PREPARATION AND REACTIVITY OF HETEROSUBSTITUTED 1,3-DIENES

By

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to the required standard

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Abstract

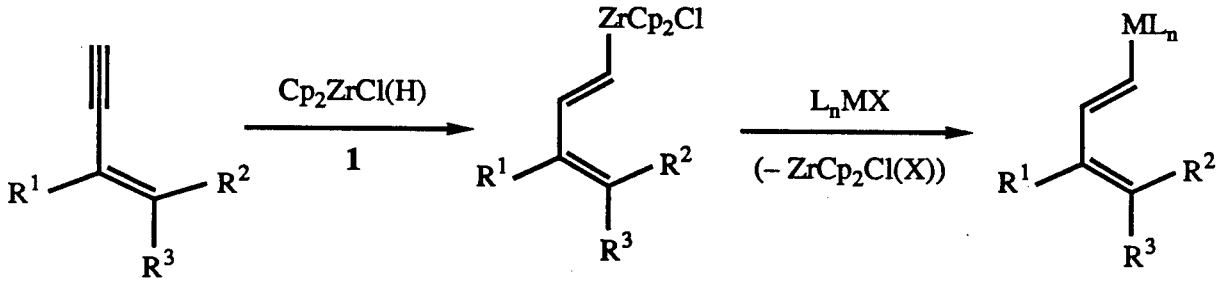
The chemoselective hydrozirconation reaction of a series of 1-ene-3-yne molecules **51a-d**, using the commercially available hydride reagent, $Cp_2ZrCl(H)$ **1**, provides an efficient route to the syntheses of 1,3-dienes **55a-d**, substituted at the 1-position by the Cp_2ZrCl moiety. Similar chemoselectivity was observed in the hydrozirconation reaction of α,β-unsaturated nitriles, to generate the corresponding 1-azadienyl complexes **68-71**.

The complexes **55a-d** were found to be useful general precursors in the preparation of other heterosubstituted 1,3-dienes. Thus, corresponding tin-, phosphorus-, boron-, selenium- and sulfur-heterosubstituted 1,3-dienes **77a-d, 79a-d, 87a-d, 88a-d** and **89a-d** were readily prepared in good to excellent yields by a stereoselective transfer reaction from zirconium. The 1-azadienyl complexes also served as useful starting materials in the preparation of selenium- and phosphorus-substituted 1-azadienes.

The selenium-substituted 1,3-dienes **88a-d** underwent a facile isomerization reaction when exposed to fluorescent light, and when thermolysed in the dark at 80°C in unsealed reactors. Mechanistic studies of this isomerization process suggested that an intermolecular pathway involving free radical intermediates was operable. A comparable photochemical isomerization reaction of the sulfur-substituted 1,3-dienes was also observed. When the cycloaddition reactions of **88a-b** and **88d** with maleic anhydride were performed in the absence of light at resonable temperatures, good yields of the expected endo-cycloadducts were obtained. However, when the same reactions were repeated in room light or at temperatures in excess of those required for formation of the endo-cycloadducts an, interesting, apparent [1,3]-shift of the phenylselenenyl moiety resulted. The results of a crossover experiment indicated that this rearrangment was intermolecular in nature.

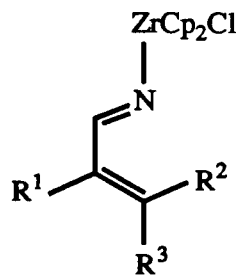
The preparation of the trialkylstannyl and phenylselenenyl 2-substituted 1,3-dienes (**128** and **129**) was achieved via a transmetalation reaction of the Grignard reagent **24**.

The Diels-Alder reactivity of 1,3-dienes **128** and **129**, with a series of electron-deficient dienophiles, was successfully investigated.

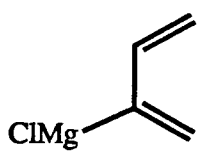


51a-d **55a-d** **M**

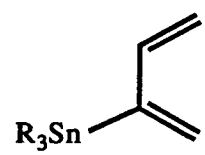
77a-d Sn
79a-d P
87a-d B
88a-d Se
89a-d S



68-71

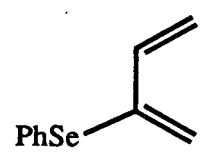


24



128

a Bu
b Me



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List of Abbreviations

atm	atmosphere(s)
Ac	acyl
acac	acetylacetonate
AIBN	azoisobisbutyronitrile
b	broad
BHT	2,6-di-*tert*-butyl-4-methylphenol
Bu	butyl group, $-(CH_2)_2CH_3$
i-Bu	*iso*-butyl group, $-CH_2CH(CH_3)_2$
t-Bu	tertiary-butyl group, $-C(CH_3)_2CH_3$
C	Celsius
$^{13}C\{^1H\}$	carbon-13 observe, broadband proton decoupling
cat.	catalyst
COD	cyclooctadiene, C_8H_{12}
Cp	η^5-cyclopentadienyl ligand, $C_5H_5^-$
Cp^*	η^5-pentamethylcyclopentadienyl ligand, $C_5(CH_3)_5^-$
d	doublet
d	deuterated
δ	chemical shift
2D	two-dimensional
dd	doublet of doublets
ddd	doublet of doublet of doublets
dddd	doublet of doublet of doublet of doublets
DIBAL	diisobutylaluminum hydride
ε	extinction coefficient
equiv	equivalent(s)

Et	ethyl group, $-CH_2CH_3$
Fp	η^5-cyclopentadienyldicarbonyliron, $[Cp(CO)_2Fe]$
GLC	gas-liquid chromatography
GCMS	gas chromatography-mass spectrometry
h	hour
$^1H\{^{31}P\}$	proton observe, phosphorus broadband decoupling
Hz	hertz, seconds^{-1}
IR	infrared
J	coupling constant
Kcal	Kilocalories
L	ligand
λ	wavelength
m	multiplet
M^+	molecular ion
max	maximum
Me	methyl group, $-CH_3$
MHz	megahertz
min	minute
mL	millilitre
mmol	millimole
mol	mole
MM2	molecular mechanics
MS	mass spectrometry
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
N-ClPSP	*N*-(4-chlorophenyl)phthalimide
N-PSP	*N*-(phenylseleno)phthalimide

N-PTP	*N*-(phenylthio)phthalimide
NMR	nuclear magnetic resonance
NOEDIFF	nuclear Overhauser effect difference
ORTEP	Oakridge Thermal Ellipsoid Plotting Program
$^{31}P\{^{1}H\}$	phosphorus-31 observe, proton broadband decoupling
Ph	phenyl group, $-C_6H_5$
ppm	parts per million
i-Pr	isopropyl group, $-CH(CH_3)_2$
PVP	poly(4-vinylpyridine)
q	quartet
R.T.	room temperature
s	singlet
$^{77}Se\{^{1}H\}$	selenium-77 observe, proton broadband decoupling
t	triplet
TEMPONE	4-oxo-2,2,6,6-tetramethylpiperidinyloxy radical
tert	tertiary
THF	tetrahydrofuran
UV	ultraviolet
UV-vis	ultraviolet-visible

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For my sister, Sandra and my father.

CHAPTER 1

Introduction

1.1 General.

The role of organometallic chemistry in the development of new synthetic methods, directed towards organic synthesis, has increased significantly over the past 20 years.[1] The use of organometallic reagents, both in catalytic and stoichiometric reactions, has undoubtedly enhanced the means by which simple and complex molecules are constructed. In this regard, two major classes of reactions which have found general use are hydrometalation and transmetalation. Both of these reactions are known to take place with a high degree of regio- and stereoselectivity. It is, perhaps, this feature which makes these reactions so attractive to the organic chemist.

The hydrometalation reaction, which encompasses such processes as hydroboration[2] (although boron is not classically regarded as a metal, it tends to be placed in this category), hydroalumination[3] and hydrostannation,[4] has found wide use in organic synthesis. A supplementary reaction to these latter processes came about with the synthesis of chlorobis(η^5-cyclopentadienyl)hydridozirconium(IV) $[Cp_2ZrCl(H)]_x$ **1**.[5]

$$M^1—R \quad + \quad M^2—X \rightleftharpoons M^2—R \quad + \quad M^1—X \qquad (1)$$

M^1 = metal M^2 = metal or non-metal

R = organic fragment X = organic fragment or halogen

The transmetalation reaction provides a method by which organic fragments can be exchanged from one metal to another in a stereochemically-controlled manner (equation 1). This process can be expanded to the more general case in which an organic moiety σ-bonded to a metal, is transferred to either another metal or a non-metal. This latter, more general process, may then be simply termed a transfer reaction. The transfer may be considered to involve the exchange of either two similar fragments (i.e where X and R are both organic moieties) or else two different fragments, such as the exchange of a σ-bound organic moiety for a halogen.

The Diels-Alder reaction has been shown to be one of the most useful carbon-carbon bond forming reactions available to the synthetic organic chemist, especially in the construction of six-membered ring systems. Greater understanding of the mechanism of this reaction has led to the preparation of heterosubstituted 1,3-dienes, since the presence of these heteroatoms has enhanced both the reactivity of the 1,3-dienes, as well as the regio- and stereoselectivity of the reaction. Also, the presence of the heteroatoms provides means for further transformations by exploiting their known chemistry. Thus, through the use of the hydrozirconation reaction and the transfer procedure, we hoped to generate a general synthetic method for the construction of a variety of stereochemically defined heterosubstituted 1,3-dienes. For ease of presentation, the majority of the 1,3-dienes in this thesis are drawn in the s-cis conformation.

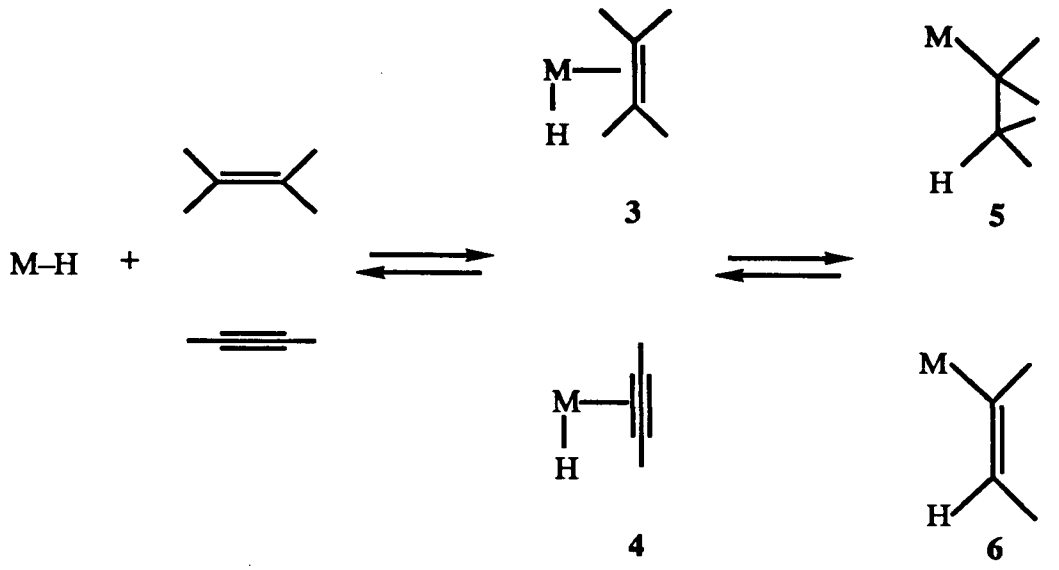
1.2 Hydrozirconation.

The hydrozirconation reaction[6] involves the insertion of unsaturated organic substrates into the metal-hydrogen bond of $[Cp_2ZrCl(H)]_x$ **1**. For simplicity, henceforth in this thesis, hydride **1** shall be represented as $Cp_2ZrCl(H)$. The synthesis of $Cp_2ZrCl(H)$ was first reported in 1969 by Wailes and co-workers.[7] In the same communication they reported the preparation of bis(η^5-cyclopentadienyl)deuteriozirconium(IV) $Cp_2ZrCl(D)$ **2** by a similar method. The infrared spectrum of these compounds strongly indicated the presence of

bridging hydrides (deuterides) in the polymeric structure. Preliminary investigation by these workers[5,8] provided evidence for the insertion reaction of alkenes and alkynes with **1**; however, the products were poorly characterized. Subsequent reports by Schwartz and co-workers brought to light the true potential of the hydrozirconation reaction.[9]

The structure of this commercially available hydride has not been clearly determined. However, due to its characteristic insolubility, it is presumed to be polymeric. The binuclear zirconocene hydride $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ has been structurally characterized by single-crystal X-ray diffraction methods.[10] This study provided the first structural evidence of bridging hydrides for binuclear hydride complexes of zirconium. During their investigations with the pentamethylcyclopentadienyl ligand (Cp^*), Bercaw and co-workers[11] synthesized the monomeric $Cp^*_2ZrCl(H)$, along with its dihydride analogue $Cp^*_2ZrH_2$. Both of these complexes are known to react with alkenes and alkynes via insertion into the Zr-H bonds.

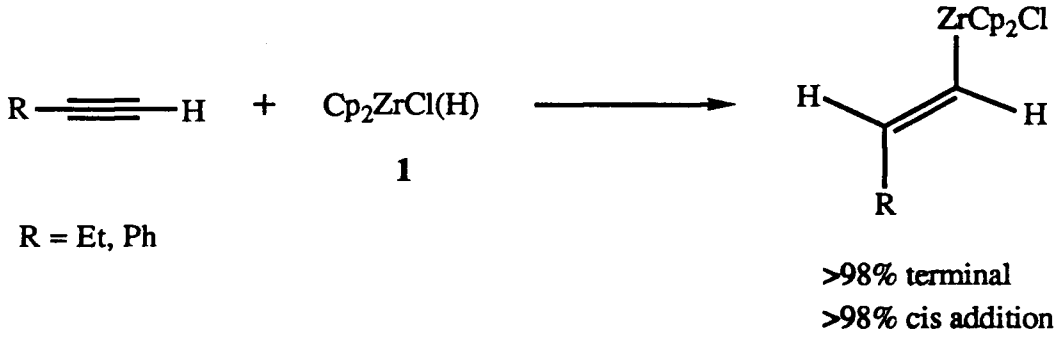
To understand why $Cp_2ZrCl(H)$ has become such a useful transition metal hydride reagent for the functionalization of unactivated alkenes and alkynes, one must examine the insertion process (Scheme 1). To achieve insertion of an alkene or alkyne into a metal-



Scheme 1

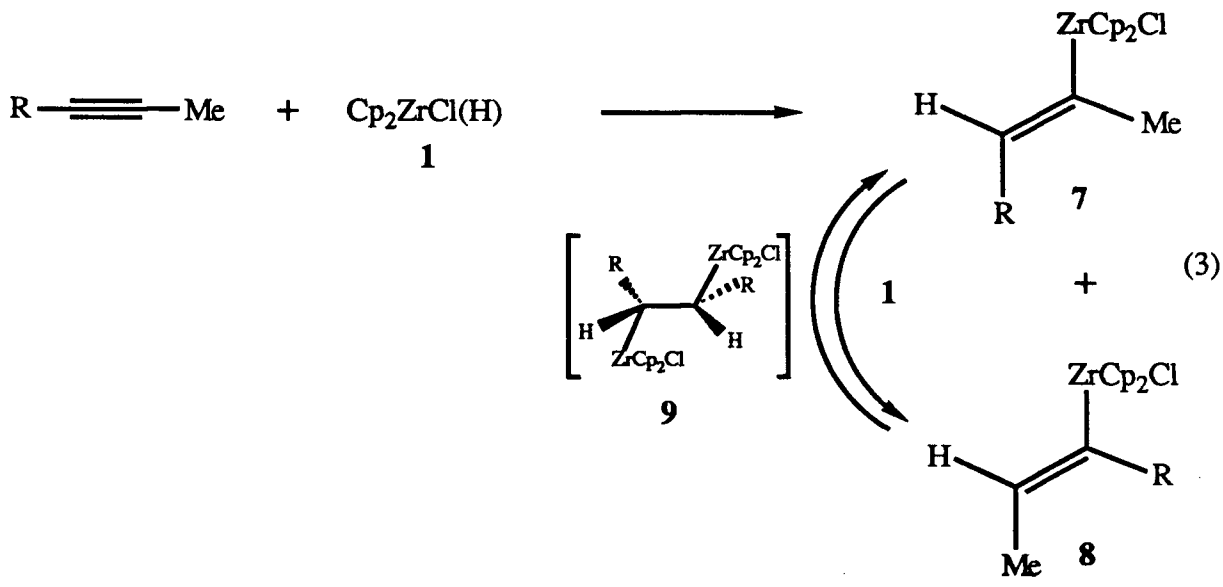
hydrogen bond, the equilibria in Scheme 1 must lie far to the right. Thus, formation of the σ-alkyl-metal complex **5** over the hydride alkene complex **3** (or the σ-alkenyl-metal complex **6** over the hydride alkyne complex **4**) must be strongly favored. For hydride complexes of transition metals in low formal oxidation states, the equilibria in Scheme 1 lie far to the left. This is presumably because alkene (π-acceptor) complexes of electron-rich metals are more stable than the corresponding alkyl (σ-donor) complexes. This rationale therefore suggests that electron-poor transition metals in high formal oxidation states should favor the formation of σ-alkyl or σ-alkenyl complexes.[12] To date, hydrozirconation is probably the most extensively studied reaction of this type and has been used to produce stable, isolable (mostly crystalline) zirconium alkyl and alkenyl complexes.

Reaction of hydride **1** with terminal alkynes has been shown to proceed stereoselectively; placing the zirconium and hydride cis to one another, with the zirconium occupying the terminal position as outlined in equation 2.[8]



(2)

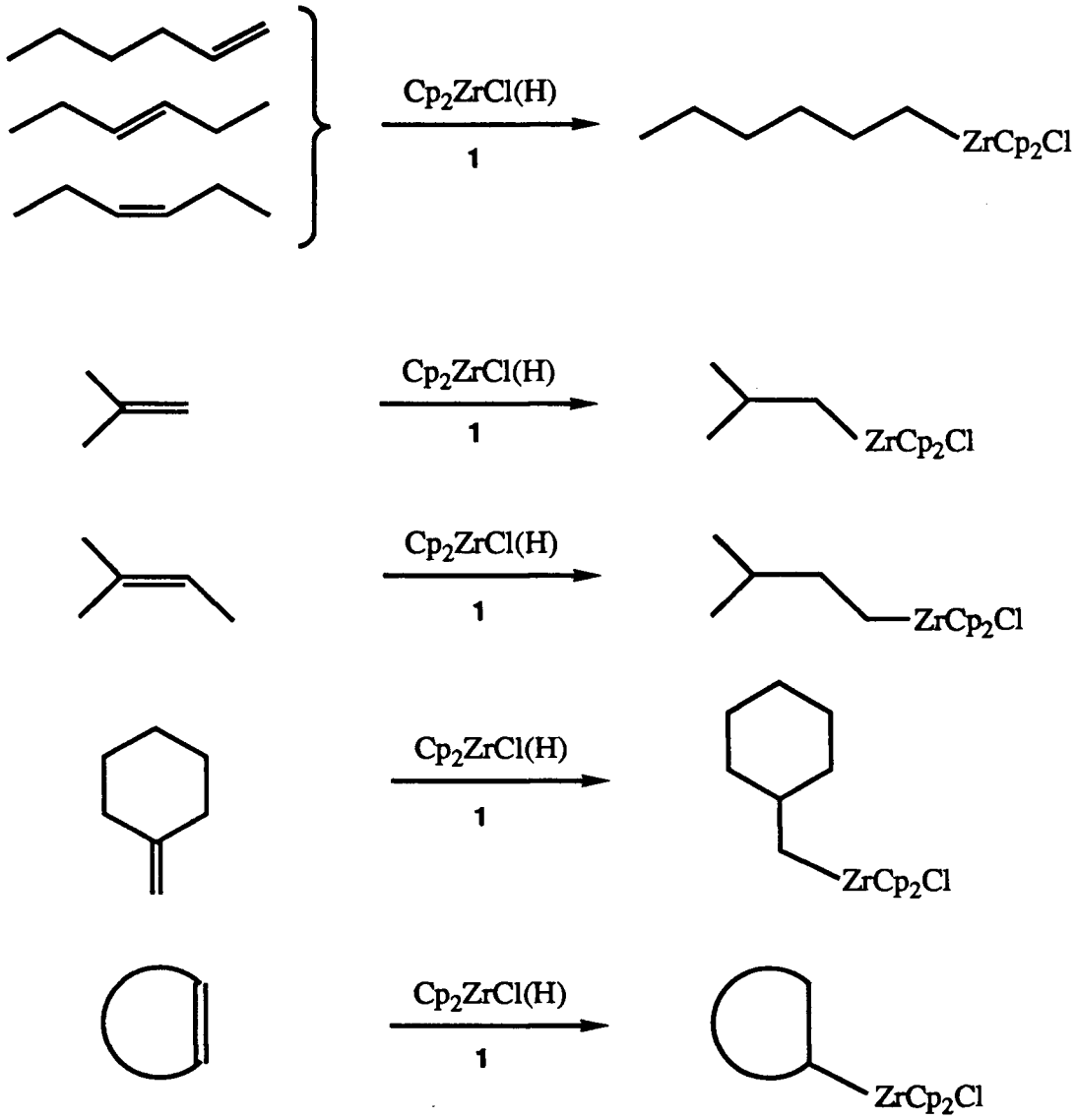
Schwartz and co-workers[13] found that addition of **1** to disubstituted alkynes also proceeded with cis stereochemistry to give a mixture of zirconium alkenyl complexes, the ratio of which was dependent on the relative steric bulk of the methyl versus an alkyl group (equation 3). Interestingly, these workers also noted that the presence of excess $Cp_2ZrCl(H)$ induced isomerization to an equilibrium mixture of zirconium alkenyls **7** and **8** at room temperature. To explain this observation, the intermediacy of a 1,2-dimetalated alkenyl



(3)

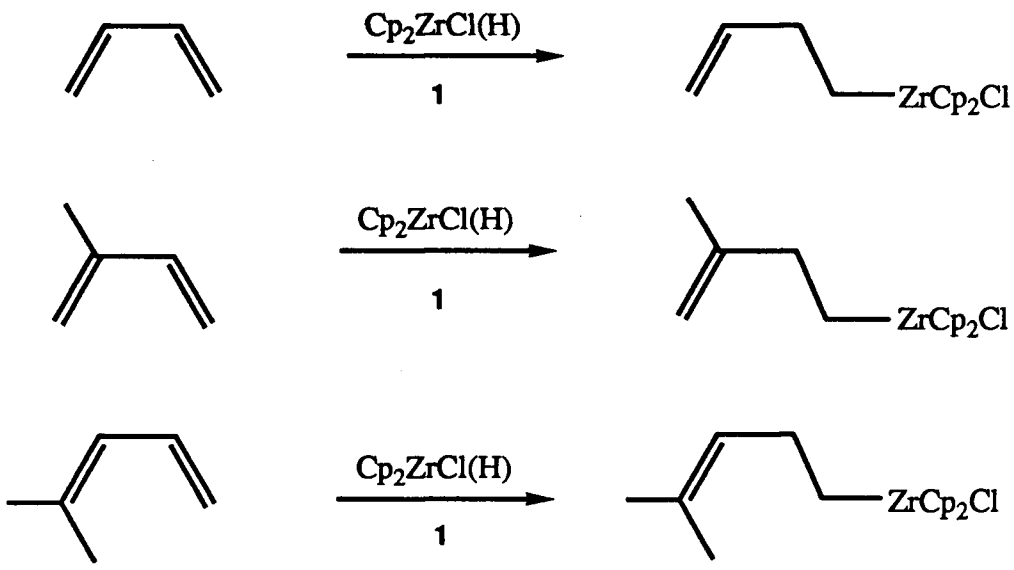
derivative **9** was proposed,[13] the formation of which could be accounted for by a second hydrozirconation reaction[8] of the mixture **7/8**. The retention of stereochemistry in the alkenyl zirconium complex, during the isomerization process, can be understood on the basis that both metal-hydride addition and elimination are known to take place with cis stereochemistry.

Hydride **1** was found to react under mild conditions with a series of terminal, internal and cyclic alkenes (Scheme 2).[9] It is evident from Scheme 2 that hydrozirconation of internal alkenes gives rise to the same product as the corresponding terminal alkene. This rearrangement is brought about by a series of β-elimination-insertion reactions which continue until the Cp_2ZrCl fragment is at the least hindered position in the alkyl chain.[9] The facile nature of this rearrangement is in contrast to the corresponding organoboron[14] or organoaluminum[15] compounds, which only undergo similar processes at elevated temperatures. From the series of reactions shown in Scheme 2, it was possible to determine relative rates of hydrozirconation. The order of reactivity was as follows: terminal alkenes > cis internal alkenes ≈ trans internal alkenes > exocyclic alkenes > cyclic alkenes > disubstituted alkenes > trisubstituted alkenes. Tetrasubstituted alkenes and trisubstituted cyclic alkenes did not react with **1** after several hours at room temperature.[9]



Scheme 2

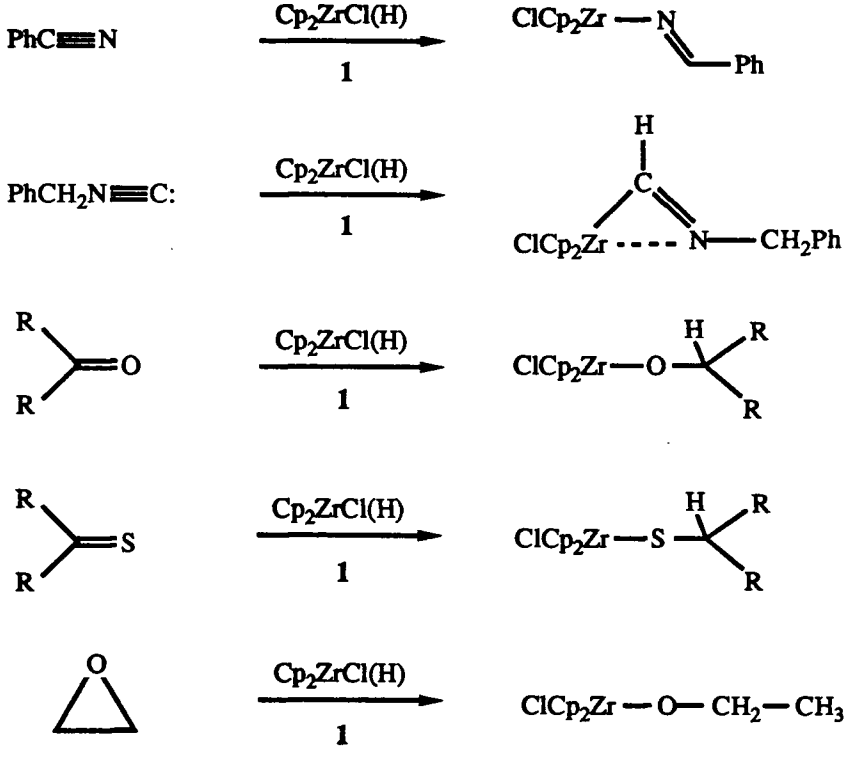
Hydrozirconation has been shown to take place with high stereo- and regioselectivity in the insertion reactions with alkynes. In addition, reaction of **1** with 1,3-dienes generally proceeds with high chemoselectivity to generate zirconium substituted γ,δ-unsaturated alkenes by insertion of the least hindered alkene, with the zirconium positioned at the least substituted carbon.[16] The regiochemistry was as observed previously, with zirconium occupying a position at the least substituted carbon (Scheme 3). The use of 3-methyl-1,3-pentadiene led to



Scheme 3

a breakdown in the high degree of regioselectivity resulting in the formation of a 10:1 mixture of regioisomers about the least substituted double bond.

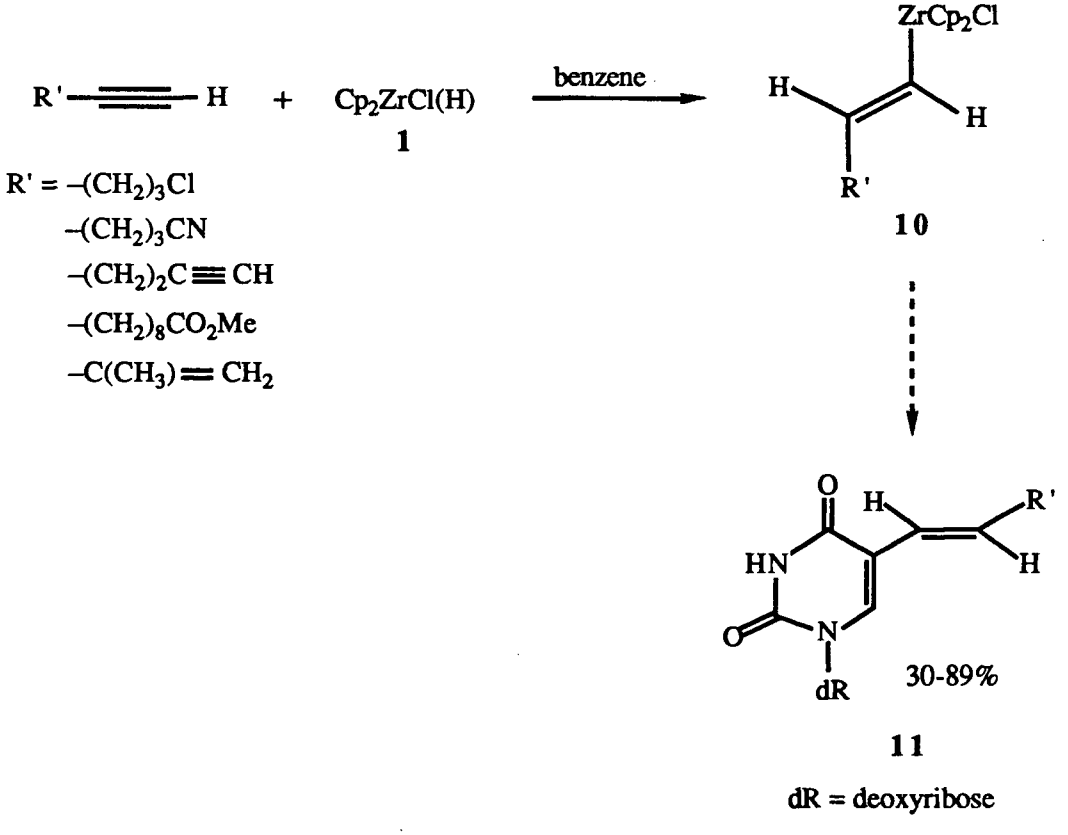
Over the years, the hydrozirconation reaction has been extended to encompass insertion



Scheme 4

reactions with nitriles,[17] isonitriles[18] (note the unusual mode of insertion), ketones,[19] thioketones[20] and epoxides[17] (Scheme 4).

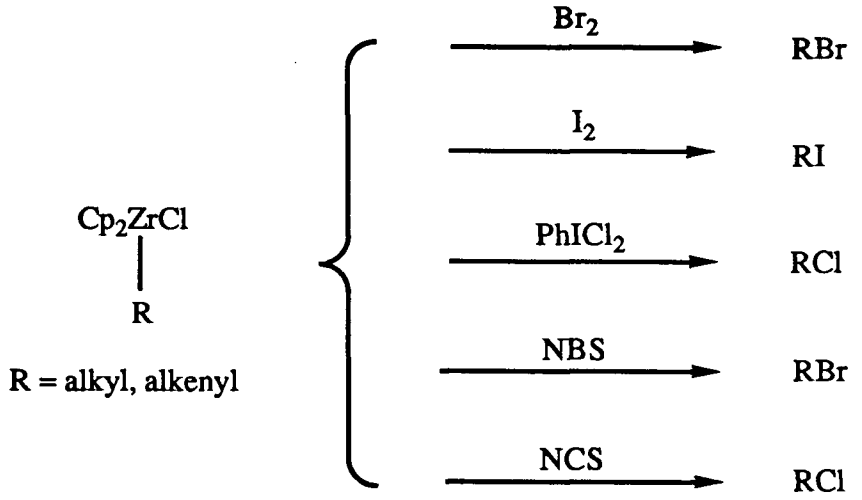
A series of hydrozirconation reactions which extended the previously observed chemoselectivity of the process has appeared in a recent communication.[21] In an effort to develop a general synthetic sequence to a series of uridine nucleosides **11**, a variety of alkenylzirconium complexes **10** was prepared. The terminal alkynes used in this procedure contained a various potentially reactive functionalities; for example, nitrile, alkyne, alkene, ester and halogen. Although the alkenyl zirconium complexes **10** were not isolated, no evidence of insertion of the secondary functionalities was observed in the final isolated products (Scheme 5).



Scheme 5

1.2.1 Reactions of Alkyl- and Alkenylzirconium Complexes.

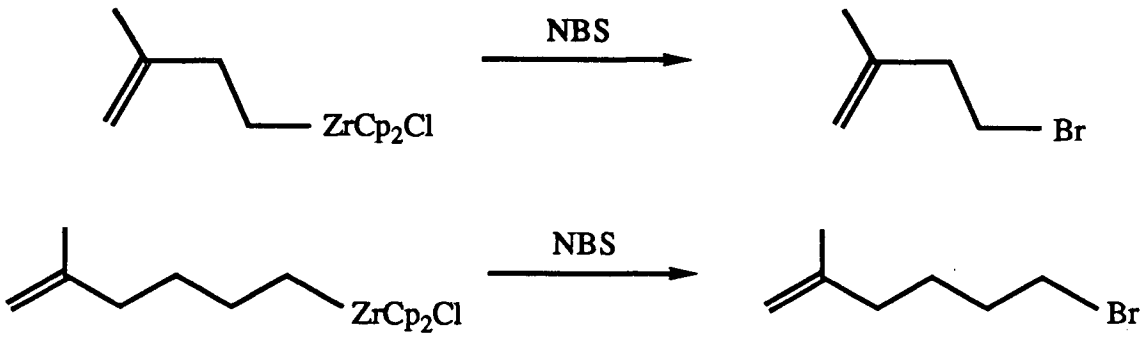
A major reason for the synthetic utility of the hydrozirconation reaction lies in the many versatile and stereochemically defined cleavage reactions available to both alkyl and alkenylzirconium complexes.[22] A wide variety of electrophilic halogenation reagents (e.g., Br_2, I_2, *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS) or iodobenzene dichloride ($PhICl_2$)) react smoothly with alkylzirconium complexes to give good to excellent yields of the corresponding alkyl halides (Scheme 6).[9] In a similar fashion, unsaturated



Scheme 6

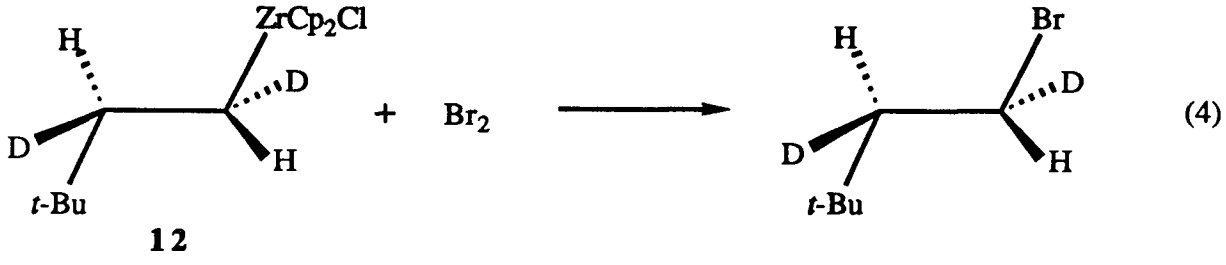
alkylzirconium complexes have been shown to react with NBS to generate the corresponding bromo-compounds (Scheme 7).[16] In general, the use of NBS rather than Br_2 in the cleavage reaction of these zirconium complexes gave higher yields.

A possible mechanism for the electrophilic cleavage of alkylzirconium complexes has been proposed,[23] based on the observation that cleavage of dideuterated-3,3-



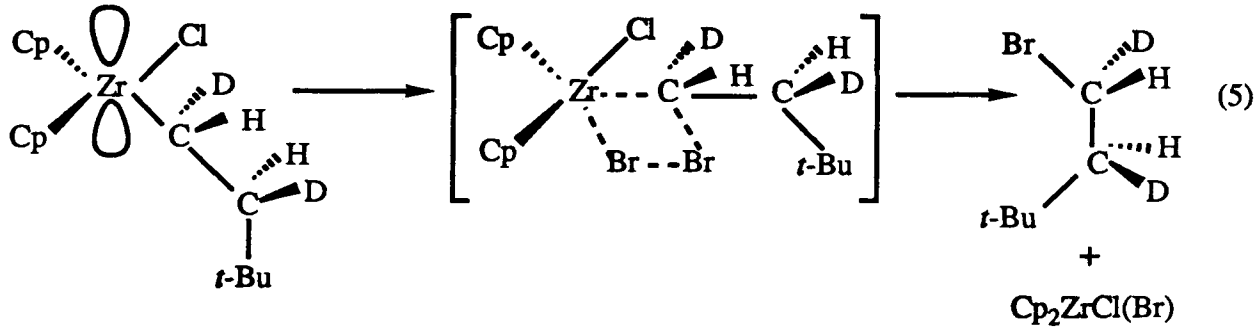
Scheme 7

dimethylbutylzirconium **12** with Br_2 proceeded with retention of configuration at carbon (equation 4). The retention of stereochemistry at carbon was accounted for by an initial



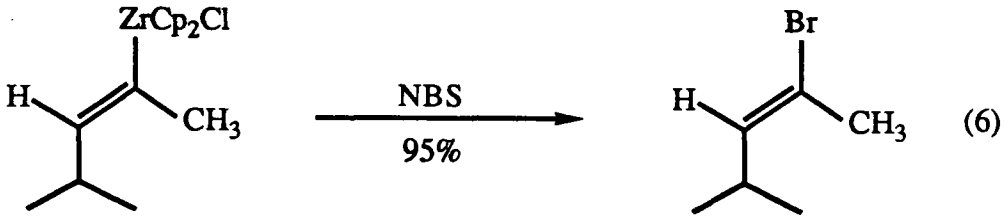
(4)

coordination of Br_2 to zirconium, through donation of a pair of electrons to its low lying orbital, thus allowing frontside attack on the C-Zr bond (equation 5).[23]



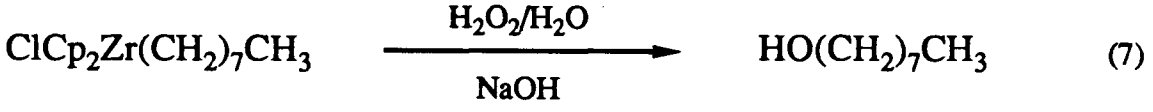
(5)

The stereochemistry observed on cleavage of alkenylzirconium complexes with NBS, can be rationalized in a similar manner to that described above for the reaction of alkylzirconium complexes with Br_2 (equation 6).[13]



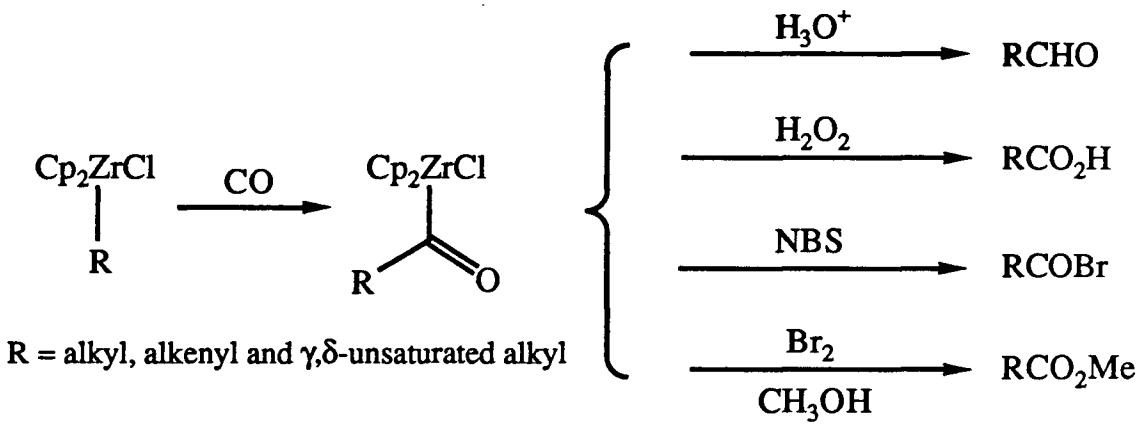
(6)

Alcohols can be prepared from alkylzirconium complexes by a variety of procedures.[24] Oxidation of these compounds with basic hydrogen peroxide gives good yields of the desired alcohol (equation 7). This is analogous to the preparation of alcohols using the hydroboration/oxidation procedure.[25]



(7)

Insertion of carbon monoxide into the Zr-C bond of alkyl[26], alkenyl[26] or γ,δ-unsaturated alkylzirconium complexes[18] proceeds smoothly at room temperature under



Scheme 8

1.5 atm of CO. The acyl complexes thus produced, serve as starting materials for a host of other compounds (Scheme 8).

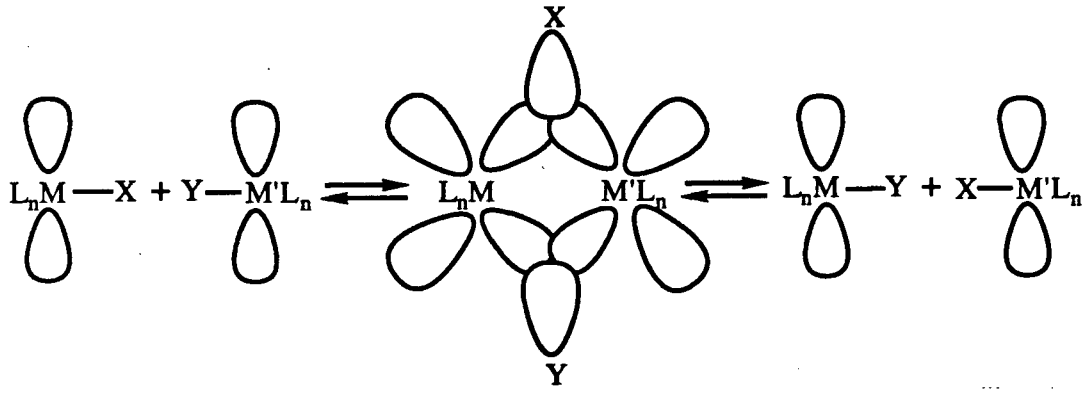
The use of alkenylzirconium complexes has been further extended by employing them as coupling partners, with a variety of other substrates, in a series of nickel(0)-catalyzed carbon-carbon bond forming reactions. These reactions, as well as a collection of other methods for the further synthetic elaboration of organozirconium species, are discussed in the following section.

1.3 Transmetalation and Transfer Reactions.

The transmetalation reaction is, as the name suggests, one in which one metal center is exchanged for another. This reaction, and the more general transfer reaction, provide an extremely useful method for the stereochemically-controlled transfer of organic moieties from one heteroatom to another. A classical example of such a process is seen in equation 8, where a transmetalation (transfer) takes place between tin and lithium.[27] It is important to note that in many cases the transmetalation reaction is a reversible process.

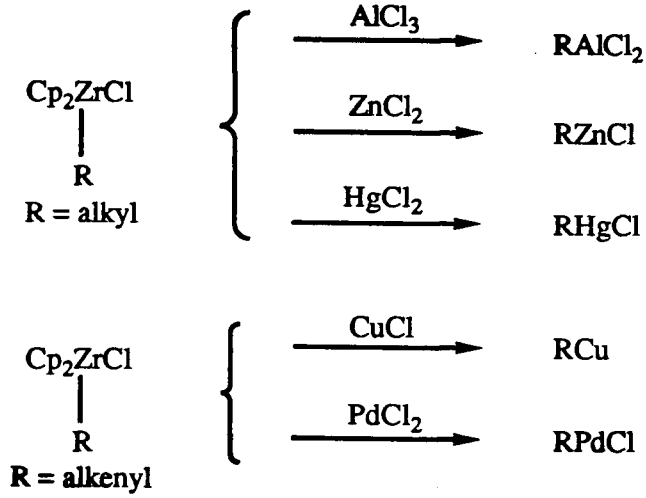
$$R_3SnR' \quad + \quad R''Li \quad \rightleftharpoons \quad R'Li \quad + \quad R_3SnR'' \qquad (8)$$

It has been proposed that replacement of zirconium in organozirconium complexes by other metals should be favorable when the other metal is more electronegative than zirconium.[28] However, further argument suggests that since this proposal is based on a thermodynamic argument, its generality may be constrained by reactions that have high kinetic barriers.[29] The mechanism by which transmetalation reactions occur is not clear. Negishi and Takahashi[29] have proposed that a four-centered process, requiring the availability of an empty orbital on each metal, may represent the most likely pathway (equation 9).



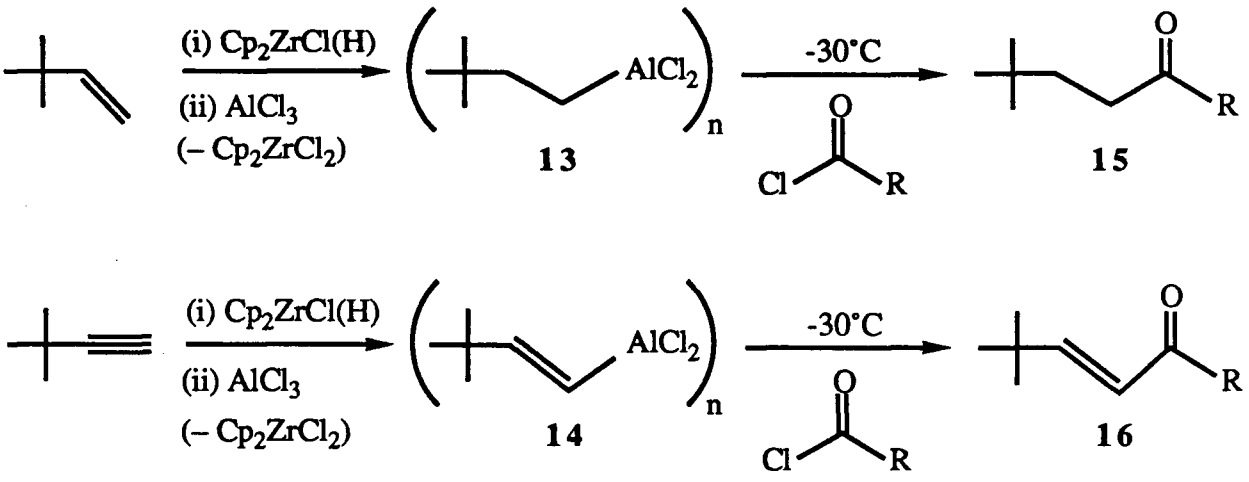
(9)

Schwartz and co-workers[30] have investigated a series of stoichiometric transmetalation reactions with Lewis acidic metal halides (Scheme 9). Reaction of alkyl or alkenylzirconium



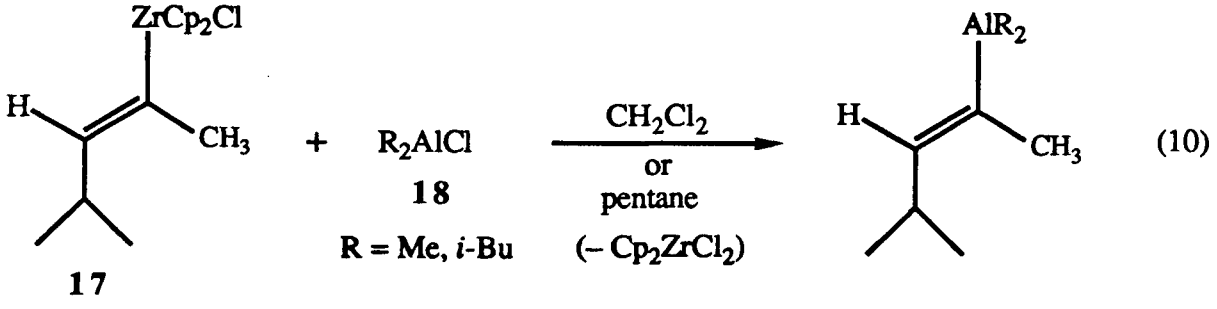
Scheme 9

complexes with aluminum trichloride at 0°C in dichloromethane proceeds quantitatively (by ^{1}H NMR spectroscopy) in less than 10 minutes. Competitive studies using mixtures of alkyl and alkenylzirconium complexes, with a deficiency of $AlCl_3$, showed that transmetalation of the alkenyl substituent is faster. Due to the thermal instability of the aluminum complexes **13** and **14**, they were immediately reacted with acid halides to generate the corresponding ketones **15** and **16** (Scheme 10).[28] Attempts to directly acylate the alkenylzirconium complexes were unsuccessful.



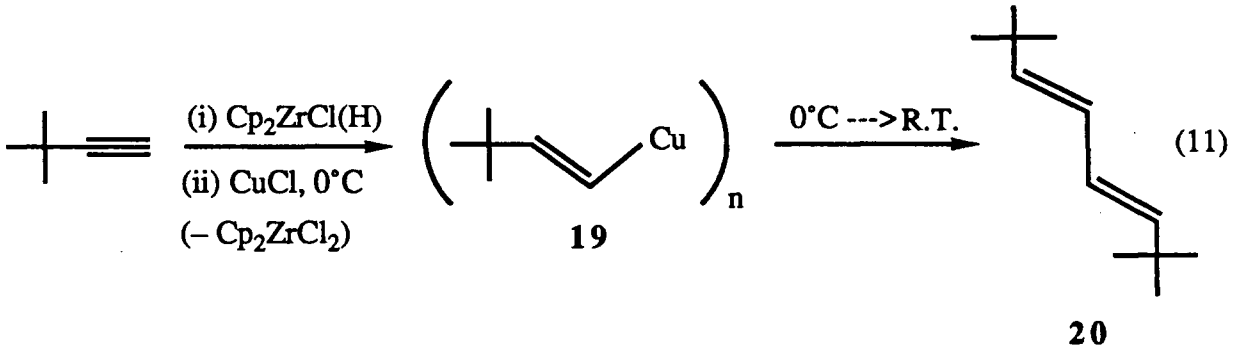
Scheme 10

By a procedure analogous to that used for the stereochemical investigation of the cleavage of alkylzirconium complexes with Br_2 (see equation 5, p 10), it was shown that transmetalation of Zr to Al proceeds with retention of stereochemistry at carbon.[28] The same stereochemical result was observed for the transmetalation of alkenylzirconium complexes. In an attempt to synthesize more robust alkenylaluminum species, the transmetalation of **17** using dialkylaluminum chlorides **18** was successfully investigated (equation 10).[28]



(10)

The transmetalation of an alkenylzirconium complex to copper using copper(I) chloride gave 1,3-diene **20**, formed by slow decomposition of the intermediate alkenylcopper compound **19**.[30b] Product analysis indicated that the 1,3-diene exhibited the regio- and stereochemistry inherent in the starting alkenyl complex (equation 11). Identical organic

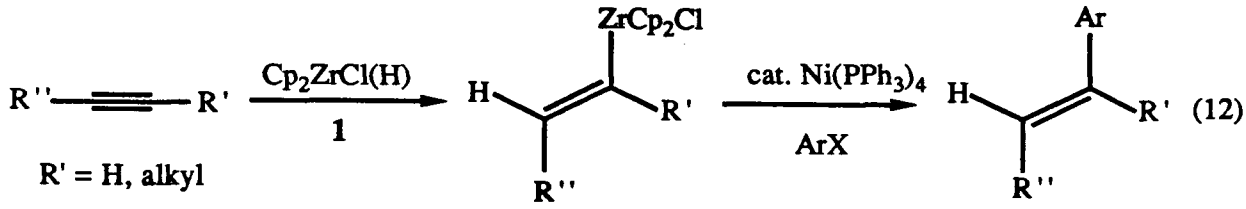


(11)

products were obtained from the transmetalation of alkenylzirconium species with palladium(II) chloride.[30b]

All of the above transformations are representative examples of stoichiometric transmetalation reactions. However, transmetalation of zirconium to other transition metals has been proposed as an important step in many catalytic carbon-carbon bond forming processes.[29] The literature abounds with examples of such processes; namely, the transition metal catalyzed reaction of organic halides using alkenylstannanes,[31] alkenyl Grignard reagents,[32] alkenylboranes,[33] alkenylzinc,[34] and others [1d] as coupling partners. Due to a tolerance of other functional groups, stereospecificity, high yields and experimental simplicity, transition metal catalyzed coupling reactions represent one of the most important new techniques for the formation of carbon-carbon bonds.

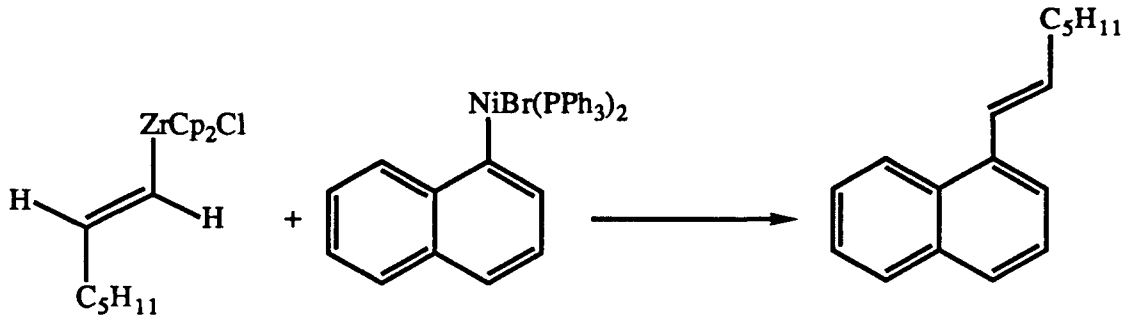
A novel nickel(0)-catalyzed cross-coupling reaction between alkenylzirconium complexes and aryl halides has been developed (equation 12).[35a] This reaction has been



(12)

R' = H, alkyl
R" = alkyl

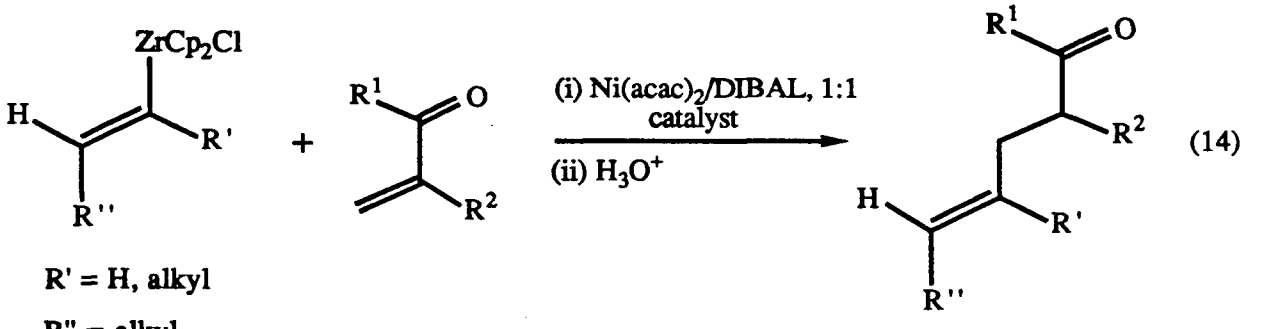
extended, using a palladium(0) complex as the catalyst, to include vinyl halides[35b] and alkynyl halides[35c] as coupling partners. In these examples, the stereochemistry of the product was >98% E, indicating retention of configuration at carbon during the coupling reaction. Reaction of the (*E*)-1-heptenylzirconium derivative **21** with one equivalent of 1-naphthylnickel complex **22** gave **23** at a rate that was comparable to that observed with use of 10 mol % $Ni(PPh_3)_4$ in the corresponding catalytic reaction (equation 13).[35a] Thus, it was proposed that a likely



21 **22** **23** (13)

catalytic cycle should involve the oxidative addition of the aryl halide to the nickel complex, followed by transmetalation from zirconium to nickel, and finally reductive elimination to yield the coupling product. A later study proposed that oxidative addition of aryl halides to reduced nickel species probably proceeds by an electron transfer mechanism.[36]

Addition of alkenylzirconium complexes to α,β-unsaturated ketones, via nickel(0) catalysis, has been shown to be an important extension of organozirconium chemistry (equation 14).[37]



R' = H, alkyl

R" = alkyl

(14)

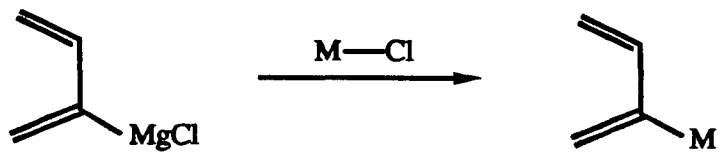
The application of the transmetalation (transfer) reaction, along with several other approaches towards the synthesis of heterosubstituted 1,3-dienes, is discussed in the following section.

1.4 Synthetic Routes to Heterosubstituted 1,3-Dienes[38]

The synthetic utility of the Diels-Alder reaction has encouraged many research groups to develop new general approaches to the preparation of functionalized 1,3-dienes. These endeavors have been made in the hope that new dienes possessing enhanced reactivity and flexibility towards further elaboration can be prepared. The following section outlines some of the general procedures that have been developed for the preparation of heterosubstitued 1,3-dienes. These procedures fall into three categories (i) use of starting materials already containing a 1,3-diene fragment, (ii) combined use of various pericyclic reactions, and (iii) trapping enolates of α,β-unsaturated ketones.

1.4.1 Use of Molecules Already Containing a 1,3-Diene Fragment.

The synthesis of 2-(1,3-butadienyl)magnesium chloride **24** by Aufdermarsh,[39]

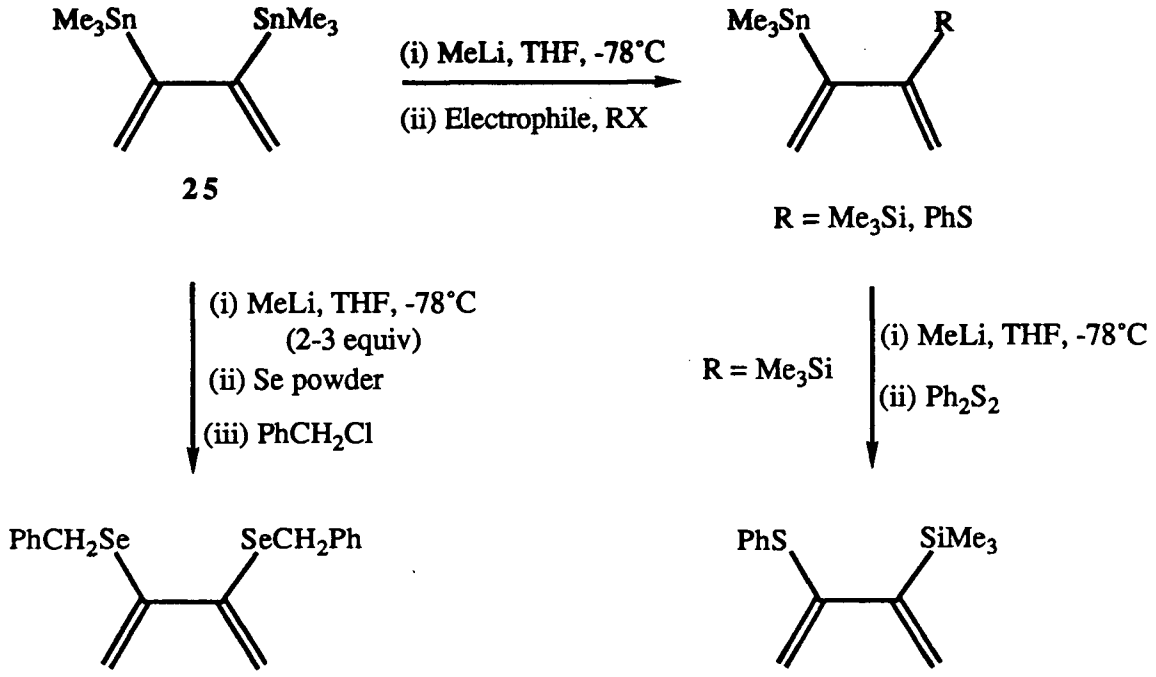


(15)

24 M = Bu_3Sn, Ph_2P, ClHg

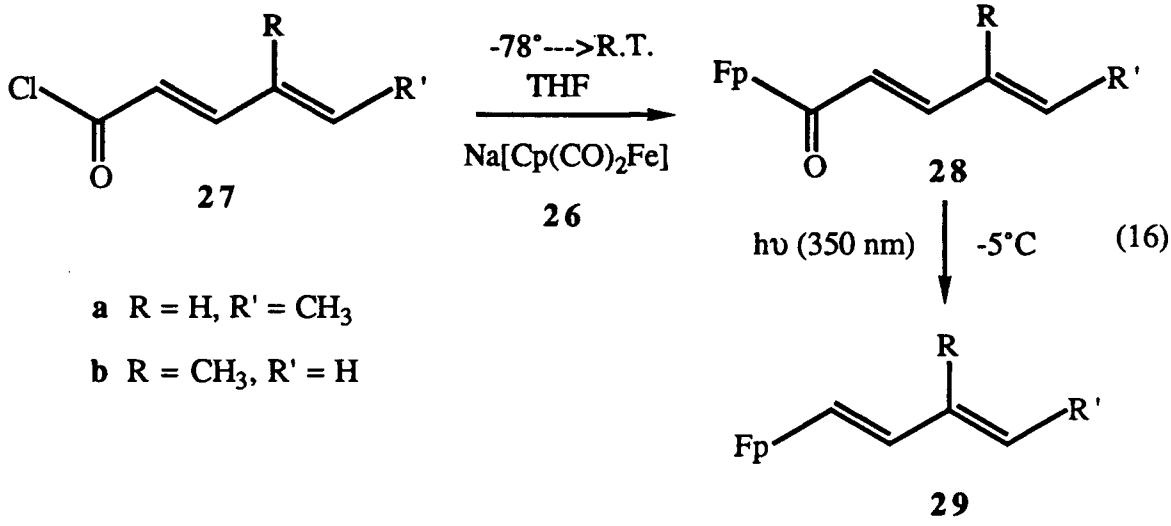
modified later by Sultanov et al.,[40] led the way to a general method for the preparation of 2-substituted-1,3-dienes via transfer of the 1,3-diene fragment from magnesium to tin, phosphorus and mercury (equation 15).

More recently, Reich et al.[41] have shown that 2,3-bis(trimethylstannyl)-1,3-butadiene **25**, via transmetalation to lithium, is a versatile reagent for the preparation of mono- and disubstituted 1,3-dienes (Scheme 11).



Scheme 11

The preparation of 1,3-dienes containing σ-bonded transition metals is rare.[42] However, a potentially general route to dienyliron complexes has been developed. The procedure involved reaction of Na[Cp(CO)$_2$Fe] (NaFp) **26** with dienoyl chlorides **27** to afford the transition metal acyl complexes **28**. These complexes were then photochemically decarbonylated to yield the desired dienes **29** (equation 16).[43] Other workers have also used NaFp to prepare dienyliron complexes; however the reaction procedures were rather elaborate and poor yielding.[44] Another example of the preparation of σ-bound transition metal dienes represents a high yielding, quite general procedure. In this reaction a hexane solution of 1,5-cyclooctadienebis(triethylphosphine)nickel(0) [Ni(PEt$_3$)$_2$(1,5-C$_8$H$_{12}$)] **30** was added to a

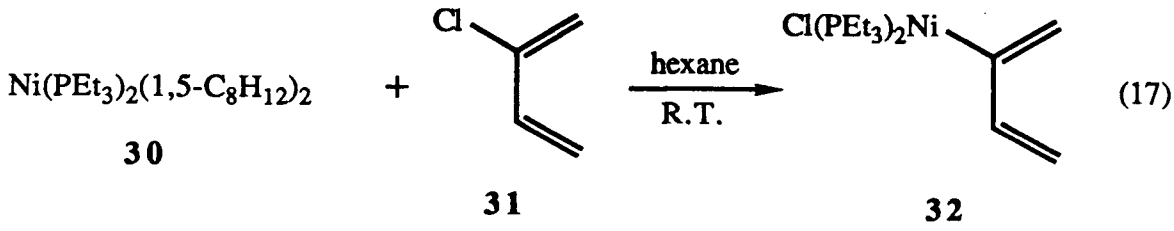


(16)

a R = H, R' = CH_3

b R = CH_3, R' = H

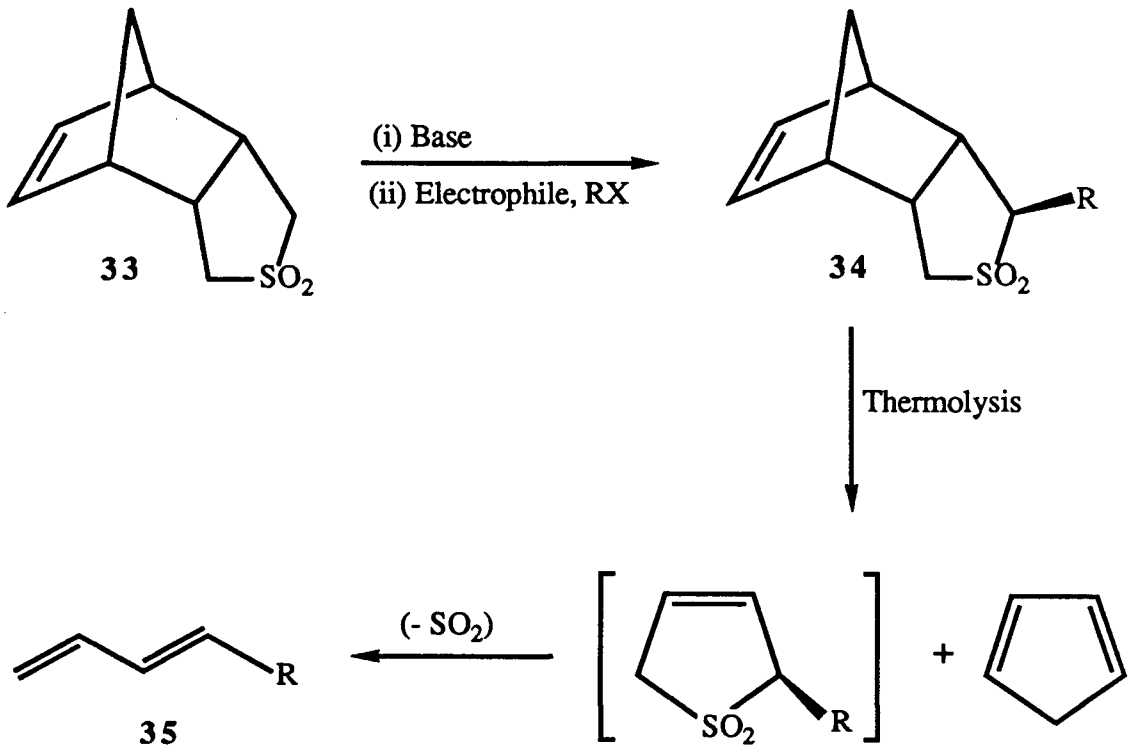
solution of 2-chloro-1,3-butadiene **31** to yield, after crystallization, the desired 1,3-dienylnickel complex **32** (equation 17).[45]



(17)

1.4.2 Pericyclic Reactions.

The retro-Diels-Alder reaction in combination with electrocyclic ring opening has proved extremely useful in providing general synthetic routes to heterosubstituted 1,3-dienes.[46] As shown in Scheme 12, deprotonation of sulfone **33** followed with trapping with an appropriate electrophile gives **34**. Thermolysis of the substituted sulfone **34** generates the desired 1,3-dienes **35** and sulfur dioxide.

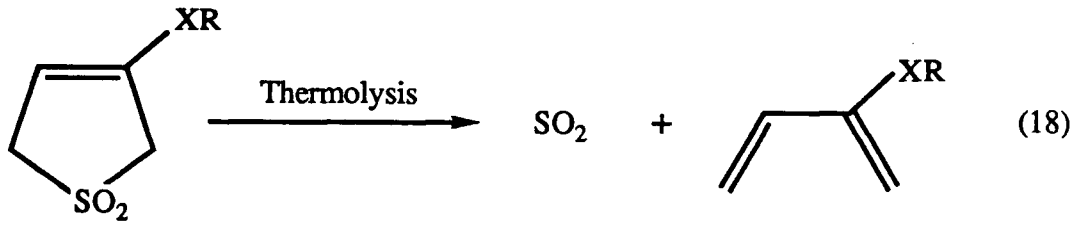


a R = Me_3Si (89%, 96% E)

b R = Me_3Sn (25%, 85% E)

Scheme 12

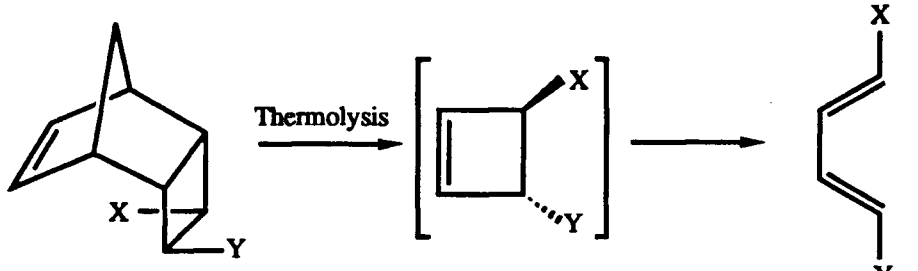
A similar procedure was used in the synthesis of 2-(phenylthio)-1,3-butadiene **36**[47a] and 2-(phenylseleno)-1,3-butadiene **37** (equation 18).[47b] The latter compound was not isolated, and was used as the sulfone for further transformations.



(18)

36 X = S, **37** X = Se

A general procedure for the preparation of 1,4-disubstituted-1,3-dienes was developed by Trost and co-workers.[48] This synthesis involved the retro-Diels-Alder reaction of **38** to give cyclobutene **39**, which on ring opening gave the 1,3-diene **40** (equation 19).



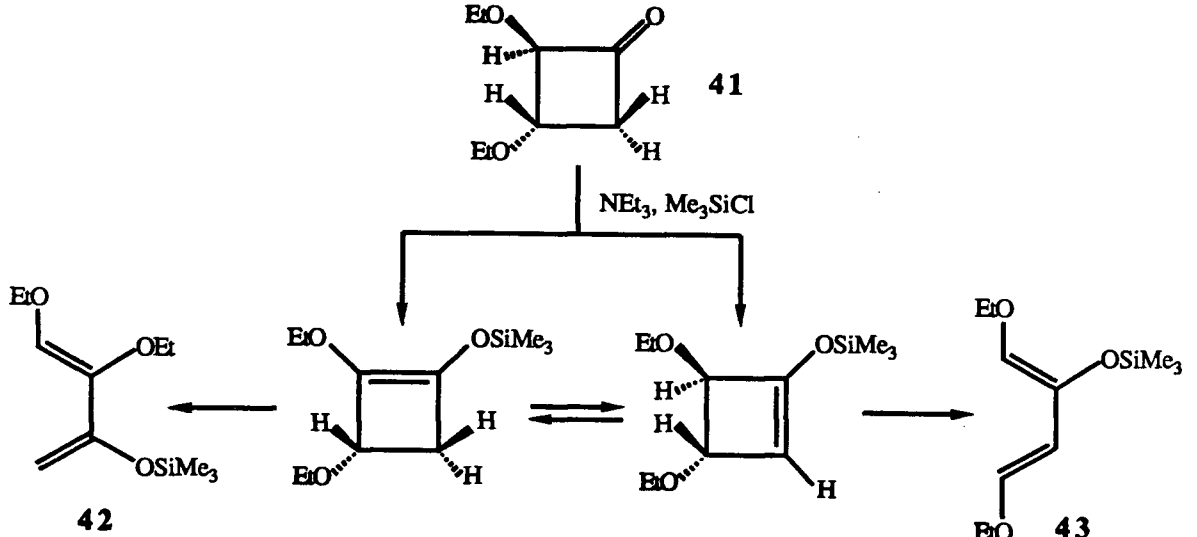
38 **39** **40**

(19)

a X = OAc, Y = SPh

b X = Y = OAc

A further example of the use of electrocyclic ring opening reactions to generate heterosubstituted 1,3-dienes, involves the preparation of dienes **42** and **43**. Silylation of **41**

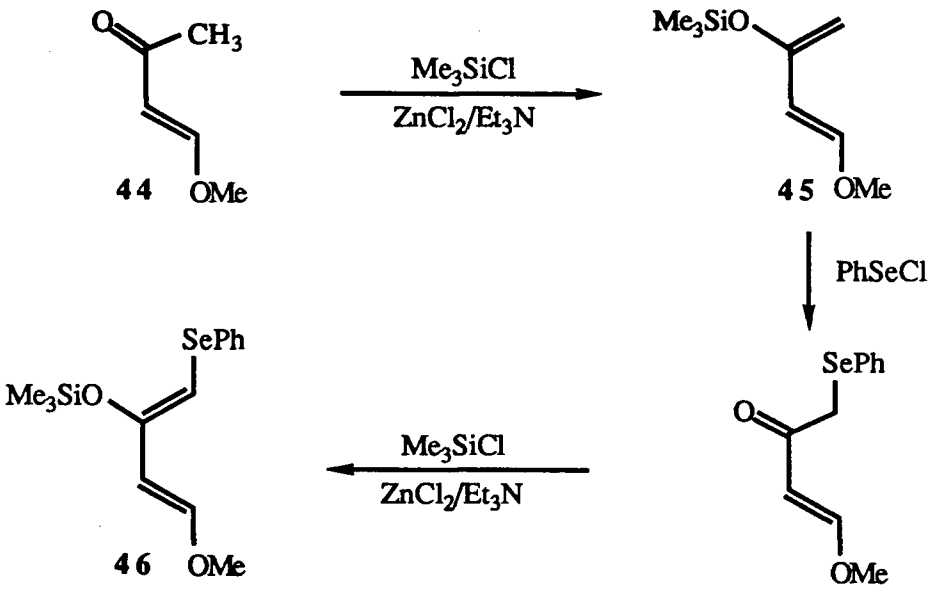


Scheme 13

followed by thermolysis, gave a 3:2 mixture of the 1,3-dienes **42** and **43** (respectively) in good overall yield (Scheme 13).[49] A similar procedure was used to prepare tetrasubstituted 1,3-dienes.[49]

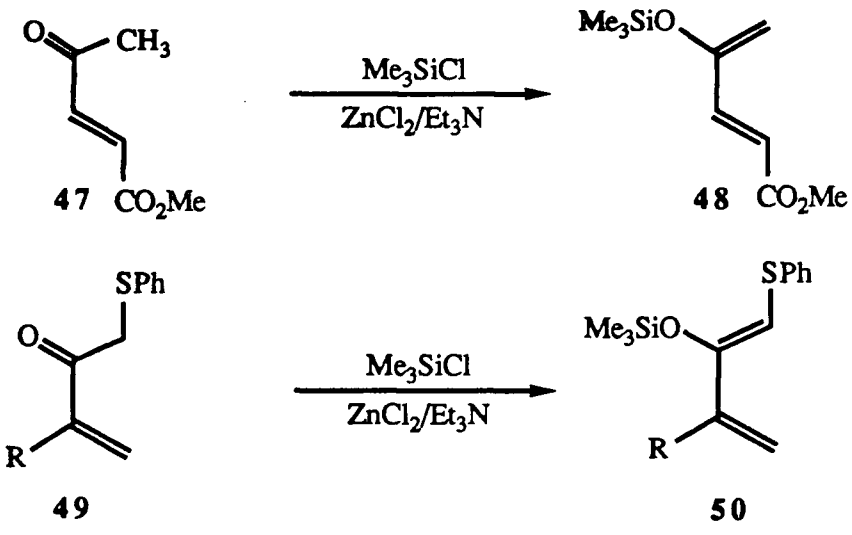
1.4.3 Trapping Enolates of α,β-Unsaturated Ketones.

A simple and general method for the preparation of heterosubstituted 1,3-dienes has been exploited by several research groups. Silylation of the enone **44** gave the 1,3-diene **45** directly in good yield.[50a] Further substitution of **45** with phenylselenenyl chloride (PhSeCl), followed by resilylation, gave the 1,3-diene **46** (Scheme 14).[50b] In a similar fashion, the



Scheme 14

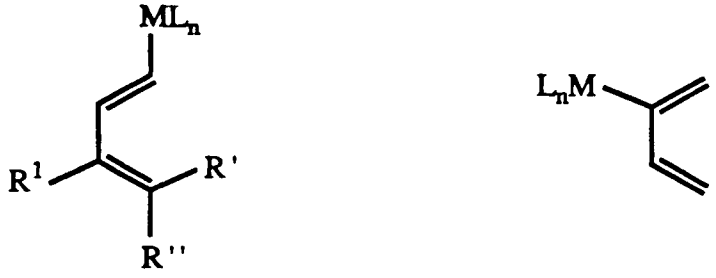
1,3-diene **48**[50c] was prepared from the enone **47**, while silylation of the enone **49** gave the 1,3-diene **50** (Scheme 15).[50d]



Scheme 15

An outline of the hydrozirconation and transmetalation (transfer) reactions and, in the latter section, a brief overview of the methods currently available for the synthesis of heterosubstituted 1,3-dienes has been presented in the Introduction.

Based on the studies presented in this Introduction, we were interested in generating general synthetic routes for the preparation of heterosubstituted 1,3-dienes. Such investigations would involve: (i) the hydrozirconation reaction of 1-ene-3-yne molecules in the hope of generating a series of σ-bonded dienylzirconium complexes of type **A** (where ML_n would be Cp_2ZrCl), (ii) the transmetalation reactions of the dienyl Grignard reagent **24** (Figure 1). It was further hoped that the dienylzirconium reagents could be exploited as



Type A Type B

Figure 1. General structures for heterosubstituted 1,3-dienes of types A and B.

general percursors in the preparation of other heterosubstituted 1,3-dienes of type **A** (where ML_n would represents some substituted heteroatom), whereas compounds such as **24** could serve as useful starting material for the synthesis of heterosubstituted 1,3-dienes of type **B**. If these procedures proved successful, the effects of the heteroatom substituents on the reactivity of these dienes could then be investigated. The following Chapters outline the progress that has been made in this regard.

CHAPTER 2

Insertion Reactions of 1-Ene-3-ynes, Nitriles and α,β-Unsaturated Nitriles: Reaction of 1,3-Dienylzirconium Complexes with Carbon Monoxide.

2.1 Hydrozirconation of 1-Ene-3-ynes.

A general synthetic procedure for the preparation of heterosubstituted 1,3-dienes of type A could be envisaged to proceed through the chemoselective hydrozirconation of 1-ene-3-ynes (Figure 2). Preferential insertion of the alkyne functionality of 1-ene-3-ynes into the metal-hydrogen bond of the hydride $Cp_2ZrCl(H)$ **1**, coupled with the well documented stereo- and regiochemical outcome of such a process, would afford the desired 1,3-dienes of the type A (where ML_n is Cp_2ZrCl).

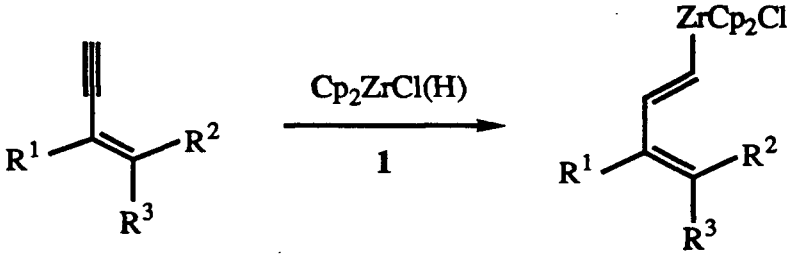
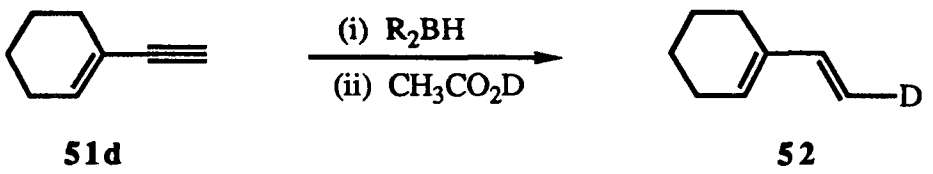


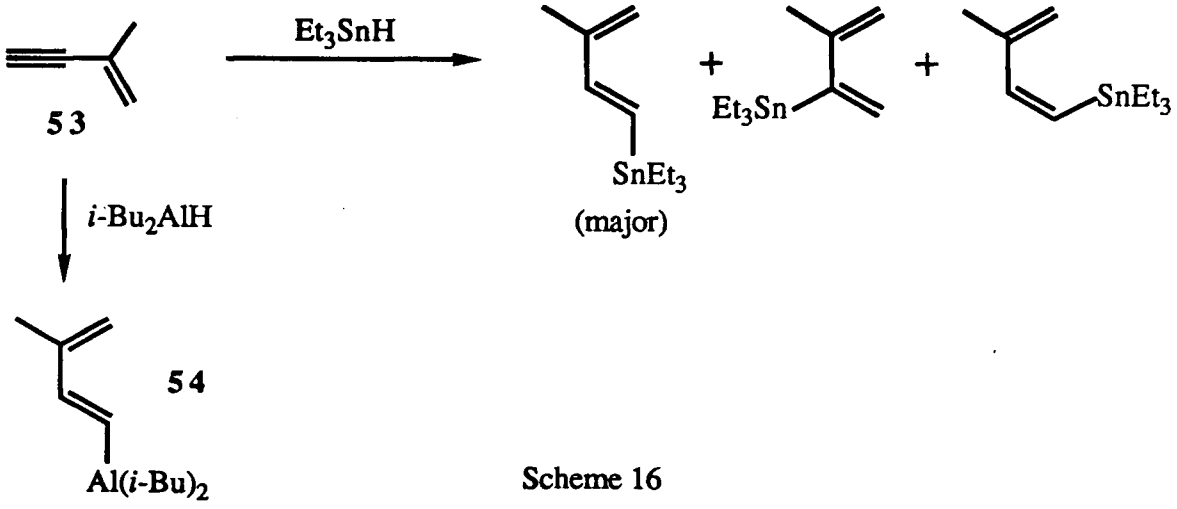
Figure 2. Proposed synthetic route to 1,3-dienylzirconium complexes of type A.

Such chemoselectivity in the insertion of 1-ene-3-ynes molecules has been observed previously for other hydrometalation reactions. Hydroboration of 1-ene-3-yne **51d** has been shown to proceed chemoselectively to give the diene **52**, after workup with acid (equation 20).[51] Other workers[52] have observed similar selectivity in the hydroalumination of



51d **52** (20)

53 with diisobutylaluminohydride (*i*-Bu_2AlH) to give the diene **54**; however, hydrostannation of the same substrate gave a mixture of products (Scheme 16).

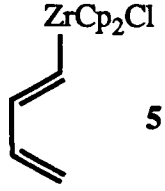
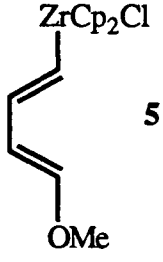
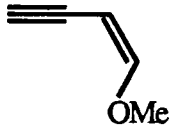
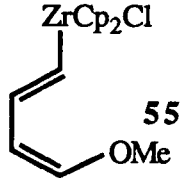
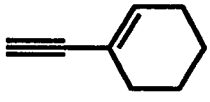
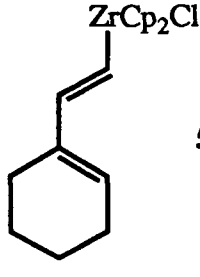


Scheme 16

It was found that the room temperature reaction of hydride **1** with a series of 1-ene-3-yne molecules **51a-d** generated the desired 1,3-dienylzirconium complexes **55a-d** in good yields (81-90%).[53] Thus, the syntheses of 1,3-dienes of the type **A** where ML_n is $ZrCp_2Cl$ can be readily achieved (Table I). Although other examples of chemoselective hydrometalation of 1-ene-3-ynes are known,[54] hydrozirconation of the unsubstituted 1-buten-3-yne **51a**, to our knowledge is the most selective and highest yielding. Dienes **55a-d** exhibited strong absorptions in the IR from 1600-1621 cm^{-1}, which are characteristic of molecules containing a 1,3-dienyl moiety.

The 1-ene-3-ynes **51a** and **51c** were commercially available, whereas **51b** and **51d** were synthesized by literature procedures.[55] The hydride $Cp_2ZrCl(H)$ **1**, although commercially available, was prepared in our laboratory by the reaction of lithium tri-*tert*-

Table I: Preparation of 1,3-dienylzirconium complexes **55a-d**.

Entry	1-ene-3-yne[a]	1,3-dienylzirconium complex	yield[b] (%)
1	 **51a**	 **55a**	81
2	 4:1 E:Z **51b**	 **55b**	85
3	 **51c**	 **55c**	83
4	 **51d**	 **55d**	90

[a] **51a** and **51c** were purchased from Pfaltz and Bauer and the Aldrich Chemical Co., respectively.

[b] Yields of isolated, crystalline products.

butoxyaluminohydride [LiAl(*t*-BuO)$_3$H] and dichlorobis(η^5-cyclopentadienyl)zirconium(IV) (Cp_2ZrCl_2) (equation 21).

$$LiAl(t\text{-}BuO)_3H \quad + \quad Cp_2ZrCl_2 \xrightarrow[\text{dark}\ \text{THF}]{\text{R.T.}} Cp_2ZrCl(H) \quad \mathbf{1} \qquad (21)$$

As shown in Table I, the 1-ene-3-yne **51b** was isolated as an inseparable mixture of geometric isomers. The ratio of these isomers was determined to be approximately 4:1 E/Z by ^{1}H NMR spectroscopy and GLC. However, reaction of this isomeric mixture, using a sufficient excess of **51b** to allow for 1 equivalent of the E isomer, gave the desired 1,3-dienylzirconium complex **55b**. The ^{1}H NMR spectrum of **55b** indicated that the required E,E isomer had been obtained (Figure 3). The most diagnostic data, obtained from the ^{1}H NMR spectrum, confirming the stereochemistry of **55b**, were the J_{AB} and J_{CD} coupling constants which were measured as 18 Hz and 13 Hz, respectively.[56] In the initial crystallized batches of **55b**, the presence of 3-5% of the E,Z isomer (**55c**), could be readily detected by ^{1}H NMR spectroscopy. This isomeric impurity was easily removed by further recrystallizations.

The hydrozirconation of **51c** proceeded more slowly than that of the isomeric mixture **51b**, when an excess of the latter is used to provide one equivalent of the E isomer. This empirical observation was made by measuring the time required for the formation of a homogeneous solution (i.e., complete reaction of the insoluble hydride **1**) in separate reactions of **51b** and **51c**. Both reactions were carried out under identical conditions. This observed difference in rate of reaction may account for the almost exclusive formation of **55b** from an E/Z mixture of the 1-ene-3-yne **51b**.

The ^{1}H NMR spectrum of **55c**, readily interpreted as that of the E,Z isomer, showed coupling constants for J_{AB} and J_{CD} of 18 Hz and 6 Hz, respectively (Figure 4).[56] There was

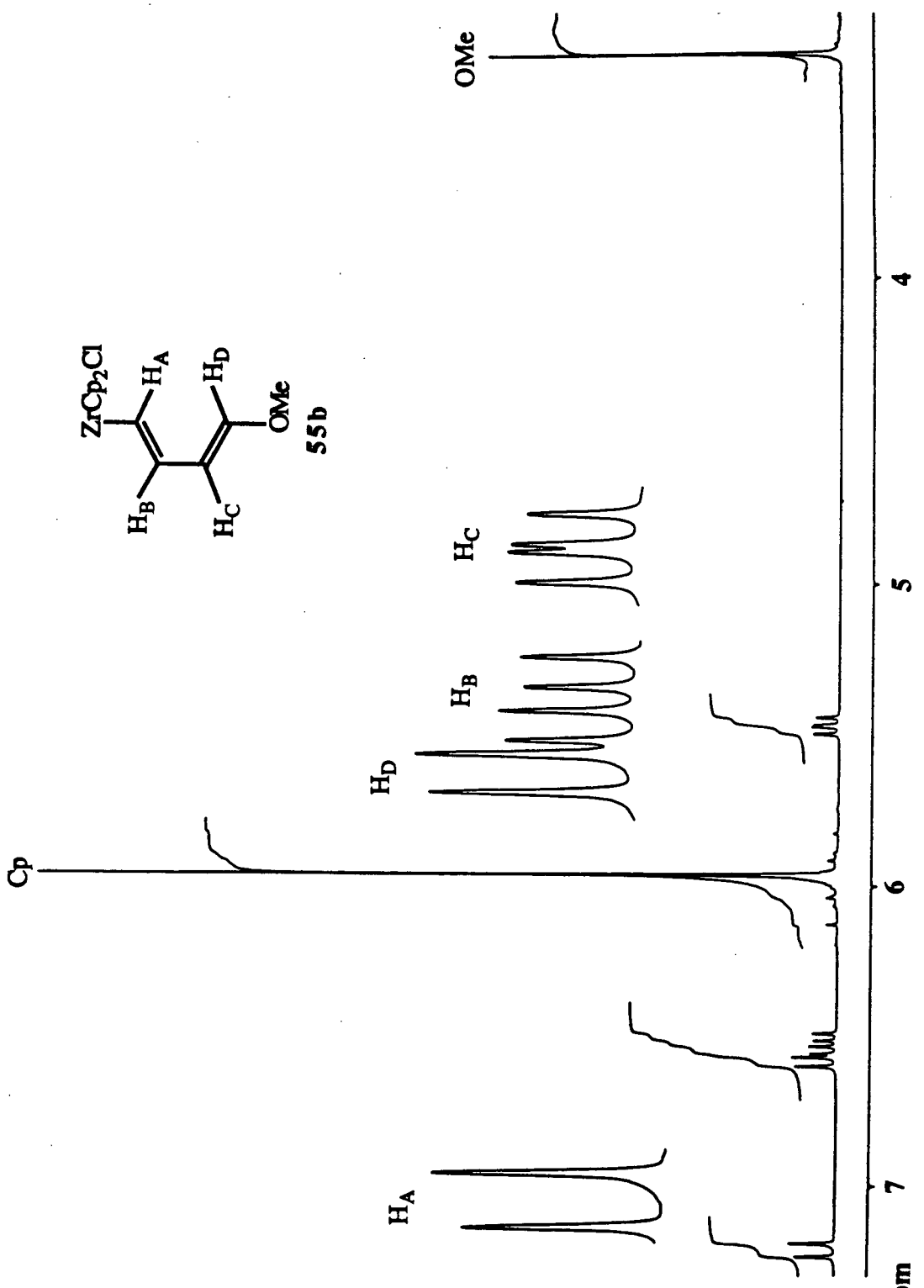


Figure 3. 400 MHz ^1H NMR spectrum of **55b** in C_6D_6.

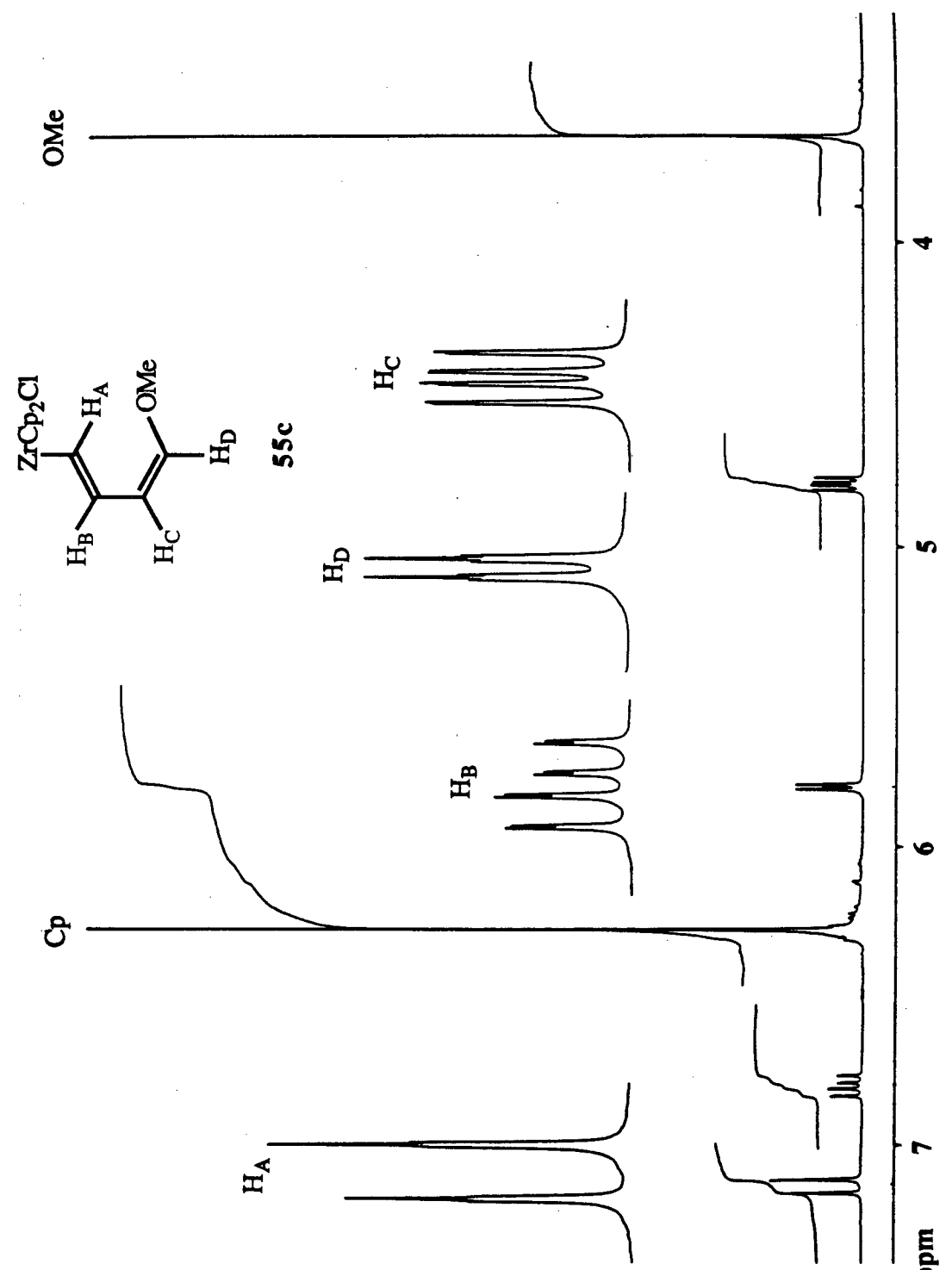


Figure 4. 400 MHz ^{1}H NMR spectrum of **55c** in $CDCl_3$.

no evidence of any double bond isomerization during the hydrozirconation of **51c**, as indicated by the absence of any of the isomeric complex **55b**.

The assignment of protons H_A and H_B for the complex **55d** derived from NOEDIFF (nuclear Overhauser effect difference) spectroscopy. Irradiation of H_C gave clean enhancement of H_B and of the neighboring allylic protons (Figure 5). Further evidence for this assignment

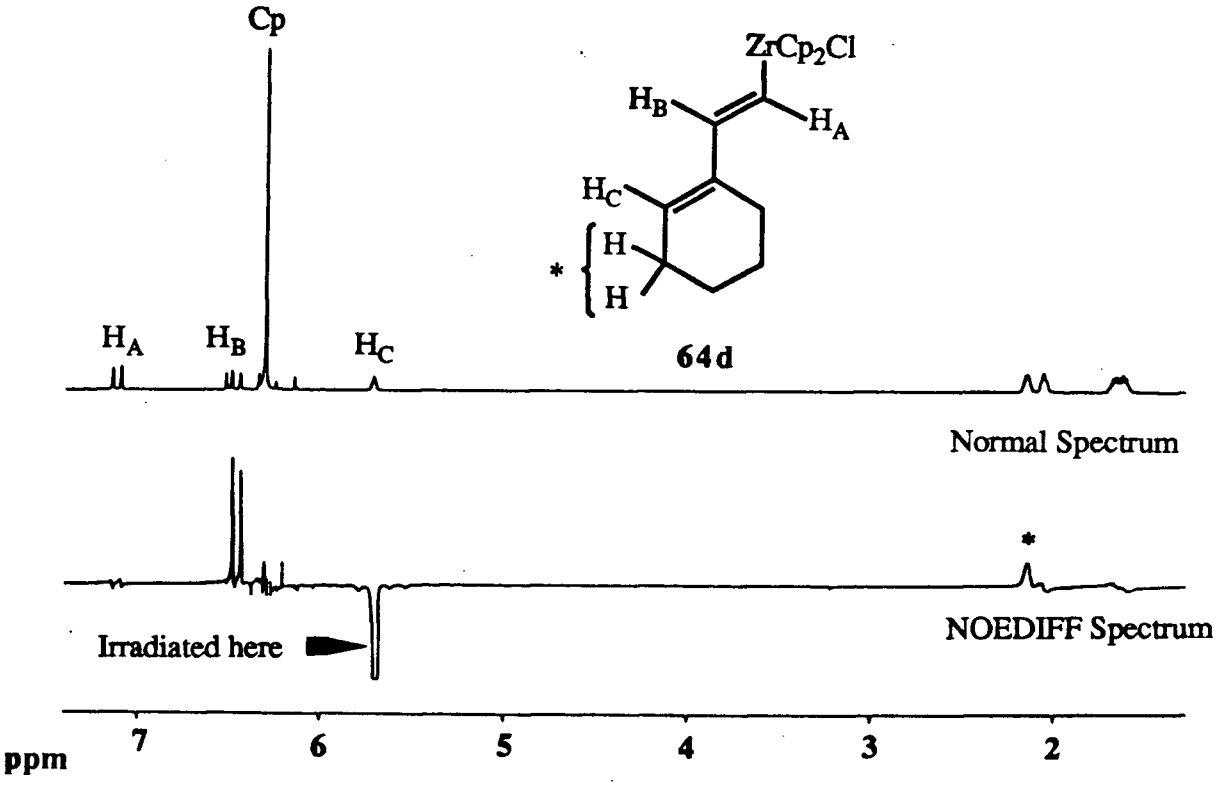
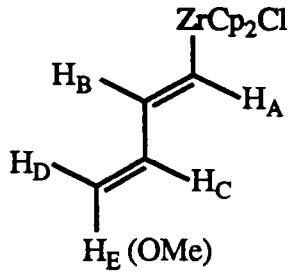


Figure 5. 400 MHz ^{1}H NMR and NOEDIFF spectra of **55d** in C_6D_6.

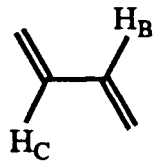
was obtained from deuterium labelling studies (vide infra). Interestingly, for the complex **55d**, decoupling experiments indicated a five-bond coupling of H_A to H_C of 0.75 Hz.[56]

Comparison of the $^3J_{BC}$ coupling constants of the dienes **55a** and **55b**, with those of 1,3-butadiene,[57] suggest that these dienes adopt the s-trans conformation in solution (Figure 6). The $^3J_{BC}$ coupling constants for **55a** and **55b** were both measured as 10.0 Hz; this correlates well with the literature value for s-trans 1,3-butadiene of 10.7 Hz.[57] The lower value of 8.5 Hz for the $^3J_{BC}$ coupling constant of the complex **55c** may represent a deviation

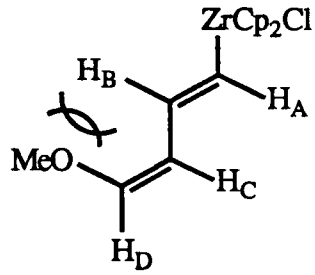


55a-b

$^3J_{BC}$ = 10.0 Hz



$^3J_{BC}$ = 10.7 Hz



55c

$^3J_{BC}$ = 8.5 Hz

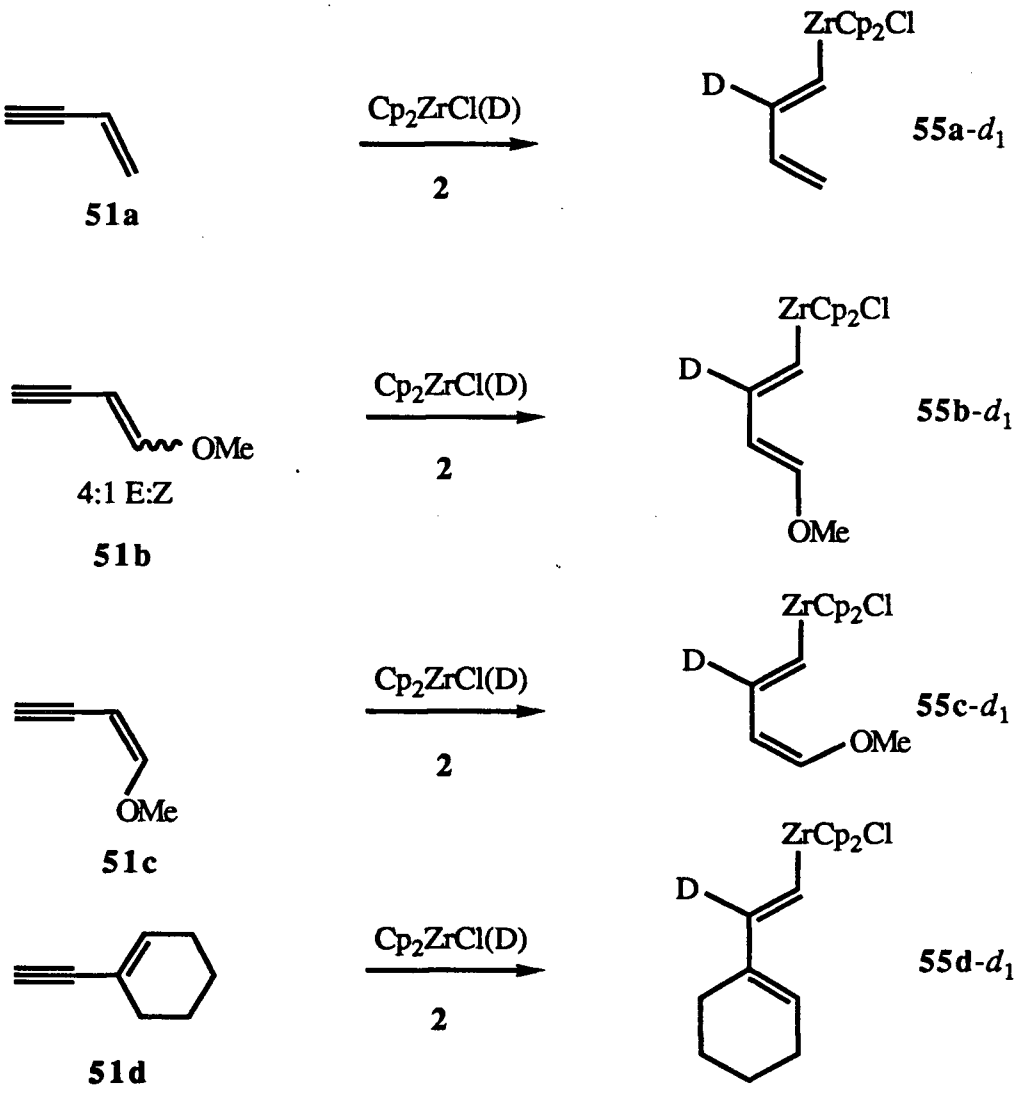
Figure 6. Conformation of **55a-c**, as related to 1,3-butadiene.

from planarity in the 1,3-butadiene fragment. This could be due to steric repulsion between the OMe group and H_B. The conformation of the diene **55d** cannot be determined by this method. However, the results of the NOEDIFF experiment (vide supra) suggest that it is likely s-trans or slightly skewed from that planar conformation. If the conformation was s-cis or close to that orientation, some enhancement of H_A would be expected.

2.1.1 Deuterium-Labelling Studies.

In an attempt to obtain some mechanistic information regarding the chemoselective hydrozirconation of 1-ene-3-ynes, the insertion reactions of the deuterated analogue of **1**, $Cp_2ZrCl(D)$ **2** were investigated.

When the reactions of **51a-d** with **2** were carried out, analysis of the products (**55a-d**-d_1) by ^1H NMR spectroscopy showed that no scrambling of the deuteron label had occurred (Scheme 17). This fact can be readily seen by comparison of the ^1H NMR spectra of



Scheme 17

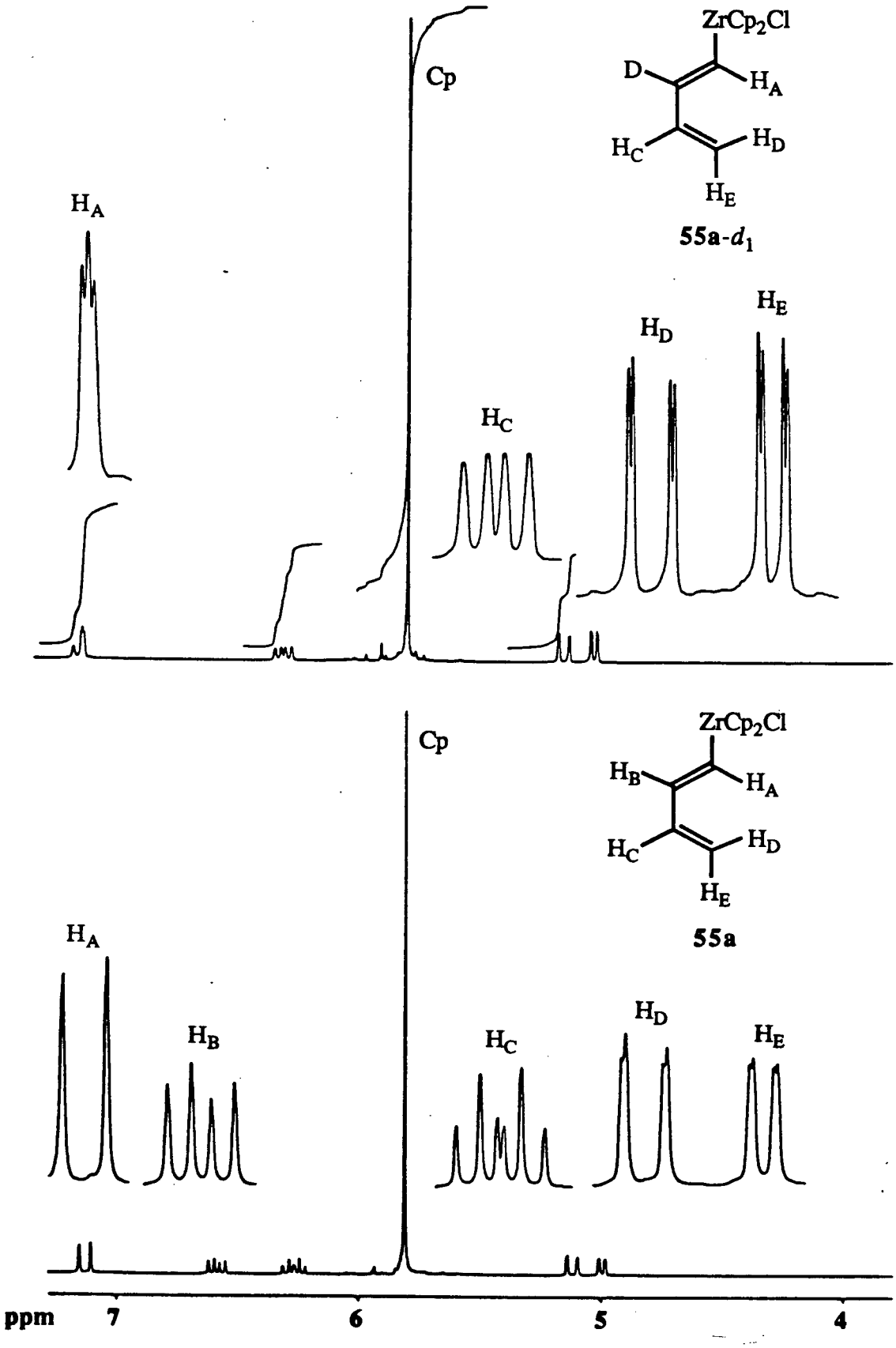


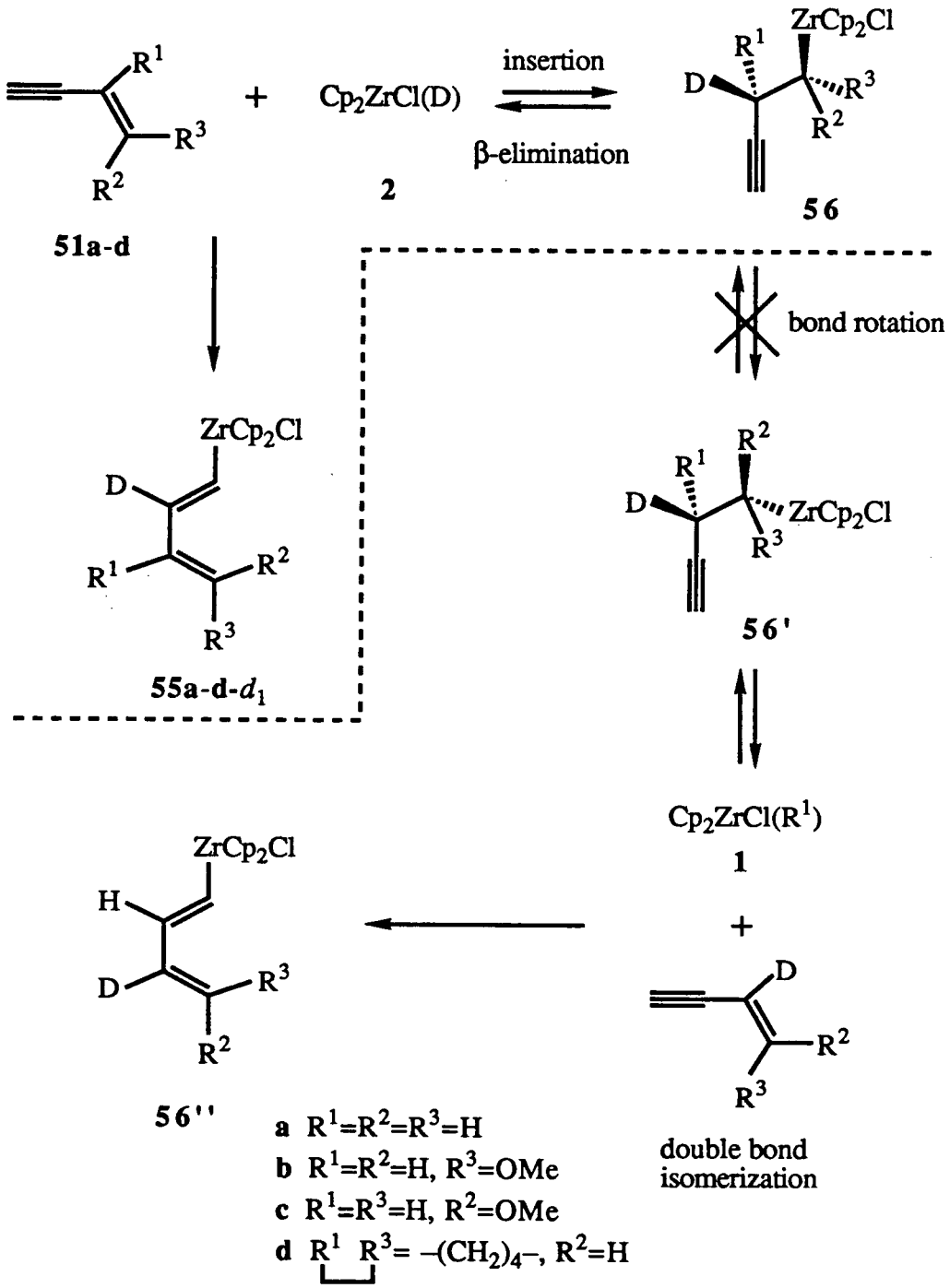
Figure 7. 400 MHz ^{1}H NMR spectra of **55a** and **55a**-d_1.

the dienes **55a** and **55a**-d_1 (Figure 7). In the ^{1}H NMR spectrum of the latter complex, the resonance attributable to H_B is now absent and the resonance for H_A has collapsed to a pseudo-1:1:1 triplet. The latter resonance shows a 2.5 Hz coupling to deuterium, which correlates well with the expected value of approximately 3 Hz. Finally, the resonance for H_C has reduced to a doublet of doublets, showing some broadening due to fine coupling to deuterium.

Similar observations were made from the ^{1}H NMR spectra of the complexes **55b-d**-d_1. Analysis of the ^{1}H NMR spectra of these deuterated complexes indicated that, as for **55a**-d_1, the deuteron label was incorporated exclusively at the β-carbon, cis to the $ZrCp_2Cl$ moiety.

The above results are consistent with a mechanism which involves direct, irreversible insertion of the alkyne functionality of **51a-d** into the Zr-D bond of hydride **2**, thereby placing the deuteron label exclusively at the β-carbon. Such a process would therefore imply a kinetic preference for insertion of the alkyne functionality over the alkene group.

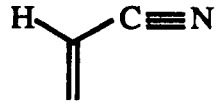
Another possible mechanism which could account for the observed chemoselectivity of this insertion reaction is shown in Scheme 18 (next page). Insertion of the alkene functionality of 1-ene-3-ynes **51a-d** would give the complex **56**. If this complex then underwent β-elimination (to regenerate starting materials) more rapidly than bond rotation to give **56'**, followed by irreversible insertion of the alkyne functionality to form **55a-d**-d_1, no scrambling of the deuteron label would be observed. However, if the reverse argument was true (i.e., bond rotation being faster than β-elimination) one would expect to observe double bond isomerization, as well as scrambling of the deuteron label (**56''**). In the hydrozirconation of **51c** no double bond isomerization was observed, thus suggesting that for **56** β–elimination is faster than bond rotation. This mechanism would suggest a thermodynamic preference for the alkyne functionality. Therefore, based on the results of the deuterium-labelling experiments it was not possible to determine whether the chemoselectivity was due to a kinetic- or thermodynamically-controlled process.


insertion
β-elimination
Cp2ZrCl(D)
2
51a-d
56
bond rotation
55a-d-d1
56'
Cp2ZrCl(R1)
1
double bond
isomerization
56''
a R1=R2=R3=H
b R1=R2=H, R3=OMe
c R1=R3=H, R2=OMe
d R1 R3= –(CH2)4–, R2=H

Scheme 18

2.2 Hydrozirconation of Nitriles and α,β-Unsaturated Nitriles.

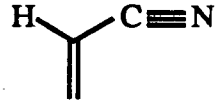
Other workers have investigated the hydrometalation of α,β-unsaturated nitriles. Reaction of acrylonitrile **57** with triphenylgermane **58** gave the addition product **59**, thus exhibiting exclusive reaction with the alkene functionality (equation 22).[58] An extensive study



$$+ \quad Ph_3GeH \longrightarrow Ph_3Ge(CH_2)_2C{\equiv}N \qquad (22)$$

57 **58** **59**

of the hydrostannation of acrylonitrile,[59] also revealed exclusive reaction with the alkene functionality of **57**, to give a mixture of α- and β-isomers **60** and **61**, respectively. The ratio of the isomers was determined by the reaction conditions and the type of stannane used (equation 23).[59]



$$+ \quad R_3SnH \longrightarrow R_3Sn{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C{\equiv}N \qquad (23)$$

57

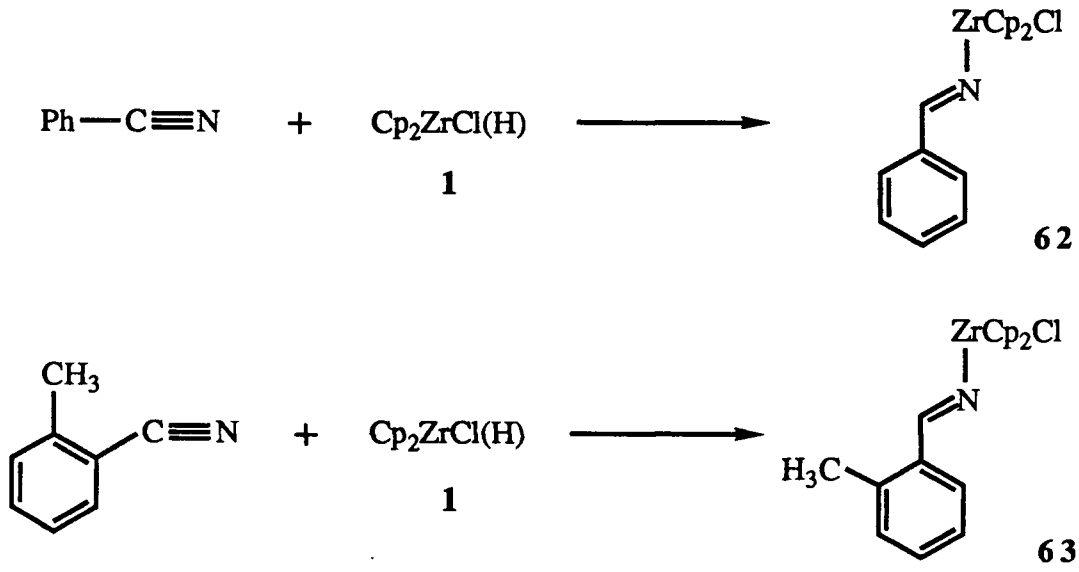
α-isomer **60**

+

$R_3Sn(CH_2)_2C{\equiv}N$

β-isomer **61**

Previous workers[17] have shown that insertion of the nitrile functionality into the metal-hydride bond of $Cp_2ZrCl(H)$ **1** is a facile process. In analogy to the insertion of alkynes with **1**, these workers assumed that the process occurred with overall cis stereochemistry, with the zirconium bonded to the nitrogen, the least sterically demanding position. The syntheses of the known imine zirconium complex **62**, and the hitherto unknown analogue **63** were performed (Scheme 19). Erker and co-workers[60] have shown, by X-ray analysis, that the



Scheme 19

complex **62** has a heteroallene-type structure, with a near linear Zr–N=C fragment (Figure 8). Such a structure is believed to arise from donation of the nitrogen lone-pair of electrons into the empty d-orbital of the zirconium, thus giving formally an 18-electron complex.[60]

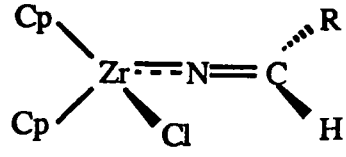
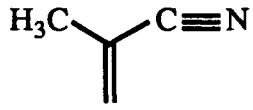
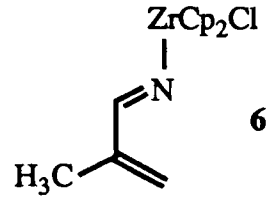
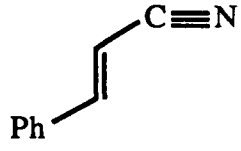
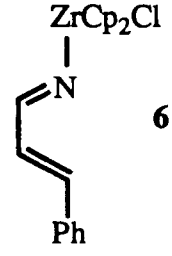
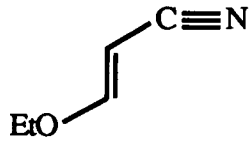
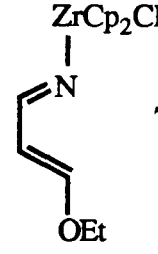
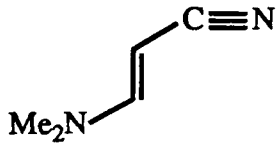
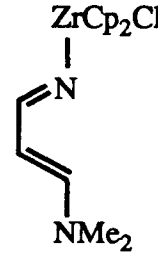


Figure 8. Heteroallene-type structure for **62**.

In line with the observed chemoselectivity in the hydrozirconation of 1-ene-3-ynes, the analogous reactions with α,β-unsaturated nitriles were investigated. It was discovered that reactions of a series of commercially available α,β-unsaturated nitriles **64-67** with the hydride **1**, at room temperature, gave the desired 1-azadienylzirconium complexes **68-71** in good yields (77-85%), as shown in Table II. As hoped, a chemoselective insertion of the nitrile functionality in the presence of the alkene group was observed.

Table II: Preparation of 1-azadienylzirconium complexes **68-71**.

Entry	α,β-unsaturated nitrile[a]	1-azadienylzirconium complex	yield[b] (%)
1	 **64**	 **68**	85
2	 **65**	 **69**	78
3	 **66**	 **70**	81
4	 **67**	 **71**	77

[a] Nitriles **64-67** were purchased from Aldrich Chemical Co., and were purified by distillation prior to use.

[b] Yields of isolated, crystalline products.

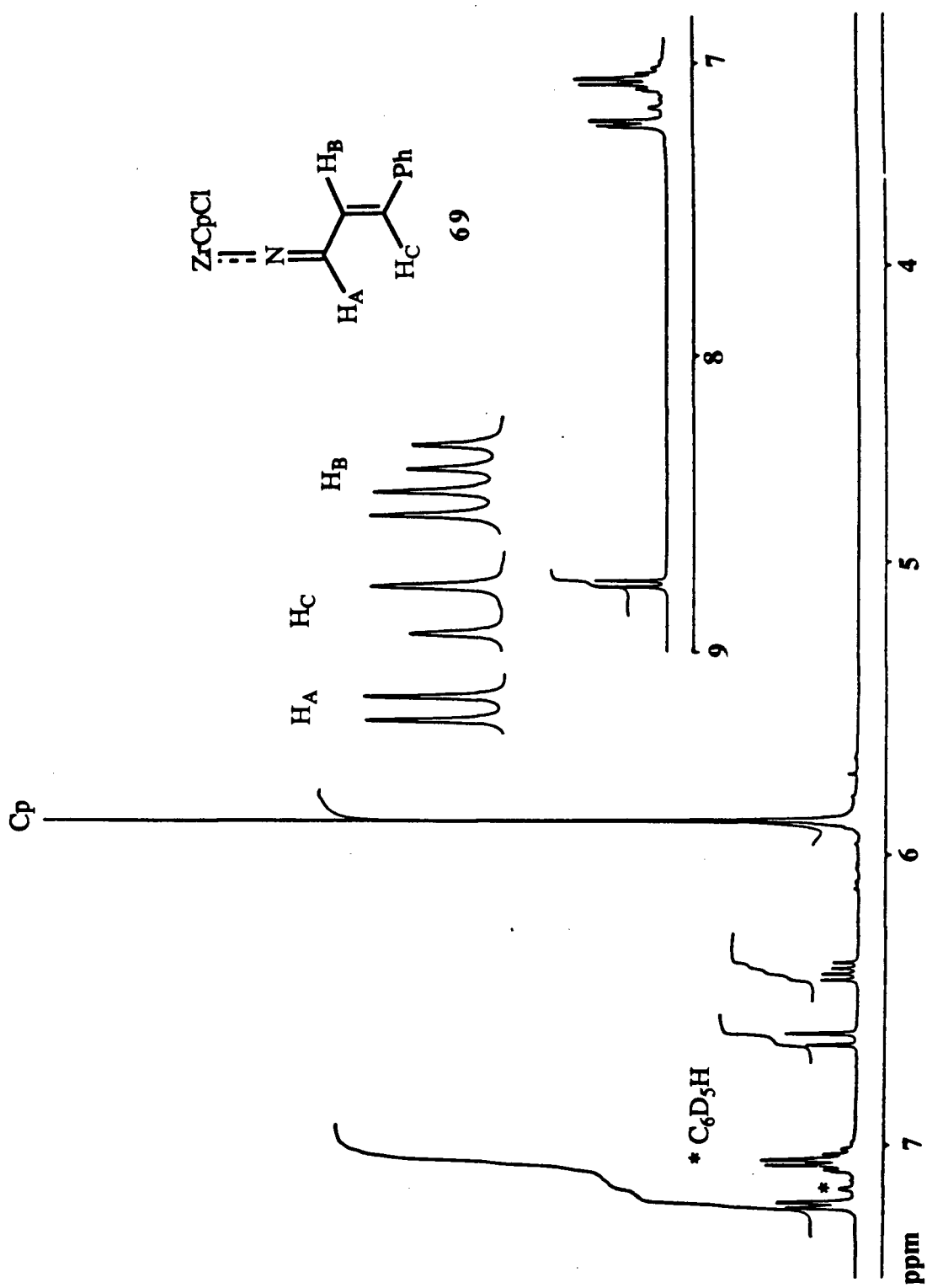


Figure 9. 400 MHz ^{1}H NMR spectrum of **69** in C_6D_6.

The exact nature of the structure in the Zr–N=C fragment of the 1-azadienylzirconium complexes **68-71** could not be clearly determined by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum for complex **69** is shown in Figure 9. To provide an answer to this structural question, crystals of the complex **69** were obtained from toluene/hexanes solution and a single crystal was subjected to X-ray analysis. The analysis was performed by Dr. R. Chadha of the University of Manitoba; the details of the data collection and refinement will be reported elsewhere. An ORTEP diagram of the molecular structure of **69**, as well as selected bond lengths and angles can be seen in Figure 10 (next page).

The most striking feature of the molecular structure of **69** is the almost linear Zr–N=C(1) fragment. The bond angle of the latter fragment was determined to be 167(2)°; this compares favorably with Erker's structure of the complex **62**, where the corresponding bond angle was measured as 170.5(5)°.[60] The Zr–N bond distance for the complex **69** was found to be 2.03(2) Å, as compared with a distance of 2.013(2) Å for **62**.

Based on the X-ray data obtained for the complex **69**, the products from the chemoselective hydrozirconation of α,β-unsaturated nitriles **64-67** cannot be, formally, regarded as 1-azadienyl complexes. Instead, it would be more correct to consider them as having the heteroallene-type structure shown in Figure 11.

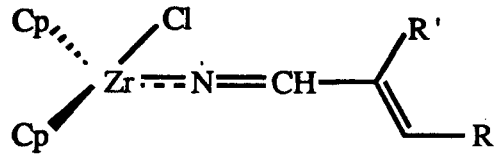
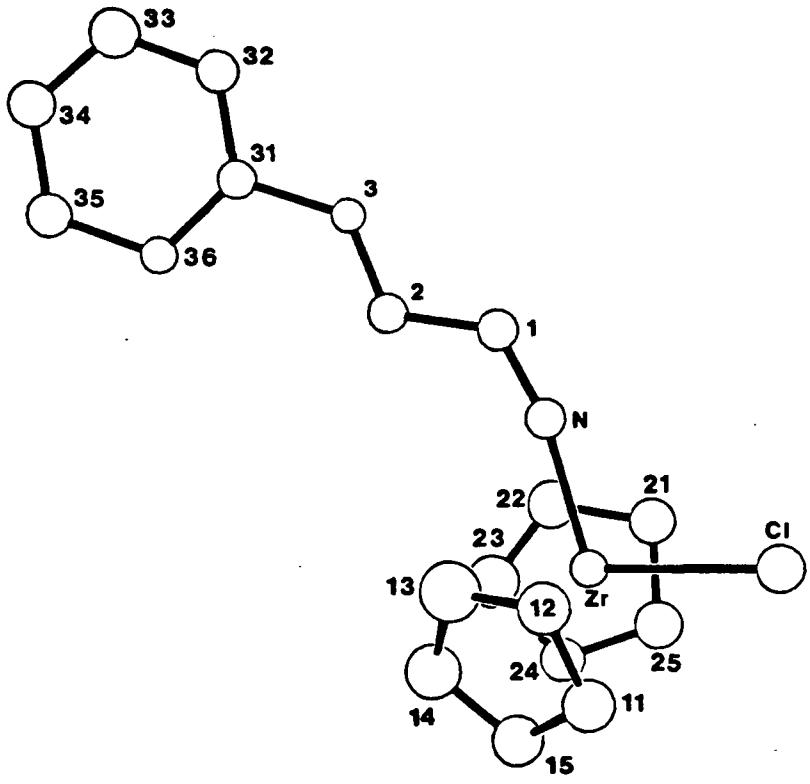


Figure 11. **Proposed solid state conformation for the complexes 68-71.**

That these compounds **68-71** can be regarded as being 18-electron species may account for their enhanced stability in air as compared to the very air sensitive, formally 16-electron, 1,3-dienylzirconium complexes **55a-d**.



Selected bond lengths (Å) and angles (°) for **69**

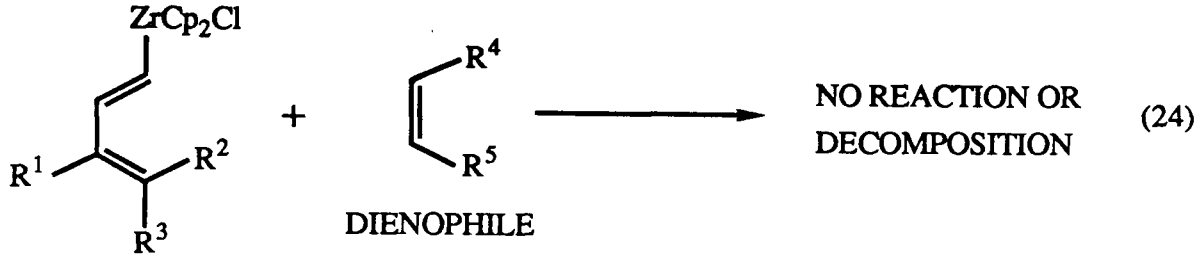
Zr—Cl	2.505(7)	C(1)—C(2)	1.44(3)
Zr—N	2.03(2)	C(2)—C(3)	1.34(3)
N—C(1)	1.28(3)	C(3)—C(31)	1.48(3)

Cl–Zr–N	102.2(6)	C(2)–C(3)–C(31)	119(2)
Zr–N–C(1)	167(2)	C(3)–C(31)–C(32)	119(2)
N–C(1)–C(2)	126(2)	C(3)–C(31)–C(36)	119(2)
C(1)–C(2)–C(3)	119(2)		

Figure 10. Molecular structure and selected bond lengths and angles for **69**.

2.3 Carbonylation and Attempted Diels-Alder Reactions of 1,3-Dienylzirconium Complexes.

Initial investigations of the reactivity of complexes **55a-d** began with the complex **55b** as a potentially reactive diene in the Diels-Alder reaction. Reaction of **55b** with a variety of dienophiles (methyl acrylate, methacrylonitrile, maleic anhydride and dimethyl acetylenedicarboxylate) at room temperature or at elevated temperatures, gave either no reaction or led to decomposition of the diene (equation 24). However, room temperature reaction of



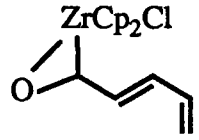
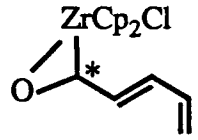
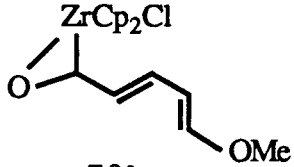
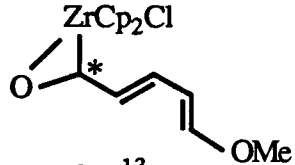
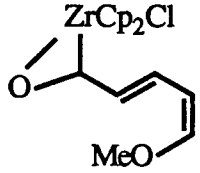
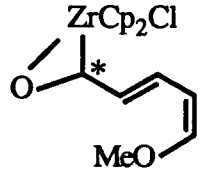
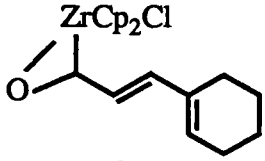
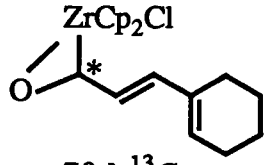
55a-d

either **55b** or **55c** with tetracyanoethene gave low yields (20-30%) of orange solids. The ^{1}H NMR spectra of these solids were extremely simple but structurally uninformative. Attempts to characterize these complexes further by IR, MS and microanalysis were unsuccessful. Therefore, due to the poor isolated yields and the inability to grow single crystals for X-ray analysis, further work on these complexes was abandoned.

The lack of reactivity of the 1,3-dienylzirconium complexes **55a-d** in the Diels-Alder reaction is, with hindsight, perhaps understandable if one considers that the bulky, electron-poor $ZrCp_2Cl$ substituent is unlikely to greatly activate the diene towards reaction with electron-deficient dienophiles.

The carbonylation reaction of alkenylzirconium complexes has been shown to be an important step in the stereocontrolled preparation of various α,β-unsaturated acyl derivatives.[26] As such, the reactivity of the complexes **55a-d** with carbon monoxide was

Table III: Carbonylation reactions of **55a-d** with CO and ^{13}CO; IR and ^{13}C NMR data.

Reaction with CO	Reaction[a] with ^{13}CO	IR (cm^{-1})[b] η^2-acyl	^{13}C NMR (ppm)[c] η^2-acyl	Yield[d] (%)
 **70a**	 **70a-^{13}C**	1499 (1439)	301	73 (66)
 **70b**	 **70b-^{13}C**	1468 (1426)	293	83 (72)
 **70c**	 **70c-^{13}C**	1492 (1447)	296	68 (61)
 **70d**	 **70d-^{13}C**	1498 (1444)	298	82 (80)

[a] The symbol * denotes the position of the ^{13}C label.

[b] The η^2-acyl absorptions for the ^{13}C-labelled complexes are shown in parenthesis.

[c] These resonances are for the ^{13}C-labelled complexes.

[d] Yields are not optimized; yields for the ^{13}C-labelled complexes are shown in parenthesis.

investigated. Exposure of a toluene solution of these dienes to one atmosphere of CO produced an immediate color change, followed within 2-3 minutes by precipitation of a yellow-orange solid, the structures of which were determined by NMR and IR spectroscopy.

Initial analysis of these CO "insertion" products **70a-d** by IR spectroscopy indicated strong absorptions characteristic of the η^2-acyl moiety (Table III). That these IR absorptions are characteristic of the η^2-acyl moiety is evident from other literature examples.[61] Further evidence for the assignment of these particular IR bands as the η^2-acyl absorptions was obtained by the preparation and characterization of the corresponding ^{13}C-labelled complexes **70a-d**-^{13}C (the ^{13}CO used was 90 atom % ^{13}C). The IR stretching frequency of these η^2-acyl complexes is shown in parenthesis in the appropriate column of Table III. The observed shifts obtained by using ^{13}CO are in good agreement with the calculated values.

Additional evidence for the η^2-acyl functionality present in the complexes **70a-d**-^{13}C was obtained from ^{13}C NMR spectroscopy. As observed by previous workers,[61] η^2-acyl complexes exhibit a resonance for the acyl carbon at remarkably low field. Resonances for the complexes **70a-d**-^{13}C were observed in the region 293-301 ppm, in good agreement with the values observed for other η^2-acyl complexes of zirconium.[61]

The ^{1}H NMR assignments for the complex **70d** were based on the results from both NOEDIFF spectroscopy and deuterium-labelling experiments. Irradiation of proton H_C resulted in a clean enhancement of proton H_B and the corresponding allylic protons (Figure 12, next page). It was possible to differentiate between protons H_A and H_B by comparison of the ^{1}H NMR spectra of the complex **70d** and its deuterium-labelled analogue **70d**-d_1 (synthesized by reaction of the complex **55d**-d_1 with CO). The ^{1}H NMR spectra of the complexes **70d** and **70d**-d_1, along with that of the ^{13}C-labelled complex **70d**-^{13}C are shown in Figure 13 (p 47). From the ^{1}H NMR spectrum of **70**-^{13}C is was possible to obtain values for the ^{13}C-^{1}H coupling constants for protons H_A and H_B. These values were measured as 2 Hz and 7.5 Hz, respectively. The magnitude of these coupling constants lends further credence to the assignments made for protons H_A and H_B.[56a]

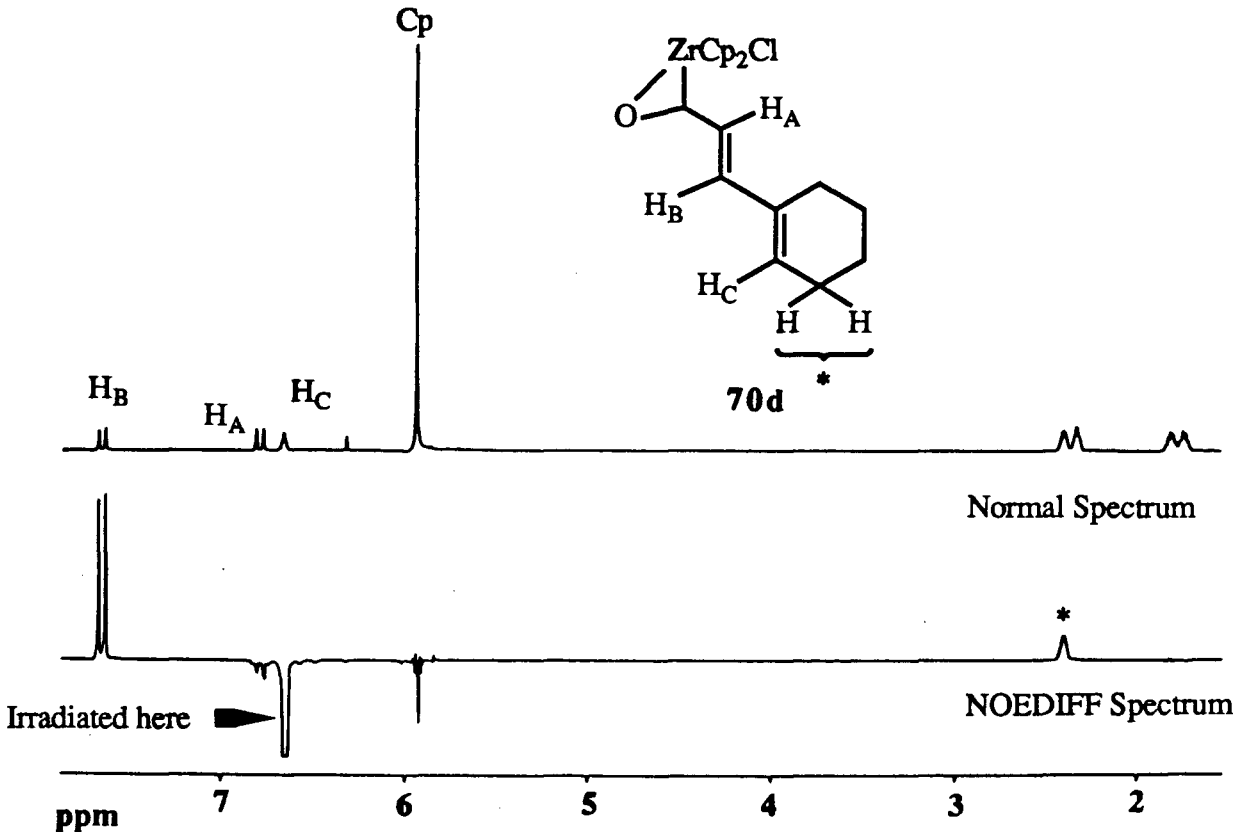


Figure 12. 400 MHz ^{1}H NMR and NOEDIFF spectra of **70d** in $CDCl_3$.

The assignments of the ^{13}C NMR spectra of complexes **70a-d**-^{13}C were determined by use of two-dimensional (2D) NMR experiments. As the dienyl-proton resonances of these complexes had already been assigned, it was possible to identify the corresponding ^{13}C resonances by analyses of the 2D ^{13}C-^{1}H heteronuclear NMR correlation maps. Having identified particular proton resonances, these connectivity maps allow the ^{13}C nucleus directly bound to each proton to be assigned. The 2D ^{13}C-^{1}H heteronuclear NMR correlation map, along with partial ^{13}C and ^{1}H NMR spectra for **70b**-^{13}C are shown in Figure 14 (p 48). The ^{13}C-^{13}C and the ^{13}C-^{1}H coupling constants for **70a-d**-^{13}C are given in Table IV (p 49). In general, for these complexes, it was observed that the two-bond ^{13}C-^{13}C coupling constants were slightly larger than the three-bond ^{13}C-^{13}C couplings constants. This observation was in

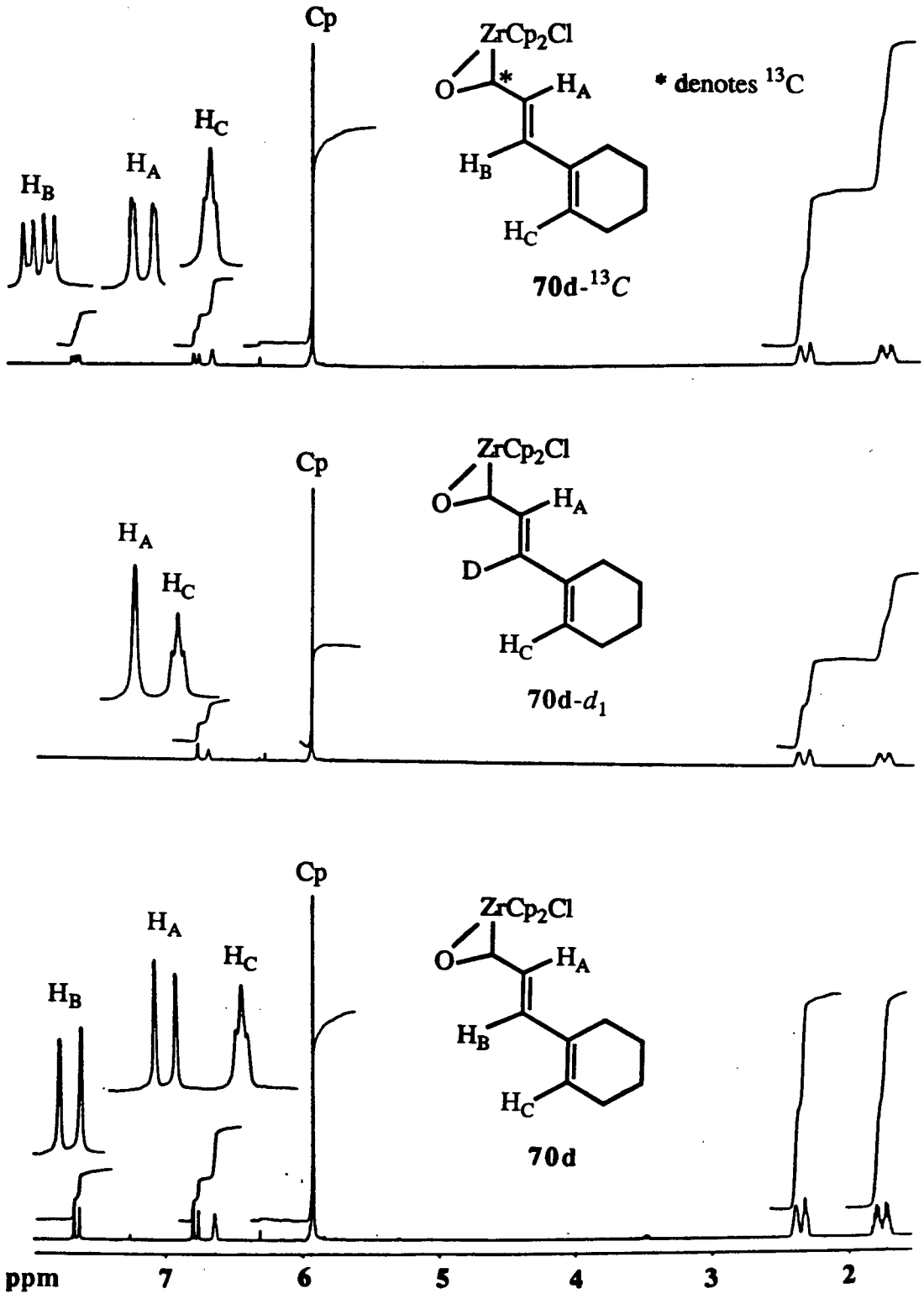


Figure 13. 400 MHz ^{1}H NMR spectra of **70d**, **70d**-d_1, **70d**-^{13}C in $CDCl_3$.

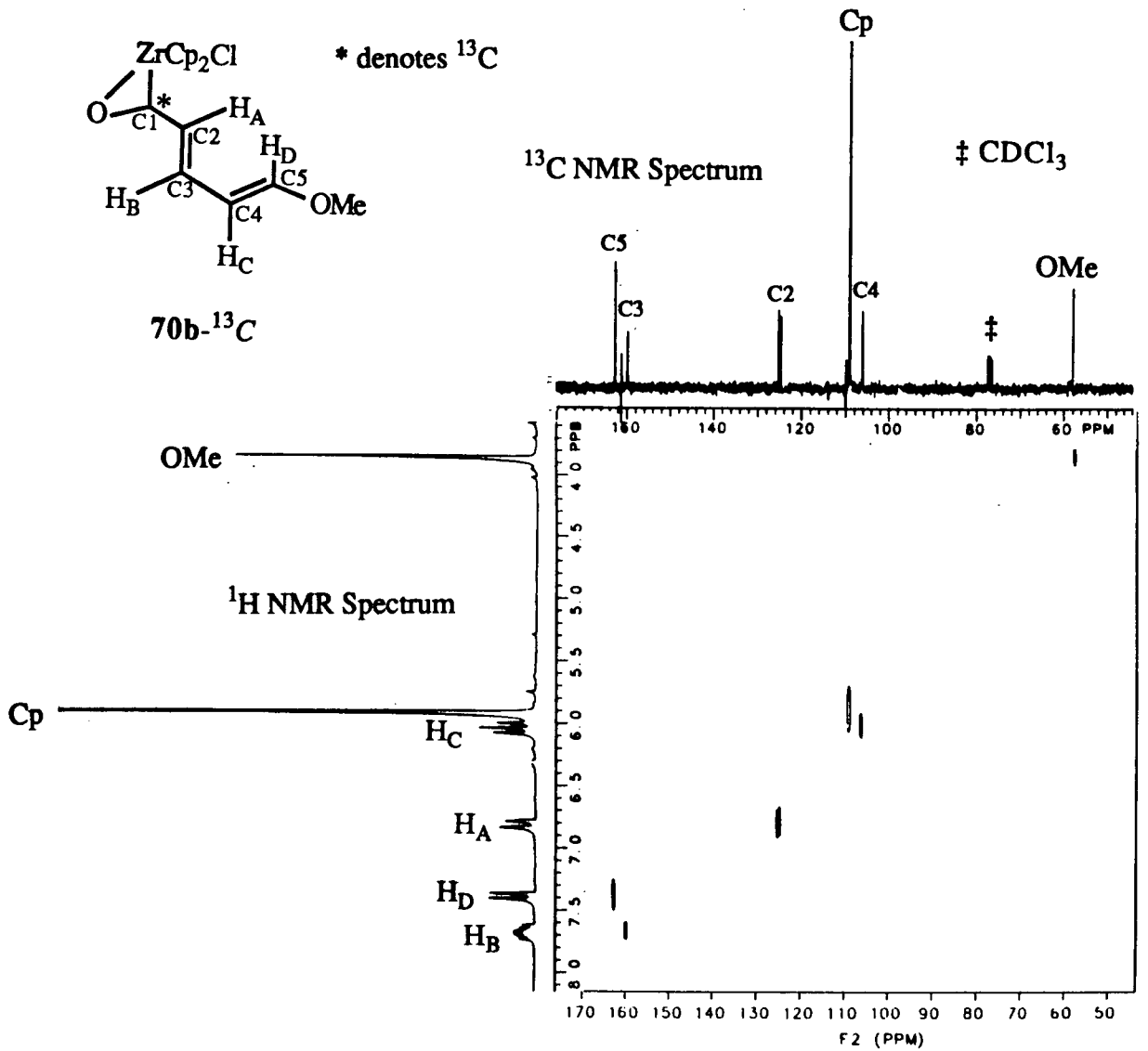
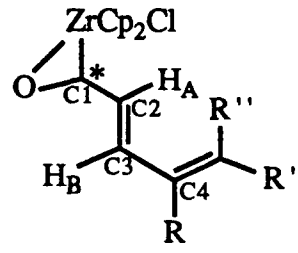
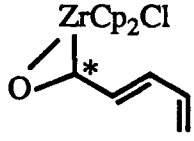
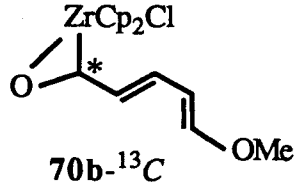
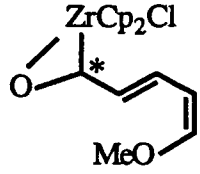
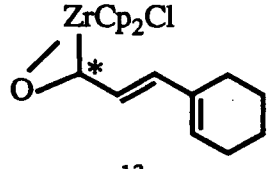


Figure 14. Portion of the ^{13}C-^{1}H heterocorrelation 75-300 MHz spectrum for **70b**-^{13}C in $CDCl_3$.

Table IV: ^{13}C–^{13}C and ^{13}C–^{1}H coupling constants for complexes **70a-d**-d_1.



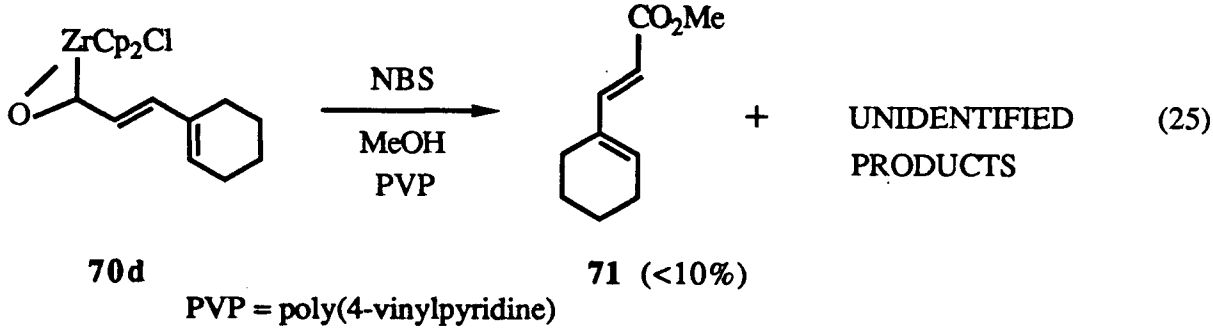
Complex[a]	$^{1}J_{C1C2}$ (Hz)	$^{2}J_{C1C3}$ (Hz)	$^{3}J_{C1C4}$ (Hz)	$^{2}J_{C1H_A}$ (Hz)	$^{3}J_{C1H_B}$ (Hz)
 **70a**-^{13}C	34.5	9.8	8.8	b	8.0
 **70b**-^{13}C	36.7	11.6	8.2	2.5	7.0
 **70c**-^{13}C	35.8	10.6	8.7	2.5	7.5
 **70d**-^{13}C	35.4	10.4	9.5	2.0	7.5

[a] The symbol * denotes the position of the ^{13}C label.

[b] No coupling was observed.

contrast to the ^{13}C-^{13}C coupling constants measured for a series of ^{13}C-labelled aromatic compounds, in which the opposite order was noted.[62]

Attempts to prepare the corresponding methyl dienyl ester of **70d** by reaction with *N*-bromosuccinimide (NBS), followed by addition of ~10 equivalents of methanol, resulted in the isolation of a mixture of products in which the desired ester **71** was present in less than 10% (by ^1H NMR spectroscopy) (equation 25). The other products were not identified. As



various changes in the reaction conditions produced no improvement in the overall yield of **71** this reaction was abandoned.

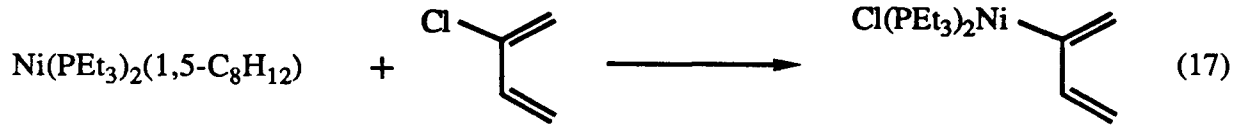
Having successfully prepared a series of 1,3-dienylzirconium complexes **55a-d**, their ability to serve as general precursors in the preparation of other heterosubstituted 1,3-dienes remained to be investigated. The results of this investigation are outlined in Chapter 3.

CHAPTER 3

Preparation of Heterosubstituted 1,3-Dienes, Imines and 1-Azadienes by a Transfer Reaction from Zirconium.

3.1 Preparation of a 1,3-Dienylnickel Complex.

As mentioned previously in Chapter 1, the synthesis of a 2-substituted 1,3-butadienylnickel complex **32** has already been achieved.[45] Complex **32** was synthesized by oxidative addition of 2-chloro-1,3-butadiene **31** to a nickel(0) complex **30** (equation 17). It



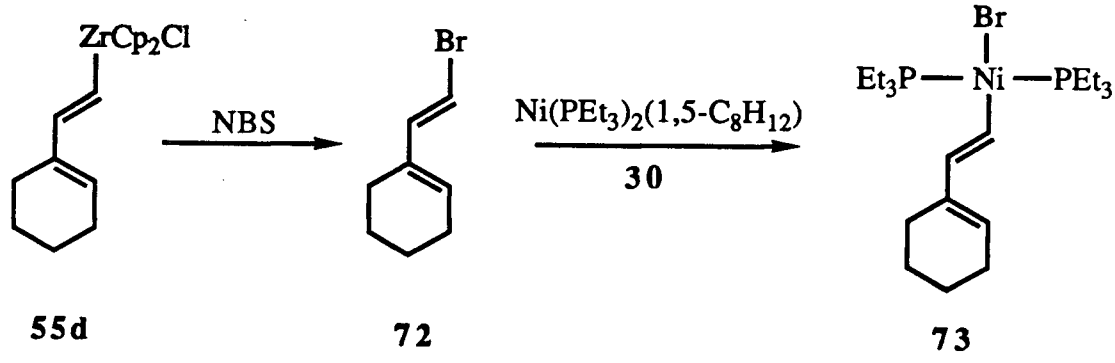
(17)

30 **31** **32**

was envisaged that by combining the chemoselective hydrozirconation reaction with the oxidative addition to nickel(0) complexes, a method for the preparation of 1-substituted 1,3-dienylnickel complexes could be developed.

Previous workers[13] have shown that reaction of alkenylzirconium complexes with *N*-bromosuccinimide (NBS) proceeds readily to generate the corresponding alkenyl bromide with retention of stereochemistry about the double bond (see equation 6, p 11). When complex **55d** was reacted with NBS at room temperature, the desired bromodiene **72** was obtained in 89% isolated yield. Oxidative addition of **72** to $Ni(PEt_3)_2(1,5\text{-}C_8H_{12})$ **30** proceeded rapidly at

room temperature to give, on workup, orange crystals of the 1,3-dienylnickel(II) complex **73** (equation 26).



55d **72** **73** (26)

The ^1H NMR spectrum of complex **73** is shown in Figure 15. The resonances for protons H_A and H_B appear as a tightly coupled ABX_2 spin system, with the AB quartet for H_A and H_B, being further coupled to two equivalent phosphines. Thus, it was not possible to directly assign the stereochemistry of complex **73** from its ^1H NMR spectrum. However, there are sufficient literature examples of oxidative addition reactions of vinyl halides to nickel(0) complexes to conclude that, in general, such processes occur with retention of stereochemistry.[35b,63] The assigned stereochemistry for bromodiene **72** is based on the $^3J_{AB}$ coupling constant of 14 Hz.[56] The trans orientation of the phosphines in the complex **73** is based on much literature precedent.[64] In accordance with these data we therefore propose the structure for the complex **73** is as shown in equation 26. Attempts to unravel the complex coupling pattern of protons H_A and H_B for **73** by using different deuterated solvents, gave either no change in the spectrum or led to decomposition of the complex.

In effect, the procedure outlined in equation 26 represents a two-step process for the stereoselective transfer of a 1,3-dienyl moiety from zirconium to nickel. Much effort was expended in an attempt to develop a method for the direct transfer of the 1,3-dienyl fragments from zirconium to other transition metals. It was hoped that this could be achieved by the reaction of the 1,3-dienylzirconium complexes **55a-d** with a series of mononuclear transition metal halide complexes of the general formula ML_nX_m (e.g., $(COD)PdCl_2$, $CpNi(PPh_3)Cl$,

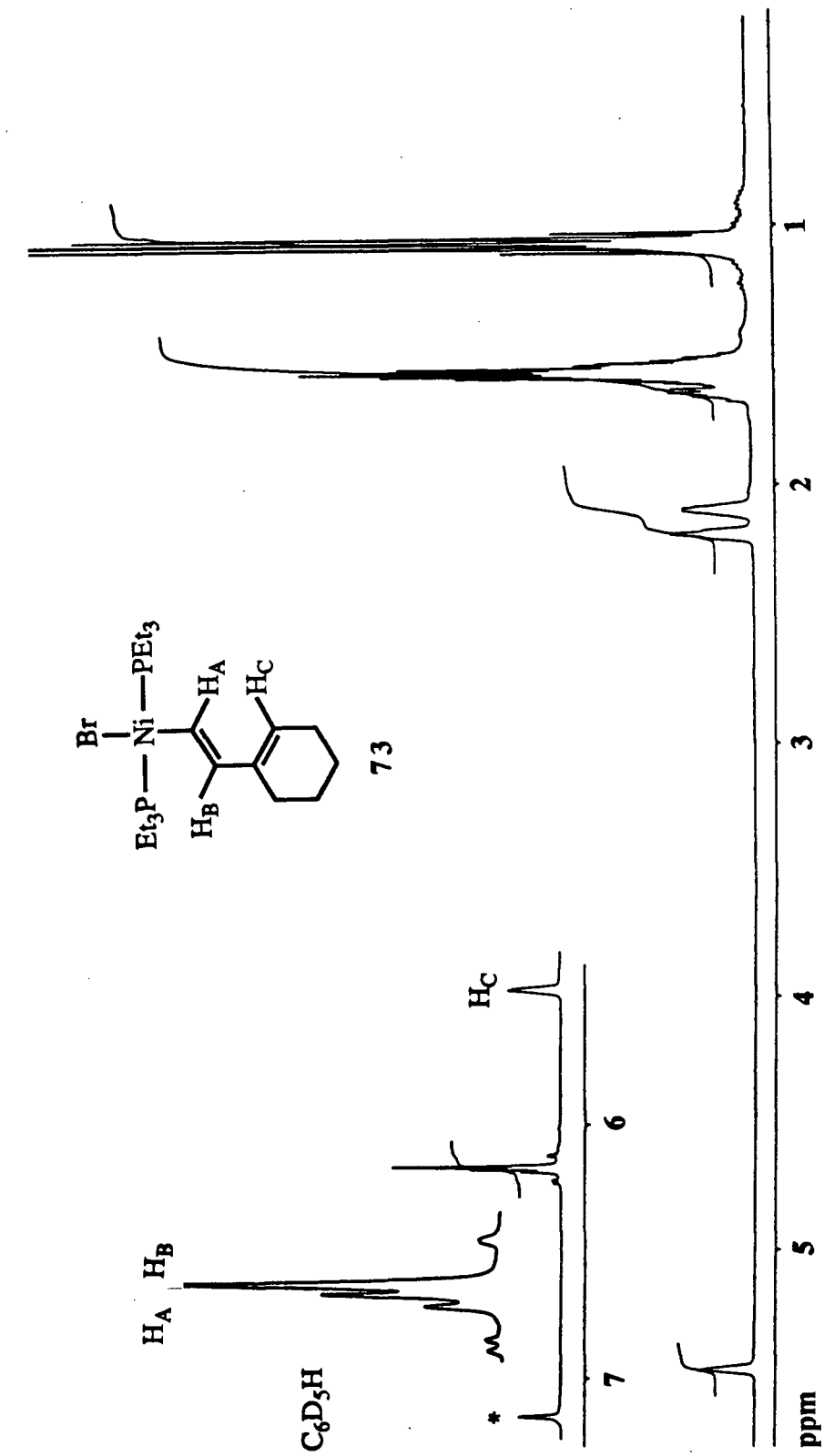
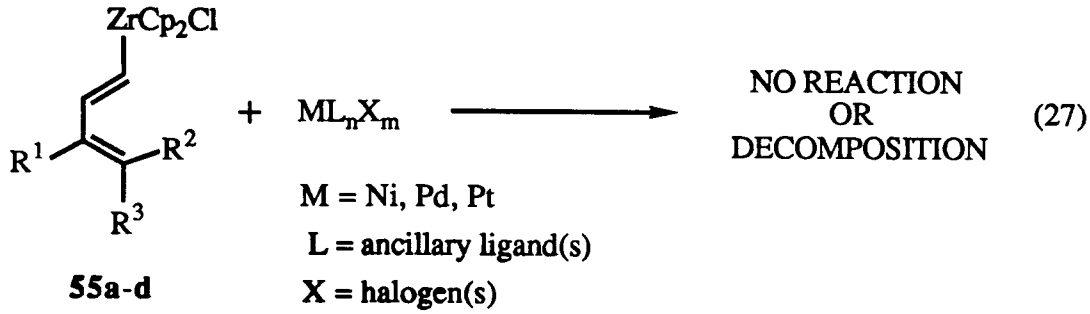


Figure 15. 400 MHz ^{1}H NMR spectrum of **73** in C_6D_6.

$(PEt_3)_2PtCl_2$, $(PEt_3)_2NiCl_2$). When the reactions were carried out at room temperature, no evidence for the transfer of the 1,3-dienyl fragments from zirconium was obtained. On performing the reactions at elevated temperatures, either no reaction or decomposition of the starting materials resulted (equation 27). A recent report has been published which presents



55a-d (27)

evidence for the intramolecular transfer of a methyl group from zirconium to platinum.[65]

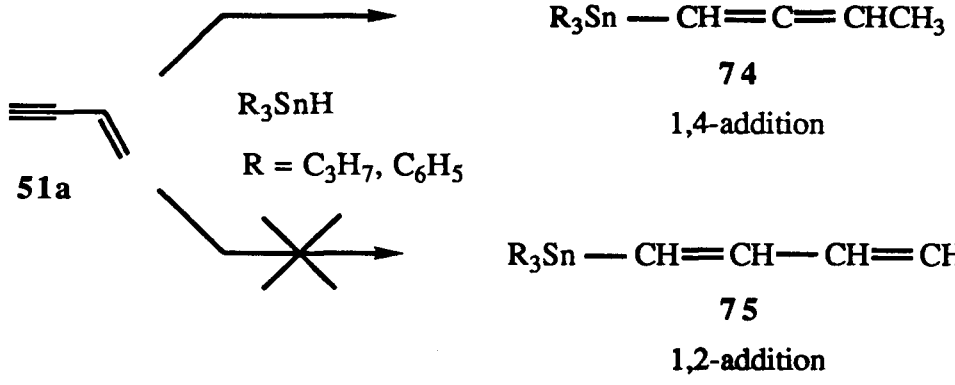
Due to the electron-rich nature of the nickel(II) center in complexes **32** and **73** (relative to the zirconium(IV) center of **55a-d**), reaction with a variety of dienophiles was attempted. When either **32** or **73** was reacted with a series dienophiles (methyl acrylate, methacrylonitrile, maleic anhydride, dimethyl acetylenedicarboxylate and tetracyanoethene) at room temperature or at elevated temperatures no reaction or decomposition of the complex was observed. This lack of reactivity may be due in part to the bulk of the triethylphosphine (PEt_3) ligands. Also, the assumption that the relatively electron-rich nickel center can activate the 1,3-dienyl fragment towards reaction with electron deficient dienophiles may be unfounded.

At present, the transfer of the 1,3-dienyl fragments from zirconium to other transition metals in a stoichiometric, high yielding process seems most attractive via the indirect cleavage-oxidative-addition method outlined in equation 26. However, this procedure would be limited to those metals which can undergo oxidative addition with vinyl halides. Attempts to transfer the 1,3-dienyl fragment of the complexes **55a-d** from zirconium to silicon, using trimethylsilyl chloride, failed even when the reaction was performed at elevated temperatures. The use of different silicon transfer reagents, such a 1-(trimethylsilyl)imidazole or trimethylsilyl

trifluromethanesulfonate also failed to generate the desired 1,3-dienylsilanes. Other workers have observed similar difficulties in obtaining transfer of organic fragments from zirconium to silicon, even with the use of silicon tetrachloride.[66] However, the direct transfer of organic moieties from zirconium to other elements such as tin, phosphorus, boron, selenium and sulfur was more successful. This procedure is discussed in detail in the following sections.

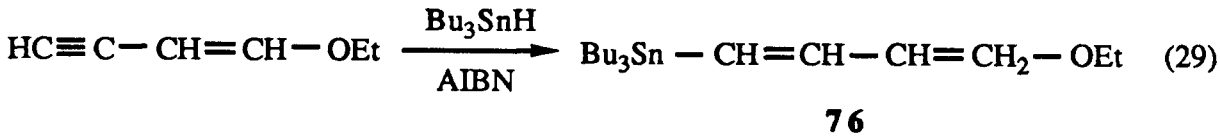
3.2 Transfer of 1,3-Dienyl Moieties from Zirconium to Tin.

Several research groups have attempted the preparation of tin-substituted 1,3-dienes by the hydrostannation of 1-ene-3-yne molecules. In general, this method appears to be very substrate dependent. The hydrostannation of 1-buten-3-yne **51a** led to 1,4-addition to generate



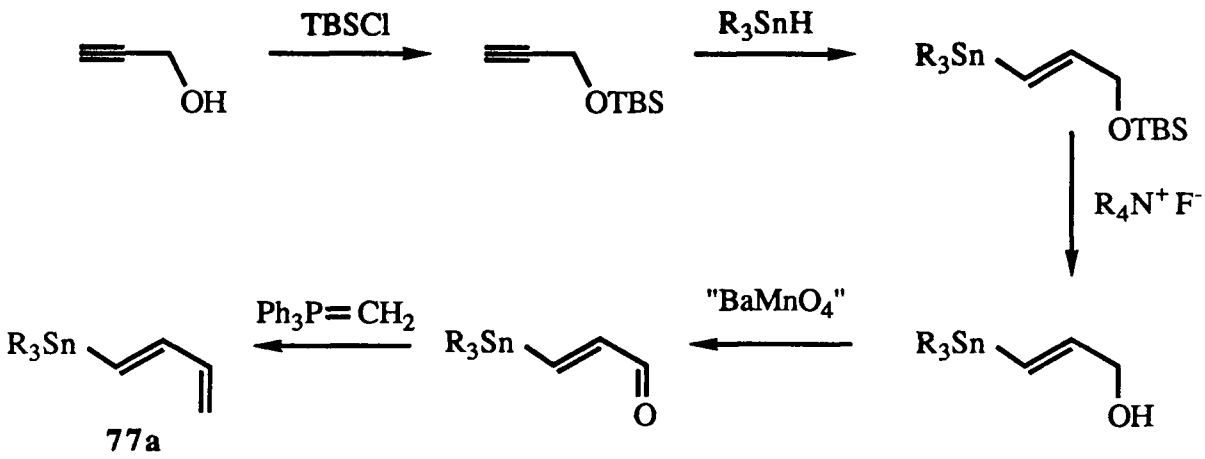
(28)

the allenic derivative **74**, rather than 1,2-addition to give the desired 1,3-diene **75** (equation 28).[54b] The reaction of 1-ethoxy-1-buten-3-yne with one equivalent of tributyltin



(29)

hydride and a catalytic amount of azobisisobutyronitrile (AIBN), gave the diene **76** as a mixture of geometric isomers (equation 29).[67] The ratio of isomers was not reported. An extensive study of the hydrostannation of alkyl substituted 1-ene-3-ynes, indicated that a wide variety of products were formed.[68] These products were shown to result from extensive isomerization, induced by trialkylstannyl radicals during and prior to addition to the 1-ene-3-ynes. The latter observations are consistent with those reported previously for the hydrostannation of 2-methyl-1-buten-3-yne.[52] The preparation of the tributylstannyl 1,3-diene **77a** was later achieved by a rather elaborate synthetic sequence (Scheme 20).[69] The

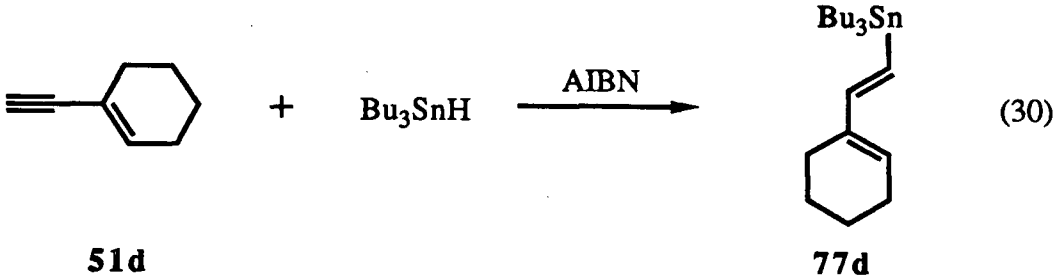


R = Bu

TBS = *t*-Bu(Me)$_2$Si

Scheme 20

stereoselective hydrostannation of the 1-ene-3-yne **51d** has been reported to give the diene **77d** (equation 30).[70] With the exception of the latter reaction, the hydrostannation of



(30)

51d **77d**

1-ene-3-yne molecules does not appear to be an efficient method for the syntheses of stereochemically defined tin-substituted 1,3-dienes.

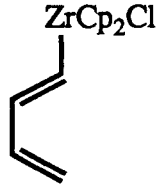
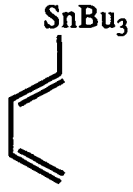
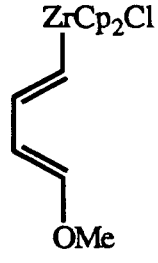
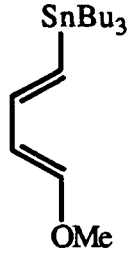
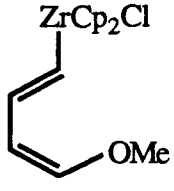
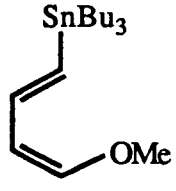
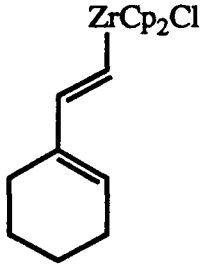
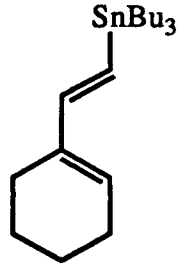
Preliminary results from another research group, indicated that the transfer of organic moieties from zirconium to tin, using tin tetrachloride, was a facile process.[28] However, due to the sensitive nature of these trichlorotin species, it was decided to investigate the reaction of the complexes **55a-d** with a trialkyltin chloride. Reaction of these complexes with tributyltin chloride in toluene, proceeded at room temperature or at elevated temperatures to afford the desired tin-substituted 1,3-dienes **77a-d** in moderate to good yields (Table V, next page).[53] These compounds were readily separated from the Cp_2ZrCl_2 by-product by extraction with hexanes and filtration.

The IR spectra of the dienes **77a-d** contained a band at 1620-1519 cm^{-1}, which is indicative of compounds containing a 1,3-dienyl moiety.[56a] Analysis of the products by ^1H NMR spectroscopy, indicated that the transfer of the 1,3-dienyl moiety from zirconium to tin had proceeded in a stereoselective manner. For example, the assignment of the diene **77b** as the E,E isomer was based on the magnitude of the $^3J_{AB}$ and $^3J_{CD}$ coupling constants of 18.5 Hz and 12.5 Hz, respectively (see Figure 16, p 59). Further evidence for the stereoselective nature of the transfer reaction, results from the $^3J_{BSn}$ coupling constant of 62 Hz. This value is consistent with previously reported cis $^3J_{HSn}$ coupling constants.[71] The corresponding $^3J_{AB}$ and $^3J_{BSn}$ coupling constants for the dienes **77a**, **77c** and **77d** can be seen in Table V.

Dienes **77a** and **77c** were prone to isomerization when stored as neat liquids at room temperature. This isomerization was inhibited by storing these compounds in the dark at -30°C. No such isomerization was observed for the dienes **77b** and **77d**, which were found to be stable for months at room temperature in the dark.

Overall, the combination of the hydrozirconation of 1-ene-3-yne molecules and the subsequent transfer reaction to tin, provides an expedient syntheses of tin-substituted 1,3-dienes.

Table V: Reaction of **55a-d** with Bu_3SnCl; $^3J_{AB}$ and $^3J_{BSn}$ for **77a-d**.

1,3-dienylzirconium reagent	1,3-dienylstannane product	$^3J_{AB}$ (Hz)	$^3J_{BSn}$ (Hz)	Yield[a] (%)
 **55a**	 **77a**	18.5	60	68
 **55b**	 **77b**	18.5	62	75
 **55c**	 **77c**	18.5	62	71
 **55d**	 **77d**	19.5	67	79

[a] Yields of isolated products.

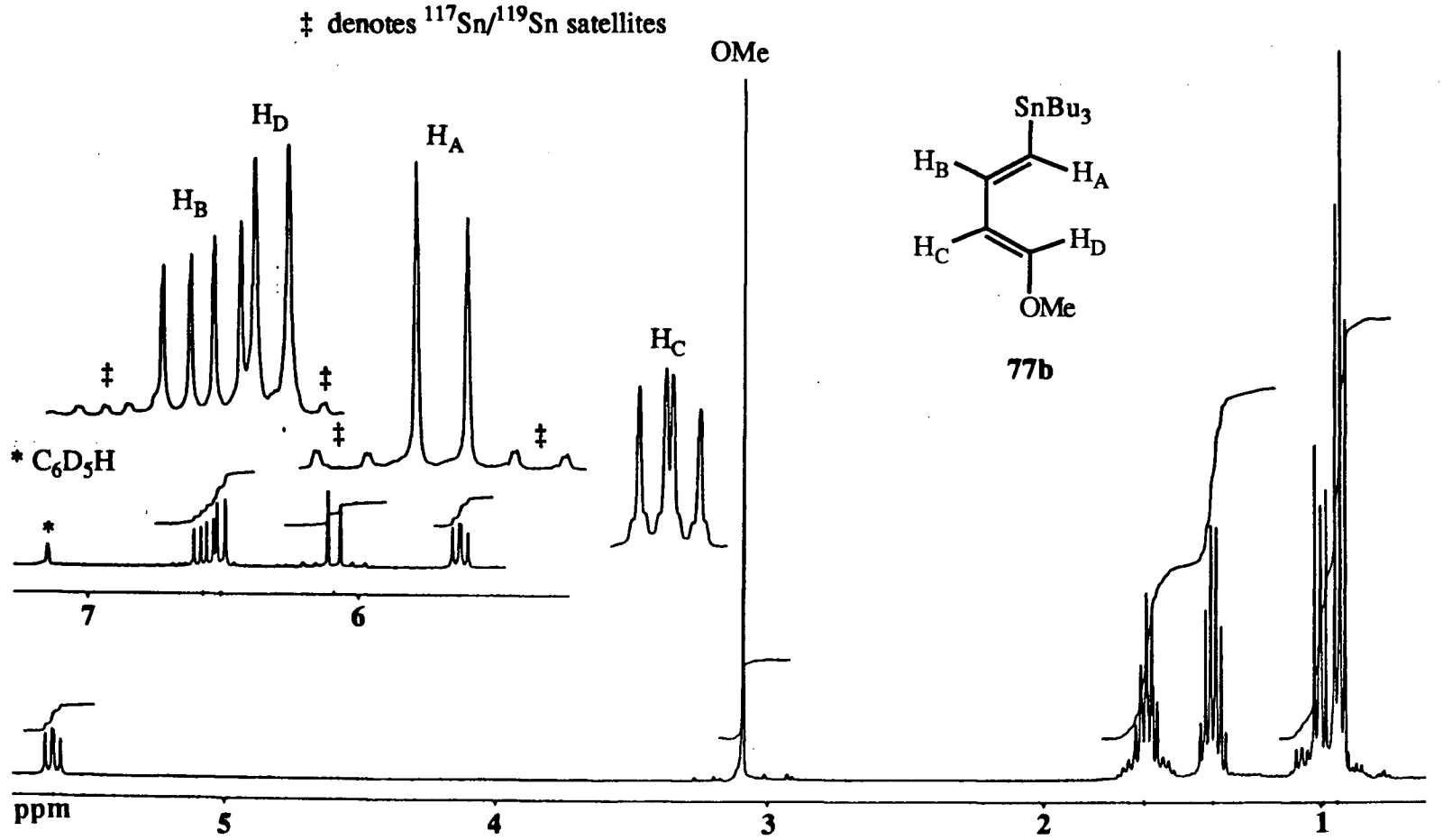
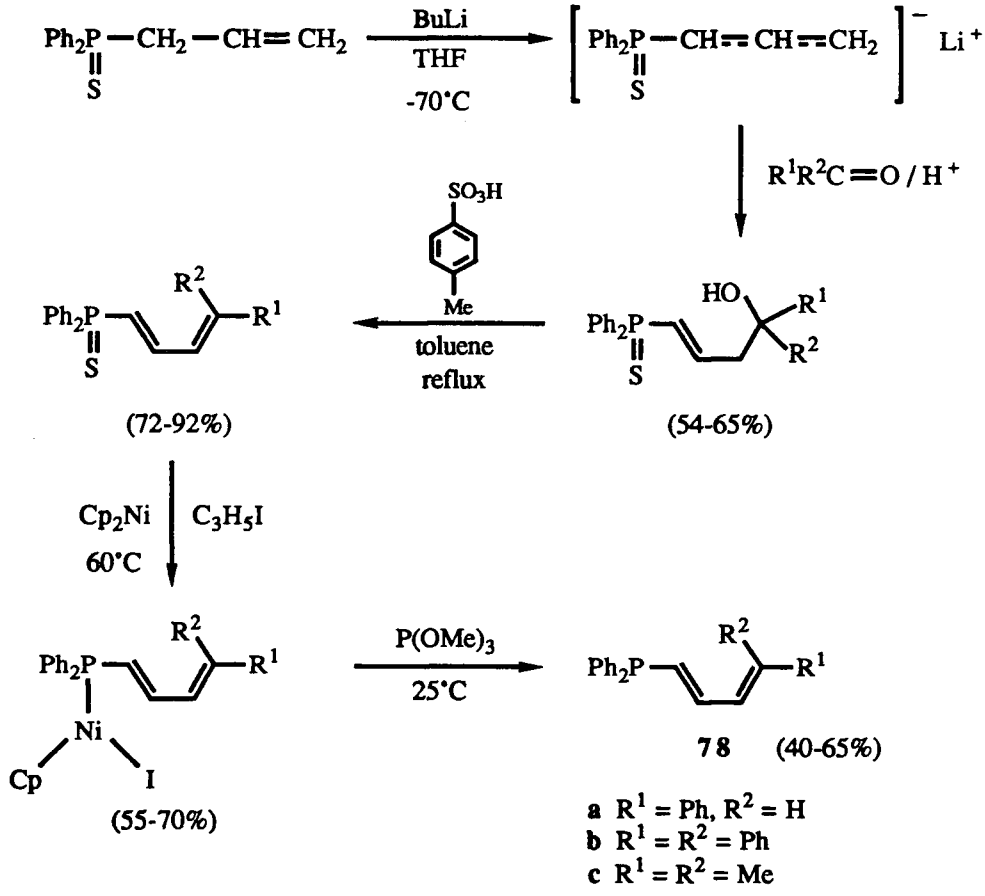


Figure 16. 400 MHz ^1H NMR spectrum of **77b** in C_6D_6.

3.3 Transfer of 1,3-Dienyl Moieties from Zirconium to Phosphorus.

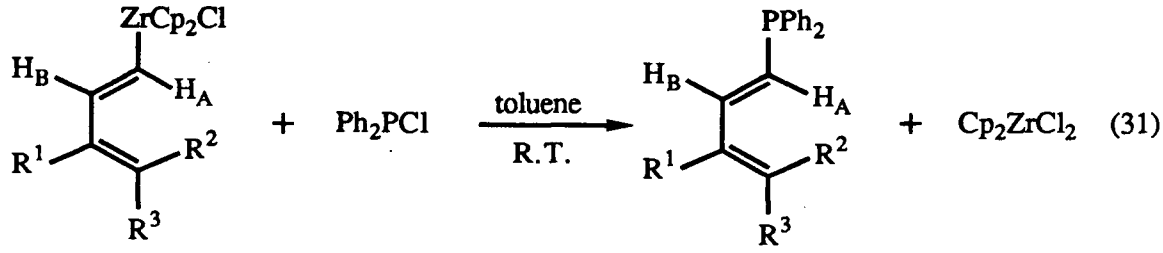
The development of a general synthetic route for the preparation of 1,3-dienylphosphines is attractive from many viewpoints. As tertiary phosphines, their coordination to transition metals and subsequent reactivity would be of potential interest. Also, as heterosubstituted dienes their reactivity with dienophiles, either as independent molecules or when bound to a transition metal, could generate interesting results.

Although there are numerous literature procedures for the syntheses of stereochemically defined 1,3-dienylphosphoryl compounds,[38,72] only one general method for the preparation of 1,3-dienylphosphines **78** has been reported (Scheme 21).[73]



Scheme 21

It was hoped, that a more direct and higher yielding syntheses of such compounds could be developed by the stereoselective transfer of the 1,3-dienyl moiety, of the complexes **55a-d**, from zirconium to phosphorus. Reaction of these complexes with one equivalent of chlorodiphenylphosphine (Ph_2PCl) in toluene at room temperature, proceeded rapidly to afford the corresponding stereochemically pure 1,3-dienylphosphines **79a-d** (equation 31).[74] Isolated yields of 79-88% were readily obtained by extraction with hexanes and filtration.



55a-d **79a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 $R^3 = -(CH_2)_4-$, $R^2 = H$

The IR spectra of **79a-d** contained a band at 1620-1516 cm^{-1}, which is indicative of compounds containing a 1,3-dienyl moiety.[56a] The assignment of the stereochemistry for these compounds was made by analysis of their ^1H NMR spectra. In all cases a large $^3J_{AB}$ coupling constant of ~17 Hz, which is indicative of a trans coupling, provided evidence for the stereoselective nature of the transfer reaction. The resonances for protons H_A and H_B were complicated by an additional coupling to the phosphorus-31 nucleus. The values for the ^1H-^{31}P coupling constants, and the ^{31}P chemical shifts for the phosphines **79a-d** are shown in Table VI. The coupling constants were determined from homonuclear or heteronuclear decoupling experiments. The ^1H NMR spectrum resulting from an experiment in which the ^{31}P chemical shift range for **79b** was broadband decoupled while observing the ^1H chemical

Table VI: ^{1}H-^{31}P coupling constants and ^{31}P NMR chemical shift data for **79a-d**.

1,3-dienylphosphine	$^{2}J_{AP}$ (Hz)	$^{3}J_{BP}$ (Hz)	δ ^{31}P NMR (ppm)
79a	10.0	11.5	–12.4
79b	3.5	14.0	–11.7
79c	4.0	14.5	–11.3
79d	5.5	15.0	–11.7

Table VII: ^{1}H-^{31}P coupling constants and ^{31}P NMR chemical shift data for **80a-d**.

1,3-dienylphosphine	$^{2}J_{AP}$ (Hz)	$^{3}J_{BP}$ (Hz)	δ ^{31}P NMR (ppm)
80a	12.0	10.5	–50.8
80b	8.0	10.0	–50.4
80c	11.0	12.0	–50.2
80d	9.0	15.0	–50.7

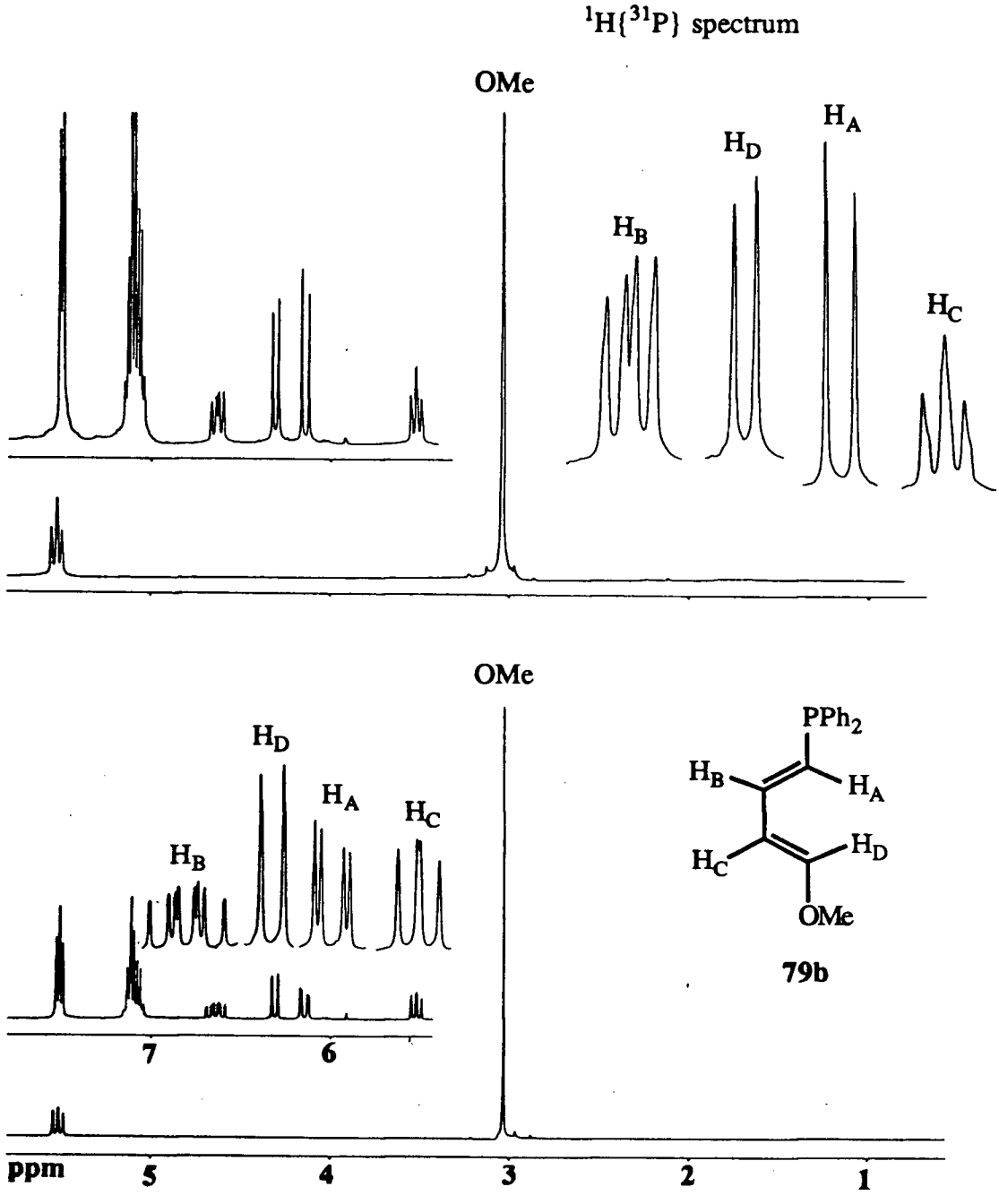
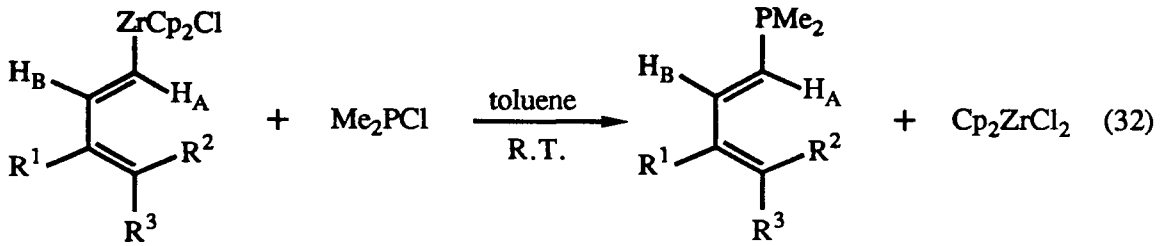


Figure 17. 400 MHz ^1H and $^1H\{^{31}P\}$ NMR spectra of **79b** in C_6D_6.

shift range (i.e , $^{1}H\{^{31}P\}$) is shown in Figure 17 . To highlight the changes made by ^{31}P broadband decoupling, the normal ^{1}H NMR spectrum of **79b** is also shown in Figure 17. Comparison of these two spectra shows that the resonances for protons H_A and H_B have collapsed to a doublet and doublet of doublets, respectively. These changes provided a clear means of determining the ^{1}H-^{31}P coupling constants. The reported values were fairly consistent throughout for these phosphines, with the exception of the $^{2}J_{AP}$ for **79a** (see Table VI). The only other $^{2}J_{AP}$ coupling constant reported for a 1,3-dienylphosphine, was for (*E,E*)-(4-phenyl-1,3-butadienyl)diphenylphosphine.[73] The value of 14 Hz given here, was in reasonable agreement with the 10 Hz coupling measured for phosphine **79a**, but in poor agreement with the corresponding coupling constants for phosphines **79b-d.**

An analogous series of 1,3-dienylphosphines was prepared in a similar way by reaction of **55a-d** with chlorodimethylphosphine (Me_2PCl). As with Ph_2PCl, the reaction with Me_2PCl was almost instantaneous at room temperature to give, after workup, the 1,3-dienylphosphines **80a-d** (equation 32). These compounds were isolated in good yields (77-82%).



55a-d **80a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 $R^3 = -(CH_2)_4-$, $R^2 = H$

The main features of the ^1H NMR spectra of phosphines **80a-d** were as observed for the diphenylphosphino 1,3-dienes **79a-d**. The ^1H NMR spectrum of the phosphine **80c** is shown in Figure 18 (next page). Measurement of the $^3J_{AB}$ coupling constants (~16 Hz) indicated that the transfer reaction had taken place with retention of stereochemistry. Interestingly, the same trend in the ^1H-^{31}P coupling constants for **79a-d**, was observed for the dimethylphosphino 1,3-dienes. The values of these coupling constants, as well as the ^{31}P chemical shifts, for phosphines **80a-d** are shown in Table VII (see p 62). Analysis of the ^1H-^{31}P coupling constants given in Tables VI and VII, highlights the anomalously large $^2J_{AP}$ coupling constant for phosphine **79a**. Also, in general, the $^2J_{AP}$ coupling constants are larger for the dimethylphosphino-substituted 1,3-dienes than for the diphenylphosphino-substituted 1,3-dienes. However, the $^3J_{BP}$ coupling constants are quite consistent throughout. This latter observation could, with further examples, lead to a general method for the assignment of stereochemistry for alkenyl- and 1,3-dienylphosphines.

In the ^1H NMR spectra of phosphines **80a-d**, small traces (~3-5%) of another compound were observed. In all cases, it was apparent from the similarity in the resonances that the impurity was isostructural with the 1,3-dienylphosphine. Measurement of the appropriate ^1H-^1H coupling constants, indicated that these impurities were not geometric isomers. Therefore, they did not arise from some isomerization process, or by a deviation from complete stereoselectivity in the transfer from zirconium to phosphorus. Interestingly, when the reaction conditions were changed, namely, if instead of using neat Me_2PCl it was added as a solution in toluene, analysis of the products by ^1H NMR spectroscopy showed no sign of the previously observed impurities.

When complexes **55a-d** were reacted with chlorodiisopropylphosphine (*i*-Pr_2PCl) at room temperature for 24 hours, less than 50% conversion to the corresponding 1,3-dienylphosphines was observed. The reaction proceeded more smoothly at 80°C, to give excellent isolated yields (83 and 92%) of the 1,3-dienylphosphines **81b** and **81d** (Scheme 22, p 67).

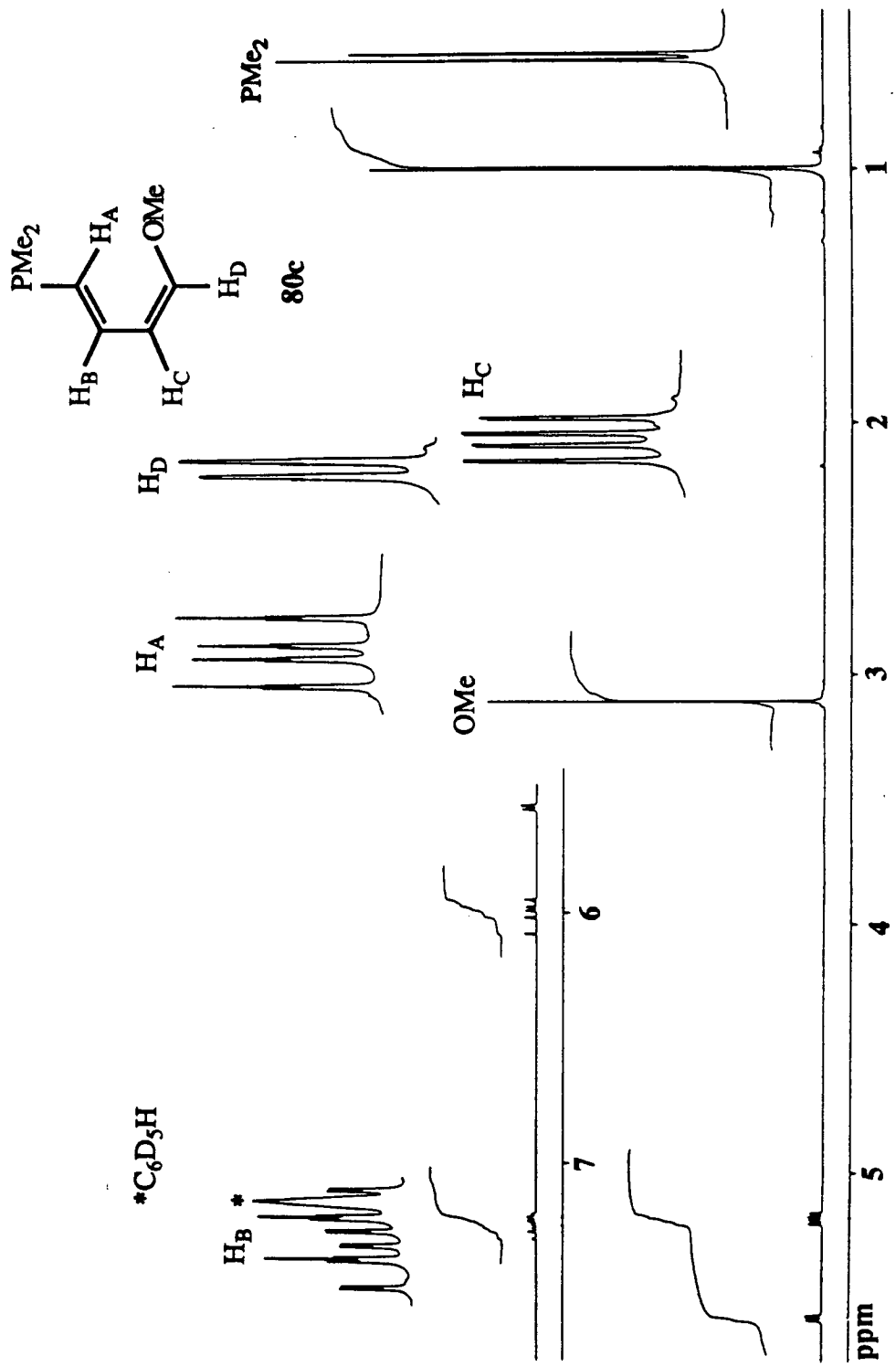
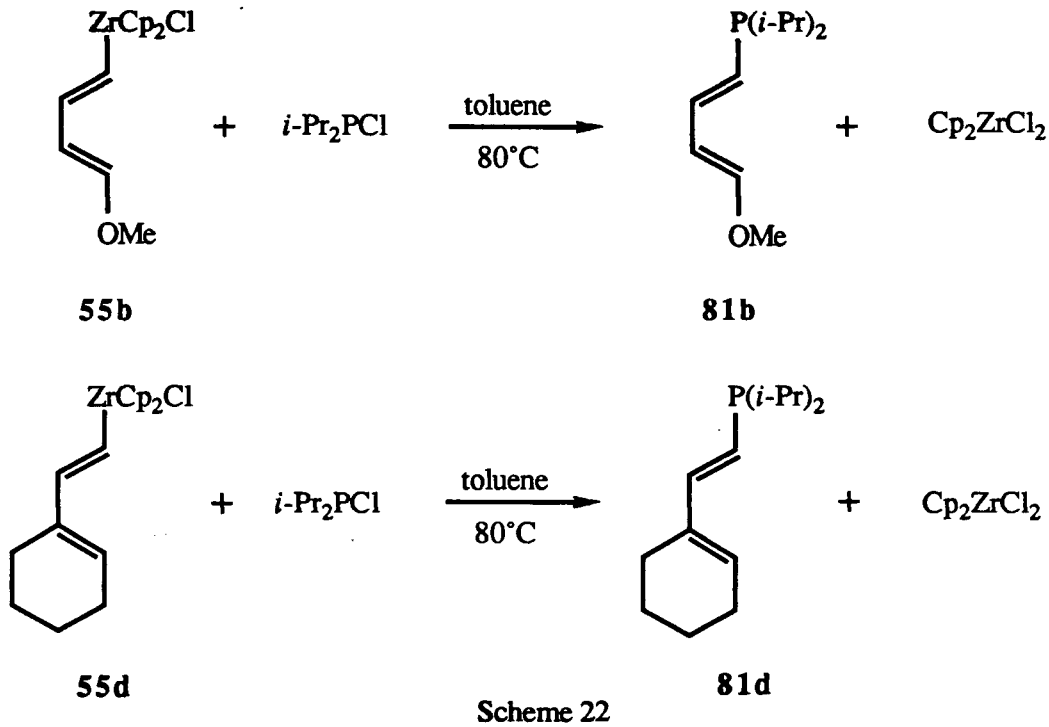


Figure 18. 400 MHz ^{1}H NMR spectrum of **80c** in C_6D_6.



Scheme 22

Analysis of these compounds by ^1H NMR spectroscopy, in each case, indicated the presence of a 2:1 mixture of isostructural compounds. These observations were similar to those made for the trace impurities seen in the preparation of phosphines **80a-d**, when neat Me_2PCl was used. The ^1H NMR spectrum of the two component mixture for **81b** is shown in Figure 19. Comparison of the relevant coupling constants ($^3J_{AB}$ and $^3J_{CD}$) for the two species, indicated that they were not geometric isomers. Although the ^1H-^1H coupling constants were identical within a given pair of isomers, the $^2J_{AP}$ as well as the $^3J_{AP}$ coupling constants were different. Also, the difference in chemical shift between the same protons for each component was greatest for proton H_A, and thereafter decreased as the distance from the phosphorus center increased. From the $^{31}P\{^1H\}$ NMR spectrum of **81b**, the difference in chemical shift of the two components was 16 ppm. These observations suggest that the structural difference between the two components, exists at or close to the phosphorus center.

The ratio of the two components of the mixture did not change on further heating for 4 days at 80°C. Also, no change in the ^1H NMR spectrum of the mixture was observed on

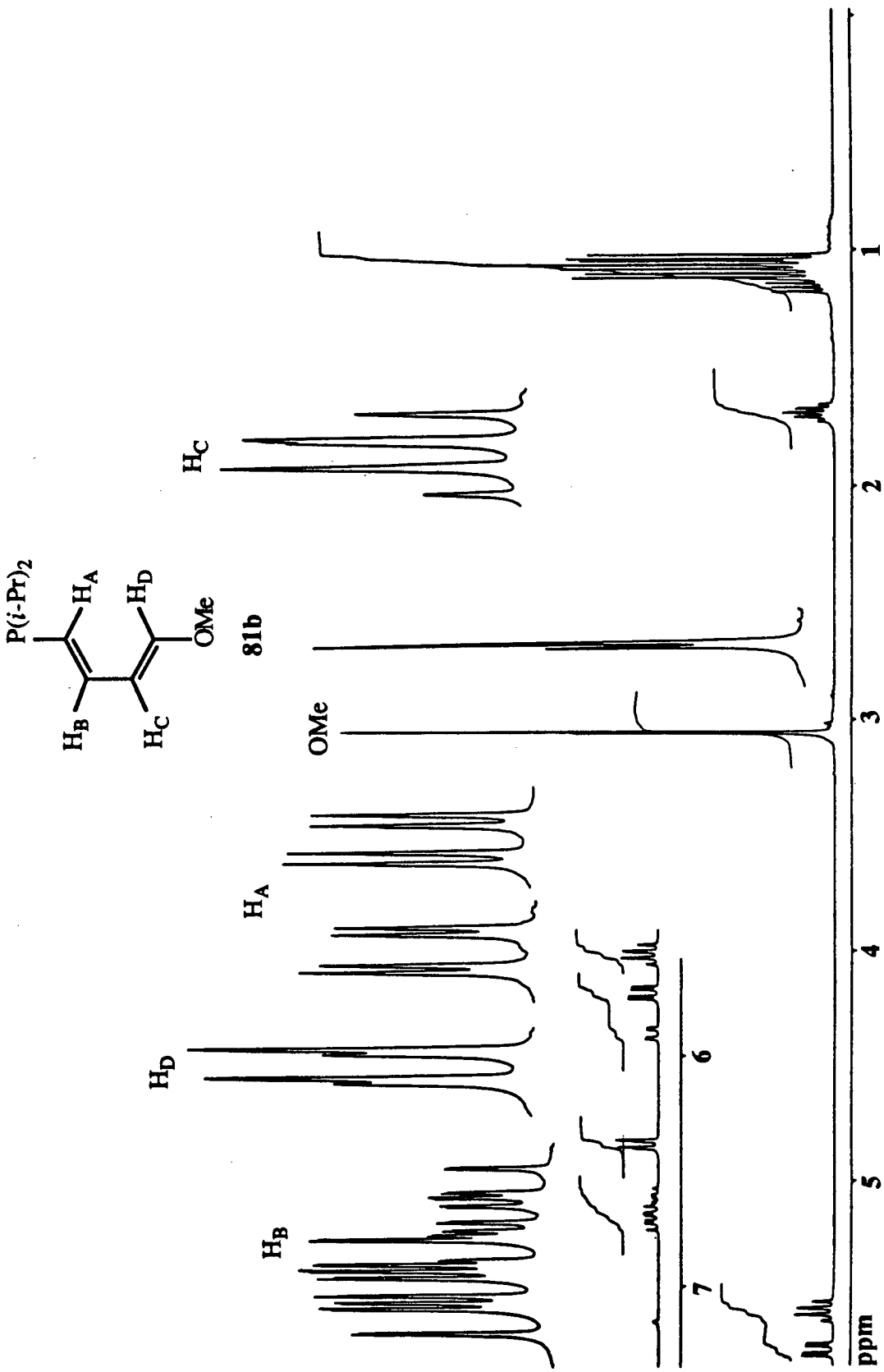


Figure 19. 400 MHz ^{1}H NMR spectrum of **81b** in C_6D_6.

increasing the probe temperature to 80°C. However, when the reaction was carried out using approximately one-third the overall concentration of the previous reactions, the ^{1}H NMR spectrum of the products **81b** and **81d** showed only one set of resonances. These resonances corresponded, in each case, to the major component of the previously observed mixture. For comparison, the ^{1}H NMR spectra of the 2:1 mixture and that of the single component, for the phosphine **81b**, are shown in Figure 20 (next page).

Based on the data outlined above, it is suggested that the two components formed in the more concentrated reaction are actually rotamers, having restricted rotation about the phosphorus-carbon bond of the 1,3-diene fragment. These rotamers may arise due to different orientations of the bulky isopropyl groups in the transition states leading to product formation (Figure 21). If the two postulated intermediates **82** and **83** are in equilibrium, the formation of

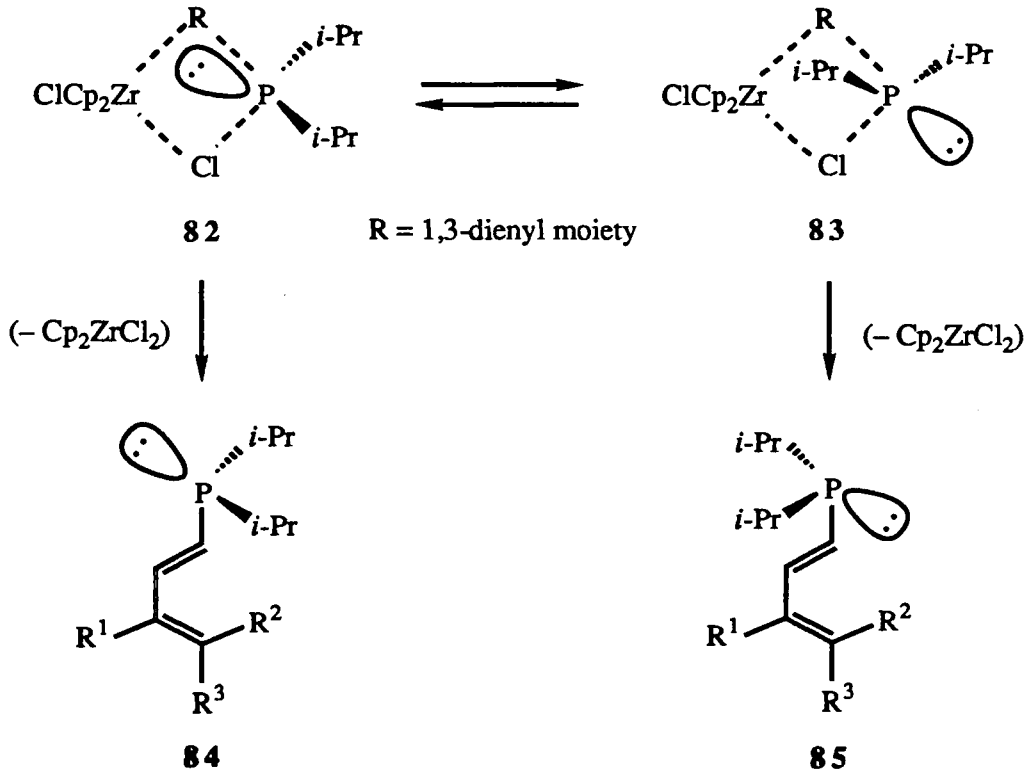


Figure 21. **Rationale for the formation of rotamers for 81b and 81d.**

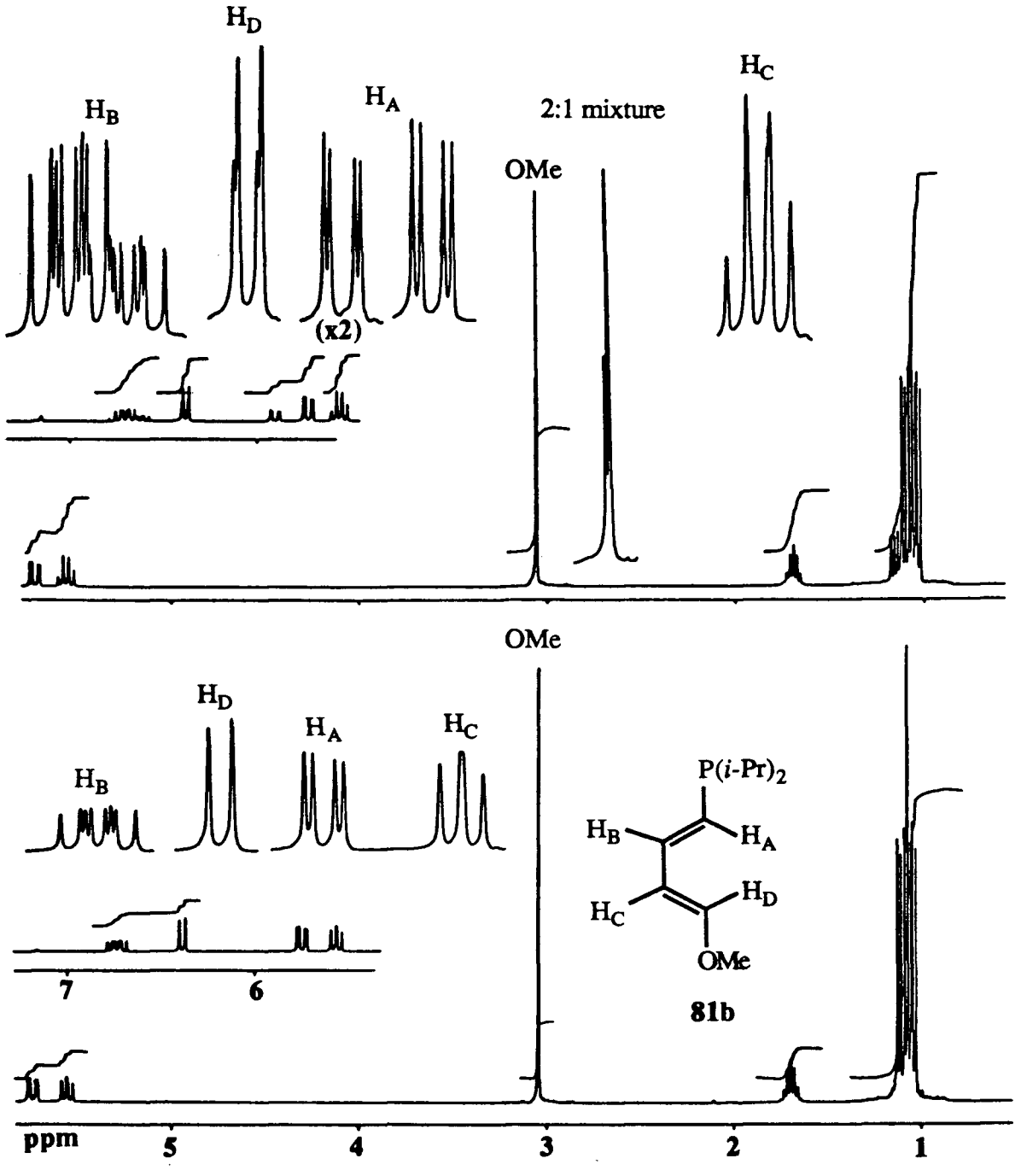
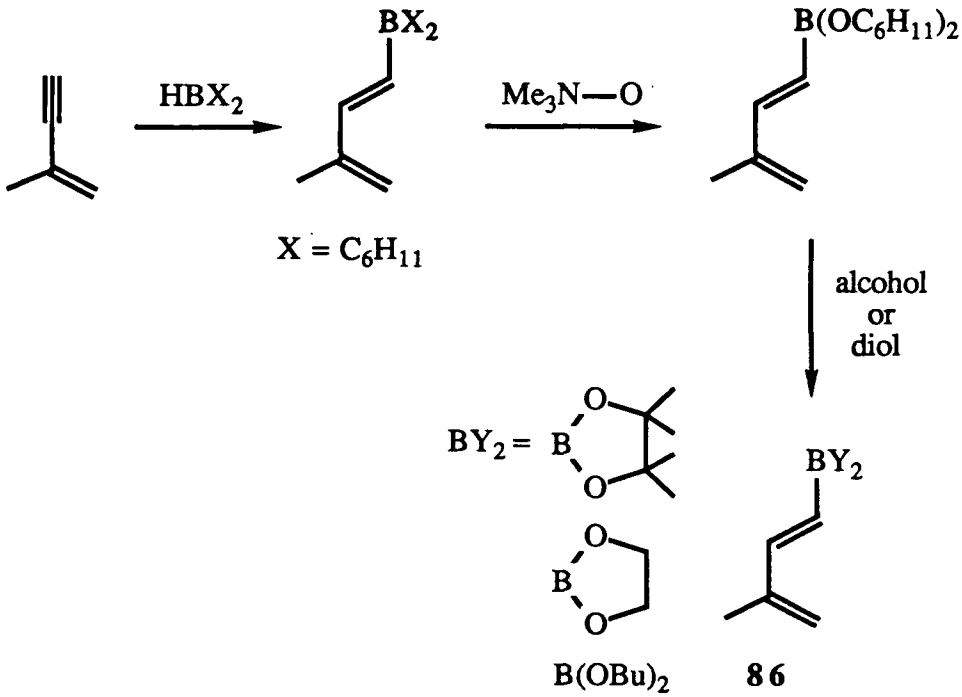


Figure 20. 400 MHz ^{1}H NMR spectra of **81b** as a single rotamer and as a 2:1 mixture of rotamers in C_6D_6.

only one rotamer due to dilution of the reaction mixture, may result from a longer induction period prior to formation of the product. Rotamers **84** and **85** would have a different orientation of the phosphorus lone-pair. For conformationally rigid systems, it has been shown that the ^{1}H-^{31}P coupling constants can depend on the orientation of the phosphorus lone pair.[75] This may account for the differences observed between the two sets of $^{2}J_{AP}$ as well as the $^{3}J_{BP}$ coupling constants, for each of the two rotamers of phosphines **81b** and **81d**. The formation of rotamers for tertiary phosphines has been observed previously for the compound diisopropylphenylphosphine (*i*-Pr_2PhP).[76]

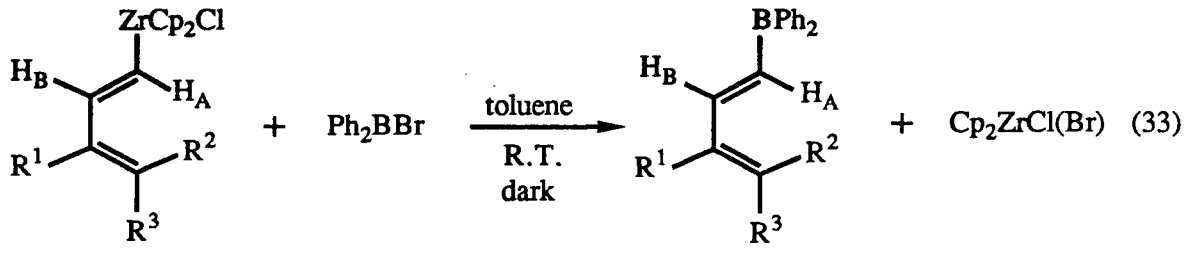
3.4 Transfer of 1,3-Dienyl Moieties from Zirconium to Boron.

Formation of 1,3-dienylboranes by direct hydroboration of 1-ene-3-yne molecules is well documented.[51,77] A recent communication outlined a general route to the preparation of a variety of 1,3-dienylboronates **86** (Scheme 23).[78] In concert with this method, we discovered



Scheme 23

that complexes **55a-d** reacted cleanly with bromodiphenylboron (Ph_2BBr) at room temperature to give the desired 1,3-dienylboranes **87a-d** (equation 33).[74] These compounds were isolated in good yields (80-88%) as white solids or colorless oils. While this two step method may not be as convenient as the hydroboration of 1-ene-3-ynes, there is the advantage that less hindered boranes can be used as the regiochemistry is defined in the hydrozirconation step. Also, to our knowledge, the direct hydroboration of the unsubstituted 1-buten-3-yne **51a** to generate 1,3-dienyls of type **87a** has not been achieved.



55a-d **87a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 $R^3 = -(CH_2)_4-$, $R^2 = H$

The IR spectra of **87a-d** contained a band at 1602-1621 cm^{-1}, which is indicative of compounds containing a 1,3-dienyl moiety.[56a] The stereochemistry of these dienes was deduced directly from their ^1H NMR spectra. The ^1H NMR spectrum of the 1,3-dienylborane **87a** is shown in Figure 22 (next page). The large $^3J_{AB}$ coupling constant of 17 Hz indicates a trans stereochemistry, confirming the stereoselective nature of the transfer reaction from zirconium to boron.

Compounds **87a-d** were found to be light sensitive, as such the best yields of pure products were obtained by performing the transfer reaction in the dark. The photochemical lability of 1,3-dienylboranes has been previously observed and investigated.[79]

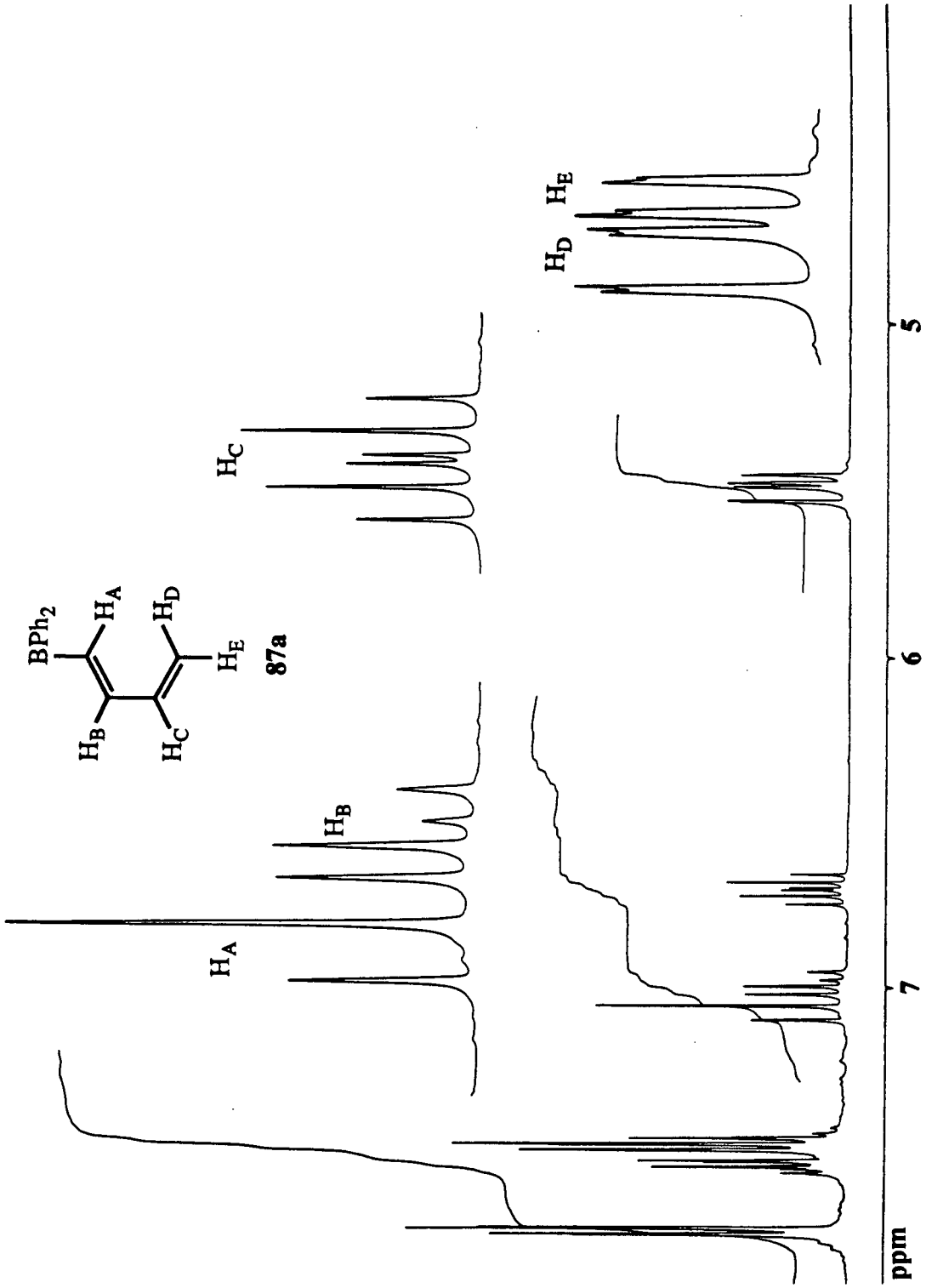
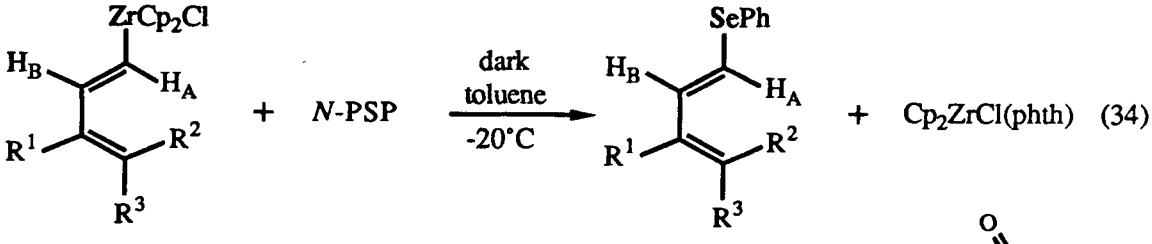


Figure 22. 400 MHz ^{1}H NMR spectrum of **87a** in $CDCl_3$.

3.5 Transfer of 1,3-Dienyl Moieties from Zirconium to Selenium and Sulfur.

While many synthetic procedures for the preparation of sulfur-functionalized 1,3-dienes are available,[38] we are aware of only two reports of stereochemically defined 1,3-dienylselenides. A methoxyselenation-elimination sequence applied to 1,3-butadiene and isoprene has been reported; however, the assignment of stereochemistry was superficial and ambiguous.[80] The other report described the preparation, stereochemical analysis and reactivity of 1-(phenylseleno)-2-(trimethylsiloxy)-4-methoxy-1,3-butadiene **46** (see Scheme 14, p 22).[50a,81]

It was found that reaction of complexes **55a-d** with *N*-(phenylseleno)phthalimide (*N*-PSP) at -20°C in the dark, gave excellent yields of the desired selenium-functionalized 1,3-dienes **88a-d** (equation 34).[82]



55a-d **88a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 R^3 = $-(CH_2)_4-$, $R^2 = H$

The IR spectra of **88a-d** contained a band at 1619-1635 cm^{-1}, which is indicative of compounds containing a 1,3-dienyl moiety.[56a] The stereoselective nature of the transfer reaction from zirconium to selenium, was determined by analysis of the products using ^1H NMR spectroscopy. The ^1H NMR spectrum of the diene **88d** is shown in Figure 23. The

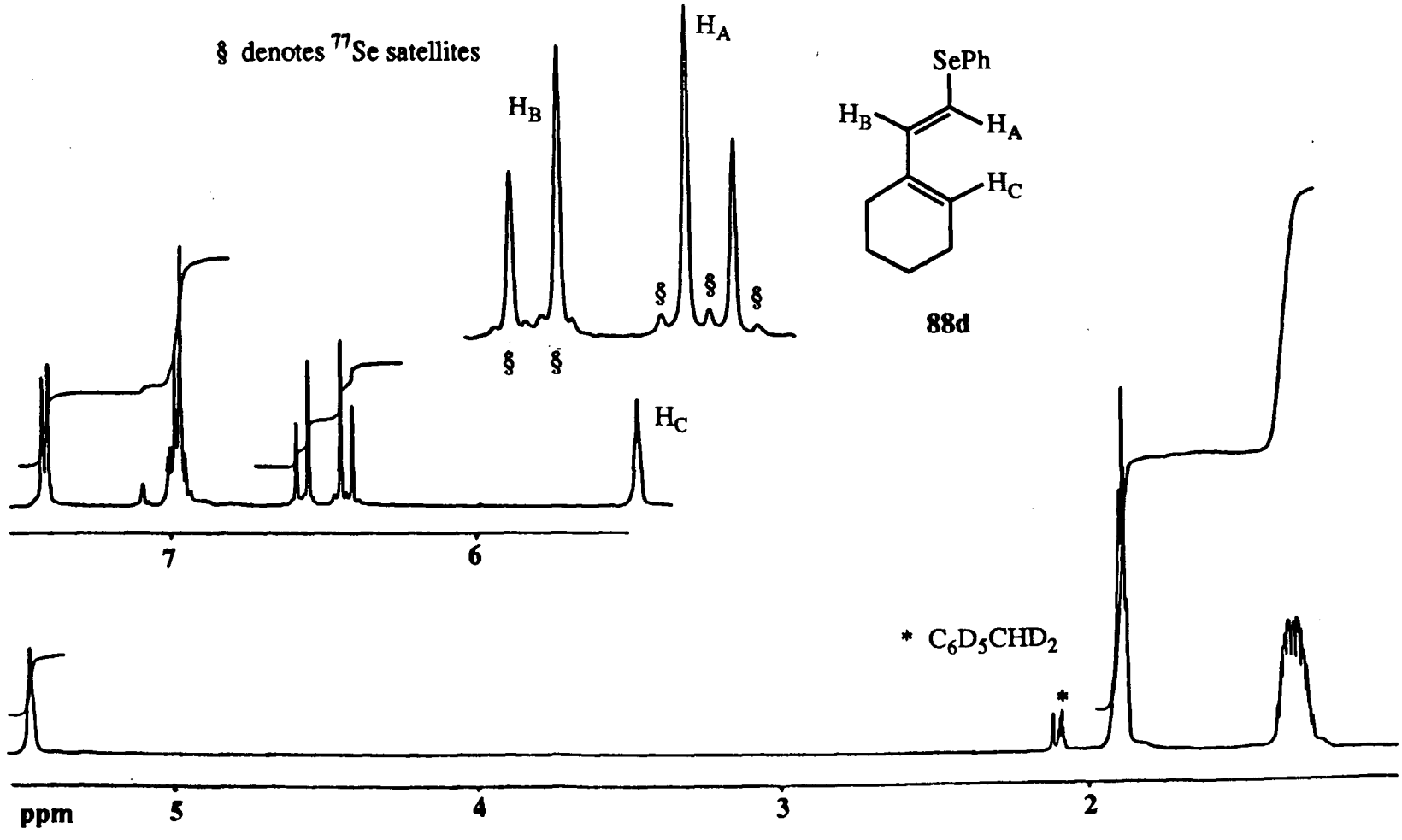


Figure 23. 400 MHz ^{1}H NMR spectrum of **88d** in C_7D_8.

large $^3J_{AB}$ coupling constant of 15.5 Hz is indicative of a trans stereochemistry. The $^2J_{ASe}$ and $^3J_{BSe}$ coupling constants, as well as the ^{77}Se NMR chemical shifts, for compounds **88a-d** are shown in Table VIII. The general observed trend is that $^2J_{ASe}$ coupling constants are larger than the corresponding $^3J_{BSe}$ values. A similar trend was reported previously for a series of phenylselenenyl-functionalized alkenes.[83] The same report gave the ^{77}Se NMR chemical shifts for the phenylselenium-functionalized alkenes. These values were in good agreement with those given in Table VIII for **88a-d.**

Table VIII: ^{1}H-^{77}Se coupling constants and ^{77}Se NMR chemical shift data for **88a-d.**

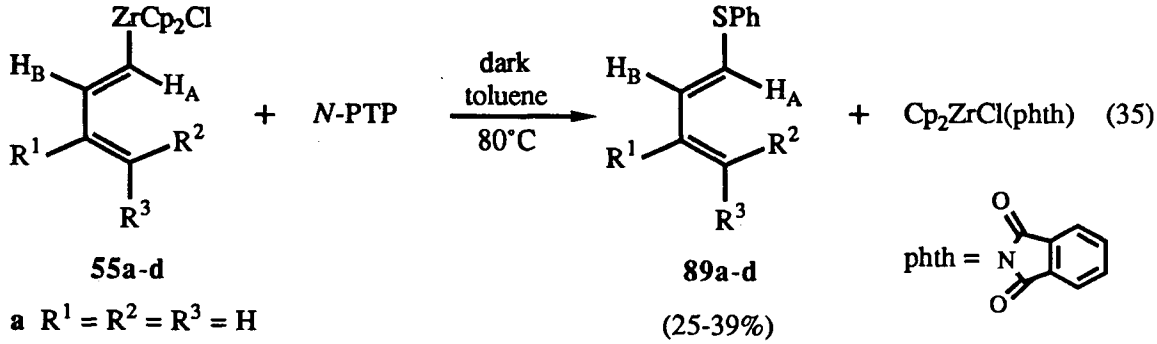
1,3-dienylselenide	$^2J_{ASe}$ (Hz)	$^3J_{BSe}$ (Hz)	δ ^{77}Se NMR (ppm)
88a	15.5	[a]	379
88b	14.5	11.0	367
88c	15.5	10.0	374
88d	15.5	10.0	369

[a] Not observed

When the transfer reaction of 1,3-dienyl moieties from zirconium to selenium was performed at room temperature under fluorescent light, mixtures of products were observed for **88a-c**. This is in contrast to the stereoselective formation of single products when the reactions were carried out at -20°C in the dark. Thus suggesting that the selenium-substituted 1,3-dienes may be photochemically and/or thermally labile. To investigate this phenomenon, a

detailed study of the photochemical and thermal reactivity of these compounds was undertaken, the results of which will be discussed later in Chapter 4.

With regard to the above study, it was decide to prepare the corresponding sulfur-substituted 1,3-dienes by a similar transfer reaction from zirconium. Reaction of the complexes **55a-d** with *N*-(phenylthio)phthalimide (*N*-PTP) at room temperature in the dark, gave no reaction after 24 hours. However, when the reaction was performed at 80°C in the dark, the sulfur-substituted 1,3-dienes **89a-d** were isolated in low yields (equation 35). Since



55a-d

89a-d

(25-39%)

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 R^3 = $-(CH_2)_4-$, $R^2 = H$

it was not our main desire to develop a synthetically useful procedure for the preparation of these 1,3-dienes, no attempt was made to optimize these low yields. It is interesting to note the difference in reactivity of the complexes **55a-d** with *N*-PTP as compared to *N*-PSP. The reasons for this dramatic difference in reactivity are unclear.

The IR spectra of **89a-d** contained a band at 1621-1634 cm^{-1}, which is diagnostic of 1,3-dienyl compounds.[56a] The stereochemical purity of these compounds was determined by ^1H NMR spectroscopy. The ^1H NMR spectrum of **89b** is shown in Figure 24. The large $^3J_{AB}$ coupling constant of 15 Hz indicates a trans stereochemistry, confirming the stereoselective nature of the transfer reaction from zirconium to sulfur.

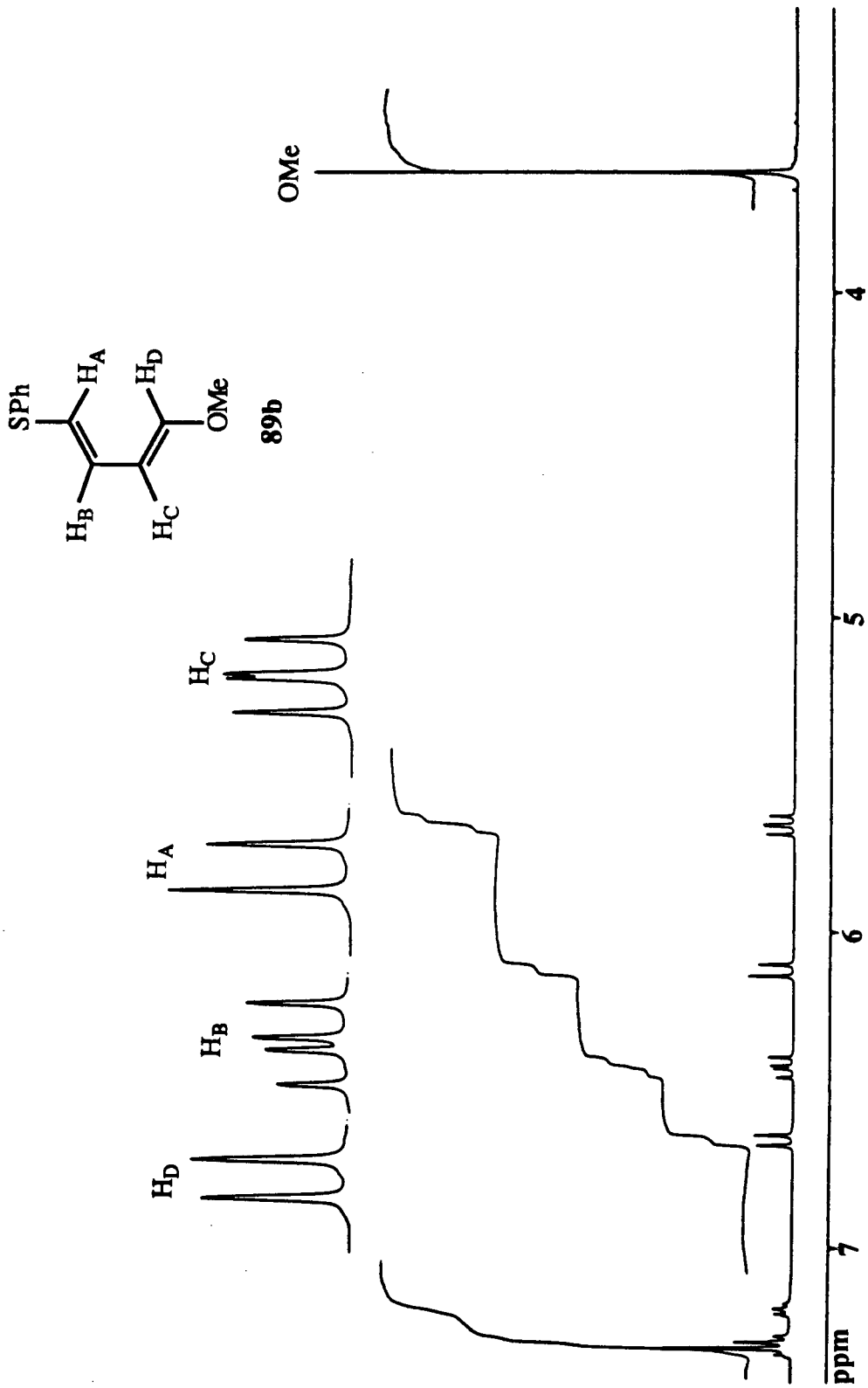
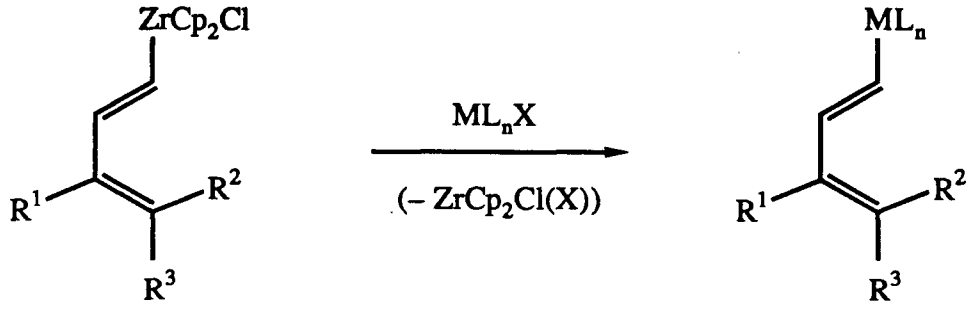


Figure 24. 400 MHz ^{1}H NMR spectrum of **89b** in $CDCl_3$.

The transfer of the 1,3-dienyl fragment from zirconium has been shown to proceed in a stereoselective manner, to generate a series of type **A** 1,3-dienes where the heteroatom (M) can be tin, phosphorus, boron, selenium or sulfur (equation 36). In general, these reactions proceed rapidly at low or moderate temperatures to give good yields of a range of heterosubstituted 1,3-dienes.



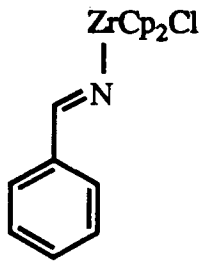
(36)

55a-d **A**

M = Sn, P, B, Se, S

3.6 Preparation of Heterosubstituted Imines and 1-Azadienes. Transfer from Zirconium to Selenium and Phosphorus.

The heteroallene-type complexes **62**, **63** and **68-71**, prepared by the hydrozirconation of nitriles and α,β-unsaturated nitriles, did not initially appear to be likely candidates as imine and 1-azadiene transfer reagents. The solid state structure of these complexes indicated



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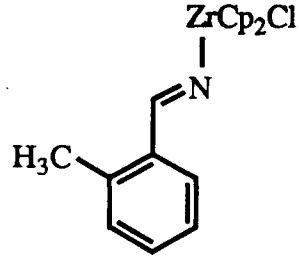

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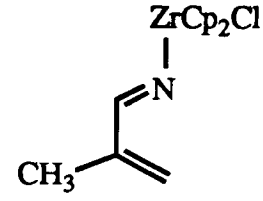

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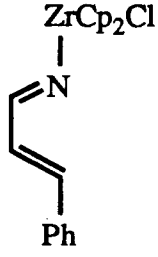

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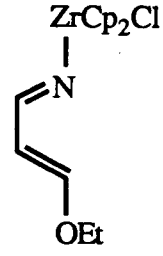

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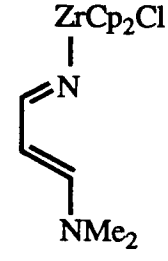


71

significant delocalization of the nitrogen lone-pair into an empty d-orbital of zirconium. Thus, as formally 18-electron complexes they lacked the empty orbital presumed necessary for the transfer of an organic moiety from one species to another, via a four-centered transition state. However, as solution state structure does not always parallel solid state structure, attempts were made to obtain imine and 1-azadiene transfer from zirconium to selenium and phosphorus.

In a very recent publication describing the synthesis and X-ray crystal structure analysis of the heteroallene-type metallocene $Cp_2Zr(N{=}CPh_2)_2$ (**90**), the authors expressed surprise at the poor correlation between solution and solid state data for this complex.[84] From the X-ray structure, it was expected that the ^1H NMR spectrum of **90** would show two sets of phenyl resonances. However, even at low temperature these workers only observed one type of aromatic resonance. They accounted for this observation by proposing a pathway in which a change in hybridization at the "azomethine" nitrogen occurred (Figure 25). This process initially involves a "decoupling" of the Zr=N multiple bond (π–interaction), followed by a rapid rotation about the Zr–N bond (σ-rotation) and finally, reformation of the Zr=N multiple bond. Such a process could account for the observed facile transfer reaction of imine and 1-azadiene moieties from zirconium to selenium and phosphorus.

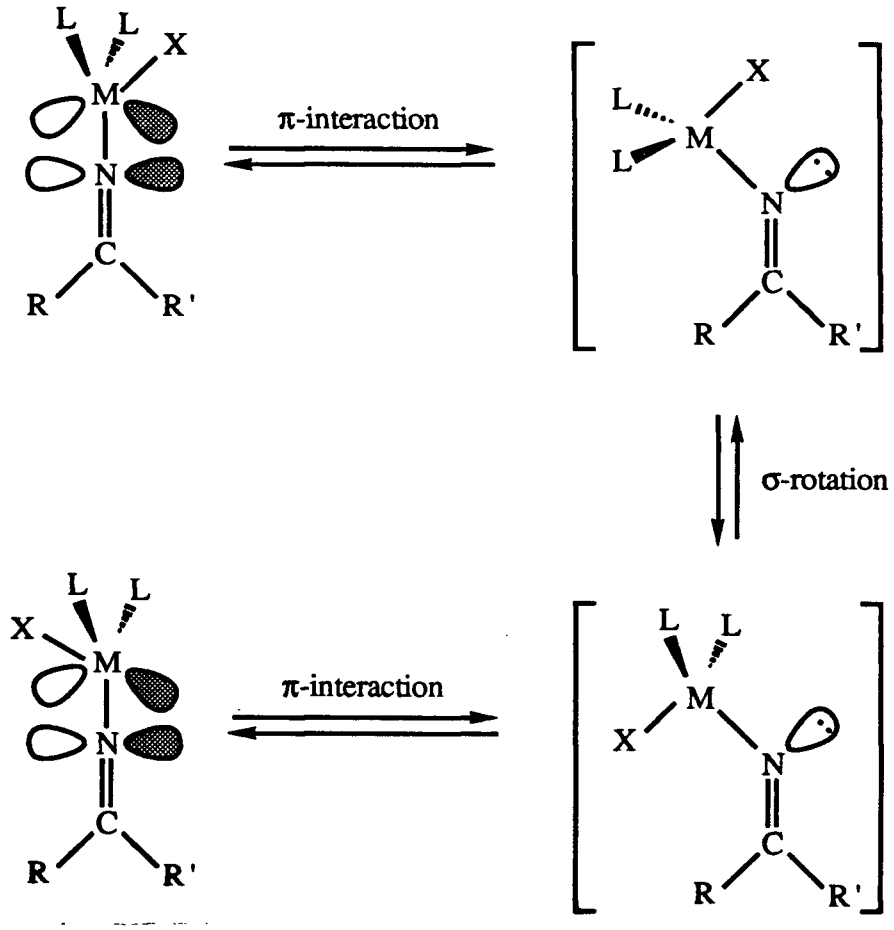
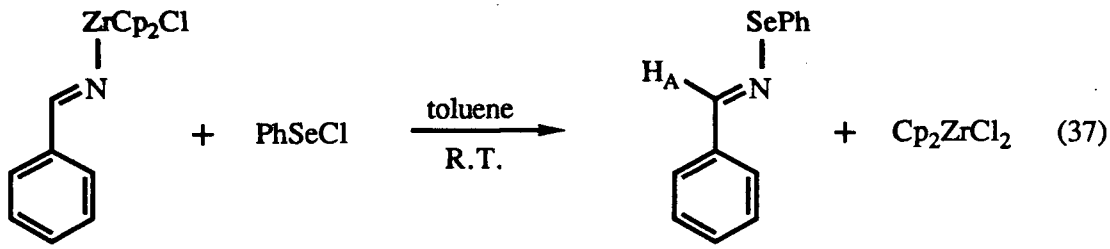


Figure 25. Rotation of heteroallene complexes via changes in hybidization.

3.6.1 Transfer of Imine and 1-Azadienyl Moieties from Zirconium to Selenium.

Although many examples of sulfinimines possessing both the imine function and a sulfur-nitrogen bond exist,[85] few examples of the corresponding selenoimines are known.[86] There are also examples of sulfur-substituted 1-azadienes in the literature,[85c] but we are unaware of any reported examples of selenium-substituted 1-azadienes. Therefore, it was our desire to investigate the preparation of imine and 1-azadiene species, substituted at nitrogen by selenium. We hoped to access such compounds by the transfer of the imine and 1-azadiene moieties from zirconium to selenium.

Reaction of **62** with phenylselenenyl chloride (PhSeCl) at room temperature in the dark, caused an immediate discharge of the deep red color of the PhSeCl. Analysis of the bright yellow oil, obtained after workup, by ^{1}H NMR spectroscopy indicated the presence of only one isomer of the desired selenoimine **91** (equation 37). Further analysis of the



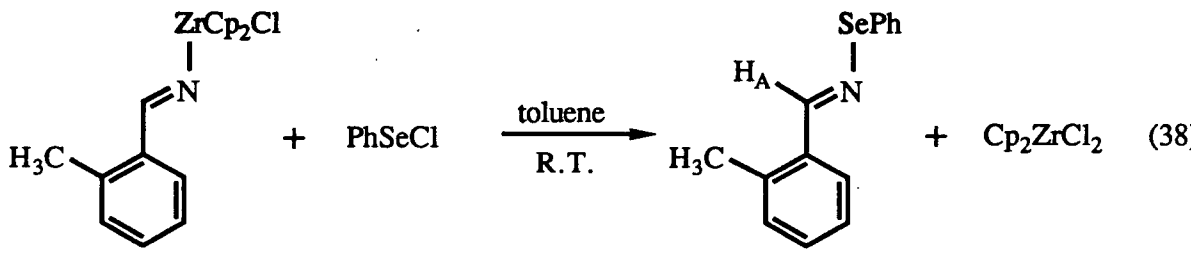
62 **91** **73%**

^{1}H NMR spectrum revealed a $^3J_{ASe}$ coupling constant of 28 Hz, the magnitude of which is probably indicative of the stereochemistry of the product. Based on this and the results of an ^{1}H NOEDIFF experiment on a related compound (**94**), it was assumed that **91** was the E isomer (vide infra).

Previous workers have used ^{1}H NOEDIFF spectroscopy to differentiate E and Z isomers of methyl enol ethers[87] and trimethylsilyl enol ethers.[88] In these experiments, the

vinyl proton was irradiated and an enhancement of the methyl of the enol ether, or the methyls of the silyl enol ether were observed only for the E isomer. Attempts to prove the stereochemistry of the selenoimine **91** by this method were unsuccessful. This was due, in part, to the poor stability of this compound. It was observed to decompose readily at room temperature, to give diphenyl diselenide (Ph_2Se_2) and some unidentified organic products. The propensity of compounds containing selenium-nitrogen bonds to decompose, generating diselenides has been previously reported.[86]

The selenoimine **92** was prepared by reaction of **63** with PhSeCl (equation 38).



63 **92** 75%

Again, only one isomer was observed by ^1H NMR spectroscopy. Attempts to prove the stereochemistry of this product by ^1H NOEDIFF spectroscopy were unsuccessful. It was assumed that selenoimine **92** has the same stereochemistry as **91**, due to the similarity of the $^3J_{ASe}$ coupling constants of 29.5 and 28 Hz, respectively. The ^1H NMR spectrum of **92** is shown in Figure 26. Although the latter compound was more stable than **91**, significant decomposition to Ph_2Se_2 was observed after 24 hours at room temperature.

Reaction of the complex **68** with PhSeCl at room temperature gave, after workup, the desired selenium-substituted 1-azadiene **93** (equation 39, p 86). Product analysis, by ^1H NMR spectroscopy, indicated that only one isomer was present. No direct evidence for the stereochemistry of the product could be obtained; however, the $^3J_{ASe}$ coupling constant of 29 Hz suggests that it has the same stereochemistry as the selenoimines **91** and **92**. This selenium-substituted 1-azadiene was found to be quite unstable at room temperature, and

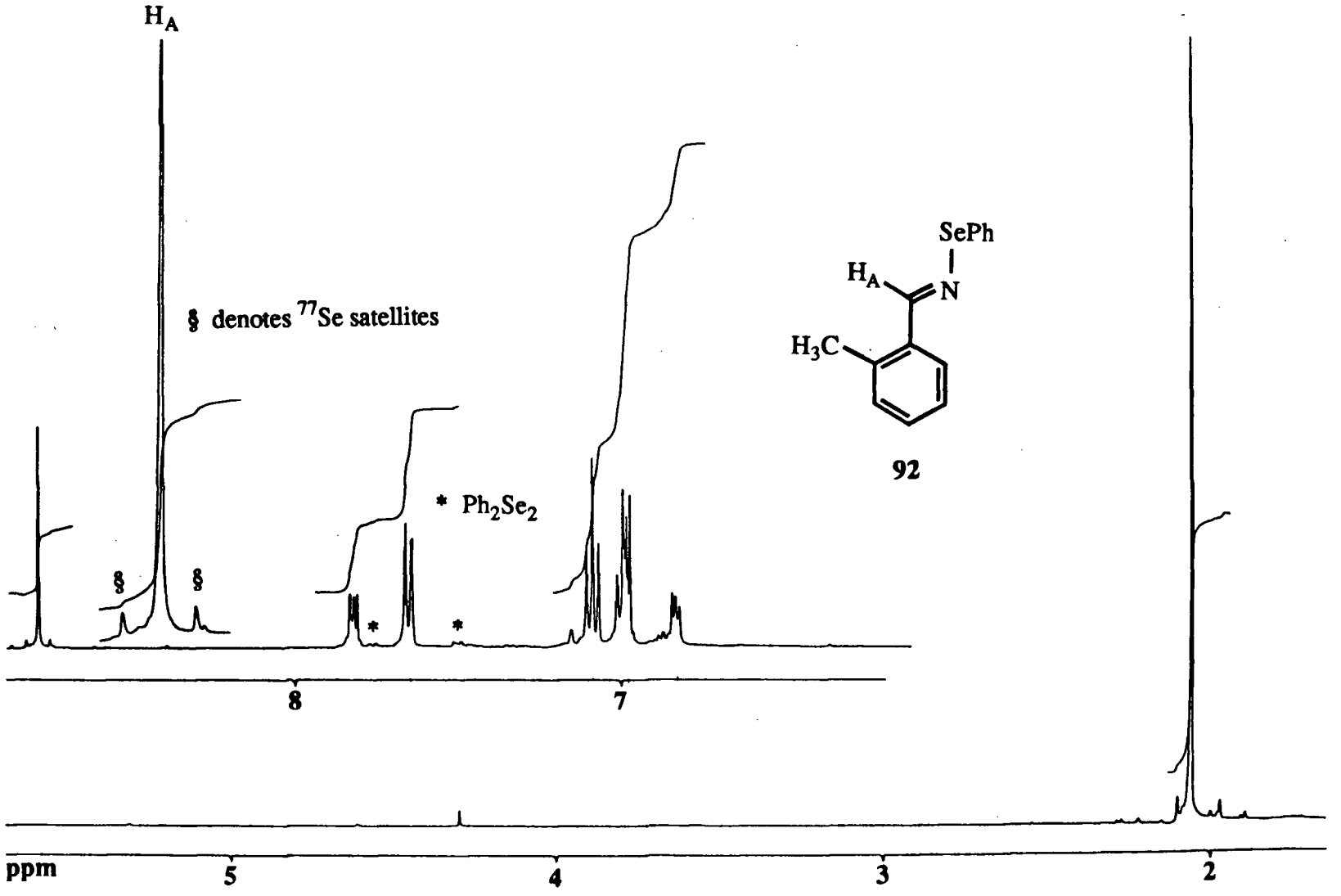
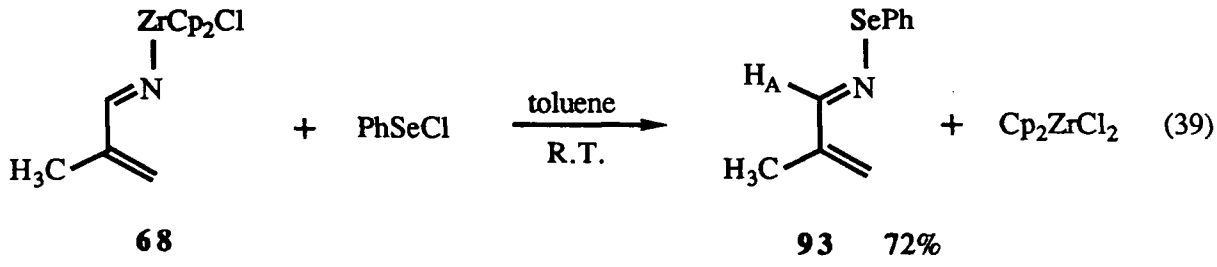


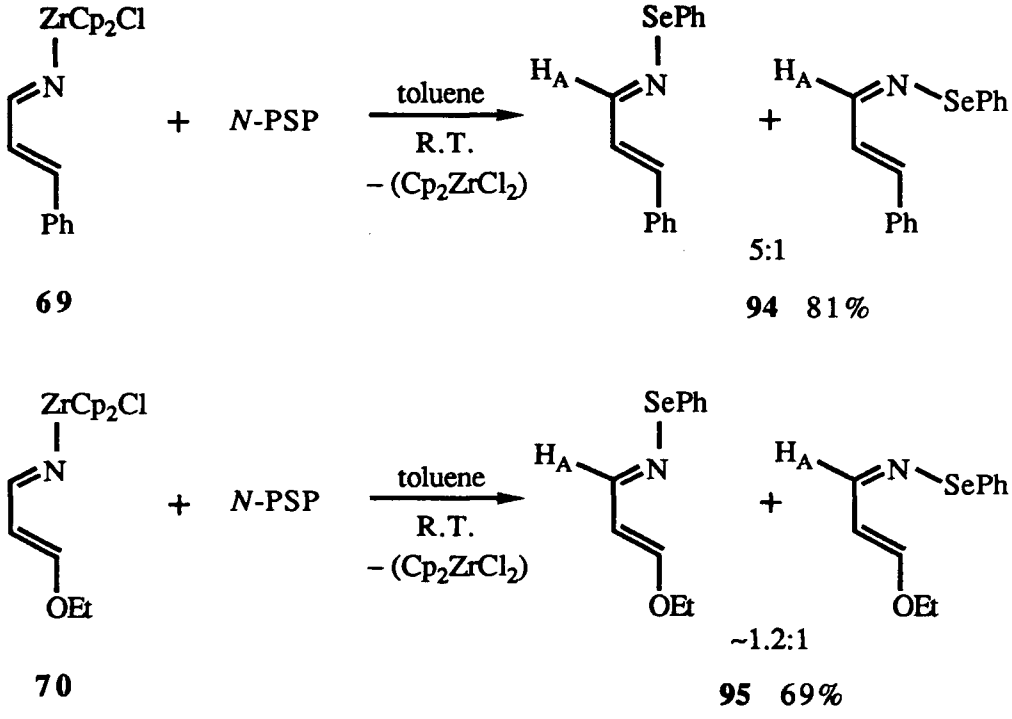
Figure 26. 400 MHz ^{1}H NMR spectrum of **92** in C_6D_6.



68 **93** 72%

decomposed readily to Ph_2Se_2. The presence of Ph_2Se_2 can be clearly seen in the ^1H NMR spectrum of **93**, shown in Figure 27 (next page).

The 1-azadienes **94** and **95** were prepared by similar procedures from complexes **69** and **70**, using *N*-PSP as the selenium transfer reagent (Scheme 24). For these compounds,



Scheme 24

^1H NMR spectroscopy indicated that a mixture of geometric isomers had been obtained. The 1-azadiene **94** was obtained as a 5:1 mixture of geometric isomers. Assignment of the stereochemistry for the major component as the E isomer was obtained by ^1H NOEDIFF

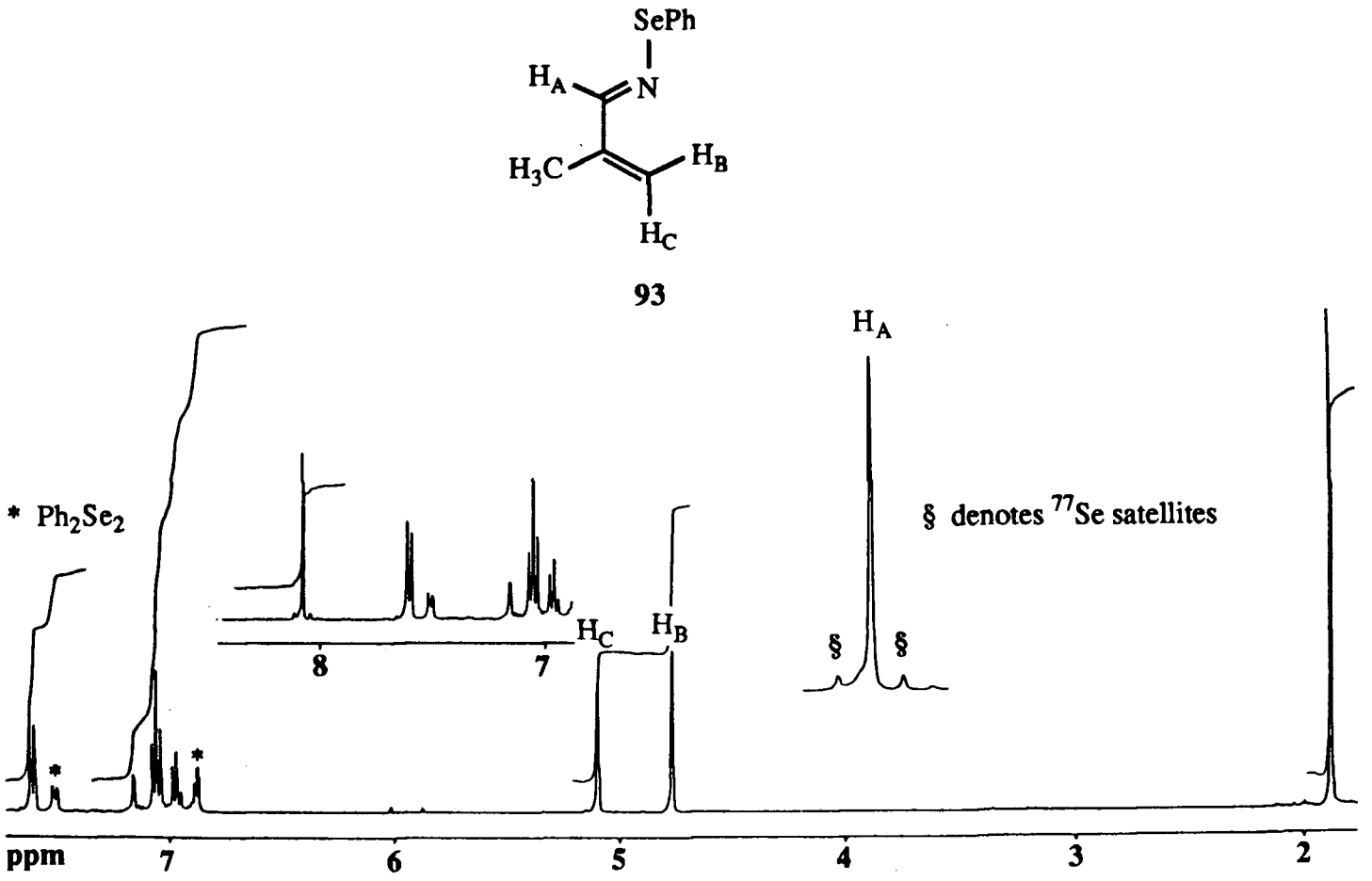


Figure 27. 400 MHz ^1H NMR spectrum of **93** in C_6D_6.

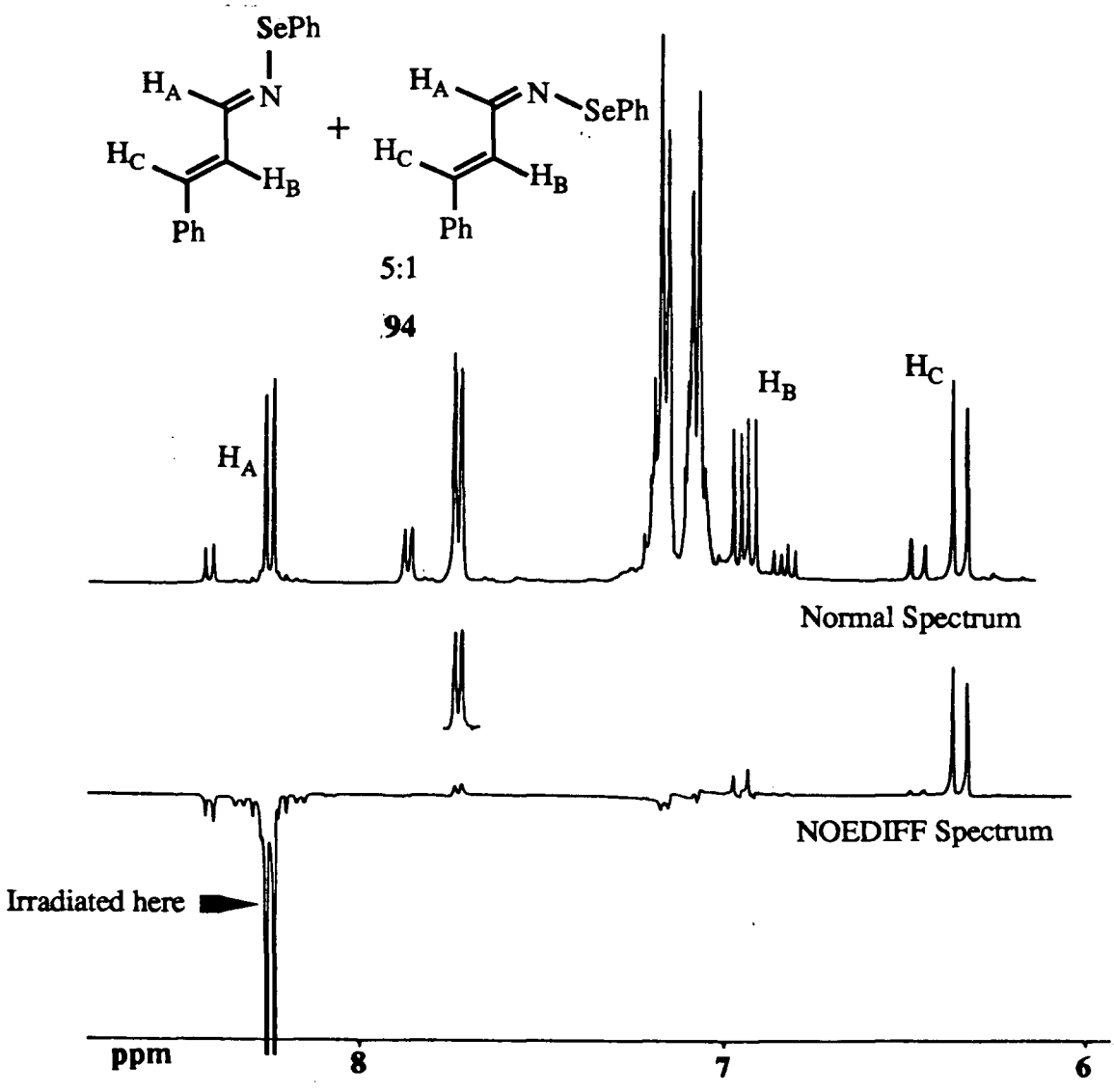


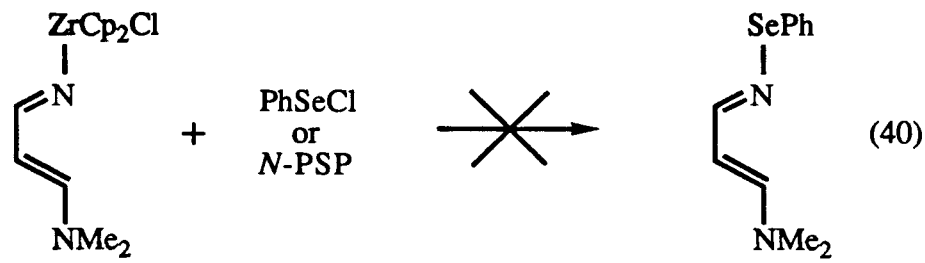
Figure 28. 400 MHz ^{1}H NMR and NOEDIFF spectra of **94** in C_6D_6.

spectroscopy (Figure 28). Irradiation of the imine proton, for the major component, gave enhancement of the *ortho*-phenyl protons of the PhSe group, and of proton H_C. The enhancement of proton H_C suggests that the 1-azadiene **121** adopts the s-trans conformation in solution. The $^3J_{ASe}$ coupling constant for the major isomer was measured as 28 Hz, due to the relative intensity of H_A for the minor isomer the magnitude of its coupling to selenium could

not be clearly determined. The $^3J_{ASe}$ coupling constant for the major isomer of **94** lends further credence to the assignment of E stereochemistry for the compounds **91-93**.

For the 1-azadiene **95**, the isomers were formed in an approximately 1.2:1 ratio. Use of ^{1}H NOEDIFF spectroscopy, to directly assign the stereochemistry of the major isomer was not possible due to the small chemical shift difference between the imine protons of the two isomers. However, the $^3J_{ASe}$ coupling constants for the major isomer was measured as 28.5 Hz; therefore by analogy to compound **94**, it was assumed that the major component was the E isomer.

It should be noted that the use of *N*-PSP for the preparation of 1-azadienes **94** and **95** gave higher isolated yields than PhSeCl, but did not effect the ratio of isomers. Also, it appears that the isomeric ratio is determined during the transfer process from zirconium to selenium, as neither irradiation with fluorescent light, nor thermolysis at 80°C brought about a change in the ratio of isomers. Attempts to prepare the 1-azadiene **96**, by reaction of the complex **71** with either *N*-PSP or PhSeCl proved unsuccessful (equation 40). The isolation of

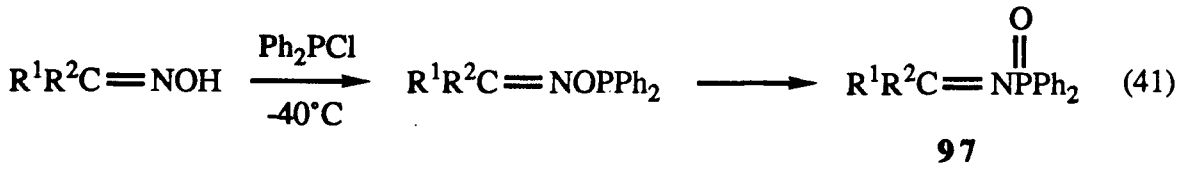


71 **96** (40)

diphenyl diselenide, in near quantitative amounts, suggests that the transfer reaction may indeed proceed; however, under the reaction conditions employed **96** is extremely unstable and readily decomposes.

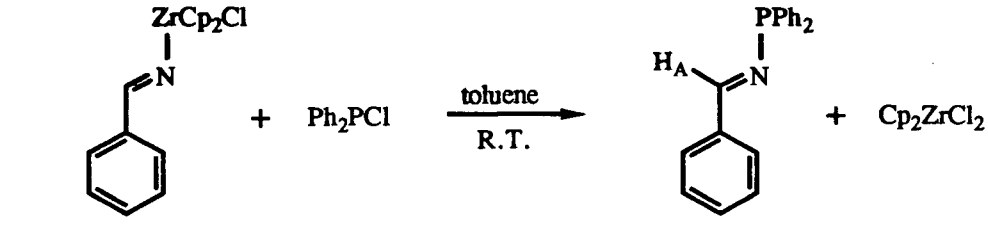
3.6.2 Transfer of Imine and 1-Azadienyl Moieties from Zirconium to Phosphorus.

The preparation of heterosubstituted imines, containing a phosphorus-nitrogen bond has been described in the general syntheses of diphenylphosphinylimines **97** (equation 41).[89]

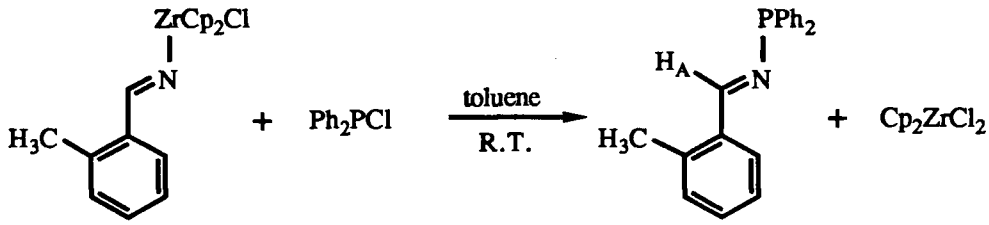


97 (41)

However, to our knowledge, there are no examples of phosphinoimines or phosphorus-substituted 1-azadienes, where phosphorus is directly bonded to nitrogen. Therefore, as a means of extending the generality of the imine and 1-azadiene transfer reaction from zirconium, and to provide a general route to phosphinoimines and phosphorus-substituted 1-azadienes, it was decided to investigate the reaction of complexes **62**, **63** and **68-71** with Ph_2PCl.



62 **98** 83%



63 **99** 86%

Scheme 25

Reaction of the complexes **62** and **63** with Ph_2PCl at 80°C gave, after workup, the desired phosphinoimines **98** and **99** (Scheme 25). In each case, product analysis by ^1H NMR spectroscopy indicated that only one isomer had been formed. The stereochemistry of compound **99** was determined by ^1H NOEDIFF spectroscopy (Figure 29). Irradiation of

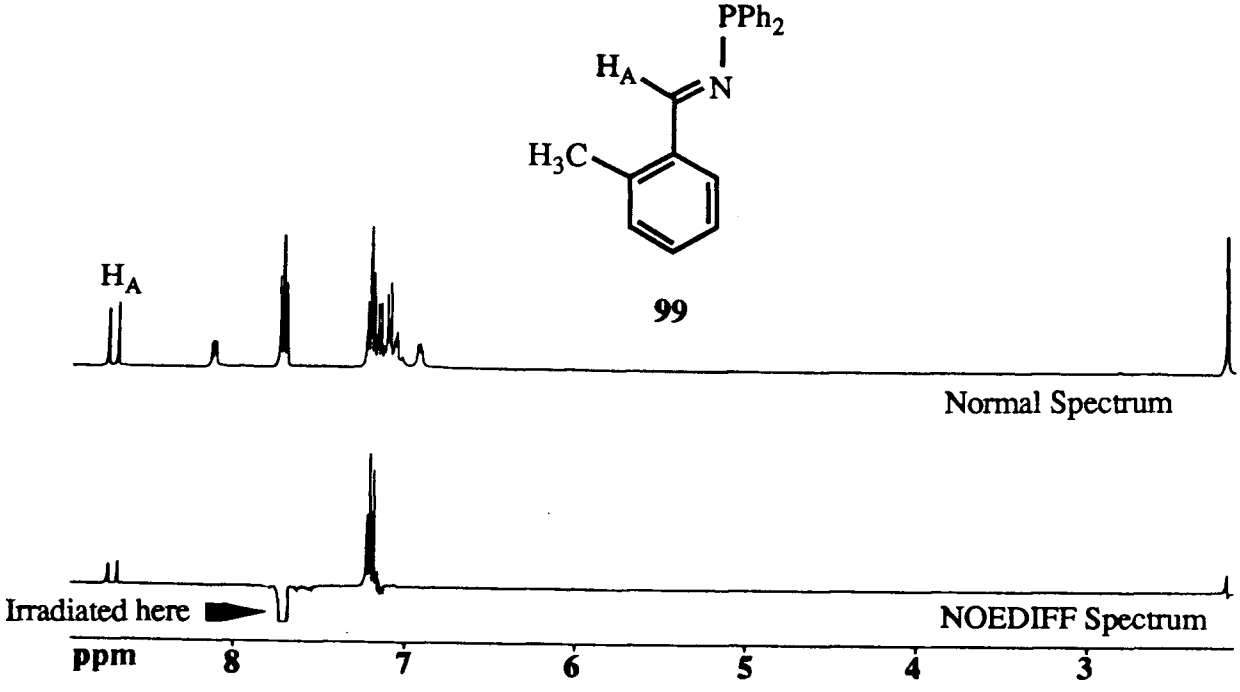
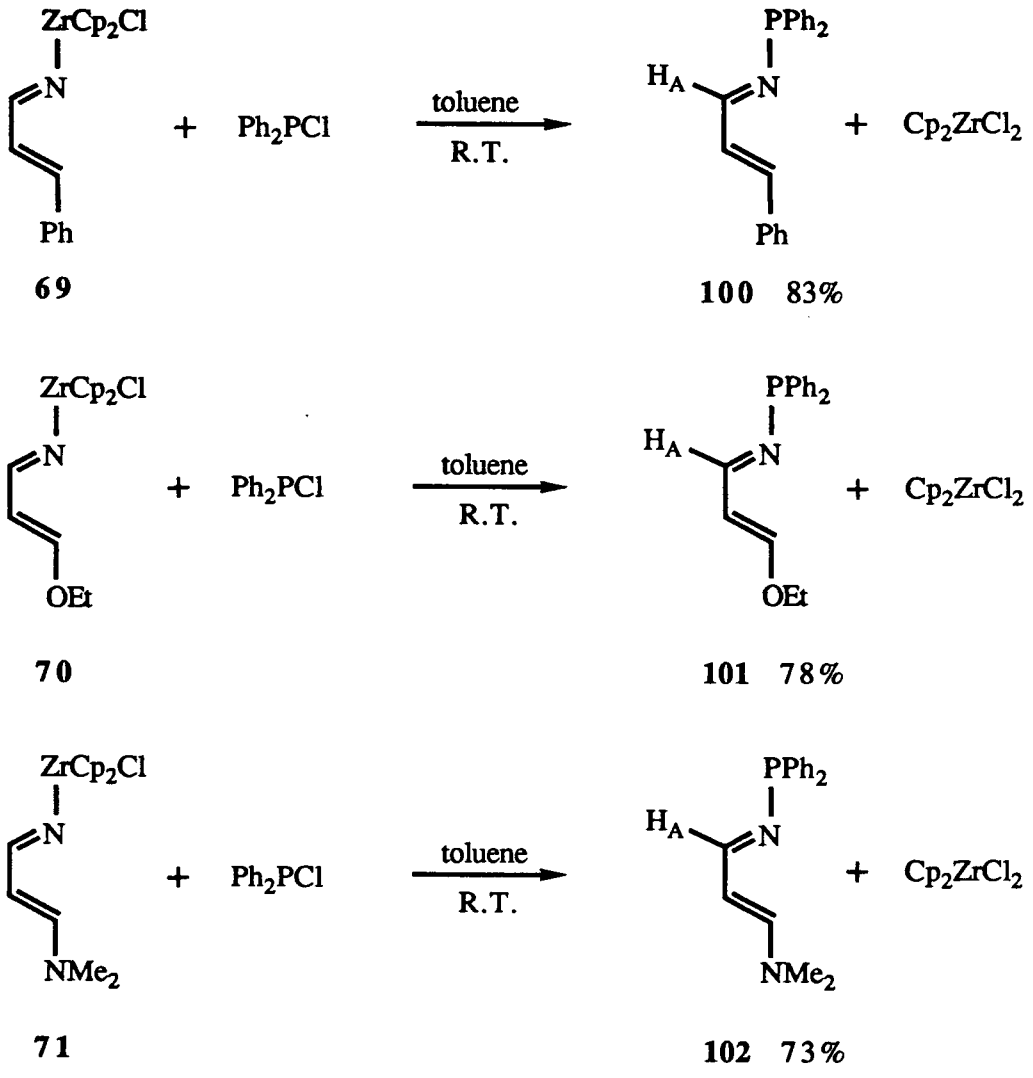


Figure 29. 400 MHz ^1H NMR and NOEDIFF spectra of **99** in C_6D_6.

the *ortho*-phenyl protons of the Ph_2P group, gave enhancement of the imine proton and of the *meta*-phenyl protons of the Ph_2P group. The stereochemistry of the latter compound was therefore assigned as the E isomer. The $^3J_{BP}$ coupling constant for this compound was measured as 22 Hz. It was assumed that the magnitude of this coupling constant would be indicative of the stereochemistry of structurally similar molecules. As such, the phosphinoimine **98** was assigned as the E isomer, due to an observed $^3J_{BP}$ coupling constant of 21 Hz.

The phosphorus-substituted 1-azadienes **100-102**, were prepared in a similar manner, by reaction at room temperature of complexes **69-71** with Ph_2PCl (Scheme 26). In each



Scheme 26

case, only one isomer was formed, the stereochemistry of which was assigned based on the magnitude of the $^3J_{BP}$ coupling constant. The $^3J_{BP}$ coupling constants for the compounds **100-102** were measured as 22, 23 and 25 Hz, respectively. It was therefore assumed that they all possessed the E configuration about the imine functionality of the 1-azadiene fragment. The ^1H NMR spectrum of **100** is shown in Figure 30.

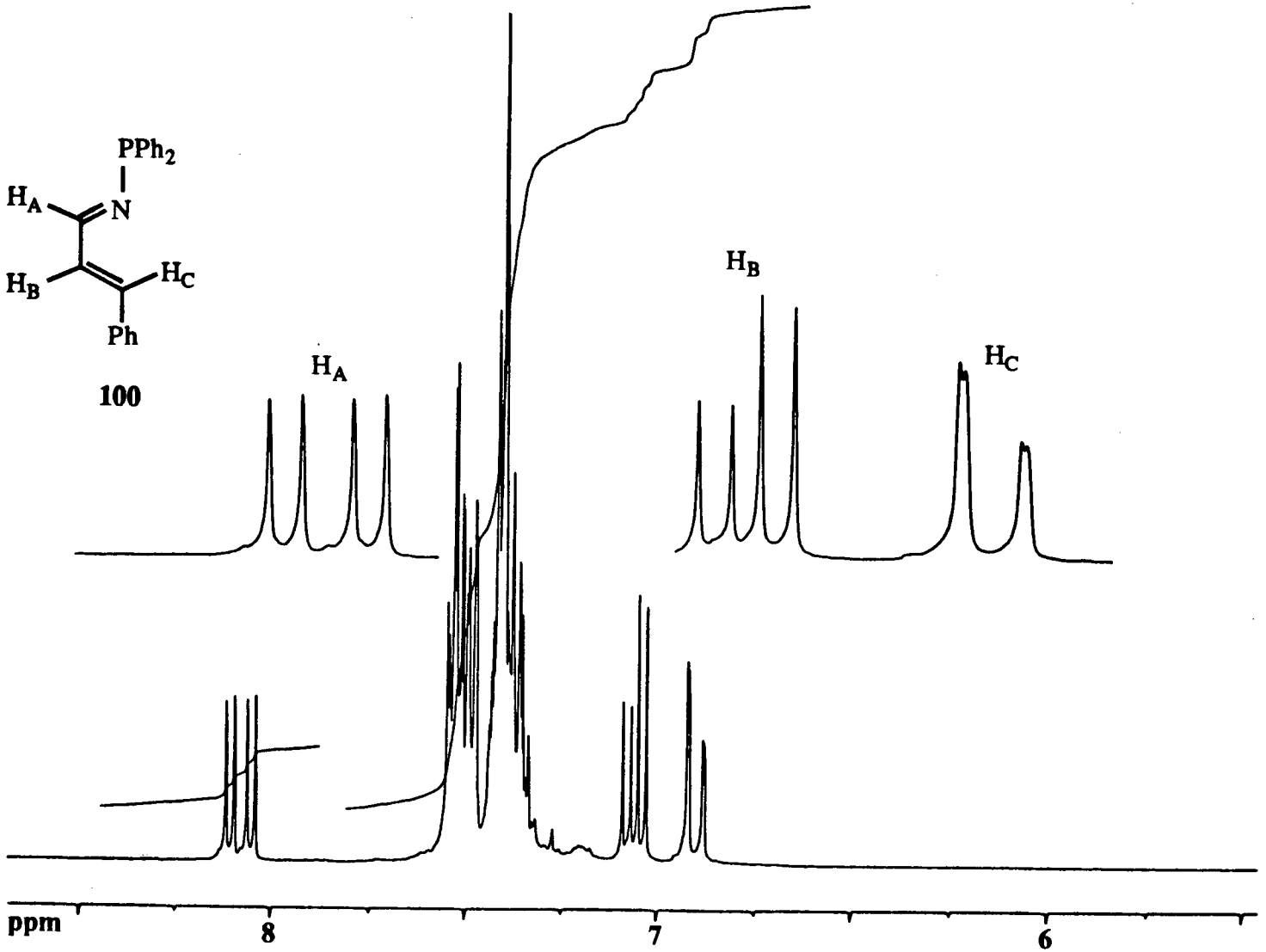
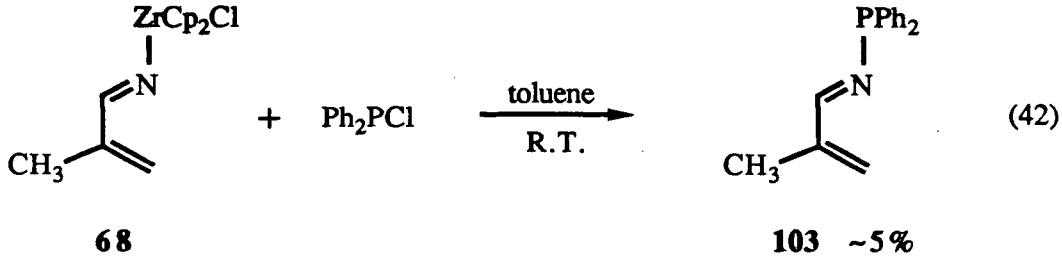


Figure 30. 400 MHz ^{1}H NMR spectrum of **100** in $CDCl_3$.

Unfortunately, reaction of complex **68** with Ph_2PCl, under a variety of conditions, gave extremely poor yields (~5% or less) of the desired 1-azadiene **103** (equation 42). At



(42)

68 **103** ~5%

temperatures below 40°C negligible product formation was observed, whereas above this temperature the product appeared to decompose as it was formed.

Through the procedures outlined above, a series of general methods has been developed for the transfer of 1,3-dienyl, imine and 1-azadienyl moieties from zirconium to various heteroatoms. In the case of the transfer of 1,3-dienyl moieties from zirconium, the reaction was observed to occur with complete stereoselectivity.

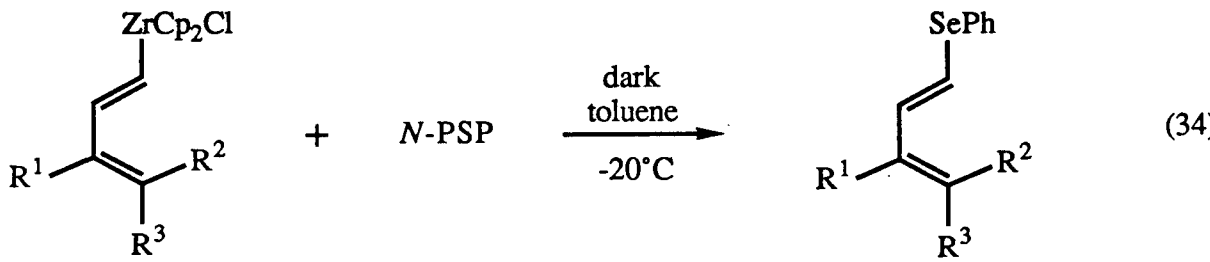
From this array of heterosubstituted organic molecules, the reactivity of the 1-(phenylseleno)-1,3-dienes **88a-d** under photochemical and thermal conditions was investigated in detail. A preliminary investigation into their Diels-Alder reactivity was also made. The results of these experiments are discussed in Chapter 4.

CHAPTER 4

Reaction of 1-(Phenylseleno)-1,3-dienes under Photochemical and Thermal Conditions. Diels-Alder Reactivity with Maleic Anhydride.

4.1 Photochemical Isomerization.

As described in Chapter 3, the stereoselective syntheses of the selenium-substituted 1,3-dienes **88a-d** were achieved by reaction of the complexes **55a-d** with *N*-PSP at -20°C in the dark (equation 34). These conditions were necessary to avoid the formation of mixtures of



(34)

55a-d **88a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

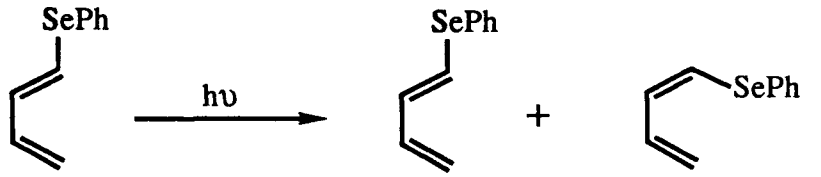
c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 R^3 = $-(CH_2)_4-$, $R^2 = H$

products when the reactions were performed at room temperature in the presence of fluorescent light; in addition, there was no beneficial effect by using other selenium transfer reagents, i.e., PhSeCl or Ph_2Se_2, under the same conditions. Analysis of these mixtures by ^1H NMR spectroscopy indicated that they were comprised of geometric isomers. Thus,

reaction of **55a** with *N*-PSP at room temperature under fluorescent light resulted in the formation of an E/Z mixture of geometric isomers of **88a**. Analysis of the ^{1}H NMR spectra of the products obtained by reaction of the complexes **55b** or **55c** under identical conditions, indicated the presence of four compounds as evidenced by four singlets in the methoxy region (3.5-3.7 ppm) of each spectrum. In each case, the mixture of compounds appeared to be identical by ^{1}H NMR spectroscopy. In contrast, the diene **88d** could be prepared isomerically pure, by the room temperature reaction of **55d** with *N*-PSP under fluorescent light. As the dienes could be synthesized isomerically pure by control of the reaction conditions, experiments were designed to determine whether the isomerization process was thermally and/or photochemically initiated.

An isomerically pure sample of **88a** (~0.20-0.25 M in C_7D_8) was placed in the probe of a 400 MHz ^{1}H NMR spectrometer held at -20°C. Great care was taken to exclude light. The probe temperature was then increased to 30°C in 10°C increments. After each temperature increase, data for a ^{1}H NMR spectrum were acquired. In all instances, no sign of isomerization was observed. The probe temperature was then increased to 90°C for 1 h. Again, no isomerization resulted. Finally, the sample was removed from the probe and taped to a fluorescent tube for approximately 1.5 h. After this exposure, the subsequent ^{1}H NMR spectrum of the sample revealed the presence of a 2:1 mixture of E/Z geometric isomers of **88a** (equation 43).[74] The ^{1}H NMR spectrum of this 2:1 mixture of geometric isomers is



(43)

88a

shown in Figure 31 (next page). Further irradiation of the sample with fluorescent light, for up to 48 h, gave no change in the observed 2:1 mixture of isomers. That this 2:1 mixture of

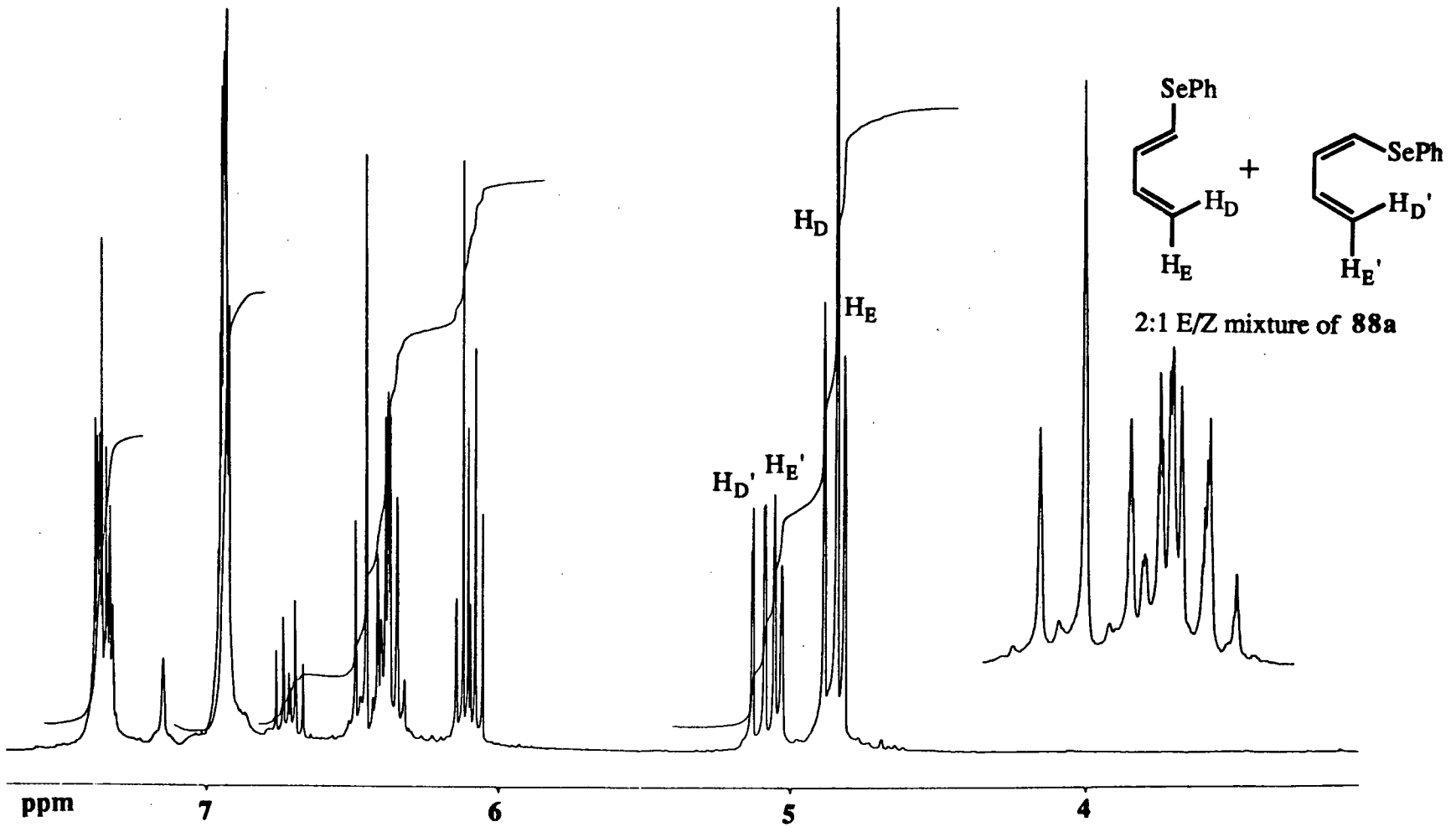
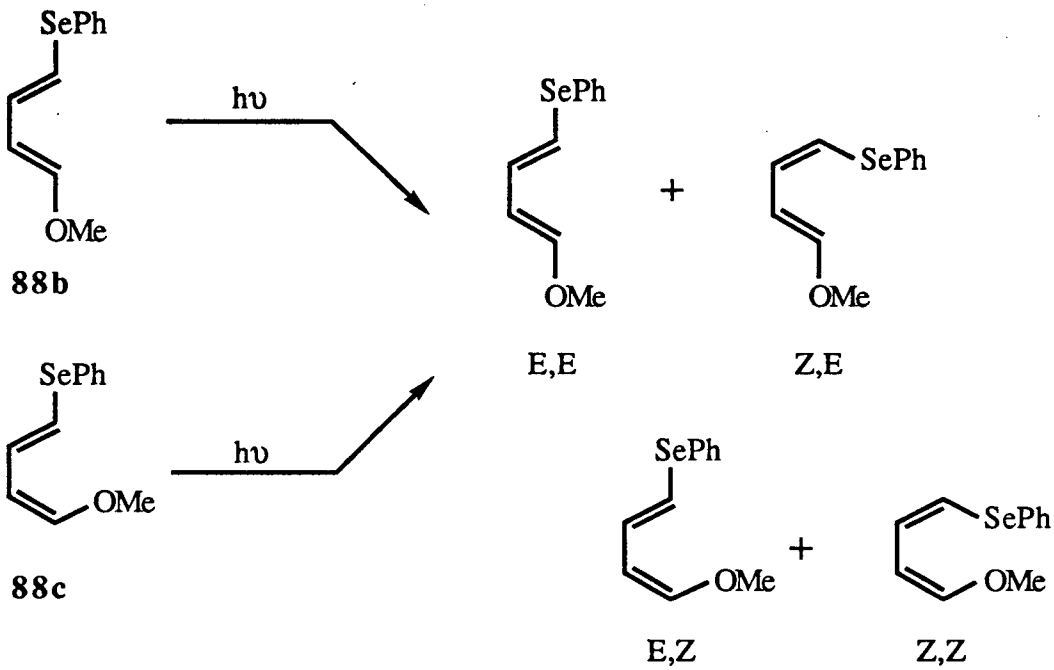


Figure 31. 400 MHz ^{1}H NMR spectrum of a 2:1 mixture of E/Z isomers of **88a** in C_6D_6.

geometric isomers for **88a** represents an equilibrium mixture was evident upon perturbing the equilibrium by addition of the isomerically pure E isomer of **88a** . Further photolysis of this new mixture of E/Z isomers resulted in the formation of the original 2:1 mixture.

When similar variable temperature ^{1}H NMR experiments were performed using **88b** and **88c**, no isomerization was observed. However, when the samples were irradiated with fluorescent light for 1.5 h, an identical mixture of all four possible stereoisomers was obtained in each case (Scheme 27). The ^{1}H NMR spectrum for the mixture of stereoisomers for **88b** is



Scheme 27

presented in Figure 32 (p 99). Through a series of ^{1}H NMR decoupling and NOEDIFF experiments, it was possible to assign all of the vinyl resonances in the region from 5-7 ppm. The spectrum of this expanded region, along with the appropriate assignments is shown in Figure 33 (p 100). Further evidence for the presence of four independent selenium-containing compounds, from the photolysis of **88b** can be seen in the ^{77}Se NMR spectrum of the mixture (Figure 34, p 101). The ratio of the four geometric isomers was obtained from

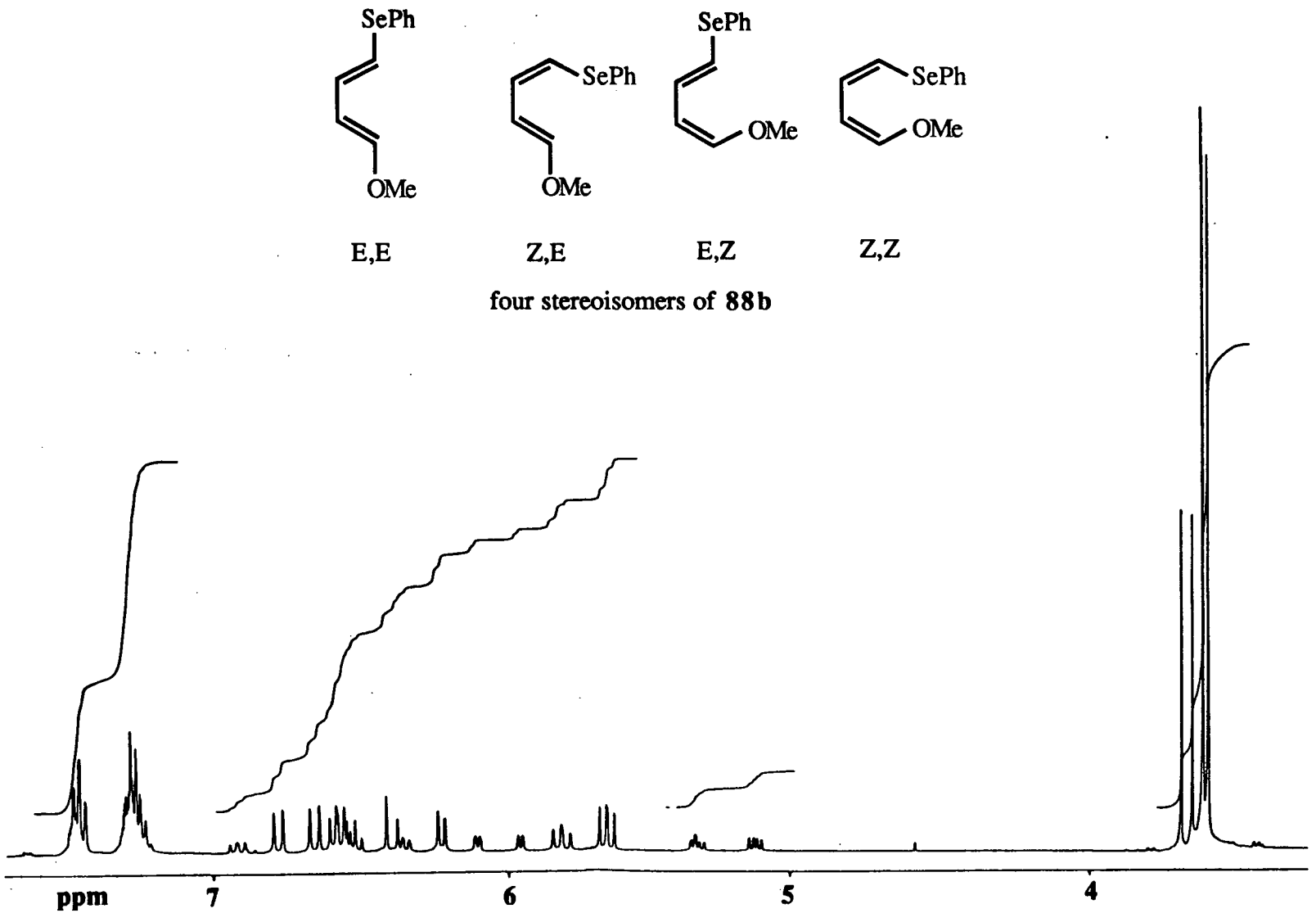


Figure 32. 400 MHz ^{1}H NMR spectrum of all four stereoisomers of **88b** in CD_2Cl_2.

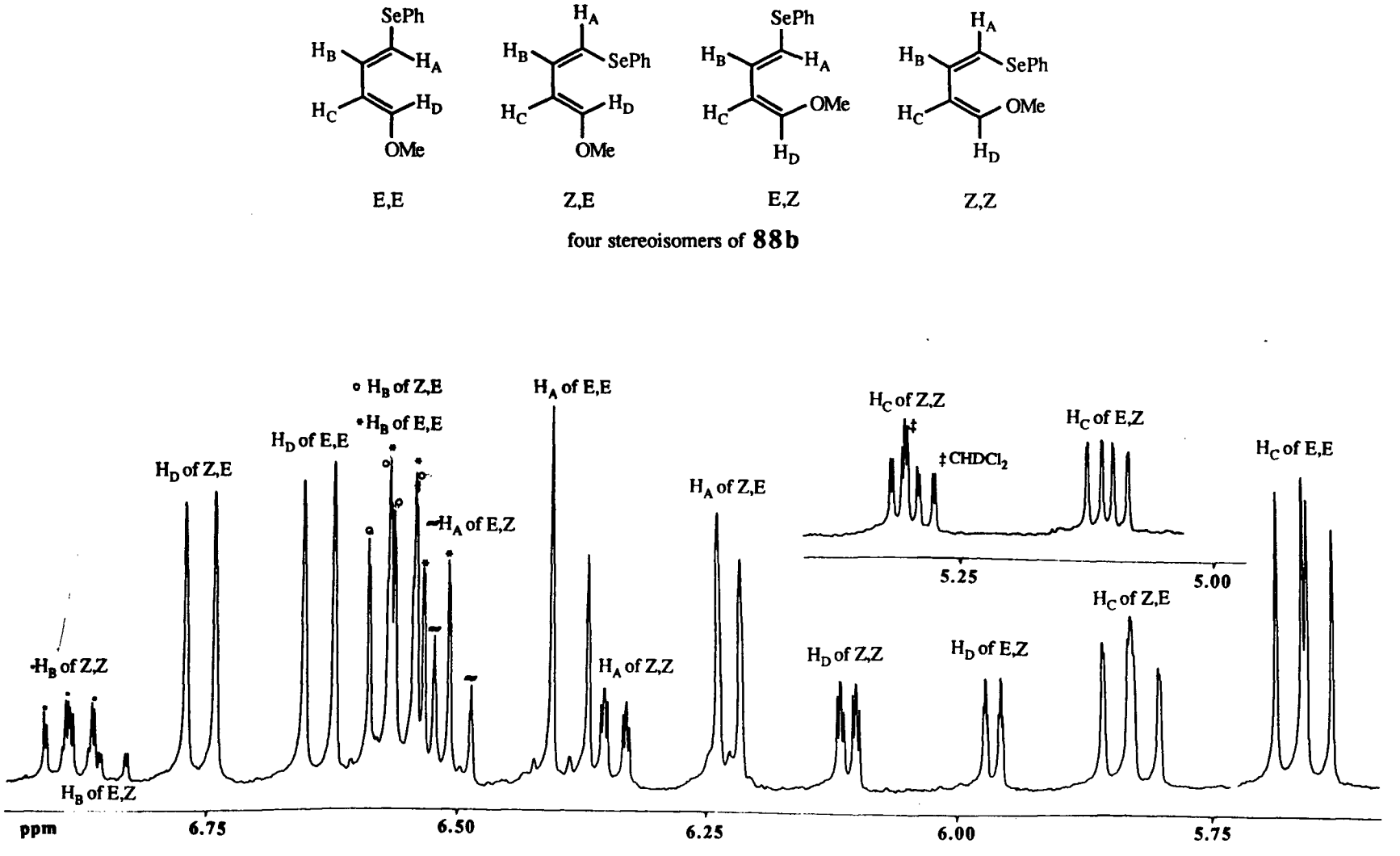


Figure 33. 400 MHz ^{1}H NMR spectrum of the expanded region from 5-7 ppm for the stereoisomers of **88b** in CD_2Cl_2.

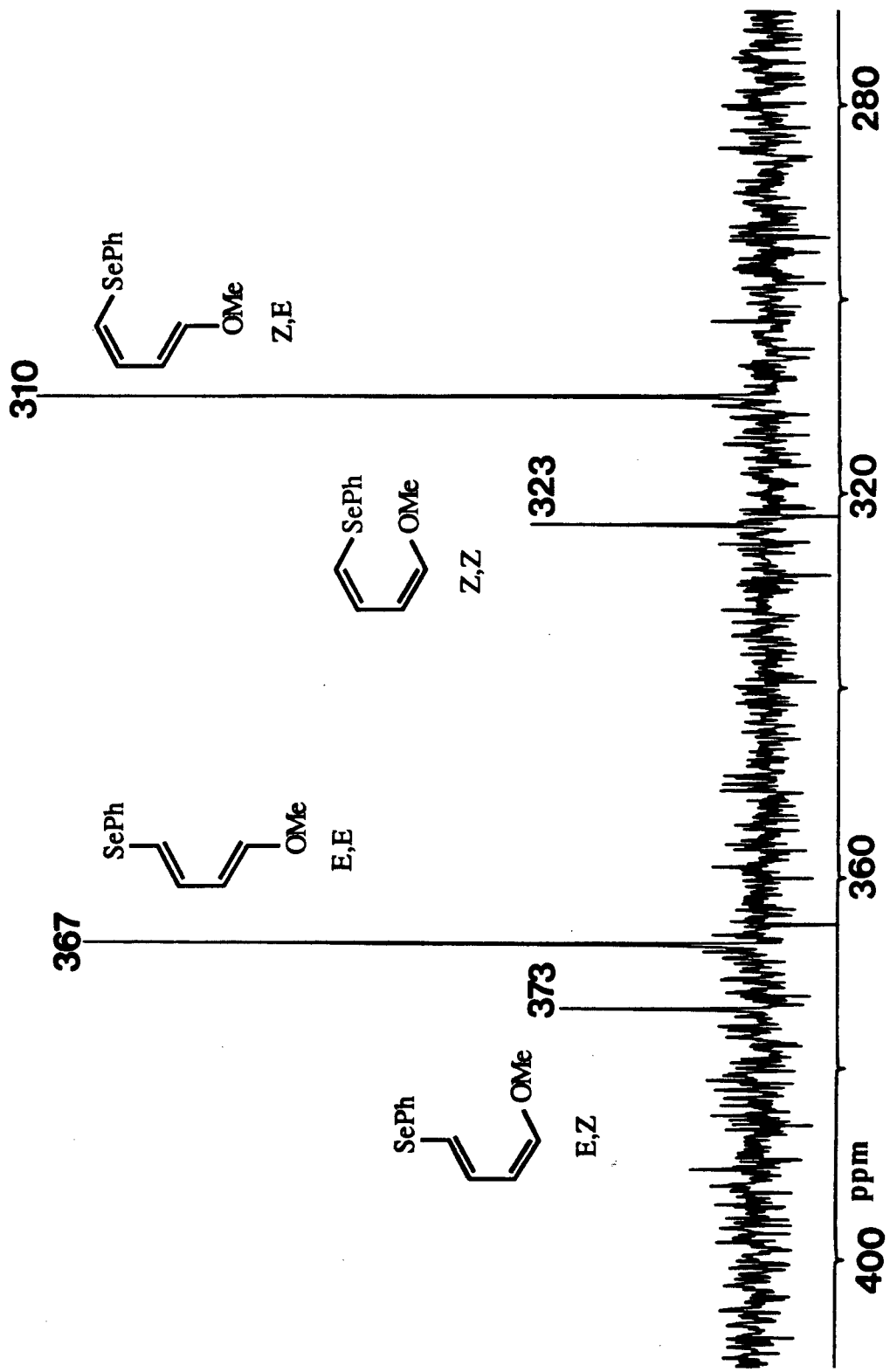


Figure 34. 76.3 MHz ^{77}Se NMR spectrum of the four stereoisomers of **88b** in $CDCl_3$.

the ^{1}H NMR spectrum. Over a series of different experiments, the ratio was observed to vary only very slightly, and was determined as 41(±2):13(±1):36(±2):10(±1) Z,E/Z,Z/E,E/E,Z. These values correlate well with those determined from the ^{77}Se NMR spectrum of the mixture.

Previous workers have observed that direct irradiation of methyl (*E*,*E*)-2,4-hexadienoate resulted in the formation of all four possible stereoisomers.[90] In this case, UV irradiation at 254 nm, close to the λ_{max} of the ester, was used. The irradiation source used in the experiments outlined here was a fluorescent lamp, which emits wavelengths from 380-800 nm. However, the possibility exists that some stray UV emission may result due to the nature of operation of a fluorescent lamp. The UV-vis spectrum of **88b** showed a broad ill-defined λ_{max} from 250-268 nm (ε 13800-14000), with **88c** exhibiting a relatively sharp λ_{max} at 270 nm (ε 15,900). The dienes **88a** and **88d** showed maximum absorptions at similar wavelengths. However, the dienes **88a-d** showed only low intensity absorptions (ε< 100) trailing into the visible region.

4.2 Mechanistic Studies on the Isomerization Process.

To determine whether the isomerization process was occurring via an intra- or intermolecular process, a crossover experiment was performed. It was assumed that if an intermolecular process was operable, cleavage would most likely occur at the selenium-carbon bond of the 1,3-diene unit. Therefore, it was required that the dienes **88a-d** be labelled in one case at the PhSe group to give **104**, and in the other case at the diene unit to give **105** (Figure 35). The crossover experiment would involve irradiation of a mixture of **104** and

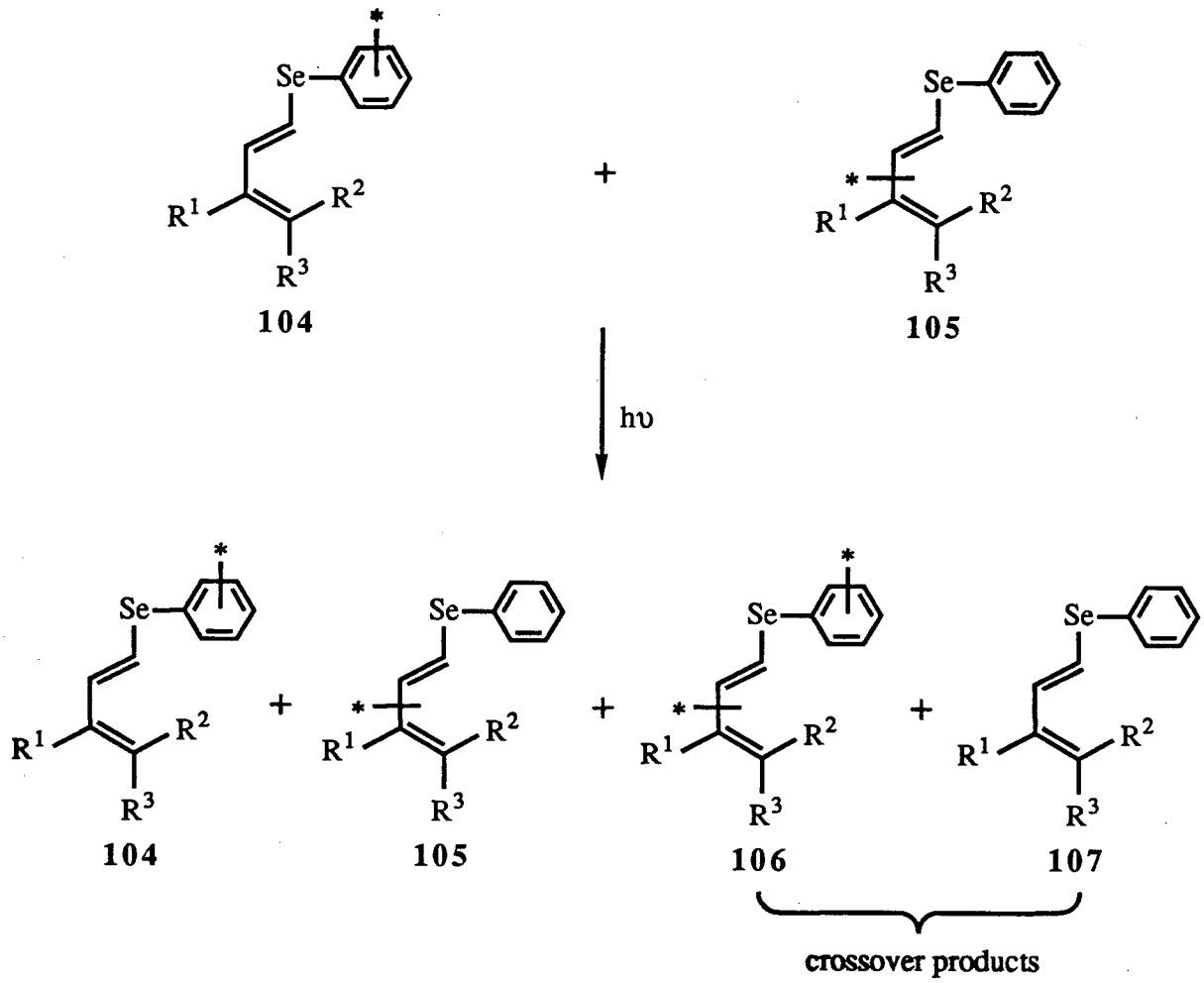
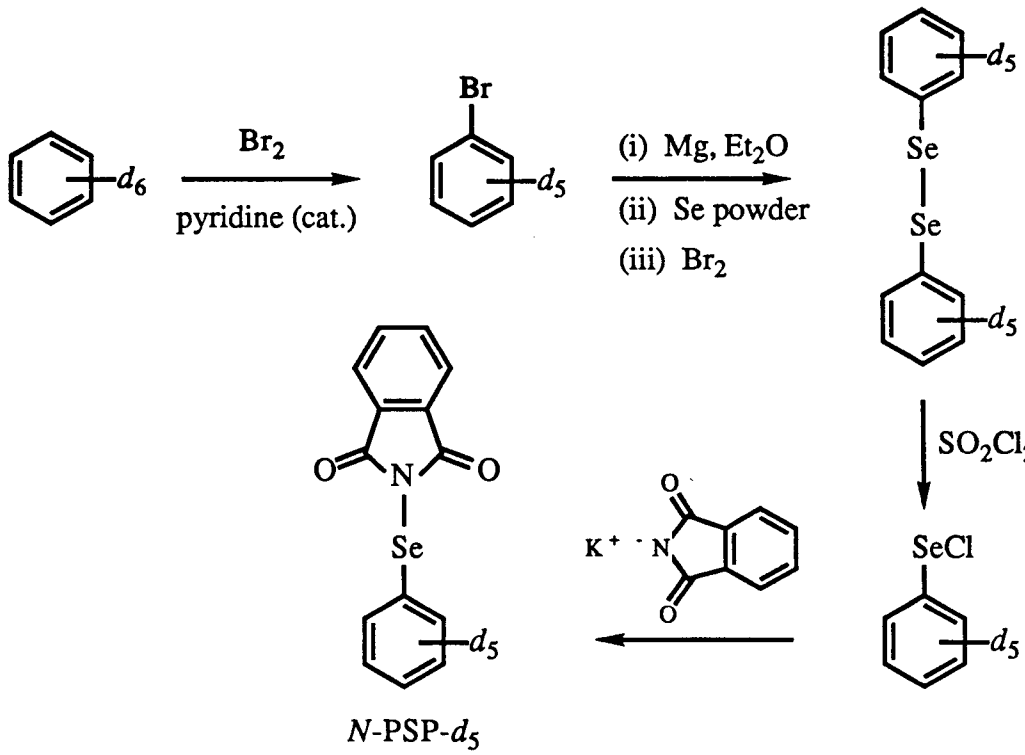
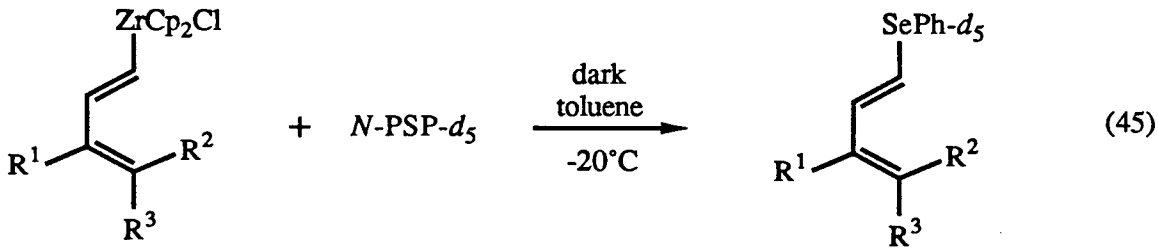


Figure 35. General design for crossover experiments using labelled (*) versions of **88a-d**.



Scheme 28



(45)

55a-d **88a-d-d_5**

a $R^1 = R^2 = R^3 = H$

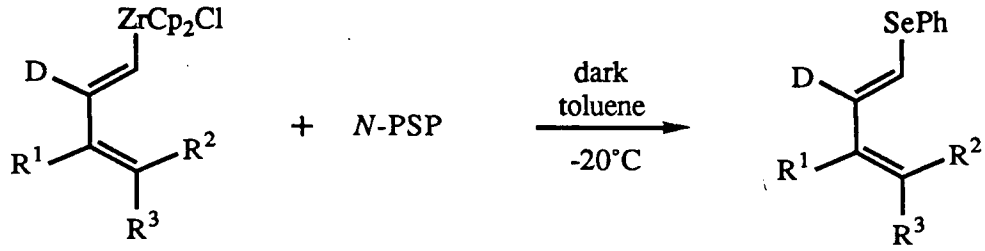
b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 R^3 = $-(CH_2)_4-$, $R^2 = H$

105. From analysis of the products, it could be determined whether or not the predominant pathway during the photochemical isomerization of **88a-d** was intra- or intermolecular. In the former case, one would not expect to see any of the crossover products **106** and **107**, whereas for an intermolecular process one would expect significant formation of these compounds.

As the deuterium-labelled complexes **55a-d**-d_1 had already been prepared by reaction of $Cp_2ZrCl(D)$ **2** with 1-ene-3-ynes **51a-d**, these could be used to label the diene unit of **88a-d** with a deuteron at the 2-position. Thus, the labelled dienes **88a-d**-d_1 were prepared according to equation 44. Analysis of these compounds by both ^1H NMR spectroscopy and



(44)

55a-d-d_1 **88a-d**-d_1

a $R^1 = R^2 = R^3 = H$

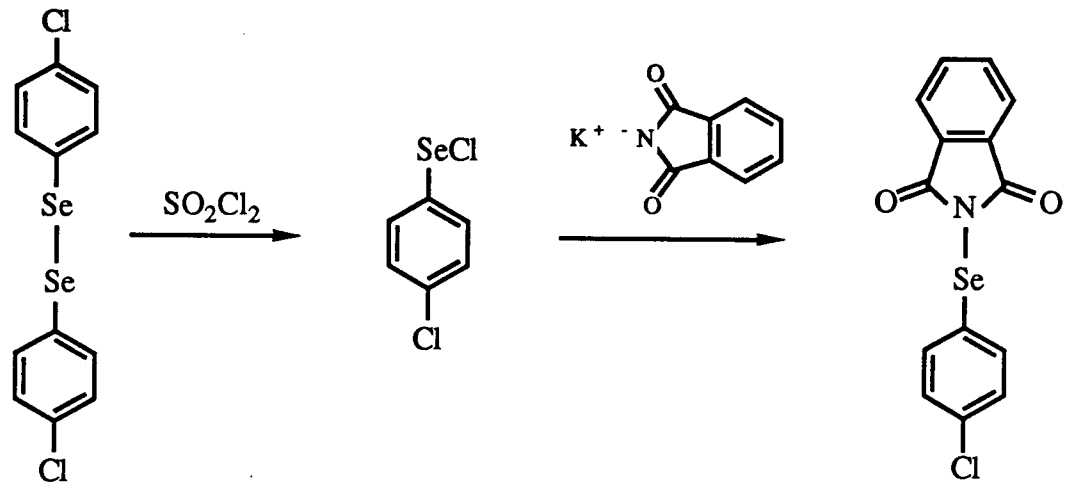
b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 $R^3 = -(CH_2)_4-$, $R^2 = H$

mass spectrometry, indicated that the deuterium incorporation was >98%. The labelling of the phenyl group of the PhSe fragment was performed in two ways. To make the change in structure as subtle as possible, so as to avoid any possible change in the mechanism of the isomerization reaction, *N*-(phenylseleno)phthalimide-d_5 (*N*-PSP-d_5) was first synthesized (Scheme 28). Reaction of *N*-PSP-d_5 with the complexes **55a-d**, as outlined in equation 45, gave the dienes **88a-d**-d_5 having the phenyl group of the PhSe fragment fully deuterated. Analysis of these compounds by ^1H NMR spectroscopy and mass spectrometry, indicated that

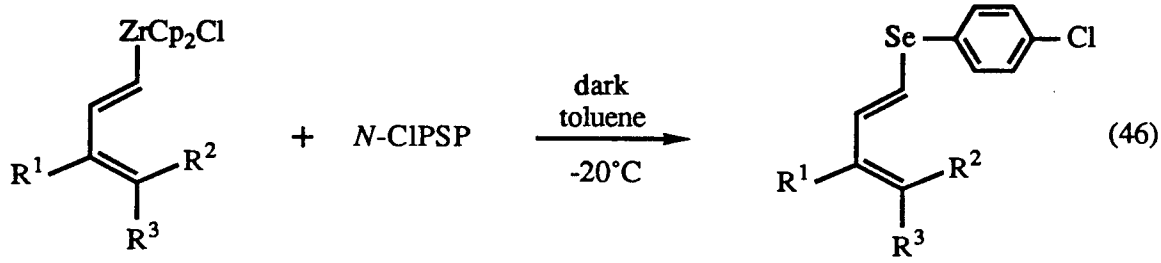
the deuterium incorporation was >98%. A different label for the PhSe fragment was developed by the synthesis of *N*-(4-chlorophenylseleno)phthalimide (*N*-ClPSP) as outlined in Scheme 29. Reaction of *N*-ClPSP with **55a-d** at -20°C in the dark proceeded cleanly to give



N-ClPSP

Scheme 29

the dienes **108a-d**, having the phenyl group of the PhSe fragment labelled with a *para*-chloro substituent (equation 46). Although the *para*-chloro substituent may affect the isomerization



(46)

55a-d **108a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 R^3 = $-(CH_2)_4-$, $R^2 = H$

process by changing the electronic nature of the selenium dienes, it was hoped that it would provide a sufficient structural difference to allow the detection of crossover products by ^{1}H NMR spectroscopy. Whereas, the combination of **88a-d**-d_1 and **88a-d**-d_5 would yield crossover products that would be indistinguishable by ^{1}H NMR spectroscopy.

Using these labelled compounds, two sets of crossover experiments were designed. In the first set of experiments, approximately equal concentrations of **88a-d**-d_1 and **88a-d**-d_5 were mixed together and the mixture was irradiated for ~1.5 h with fluorescent light. The products were then analyzed by ^{1}H NMR spectroscopy and mass spectrometry. Analysis of the photolyzed mixture by ^{1}H NMR spectroscopy was performed to establish that isomerization had taken place to yield the equilibrium mixture of isomers. It was envisaged that the use of mass spectrometry for this determination could prove difficult, as the masses of the products would only differ by one and five units. Also, each molecular ion fragment would be extremely complex due to the six isotopes of selenium. Five of these isotopes occur in reasonable natural abundance, namely, ^{76}Se (9.0%), ^{77}Se (7.6%), ^{78}Se (23.5%), ^{80}Se (49.8%), ^{82}Se (9.2%), with ^{74}Se being present in only 0.9% natural abundance. Therefore, to avoid any ambiguity in the determination of crossover products by mass spectrometry, a control experiment was designed in which approximately equal concentrations of **88b**-d_1 and **88b**-d_5 were irradiated independently, and then mixed prior to analysis by mass spectrometry. The molecular ion fragmentation pattern for this experiment was then compared with the one resulting from the crossover experiment in which **88b**-d_1 and **88b**-d_5 were mixed and then irradiated with fluorescent light. The results of these experiments are shown in Figure 36. Using ^{80}Se as the major isotope, molecular weights for **88b**-d_1 and **88b**-d_5 were calculated to be 241 and 245, respectively. The two compounds resulting from crossover would therefore have the unit masses of 240 (**88b**) and 246 (**88b**-d_6). The molecular ion fragmentation patterns for the control and crossover experiments are distinctly different, indicating that some degree of crossover has indeed taken place, and that the photochemical isomerization reaction does involve an intermolecular process.

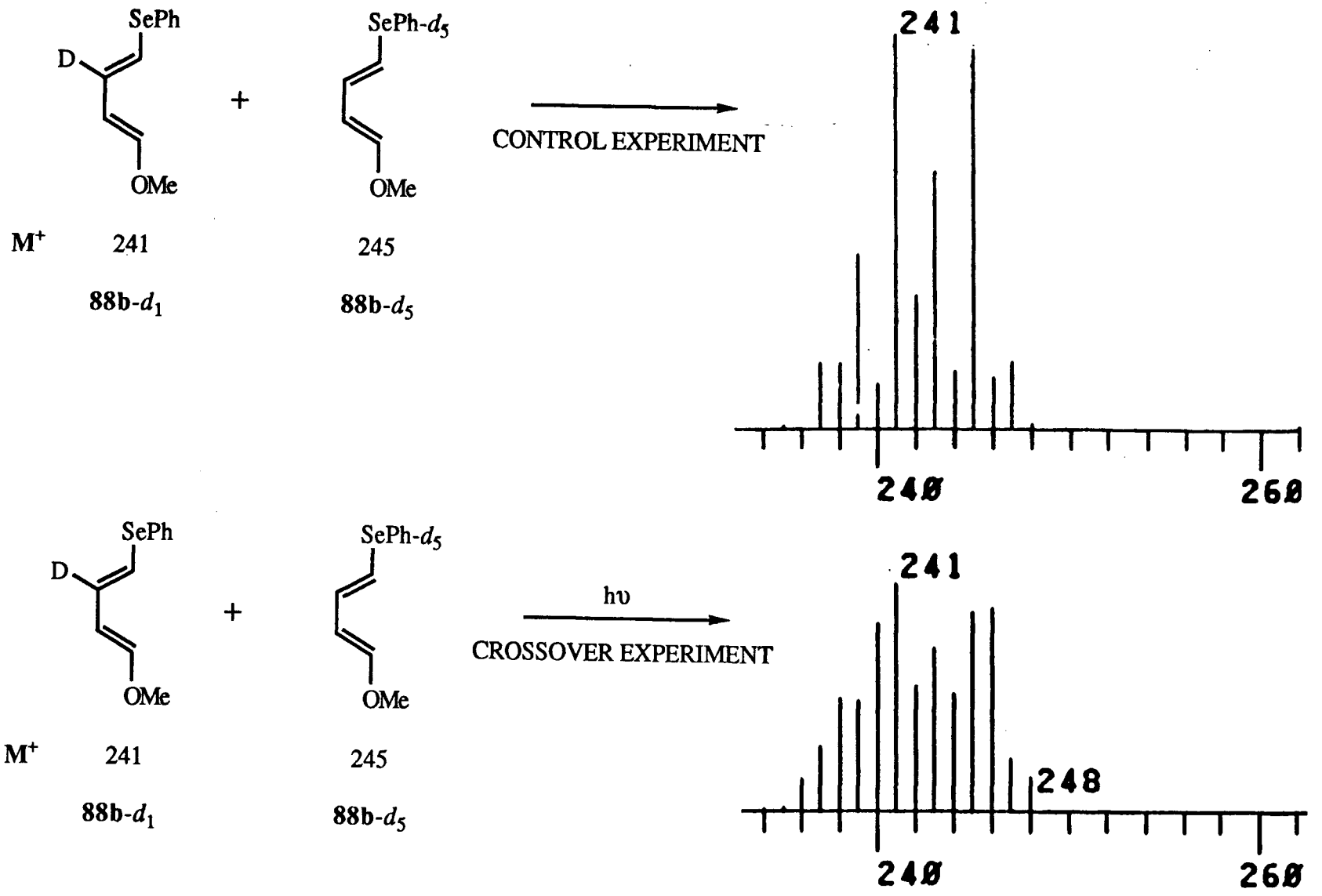
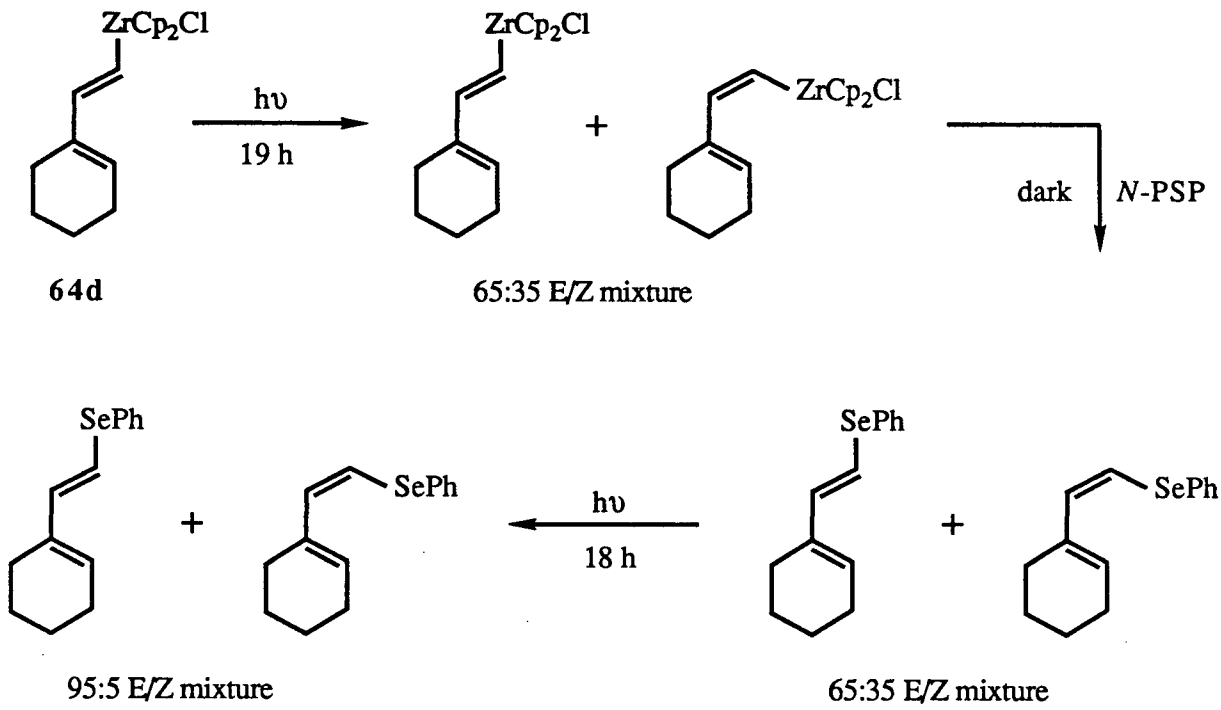


Figure 36. Molecular ion fragmentation patterns for the control and crossover experiments using **88b**-d_1 and **88b**-d_5.

Similar experiments were performed for the mixtures **88a**-d_1/**88a**-d_5 and **88c**-d_1 /**88c**-d_5; in each case crossover products were evident by mass spectrometry. When the crossover experiment was performed with the mixture of **88d**-d_1 and **88d**-d_5, analysis by mass spectrometry indicated that significant crossover had taken place. Assuming that the isomerization reaction and the presence of crossover products are directly linked, this result was somewhat surprising as **88d** had shown no sign of isomerization by ^{1}H NMR spectroscopy. It was therefore concluded that since the isomerization process yields equilibrium mixtures of geometric isomers, perhaps the E isomer of **88d** was by far the predominant one in equilibrium, with only a small concentration of the Z-isomer. If this was the case, such small quantities of the Z isomer may not have been detectable by ^{1}H NMR spectroscopy. To investigate this postulate, a sample of the Z isomer of **88d** was prepared and irradiated with fluorescent light to determine if isomerization to a mixture of geometric isomers greatly dominated by the E isomer would be obtained.

Previous workers have reported the isomerization of alkenylzirconium complexes upon irradiation with UV-light.[18] It was thought that **55d** would undergo a similar isomerization, thereby allowing for the preparation of a mixture of geometric isomers of **88d** via a transfer reaction with *N*-PSP. Irradiation of **55d** with fluorescent light for 19 h resulted in the formation of a 65:35 E/Z mixture of stereoisomers. This mixture was then reacted with *N*-PSP to give a 65:35 mixture of E/Z geometric isomers of **88d**. *This result thus represents the first example of stereospecific transfer of an organic moiety from zirconium.* When the 65:35 E/Z mixture of **88d** was irradiated with fluorescent light, isomerization was observed to take place by ^{1}H NMR spectroscopy to give, after 18 h, a 95:5 E/Z mixture of **88d** (Scheme 30, next page). Thus, under conditions where equilibration between the E and Z isomers of **88d** can occur, the former species was found to compose 95% of the mixture. It is believed that this result accounts for the apparent absence of isomerization, and the observation of crossover on irradiation of **88d**.



Scheme 30

The second set of crossover experiments involved the use of the dienes **108a-d**, which contain the *para*-chloro substituent on the PhSe fragment. A similar series of crossover experiments, as described previously, were performed using mixtures of **108a-d** and **88a-d**-d_1. In all cases, the differences between the molecular ion fragmentation patterns for the control experiments versus the crossover experiments were sufficiently great to conclude that crossover had taken place. These results are exemplified for the mixture **108b** and **88b**-d_1 which, after irradiation with fluorescent light, resulted in the molecular ion fragmentation patterns shown in Figure 37 (next page). As predicted, the presence of the *para*-chloro substituent provided a sufficiently different environment for the nearby protons that the presence of crossover products could be readily identified by ^{1}H NMR spectroscopy. This observable difference by ^{1}H NMR spectroscopy is most easily seen in the ^{1}H NMR spectrum of the photolyzed mixture of **108d** and **88d**-d_1. The ^{1}H NMR spectra of the **108d** and **88d**-d_1 mixture before and after photolysis are shown in Figure 38 (p 112). Analysis of

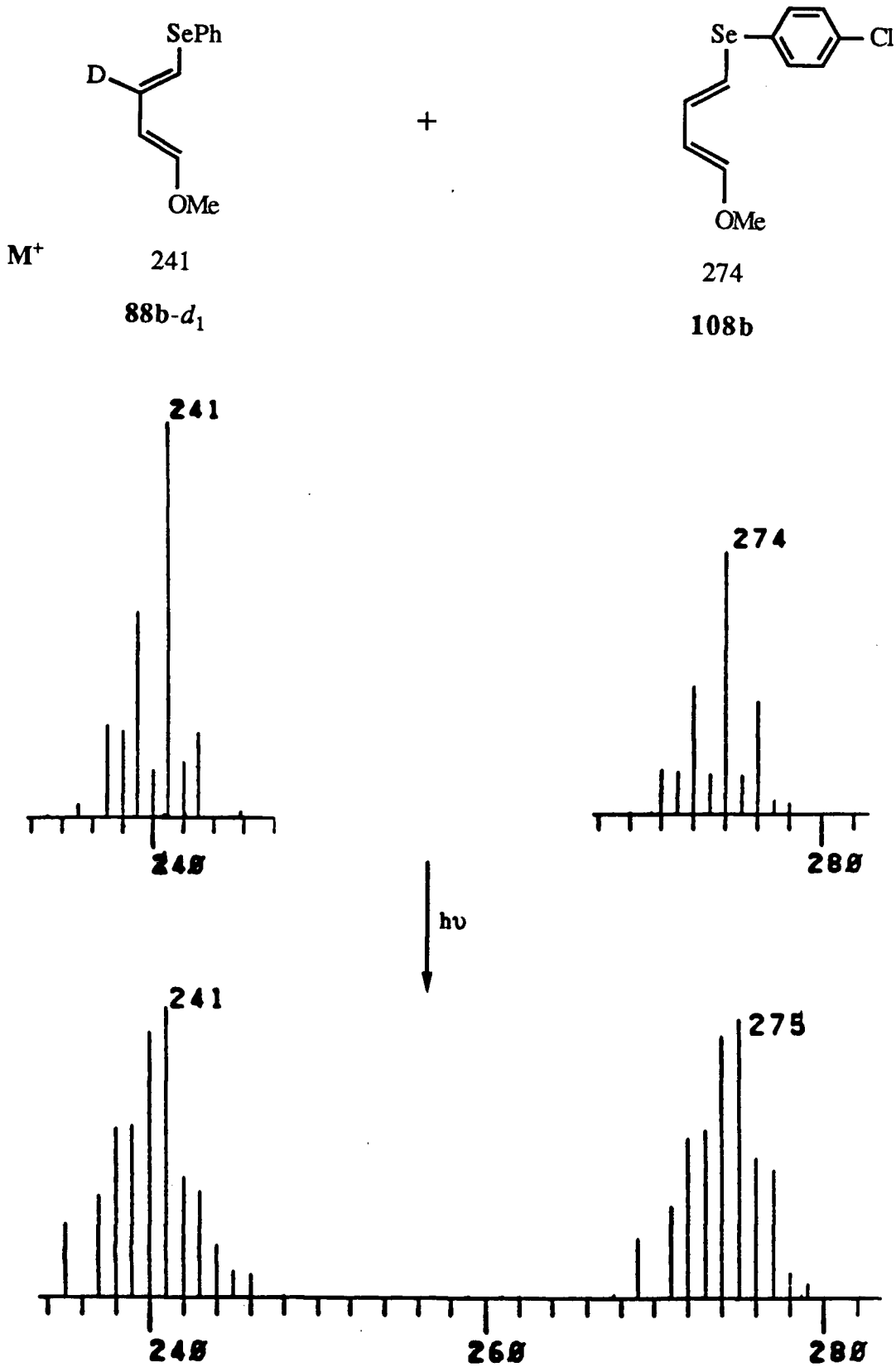


Figure 37. Molecular ion fragmentation patterns for the control and crossover experiments using **108b** and **88b**-d_1.

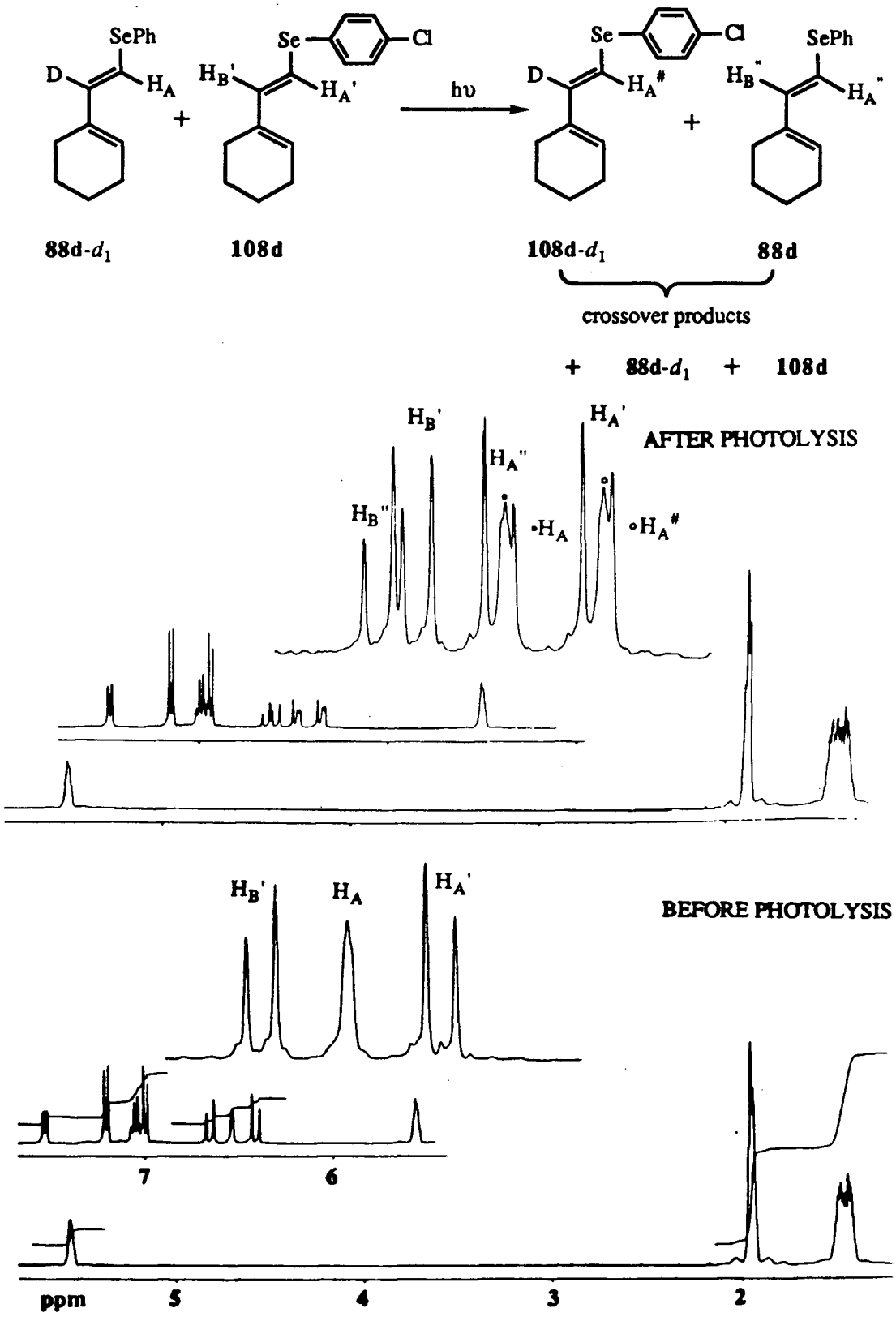


Figure 38. 400 MHz ^{1}H NMR spectra of the mixture **108d** and **88d**-d_1 before and after photolysis in C_6D_6.

these crossover experiments by ^{1}H NMR spectroscopy made it possible to obtain qualitative information on the degree of crossover. In general, crossover was observed to give an approximately equal mixture of all possible products. This can be seen by examination of the ^{1}H NMR spectrum of the **108d** and **88d**-d_1 mixture after photolysis (Figure 38). By observing that there was a strong correlation between the degree of crossover and the time of exposure of the mixtures to fluorescent light, it is proposed that the extent of isomerization is indeed directly linked to the amount of crossover. The results outlined above suggest that the photochemical isomerization of the dienes **88a-d** occurs by an intermolecular process, which likely involves cleavage of the selenium-carbon bond of the 1,3-diene fragment.

The reaction was investigated further to determine if the process leading to diene isomerization involved an ionic or free radical pathway. The empirical observation that both the rate of isomerization and the degree of crossover were unaffected by changing the solvent from either C_6D_6 or C_7D_8 to CD_2Cl_2 or $CDCl_3$, tends to rule against an ionic process. To probe the mechanism further, the effects of 2,6-*tert*-butyl-4-methylphenol (BHT), 4-oxo-2,2,6,6-tetramethylpiperidinyloxy radical (TEMPONE) and 1,4-cyclohexadiene on the isomerization process were examined. These reagents were chosen for their ability to intercept and, in general, effect in some way a change in reactions which involve free radicals. The presence of up to two equivalents of BHT was necessary to cause a significant rate change in the isomerization of **88b**, as observed by ^{1}H NMR spectroscopy. As TEMPONE is itself a free radical, amounts greater than approximately 5 mol % concentrations of this reagent caused significant deterioration of the spectral resolution, such that its effect on the isomerization process could not be clearly demonstrated by ^{1}H NMR spectroscopy. The most extensive studies were performed using 1,4-cyclohexadiene as a free radical trapping agent. Photolysis of a 0.20-0.25 M solution of **88a** in 1,4-cyclohexadiene showed significant retardation of the isomerization process. A 9:1 E/Z mixture of products resulted after a 2 h irradiation with fluorescent light. This ratio differs considerably from the 2:1 E/Z mixture obtained when photolysis was performed in the absence of 1,4-cyclohexadiene. When similar

experiments were performed for **88b** and **88c** the isomerization process was also retarded, but to a lesser extent to that observed for **88a**. When the crossover experiment for the mixture **88d**-d_1 and **88d**-d_5 was performed in neat 1,4-cyclohexadiene, there was no evidence of any crossover products as determined by ^{1}H NMR spectroscopy and mass spectrometry. These results provide evidence for the involvement of free radicals in the photochemical isomerization of **88a-d**.

Further to the proposal of free radicals as intermediates in the photochemical isomerization process, was the presence of small amounts (<5%) of Ph_2Se_2 detected by ^{1}H NMR spectroscopy after irradiation of **88a-d**. The ability of Ph_2Se_2 to form PhSe$^{\cdot}$ free radicals by cleavage of the selenium-selenium bond under the photochemical conditions necessary for isomerization was therefore investigated. In this regard, a 1:1 mixture of Ph_2Se_2 (*m/e* 314) and Ph_2Se_2-d_{10} (*m/e* 324) was irradiated with fluorescent light for 2 h and analyzed by mass spectrometry for the presence of Ph_2Se_2-d_5 (*m/e* 319). A control experiment was also performed to exclude the possibility of formation of the crossover product Ph_2Se_2-d_5, in the mass spectrometer during analysis. In the latter experiment a 1:1 mixture of Ph_2Se_2 and Ph_2Se_2-d_{10} was analyzed by mass spectrometry immediately after mixing. Comparison of the results obtained from these experiments showed significant differences in the molecular ion fragmentation patterns of the control versus the crossover reaction (Figure 39, next page). It is proposed that these differences are due to the presence of Ph_2Se_2-d_5 (*m/e* 319), thus indicating the formation of PhSe$^{\cdot}$ radicals during photolysis .

When a 1:1 mixture of Ph_2Se_2-d_{10} and **88b** was irradiated with fluorescent light for 2 h, mass spectrometry indicated the presence of significant amounts of **88b**-d_5 (*m/e* 245) and Ph_2Se_2-d_5 (Figure 40, p 116). This result provides evidence for the exchange of PhSe$^{\cdot}$ radicals produced from the cleavage of Ph_2Se_2-d_{10} with the PhSe group of **88b**. A similar control experiment to that described above was performed to ensure that formation of the crossover products **88b**-d_5 and Ph_2Se_2-d_5 did not occur to any great extent in the mass spectrometer (Figure 40). When these experiments were repeated for a mixture of Ph_2Se_2-d_{10}

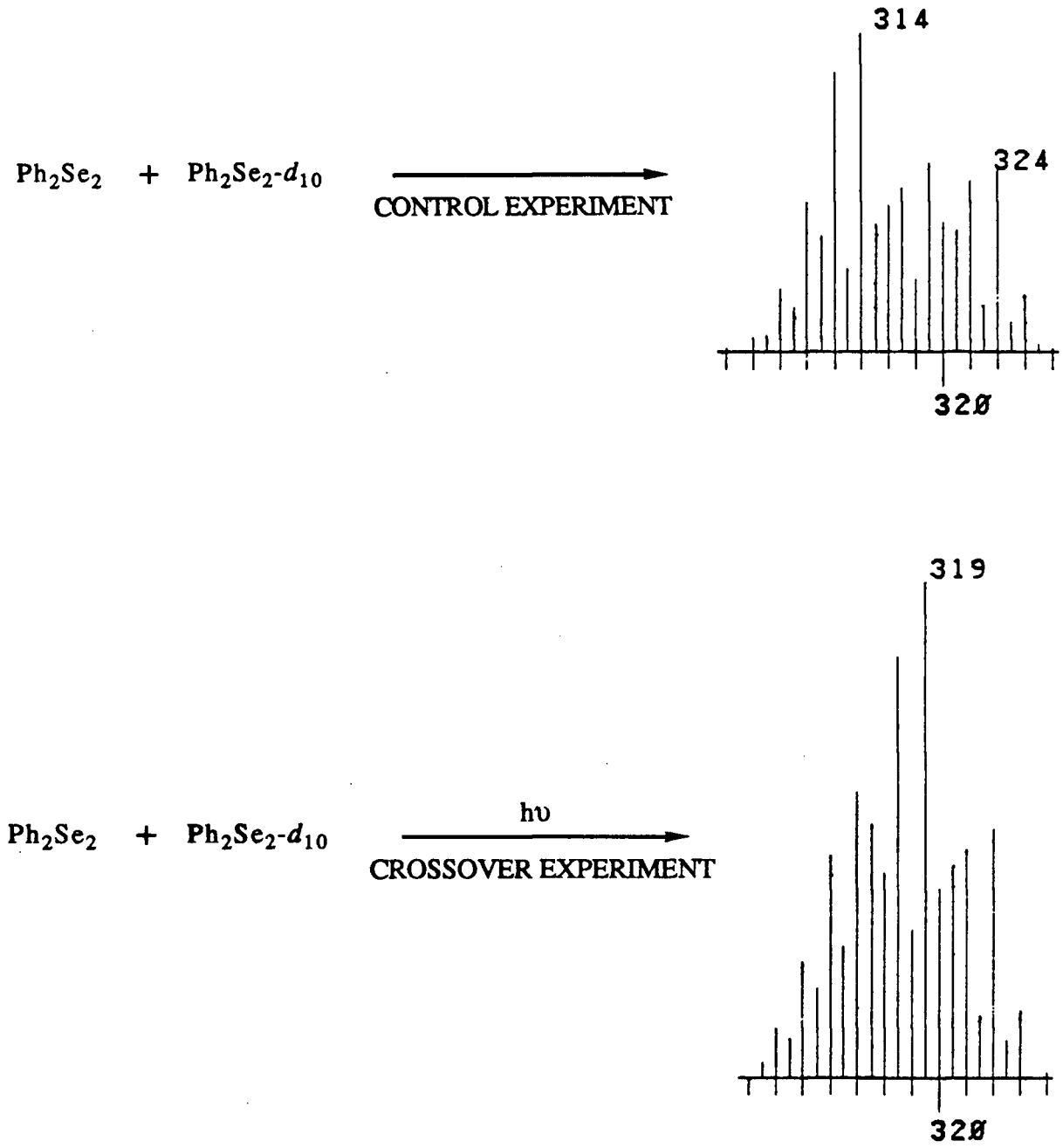


Figure 39. Molecular ion fragmentation patterns for the control and crossover experiments for the mixture of Ph_2Se_2 and Ph_2Se_2-d_{10}.

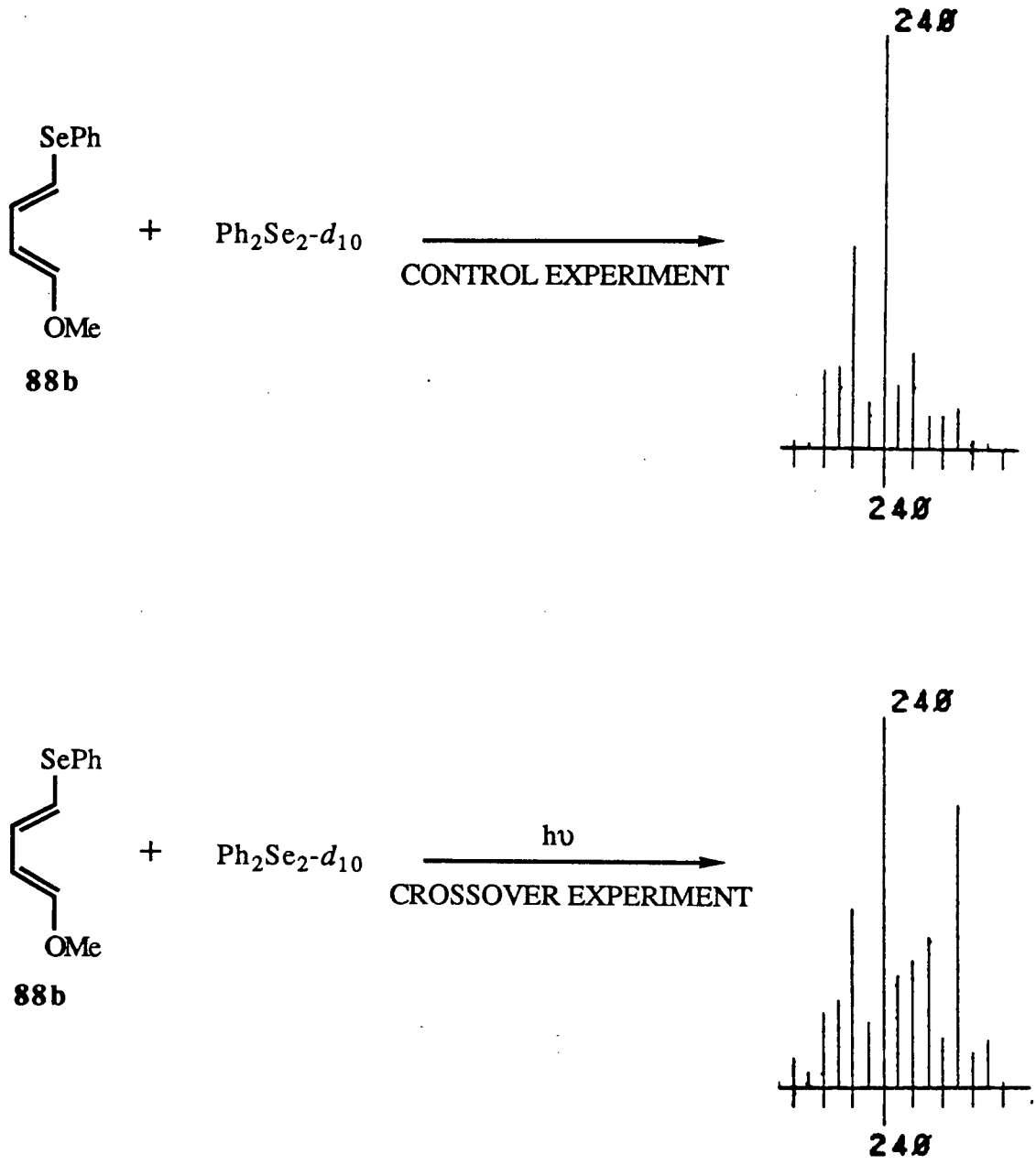
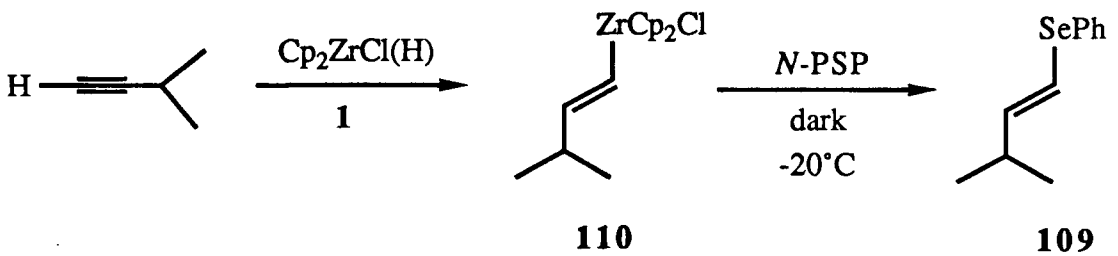


Figure 40. Molecular ion fragmentation patterns for the control and crossover experiments for the mixture of **88b** and Ph_2Se_2-d_{10}.

and **88a**, similar results were obtained, namely, the formation of large amounts of **88a**-d_5 and Ph_2Se_2-d_5. Although the reactions with Ph_2Se_2-d_{10} provide further evidence for the involvement of free radicals in the isomerization process, they also present an added complexity. As Ph_2Se_2 is seen by ^1H NMR spectroscopy in small amounts by the photolysis of **88a-d**, there exists the possibility that it may play some part in the mechanism leading to diene isomerization. This postulate is not unreasonable since catalytic amounts of diphenyl disulfide have been employed in the cis to trans isomerization of polybutadiene.[91]

To determine if this photochemical isomerization process is a general reaction for molecules having the PhSe group attached to unsaturated organic fragments, it was decided to investigate the photochemical stability of a vinylselenide. The E isomer of **109** was synthesized by the hydrozirconation of isopropylacetylene to give **110**, followed by reaction with *N*-PSP to generate the desired product (equation 47). Photolysis of a deuteriobenzene

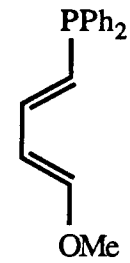


110 **109** (47)

solution of **109** under identical conditions to those used for **88a-d**, produced no isomerization as determined by ^1H NMR spectroscopy. However, after 24 h irradiation with fluorescent light a 92:8 E/Z mixture of geometric isomers resulted. The UV-vis spectrum of **109** has a λ_{max} at 258 nm (ε 9500), with only background level absorptions in the visible region. After 19 h of irradiation with UV light an 86:14 E/Z mixture was obtained. Following irradiation of **109** with UV light (330-380 nm), the presence of small amounts of Ph_2Se_2 was detected by ^1H NMR spectroscopy. As Ph_2Se_2 has been shown to produce PhSe$^{\cdot}$ radicals on irradiation with fluorescent light, a solution of **109** was photolyzed in the presence of a catalytic amount of Ph_2Se_2. After 24 h irradiation with fluorescent light, this

mixture produced an 87:13 ratio of E/Z geometric isomers, similar to that obtained by UV irradiation. If, as proposed, the isomerization of **88a** involves the free radical PhSe$^{\cdot}$, then photolysis of a mixture of **88a** and **109** should result in isomerization of the latter species. Thus, a mixture of **88a** (70 mol %) and **109** was irradiated with fluorescent light for 24 h. As expected, this resulted in isomerization of **88a** to a 2:1 mixture of E/Z isomers. In turn, the vinylselenide had isomerized to give an 86:14 E/Z mixture; the same ratio observed by both UV irradiation, and fluorescent light irradiation in the presence of Ph_2Se_2. In conclusion, the photochemical isomerization of **109** occurs under a variety of conditions, with the extent of isomerization being enhanced by the presence of Ph_2Se_2 and **88a**.

The effect of the PhSe$^{\cdot}$ radical on the photochemical isomerization of a stereochemically stable 1,3-diene was then investigated. Irradiation of the phosphorus-substituted 1,3-diene **79b** for up to 48 h with fluorescent light showed no signs of



79b

isomerization by ^{1}H NMR spectroscopy. However, after only 1.5 h irradiation of this diene with fluorescent light in the presence of a catalytic amount of Ph_2Se_2, isomerization was observed to yield a 69:17 mixture of E,E/E,Z isomers with the remainder being an unidentified isomer. When the experiment was repeated using **88a** (70 mol %) instead of Ph_2Se_2, no isomerization of **79b** occurred until **88a** began to isomerize, implying that the presence of **79b** was somehow inhibiting the isomerization of **88a**. After 18 h of irradiation with fluorescent light **88a** began to isomerize, resulting in the concomitant isomerization of **79b**. After a total of 65 h irradiation a 64:16 mixture of E,E/E,Z isomers resulted, the remainder being composed of a mixture of unidentified stereoisomers. The presence of any Ph_2Se_2

could not be determined due to the complexity of the ^1H NMR spectrum. Once again, Ph_2Se_2 and **88a** have induced photochemical isomerization of an molecule which in the absence of these selenium-containing compound is photochemically stable.

The following mechanism is proposed for the photochemical isomerization of the dienes **88a-d** (Figure 41). This mechanism embodies the main experimental results,

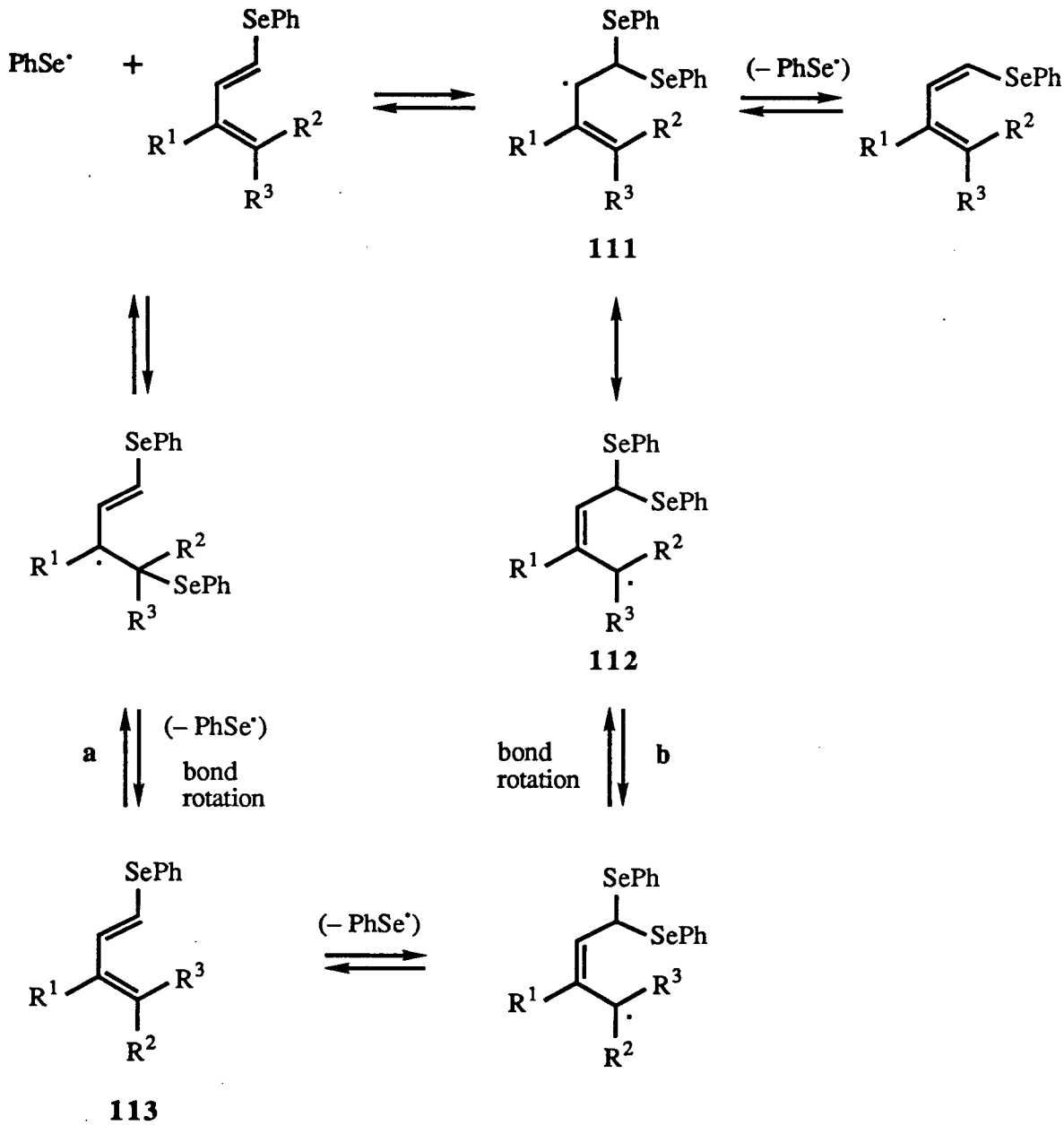
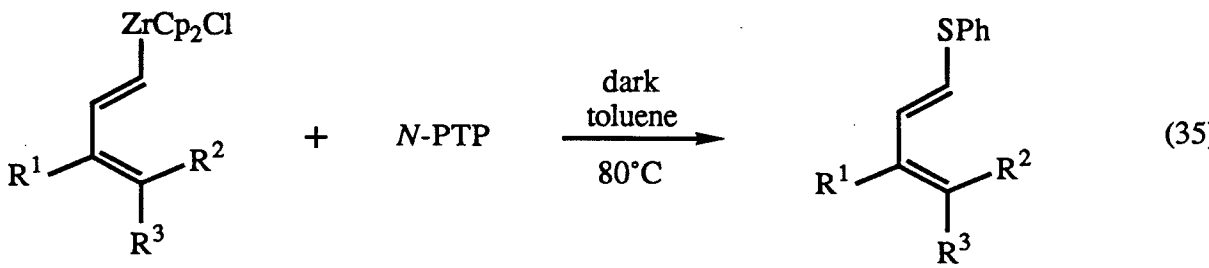


Figure 41. Proposed mechanism for the photochemical isomerization of **88a-d**.

indicating an intermolecular process which involves the PhSe· radical operating in a series of addition-elimination reactions resulting in the observed isomerization. Thus, the propagation step is proposed to involve addition of the PhSe· radical to the diene resulting in the formation of the allylic radical **111**. Isomerization of the "upper" double bond can then occur, by elimination of the PhSe· radical. The isomerization about the "lower" double bond could occur by a similar process (pathway **a**). Alternatively, bond rotation of **112**, followed by loss of PhSe· radical to generate **113** would also result in the observed isomerization (pathway **b**).

4.3 Photochemical Isomerization of 1-(Phenylthio)-1,3-dienes

To explore the generality of the photochemical isomerization reaction described above for the selenium-substituted dienes **88a-d**, the closely related sulfur-functionalized dienes **89a-d** were synthesized (equation 35). The UV-vis spectra of these dienes were very similar



(35)

55a-d **89a-d**

a $R^1 = R^2 = R^3 = H$

b $R^1 = R^2 = H$, $R^3 = OMe$

c $R^1 = R^3 = H$, $R^2 = OMe$

d R^1 $R^3 = -(CH_2)_4-$, $R^2 = H$

to **88a-d**, with the replacement of the PhS group with the PhSe group resulting in a bathochromic shift of the λ_{max} by approximately 10 nm. Irradiation of **89a** with fluorescent light for 5 h resulted in isomerization to afford a 2:1 E/Z mixture of geometric isomers. This result is in direct analogy to the previously reported data for the photolysis of **88a**. Similar photochemical reactions of **89b** and **89c** resulted in isomerization to give identical mixtures of all four possible stereoisomers. The ratio of the isomers was determined from the ^{1}H NMR spectra of several different experiments, and was found to vary only slightly to give a 39(±2):13(±1):35(±2)13(±1) mixture of Z,E/Z,Z/E,E/E,Z geometric isomers. In a fashion similar to that described previously for **88b**, the vinyl resonances of these isomers were identified. The ^{1}H NMR spectrum and the expanded region from 5-7 ppm indicating the relevant assignments for the stereoisomeric mixture of **89b** are shown in Figures 42 and 43 (pp 122 and 123). Irradiation of a solution of **89d** for up to 24 h with fluorescent light gave no isomerization. This apparent absence of isomerization for **89d** was assumed to result from an equilibrium mixture of geometric isomers which greatly favored the E isomer, as shown previously for **88d**. In all cases, small quantities of diphenyl disulfide were observed in the ^{1}H NMR spectra of the photolyzed dienes **89a-d**. Although detailed experiments were not performed to probe the mechanism of the isomerization of **89a-d**, it is assumed that they isomerize by a similar process to that outlined above for **88a-d**.

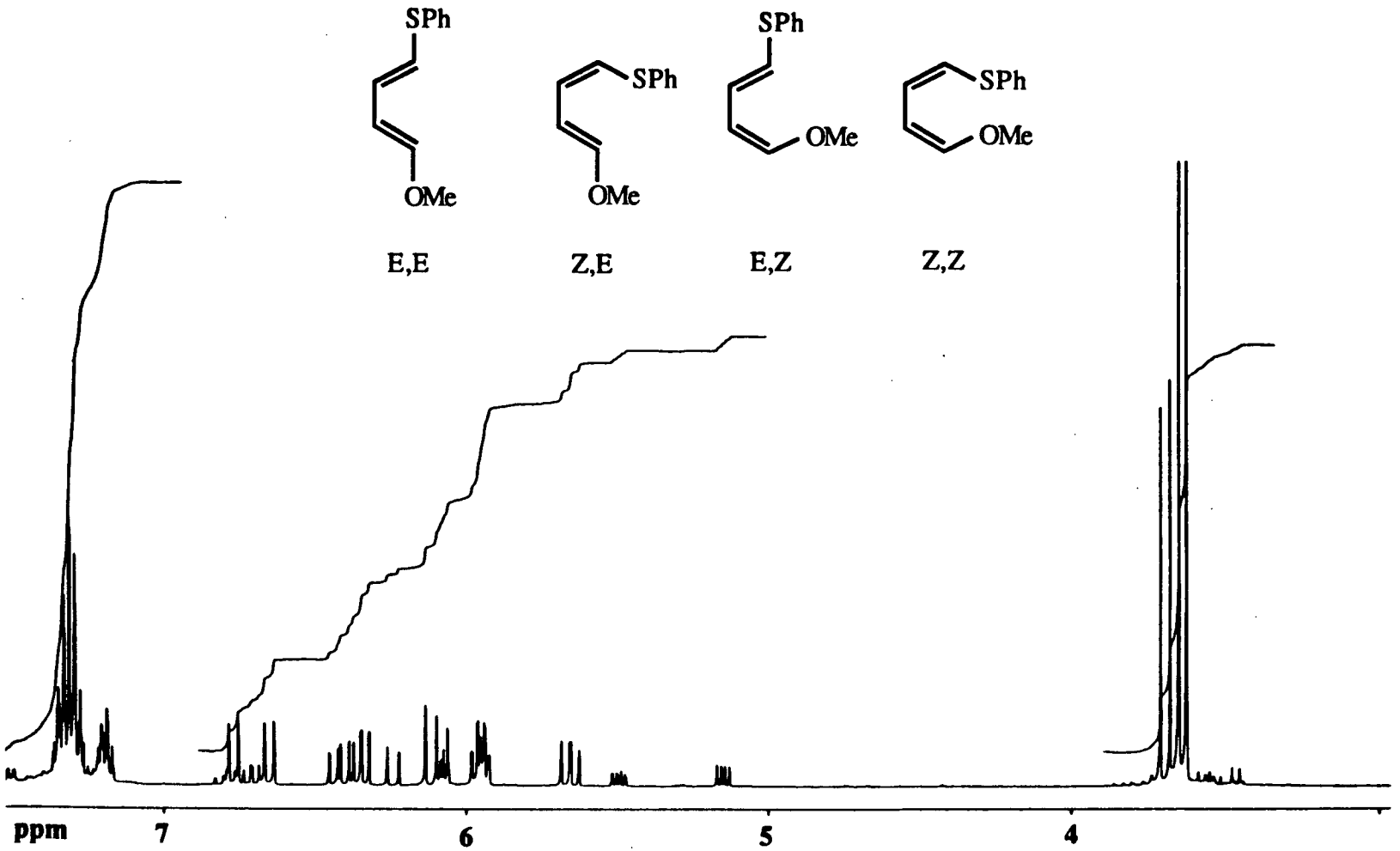
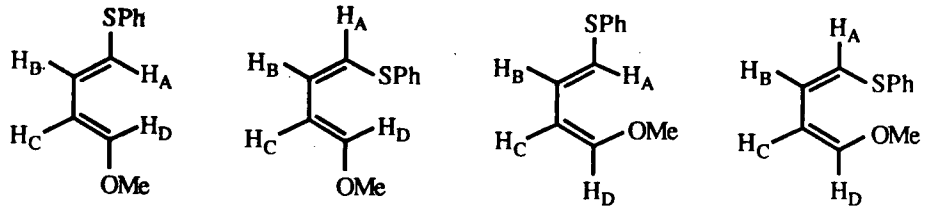


Figure 42. 400 MHz ^{1}H NMR spectrum of the four stereoisomers of **89b** in $CDCl_3$.



four stereoisomers of **89b**

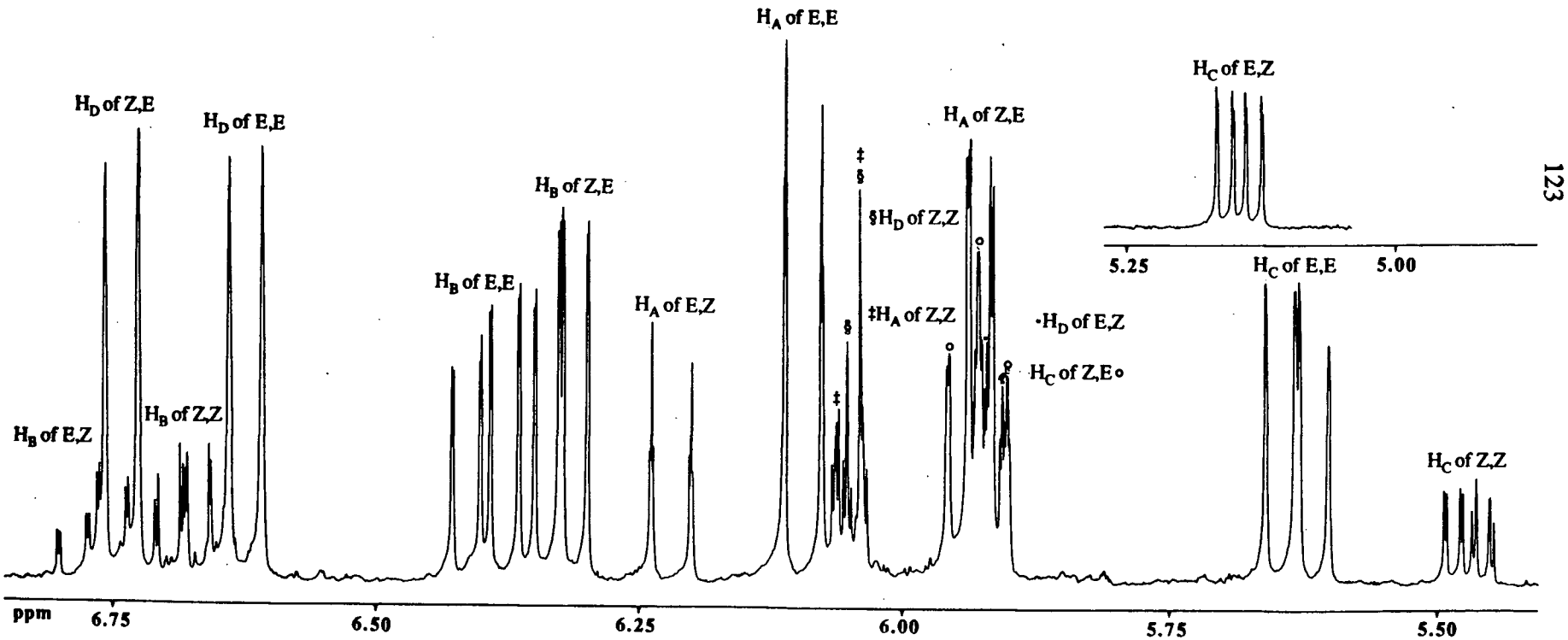


Figure 43. 400 MHz ^{1}H NMR spectrum of the expanded region from 5-7 ppm for the stereoisomers of **89b** in $CDCl_3$.

4.4 Thermal Isomerization.

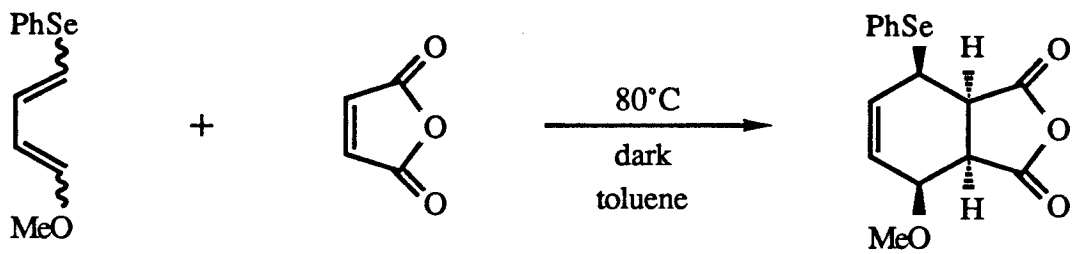
Under thermal conditions, the dienes **88a-c** were observed to isomerize to ratios of stereoisomers identical to those already outlined for the photochemical process. However, in contrast to the photochemical reaction, the thermal isomerization was rather sluggish and less reproducible. Initial experiments involved thermolysis of the dienes **88a-d** in capped NMR tubes at 80°C in the dark for 24-48 h. Using these conditions, **88a** gave a 2:1 mixture of E/Z geometric isomers, while both dienes **88b** and **88c** gave the previously observed mixtures of all four possible stereoisomers. The presence of trace amounts of Ph_2Se_2 was again observed by ^1H NMR spectroscopy. As with the photochemical reaction, thermolysis of **88d** under the conditions described above did not result in any detectable isomerization. As proposed previously for the photochemical reaction, the apparent lack of isomerization for **88d** by thermolysis, is due to the relative stability of the Z isomer under these equilibrating conditions. Crossover experiments, identical to those described previously for the photochemical isomerization of **88a-d**, were performed for the thermal isomerization reactions. The results of these experiments indicated that once again a predominantly intermolecular process was operable. Isomerization rate inhibition experiments, using BHT and 1,4-cyclohexadiene, provided evidence for the presence of free radicals during the thermally-induced isomerizations of **88a-d**.

When solutions of **88a-c** were heated at 80°C in the dark for up to 48 h in NMR tubes sealed under pre-purified nitrogen, no isomerization was observed for **88a**, and isomerizations of **88b-c** were strongly inhibited. When the crossover experiments were performed under identical conditions, the degree of crossover correlated well with the changes in the isomerization in that the presence of crossover products was greatly reduced. From these results it appears that the thermal isomerization of **88a-d** may be initiated by some contaminant which can permeate the capped NMR tubes but not the sealed tubes. Various experiments were performed to determine the source of this contamination.

Thermolysis of **88a** was performed in a sealed NMR tube under an atmosphere of pre-dried air to determine the effect of oxygen on the isomerization reaction. After 48 h at 80°C in the dark, no isomerization was observed by ^{1}H NMR spectroscopy. The same observation was made when **88a** was thermolyzed in an HCl-washed NMR tube sealed under pre-purified nitrogen. Thus, it does not appear that the thermal isomerization of **88a-d** is promoted by oxygen or by traces of mineral acids. However, when the thermolysis of **88a** was carried out in a sealed NMR tube under nitrogen, containing a catalytic amount of the free-radical initiator AIBN, isomerization of **88a** to a 2:1 E/Z mixture of geometric isomers was observed after only 3 h at 80°C in the dark. This provides strong evidence for the involvement of free radicals in the thermal isomerization process. In general, it is believed that the mechanism involved in the thermal process is similar to that described for the photochemical isomerization reaction. Thus, although **88a-d** are photochemically labile, they exhibit stereochemical rigidity under thermolysis in sealed reactors at 80°C in the dark for several hours. We hoped to take advantage of this selective thermal stability to investigated the Diels-Alder reactivity of dienes **88a-d**. The reactivity of the latter compounds with maleic anhydride is discussed in the following section.

4.5 Diels-Alder Reaction of 1-(Phenylseleno)-1,3-dienes with Maleic Anhydride.

The reactivity of the selenium-substituted 1,3-dienes **88a-d** with maleic anhydride in the Diels-Alder reaction was investigated. As functionalities such as methyl ether functionalities are known to activate 1,3-dienes towards reaction with electron-deficient dienophiles, it was thought that **88b** would be the most reactive member of this series of dienes. In addition, the E,E stereochemistry should enable **88b** to more easily adopt the necessary s-cis conformation, required for the Diels-Alder reaction, than **88c** which has the E,Z geometry. Interestingly, the reaction of an equilibrium mixture of all four geometric isomers of **88a** with maleic anhydride in the dark at 80°C, resulted in the formation of a *single* stereoisomeric product in 78% isolated yield (equation 48).[74] The stereochemistry of this



(48)

88b
isomeric mixture

114

Diels-Alder cycloadduct (**114**) was confirmed by ^{1}H NMR decoupling and NOEDIFF experiments. Proton H_C was identified both from its chemical shift,[56a] and from an NOEDIFF experiment in which irradiation of the methyl protons of the OMe group gave strong enhancement of this proton. In turn, irradiation of H_C gave enhancement of H_A and H_E, which permitted differentiation between the two vinyl and the two ring-junction resonances (Figure 44). Also, irradiation of proton H_B resulted in enhancements of H_A and H_D. These latter results provide evidence for the cis stereochemistry for the ring junction of the 6/5-bicyclic system and confirm that **114** is the endo-cycloadduct, resulting from

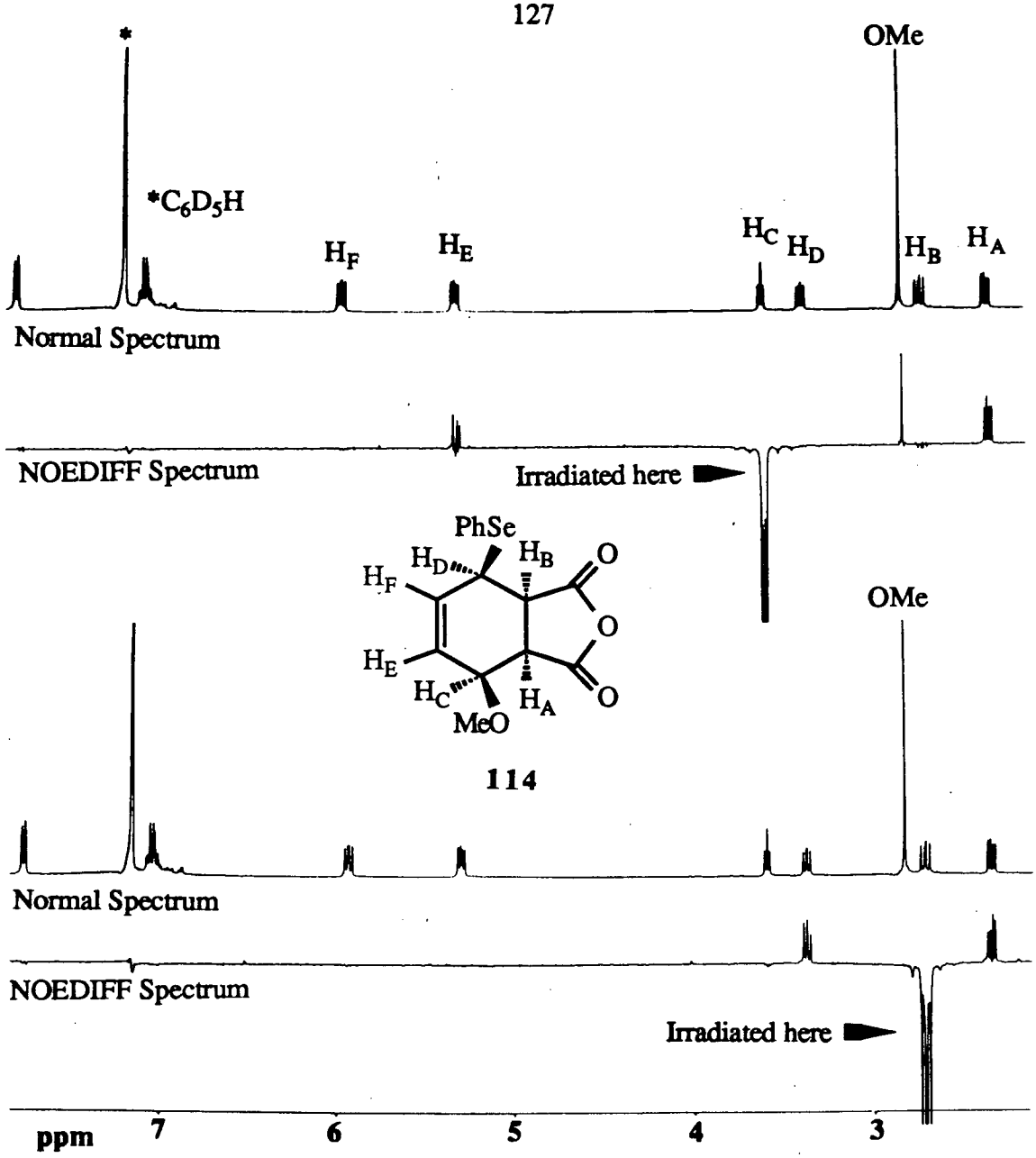
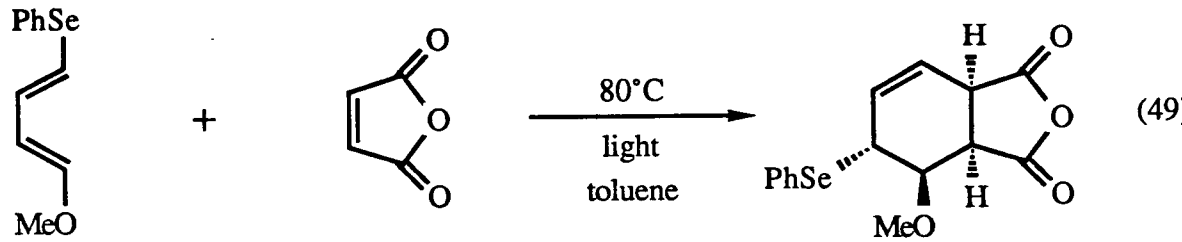


Figure 44. 400 MHz ^{1}H NMR and NOEDIFF spectra for **114** in C_6D_6.

exclusive reaction of the E,E isomer of **88b** with maleic anhydride. As the isolated yield of **114** is far in excess of the amount of E,E isomer (of **88b**) present in the equilibrium mixture, it appears that the latter compound has been kinetically depleted from the equilibrium mixture of stereoisomers.

Not surprisingly, this cycloadduct was also prepared in good yield by reaction of an isomerically pure sample of **88b** at 80°C in the dark with maleic anhydride. As the presence

of all four geometric isomers of **88b** had not affected the ultimate formation of **114**, it was decided to attempt the reaction of isomerically pure **88b** with maleic anhydride at 80°C while exposing the reaction to room light. Workup of the crude yellow oil obtained from this reaction, afforded a 70% yield of what appeared to be a stereoisomer of **114**, along with a 10% yield of cycloadduct **114**; the remaining material was identified as Ph_2Se_2. The ^1H NMR spectra of **114** and its stereoisomer **115** are shown in Figure 45 (next page). Comparison of these two spectra shows that the resonances of the latter cycloadduct are more strongly coupled than the former, suggesting that some change in geometry of the 6/5-bicyclic system has taken place. Based on a series of ^1H NMR decoupling and NOEDIFF experiments similar to those outlined above for **114**, the structure of the cycloadduct has been tentatively assigned as **115** (equation 49). Although, it was clear that the PhSe group



(49)

had undergone an apparent [1,3]-shift, the relative stereochemistry of the latter group with respect to the methoxy group was uncertain. It was expected that there would be a significant energy difference between the cycloadduct **115** and its epimer **115'**, where the PhSe and OMe groups are oriented cis to one another (Figure 46, p 130). Based on this assumption, molecular mechanics calculations were performed for the two epimers to determine which one possessed the lower energy. For these calculations the parameters of the 1985 MM2 force field were used[92], with the exception of the bond lengths $C_{sp}3$–Se and $C_{sp}2$–Se and the bond angle $C_{sp}3$–Se–$C_{sp}2$, which were obtained from another literature source.[93] The results of such calculations for the epimers **115'** and **115** indicated that the latter compound was

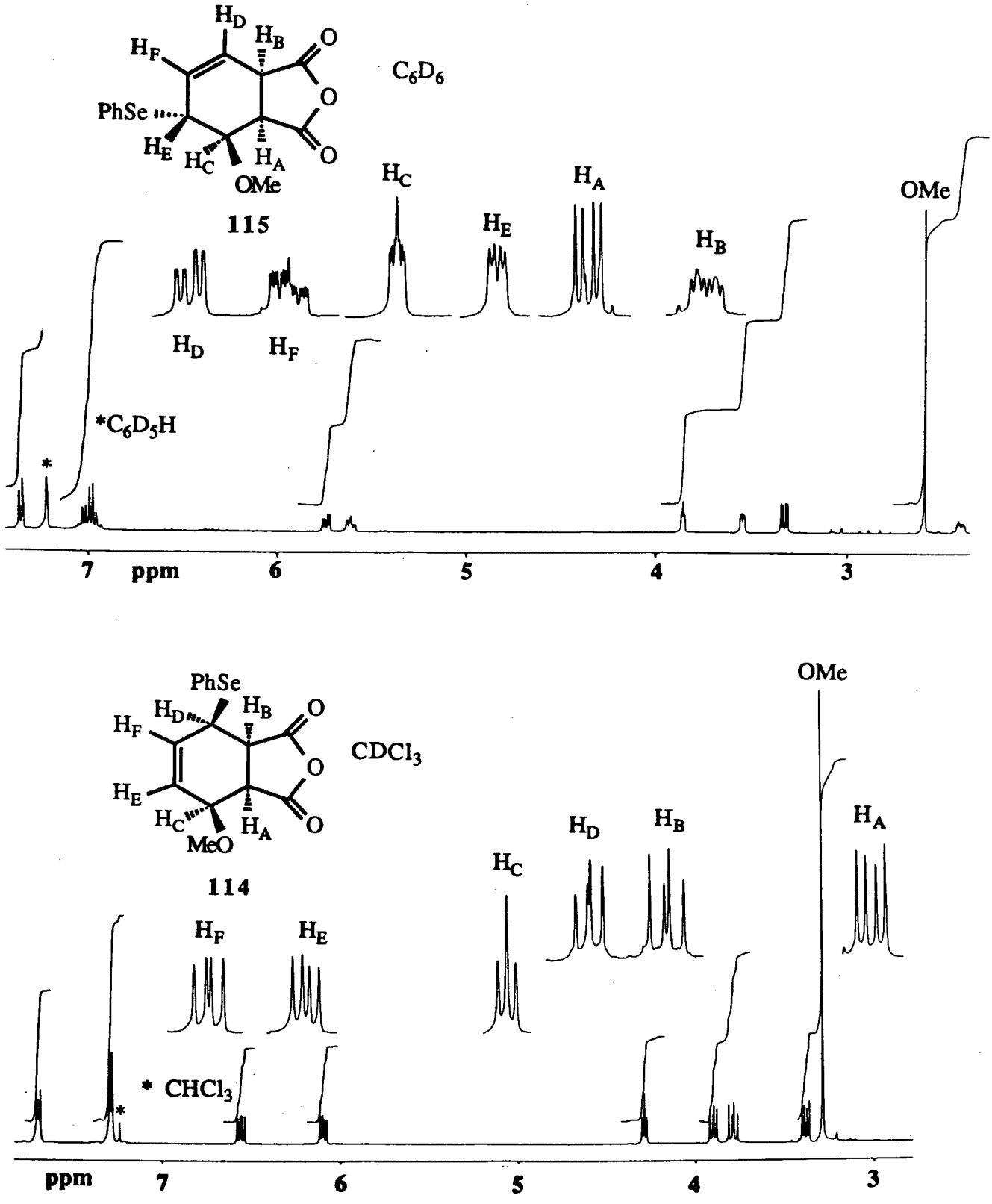
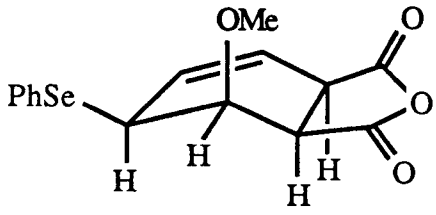
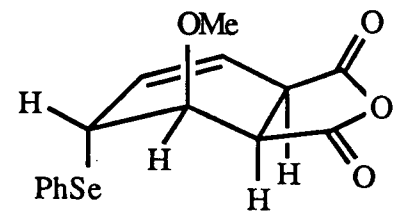


Figure 45. 400 MHz ^{1}H NMR spectra of **114** and **115** in $CDCl_3$ and C_6D_6, respectively.



3.6 kcal/mol

115'



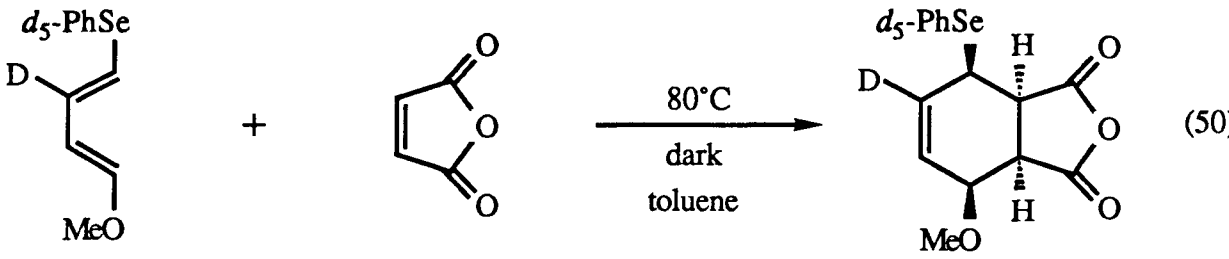
0 kcal/mol

115

Figure 46. **Proposed structures for the epimers of 115.**

approximately 3.6 kcal/mol more stable than the former. This difference in energy corresponds to an equilibrium mixture of >99:1 in favor of **115** over **115'** at 80°C. Therefore, based on the results of these calculations and on the assignments made for a previously investigated system[94] (vide infra), cycloadduct **115** was assigned the structure in which the OMe and PhSe groups are trans to one another.

Allylselenides have been previously observed to undergo [1,3]-shifts induced by mild thermolysis.[95] However, in our case it is obvious that the rearrangement is promoted by light. Thermolysis of **114** at 80°C in the dark for up to 24 h showed no signs of the apparent [1,3]-shifted compound **115**, by ^{1}H NMR spectroscopy. However, irradiation of a deuteriochloroform solution of **114** with fluorescent light for 18 h resulted in an 80% conversion to **115**. Further irradiation of this mixture gave an almost quantitative yield of Ph_2Se_2 along with other unidentified organic materials. The formation of the Ph_2Se_2 again suggested the possible involvement of free radicals in the rearrangement process. To determine if the apparent [1,3]-shift was proceeding by an intra- or intermolecular process, a crossover experiment was performed. This experiment required the synthesis of the cycloadduct **114**-d_6, which was readily prepared by reaction of maleic anhydride with **88b**-d_6 (equation 50). The latter compound was prepared by a transfer reaction of the complex **55b**-d_1 with *N*-PSP-d_5. The ^{1}H NMR spectrum of **114**-d_6 is shown in Figure 47 (p 132).

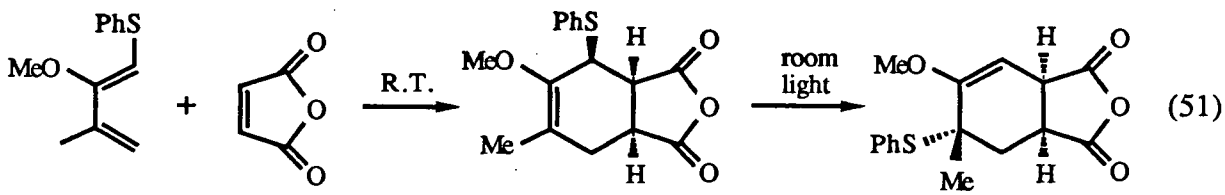


(50)

88b-d_6 **114**-d_6

To facilitate the assignment of crossover products by mass spectrometry, a control experiment was designed in which **114** and **114**-d_6 were independently irradiated with fluorescent light and then mixed prior to analysis. The crossover experiment involved the photolysis of a 1:1 mixture of **114** (*m/e* 338) and **114**-d_6 (*m/e* 344) for 15 h and subsequent analysis by mass spectrometry. The molecular ion fragmentation patterns for the control and crossover experiments are shown in Figure 48 (p 133). There is a clear difference in the pattern shown for the control as compared to the crossover experiment, thus strongly suggesting that crossover has taken place. This result indicates that a significant intermolecular process is involved in the apparent [1,3]-allylic rearrangement.

Other workers have observed a similar apparent [1,3]-shift of an allylsulfide for the cycloadduct **116**.[94] These workers reported that exposure of a deuteriochloroform solution



(51)

116 **117**

of **116** to room light for 1.5-2 days resulted in quantitative rearrangement to the isomer **117** (equation 51). The X-ray crystal structure analysis of **117** showed that the phenylthio group was attached to the opposite face of the cycloadduct, indicating that it had

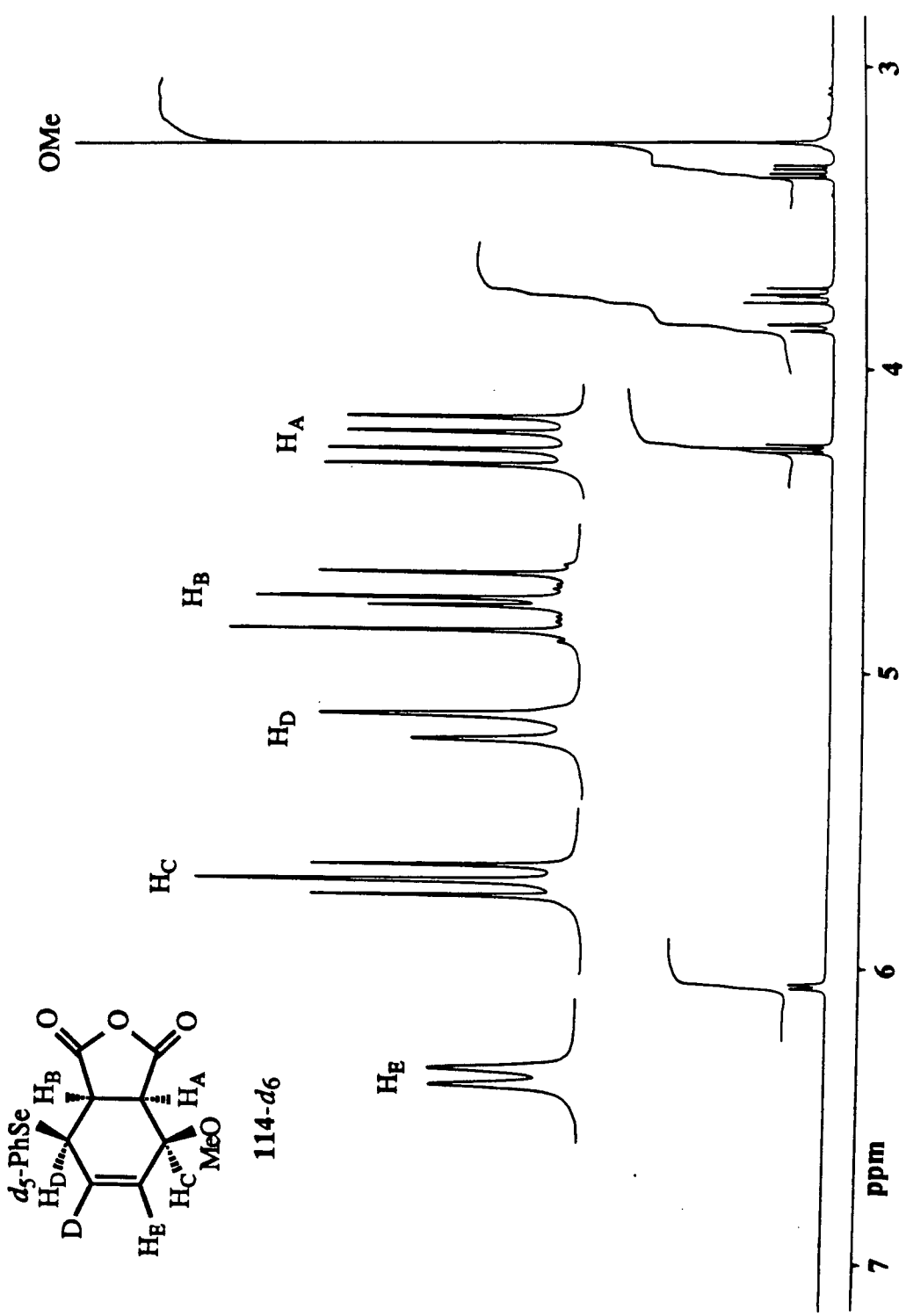


Figure 47. 400 MHz ^{1}H NMR spectrum of **114**-d_6 in $CDCl_3$.

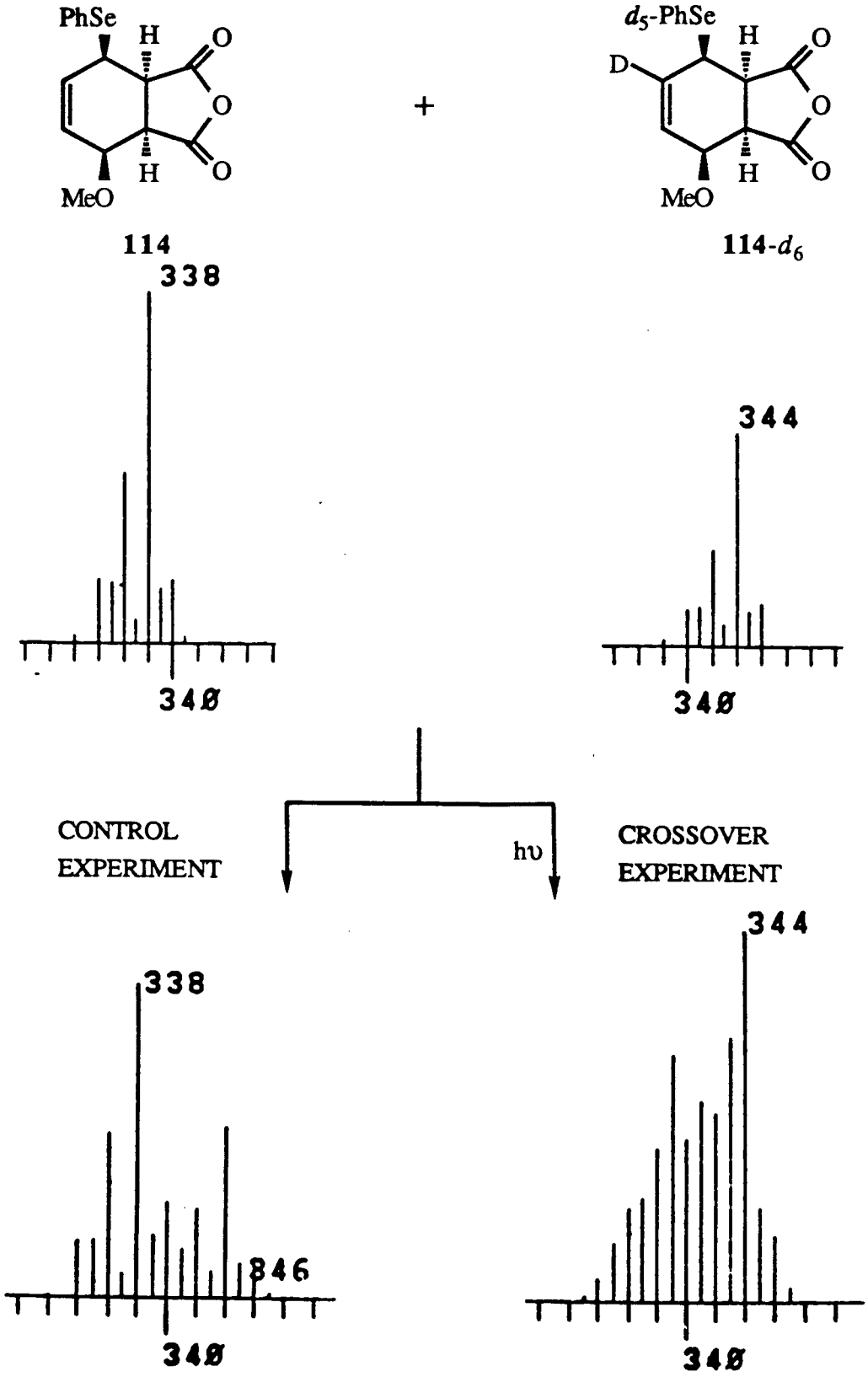


Figure 48. Molecular ion fragmentation patterns for the control and photochemical crossover experiments using mixtures of **114** and **114**-d_6.

moved from one face of the six-membered ring to the other during the rearrangement process. They concluded that this observation was consistent with a free radical chain mechanism, whereby the incoming phenylthio radical approaches opposite to the bulky resident phenylthio group (Figure 49.). A similar argument can be used to account for the stereochemistry observed for the apparent [1,3]-shifted cycloadduct **115**.

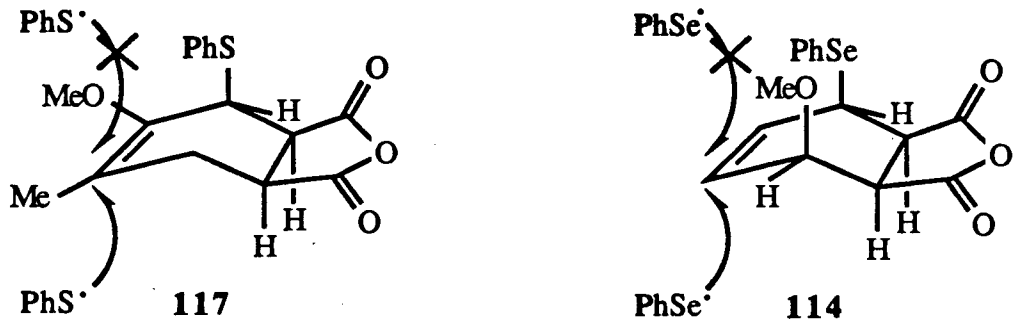
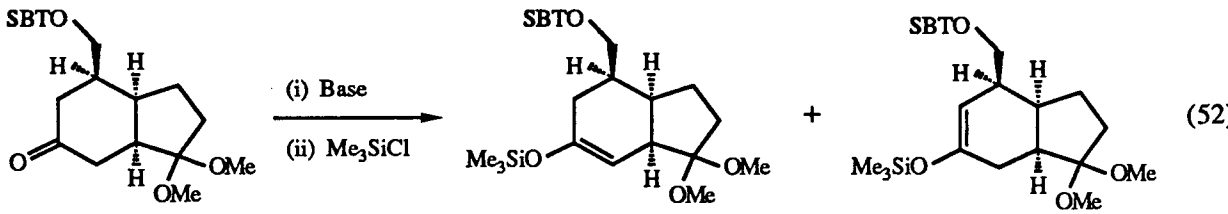


Figure 49. **Proposed rationale for the formation of 116 and 114.**

To understand why the rearrangement of **114** to **115** should be such a facile process, it is necessary to consider the angle strain inherent in a cis-fused 6/5-bicyclic system. To account for the formation of a single product (**119**) in the thermodynamic deprotonation and subsequent silylation of **118**, earlier workers proposed that the presence of a double bond opposite to the ring junction of a cis-fused 6/5-bicyclic system (compound **120**) enhanced the angle strain at that junction (equation 52).[96] This strain can be relieved somewhat by removal



(52)

118
SBT = $(Me)_2t$-BuSi

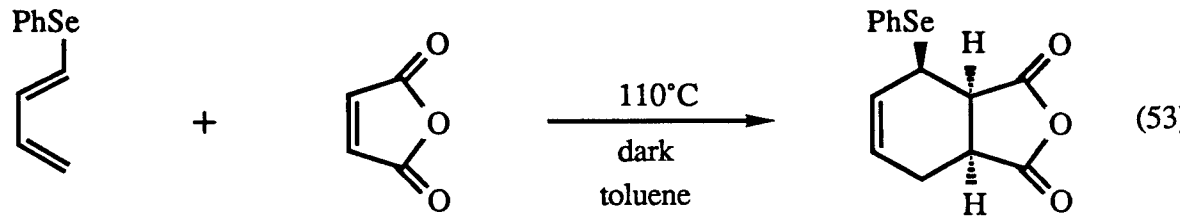
119
formed exclusively

120
not observed

of the double bond or by changing its position in the structure. These workers performed force field calculations which showed an energy difference of 1.9 kcal/mol at 25°C between compounds **119** and **120**, the former compound possessing the lower energy.

It is therefore proposed that the apparent [1,3]-rearrangement from **114** to **115** is promoted by the relief of angle strain inherent in having a double bond opposite the ring junction of a cis-fused 6/5-bicyclic system. To gain further evidence for this proposal, attempts were made to prepare the Diels-Alder cycloadducts of **88b** with either dimethyl fumarate or dimethyl maleate. As these cycloadducts would no longer possess the bicyclic structure of **114**, their photochemical stability would lend credence to the proposed argument for the driving force inherent in the rearrangement process. Unfortunately, attempts to prepare these cycloadducts were unsuccessful. Reaction of **88b** with either dimethyl fumarate or dimethyl maleate at temperatures up to 140°C failed to yield anything more than trace amounts of the desired cycloadducts, suggesting that these dienophile are insufficiently reactive to undergo Diels-Alder reaction with **88b**.

The reaction of **88a** with maleic anhydride proceeded smoothly at 110°C in the dark to give the desired cycloadduct **121** after 22 h (equation 53). One product was formed which



(53)

88a **121**

was identified as the endo-adduct by ^{1}H NOEDIFF spectroscopy, since irradiation of H_B resulted in enhancement of protons H_A and H_D (Figure 50, next page). The proton assignments for this cycloadduct resulted from experiments similar to those described previously for **114**. Attempts to induce a similar rearrangement of the PhSe group of **121** by

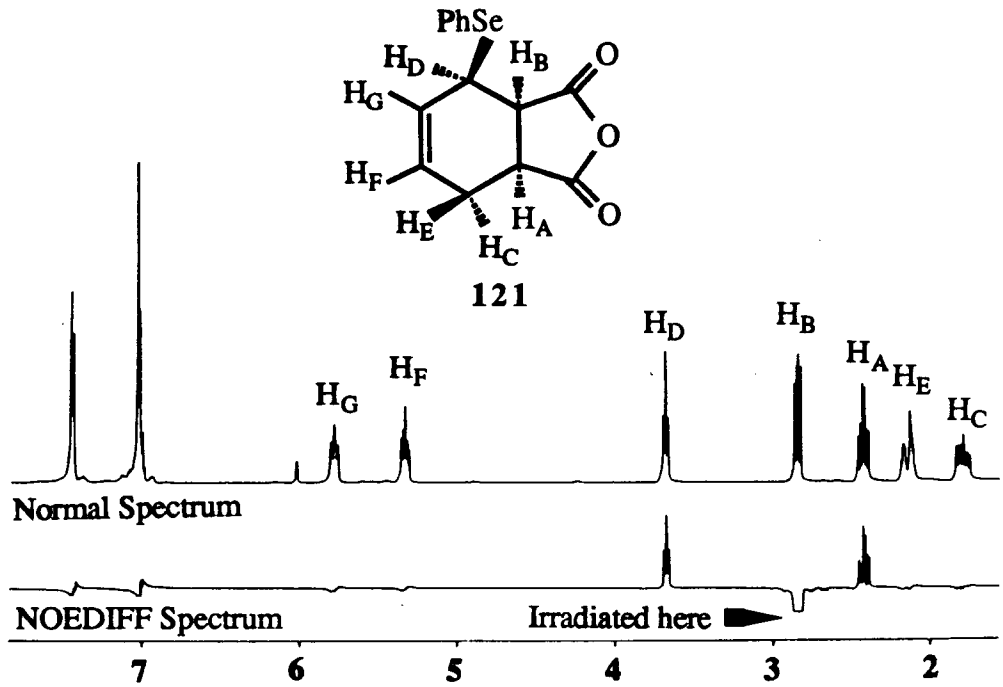
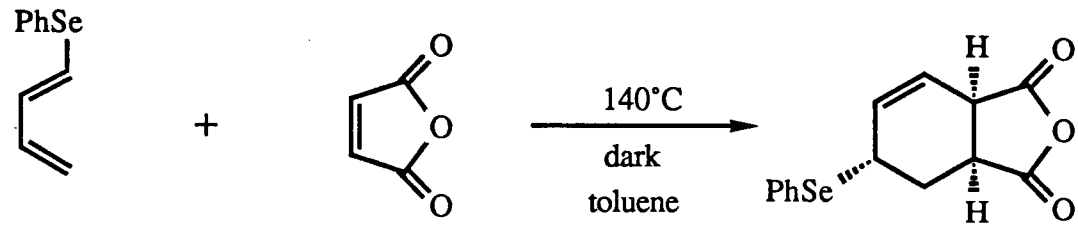


Figure 50. 400 MHz ^{1}H NMR and NOEDIFF spectra for **121** in C_7D_8.

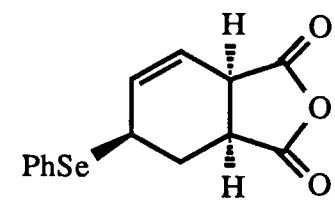
repeating the reaction in the presence of room light or by photolysis of the preformed cycloadduct, resulted in decomposition to Ph_2Se_2 and other unidentified organic products. However, when the Diels-Alder reaction was performed at 140°C in the dark, a 1:1 mixture of stereoisomeric products **122** and **123** was formed after 24 h. The formation of this mixture was accompanied by some decomposition to Ph_2Se_2 (~5%) and other unidentified materials. After further thermolysis up to 63 h, a 2:1 mixture of stereoisomers was present by ^{1}H NMR spectroscopy. Continued thermolysis resulted in significant decomposition to Ph_2Se_2. A similar mixture was obtained by thermolysis, in the dark, of the preformed cycloadduct **121** at 140°C for 48 h. Analysis of the complex ^{1}H NMR spectrum of this mixture indicated that both products had arisen from an apparent [1,3]-allylic rearrangement of the PhSe group. Through a series of ^{1}H NMR decoupling and NOEDIFF experiments, it was possible to

assign the protons for each isomer. The two stereoisomers were tentatively assigned the structures shown in equation 54. Unfortunately, it was not possible to clearly determine by



88a **122**

\+ (54)



123

^{1}H NMR spectroscopy which was the major isomer . However, by use of the molecular mechanics program (MM2) it was possible to determine that cycloadduct **122** possessed the lower energy structure. For cycloadduct **123** two possible conformations were calculated, both of which were of higher energy than **122** (Figure 51, next page). Using this calculated energy difference an equilibrium ratio of 2:1 at 140°C was determined for **122**:**123**. This ratio is in excellent agreement with the ratio of stereoisomers determined by ^{1}H NMR spectroscopy. Also, the assignment of **122** as the major isomer is consistent with the argument that the apparent [1,3]-shift occurs by attack of the PhSe$^{\cdot}$ radical on the face of the six-membered ring opposite to the bulky resident PhSe group. Presumably, the minor isomer is formed as a result of free radical epimerization at the carbon bearing the PhSe group.

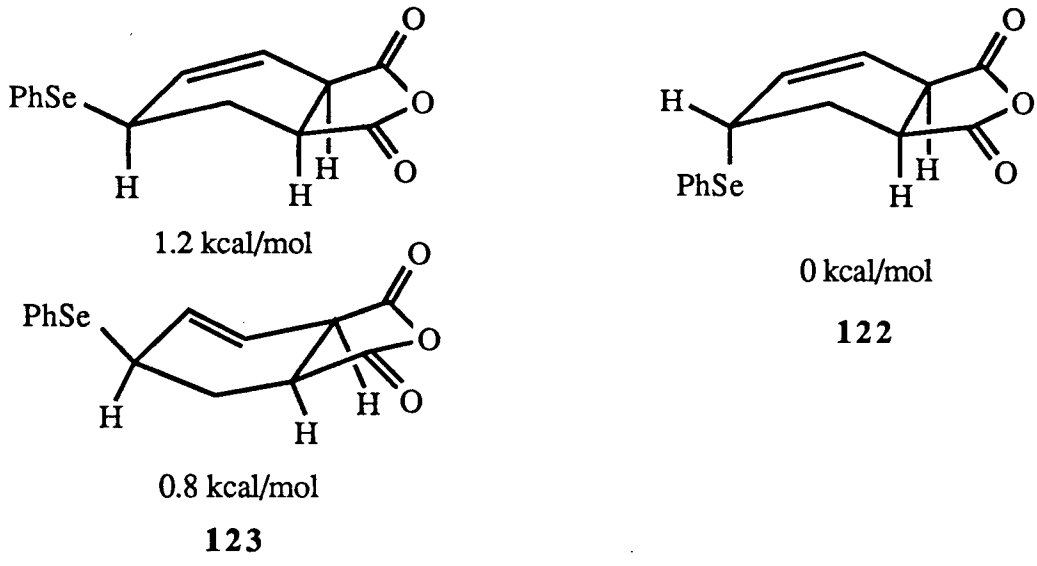
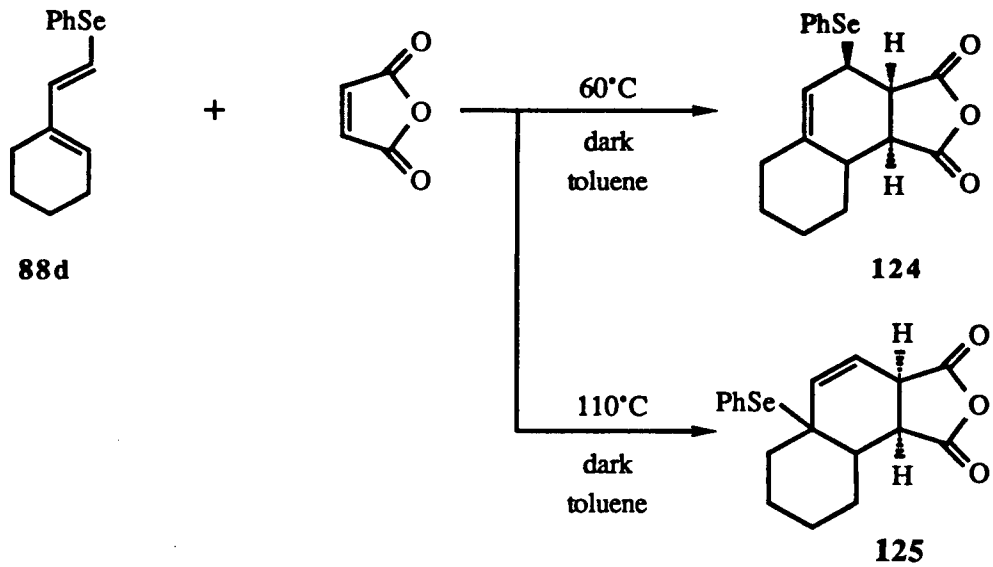


Figure 51. Possible structures for the apparent [1,3]-shift cycloadducts **122** and **123**.

The reaction of **88d** with maleic anhydride occurred at 60°C in the dark to yield the expected cycloadduct **124** (Scheme 31). At higher temperatures this reaction led to the



Scheme 31

formation of significant amounts of the apparent [1,3]-shifted cycloadduct **125**. The ^{1}H NMR spectrum of **124** is shown in Figure 52. The structural assignment of this

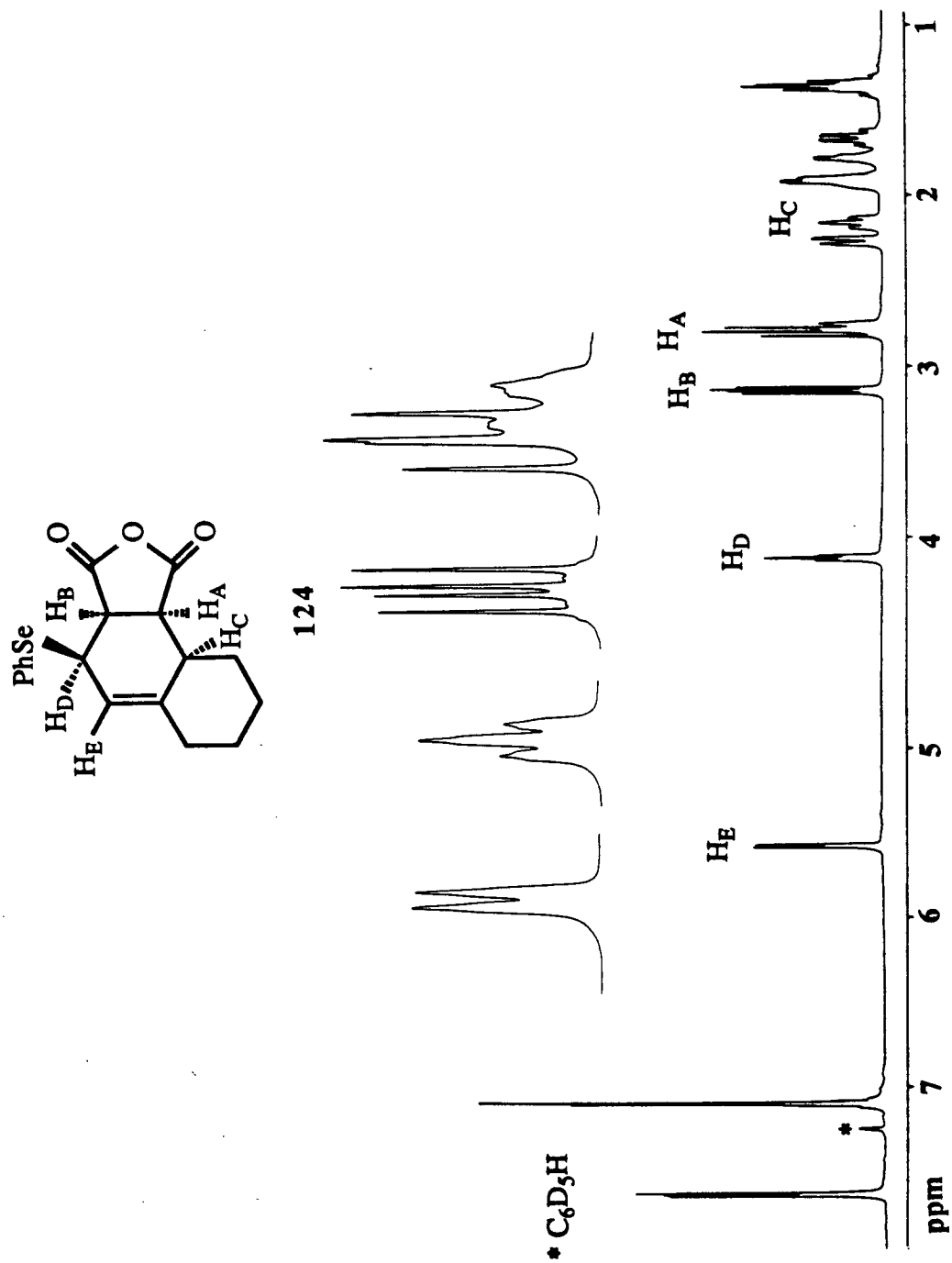
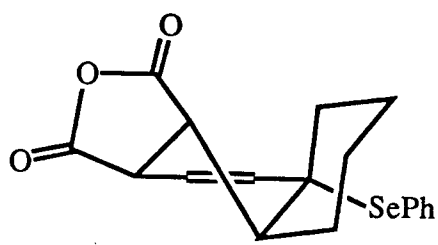


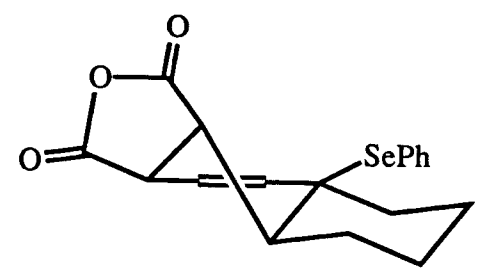
Figure 52. 400 MHz ^{1}H NMR spectrum of **124** in C_6D_6.

cycloadduct resulted from ^1H NMR decoupling and NOEDIFF experiments. The proposed stereochemistry was arrived at from the latter experiments which showed enhancement of the protons H_A and H_D by irradiation of H_B, and enhancement of protons H_A from irradiation of H_C (Figure 53, next page). Attempts to prepare **125** directly via the reaction at 60°C in room light or by photolysis of preformed **124**, resulted in decomposition to Ph_2Se_2 and other unidentified products. However, reaction of **88d** with maleic anhydride at 110°C for 18 h in the dark, gave the cycloadduct **125** in 78% yield. That this product resulted from an apparent [1,3]-rearrangement of the PhSe group was immediately apparent from the presence of two vinyl resonances in the ^1H NMR spectrum. The ^1H NMR spectrum of the cycloadduct **125** is shown in Figure 54 (p 142). Although many of the protons were readily assigned by ^1H NMR decoupling and NOEDIFF experiments, it was not possible to determine the relative stereochemistry of the PhSe group. The molecular mechanics program MM2 was used once more to determine which of the two epimers **126** or **127** represented the lower energy conformation (Figure 55). Calculations indicated that there was an approximate 4 kcal/mol



126

4.0 kcal/mol



127

0 kcal/mol

Figure 55. Proposed structures for the epimers **126** and **127**.

energy difference between the lowest energy conformations of these two epimers, with the cycloadduct **127** possessing the lower energy. This implies that in an equilibrium mixture of these two epimers at 80°C, **127** would compose >99% of the mixture. The stereochemistry of this compound is in contrast to the other apparent [1,3]-shifted products described here, in

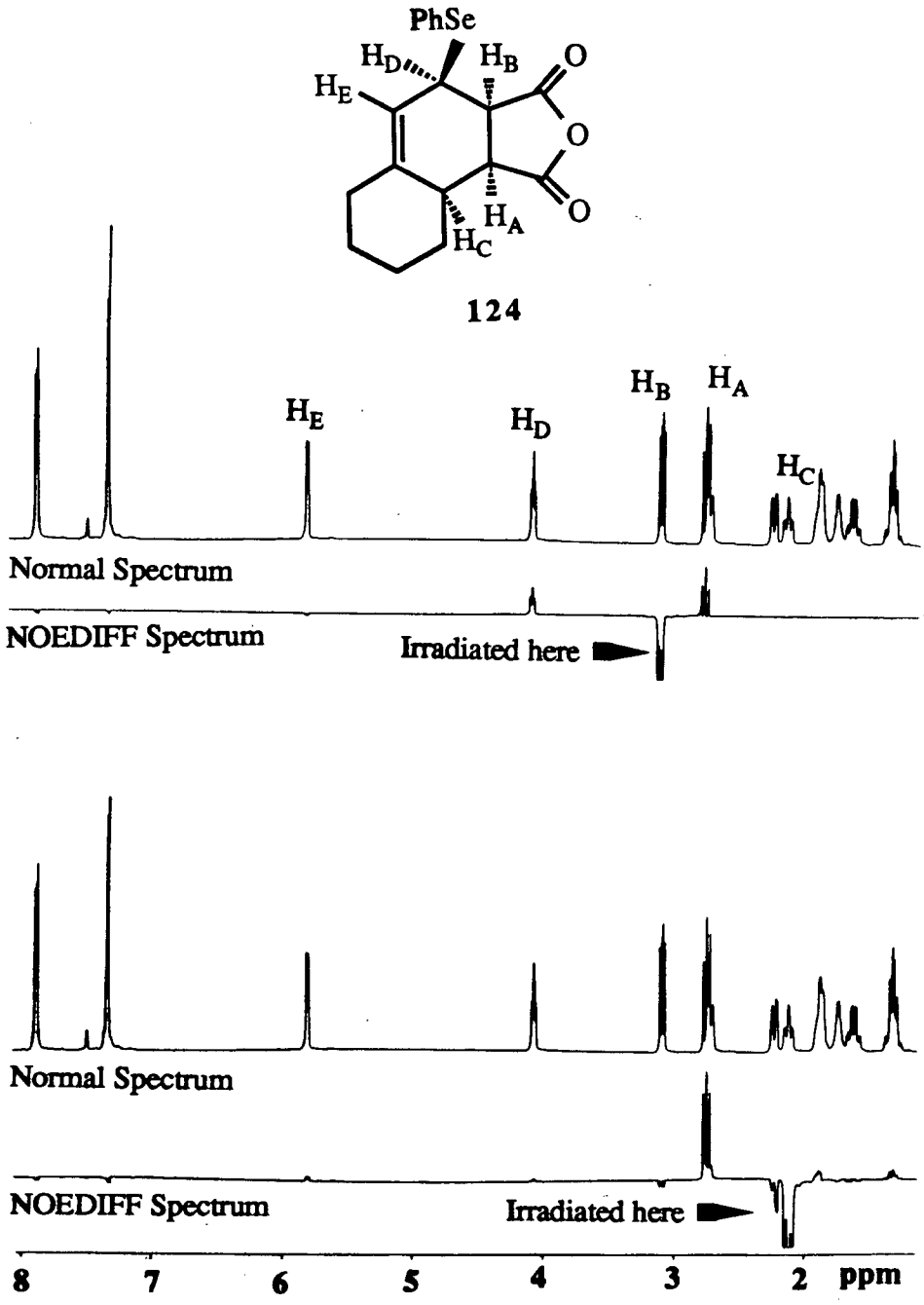


Figure 53. 400 MHz ^1H and NOEDIFF spectra of **124** in C_6D_6.

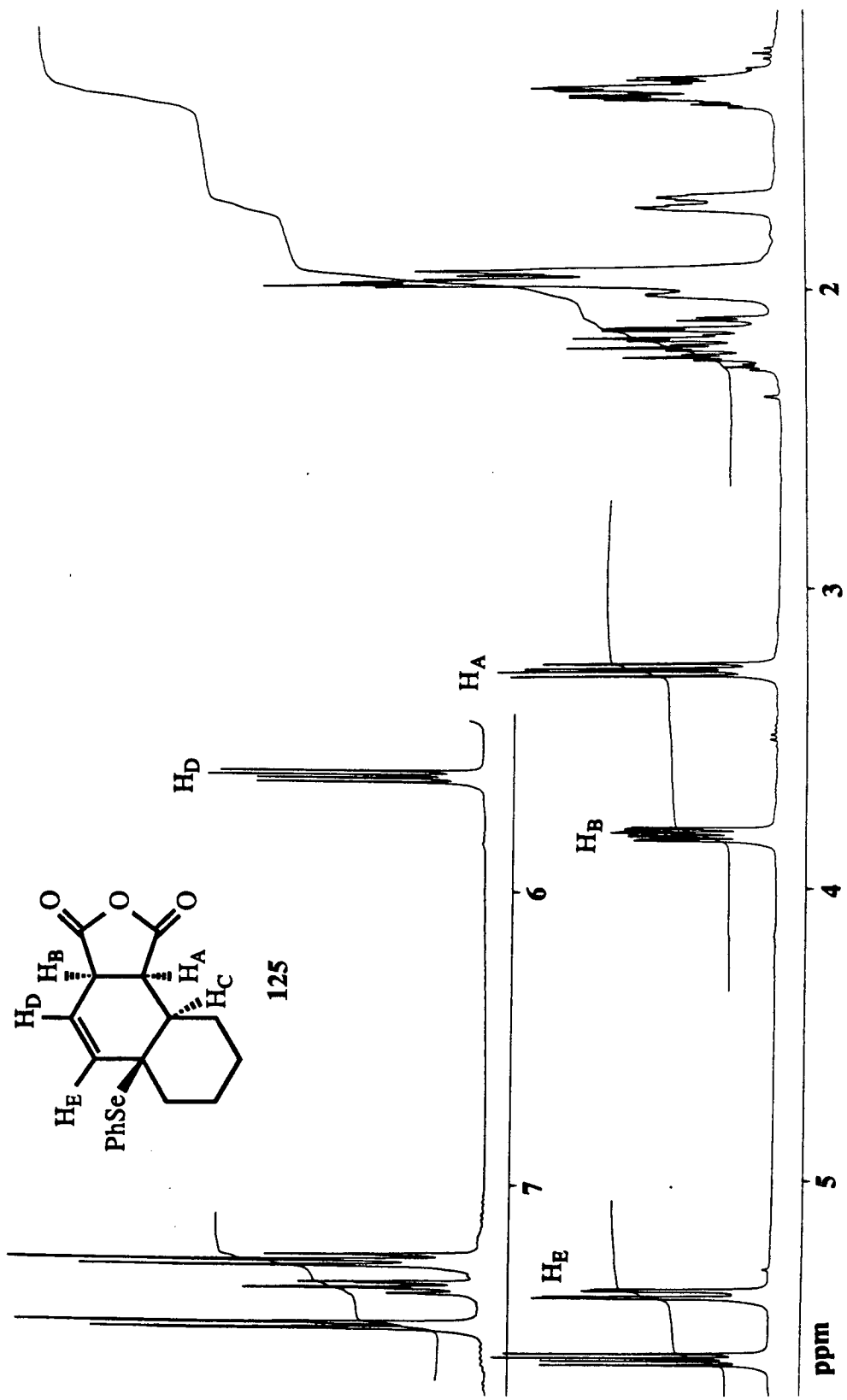


Figure 54. 400 MHz ^{1}H NMR spectrum of **125** in C_6D_6.

that it could not have been formed directly by attack of the PhSe· radical on the face opposite the resident PhSe group. It may have formed indirectly by this latter mechanism, followed by free radical epimerization to the more stable stereoisomer.

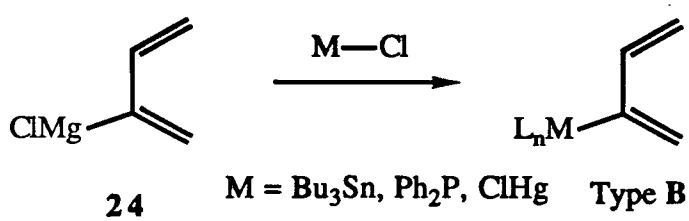
The Diels-Alder reactivity of the dienes **88a-b** and **88d** with maleic anhydride has presented some interesting results. By varying the reaction conditions, the preparation of two distinct sets of compounds can be achieved using the same starting materials.

CHAPTER 5

Preparation and Diels-Alder Reactivity of 2-(Trialkylstannyl)-1,3-butadienes and 2-(Phenylseleno)-1,3-butadiene.

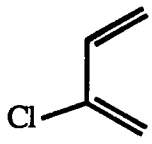
5.1 Synthesis and Cycloaddition Reactions of 2-(Phenylseleno)-1,3-butadiene and 2-(Trialkylstannyl)-1,3-butadienes.

Further to the major theme of this thesis, the preparation and Diels-Alder reactivity of type **B** 1,3-dienes (ML_n = metalloid or transition metal complex) were examined. A rational approach to the syntheses of these compounds was to use the readily available, inexpensive, starting material chloroprene **31**, and examine its conversion to type **B** 1,3-dienes via the Grignard reagent **24**. It had been reported that attempts to prepare **24** from chloroprene gave polymers; however, the preparation of this Grignard reagent was achieved from the less accessible 4-chloro-1,2-butadiene.[39] More recently, a modification was published that allowed **24** to be prepared directly from **31** by first activating the magnesium with zinc chloride and 1,2-dibromoethane.[40] As noted previously, Grignard reagent **24** has been shown to be a

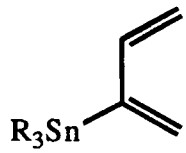


24 M = Bu_3Sn, Ph_2P, ClHg **Type B** + $MgCl_2$ (15)

useful starting material for the syntheses of other 2-substituted-1,3-butadienes, via a transfer reaction from magnesium (equation 15).[39] It was decided to use this procedure to prepare



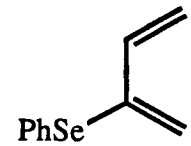
31



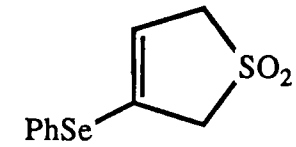
128

a R = Bu

b R = Me



129

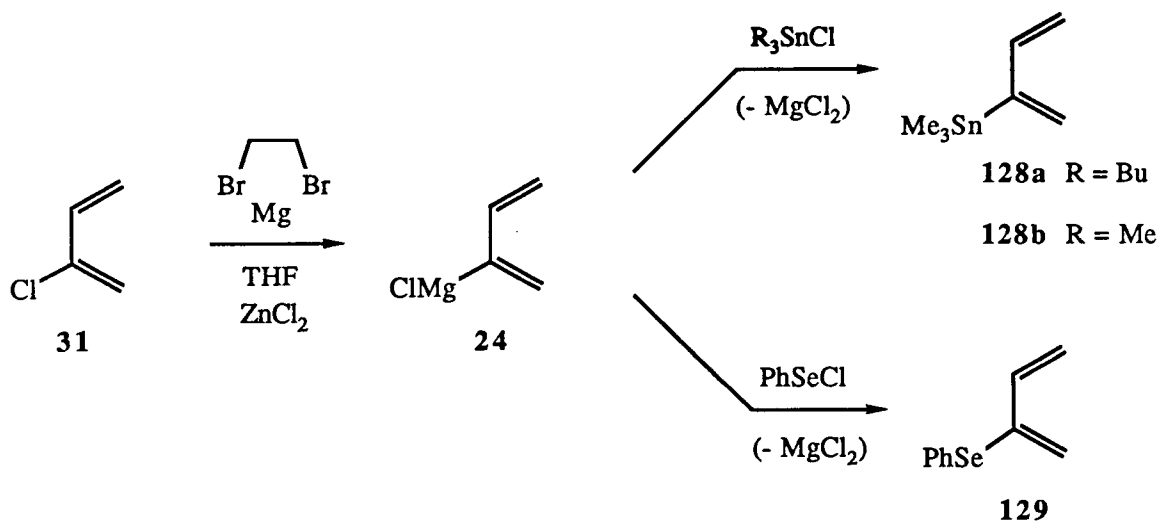


130

2-trialkylstannyl-1,3-butadienes **128** and 2-phenylseleno-1,3-butadiene **129**. Previous workers have reported on alternative syntheses and Diels-Alder reactivity of **128a-b**; a "tin-cupration" of 2-butyne-1,4-diol followed by "silyl-cupration" generated **128a** in reasonable yield,[97] while an equally elaborate Wurtz-type coupling yielded **128b**.[98] No report on the preparation of **129** was found, although the synthesis of the SO_2-masked derivative **130** has been recently described along with a study of its Diels-Alder reactivity.[99]

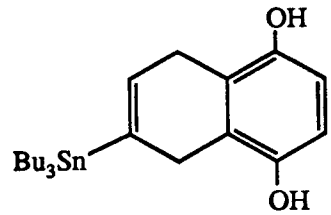
5.1.1 Diene Synthesis and Diels-Alder Reactivity.

Chloroprene **31** was readily converted into the corresponding Grignard reagent **24** by activating the magnesium with 1-3 mol % anhydrous $ZnCl_2$ and small amounts of 1,2-dibromoethane. In this fashion, 0.25-0.60 M solutions of **24** in THF were prepared. Subsequent reaction with tributyltin chloride, trimethyltin chloride and phenylselenenyl chloride allowed for the convenient, one-pot preparation of the dienes **128a-b** and **129** on a multi-gram scale (Scheme 32, next page). Diene **129**, previously uncharacterized due to its ready polymerization,[105] was isolated and found to be stable for months at -20°C under nitrogen in the dark. The ^1H NMR spectrum of this compound is shown in Figure 56 (p 147).



Scheme 32

The 2-tributylstannyl-1,3-butadiene **128a** underwent facile reaction with electron-deficient dienophiles, as is evidenced by the reactions summarized in Table IX (p 148). The corresponding reaction of **128a** with the electron-rich dienophile diphenylacetylene failed to yield any cycloaddition product, even after extended periods (several days) at reflux in toluene. In general, the reactions with electron-deficient dienophiles proceeded smoothly at elevated temperatures to give good yields of the Diels-Alder cycloadducts (**131-135**). However, reaction of **128a** with maleic anhydride for extended periods of time at room temperature gave the best yields of cycloadduct **131**. In the workup of **133**, by column chromatography on silica, enolization took place producing small quantities of the corresponding hydroquinone **136**. The ^{1}H NMR spectra of **133** and **136** are shown in



136

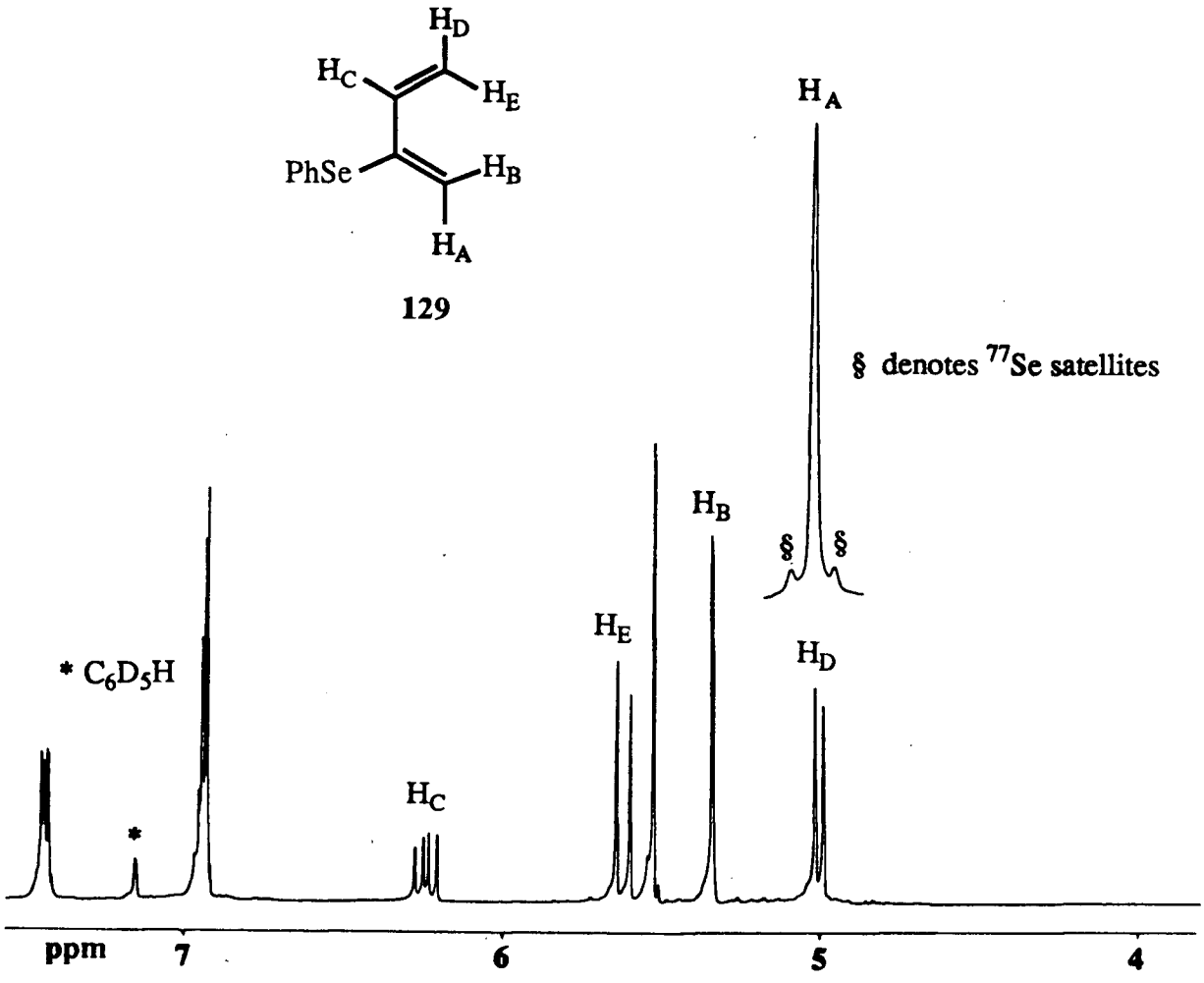
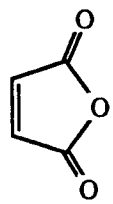
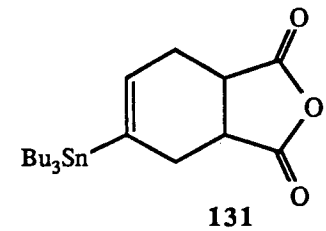
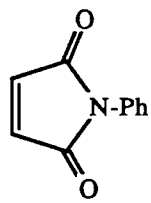
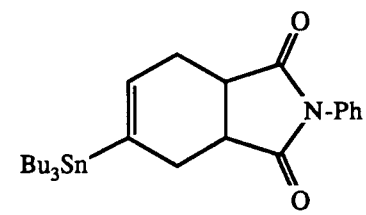
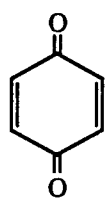
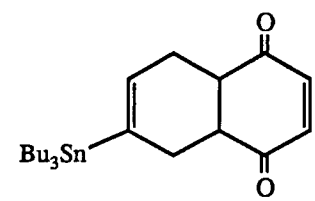
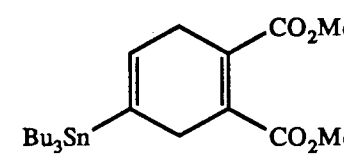
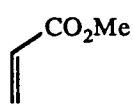
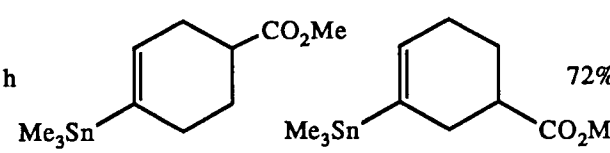


Figure 56. 400 MHz ^{1}H NMR spectrum of **129** in C_6D_6.

Figure 57 (p 149). Hydroquinone production was also observed when reaction times in excess of 12 h were used. Similar results were noted in the preparation and workup of **139** (see Table X, p 150), albeit to a lesser extent.

The results of the cycloaddition reactions of the phenylseleno diene **129** with a variety of activated dienophiles is outlined in Table X. The reaction of **129** at room temperature with maleic anhydride and at elevated temperature with less activated dienophiles yielded cycloadducts **137-141**. Thermolysis of **129** with diphenylacetylene for several days at reflux in toluene resulted in the quantitative recovery of starting materials, suggesting that as with the

Table IX. Reaction of 2-(Trialkylstannyl)-1,3-butadienes **128a-b**.

Entry	Dienophile[a]	Conditions	Products	Yields
1		$PhCH_3$, R.T., 2 days	 **131**	75%
2		$PhCH_3$, reflux, 8 h	 **132**	90%
3		$PhCH_3$, reflux, 5 h	 **133**	69%
4	$MeO_2CC{\equiv}CCO_2Me$	$PhCH_3$, reflux, 18 h	 **134**	71%
5		$PhCH_3$, reflux, 18 h	 **135a** **135b** 2 : 1	72%

[a] No reaction with diphenylacetylene

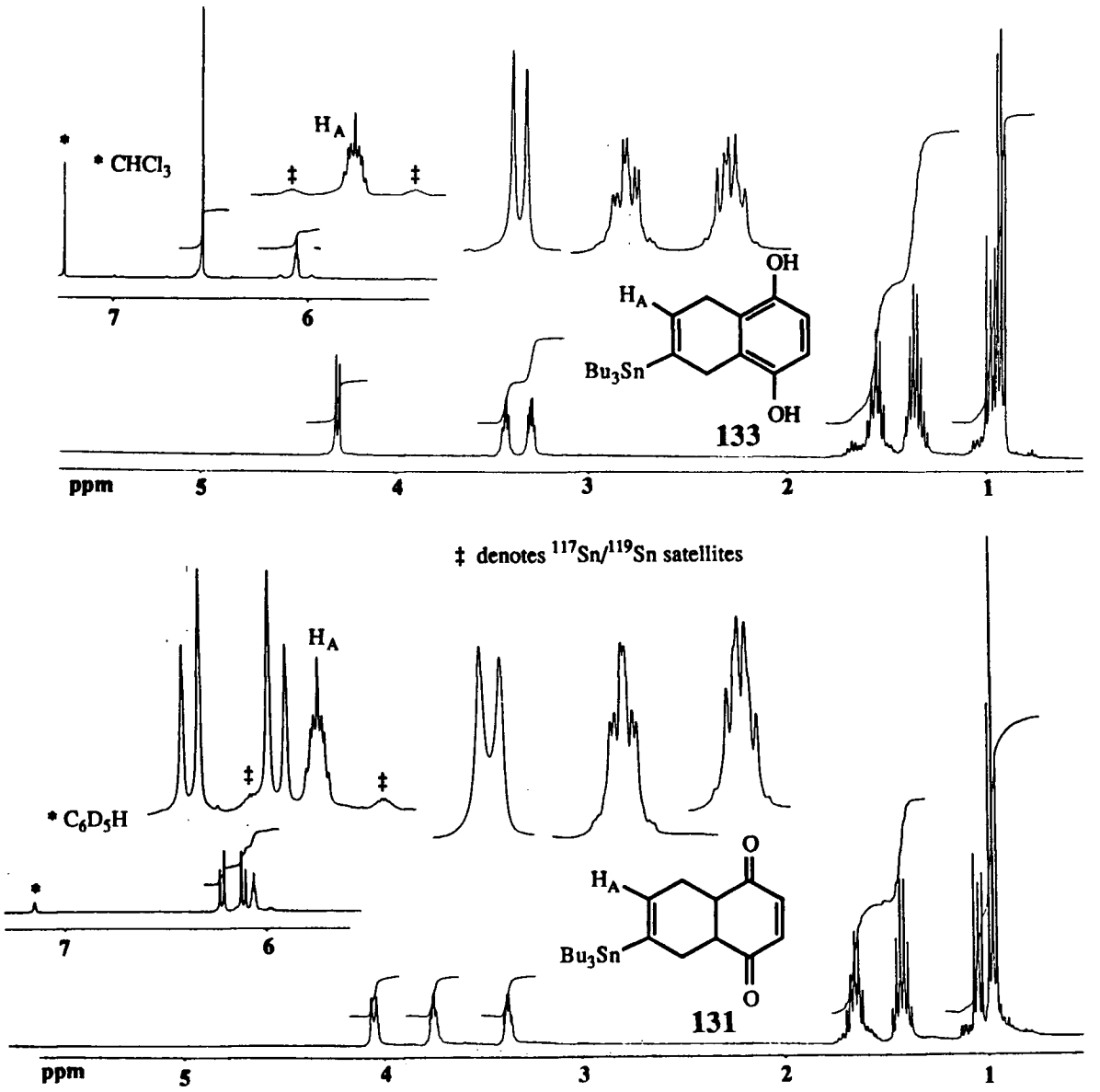
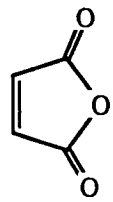
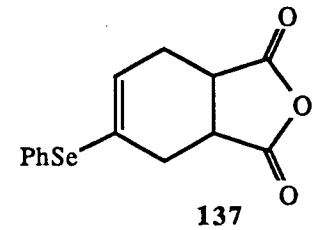
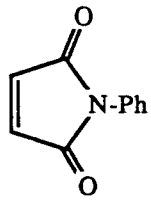
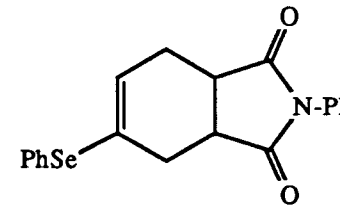
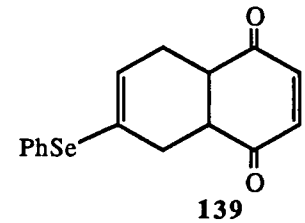
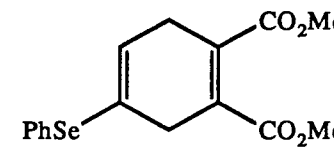
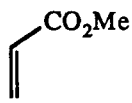
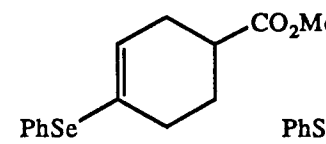
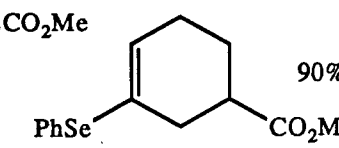


Figure 57. 400 MHz ^{1}H NMR spectrum of **131**and **133** in C_6D_6 and $CDCl_3$, respectively.

Table X. Reaction of 2-(Phenylseleno)-1,3-butadiene **129**.

Entry	Dienophile[a]	Conditions	Products	Yields
1		$PhCH_3$, R.T., 2 days	 **137**	70%
2		$PhCH_3$, reflux, 8 h	 **138**	76%
3		$PhCH_3$, reflux, 2 h	 **139**	64%
4	$MeO_2CC{\equiv}CCO_2Me$	$PhCH_3$, reflux, 18 h	 **140**	81%
5		$PhCH_3$, reflux, 18 h	 **141a**  **141b** 4 : 1	90%

[a] No reaction with diphenylacetylene

stannyl functionality the selenenyl moiety does not activate the 1,3-diene towards reaction with electron-rich dienophiles. The structural assignments for these cycloadducts followed from analysis of their ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum of **137** is shown in Figure 58 (next page).

In an attempt to determine the directing effect of the stannyl moiety, the reaction of **128b** with methyl acrylate at reflux in toluene was examined. In analogy to results previously observed in cycloaddition reactions of silylbutadienes,[100] the stannyl moiety was found to exhibit only a weak directing effect, resulting in a 2:1 mixture of *para*:*meta* regioisomers **135a/135b**, as determined by GLC and ^{1}H NMR spectroscopy. Other workers have shown that use of 15 mol % Et_2AlCl in the reaction of **128a** with ethyl acrylate gave a 10:1 ratio of *para*:*meta* regioisomers.[97a] This latter observation suggests that the poor regioselectivity seen in the uncatalyzed reaction of **128b** with methyl acrylate should be significantly improved by the use of a Lewis acid catalyst.

The assignment of **135a** as the major regioisomer was based on literature precedent.[105,108] Attempts to separate mixtures of **135a/135b** using column chromatography proved difficult; however, an enriched 7:1 (**135a/135b**) mixture was obtained. It was hoped that by use of ^{1}H NOEDIFF spectroscopy on this enriched mixture, more physical evidence for the assignment of the major regioisomer could be achieved. Unfortunately, the results of such experiments at 400 MHz were equivocal.

Regiochemical investigation of the Diels-Alder reactivity of **129** involved reaction with methyl acrylate at reflux in toluene. An excellent yield of **141a/141b** (90%) was obtained; the ratio of regioisomers being 4:1 (*para*:*meta*) as determined by GLC and ^{1}H NMR spectroscopy. This result was in agreement with published data on the products obtained by reaction of **129** with ethyl acrylate.[99] The results of this study show that, in reaction with methyl acrylate, the selenenyl moiety has a greater directing effect than the stannyl substituent.

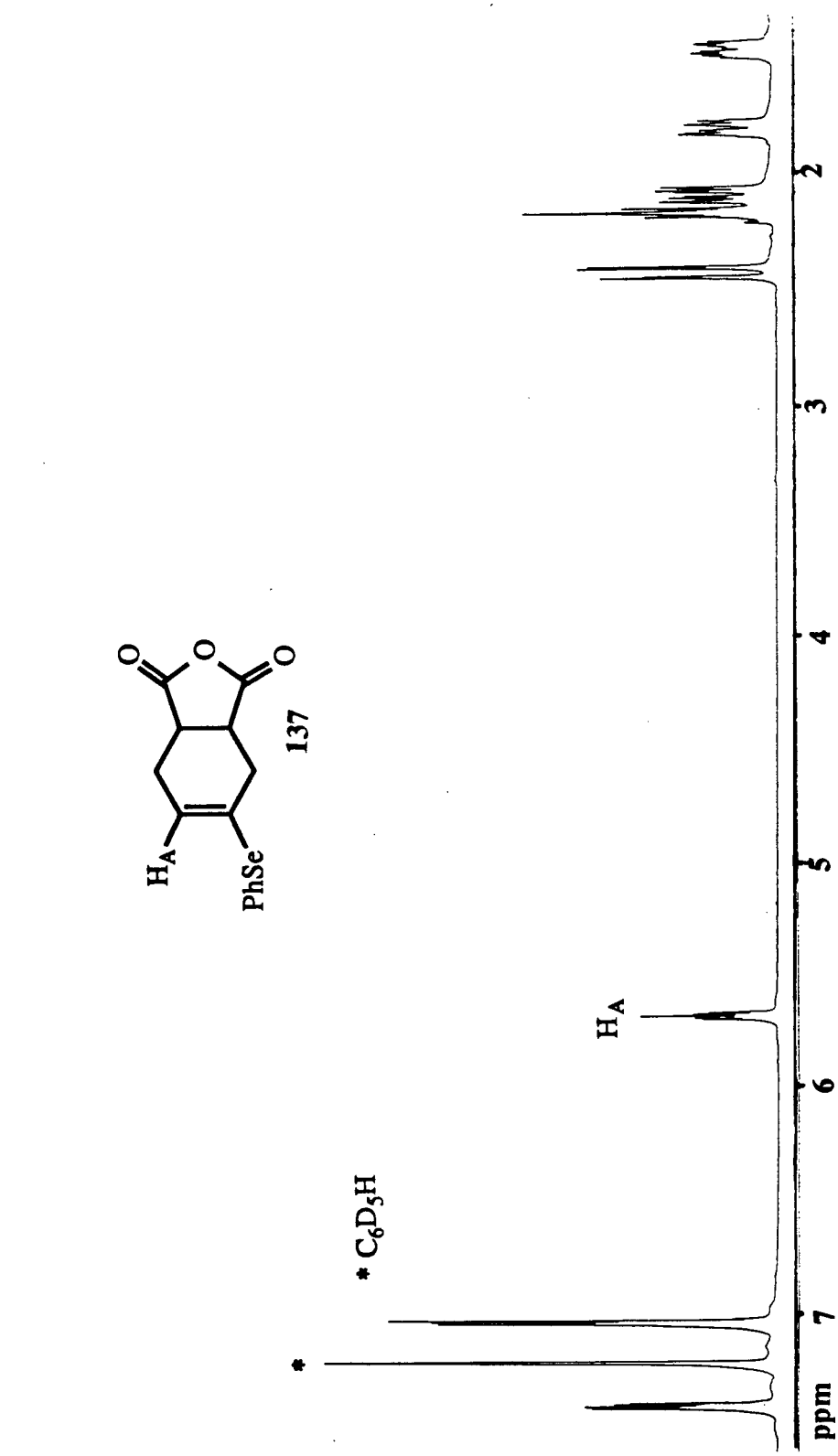
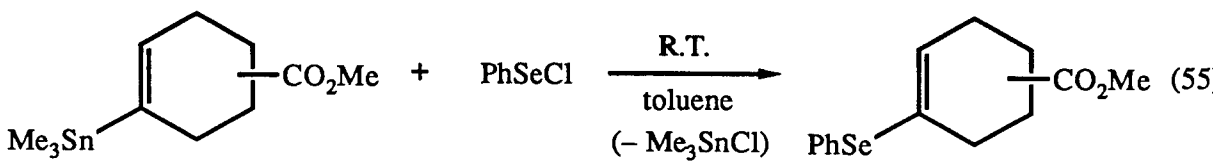


Figure 58. 400 MHz ^1H NMR spectrum of **137** in C_6D_6.

5.1.2 Transmetalation from Tin to Selenium.

Addition of PhSeCl to a solution of the 1,3-dienylzirconium complexes **55a-d** resulted in smooth transfer of the dienyl unit from zirconium to selenium with immediate discharge of the deep red color of PhSeCl. In an attempt to gain further comparative information on the reaction of dienylstannane **128b** and dienylselenide **129** with methyl acrylate, a solution of PhSeCl was added to a 2:1 mixture of **135a/135b**. Stirring the mixture overnight at room temperature caused discharge of the deep red color of the PhSeCl, which on workup yielded a 2:1 (*para:meta*) mixture of **141a/141b** as determined by ^{1}H NMR spectroscopy (equation 55).

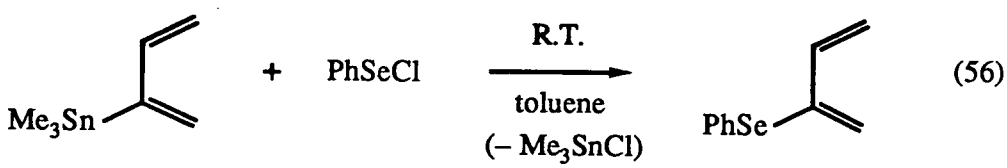


135a/135b
2:1
para:meta

141a/141b
2:1
para:meta

(55)

This result indicates that the major regioisomer formed in the reaction of **128b** with methyl acrylate has the same regiochemistry (i.e., the *para* isomer) as that observed from the corresponding reaction of **129** with methyl acrylate. The reaction appears to be quite general for vinylstannanes as evidenced in the reaction of **128b** with PhSeCl to give **129** (equation 56). The latter reaction is also highly chemoselective as no products of the addition of PhSeCl to the isolated double bond are observed.

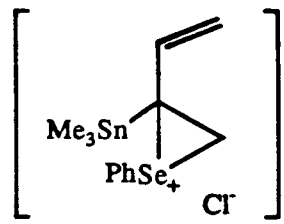


128b **129**

(56)

Transmetalation of tin in vinylstannanes has precedent in reactions at low temperature with alkyllithium reagents,[27] and in coupling reactions catalyzed by palladium(0) complexes.[31] Stereoselective transmetalation from mercury to selenium by reaction of vinyl mercuric compounds with PhSeCl has also been observed.[102] *However, the above observations are, to the best of our knowledge, the first reported examples of transmetalation from tin to selenium.*

The reaction of vinylstannanes with PhSeCl may be analogous to a previously reported reaction in which iodine is used to cleave the tin-carbon bond producing a vinyl iodide.[103] Much work has already been done on the mechanism of areneselenenyl chloride addition to alkenes. Schmid and Garratt[104] proposed three possible mechanisms, which differ only in the relative amount of carbon-selenium bond making and selenium-chlorine bond breaking leading up to the formation of a seleniranium ion. For the system described here, collapse of

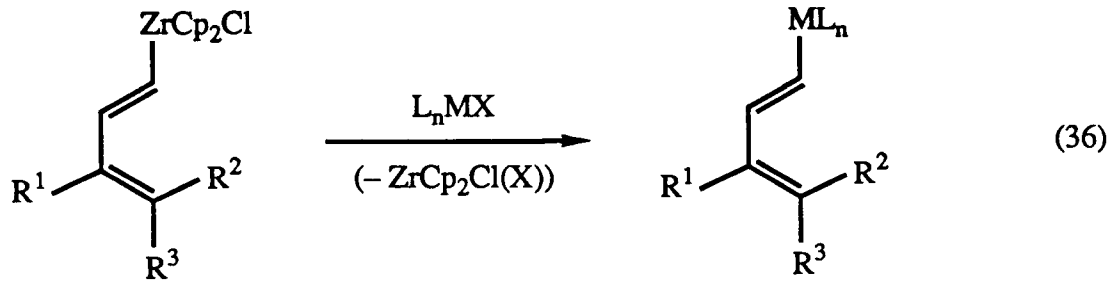


142

the analogous seleniranium ion **142** to give **129** could proceed via attack of the chloride at the least-substituted carbon or at the tin, followed by loss of Me_3SnCl.

5.2 Attempted Syntheses of Type B 1,3-Dienes where ML_n is Cp_2ZrCl.

The Grignard reagent **24** has proved to be a useful starting material for the syntheses of type **B** 1,3-dienes. However, the method appears to lack the generality of the transfer reaction of organic fragments from zirconium (equation 36), as regards the ease with which other

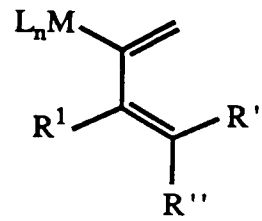


(36)

55a-d Type **A**

M = Sn, P, B, Se, S

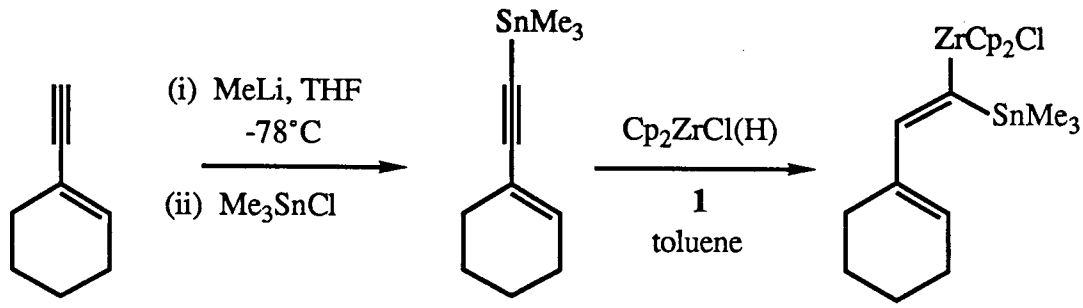
functionalities can be introduced. To address this deficiency, preliminary investigations into the syntheses of type **B** 1,3-dienes, having the Cp_2ZrCl fragment at the 2-position, were performed.



Type **B**

The initial plan centered around the fact that in the hydrozirconation reaction of disubstituted acetylenes, the Cp_2ZrCl fragment always occupied the least sterically crowded position.[13] With this in mind, the trimethylstannyl-substituted 1-ene-3-yne **143** was prepared by reaction of the lithium salt of **51d** with trimethyltin chloride. The presence of the trialkylstannyl group was also attractive as it introduced another functionality which could prove useful for further synthetic elaboration. Subsequent reaction of **143** with a slight excess

of $Cp_2ZrCl(H)$ **1**, resulted in a 95:5 mixture of stereoisomers in which compound **144** was identified (by ^1H NOEDIFF experiments) as the major isomer (Scheme 33). The

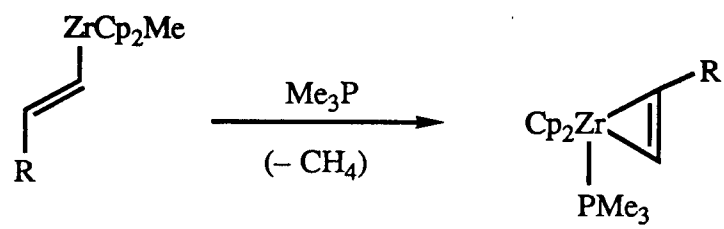


51d **143** **144**

Scheme 33

regiochemical outcome of this reaction was initially somewhat surprising, as it had been anticipated that the Me_3Sn group would prove more sterically demanding than the cyclohexenyl group. However, it is likely that the effective steric bulk of the Me_3Sn group is somewhat lessened by the length of the tin-carbon bond (~2.1 Å).

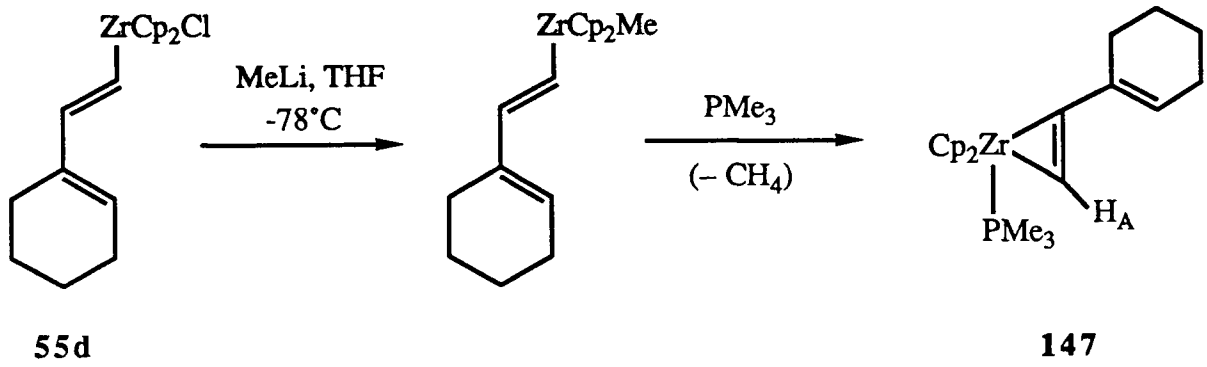
Another possible route to type **B** 1,3-dienes involves the preparation of zirconium η^2-alkyne complexes **146**, by reaction of **145** with an excess of Me_3P (equation 57).[105] The



(57)

145 **146**

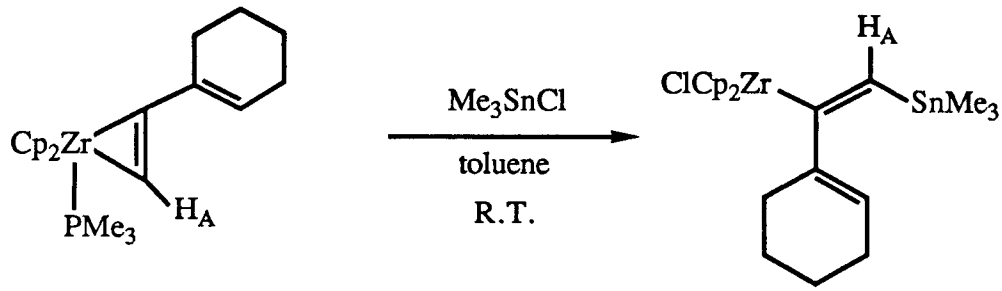
η^2-alkyne functionality of these complexes is very reactive, and undergoes a series of cleavage and insertion reactions.[100] Based on these precedents, the preparation of **147** was carried out using the procedure outlined in Scheme 34 (next page). The ^1H NMR spectrum of **147** is



55d **147**

Scheme 34

shown in Figure 59 (next page). The assigned structure is consistent with the results of a ^1H NOEDIFF experiment in which irradiation of the methyls of the Me_3P group gave enhancement of proton H_A and the cyclopentadienyl ligands (Figure 60, p 159). In the anticipation that cleavage of the η^2-alkyne would occur to place the Cp_2ZrCl group at the 2 position, leaving the Me_3Sn group at the 1-position, **147** was reacted with trimethyltin chloride. This reaction proceeded smoothly at room temperature to give a single crystalline product **148**, tentatively assigned the structure shown in equation 58. The ^1H NMR spectrum



(58)

147 **148**

of **148** is shown in Figure 61 (p 160). Analysis of the spectrum shows a 43 Hz $^1H^{117/119}Sn$ coupling for proton H_A. The magnitude of this coupling strongly suggested that the Me_3Sn group and proton H_A are geminal.[71] The results of ^1H NOEDIFF experiments confirmed this assignment; however, the determination of the relative stereochemistry of the

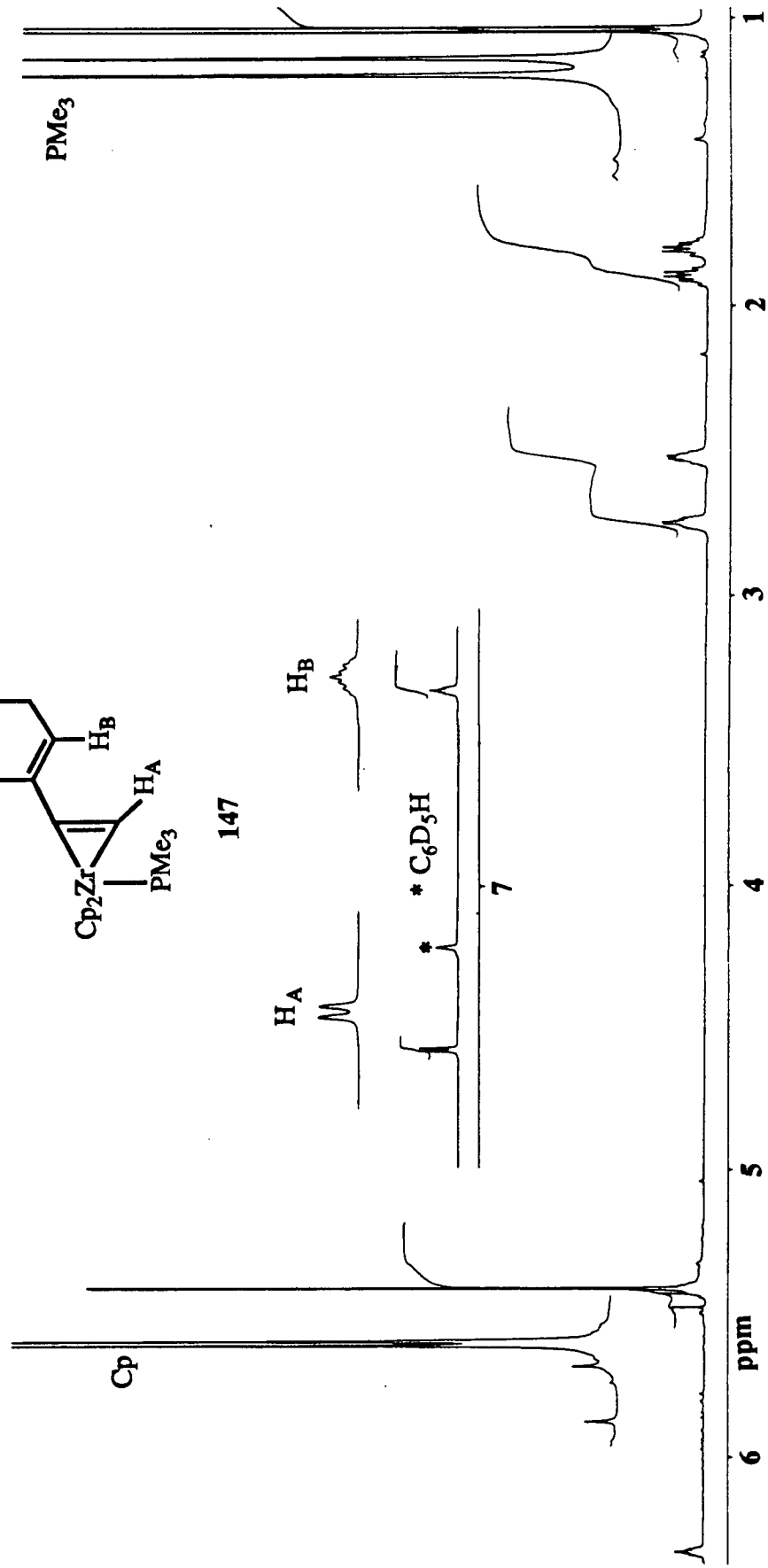


Figure 59. 400 MHz ^{1}H NMR spectrum of **147** in C_6D_6.

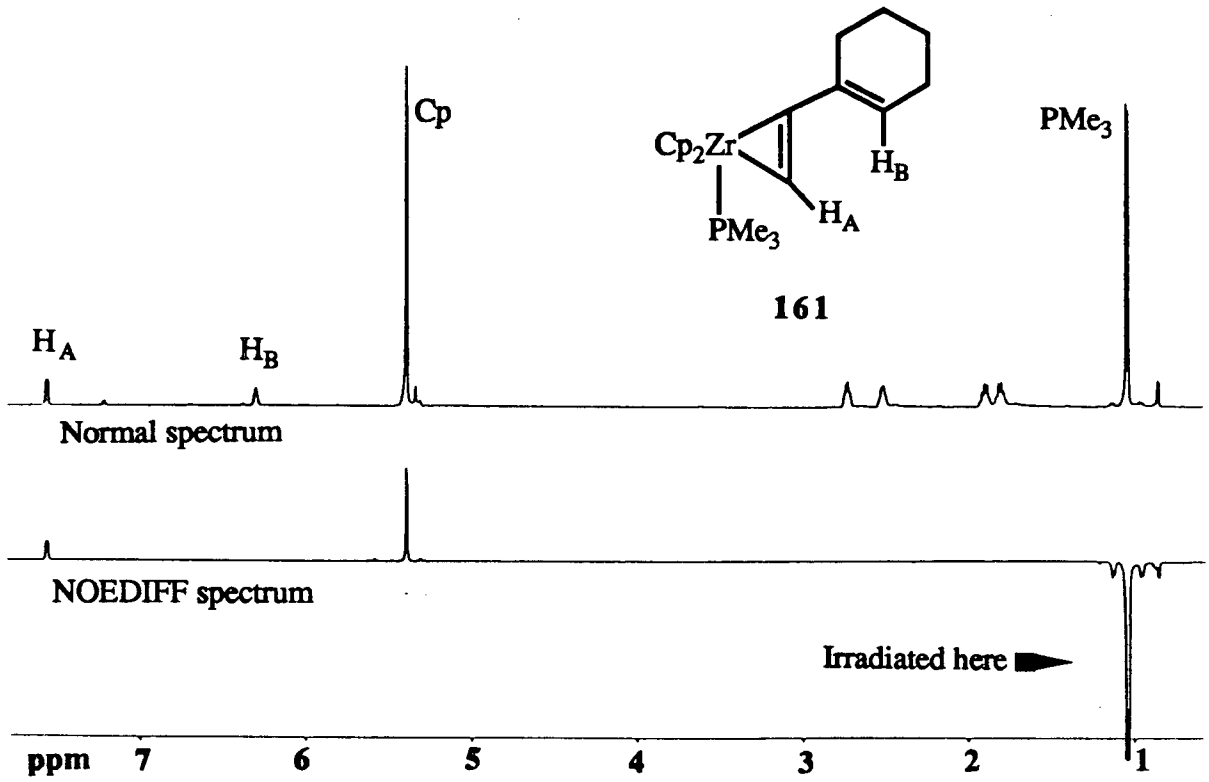


Figure 60. 400 MHz ^{1}H NMR and NOEDIFF spectra of **147** in C_6D_6.

Cp_2ZrCl and Me_3Sn groups remained uncertain. To remove this ambiguity a single crystal (prepared by Dr. Randy Alex) was subjected to X-ray structure analysis. The solid state structure for **148** is shown in Figure 62 (p 161), along with selected bond lengths and angles. It is clear from this structure determination that the Cp_2ZrCl and Me_3Sn groups are oriented trans to one another.

Utilization of the literature procedure,[105] followed by cleavage of the η^2-alkyne functionality provides a path to the desired 1,3-dienes of type **B**, substituted at the 1-position with a Me_3Sn group.[106] The removal of the latter functionality could be achieved by selective "lithiation", followed by an aqueous workup. Also, further work in this area suggests that cleavage of the η^2-alkyne functionality of **147** with gaseous HCl may provide a direct route to type **B** 1,3-dienes.[107]

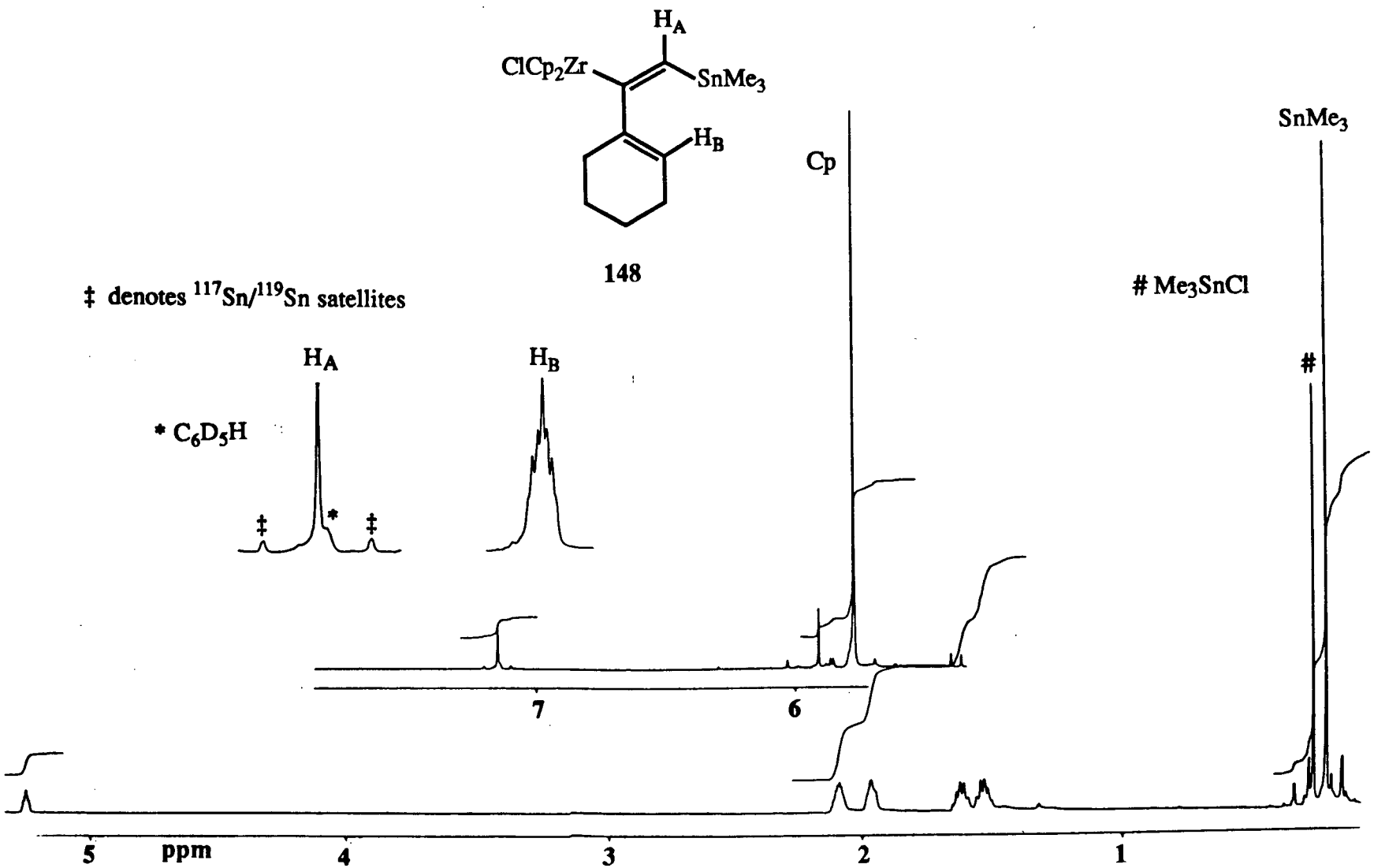
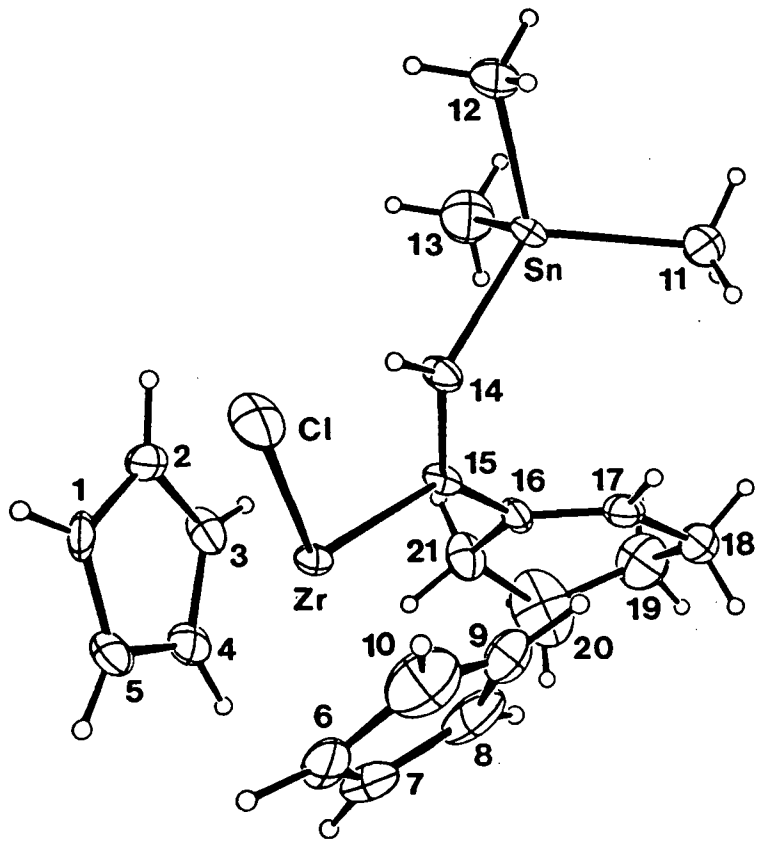


Figure 61. 400 MHz ^{1}H NMR spectrum of **148** in C_6D_6.



Selected bond lengths (Å) and angles (°) for **148**

Zr—Cl	2.52(2)	C(14)—C(15)	1.34(8)
Zr—C(15)	2.24(7)	C(15)—C(16)	1.48(9)
Sn—C(14)	2.14(6)	C(16)—C(17)	1.32(9)

Cl–Zr–C(15)	115(2)	Zr–C(15)–C(16)	140(4)
Sn–C(14)–C(15)	128(5)	C(15)–C(16)–C(17)	121(7)
Zr–C(15)–C(14)	95(5)	C(15)–C(16)–C(21)	118(6)
C(14)–C(15)–C(16)	125(6)	C(17)–C(16)–C(21)	122(6)

Figure 62. Molecular structure and selected bond lengths and angles for **148**.

Conclusion

The reaction of the hydride reagent $Cp_2ZrCl(H)$ **1** with bifunctional molecules such as 1-ene-3-ynes and α,β-unsaturated nitriles has been shown to proceed in a chemoselective manner to provide general synthetic methods for the preparation of 1-substituted 1,3-dienyl- and 1-azadienylzirconium complexes in good to excellent yields. The reactions of 1-ene-3-ynes with the deuterium-labelled reagent $Cp_2ZrCl(D)$ **2**, failed to provide clear evidence as to the nature of the observed chemoselectivity. The 1,3-dienylzirconium reagents underwent a facile reaction with carbon monoxide to generate a series of well-characterized η^2-acyl-1,3-dienyl complexes.

The 1,3-dienylzirconium reagents (**55a-d**) were successfully employed as general precursors for the preparation of other heterosubstituted 1,3-dienes. In this reaction the 1,3-dienyl fragment was stereoselectively transferred from zirconium to tin, phosphorus, boron, selenium and sulfur. Although this transfer reaction was a clean and efficient procedure for the syntheses of these 1,3-dienes, attempts to transfer of the 1,3-dienyl moiety from zirconium to silicon or to various transition metals (e.g., Ni, Pd and Pt) were unsucessful.

An X-ray crystal structure of the 1-azadienylzirconium complex **69**, indicated that significant double-bond character was present in the zirconium-nitrogen linkage; suggesting that these complexes were formally 18-electron species and as such were unlikely to undergo transfer reactions. However, for the most part, reaction of these 1-azadienyl complexes with selenium and phosphorus transfer reagents proceeded smoothly to afford in reasonable yields a quite novel series of heterosubstituted 1-azadienes.

During investigations into the transfer of the 1,3-dienyl moiety from zirconium to selenium, the formation of isomeric mixtures of products was observed. This could be avoided through careful control of the reaction conditions, namely by performing the reaction at -20°C in the dark. Separate studies indicated that the formation of isomeric mixtures for these compounds could be induced by photolysis with fluorescent light or by thermolysis in the dark

at 80°C. Mechanistic studies of this isomerization reaction involved the use of crossover experiments and free radical traps and initiators. These studies indicated that an intermolecular process involving free radicals was likely responsible for the observed isomerization. Similar isomerization of the sulfur-substituted 1,3-dienes was noted after several hours of irradiation with fluorescent light. The Diels-Alder reactivity of the selenium-substituted 1,3-dienes (**88a-b, 88c**) with maleic anhydride uncovered an interesting photochemically and thermally induced apparent [1,3]-shift of the PhSe group in the pre-formed cycloadducts.

The Grignard reagent 2-chloromagnesium-1,3-butadiene (**24**) proved to be a useful starting material for the prepartion of the corresponding tin- and selenium-substituted 1,3-dienes (**128** and **129**). These 1,3-dienes reacted efficiently with a variety of electron-deficient dienophiles to afford a series of cyclohexenes containing the vinylstannane or the vinylselenide functionality. Reaction of trimethylstannyl-1,3-butadiene (**128b**) with PhSeCl yielded exclusively the corresponding selenium-substituted 1,3-diene (**129**) via a novel transmetalation reaction from tin to selenium. Attempts to provide a more general route to 2-substituted 1,3-dienes involved the preparation of a dimetalated 1,3-diene (**148**), containing the Cp_2ZrCl substituent at the 2-position and the Me_3Sn group at the 1-position. It was envisaged that such a molecule would undergo similar transfer reactions of the 1,3-dienyl fragment, as outlined for **55a-d** (Chapter 3), to generate the corresponding series of 2-heterosubstituted 1,3-dienes.

Opportunities for further research regarding the material presented in this thesis could involve: (i) investigation of the directing influence of the various heterosubstituted 1,3-dienes in cycloaddition reactions with unsymmetrical dienophiles, (ii) use of the 1,3-dienylzirconium complexes in natural product synthesis for the stereocontrolled introduction of a 1,3-dienyl unit, and (iii) further effort directed towards the synthesis of 1,3-dienes substituted at the 2-position by the Cp_2ZrCl moiety.

CHAPTER 6

Experimental

6.1 General.

All manipulations were performed under prepurified nitrogen[108] in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purifier, or in standard Schlenk-type glassware under argon (as supplied) or prepurified nitrogen. The term "reactor bomb" refers to a cylindrical, thick-walled Pyrex® vessel (50-75 mL in volume) equipped with a 5 mm Kontes® needle valve and a ground glass joint for attachment to a vacuum line. Larger reactor bombs (250-500 mL in volume) are equipped with 10 mm Kontes® valves.

Infrared spectra (IR) were recorded on a Nicolet 5D-X spectrophotometer (internal calibration) as KBr pellets, or on NaCl plates as Nujol mulls or liquid films, or as solutions in dichloromethane (CH_2Cl_2), and are reported in cm^{-1}. UV-vis spectra were performed on a Hewlett-Packard 8452A Diode Array spectrophotometer using spectroscopic-grade hexane and a 1 cm quartz cell; λ_{max} values are reported in nm. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker WH-400 spectrometer (at 400 MHz) as solutions in chloroform-d_1 ($CDCl_3$), dichloromethane-d_2 (CD_2Cl_2), benzene-d_6 (C_6D_6) or toluene-d_8 (C_7D_8). Signal positions are given on the delta (δ) scale in ppm with reference to $CHCl_3$ at 7.25 ppm, $CHDCl_2$ at 5.32 ppm, C_6D_5H at 7.15 ppm, or $C_6D_5CHD_2$ at 2.09 ppm.[56a] $^{13}C\{^1H\}$ NMR measurements were performed at 75.4 MHz on a Varian XL-300 spectrometer, signal positions were measured in δ relative to $CDCl_3$ at 77.0 ppm.[56a] $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP-80 (32.4 MHz), Bruker WH–400 (162.2 MHz) or on a Varian XL-300 (121.5 MHz); signal positions are given on the δ scale with reference to

external trimethylphosphite at 141 ppm.[56a] $^{77}Se\{^{1}H\}$ NMR data were obtained on a Bruker WH-400 (76.3 MHz); signal positions are given relative to an external sample of diphenylselenide (Ph_2Se, 60% v/v in $CDCl_3$) at 416 ppm.[109] Where reported, hydrogen-tin coupling constants (J_{HSn}) are quoted as an average of the ^{117}Sn and ^{119}Sn values. Low and high resolution mass spectra were recorded on a Kratos/AEI MS-50 mass spectrometer. For compounds containing the η^5-cyclopentadienyl ligand (Cp), the integral for this resonance was consistently less than the expected value. This phenomenom has be previously observed and is believed to result from a long spin-lattice relaxation time for the Cp ligand.[110] Gas chromatography-mass spectroscopy (GCMS) analyses were performed using a Varian Vista 6000 (DB1-100% Dimethyl-polysiloxane 5 μm film thickness x 30 m) coupled to a Delsi-Nermag R10-10C mass spectrometer.

Gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 5880a gas chromatograph using a 12 m x 0.2 mm column (Carbowax 10M). Column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh ASTM). For thin-layer chromatography silica gel 13181 (Eastman chromagram®) sheets were used. Microanalyses were performed by Mr. P. Borda of this department. X-ray crystal structure determination were performed by Dr. R. Chadha at the University of Manitoba. Mr. Tom Keller is acknowledged for the performance of the reported MM2 calculations.

For reactions carried out at -20°C, the reagents were cooled to this temperature in a refrigerator contained in the glovebox. Removal of bis(η^5–cyclopentadienyl)zirconium(IV) dichloride (Cp_2ZrCl_2), produced as a by-product in most of the zirconium transfer reactions, was performed (unless stated otherwise) by filtration through basic alumina, Brockman Activity 1 (80-200 mesh). For reactions carried out in the dark, the appropriate vessel was simply covered with aluminum foil. All photolysis reactions were carried out in capped (or sealed) 5 mm 507PP NMR tubes under prepurified nitrogen (unless stated otherwise) using a Sylvania (GTE) 34 W *Cool White* fluorescent light. The irradiation source emitted white light covering the spectrum of wavelengths from 380 to 800 nm. Samples for photolysis were

simply taped to the fluorescent light, the solution being ~3-4 cm from the source. Measurements indicated that the temperature of the sample did not exceed 29°C.

6.2 Solvents and Reagents

NMR solvents $CDCl_3$, CD_2Cl_2, C_6D_6 and C_7D_8 were purchased from MSD Isotopes, and were dried over 3Å molecular sieves, with the exception of $CDCl_3$ which was distilled from calcium hydride (CaH_2). All solvents were dried under argon. Hexanes and diethyl ether (Et_2O) were dried over sodium-benzophenone ketyl. Toluene and tetrahydrofuran (THF) were predried over sodium wire and CaH_2, respectively, and then distilled from sodium-benzophenone ketyl. Dichloromethane and petroleum ether (30-60°C) were dried by refluxing over CaH_2.

Methyllithium in Et_2O, bis(η^5-cyclopentadienyl)zirconium(IV) dichloride (Cp_2ZrCl_2), trimethyltin chloride, tributyltin chloride, phenylselenenyl chloride (PhSeCl), diphenyl diselenide (Ph_2Se_2), cyclooctadiene (COD), 2,6-di-*tert*-butyl-4-methylphenol (BHT), 1,4-cyclohexadiene, *N*-bromosuccinimide, azobisisobutyronitrile (AIBN), chlorodiphenylphosphine (Ph_2PCl), methyl acrylate, methacrylonitrile, benzonitrile, *o*-tolunitrile, maleic anhydride, *N*-phenylmaleimide *p*-benzoquinone, dimethyl acetylenedicarboxylate, cinnamonitrile, (*E*)-3-ethoxyacrylonitrile, (*E*)-3-dimethylaminoacrylonitrile, *p*-toluenesulfonyl chloride and (*Z*)-1-methoxy-1-buten-3-yne were all purchased from the Aldrich Chemical Co., Inc.. All of the above reagents were purified by standard means prior to use. The reagents 2-chloro-1,3-butadiene and 1-buten-3-yne were purchased from Pfaltz and Bauer Chemicals, Inc.; both were obtained as solutions in xylene. The former was dried over 4Å molecular sieves and vacuum transferred several times to remove any xylene, the latter compound was simply vacuum transferred twice prior to use. Chlorodimethylphosphine (Me_2PCl), trimethylphosphine (PMe_3) and triethylphosphine (PEt_3)

were purchased from Strem Chemical Co., and were used without further purification. Bromodiphenylboron was purchased from Alfa Chemical Co., isopropylacetylene was purchased from Farchan Chemical Co., and ^{13}CO (90 atom %) was purchased from MSD Isotopes; these reagents were used as supplied. Carbon monoxide was obtained from Matheson Gas Products and was used without further purification. Gratitude is expressed to Mr. J. B. Ng (UBC) for providing a sample of chlorodiisopropylphosphine (*i*-Pr_2PCl), Dr. G. Herring for a loan of 4-oxo-2,2,6,6-tetramethylpiperidinyloxy radical (TEMPONE) and to Dr. M. Pinto (Simon Fraser University) for his kind gift of bis(4-chlorophenyl)diselenide.

6.2.1 Reagents Prepared by Literature Procedures

The following reagents were prepared by literature procedures: 1-methoxy-1-buten-3-yne (~4:1 E/Z),[55] 1-ethynylcyclohexene,[55] lithium tri-*tert*-butoxyaluminohydride,[111] lithium tri-*tert*-butoxyaluminodeuteride,[111] chlorobis(η^5-cyclopentadienyl)hydridozirconium(IV) [$Cp_2ZrCl(H)$],[7] chlorobis(η^5-cyclopentadienyl)deuteriozirconium(IV) [$Cp_2ZrCl(D)$][7] *N*-(phenylseleno)phthalimide (*N*-PSP),[112] *N*-(phenylthio)phthalimide (*N*-PTP),[112] 2-chloromagnesium-1,3-butadiene,[40] bis(1,5-cyclooctadiene)nickel(0) [$Ni(COD)_2$],[113] and (benzenemethaniminato)chlorobis(η^5-cyclopentadienyl)zirconium(IV).[17]

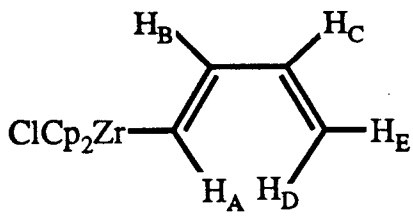
6.3 Insertion Reactions of 1-Ene-3-ynes, Nitriles and α,β-Unsaturated Nitriles. Reaction of 1,3-Dienylzirconium complexes with Carbon Monoxide.

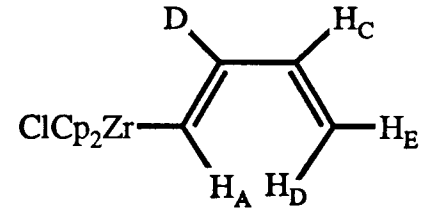
General Procedure 1: Preparation of $ZrCp_2Cl(CH{=}CH{-}CR{=}CR'R'')$, $ZrCp_2Cl(N{=}CH{-}R)$ and $ZrCp_2Cl(N{=}CH{-}CR{=}CR'R'')$

The hydride $Cp_2ZrCl(H)$ **1** was added in three portions, at room temperature in the dark, to a stirred solution in toluene of the appropriate 1-ene-3-yne or nitrile or α,β-unsaturated nitrile (1 equiv, respectively). The resulting white slurry was stirred in the dark (reaction vessel was simply covered with aluminum foil), until a homogeneous solution was obtained. The solvent was evaporated to approximately one-third of its original volume, at which point hexanes was added and the solution was allowed to crystallize at -30°C.

6.3.1 Reaction of 1-Ene-3-ynes with $Cp_2ZrCl(H)$ 1 and $Cp_2ZrCl(D)$ 2.

(*E*)-1,3-Butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV) **55a** and (*E*)-1,3-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* **55a**-d_1



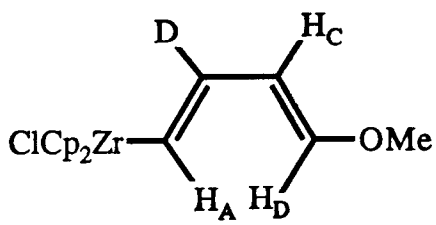


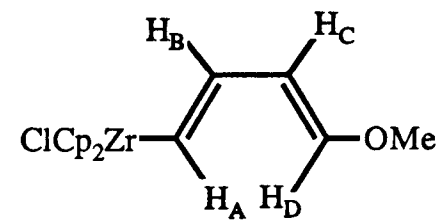
The preparation of **55a** deviated slightly from general procedure 1 due to the low boiling point of 1-buten-3-yne (2°C). To a stirred slurry of $Cp_2ZrCl(H)$ **1** (3.00 g, 11.63 mmol) in 60 mL of toluene, contained in a large reactor bomb, was vacuum transferred 1-buten-3-yne (1.82 g, 34.90 mmol). The mixture was stirred in the dark at room temperature until a red homogeneous solution resulted. Workup as described in general procedure 1 gave **55a** as yellow-orange crystals (2.92 g, 81%); IR (KBr): 3095, 2890, 1600, 1532, 1441, 1020, 1000, 908 and 629 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR) 4.99 (1H, ddd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz, J_{EB} = 0.75 Hz), 5.12 (1H, ddd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz, J_{DB} = 0.75 Hz), 5.80 (10H, s, Cp), 6.27 (1H, dddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz, J_{CA} = 0.75 Hz), 6.59 (1H, dddd, H_B, J_{BA} = 19 Hz, J_{BC} = 10 Hz, J_{BD} = J_{BE} = 0.75 Hz), 7.12 (1H, dd, H_A, J_{AB} = 19 Hz, J_{AC} = 0.75 Hz). *Anal.* calcd. for $C_{14}H_{15}ClZr$: C 54.24, H 4.84, Cl 11.46; found: C 53.85, H 4.72, Cl 11.65.

Reaction of $Cp_2ZrCl(D)$ **2** (1.00 g, 3.86 mmol) and 1-buten-3-yne (0.60 g, 11.59 mmol) afforded yellow crystals of **55a**-d_1 (0.99 g, 82%); δ (C_6D_6, 400 MHz, ^1H NMR): 5.02 (1H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.14 (1H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 5.78 (10H, s, Cp), 6.28 (1H, b dd, H_C, J_{CD} = 17 Hz, J_{CE} = 10 Hz), 7.11 (1H, b t, H_A, J_{Ad} = 2.5 Hz).

(*E*,*E*)-Chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) **55b** and

(*E*,*E*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) -2-*d* **55b**-d_1



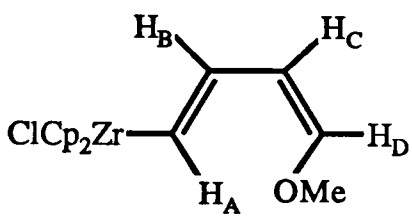


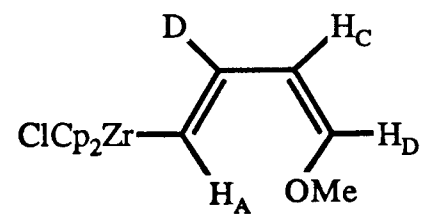
To a stirred solution of 1-methoxy-1-buten-3-yne (~4:1 E/Z) (1.19 g, 13.96 mmol) in 60 mL of toluene was added $Cp_2ZrCl(H)$ **1** (3.00 g, 11.63 mmol), in three portions. Upon formation of an orange-red homogeneous solution workup of the reaction mixture, as described in general procedure 1, was performed to yield yellow crystals of **55b** (3.36 g, 85%); IR (Nujol): 3104, 3048, 1617, 1543, 1294, 1214, 1144, 1018, 984, 913 and 802 cm^{-1};δ (C_6D_6, 400 MHz, ^1H NMR): 3.19 (3H, s, OMe), 5.47 (1H, ddd, H_C, J_{CD} = 13 Hz, J_{CB} = 10 Hz, J_{CA} = 0.75 Hz), 5.86 (10H, s, Cp), 6.51 (1H, ddd, H_B, J_{BA} = 18 Hz, J_{BC} = 10 Hz, J_{BD} = 0.75 Hz), 6.58 (1H, dd, H_D, J_{DC} = 13 Hz, J_{DB} = 0.75 Hz), 7.17 (1H, dd, H_A, J_{AB} = 18 Hz, J_{AC} = 0.75 Hz). *Anal.* calcd. for $C_{15}H_{17}ClOZr$: C 52.98, H 5.00, Cl 10.45; found: C 52.81, H 5.07, Cl 10.66.

Reaction of $Cp_2ZrCl(D)$ **2** (1.00 g, 3.86 mmol) and 1-methoxy-1-buten-3-yne (~4:1 E/Z) (0.40 g, 4.83 mmol) afforded yellow crystals of **55b**-d_1 (1.14 g, 87%); δ (C_6D_6, 400 MHz, ^1H NMR): 3.19 (3H, s, OMe), 5.47 (1H, b d, H_C, J_{CD} = 12.5 Hz), 5.86 (10H, s, Cp), 6.58 (1H, d, H_D, J_{DC} = 12.5 Hz), 7.15 (1H, b s, H_A).

(*E,Z*)-Chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) **55c** and

(*E,Z*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) -2-*d* **55c**-d_1





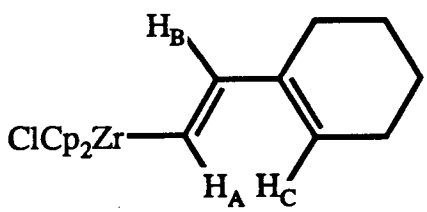
To a stirred solution of (*Z*)-1-methoxy-1-buten-3-yne (0.95 g, 11.63 mmol) in 60 mL of toluene was added $Cp_2ZrCl(H)$ **1** (3.00 g, 11.63 mmol) in three portions. The resulting orange-red homogeneous solution was worked up as described in general procedure 1, to yield

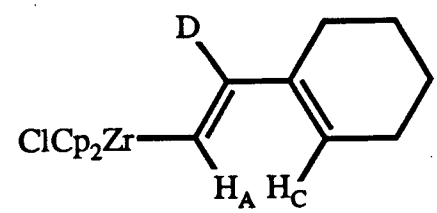
yellow crystals of **55c** (3.28 g, 83%); IR (Nujol): 3097, 1617, 1517, 1260, 1113, 1070, 990 and 805 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 3.15 (3H, s, OMe), 5.04 (1H, ddd, H_C, J_{CB} = 8.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 5.60 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DA} = J_{DB} = 0.75 Hz), 5.83 (10H, s, Cp), 7.20 (1H, ddd, H_B, J_{BA} = 18 Hz, J_{BC} = 8.5 Hz, J_{BD} = 0.75 Hz), 7.27 (1H, ddd, H_A, J_{AB} = 18 Hz, J_{AC} = J_{AD} = 0.75 Hz). *Anal.* calcd. for $C_{15}H_{17}ClOZr$: C 52.98, H 5.00, Cl 10.45; found: C 52.69, H 4.83, Cl 10.52.

Reaction of $Cp_2ZrCl(D)$ **2** (1.00 g, 3.86 mmol) and (*Z*)-1-methoxy-1-buten-3-yne (0.32 g, 3.86 mmol) afforded yellow crystals of **55c**-d_1 (1.08 g, 82%); δ (C_6D_6, 400 MHz, ^1H NMR): 3.15 (3H, s, OMe), 5.07 (1H, b d, H_C, J_{CD} = 6 Hz), 5.60 (1H, dd, H_D, J_{DC} = 6 Hz, J_{DA} = 0.5 Hz), 5.83 (10H, s, Cp), 7.25 (1H, b t, H_A, J_{Ad} = 2.75 Hz).

(*E*)-Chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η5-cyclopentadienyl)zirconium(IV) **55d** and

(*E*)-chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η5-cyclopentadienyl)zirconium(IV)-2-*d* **55d**-d_1





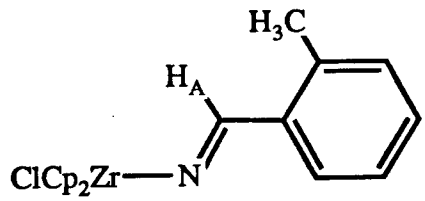
To a stirred solution of 1-ethynylcyclohexene (1.23 g, 11.63 mmol) in 60 mL of toluene was added $Cp_2ZrCl(H)$ **1** (3.00 g, 11.63 mmol) in three portions. Workup of the resulting red solution, as described in general procedure 1, afforded pale yellow crystals of **55d** (3.81 g, 90%); IR (KBr): 3102, 2926, 2853, 1621, 1522, 1439, 1316, 1018, 988 and 804 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.54 (2H, m), 1.61 (2H, m), 2.08 (2H, m), 2.15 (2H, m), 5.74 (1H, m, H_C), 5.87 (10H, s, Cp), 6.66 (1H, d, H_B, J_{BA} = 18.5 Hz), 7.14 (1H,

dd, H_A, J_{AB} = 18.5 Hz, J_{AC} = 0.75 Hz). *Anal.* calcd. for $C_{20}H_{21}ClZr$: C 59.37, H 5.77, Cl 9.76; found: C 59.17, H 5.67, Cl 10.00.

Reaction of $Cp_2ZrCl(D)$ **2** (1.00 g, 3.86 mmol) and 1-ethynylcyclohexene (0.39 g, 3.86 mmol) afforded pale yellow crystals of **55d**-d_1 (1.25 g, 89%); δ (C_6D_6, 400 MHz, ^1H NMR): 1.54 (2H, m), 1.61 (2H, m), 2.08 (2H, m), 2.15 (2H, m), 5.74 (1H, m, H_C), 5.87 (10H, s, Cp), 7.13 (1H, b t, H_A, J_{Ad} = 2.5 Hz).

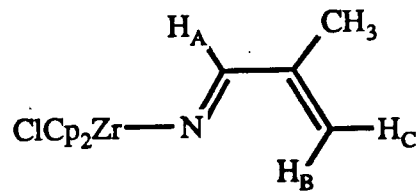
6.3.2 Reaction of Nitriles and α,β–Unsaturated Nitriles with $Cp_2ZrCl(H)$ 1.

Chlorobis(η^5-cyclopentadienyl)(2-methylbenzenemethaniminato)zirconium(IV) **63**



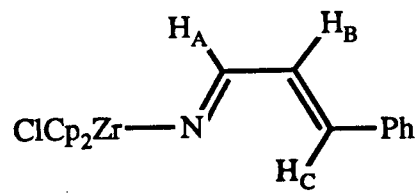
To a stirred solution of *o*-tolunitrile (0.45 g, 3.88 mmol) in 50 mL of toluene was added $Cp_2ZrCl(H)$ **1** (1.00 g, 3.88 mmol) in three portions. Workup of the resulting orange-red homogeneous solution, as described in general procedure 1, afforded bright yellow microcrystals of **63** (1.15 g, 79%); IR (Nujol): 1650, 1595, 1204, 1027, 826, 803, 756 and 660 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 2.37 (3H, s, $C\underline{H}_3$), 5.92 (10H, s, Cp), 6.97 (1H, b d, H_E J = 7.5 Hz), 7.11 (1H, td, H_D, J = 7.5 Hz, J_{BD} = 1.50 Hz), 7.21 (1H, b t, H_C, J = 7.5 Hz), 7.81 (1H, b d, H_B, J = 7.5 Hz), 9.38 (1H, s, H_A). *Anal.* calcd. for $C_{18}H_{18}ClNZr$: C 57.65, H 4.84, N 3.73; found: C 57.36, H 4.85, N 3.62.

Chlorobis(η^5-cyclopentadienyl)[2-(2-propen-1-yl)methaniminato]zirconium(IV) **68**



To a stirred solution of methacrylonitrile (0.26 g, 3.88 mmol) in 50 mL of toluene was added $Cp_2ZrCl(H)$ **1** (1.00 g, 3.88 mmol) in three portions. Workup of the resulting red homogeneous solution, as described in general procedure 1, afforded yellow microcrystals of **68** (1.07 g, 85%); IR (Nujol): 3104, 2802, 1656, 1016, 928, 803 and 677 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.77 (3H, s, CH_3), 5.11 (1H, m, H_B), 5.33 (1H, m, H_C), 5.79 (10H, s, Cp), 8.60 (1H, s, H_A). *Anal.* calcd. for $C_{14}H_{16}ClNZr$: C 51.74, H 4.98, N 4.31; found: C 51.96, H 4.77, N 4.08.

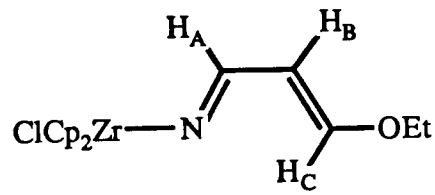
(*E*)-Chlorobis(η^5-cyclopentadienyl)[2-(2-phenylethenyl)methaniminato]zirconium(IV) **69**



To a stirred solution of cinnamonitrile (0.50 g, 3.88 mmol) in 50 mL of toluene was added $Cp_2ZrCl(H)$ **1** (1.00 g, 3.88 mmol) in three portions. Workup of the resulting red homogeneous solution, as described in general procedure 1, afforded orange crystals of **69** (1.17 g, 78%); IR (Nujol): 1641, 1611, 1015, 987, 975, 800, 742, 688 and 646 cm^{-1};

δ (C_6D_6, 400 MHz, ^1H NMR): 5.88 (10H, s, Cp), 6.39 (1H, dd, H_B, J_{BC} = 16 Hz, J_{BA} = 8 Hz), 6.63 (1H, d, H_C, J_{CB} = 16 Hz), 7.02-7.10 (3H, m), 7.20 (2H, m), 8.75 (1H, d, H_A, J_{AB} = 8 Hz). *Anal.* calcd. for $C_{19}H_{18}ClNZr$: C 58.96, H 4.69, N 3.62; found: C 58.97, H 4.77, N 3.45.

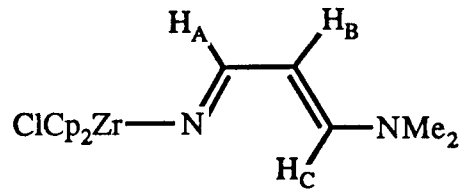
(*E*)-Chlorobis(η^5-cyclopentadienyl)[2-(2-ethoxyethenyl)methaniminato]zirconium(IV) **70**



To a stirred solution of (*E*)-3-ethoxyacrylonitrile (0.38 g, 3.88 mmol) in 50 mL of toluene was added $Cp_2ZrCl(H)$ **1** (1.00 g, 3.88 mmol) in three portions. Workup of the resulting deep-red homogeneous solution, as described in general procedure 1, afforded orange-brown crystals of **70** (1.12 g, 81%); IR (Nujol): 3097, 1649, 1613, 1318, 1201, 1021, 801, 728 and 662 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.88 (3H, t, $C\underline{H}_3$, J = 8 Hz), 3.24 (2H, q, $C\underline{H}_2$, J = 8 Hz), 5.25 (1H, dd, H_B, J_{BC} = 13 Hz, J_{BA} = 8.5 Hz), 5.91 (10H, s, Cp), , 6.55 (1H, d, H_C, J_{CB} = 13 Hz), 8.45 (1H, d, H_A, J_{AB} = 8.5 Hz). *Anal.* calcd. for $C_{15}H_{18}ClNOZr$: C 50.75, H 5.11, N 3.95; found: C 51.00, H 5.09, N 4.03.

(*E*)-Chlorobis(η^5-cyclopentadienyl)[2-(2-dimethylaminoethenyl)methaniminato]zirconium(IV)

71



To a stirred solution of (*E*)-3-dimethylaminoacrylonitrile (0.37 g, 3.88 mmol) in 70 mL of toluene was added $Cp_2ZrCl(H)$ **1** (1.00 g, 3.88 mmol) in three portions. Workup of the resulting deep-red homogeneous solution, as described in general procedure 1, afforded orange crystals of **71** (1.06 g, 77%); IR (Nujol): 3104, 2795, 1635, 1590, 1438, 1286, 1108, 970, 798 and 645 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 2.90 (6H, s, NMe_2), 4.55 (1H, dd, H_B, J_{BC} = 13 Hz, J_{BA} = 9 Hz), 6.11 (10H, s, Cp), 6.60 (1H, d, H_C, J_{CB} = 13 Hz), 8.38 (1H, d, H_A, J_{AB} = 9 Hz). *Anal.* calcd. for $C_{15}H_{19}ClN_2Zr$: C 50.89, H 5.41, N 7.91; found: C 50.95, H 5.38, N 7.91.

6.3.3 Carbonylation Reactions of 1,3-Dienylzirconium Complexes.

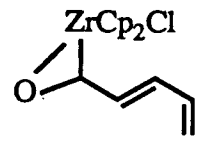
General Procedure 2: Preparation of $ClCp_2Zr(CO–CH=CH–CR=CR'R")$ and $ClCp_2Zr(CO–CH=CH–CR=CR'R")$-1-$^{13}C$

Carbonylation reactions were carried out in reactor bombs with 250 mg of the appropriate (*E*)-1-chlorobis(η^5-cyclopentadienylzirconium(IV) 1,3-dienes **55a-d** dissolved in 2 mL of toluene. After several *freeze-pump-thaw* cycles, to remove nitrogen from the bomb and the solution, the reactor bomb was left under vacuum (~10^{-2} Torr). The stirred solution

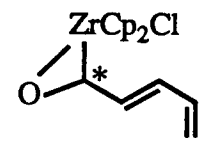
was then placed under 1 atmosphere of carbon monoxide (CO or ^{13}CO) at room temperature. On addition of CO, there was an immediate color change (yellow to orange/red), followed by precipitation of the product from solution. The slurry was diluted with hexanes and the product collected by filtration. Analytical samples were obtained by recrystallization from dichloromethane/hexanes at low temperature (-30°C). The position of dienyl protons H_A, H_B, H_C, etc., for complexes **70a-d**, **70a-d-^{13}C** are as shown for the corresponding complexes **55a-d**.

(*E*)-1-η^2-Acyl-2,4-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV) **70a** and

(*E*)-1-η^2-acyl-2,4-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV)-1-^{13}C **70a-^{13}C**



70a

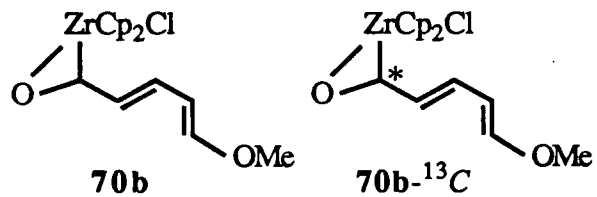


70a-^{13}C

Carbonylation of **55a** (250 mg, 0.81 mmol) was carried out according to general procedure 2. On addition of CO, the orange solution darkened to orange-red. After ~3 min stirring at room temperature, an orange-red slurry resulted. Recrystallization gave orange crystals of **70a** (246 mg, 73%); IR (KBr): 3106, 3081, 2926, 2853, 1627, 1582, 1512, 1499 (η^2-acyl), 1194, 1015 and 809 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 5.87 (1H, d, H_E, J_{EC} = 10 Hz), 5.94 (10H, s, Cp), 6.02 (1H, d, H_D, J_{CD} = 17 Hz), 6.83 (1H, ddd, H_C, J_{CD} = 17 Hz, J_{CE} = 10 Hz, J_{CB} = 10.5 Hz), 6.85 (1H, d, H_A, J_{AB} = 15.5 Hz), 7.63 (1H, dd, H_B, J_{BA} = 15.5 Hz, J_{BC} = 10.5 Hz). *Anal.* calcd. for $C_{15}H_{15}ClOZr$: C 53.31, H 4.47; found: C 53.50, H 4.55.

In the case where, **55a** (150 mg, 0.48 mmol) was carbonylated with ^{13}CO; recrystallization yielded orange crystals of **70a**-^{13}C (109 mg, 66%); IR (Nujol): 3090, 1623, 1439 (η^2-acyl), 1182, 1014 and 804 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 5.87 (1H, d, H_E, J_{EC} = 10 Hz), 5.94 (10H, s, Cp), 6.02 (1H, d, H_D, J_{CD} = 17 Hz), 6.83 (1H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = 10.5 Hz, J_{CE} = 10 Hz), 6.85 (1H, b d, H_A, J_{AB} = 15.5 Hz), 7.61 (1H, ddd, H_B, J_{BA} = 15.5 Hz, J_{BC} = 10.5 Hz, J_{B13C} = 8 Hz); δ ($CDCl_3$, 75.4 MHz, $^{13}C\{^1H\}$ NMR): 109.40 (s, Cp), 129.71 (d, C2, J_{C2C1} = 34.5 Hz), 129.84 (s, C5), 135.2 (d, C4, J_{C4C1} = 8.8 Hz), 159.14 (d, C3, J_{C3C1} = 9.8 Hz), 301.44 (s, C1).

(*E*,*E*)-1-η^2-Acyl-chlorobis(η^5-cyclopentadienyl)(4-methoxy-2,4-butadienyl)zirconium(IV) **70b** and (*E*,*E*)-1-η^2-acyl-chlorobis(η^5-cyclopentadienyl)(4-methoxy-2,4-butadienyl)zirconium(IV)-1-^{13}C **70b**-^{13}C

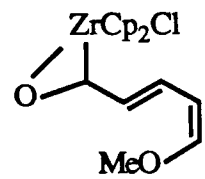


70b **70b**-^{13}C

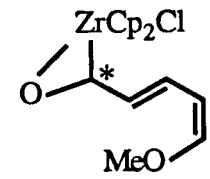
Carbonylation of **55b** (250 mg, 0.74 mmol) was carried out according to general procedure 2. On addition of CO, the yellow solution darkened to yellow-orange. After ~3 min stirring at room temperature, a yellow-orange slurry resulted. Recrystallization gave yellow crystals of **70b** (225 mg, 83%); IR (KBr): 3077, 2933, 1617, 1589, 1468 (η^2-acyl), 1200, 1009, 807 and 654 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.86 (3H, s, OMe), 5.92 (10H, s, Cp), 6.03 (1H, dd, H_C, J_{CD} = J_{CB} = 12 Hz), 6.82 (1H, d, H_A, J_{AB} = 15 Hz), 7.34 (1H, d, H_D, J_{DC} = 12 Hz), 7.64 (1H, dd, H_B, J_{BA} = 15 Hz, J_{BC} = 12 Hz). *Anal.* calcd. for $C_{16}H_{17}ClOZr$: C 52.22, H 4.66; found: C 52.32, H 4.80.

In the case where, **55b** (150 mg, 0.44 mmol) was carbonylated with ^{13}CO; recrystallization yielded yellow crystals of **70b**-^{13}C (117 mg, 72%); IR (Nujol): 3076, 1617, 1590, 1426 (η^2-acyl), 1184, 1010, 808 and 654 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.86 (3H, s, OMe), 5.90 (10H, s, Cp), 6.03 (1H, dd, H_C, $J_{CD} = J_{CB}$ = 12 Hz), 6.81 (1H, dd, H_A, J_{AB} = 15 Hz, J_{A13C} = 2.5 Hz), 7.34 (1H, d, H_D, J_{DC} = 12 Hz), 7.67 (1H, ddd, H_B, J_{BA} = 15 Hz, J_{BC} = 12 Hz, J_{B13C} = 7 Hz); δ ($CDCl_3$, 75.4 MHz, $^{13}C\{^1H\}$ NMR): 58.14 (s, OCH_3), 106.32 (d, C4, J_{C4C1} = 9.6 Hz), 109.19 (s, Cp), 125.02 (d, C2, J_{C2C1} = 36.7 Hz), 159.28 (d, C3, J_{C3C1} = 11.2 Hz), 162.59 (s, C5), 293.22 (s, C1).

(*E*,*Z*)-1-η^2-Acyl-chlorobis(η^5-cyclopentadienyl)(4-methoxy-2,4-butadienyl)zirconium(IV) **70c** and (*E*,*Z*)-1-η^2-acyl-chlorobis(η^5-cyclopentadienyl)(4-methoxy-2,4-butadienyl)zirconium(IV)-1-^{13}C **70c**-d_1



70c



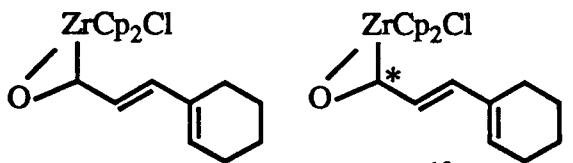
70c-^{13}C

Carbonylation of **55c** (250 mg, 0.74 mmol) was carried out according to general procedure 2. On addition of CO, the yellow solution darkened to deep red. In this case, precipitation of the product occurred only after cooling the solution to -30°C. Recrystallization gave orange-red crystals of **70c** (183 mg, 68%); IR (Nujol): 3111, 1614, 1587, 1492 (η^2-acyl), 1275, 1191, 1085, 800 and 724 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.96 (3H, s, OMe), 5.59 (1H, dd, H_C, J_{CB} = 11.5 Hz, J_{CD} = 6 Hz), 5.93 (10H, s, Cp), 6.57 (1H, d,

H_D, J_{DC} = 6 Hz), 6.75 (1H, d, H_A, J_{AB} = 15 Hz), 8.04 (1H, dd, H_B, J_{BA} = 15 Hz, J_{BC} = 11.5 Hz). *Anal.* calcd. $C_{16}H_{17}ClOZr$: C 52.22, H 4.66; found: C 52.35, H 4.74.

In the case where, **55c** (150 mg, 0.44 mmol) was carbonylated with ^{13}CO; recrystallization yielded orange-red crystals of **70c**-^{13}C (98 mg, 61%); IR (Nujol): 3097, 1620, 1587, 1447 (η^2-acyl), 1275, 1185, 1081, 800 and 723 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.96 (3H, s, OMe), 5.59 (1H, dd, H_C, J_{CB} = 11.5 Hz, J_{CD} = 6 Hz), 5.93 (10H, s, Cp), 6.57 (1H, dd, H_D, J_{DC} = 6 Hz, J_{DB} = 0.75 Hz), 6.75 (1H, dd, H_A, J_{AB} = 15 Hz, J_{A13C} = 2.5 Hz), 8.04 (1H, dddd, H_B, J_{BA} = 15 Hz, J_{BC} = 11.5 Hz, J_{B13C} = 7.5 Hz, J_{BD} = 0.75 Hz); δ ($CDCl_3$, 75.4 MHz, $^{13}C\{^1H\}$ NMR): 61.87 (s, OCH_3), 105.89 (d, C4, J_{C4C1} = 8.7 Hz), 109.19 (s, Cp), 125.57 (d, C2, J_{C2C1} = 35.8 Hz), 153.65 (d, C3, J_{C3C1} = 10.6 Hz), 157.68 (s, C5), 296.25 (s, C1).

(*E*)-1-η^2-Acylchloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) **70d**, (*E*)-1-η^2-acylchloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV)-1-^{13}C **70d**-^{13}C and (*E*)-1-η^2-acylchloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* **70d**-d_1



70d **70d**-^{13}C

Carbonylation of **55d** (250 mg, 0.69 mmol) was carried out according to general procedure 2. On addition of CO, the yellow solution darkened to orange. After ~3 min stirring at room temperature an orange slurry resulted. Recrystallization gave yellow-orange crystals of

70d (221 mg, 82%); IR (Nujol): 1620, 1588, 1498 (η^2-acyl), 1190, 985, 829, 800 and 726 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.73 (2H, m), 1.80 (2H, m), 2.33 (2H, m), 2.39 (2H, m), 5.93 (10H, s, Cp), 6.64 (1H, m, H_C), 6.78 (1H, dd, H_A, J_{AB} = 15.5 Hz, J_{AC} = 0.75 Hz), 7.64 (1H, d, H_B, J_{BA} = 15.5 Hz). *Anal.* calcd.for $C_{21}H_{21}ClOZr$: C 57.99, H 5.76; found: C 57.93, H 5.70.

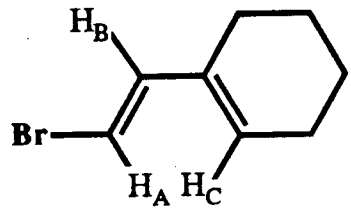
In the case where, **55d** (150 mg, 0.41 mmol) was carbonylated with ^{13}CO; recrystallization yielded orange crystals of **70d**-^{13}C (129 mg, 80%); IR (Nujol): 1620, 1588, 1444 (η^2-acyl), 1167, 984, 828, 799 and 725 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.73 (2H, m), 1.80 (2H, m), 2.33 (2H, m), 2.39 (2H, m), 5.93 (10H, s, Cp), 6.64 (1H, m, H_C), 6.78 (1H, dd, H_A, J_{AB} = 15.5 Hz, J_{A13C} = 2 Hz), 7.64 (1H, dd, H_B, J_{BA} = 15.5 Hz, J_{B13C} = 7.5 Hz); δ ($CDCl_3$, 75.4 MHz, $^{13}C\{^1H\}$ NMR): 21.94 (s), 21.98 (s), 24.41 (s), 27.30 (s), 109.26 (s, Cp), 123.15 (d, C2, J_{C2C1} = 35.4 Hz), 136.64 (d, C4, J_{C4C1} = 9.5 Hz), 144.85 (s, C5), 164.14 (d, C3, J_{C3C1} = 10.4 Hz), 297.91 (s, C1).

Carbonylation of **55d**-d_1 (75 mg, 0.21 mmol) was carried out according to general procedure 2. On addition of CO, the yellow solution darkened to orange. After ~3 min stirring at room temperature an orange slurry formed, from which was obtained, after filtration, an orange powder **70d**-d_1 (68 mg, 84%); δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.73 (2H, m), 1.80 (2H, m), 2.33 (2H, m), 2.39 (2H, m), 5.93 (10H, s, Cp), 6.64 (1H, m, H_C), 6.80 (1H, b s, H_A).

6.4 Preparation of Heterosubstituted 1,3-Dienes, Imines and 1-Azadienes.

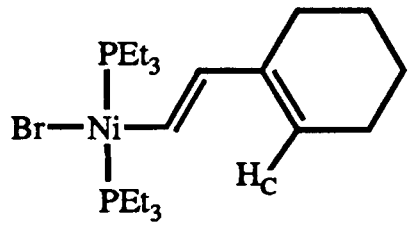
6.4.1 Preparation of a 1,3-Dienylnickel Complex.

(*E*)-1-Bromo[2-(1-cyclohexen-1-yl)ethene] **72**



To a stirred solution of **55d** (500 mg, 1.37 mmol) in 3 mL of THF was added *N*-bromosuccinimide (271 mg, 1.52 mmol). The white slurry was stirred at room temperature for 3 h. The mixture was diluted with 10 mL of hexanes and filtered through basic alumina to remove $Cp_2ZrCl(Br)$. After careful evaporation of the solvent, a colorless liquid resulted **72** (225 mg, 89%); IR (film): 3083, 1678, 1586, 1434, 1202, 942, 760 and 745 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.59 (2H, m), 1.67 (2H, m), 2.08 (4H, m), 5.76 (1H, m, H_C), 6.12 (1H, dd, H_A, J_{AB} = 14 Hz, J_{AC} = 0.5 Hz), 6.68 (1H, d, J_{BA} = 14 Hz). *Anal.* calcd. for $C_8H_{11}Br$: C 51.36, H 5.93, Br 42.71; found: C 51.27, H 6.07, Br 42.50.

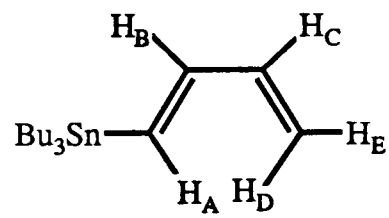
(*E*)-Bromo[2-(1-cyclohexen-1-yl)ethenyl]bis(triethylphosphine)nickel(II) **73**



A solution of $Ni(PEt_3)_2(COD)$ was prepared by stirring $Ni(COD)_2$ (300 mg, 1.09 mmol) and PEt_3 (256 mg, 2.18 mmol) in 2 mL of hexane. The yellow-brown solution was then slowly added to (*E*)-1-bromo[2-(1-cyclohexen-1-yl)ethene] **72** (206 mg, 1.11 mmol) in 3 mL of hexane at room temperature. After the addition was complete, the orange-brown solution was cooled to -30°C to allow for crystallization. This yielded orange crystals of **73** (403 mg, 77%); IR (Nujol): 1627, 1542, 1410, 1258, 1038, 1000, 959, 761, 723 and 629 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.07 (18H, m, $PCH_2C\underline{H}_3$), 1.58 (12H, m, $PC\underline{H}_2CH_3$), 1.60 (2H, m), 1.65 (2H, m), 2.09 (2H, m), 2.19 (2H, m), 5.47 (1H, m), 6.13 (1H, m), 6.20 (1H, m); δ (C_6D_6, 121.5 MHz, $^{31}P\{^1H\}$ NMR): 10.4 (s). *Anal.* calcd.for $C_{20}H_{41}BrP_2Ni$: C 49.82, H 8.57, Br 16.57; found: C 50.03, H 8.66, Br 16.30.

6.4.2 Preparation of 1,3-Dienylstannanes.

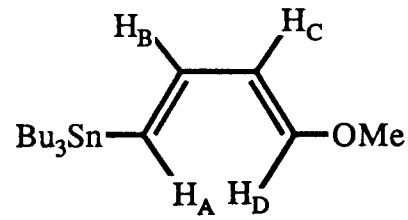
(*E*)-1,3-Butadienyl-1-tributylstannane **77a**



Tributyltin chloride (368 mg, 1.13 mmol) was added to a stirred solution of **55a** (350 mg, 1.13 mmol) dissolved in 1.5 mL of toluene. Upon addition, the solution changed from orange to yellow. The mixture was then stirred at room temperature in the dark for 2-3 days. After this time, a pale yellow slurry was observed. The reaction mixture was diluted with hexanes and filtered through basic alumina. Evaporation of the solvent yielded a pale

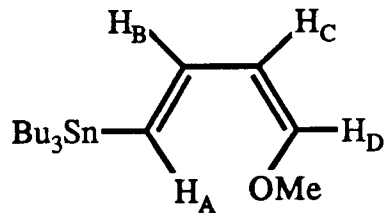
yellow oil **77a** (264 mg, 68%); IR (film): 2958, 2934, 2856, 1635, 1565, 1460, 1375, 1071, 984, 748 and 667 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.92 (9H, t, J = 7.5 Hz), 0.96 (6H, t, J = 7.5 Hz), 1.35 (6H, dt, J = 7.5 Hz), 1.56 (6H, m), 4.98 (1H, ddd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz, J_{EB} = 0.75 Hz), 5.11 (1H, ddd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz, J_{DB} = 0.75 Hz), 6.34 (1H, dd, H_A, J_{AB} = 18.5 Hz, J_{AC} = 1 Hz), 6.36 (1H, dddd, H_C, J_{CD} = 17 Hz, J_{CE} = 10 Hz, J_{CB} = 10 Hz, J_{CA} = 1 Hz), 6.63 (1H, dddd, H_B, J_{BA} = 18.5 Hz, J_{BC} = 10 Hz, J_{BD} = J_{BE} = 0.75 Hz, J_{BSn} = 60 Hz). *Anal.* calcd. for $C_{16}H_{32}Sn$: C 56.01, H 9.40; found: C, 55.76, H 9.40.

(*E*,*E*)-(4-Methoxy-1,3-butadienyl)-1-tributylstannane **77b**



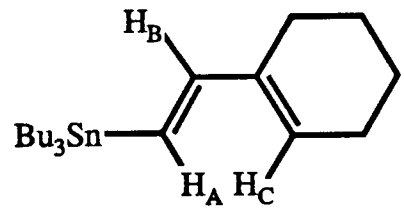
The preparation of **77b** was identical to that described above for **77a**. In this case, tributyltin chloride (335 mg, 1.03 mmol) and **55b** (350 mg, 1.03 mmol) were reacted to give, after distillation under vacuum (10^{-2} Torr), **77b** (288 mg, 75%) as a colorless oil; IR (film): 2958, 2928, 2872, 2852, 1631, 1462, 1217, 1143, 958 and 664 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.94 (9H, t, J = 7.5 Hz), 0.99 (6H, t, J = 7.5 Hz), 1.39 (6H, dt, J = 7.5 Hz), 1.65 (6H, m), 3.10 (3H, s, OMe), 5.63 (1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10 Hz), 6.09 (1H, d, H_A, J_{AB} = 18.5 Hz, J_{ASn} = 73 Hz), 6.51 (1H, d, H_D, J_{DC} = 12.5 Hz), 6.57 (1H, dd, H_B, J_{BA} = 18.5 Hz, J_{BC} = 10 Hz, J_{BSn} = 62 Hz). *Anal.* calcd. for $C_{17}H_{34}OSn$: C 54.72, H 9.18; found: C, 54.54, H 9.15.

(*E*,*Z*)-(4-Methoxy-1,3-butadienyl)-1-tributylstannane **77c**



The preparation of **77c** was identical to that described above for **77a**. In this case, tributyltin chloride (335 mg, 1.03 mmol) and **55c** (350 mg, 1.03 mmol) were reacted to give, after distillation under vacuum (10^{-2} Torr), **77c** (274 mg, 71%) as a colorless oil; IR (film): 2956, 2921, 2851, 1639, 1462, 1263, 1123, 994, 806 and 664 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.89 (9H, t, J = 7.5 Hz), 0.95 (6H, t, J = 7.5 Hz), 1.35 (6H, dt, J = 7.5 Hz), 1.59 (6H, m), 3.06 (3H, s, OMe), 5.22 (1H, ddd, H_C, J_{CB} = 10.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 5.50 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DA} = J_{DB} = 0.75 Hz), 6.28 (1H, ddd, H_A, J_{AB} = 18.5 Hz, J_{AC} = J_{AD} = 0.75 Hz, J_{ASn} = 75 Hz), 7.37 (1H, ddd, H_B, J_{BA} = 18.5 Hz, J_{BC} = 10.5 Hz, J_{BD} = 0.75 Hz, J_{BSn} = 62 Hz). *Anal.* calcd. for $C_{17}H_{34}OSn$: C 54.72, H 9.18; found: C, 54.45, H 9.20.

(*E*)- [2-(1-Cyclohexen-1-yl)ethenyl]-1-tributylstannane **77d**



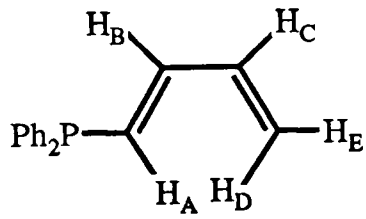
A solution of tributyltin chloride (313 mg, 0.96 mmol) and **55d** (350 mg, 0.96 mmol) in 1.5 mL of toluene were heated in a reactor bomb, in the dark, at 80°C for 16 h. The workup as described above gave, after distillation under vacuum (10^{-2} Torr), a colorless oil **77d** (313 mg, 79%); IR (film): 2967, 2925, 2872, 2854, 1620, 1558, 1464, 1377, 1010, 903 and 663 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.94 (9H, t, J = 7.5 Hz), 1.00 (6H, t, J = 7.5 Hz), 1.36 (6H, dt, J = 7.5 Hz), 1.58 (6H, m), 1.42 (2H, m), 1 51 (1H, m), 2.00 (2H, m), 2.17 (2H, m), 5.63 (1H, m, H_C), 6.24 (1H, dd, H_A, J_{AB} = 19.5 Hz, J_{AC} = 0.75 Hz, J_{ASn} = 74 Hz), 6.80 (1H, d, J_{BA} = 19.5 Hz, J_{BSn} = 67 Hz). *Anal.* calcd. for $C_{20}H_{38}Sn$: C 60.48, H 9.64; found: C, 60.44, H 9.55.

6.4.3 Preparation of 1,3-Dienylphosphines.

General Procedure 3: Preparation of Dimethyl and Diphenylphosphino 1,3-Dienes **79a-d** and **80a-d**

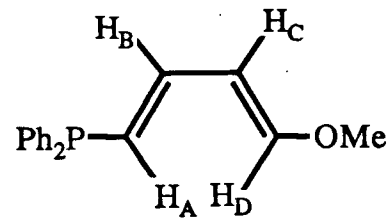
To a stirred solution of the appropriate (*E*)-1-chlorobis(η^5-cyclopentadienylzirconium(IV) 1,3-dienes **55a-d** in 1 mL of toluene at room temperature, was added a solution of Ph_2PCl or Me_2PCl (1 equiv in ~1 mL of toluene). On addition of the phosphine, there was an immediate color change from yellow (or orange in the case of **55a**) to colorless. The reaction was complete within 5 min, and the solution was then diluted with hexanes to produce a white slurry. The slurry was filtered through basic alumina and evaporated to give the product as a white solid or colorless liquid.

(*E*)-1,3-Butadienyl-1-diphenylphosphine **79a**



According to general procedure 3, **55a** (150 mg, 0.48 mmol) was reacted with Ph_2PCl (107 mg, 0.48 mmol) to give, after workup, a white solid **79a** (96 mg, 83%); IR (Nujol): 1620, 1584, 1479, 1005, 911, 741 and 697 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 4.91 (1H, d, H_E, J_{EC} = 10 Hz), 4.95 (1H, d, H_D, J_{DC} = 17 Hz), 6.27 (1H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = 10.5 Hz, J_{CE} = 10 Hz), 6.33 (1H, dd, H_A, J_{AB} = 17 Hz, J_{AP} = 10 Hz), 6.59 (1H, ddd, H_B, J_{BA} = 17 Hz, J_{BP} = 11.5 Hz, J_{BC} = 10.5 Hz), 7.06 (6H, m), 7.44 (4H, m); δ (C_6D_6, 32.4 MHz, $^{31}P\{^1H\}$ NMR): -12.4 (s). *Anal.* calcd. for $C_{16}H_{15}P$: C 80.66, H 6.35; found: C 80.39, H 6.36.

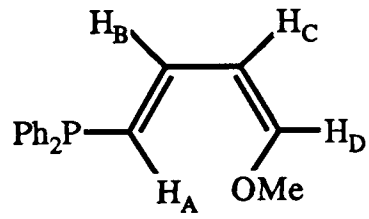
(*E*,*E*)-(4-Methoxy-1,3-butadienyl)-1-diphenylphosphine **79b**



According to general procedure 3, **55b** (150 mg, 0.44 mmol) was reacted with Ph_2PCl (97 mg, 0.44 mmol) to give, after workup, a white solid **79b** (99 mg, 85%); IR (Nujol): 1631, 1444, 1227, 1146, 981, 739 and 696 cm^{-1}; λ_{max} (hexane): 256 nm (ε 17,500), 250 nm (ε 16,700) and 260 nm (ε 16,500); δ (C_6D_6, 400 MHz, ^1H NMR): 3.03 (3H, s, OMe), 5.52

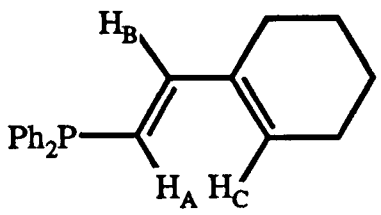
(1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 11 Hz), 6.14 (1H, dd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 3.5 Hz), 6.32 (1H, d, H_D, J_{DC} = 12.5 Hz), 6.64 (1H, ddd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 14 Hz, J_{BC} = 11 Hz), 7.11 (6H, m), 7.60 (4H, m); δ (C_6D_6, 32.4 MHz, $^{31}P\{^1H\}$ NMR): -11.7 (s). *Anal.* calcd. for $C_{17}H_{17}OP$: C 76.11, H 6.39; found: C 76.10, H 6.50.

(*E,Z*)-(4-Methoxy-1,3-butadienyl)-1-diphenylphoshine **79c**



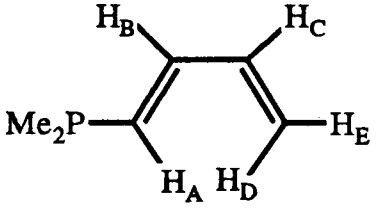
According to general procedure 3, **55c** (150 mg, 0.44 mmol) was reacted with Ph_2PCl (97 mg, 0.44 mmol) to give, after workup, a colorless oil **79c** (92 mg, 79%); IR (film): 1636, 1480, 1433, 1389, 1265, 1126, 1086, 825, 741 and 696 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.67 (3H, s, OMe), 5.23 (1H, ddd, H_C, J_{CB} = 11 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 5.98 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.75 Hz), 6.23 (1H, dddd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 4 Hz, J_{AC} = J_{AD} = 0.75 Hz), 7.07 (1H, dddd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 14.5 Hz, J_{BC} = 11 Hz, J_{BD} = 1 Hz), 7.32 (6H, m), 7.42 (4H, m); δ (C_6D_6, 162.2 MHz, $^{31}P\{^1H\}$ NMR): -11.4 (s); *m/e* (relative intensity): 107 (23.2), 108 (22.1), 109 (25.1), 115 (27.5), 133 (18.9), 159 (27.7), 183 (28.7), 237 (100), 238 (30.3) and 268 (M^+, 30.0). *Exact Mass* calcd. for $C_{17}H_{17}OP$: 268.1019; found: 268.1012.

(*E*)-[2-(1-Cyclohexen-1-yl)ethenyl]-1-diphenylphosphine **79d**



According to general procedure 3, **55d** (150 mg, 0.41 mmol) was reacted with Ph_2PCl (91 mg, 0.41 mmol) to give, after workup, a white solid **79d** (107 mg, 88%); IR (Nujol): 1631, 1578, 1432, 974, 823, 741 and 695 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.39 (4H, m), 1.92 (4H, m), 5.59 (1H, m, H_C), 6.31 (1H, dd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 5.5 Hz), 6.82 (1H, dd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 15 Hz), 7.09 (6H, m), 7.52 (4H, m); δ (C_6D_6, 162.2 MHz, $^{31}P\{^1H\}$ NMR): -11.7 (s). *Anal.* calcd. for $C_{20}H_{21}P$: C 82.17, H 7.24; found: C 82.37, H 7.30.

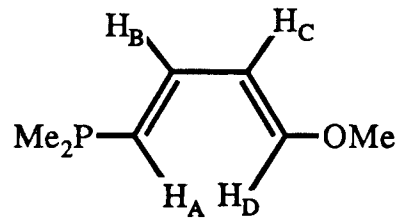
(*E*)-1,3-Butadienyl-1-dimethylphosphine **80a**



According to general procedure 3, **55a** (150 mg, 0.48 mmol) was reacted with Me_2PCl (47 mg, 0.48 mmol) to give, after workup, a colorless oil **80a** (74 mg, 81%); IR (CH_2Cl_2): 1620, 1578, 1430, 1294, 1007, 943 and 904 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.87 (6H, d, P<u>Me</u>2, J_{HP} = 3 Hz), 4.93 (1H, ddd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.5 Hz, J_{EB} = 1 Hz), 5.04 (1H, ddd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.5 Hz, J_{DB} = 1 Hz), 5.93 (1H, ddd, H_A, J_{AB} = 16.5

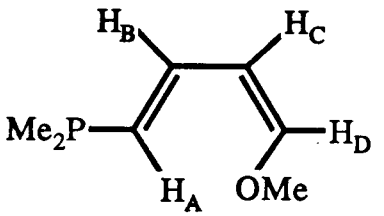
Hz, J_{AP} = 12 Hz, J_{AC} = 1 Hz), 6.27 (1H, dddd, H_C, J_{CD} = 17 Hz, J_{CB} = 10 Hz, J_{CE} = 10 Hz, J_{CA} = 1 Hz), 6.41 (1H, ddddd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 10.5 Hz, J_{BC} = 10 Hz, J_{BD} = J_{BE} = 1 Hz); δ (C_6D_6, 162.2 MHz, $^{31}P\{^1H\}$ NMR): -50.8 (s); *m/e* (relative intensity): 43 (30.3), 44 (49.5), 53 (19.1), 57 (76.5), 59 (22.4), 69 (40.9), 97 (67.8), 99 (100), 113 (79.0) and 114 (M^+,95.5). *Exact Mass* calcd. for $C_6H_{11}P$: 114.0598; found: 114.0597.

(*E*,*E*)-(4-Methoxy-1,3-butadienyl)-1-dimethylphosphine **80b**



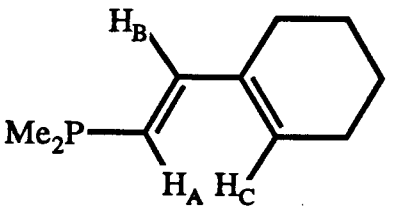
According to general procedure 3, **55b** (150 mg, 0.44 mmol) was reacted with Me_2PCl (43 mg, 0.44 mmol) to give, after workup, a colorless oil **80b** (65 mg, 77%); IR (CH_2Cl_2): 1635, 1265, 1228, 1146, 979, 940 and 907 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.97 (6H, d, PMe$_2$, J_{HP} = 3.5 Hz), 3.13 (3H, s, OMe), 5.48 (1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} =10.5 Hz), 5.72 (1H, dd, H_A, J_{AB} = 16 Hz, J_{AP} = 8 Hz), 6.37 (1H, d, H_D, J_{DC} = 12.5 Hz), 6.54 (1H, ddd, H_B, J_{BA} = 16 Hz, J_{BP} = 13 Hz, J_{BC} = 10.5 Hz); δ (C_6D_6, 121.5 MHz, $^{31}P\{^1H\}$ NMR): -50.4 (s); *m/e* (relative intensity): 97 (27.6), 99 (25.0), 113 (100), 114 (25.4), 129 (16.3) and 144 (M^+, 62.3). *Exact Mass* calcd. for $C_7H_{13}OP$: 144.0704; found: 144.0702.

(*E,Z*)-(4-Methoxy-1,3-butadienyl)-1-dimethylphosphine **80c**



According to general procedure 3, **55c** (150 mg, 0.44 mmol) was reacted with Me_2PCl (43 mg, 0.44 mmol) to give, after workup, a colorless oil **80c** (67 mg, 79%); IR (CH_2Cl_2): 1640, 1497, 1390, 1279, 1264, 1086, 977, 940 and 903 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.93 (6H, d, P<u>Me2</u>, J_{HP} = 2.5 Hz), 3.04 (3H, s, O<u>Me</u>), 5.11 (1H, ddd, H_C, J_{CB} = 10.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 5.51 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.75 Hz), 5.92 (1H, dddd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 11 Hz, J_{AC} = J_{AD} = 0.75 Hz), 7.18 (1H, dddd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 12 Hz, J_{BC} = 10.5 Hz, J_{BD} = 1 Hz); δ (C_6D_6, 162.2 MHz, $^{31}P\{^1H\}$ NMR): -50.2 (s); *m/e* (relative intensity): 41 (19.8), 57 (15.4), 97 (14.6), 113 (100) and 144 (M^+,12.4). *Exact Mass* calcd. for $C_7H_{13}OP$: 144.0704; found: 144.0705.

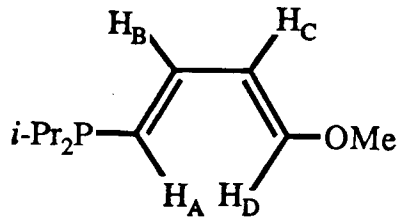
(*E*)-[2-(1-Cyclohexen-1-yl)ethenyl]-1-dimethylphosphine **80d**



According to general procedure 3, **55d** (150 mg, 0.41 mmol) was reacted with Me_2PCl (40 mg, 0.41 mmol) to give, after workup, a colorless oil **80d** (95 mg, 82%); IR (film): 1635, 1429, 971, 962, 939 and 905 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.98 (6H, d,

P<u>Me</u>$_2$, J_{HP} = 3 Hz), 1.45 (4H, m), 1.92 (4H, m), 5.65 (1H, m, H_C), 5.90 (1H, dd, H_A, J_{AB} = 17 Hz, J_{AP} = 9 Hz), 6.61 (1H, dd, H_B, J_{BA} = 17 Hz, J_{BP} = 13 Hz); δ (C_6D_6, 32.4 MHz, $^{31}P\{^1H\}$ NMR): -50.7 (s); *m/e* (relative intensity): 79 (41.7), 105 (18.4), 125 (21.7), 139 (86.4), 140 (58.0), 153 (25.2), 167 (100) and 168 (M^+, 99.0). *Exact Mass* calcd. for $C_{10}H_{17}P$: 168.1075; found: 168.1068.

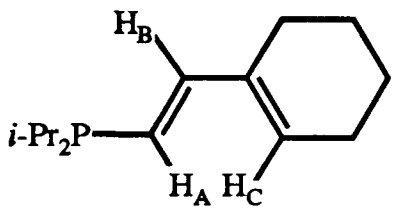
<u>(*E*,*E*)-(4-Methoxy-1,3-butadienyl)-1-diisopropylphosphine **81b**</u>



To a stirred solution of **55b** (200 mg, 0.58 mmol) in 5 mL of toluene was added *i*-Pr_2PCl (90 mg, 0.58 mmol). The solution was then transferred to a reactor bomb and heated at 80°C, in the dark, for 18 h. On cooling the mixture to room temperature, a white crystalline material deposited (Cp_2ZrCl_2) from the pale yellow (initially bright yellow) solution. The mixture was then diluted with hexanes and filtered through basic alumina to give a colorless oil **89b** (98 mg, 83%); IR (film): 1636, 1462, 1226, 1147, 982 and 802 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.08 (12H, m, PCH<u>Me</u>$_2$), 1.70 (2H, m, PC<u>H</u>Me$_2$), 3.05 (3H, s, O<u>Me</u>), 5.56 (1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10 Hz), 5.74 (1H, dd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 4.5 Hz), 6.38 (1H, d, H_D, J_{DC} = 12.5 Hz), 6.73 (1H, ddd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 13.5 Hz, J_{BC} = 10 Hz); δ (C_6D_6, 121.5 MHz, $^{31}P\{^1H\}$ NMR): 5.3 (s); *m/e* (relative intensity): 41 (45.2), 83 (28.2), 85 (75.8), 99 (19.0), 115 (59.1), 169 (100) and 200 (M^+, 38.1). *Exact Mass* calcd. for $C_{11}H_{21}OP$: 200.1330; found; 200.1323.

When the above reaction was performed in a more concentrated solution of **55b** (250 mg, 0.74 mmol) and 1 equiv *i*-Pr_2PCl dissolved in 2 mL of toluene, a 2:1 mixture of rotamers was formed. In this mixture, the major component has the ^1H and $^{31}P\{^1H\}$ NMR data described above. The ^1H and $^{31}P\{^1H\}$ NMR data for the minor component, taken from spectra of the 2:1 mixture, were as follows; δ (C_6D_6, 400 MHz, ^1H NMR): 1.11 (12H, m, PCH<u>Me</u>$_2$), 1.70 (2H, m, PC<u>H</u>Me$_2$), 3.07 (3H, s, O<u>Me</u>), 5.54 (1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10 Hz), 5.90 (1H, dd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 3 Hz), 6.34 (1H, d, H_D, J_{DC} = 12.5 Hz), 6.70 (1H, ddd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 12.5 Hz, J_{BC} = 10 Hz); δ (C_6D_6, 121.5 MHz, $^{31}P\{^1H\}$ NMR): -9.00 (s)

<u>(*E*)-[2-(1-Cyclohexen-1-yl)ethenyl]-1-diisopropylphosphine **81d**</u>



The preparation of **81d** was identical to that described above for **81b**. In this case, **55d** (300 mg, 0.82 mmol) and 1 equiv *i*-Pr_2PCl were dissolved in 5 mL of toluene and heated at 80°C for 18 h. After workup, a colorless oil **81d** (170 mg, 92%) was isolated; IR (film): 2828, 2864, 1635, 1577, 1460, 1381, 1362, 926 and 785 cm^{-1}; δ (C_7D_8, 400 MHz, ^1H NMR): 1.06 (12H, m, PCH<u>Me</u>$_2$), 1.41 (2H, m), 1.50 (2H, m), 1.70 (2H, m, PC<u>H</u>Me$_2$), 1.93 (2H, m), 2.07 (2H, m), 5.65 (1H, m, H_C), 5.82 (1H, ddd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 3.5 Hz, J_{AC} = 0.75 Hz), 6.86 (1H, dd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 14.5 Hz); δ (C_7D_8, 121.5 MHz, $^{31}P\{^1H\}$ NMR): 4.8 (s); *m/e* (relative intensity): 43 (41.4), 79 (30.8), 111 (21.1), 139

(100), 181 (75.7), 182 (67.6) and 224 (M^+, 58.8). *Exact Mass* calcd. for $C_{14}H_{25}P$: 224.1694; found; 224.1698.

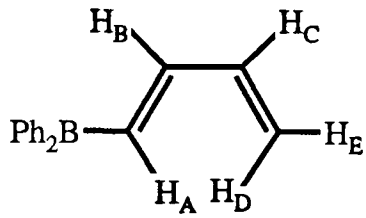
As observed for **81b**, when the reaction was performed in a more concentrated solution of **55d** (250 mg 0.69 mmol) and 1 equiv *i*-Pr_2PCl in 2 mL of toluene a 2:1 mixture of rotamers was observed by ^1H and $^{31}P\{^1H\}$ NMR. The ^1H and $^{31}P\{^1H\}$ NMR data (taken from the spectra of the 2:1 mixture) for the minor isomer were; δ (C_6D_6, 400 MHz, ^1H NMR): 1.12 (12H, m, PCH$\underline{Me_2}$), 1.40 (2H, m), 1.48 (2H, m), 1.71 (2H, m, PC$\underline{H}Me_2$), 1.91 (2H, m), 2.07 (2H, m), 5.62 (1H, m, H_C), 6.08 (1H, ddd, H_A, J_{AB} = 16.5 Hz, J_{AP} = 3.5 Hz, J_{AC} = 0.75 Hz), 6.84 (1H, dd, H_B, J_{BA} = 16.5 Hz, J_{BP} = 13 Hz); δ (C_6D_6, 121.5 MHz, $^{31}P\{^1H\}$ NMR): -9.66 (s).

6.4.4 Preparation of 1,3-Dienylboranes.

General Procedure 4: Preparation of Diphenylboron 1,3-dienes **87a-d**

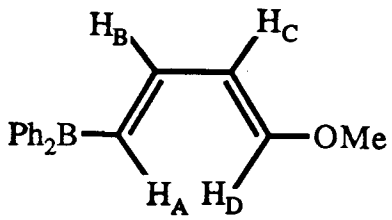
To a stirred solution, in the dark, of the appropriate (*E*)-1-chlorobis(η^5-cyclopentadienylzirconium(IV) 1,3-diene **55a-d** in 1 mL of toluene, at room temperature, was added Ph_2BBr (1 equiv). An immediate color change from yellow (or orange in the case of **55a**) to colorless was observed on addition of the neat Ph_2BBr; this was closely followed by formation of a white slurry (precipitation of $Cp_2ZrCl(Br)$). The reaction was diluted with hexanes, filtered through basic alumina, and evaporated to give the product as a white solid or colorless oil.

(*E*)-1,3-Butadienyl-1-diphenylborane **87a**



As outlined in general procedure 4, **55a** (150 mg, 0.48 mmol) was reacted with Ph_2BBr (119 mg, 0.48 mmol) at room temperature, in the dark. Workup provided, as a colorless oil, **87a** (84 mg, 82%); IR (film): 1620, 1593, 1570, 1433, 1273, 1198, 1018, 919, 750 and 695 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 5.46 (1H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.52 (1H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.70 (1H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = 10 Hz, J_{CE} = 10 Hz), 6.98 (1H, dd, H_B, J_{BA} = 17 Hz, J_{BC} = 10 Hz), 7.08 (1H, d, H_A, J_{AB} = 17 Hz), 7.47 (2H, m), 7.56 (4H, m), 7.75 (4H, m); *m/e* (relative intensity): 54 (21.8), 84 (31.2), 87 (24.7), 89 (32.3), 103 (20.1), 113 (49.3), 114 (40.1), 126 (36.1), 127 (29.9), 128 (52.6), 139 (57.0), 140 (100), 163 (21.6) and 218 (M^+, 37.3). *Exact Mass* calcd. for $C_{16}H_{15}{}^{11}B$: 218.1267; found: 218.1269.

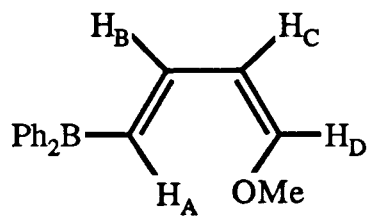
(*E*,*E*)-(4-Methoxy-1,3-butadienyl)-1-diphenylborane **87b**



As outlined in general procedure 4, **55b** (150 mg, 0.44 mmol) was reacted with Ph_2BBr (108 mg, 0.44 mmol) at room temperature, in the dark. Workup provided, as a

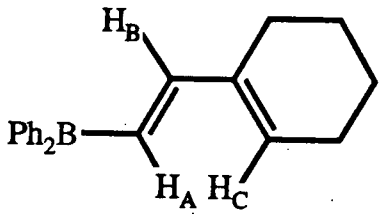
colorless oil, **87b** (92 mg, 84 %); IR (film): 1602, 1438, 1328, 1301, 1025, 970, 748 and 697 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.71 (3H, s, OMe), 5.93 (1H, dd, H_C, J_{CD} = 13 Hz, J_{CB} =10 Hz), 6.88 (1H, d, H_A, J_{AB} = 17 Hz), 6.89 (1H, d, H_D, J_{DC} = 13 Hz), 7.04 (1H, dd, H_B, J_{BA} = 17 Hz, J_{BC} = 10 Hz), 7.41-7.53 (6H, m), 7.70 (4H, m); *m/e* (relative intensity): 39 (100), 41 (83.6), 51 (42.3), 69 (75.8), 84 (93.5), 105 (27.5), 115 (47.8), 117 (36.0), 119 (51.0), 128 (48.7), 129 (70.4), 154 (32.3), 160 (41.1), 182 (24.3), 233 (12.2) and 248 (M^+, 1.6). *Exact Mass* calcd. for $C_{17}H_{17}{}^{11}BO$: 248.1373; found: 248.1379.

(*E,Z*)-(4-Methoxy-1,3-butadienyl)-1-diphenylborane **87c**



As outlined in general procedure 4, **55c** (150 mg, 0.44 mmol) was reacted with Ph_2BBr (108 mg, 0.44 mmol) at room temperature, in the dark. Workup provided, as a colorless oil, **87c** (88 mg, 80 %); IR (film): 1602, 1440, 1349, 1274, 1093, 1027, 970, 749 and 701 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 2.90 (3H, s, OMe), 5.44 (1H, ddd, H_C, J_{CB} = 11 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 5.64 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.75 Hz), 7.14 (1H, ddd, H_A, J_{AB} = 17 Hz, J_{AC} = J_{AD} = 0.75 Hz), 7.91 (1H, ddd, H_B, J_{BA} = 17 Hz, J_{BC} = 11 Hz, J_{BD} = 1 Hz), 7.30 (6H, m), 7.82 (4H, m); *m/e* (relative intensity): 39 (100), 41 (83.4), 51 (36.5), 69 (83.1), 84 (82.9), 115 (43.0), 117 (29.7), 119 (41.4), 128 (42.8), 129 (59.1), 160 (31.4), 233 (10.0) and 248 (M^+,1.0). *Exact Mass* calcd. for $C_{17}H_{17}{}^{11}BO$: 248.1373; found: 248.1382.

(*E*)-[2-(1-Cyclohexen-1-yl)ethenyl]-1-diphenylborane **87d**



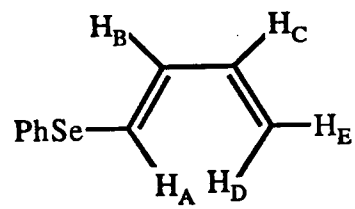
As outlined in general procedure 4, **55d** (150 mg, 0.41 mmol) was reacted with Ph_2BBr (101 mg, 0.41 mmol) at room temperature, in the dark. Workup provided, as a white solid, **87d** (99 mg, 88 %); IR (Nujol): 1621, 1593, 1573, 1458, 1376, 1234, 1007, 892, 755 and 697 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.39 (2H, m), 1.49 (2H, m), 1.87 (2H, m), 2.22 (2H, m), 5.67 (1H, m, H_C), 7.05 (1H, d, H_A, J_{AB} = 18 Hz), 7.19 (1H, d, H_B, J_{BA} = 18 Hz), 7.30 (6H, m), 7.83 (4H, m); *m/e* (relative intensity): 77 (43.0), 78 (47.9), 79 (75.9), 89 (33.3), 93 (51.3), 103 (33.8), 108 (28.6), 113 (47.7), 115 (31.4), 126 (33.2), 137 (24.9), 141 (21.8), 153 (21.9), 154 (21.6), 163 (63.0), 165 (100), 182 (63.0), 191 (32.1), 192 (27.7), 194 (43.7), 204 (23.1) and 272 (M^+, 55.3). *Exact Mass* calcd. for $C_{20}H_{21}{}^{11}B$: 272.1739; found: 272.1738.

6.4.5 Preparation of 1-(Phenylseleno)- and 1-(Phenylthio)-1,3-Dienes.

General Procedure 5: Preparation of 1-Arylseleno 1,3-Dienes

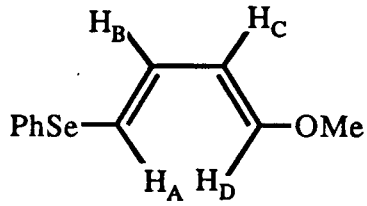
To a stirred solution of the appropriate (*E*)-1-chlorobis(η^5-cyclopentadienylzirconium(IV) 1,3-diene **55a-d** in 1 mL of toluene, in the dark at -20°C, was added 1 equiv of ArSeX. ArSeX = phenylselenenyl chloride (PhSeCl, added as a solution in 0.5 mL of toluene), diphenyldiselenide (Ph_2Se_2, added as a solution in 0.5 mL of toluene), *N*-(phenylseleno)phthalimide (*N*-PSP, added as a solid), *N*-(phenylseleno)phthalimide-d_5 (*N*-PSP-d_5) or *N*-(4-chlorophenylseleno)phthalimide (*N*-ClPSP). All reactions were complete within 5 min at -20°C. The initial yellow (or orange in the case of **55a**) color of the zirconium 1,3 diene changed to colorless or pale yellow on addition of ArSeX. Workup of the reaction involved dilution with hexanes, resulting in precipitation of the zirconium by-product, and filtration through basic alumina. Solvent evaporation yielded the desired products as colorless to pale yellow oils. Identical products were obtained with use of either PhSeCl, Ph_2Se_2 or *N*-PSP. However, when *N*-PSP was employed, the yield and ease of separation of the required products was facilitated.

(*E*)-1-(Phenylseleno)-1,3-butadiene **88a**



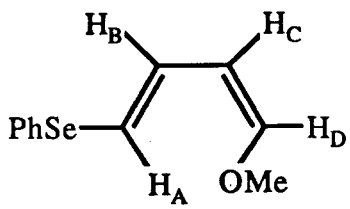
As outlined in general procedure 5, **55a** (75 mg, 0.24 mmol) was reacted with *N*-PSP (73 mg, 0.24 mmol) to yield a pale yellow oil **88a** (45 mg, 90%); IR (film): 3074, 3059, 3022, 2997, 1619, 1579, 1476, 1215, 996, 735 and 690 cm^{-1}; λ_{max} (hexane): 278 nm (ε 16,900); δ (C_6D_6, 400 MHz, ^1H NMR): 4.83 (1H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 4.87 (1H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.10 (1H, ddd, H_C, J_{CD} = 17 Hz, $J_{CB} = J_{CE}$ = 10 Hz), 6.39 (1H, dd, H_B, J_{BA} = 15.5 Hz, J_{BC} = 10 Hz), 6.48 (1H, d, H_A, J_{AB} = 15.5 Hz, J_{ASe} = 15.5 Hz), 6.95 (3H, m), 7.38 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 379 (s). *Anal.* calcd. for $C_{10}H_{10}Se$: C 57.43, H 4.82; found: C 57.10, H 4.86.

(*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene **88b**



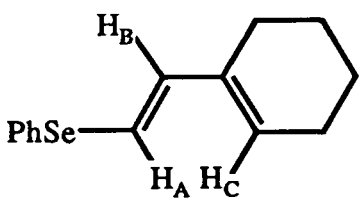
As outlined in general procedure 5, **55b** (75 mg, 0.22 mmol) was reacted with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil **88b** (49 mg, 92%); IR (film): 3054, 3020, 2935, 2837, 1633, 1578, 1474, 1438, 1220, 1144, 966, 735, 689 and 626 cm^{-1}; λ_{max} (hexane): 250 nm (ε 14,000), 264 nm (ε 13,800) and 268 nm (ε 13,900); δ (CD_2Cl_2, 400 MHz, ^1H NMR): 3.60 (3H, s, OMe), 5.64 (1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10.5 Hz), 6.39 (1H, d, H_A, J_{AB} = 15 Hz, J_{ASe} = 14.5 Hz), 6.55 (1H, ddd, H_B, J_{BA} = 15 Hz, J_{BC} = 10.5 Hz, J_{BD} = 0.75 Hz, J_{BSe} = 11 Hz), 6.65 (1H, d, H_D, J_{DC} = 12.5 Hz), 7.23-7.27 (3H, m), 7.43 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 367 (s). *Anal.* calcd. for $C_{11}H_{12}OSe$: C 55.24, H 5.06; found: C 55.44, H 5.04.

(*E,Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene **88c**



As outlined in general procedure 5, **55c** (75 mg, 0.22 mmol) was reacted with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil **88c** (47 mg, 90%); IR (film): 3054, 2928, 2837, 1635, 1573, 1475, 1433, 1219, 1107, 926, 732 and 690 cm^{-1}; λ_{max} (hexane): 270 nm (ε 15,900); δ (CD_2Cl_2, 400 MHz, ^1H NMR): 3.66 (3H, s, OMe), 5.11 (1H, ddd, H_C, J_{CB} = 10.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.5 Hz), 5.96 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.5 Hz), 6.52 (1H, ddd, H_A, J_{AB} = 15.5 Hz, J_{AC} = J_{AD} = 0.5 Hz, J_{ASe} = 15.5 Hz), 6.89 (1H, ddd, J_{BA} = 15.5 Hz, J_{BC} = 10.5 Hz, J_{BD} = 1 Hz, J_{BSe} = 10 Hz), 7.27 (3H, m), 7.46 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 374 (s). *Anal.* calcd. for $C_{11}H_{12}OSe$: C 55.24, H 5.06; found: C 55.28, H 5.00.

(*E*)-1-Phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d**



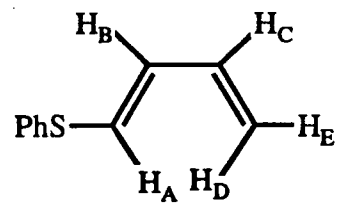
As outlined in general procedure 5, **55d** (75 mg, 0.21 mmol) was reacted with *N*-PSP (64 mg, 0.21 mmol) to yield a pale yellow oil **88d** (55 mg, 95%); IR (film): 3034, 2928, 2854, 2830, 1630, 1577, 1476, 1437, 949, 740, 690 and 668 cm^{-1}; λ_{max} (hexane): 280 nm

(ε 15,500), 270 nm (ε 14,900) and 284 nm (ε 15,000); δ (CD_2Cl_2, 400 MHz, ^1H NMR): 1.39 (4H, m), 1.88 (4H, m), 5.48 (1H, m, H_C), 6.48 (1H, dd, H_A, J_{AB} = 15.5 Hz, J_{AC} = 0.75 Hz, J_{ASe} = 15.5 Hz), 6.65 (1H, d, H_B, J_{BA} = 15.5 Hz, J_{BSe} = 10 Hz), 6.95-7.01 (3H, m), 7.48 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 369 (s). *Anal.* calcd. for $C_{14}H_{16}Se$: C 63.88, H 6.13; found: C 64.13, H 6.17.

General Procedure 7: Preparation of 1-(phenylthio)-1,3-dienes **89a-d**

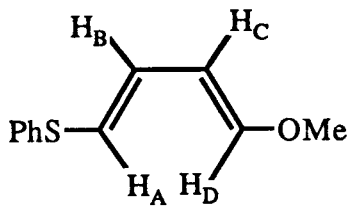
To a stirred solution, in the dark, of the appropriate (*E*)-1-chlorobis(η^5-cyclopentadienylzirconium(IV) 1,3-diene **55a-d** in 2 mL of toluene, was added 1 equiv of *N*-(phenylthio)phthalimide (*N*-PTP, added as a solid). The mixture was then heated in a reactor bomb at 80°C for 2 h. The initial yellow (or orange in the case of **55a**) color of the zirconium 1,3-diene changed to an orange-brown slurry. Partial evaporation of the toluene, dilution with hexanes, and filtration through basic alumina yielded the desired products as colorless to pale yellow oils.

(*E*)-1-(Phenylthio)-1,3-butadiene **89a**



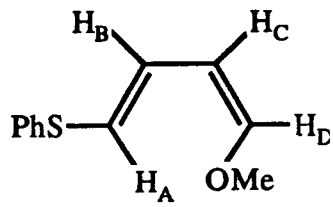
As outlined in general procedure 7, **55a** (250 mg, 0.81 mmol) was reacted with *N*-PTP (206 mg, 0.81 mmol) to yield a colorless oil **89a** (39 mg, 30%); IR (film): 3062, 3020, 1621, 1583, 1478, 996, 743 and 691 cm^{-1}; λ_{max} (hexane): 288 nm (ε 7,000), 282 nm (ε 6,200), 294 nm (ε 6,300); δ (C_6D_6, 400 MHz, ^1H NMR): 4.81 (1H, dd, H_E, J_{ED} = 10 Hz, J_{ED} = 1.75 Hz), 4.90 (1H, dd, H_D, J_{DC} = 16.5 Hz, J_{DE} = 1.75 Hz), 6.13 (1H, ddd, H_C, J_{CD} = 16.5 Hz, J_{CB} = 10.5 Hz, J_{CE} = 10 Hz), 6.19 (1H, d, H_A, J_{AB} = 15 Hz), 6.29 (1H, dd, H_B, J_{BA} = 15 Hz, J_{BC} = 10.5 Hz), 6.95 (3H, m), 7.24 (2H, m); *m/e* (relative intensity): 51 (15.6), 85 (100), 128 (24.2), 129 (58.2) and 162 (M^+, 59.0). *Exact Mass* calcd. for $C_{10}H_{10}S$: 162.0503; found: 162.0501.

(*E*,*E*)-1-(Phenylthio)-4-methoxy-1,3-butadiene **89b**



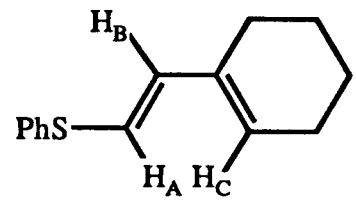
As outlined in general procedure 7, **55b** (250 mg, 0.74 mmol) was reacted with *N*-PTP (188 mg, 0.74 mmol) to yield a pale yellow oil **88b** (42 mg, 30%); IR (film): 3113, 2935, 2828, 1634, 1578, 1479, 1229, 1157, 1118, 966, 740 and 690 cm^{-1}; λ_{max} (hexane): 290 nm (ε 13,000); δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.66 (3H, s, OMe), 5.74 (1H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10.5 Hz), 6.21 (1H, d, H_A, J_{AB} = 14.5 Hz), 6.50 (1H, ddd, H_B, J_{BA} = 14.5 Hz, J_{BC} = 10.5 Hz), 6.74 (1H, d, H_D, J_{DC} = 12.5 Hz), 7.27 (1H, m), 7.35-7.42 (4H, m); *m/e* (relative intensity): 39 (19.1), 115 (46.5), 116 (31.9), 147 (33.8), 161 (32.7) and 192 (M^+, 100). *Exact Mass* calcd. for $C_{11}H_{12}OS$: 192.0609; found: 192.0603.

(*E*,*Z*)-1-(Phenylthio)-4-methoxy-1,3-butadiene **89c**



As outlined in general procedure 7, **55c** (250 mg, 0.74 mmol) was reacted with *N*-PTP (188 mg, 0.74 mmol) to yield a colorless oil **89c** (55 mg, 39%); IR (film): 2928, 2830, 1631, 1579, 1476, 1228, 1115, 964, 739 and 692 cm^{-1}; λ_{max} (hexane): 298 nm (ε 15,400), 296 nm (ε 15,300), 306 nm (ε 14,300); δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.72 (3H, s, OMe), 5.23 (1H, ddd, H_C, J_{CB} = 11 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 6.01 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.75 Hz), 6.32 (1H, ddd, H_A, J_{AB} = 15 Hz, J_{AC} = J_{AD} = 0.75 Hz), 6.87 (1H, ddd, H_B, J_{BA} = 15 Hz, J_{BC} = 11 Hz, J_{BD} = 1 Hz), 7.24 (1H, m), 7.35 (4H, m); *m/e* (relative intensity): 39 (19.6), 109 (31.6), 115 (51.8), 116 (32.7), 147 (34.8), 161 (33.7) and 192 (M^+, 100). *Exact Mass* calcd. for $C_{11}H_{12}OS$: 192.0609; found: 192.0608.

(*E*)-1-Phenylthio-[2-(1-cyclohexen-1-yl)ethene] **89d**

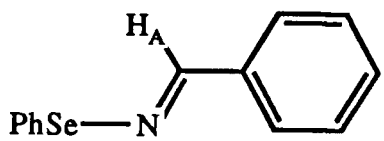


As outlined in general procedure 7, **55d** (250 mg, 0.69 mmol) was reacted with *N*-PTP (175 mg, 0.69 mmol) to yield a pale yellow oil **89d** (38 mg, 25%); IR (film): 3027, 2928, 2858, 1632, 1582, 1532, 1478, 949, 739 and 689 cm^{-1}; λ_{max} (hexane): 290 nm

(ε-12,000), 294 nm (ε 11,500) and 284 nm (ε 11,400); δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.61 (2H, m), 1.71 (2H, m), 2.18 (4H, m), 5.77 (1H, m, H_C), 6.24 (1H, dd, H_A, J_{AB} = 15.5 Hz, J_{AC} = 0.75 Hz), 6.46 (1H, d, H_B, J_{BA} = 15.5 Hz), 7.21 (1H, m), 7.33 (4H, m). *Anal.* calcd. for $C_{14}H_{16}S$: C 77.73, H 7.45; found: C 77.50, H 7.40.

6.4.6 Preparation of Heterosubstituted Imines and 1-Azadienes: Transfer of Zirconium to Selenium and Phosphorus

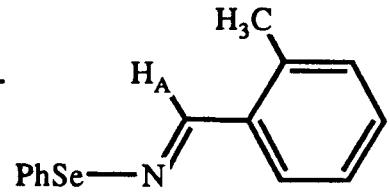
(*E*)-1-(Phenylseleno)benzenemethanimine **91**



To a stirred solution of (benzenemethaniminato)chlorobis(η^5-cyclopentadienyl)zirconium(IV) **62** (150 mg, 0.42 mmol) in 1 mL of toluene, at room temperature, was added a solution (in 2 mL of toluene) of phenylselenenyl chloride (PhSeCl) (80 mg, 0.42 mmol). On addition, the deep red color of the PhSeCl was immediately discharged and the initially bright yellow solution changed to pale yellow. Shortly after the addition was complete, a pale yellow slurry formed. Dilution with hexanes, followed by filtration through Celite®, gave a pale yellow oil **91** (80 mg, 73%); δ (C_6D_6, 400 MHz, ^1H NMR): 7.00 (1H, m), 7.00-7.05 (3H, m), 7.10 (2H, m), 7.46 (2H, m), 7.64 (2H, m), 8.34 (1H, s, H_A, J_{ASe} = 28 Hz); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 897 (s); *m/e* (relative

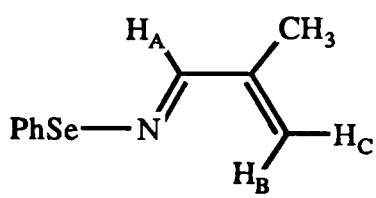
intensity): 39 (32.5), 50 (59.5), 51 (72.4), 77 (100), 83 (48.0), 85 (32.2), 103 (41.4) and 261 (M^+, 15.8). *Exact Mass* calcd. for $C_{13}H_{11}N^{80}Se$: 261.0057; found: 261.0056.

(*E*)-1-(phenylseleno)-2-methylbenzenemethanimine **92**



Preparation of **92** was identical to that described above for **91**. Chlorobis(η^5-cyclopentadienyl)(2-methylbenzenemethaniminato)zirconium(IV) **63** (150 mg, 0.40 mmol) was reacted with PhSeCl (77 mg, 0.40 mmol) to produce, after workup, a pale yellow oil **92** (82 mg, 75%); δ (C_6D_6, 400 MHz, ^1H NMR): 2.07 (3H, s, $C\underline{H}_3$), 6.83 (1H, m), 6.98 (2H, m), 7.01 (1H, m), 7.09 (2H, m), 7.65 (2H, m), 7.82 (1H, m), 8.74 (1H, s, J_{ASe} = 29.5 Hz); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 903 (s); *m/e* (relative intensity): 39 (56.7), 50 (86.2), 51 (46.1), 63 (31.3), 65 (48.5), 76 (100), 77 (50.4), 91 (68.9), 103 (43.2), 104 (60.4), 117 (47.2), 118 (58.8), 119 (30.2), 147 (47.4) and 275 (M^+, 1.5). *Exact Mass* calcd. for $C_{14}H_{13}N^{80}Se$: 275.0213; found: 275.0210.

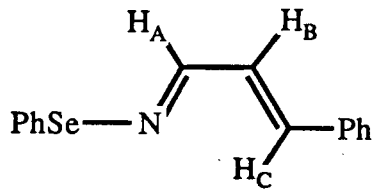
(*E*)-1-(Phenylseleno)-3-methyl-1,3-azadiene **93**



Preparation of **93** was identical to that described above for **91**. Chlorobis(η^5-cyclopentadienyl)[2-(2-propen-1-yl)methaniminato]zirconium(IV) **68** (150 mg, 0.46 mmol)

was reacted with PhSeCl (88 mg, 0.46 mmol) to yield, after workup, a yellow oil **93** (75 mg, 72%); δ (C_6D_6, 400 MHz, ^1H NMR): 1.87 (3H, s, CH_3), 4.77 (1H, m, H_B), 5.10 (1H, m, H_C), 6.69 (1H, m), 7.06 (2H, m), 7.59 (2H, m), 8.08 (1H, s, H_A, J_{ASe} = 29 Hz); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 882 (s); *m/e* (relative intensity): 39 (100), 41 (72.5), 55 (46.0), 68 (75.0), 122 (81.3), 144 (18.8), 157 (25.0) and 225 (M^+, 13.4). *Exact Mass* calcd. for $C_{10}H_{11}N^{80}Se$: 225.0056; found: 225.0055.

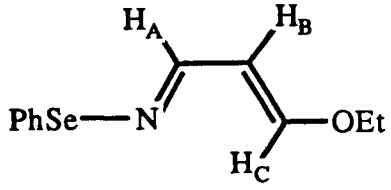
(*E*,*E*)-1-(Phenylseleno)-4-phenyl-1,3-azadiene **94**



Preparation of **94** was as described above for **91**, except that, *N*-(phenylseleno)phthalimide (*N*-PSP) was used as the selenium transfer reagent. (*E*)-Chlorobis(η^5-cyclopentadienyl)[2-(2-phenylethenyl)methaniminato]zirconium(IV) **69** (150 mg, 0.39 mmol) and *N*-PSP (117 mg, 0.39 mmol) were reacted at room temperature in the dark, to yield a pale yellow oil **94** (91 mg, 81%) on workup. It was evident from the ^1H and ^{77}Se NMR spectra that **94** was actually a mixture of two isomers; namely, a 5:1 mixture of geometric isomers about the C=N bond (as shown in the structures above). Evidence that the major isomer was the (E,E)-isomer was obtained from ^1H nuclear Overhauser effect difference (NOEDIFF) spectroscopy; irradiation of H_A of the major isomer, produced enhancement of the *ortho*-phenyl protons of the PhSe group and of proton H_C. All data presented were obtained by analysis of the mixture. Major isomer ; δ (C_6D_6, 400 MHz, ^1H NMR): 6.28 (1H, d, H_C, J_{CB} = 16 Hz), 6.90 (1H, dd, H_B, J_{BC} = 16 Hz, J_{BA} = 9 Hz), 6.96-7.13 (8H, m), 7.67 (2H,

m), 8.17 (1H, d, J_{AB} = 9 Hz, J_{ASe} = 28 Hz); δ (C_6D_6, 76.3 MHz, ^{77}Se NMR): 859 (s); Minor isomer ; δ (C_6D_6, 400 MHz, ^{1}H NMR): 6.37 (1H, d, $H_{C'}$, $J_{C'B'}$ = 16 Hz), 6.79 (1H, dd, $H_{B'}$, $J_{B'C'}$ = 16 Hz, $J_{B'A'}$ = 9 Hz), 6.96-7.13 (8H, m), 7.82 (2H, m), 8.34 (1H, d, $H_{A'}$, $J_{A'B'}$ = 9 Hz); δ (C_6D_6, 76.3 MHz, ^{77}Se NMR): 801 (s). Mass spectra data for the mixture were; *m/e* (relative intensity): 50 (58.7), 51 (46.0), 74 (32.5), 75 (27.4), 76 (68.5), 77 (68.8), 78 (57.3), 103 (55.4), 130 (100), 147 (33.4), 157 (29.1) and 287 (M^+, 10.4). *Exact Mass* calcd. for $C_{15}H_{13}N^{80}Se$: 287.0213; found: 287.0211.

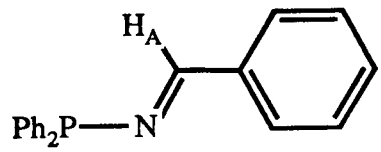
(*E*,*E*)-1-(Phenylseleno)-4-ethoxy-1,3-azadiene **95**



Preparation of **95** was as described above for **94**. (*E*)-chlorobis(η^5-cyclopentadienyl)[2-(2-ethoxyethenyl)methaniminato]zirconium(IV) **70** (150 mg, 0.42 mmol) was reacted with *N*-PSP (80 mg, 0.42 mmol) to yield, on workup, a yellow oil (74 mg, 69%). ^{1}H and ^{77}Se NMR spectra indicated that **95** was actually a mixture of two isomers (~1.2:1). In this case, the use of ^{1}H NOEDIFF spectroscopy to determine the stereochemistry of the major component was not successful. However, the chemical shift of the ^{77}Se NMR resonance, and J_{ASe} value for the major isomer indicate that it is likely the (E,E)-isomer. All data were determined by analysis of the mixture. Major isomer ; δ (C_6D_6, 400 MHz, ^{1}H NMR): 0.91 (3H, t, J = 7 Hz), 3.28 (2H, q, J = 7 Hz), 5.83 (1H, dd, H_B, J_{BC} = 12.5 Hz, J_{BA} = 9 Hz), 6.38 (1H, d, H_C, J_{CB} = 12.5 Hz), 7.05 (1H, m), 7.21 (2H, m), 7.78 (2H, m), 8.07 (1H, d, H_A, J_{AB} = 9 Hz, J_{ASe} = 28.5 Hz); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 893 (s);

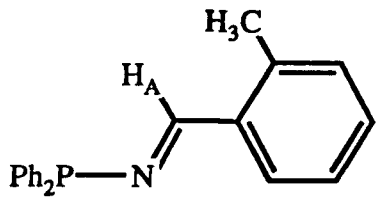
Minor isomer ; δ (C_6D_6, 400 MHz, ^1H NMR): 0.91 (3H, t, J = 7 Hz), 3.22 (2H, q, J = 7 Hz), 5.64 (1H, dd, H_B, J_{BC} = 12.5 Hz, J_{BA} = 9 Hz), 6.38 (1H, d, H_C, J_{CB} = 12.5 Hz), 7.05 (1H, m), 7.17 (2H, m), 7.92 (2H, m), 8.12 (1H, d, H_A, J_{AB} = 9 Hz); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 819 (s). Mass spectra data for the mixture were; *m/e* (relative intensity): 56 (26.8), 82 (10.2), 84 (100), 147 (5.3) and 255 (M^+, 4.4). *Exact Mass* calcd. for $C_{11}H_{13}NO^{80}Se$: 255.0162; found: 255.0155.

(*E*)-1-(Diphenylphosphino)benzenemethanimine **98**



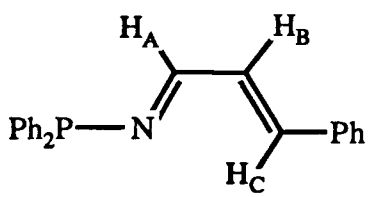
To a stirred solution of **62** (150 mg, 0.42 mmol) in 1.5 mL of toluene was added Ph_2PCl (93 mg, 0.42 mmol). The yellow solution was then transferred to a reactor bomb and heated, in the dark, at 80°C for 1 h. On cooling to room temperature, a white crystalline material (Cp_2ZrCl_2) precipitated from a pale yellow solution. The mixture was diluted with hexanes and filtered through basic alumina to give, after evaporation of the solvent, a white solid **98** (100 mg, 83%); IR (Nujol): 3063, 3046, 1625, 1611, 1576, 1433, 1311, 1215, 1092, 1024, 844, 776, 743 and 696 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 7.00-7.20 (9H, m), 7.54-7.68 (6H, m), 8.26 (1H, d, H_A, J_{AP} = 21 Hz); δ (C_6D_6, 121.5 MHz, ^{31}P NMR): 49.9 (s). *Anal.* calcd. for $C_{19}H_{16}NP$: C 78.88, H 5.57, N 4.84; found: C 79.12, H 5.70, N 4.81.

(*E*)-1-(Diphenylphosphino)(2-methyl-benzenemethanimine **99**



Preparation of **99** was identical to that described above for **98**. Ph_2PCl (88 mg, 0.40 mmol) and **63** (150 mg, 0.40 mmol) afforded, after workup, a pale yellow oil **99** (104 mg, 86%); IR (film): 3070, 3052, 3020, 1614, 1593, 1568, 1480, 1434, 1282, 1221, 1093, 1025, 807, 741 and 696 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 2.11 (3H, s, $C\underline{H}_3$), 6.83 (1H, m), 7.01 (1H, m), 7.03-7.15 (7H, m), 7.63 (4H, m), 8.03 (1H, m), 8.63 (1H, d, H_A, J_{AP} = 22 Hz); δ (C_6D_6, 121.5 MHz, ^{31}P NMR): 51.9 (s); *m/e* (relative intensity): 91 (36.2), 107 (20.5), 108 (44.9), 117 (27.0), 118 (100), 183 (34.1), 288 (19.5) and 303 (M^+, 10.0). *Exact Mass* calcd. for $C_{20}H_{18}NP$: 303.1177; found: 303.1183.

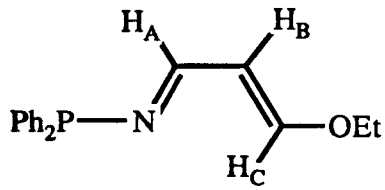
(*E,E*)-1-(Diphenylphosphino)-4-phenyl-1,3-azadiene **100**



To a stirred solution of **69** (150 mg, 0.39 mmol) in 2 mL of toluene, at room temperature, was added Ph_2PCl (86 mg, 0.39 mmol). There was an immediate color change from orange to pale yellow, closely followed by precipitation of a white solid (Cp_2ZrCl_2). After stirring at room temperature for a further 30 min, the reaction was diluted with hexanes

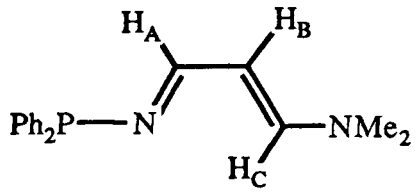
and filtered through basic alumina. Evaporation of the solvent gave a pale yellow solid **100** (102 mg, 83%); IR (Nujol): 3052, 3035, 1601, 1585, 1434, 1146, 1102, 980, 747 and 695 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 6.90 (1H, dd, H_C, J_{CB} = 16 Hz, J_{CH} = 1.25 Hz), 7.05 (1H, dd, H_B, J_{BC} = 16 Hz, J_{BA} = 8.5 Hz), 7.32-7.46 (9H, m), 7.48 (2H, m), 7.51 (4H, m), 8.07 (1H, dd, H_A, J_{AP} = 22 Hz, J_{AB} = 8.5 Hz); δ (C_6D_6, 121.5 MHz, ^{31}P NMR): 49.9 (s); *m/e* (relative intensity): 108 (39.9), 109 (30.6), 130 (33.5), 183 (60.1), 185 (25.5), 238 (32.2) and 315 (M^+, 100). *Exact Mass* calcd. for $C_{21}H_{18}NP$: 315.1177; found: 315.1181

(*E*,*E*)-1-(Diphenylphosphino)-4-ethoxy-1,3-azadiene **101**



The preparation of **101** was identical to that described above for **100**. Ph_2PCl (93 mg, 0.42 mmol) and **70** (150 mg, 0.42 mmol) were reacted to yield, after workup, a yellow oil **101** (93 mg, 78%); IR (film): 3055, 2977, 1638, 1619, 1479, 1435, 1321, 1207, 1093, 743 and 696 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.79 (3H, t, *J* = 7 Hz), 3.19 (2H, q, *J* = 7 Hz), 6.90 (1H, dd, H_B, J_{BC} = 13 Hz, J_{BA} = 9 Hz), 7.30 (1H, d, H_C, J_{CB} = 13 Hz), 8.07 (2H, m), 8.15 (4H, m), 8.74 (4H, m), 9.01 (1H, dd, H_A, J_{AP} = 23 Hz, J_{AB} = 9 Hz); δ (C_6D_6, 121.5 MHz, ^{31}P NMR): 51.2 (s); *m/e* (relative intensity): 39 (29.8), 77 (9.2), 105 (5.54), 125 (4.1), 183 (9.3), 210 (30.0), 238 (31.4), 254 (100) and 283 (M^+, 2.5). *Exact Mass* calcd. for $C_{17}H_{18}NOP$: 283.1126; found: 283.1128.

(*E*,*E*)-1-(Diphenylphosphino)-4-(dimethylamino)-1,3-azadiene **102**



The preparation of **102** was carried out as described above for **100**. Ph_2PCl (93 mg, 0.42 mmol) was added to a slurry of **71** (150 mg, 0.42 mmol) in 2 mL of toluene. After 5 min at room temperature the slurry had become homogeneous. Workup of the reaction mixture yielded a yellow oil **102** (87 mg, 73%); IR (film): 3055, 2907, 1629, 1588, 1564, 1388, 1109, 943, 792 and 696 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.97 (6H, s, NMe_2), 5.45 (1H, b dd, H_B, J_{BC} = 13 Hz, J_{BA} = 9 Hz), 5.96 (1H, b d, H_C, J_{CB} = 13 Hz), 7.07 (2H, m), 7.18 (4H, m), 7.88 (4H, m), 8.28 (1H, dd, H_A, J_{AP} = 9 Hz, J_{AB} = 9 Hz); δ (C_6D_6, 121.5 MHz, ^{31}P NMR): 51.8 (b s); *m/e* (relative intensity): 42 (26.4), 56 (22.2), 97 (88.0), 108 (41.2), 109 (53.5), 154 (35.8), 162 (26.0), 183 (65.5), 185 (27.6), 201 (53.7), 205 (41.2), 222 (30.5), 238 (20.5) and 282 (M^+, 100). *Exact Mass* calcd. for $C_{17}H_{19}N_2P$: 282.1286; found: 282.1282.

6.5 Photochemical Isomerization of 1-(Phenylseleno)- and 1-(Phenylthio)-1,3-dienes. Thermal Isomerization of 1-(Phenylseleno)-1,3-dienes and Diels-Alder Reactivity with Maleic Anhydride.

6.5.1 Photolysis of 1-(Phenylseleno)-1,3-dienes.

Photolysis of (*E*)-1-(phenylseleno)-1,3-butadiene **88a**

A solution of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (30 mg, 0.14 mmol) in 0.5 mL of C_6D_6 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then irradiated with fluorescent light for 2 h. ^1H and ^{77}Se NMR of the solution, after photolysis, indicated that isomerization of **88a** had taken place to give a 2:1 mixture of E/Z isomers. Addition of (*E*)-1-(phenylseleno)-1,3-butadiene to the 2:1 E/Z mixture resulted in a change in this ratio, which was reestablished after a further 2 h irradiation with fluorescent light. Continued irradiation up to 24 h gave no change in the E/Z ratio. ^1H and ^{77}Se NMR data, taken from the spectrum of the mixture, of (*Z*)-1-(phenylseleno)-1,3-butadiene were; δ (C_6D_6, 400 MHz, ^1H NMR): 5.04 (1H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.11 (1H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.35 (1H, dd, H_B, J_{BA} = 9 Hz, J_{BC} = 10 Hz), 6.40 (1H, d, H_A, J_{AB} = 9 Hz), 6.71 (1H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz), 6.93 (2H, m), 7.33 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 341 (s).

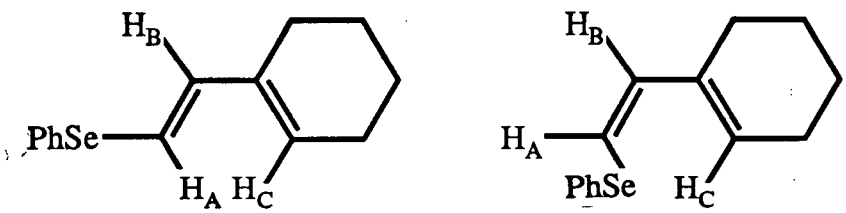
Photolysis of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b**

A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (32 mg, 0.13 mmol) in 0.5 mL of CD_2Cl_2 was photolyzed with fluorescent light for 1.5 h. ^1H and ^{77}Se NMR of the solution, after photolysis, indicated that isomerization of **88b** had taken place to give a 41(±2):13(±1):36(±2):10(±1) mixture of Z,E/Z,Z/E,E/E,Z isomers. These ratios were determined, from the ^1H NMR, by integration of the OMe resonances. That these were representative of the equilibrium composition of these isomers was determined by continuing the photolysis for a further 24 h, during which time the ratios did not change beyond those values stated above. When the equilibrium was disturbed by addition of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene, further photolysis (~1.5 h) reestablished the equilibrium values. ^1H and ^{77}Se NMR data, taken from the spectrum of the mixture, were: (*Z*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene; δ (CD_2Cl_2, 400 MHz, ^1H NMR): 3.62 (3H, s, OMe), 5.63 (1H, ddd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10.5 Hz, J_{CA} = 0.75 Hz), 6.22 (1H, ddd, H_A, J_{AB} = 9 Hz, J_{AC} = J_{AD} = 0.75 Hz), 6.52 (1H, ddd, H_B, J_{BC} = 10.5 Hz, J_{BA} = 9 Hz, J_{BD} = 0.5 Hz), 6.78 (1H, d, H_D, J_{DC} = 12.5 Hz), 7.20-7.32 (3H, m), 7.42-7.51 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 310 (s); (*Z*,*Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene; δ (CD_2Cl_2, 400 MHz, ^1H NMR): 3.69 (3H, s, OMe), 5.31 (1H, ddd, H_C, J_{CB} = 11 Hz, J_{CD} = 6.5 Hz, J_{CA} = 1 Hz), 6.11 (1H, ddd, H_D, J_{DC} = 6.5 Hz, J_{DA} = 1.5 Hz, J_{DB} = 1 Hz), 6.34 (1H, ddd, H_A, J_{AB} = 9 Hz, J_{AD} = 1.5 Hz, J_{AC} = 1 Hz), 6.92 (1H, ddd, H_B, J_{BC} = 11 Hz, J_{BA} = 9 Hz, J_{BD} = 1 Hz), 7.20-7.32 (3H, m), 7.42-7.51 (2H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR): 323 (s).

Photolysis of (*E*,*Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88c**

A solution of (*E*,*Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88c** (31 mg, 0.13 mmol) in 0.5 mL of CD_2Cl_2 was photolyzed with fluorescent light for 1.5 h. By ^1H and ^{77}Se NMR, an isomeric mixture identical to that described above for the photolysis of **88b** was observed.

Preparation and photolysis of a 65:35 E/Z mixture of 1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d**



65:35 E/Z

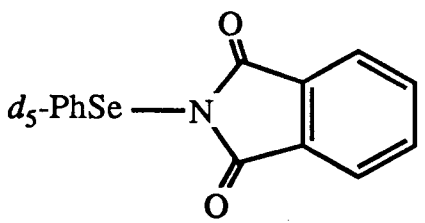
A solution of (*E*)-chloro[2-(1-cyclohexen-1-yl-ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) **55d** (80 mg, 0.22 mmol) in 0.5 mL of C_6D_6 was photolyzed with fluorescent light in a sealed (under nitrogen) 5 mm NMR tube for 19 h. The ^1H NMR indicated the formation of a 65:35 E/Z mixture of chloro[2-(1-cyclohexen-1-yl-ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV). The orange solution (initially yellow) was then reacted with *N*-PSP (66 mg, 0.22 mmol) according to general procedure 5. Workup yielded a yellow oil (48 mg, 83%) which by ^1H NMR spectroscopy was identified as a 65:35 E/Z mixture of 1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d**. Photolysis of this mixture with fluorescent light, for up to 18 h, gave a 95:5 E/Z mixture of **88d**. (*E*)-1-Phenylseleno-[2-(1-cyclohexen-1-yl)ethene] did not isomerize under the same photochemical conditions. (*Z*)-Chloro[2-(1-cyclohexen-1-yl-ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV); δ (C_6D_6,

400 MHz, ^{1}H NMR): 1.54-1.71 (4H, m), 2.00 (2H, m), 2.16 (2H, m), 5.47 (1H, m, H_C), 5.98 (10H, s, Cp), 6.13 (1H, d, H_A, J_{AB} = 13 Hz), 7.24 (1H, d, H_B, J_{BA} = 13 Hz); (*Z*)-1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene]; δ ($CDCl_3$, 400 MHz, ^{1}H NMR): 1.55-1.75 (4H, m), 2.14 (2H, m), 2.32 (2H, m), 5.80 (1H, m, H_C), 6.39 (2H, AB_q, H_A/H_B), 7.25 -7.35 (3H, m), 7.56 (2H, m).

6.5.2 Mechanistic Studies on the Isomerization of 1-(Phenylseleno)-1,3-dienes.

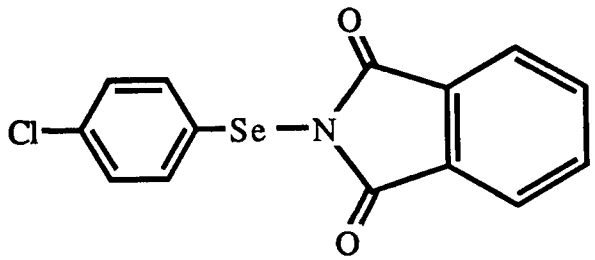
Crossover Experiments, a Mechanistic Probe: Intramolecular vs. Intermolecular Process

N-(Phenylseleno)phthalimide-d_5 (*N*-PSP-d_5)



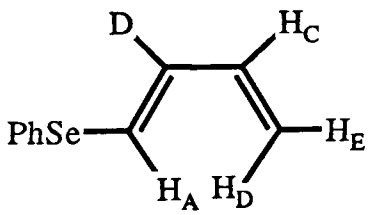
N-(phenylseleno)phthalimide-d_5 was prepared according to literature procedure[104,114] starting from benzene-d_6 to yield white crystals (3.23 g, 64% over 4 steps). The following data were recorded for this compound; IR (Nujol): 2274, 1774, 1720, 1343, 1280, 1066, 710 and 676 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^{1}H NMR): 7.73 (2H, m), 7.90 (2H, m). *Anal.* calcd. for $C_{14}H_4D_5NSe$: C 54.73, H 2.95, N 4.56; found: C 55.00, H 3.00, N 4.49.

N-(4-Chlorophenylseleno)phthalimide (*N*-ClPSP)



N-(4-chlorophenylseleno)phthalimide was prepared according to literature procedures[104,112] using bis(4-chlorophenyl)diselenide (2.5 g, 6.60 mmol) to a yield pale yellow microcrystalline material (2.87 g, 75%); IR (Nujol): 1775, 1725, 1344, 1277, 1064, 1011, 731 and 711 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 7.31 (2H, m), 7.76 (2H, m), 7.81 (2H, m), 7.91 (2H, m). *Anal.* calcd. for $C_{14}H_8ClNSe$: C 49.95, H 2.40, N 4.16; found: C 50.12, H 2.44, N 4.14.

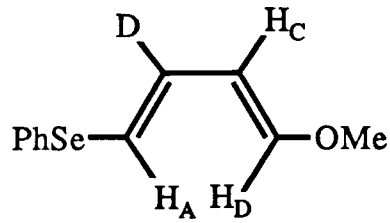
(*E*)-1-(phenylseleno)-1,3-butadiene-2-*d* **88a**-d_1



As outlined in general procedure 5, (*E*)-1,3-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* **55a**-d_1 (75 mg, 0.24 mmol) was reacted with *N*-PSP (73 mg, 0.24 mmol) to yield a pale yellow oil **88a**-d_1 (43 mg, 85%); IR (film): 3075, 2985, 1617, 1578, 1475, 1215, 996, 737 and 690 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 5.06 (1H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.13 (1H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.34 (1H, b dd, H_A, J_{CD} = 17 Hz, J_{CE} = 10 Hz), 6.70 (1H, b t, H_A, J_{Ad} = 2.5 Hz), 7.30

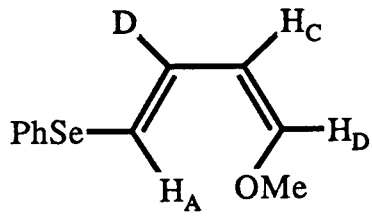
(3H, m), 7.51 (2H, m); *m/e* (relative intensity): 51 (25.2), 77 (25.3), 78 (24.7), 129 (41.1), 130 (100), 131 (28.3), 134 (29.7) and 211 (M^+, 25.4). *Exact Mass* calcd. for $C_{10}H_9{}^2H^{80}Se$: 211.0011; found: 211.0007.

(*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-2-*d* **88b**-d_1



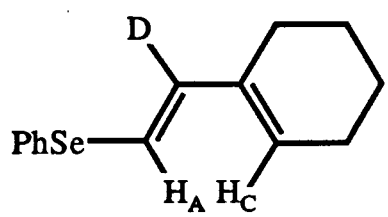
As outlined in general procedure 5, (*E*,*E*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* **55b**-d_1 (75 mg, 0.22 mmol) was reacted with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil **88b**-d_1 (48 mg, 91%); IR (film): 3060, 2932, 2832, 1632, 1577, 1478, 1219, 1145, 968, 734 and 691 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.64 (3H, s, OMe), 5.64 (1H, b d, H_C, J_{CD} = 12.5 Hz), 6.41 (1H, b t, H_A, J_{Ad} = 2.5 Hz), 6.66 (1H, d, H_D, J_{DC} = 12.5 Hz), 7.27 (3H, m), 7.48 (2H, m); *m/e* (relative intensity): 51 (30.0), 77 (44.6), 78 (24.5), 116 (52.8), 117 (38.3), 145 (36.6), 146 (21.9), 157 (41.0), 160 (87.9), 161 (100) and 241 (M^+, 71.7). *Exact Mass* calcd. for $C_{11}H_{11}{}^2HO^{80}Se$: 241.0116; found: 241.0117.

(*E*,*Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-2-*d* **88c**-d_1



As outlined in general procedure 5, (*E*,*Z*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* **55c**-d_1 (75 mg, 0.22 mmol) was reacted with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil **88c**-d_1 (44 mg, 83%); IR (film): 2935, 2830, 1628, 1577, 1476, 1437, 1213, 1109, 929, 736 and 688 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.61 (3H, s, OMe), 5.06 (1H, b d, H_C, J_{CD} = 6 Hz), 5.87 (1H, dd, H_D, J_{DC} = 6 Hz, J_{DA} = 0.5 Hz), 6.46 (1H, b t, H_A, J_{Ad} = 2.5 Hz), 7.22 (3H, m), 7.42 (2H, m); *m/e* (relative intensity): 51 (21.0), 77 (38.1), 78 (32.3), 116 (42.6), 117 (25.5), 118 (24.2), 129 (38.1), 130 (34.6), 145 (28.6), 146 (16.3), 155 (19.1), 160 (74.8), 161 (100) and 241 (M^+, 54.9). *Exact Mass* calcd. for $C_{11}H_{11}{}^2HO^{80}Se$: 241.0116; found: 241.0119.

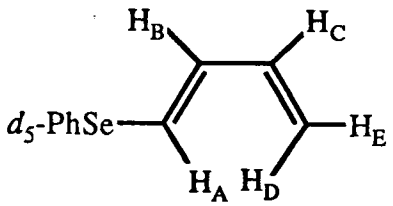
(*E*)-1-Phenylseleno-[2-(1-cyclohexen-1-yl)ethene]-2-*d* **88d**-d_1



As outlined in general procedure 5, (*E*)-chloro[2-(1-cyclohexen-1-yl-ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* **55d**-d_1 (75 mg, 0.21 mmol) was reacted with *N*-PSP (64 mg, 0.21 mmol) to yield a pale yellow oil **88d**-d_1 (52 mg, 93%); IR (film): 1628, 1578,

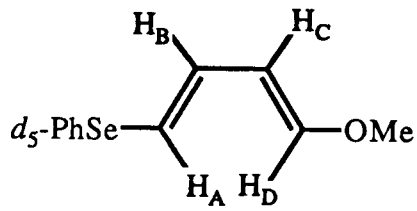
1477, 1438, 829, 733, 690 and 669 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.62 (2H, m), 1.70 (2H, m), 2.17 (4H, m), 5.79 (1H, m, H_C), 6.51 (1H, b s), 7.25-7.34 (3H, m), 7.50 (2H, m); *m/e* (relative intensity): 51 (58.1), 65 (22.0), 77 (75.2), 78 (94.2), 80 (99.6), 106 (50.0), 141 (21.4), 142 (100), 143 (30.1), 156 (25.8), 184 (67.8), 186 (34.3), 188 (61.0) and 265 (M^+, 54.4). *Exact Mass* calcd. for $C_{14}H_{15}{}^2H^{80}Se$: 265.0480; found: 265.0481.

(*E*)-1-(Phenylseleno)-1,3-butadiene-d_5 **88a**-d_5



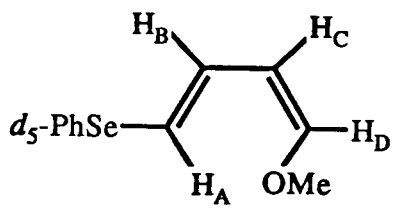
As outlined in general procedure 5, (*E*)-1,3-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV) **55a** (75 mg, 0.24 mmol) was reacted with *N*-PSP-d_5 (74 mg, 0.24 mmol) to yield a pale yellow oil **88a**-d_5 (42 mg, 82%); IR (film): 2288, 2274, 1620, 1568, 1545, 1341, 1215, 993, 936, 900, 806 and 641 cm^{-1}; ^1H NMR was identical to **88a** with the absence of the aromatic resonances; *m/e* (relative intensity): 54 (41.9), 82 (37.3), 83 (38.0), 131 (28.0), 132 (37.1), 133 (100) and 215 (M^+, 20.2). *Exact Mass* calcd. for $C_{10}H_{15}{}^2H_5{}^{80}Se$: 215.0261; found: 215.0264.

(*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-d_5 **88b**-d_5



As outlined in general procedure 5, (*E*,*E*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) **55b** (75 mg, 0.22 mmol) was reacted with *N*-PSP-d_5 (68 mg, 0.22 mmol) to yield a pale yellow oil **88b**-d_5 (45 mg, 84%); IR (film): 2290, 2276, 1630, 1578, 1542, 1222, 1145, 965, 827 and 628 cm^{-1}; ^1H NMR was identical to **88b** with the absence of the aromatic resonances; *m/e* (relative intensity): 54 (25.4), 82 (38.9), 119 (29.9), 120 (32.4), 121 (23.8), 132 (24.8), 133 (22.5), 134 (35.1), 149 (25.2), 160 (25.8), 162 (50.5), 163 (54.8), 164 (34.8), 165 (100) and 245 (M^+, 87.7). *Exact Mass* calcd. for $C_{11}H_7{}^2H_5O^{80}Se$: 245.0367; found: 245.0362.

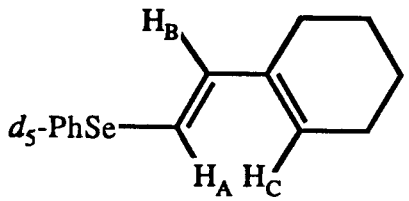
(*E*,*Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-d_5 **88c**-d_5



As outlined in general procedure 5, (*E*,*Z*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) **55c** (75 mg, 0.22 mmol) was reacted with *N*-PSP-d_5 (68 mg, 0.22 mmol) to yield a pale yellow oil **88c**-d_5 (46 mg, 86%); IR (film): 2274, 1633, 1575, 1546, 1227, 1146, 962, 828 and 630 cm^{-1}; ^1H NMR was identical to **88c** with the absence of

the aromatic resonances; *m/e* (relative intensity): 54 (23.7), 82 (36.7), 119 (28.3), 120 (32.5), 121 (38.3), 149 (22.4), 160 (24.9), 162 (50.4), 163 (55.1), 165 (100) and 245 (M^+, 74.3). *Exact Mass* calcd. for $C_{11}H_{17}{}^2H_5O^{80}Se$: 245.0367; found: 245.0364.

(*E*)-1-Phenylseleno-[2-(1-cyclohexen-1-yl)ethene]-d_5 **88d**-d_5



As outlined in general procedure 5, (*E*)-chloro[2-(1-cyclohexen-1-yl-ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) **55d** (75 mg, 0.21 mmol) was reacted with *N*-PSP-d_5 (65 mg, 0.21 mmol) to yield a pale yellow oil **88d**-d_5 (51 mg, 91%); IR (film): 3027, 2991, 2928, 2274, 1630, 1578, 1544, 1435, 1339, 1022, 952, 764 and 639 cm^{-1}; ^1H NMR was identical to **88d** with the absence of the aromatic resonances; *m/e* (relative intensity): 54 (30.5), 78 (44.8), 79 (100), 80 (21.7), 82 (36.9), 83 (40.9), 105 (41.3), 107 (25.7), 145 (36.9), 146 (65.6), 159 (19.5), 160 (19.9), 185 (27.4), 187 (54.8), 188 (45.2) and 269 (M^+, 42.7). *Exact Mass* calcd. for $C_{14}H_{11}{}^2H_5{}^{80}Se$: 269.0731; found: 269.0736.

General Procedure 6: Crossover Experiments for Photochemical and Thermal Isomerization Process.

A known ratio (approximately 1:1) of 1-(phenylseleno)-1,3-diene-d_5 [or 1-(4-chlorophenylseleno)-1,3-diene] and 1-(phenylseleno)-1,3-diene-2-*d* were dissolved in 0.5 mL of $CDCl_3$ (C_6D_6 or C_7D_8 for thermolysis reactions) and placed in a capped (or sealed) 5 mm NMR tube. The mixture was then photolyzed (1.5 h with fluorescent light) or heated at 80°C in the dark (48 h). Analyses for crossover products were performed by ^1H NMR and low resolution mass spectrometry. See pp 107-112 and 124-125 for a discussion of these results.

Effect of 1,4-cyclohexadiene on crossover

When crossover experiments (thermal and photochemical) were carried out according to general procedure 6, using 1,4-cyclohexadiene as the solvent instead of deuterated solvents, a reduction in the amount of crossover was observed by ^1H NMR and low resolution mass spectrometry.

Effect of 2,6-*tert*-butyl-4-methylphenol (BHT)

Photolysis of a solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (29 mg, 0.12 mmol) in 0.5 mL of C_7D_8, containing BHT (2 equiv), showed a significant decrease in the rate of isomerization. It was necessary to photolyze the solution for 20 h before the Z,E/Z,Z/E,E/E,Z ratio approached the equilibrium value (see above).

A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (27 mg, 0.11 mmol) in 0.5 mL of C_7D_8, containing BHT (2 equiv), gave an isomeric mixture of 15:4:69:12 Z,E/Z,Z/E,E/E,Z after 48 h thermolysis at 80°C in the dark. This ratio shows a concentration of the E,E-isomer far in excess of the equilibrium value. Subsequent photolysis of this solution, for 20 h with fluorescent light, gave the equilibrium ratios for the Z,E/Z,Z/E,E/E,Z isomeric mixture.

Effect of 4-oxo-2,2,6,6-tetramethylpiperidinyloxy radical (TEMPONE)

Photolysis of a solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (28 mg, 0.12 mmol) in 0.5 mL of C_7D_8, containing TEMPONE (1 mg, 5 mol %) showed little effect on the rate of isomerization. Equilibrium values of Z,E/Z,Z/E,E/E,Z were reached within 2 h of photolysis with fluorescent light.

A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (27 mg, 0.11 mmol) in 0.5 mL of C_7D_8, containing TEMPONE (1 mg, 5 mol %), had little effect on the thermal isomerization process, with equilibrium values for Z,E/Z,Z/E,E/E,Z attained after 48 h at 80°C in the dark.

Effect of 1,4-cyclohexadiene

A solution of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (28 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was photolyzed, in a capped 5 mm NMR tube, for 2 h with fluorescent

light. A 9:1 E/Z mixture was observed by ^{1}H NMR, indicating significant retardation of the isomerization process.

A solution of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (28 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was heated at 80°C in capped NMR tube for 48 h. A 20:1 E/Z mixture was observed by ^{1}H NMR, indicating significant retardation of the isomerization process.

A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (28 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was photolyzed, in capped NMR tube, for 1.5 h with fluorescent light. An isomeric ratio of 29:13:34:15 Z,E/Z,Z/E,E/E,Z was obtained, indicating a slight retardation of the isomerization process.

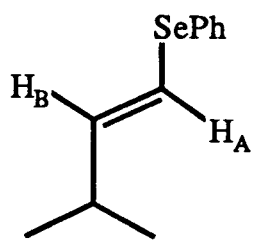
A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (30 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was heated at 80°C in capped NMR tube for 48 h. An equilibrium ratio was obtained after 48 h, but a significant retardation in the initial stages was observed with 92% of the E,E isomer remaining in solution after 24 h.

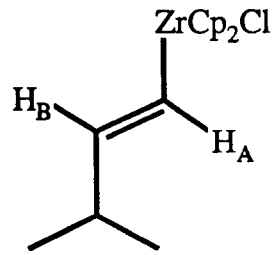
Effect of diphenyldiselenide-d_{10} (Ph_2Se_2-d_{10})[114]

It was shown, by mass spectroscopy, that when 1:1 mixtures of Ph_2Se_2-d_{10} and Ph_2Se_2 were photolyzed with fluorescent light in C_6D_6 significant quantities of Ph_2Se_2-d_5 were produced. A similar result was seen on thermolysis (80°C in the dark for 24 h) of such a mixture. A solution of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (26 mg, 0.12 mmol) in 0.5 mL of C_6D_6 [or (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (30 mg, 0.13 mmol) in $CDCl_3$] containing Ph_2Se_2-d_{10} (1 equiv) was photolyzed, in a capped 5 mm

NMR tube, for 2 h with fluorescent light. Mass spectroscopy indicated the presence of significant amounts of 1-(phenylseleno)-1,3-butadiene-d_5 [or 1-(phenylseleno)-4-methoxy-1,3-butadiene-d_5] and Ph_2Se_2-d_5. A similar result was observed on thermolysis (at 80°C), in the dark, of these mixtures.

(*E*)-Chlorobis(η^5-cyclopentadienyl)(3-methylbuten-1-yl)zirconium(IV) **110** and 1-(phenylseleno)-3-methylbut-1-ene **109**





Isopropyacetylene (0.53 g, 7.76 mmol) was vacuum transferred to a stirred slurry of $Cp_2ZrCl(H)$ **1** (1.00 g, 3.88 mmol) in 25 mL of toluene, contained in reactor bomb. The mixture was stirred in the dark at room temperature until a pale yellow homogeneous solution resulted. The amount of solvent was reduced to ~10 mL and, after addition of hexanes, the solution was left to crystallize at -30°C. The desired product was isolated as white crystals **110** (1.05 g, 83%); IR (Nujol): 3111, 3093, 1653, 1570, 1309, 1018, 990, 810 and 734 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.92 (6H, d, $CH\underline{Me}_2$, J = 7 Hz), 2.06 (1H, m, $C\underline{H}Me_2$, J = 7 Hz, J_{CB} = 6 Hz, J_{CA} = 1 Hz), 5.73 (1H, dd, H_B, J_{BA} = 18 Hz, J_{BC} = 6 Hz), 6.25 (10H, s, Cp), 6.72 (1H, dd, J_{AB} = 18 Hz, J_{AC} = 1 Hz). *Anal.* calcd. for $C_{15}H_{19}ClZr$: C 55.27, H 5.78; found: C 55.42, H 5.78.

To a stirred solution of **110** (75 mg, 0.23 mmol) in 1 mL of toluene at -20°C, in the dark, was added *N*-PSP (70 mg, 0.23 mmol). Workup according to general

procedure 5yielded a colorless oil **109** (43 mg, 83%); λ_{max} (hexane): 258 nm (ε 9,500); δ ($CDCl_3$, 400 MHz, ^1H NMR): 0.81 (6H, d, $CH\underline{Me}_2$, J = 7 Hz), 2.09 (1H, m, $C\underline{H}Me_2$, J = 7 Hz, J_{CB} = 7 Hz, J_{CA} = 1 Hz), 6.00 (1H, dd, H_B, J_{BA} = 15 Hz, J_{BC} = 7 Hz, J_{BSe} = 10.5 Hz), 6.30 (1H, dd, J_{AB} = 15 Hz, J_{AC} = 1 Hz), 6.94-7.02 (3H, m), 7.40 (3H, m).

Photolysis of 1-(phenylseleno)-3-methylbut-1-ene **109**

A solution of 1-(phenylseleno)-3-methylbut-1-ene **109** (43 mg, 0.19 mmol) in 0.5 mL of C_6D_6, in a capped 5 mm NMR tube, was photolyzed with fluorescent light for 24 h. ^1H NMR spectroscopy indicated that isomerization had taken place to give a 92:8 E/Z isomeric mixture.

Effect of diphenyldiselenide (Ph_2Se_2) on the photolysis of (*E*,*E*)-1,3-butadienyl-4-methoxy-1-diphenylphosphine **79b** and 1-(phenylseleno)-3-methylbut-1-ene **88a**

To a solution of (*E*,*E*)-1,3-butadienyl-4-methoxy-1-diphenylphosphine **79b** (35 mg, 0.13 mmol) in 0.5 mL of C_6D_6 was added Ph_2Se_2 (3 mg, 7 mol %). The mixture was then photolyzed with fluorescent light. ^1H NMR spectroscopy indicated that isomerization had taken place to give a 69:17 of E,E/E,Z:unknown mixture of stereoisomers after only 1.5 h irradiation.

To a solution of 1-(phenylseleno)-3-methylbut-1-ene **109** (34 mg, 0.15 mmol) in 0.5 mL of of C_6D_6 was added Ph_2Se_2 (3 mg, 6 mol %). The mixture was then photolyzed

with fluorescent light. ^{1}H NMR spectroscopy indicated that isomerization had taken place to give a 87:13 E/Z mixture of stereoisomers after 24 h irradiation.

Effect of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** on the photolysis of (*E*,*E*)-1,3-butadienyl-4-methoxy-1-diphenylphosphine **79b** and 1-(phenylseleno)-3-methylbut-1-ene **109**

To a solution of (*E*,*E*)-1,3-butadienyl-4-methoxy-1-diphenylphosphine **79b** (39 mg, 0.15 mmol) in 0.5 mL of C_6D_6 was added (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (21 mg, 0.10 mmol, 0.70 mol %). The mixture was then photolyzed with fluorescent light. No isomerization of **79b** was observed until **88a** began to isomerize. ^{1}H NMR spectroscopy indicated that isomerization had taken place to give a 64:16 of E,E/E,Z:unknown mixture of stereoisomers after 65 h irradiation. At this point **88a** was present as an 2:1 E/Z isomeric mixture.

To a solution of 1-(phenylseleno)-3-methylbut-1-ene **109** (32 mg, 0.14) in 0.5 mL of C_6D_6 was added (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (21 mg, 0.10 mmol, 0.70 mol %). The mixture was then photolyzed with fluorescent light. ^{1}H NMR spectroscopy indicated that isomerization had taken place to give an 86:14 E/Z mixture of stereoisomers after 24 h irradiation. At this point **88a** was present as an 2:1 E/Z isomeric mixture.

6.5.3 Photolysis of 1-Phenylthio-1,3-dienes

Photolysis of (*E*)-1-(phenylthio)-1,3-butadiene **89a**

A solution of (*E*)-1-(phenylthio)-1,3-butadiene **89a** (25 mg, 0.15 mmol) in 0.5 mL of C_6D_6 was placed in a capped NMR tube under nitrogen. The solution was then irradiated with fluorescent light for 5 h. The ^1H NMR spectrum of the solution, after photolysis, indicated that isomerization of **89a** had taken place to give a 2:1 mixture of E/Z isomers. ^1H NMR data, taken from the spectrum of the mixture, of (Z)-1-(phenylthio)-1,3-butadiene were; δ (C_6D_6, 400 MHz, ^1H NMR): 5.03 (1H, dddd, H_E, J_{ED} = 10 Hz, J_{ED} = 1.75 Hz, J_{EB} = 0.75 Hz, J_{EA} = 0.5 Hz), 5.11 (1H, dddd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz, J_{DA} = 1 Hz, J_{DB} = 0.75 Hz), 5.99 (1H, dddd, H_A, J_{AB} = 9 Hz, J_{AD} = 1 Hz, J_{AC} = 0.75 Hz, J_{AE} = 0.5 Hz), 6.10 (1H, dddd, H_B, J_{BC} = 10 Hz, J_{BA} = 9 Hz, J_{BD} = J_{BE} = 0.75 Hz), 6.13 (1H, dddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz, J_{CA} = 0.75 Hz), 6.89 (1H, m), 6.95 (2H, m), 7.23 (2H, m).

Photolysis of (*E*,*E*)-1-phenylthio-4-methoxy-1,3-butadiene **89b**

A solution of (*E*,*E*)-1-(phenylthio)-4-methoxy-1,3-butadiene **89b** [or (*E*,*Z*)-1-(phenylthio)-4-methoxy-1,3-butadiene **89c**] (27 mg, 0.14 mmol) in 0.5 mL of $CDCl_3$ was photolyzed with fluorescent light for 1.5 h. ^1H NMR of the solution, after photolysis, indicated that isomerization of **89b** had taken place to give a 39(±2):13(±1):35(±2)13(±1) mixture of Z,E/Z,Z/E,E/E,Z isomers. These ratios were determined, from the ^1H NMR, by integration of the OMe resonances. ^1H NMR data, taken from the spectrum of the mixture, were: (*Z*,*E*)-1-(phenylthio)-4-methoxy-1,3-butadiene; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.63 (3H, s, OMe), 5.98 (1H, ddd,.H_A, J_{AB} = 9 Hz, J_{AC} = 0.75 Hz, J_{AD} = 0.5 Hz), 5.99

(1H, ddd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10.5 Hz, J_{CA} = 0.75 Hz), 6.39 (1H, ddd, H_B, J_{BC} = 10.5 Hz, J_{BA} = 9 Hz, J_{BD} = 0.5 Hz), 6.82 (1H, d, H_D, J_{DC} = 12.5 Hz), 7.21-7.27 (1H, m), 7.30-7.42 (4H, m); (Z,Z)-1-(phenylthio)-4-methoxy-1,3-butadiene; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.69 (3H, s, OMe), 5.19 (1H, ddd, H_C, J_{CB} = 10.5 Hz, J_{CD} = 6 Hz, J_{CA} = 1 Hz), 6.11 (1H, ddd, H_D, J_{DC} = 6 Hz, J_{DA} = 1.5 Hz, J_{DB} = 1 Hz), 6.13 (1H, ddd, H_A, J_{AB} = 9 Hz, J_{AD} = 1.5 Hz, J_{AC} = 1 Hz), 6.74 (1H, ddd, H_B, J_{BC} = 10.5 Hz, J_{BA} = 9 Hz, J_{BD} = 1 Hz), 7.21-7.27 (1H, m), 7.30-7.42 (4H, m).

6.5.4 Thermal Isomerization of 1-(Phenylseleno)-1,3-dienes in Capped and Sealed 5 mm NMR Tubes

A solution of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** (28 mg, 0.13 mmol) in 0.5 mL of C_6D_6 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then heated in the dark at 80°C for 48 h. ^1H NMR spectroscopy of the solution indicated that isomerization had taken place to give an 2:1 E/Z mixture of 1-(phenylseleno)-1,3-butadiene.

A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (30 mg, 0.13 mmol) in 0.5 mL of C_7D_8 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then heated in the dark at 80°C for 48 h. ^1H NMR spectrum of the solution indicated that isomerization had taken place to a give a mixture of isomers (Z,E/Z,Z/E,E/E,Z) of the composition described above.

A solution of (*E*,*Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88c** (29 mg, 0.12 mmol) in 0.5 mL of C_7D_8 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then heated in the dark at 80°C for 48 h. ^1H NMR spectrum of the solution indicated that isomerization had taken place to a give a mixture of isomers (Z,E/Z,Z/E,E/E,Z) of the composition described above for the thermolysis of **88b**.

Thermolysis at 80°C of a solution of (*E*)-1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d** (34 mg, 0.13 mmol) in 0.5 mL of C_6D_6 in the dark showed no isomerization after 4 days.

Thermolysis, at 80°C in the dark, of a solution of 1-(phenylseleno)-1,3-butadiene **88a** (27 mg, 0.13 mmol) in 0.5 mL of C_6D_6 in a sealed tube under nitrogen for 48 h resulted in no isomerization. When the experiment was repeated (same concentration of **88a**) with the tube sealed under dry air (air was passed through a 20 x 2 cm column of Drierite®) or under nitrogen in an acid-washed tube (tube was soaked in 12 M HCl for 3 h, then dried at 120°C for 3 h) the same results were obtained: no isomerization.

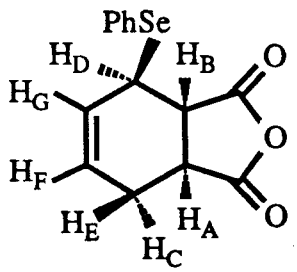
A solution of **88a** (35 mg, 0.17 mmol) in 0.5 mL of C_6D_6 containing azobisisobutyronitrile (AIBN) (2 mg, ~5 mol %) when heated at 80°C in the dark for 3 h resulted in a 2:1 E/Z mixture of stereoisomers.

Thermolysis, at 80°C in the dark, of a solution of 1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (29 mg, 0.12 mmol) in 0.5 mL of C_7D_8 contained in a sealed tube under nitrogen for 48 h resulted in only limited isomerization (less than 30% conversion of the E,E isomer of **88b**). When the experiment was repeated (same concentration of **88b**) with a tube sealed under dry air or under nitrogen in an acid-washed tube, both reactions gave rise to pre-equilibrium isomeric mixtures (~40% conversion of the E,E isomer of **88b**).

A solution of **88b** (33 mg, 0.14 mmol) in 0.5 mL of C_7D_8 containing azobisisobutyronitrile (AIBN) (2 mg, ~5 mol) when heated at 80°C in the dark for 3 h resulted in an equilibrium mixture of E,Z/Z,Z/E,E/Z,E stereoisomers.

6.5.5 Diels-Alder Reactivity of 1-(Phenylseleno)-1,3-dienes with Maleic Anhydride.

Diels-Alder adducts of (*E*)-1-(phenylseleno)-1,3-butadiene **88a** and maleic anhydride **121, 122 and 123**



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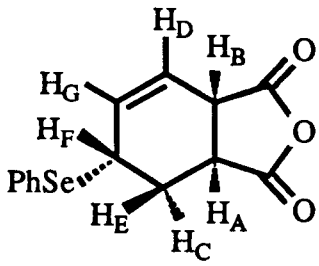
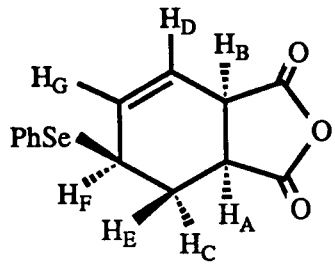


122



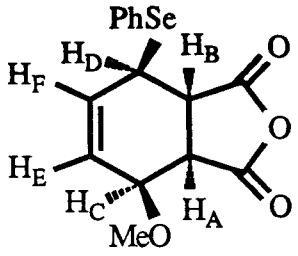
123

To a pale yellow solution of 1-(phenylseleno)-1,3-butadiene **88a** (137 mg, 0.66 mmol) in 2 mL of toluene was added maleic anhydride (64 mg, 0.66 mmol). The solution immediately turned bright yellow, and was transferred to a reactor bomb and heated in the dark for 22 h at 110°C. On evaporation of the pale yellow solution a yellow oil was obtained. Crystallization from a toluene/hexanes mixture at -30°C gave a white solid **121** (156 mg, 78%); IR (Nujol): 1855, 1778, 1577, 1241, 1023, 968, 733 and 687 cm^{-1}; δ (C_7D_8, 400 MHz, ^1H NMR): 1.79 (1H, dddd, H_C, J_{CE} = 17 Hz, J_{CA} = 11 Hz, J_{CF} = 6 Hz, J_{CG} = 1.75 Hz), 2.14 (1H, dddd, H_E, J_{EC} = 17 Hz, J_{EA} = 7 Hz, J_{EF} = 2.75 Hz, J_{EG} = 2.25 Hz), 2.42 (1H, ddd, H_A, J_{AC} = 11 Hz, J_{AB} = 10.5 Hz, J_{AC} = 7 Hz), 2.84 (1H, dd, H_B, J_{BA} = 10.5 Hz, J_{BD} = 5.5 Hz), 3.68 (1H, dd, H_D, J_{DG} = 6 Hz, J_{DB} = 5.5 Hz), 5.32 (1H, ddd, H_F, J_{FG} = 10 Hz, J_{FC} = 6 Hz, J_{FE} = 2.75 Hz), 5.76 (1H, dddd, H_G, J_{GF} = 10 Hz, J_{GD} = 6 Hz, J_{GE} = 2.25 Hz, J_{GC} = 1.75 Hz), 7.00 (3H, m), 7.43 (2H, m). *Anal.* calcd. for $C_{14}H_{12}O_3Se$: C 54.74, H 3.94; found: C 54.47, H 3.91.

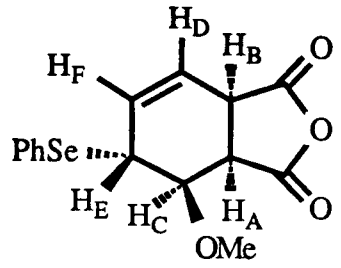
To a pale yellow solution of 1-(phenylseleno)-1,3-butadiene **88a** (68 mg, 0.33 mmol) in 0.5 mL of C_7D_8 was added maleic anhydride (32 mg, 0.33 mmol). The solution

immediately turned bright yellow, and was sealed under nitrogen in a 5 mm NMR tube and heated in the dark for 63 h at 140°C. On evaporation of the pale yellow solution a yellow oil was obtained. The oil was washed with hexanes to remove Ph_2Se_2 formed during the reaction; all attempts at crystallization failed. The pale yellow oil **122/123** (74 mg, 70%) was seen to be a 2:1 mixture of cycloadducts by ^1H NMR. The following data were obtained for the mixture; IR (film): 1870, 1783, 1478, 1435, 1220, 1107, 932, 745 and 694 cm^{-1}; Major isomer **122** δ (C_7D_8, 400 MHz, ^1H NMR): 1.47 (1H, dddd, H_C, J_{CE} = 14 Hz, J_{CA} = 9.5 Hz, J_{CF} = 5 Hz, J_{CB} = 0.5 Hz), 1.74 (1H, ddd, H_E, J_{EC} = 14 Hz, J_{EA} = J_{EF} = 5.5 Hz), 2.59 (1H, dddd, H_B, J_{BA} = 10 Hz, J_{BD} = 4.5 Hz, J_{BG} = 2.5 Hz, J_{BC} = 0.5 Hz), 2.86 (1H, ddd, H_A, J_{AB} = 10 Hz, J_{AC} = 9.5 Hz, J_{AE} = 5.5 Hz), 3.32 (1H, dddd, H_F, J_{FE} = J_{FG} = 5.5 Hz,J_{FC} = 5 Hz, J_{FD} = 1.25 Hz), 5.45 (1H, ddd, H_D, J_{DG} = 9.5 Hz, J_{DB} = 4.5 Hz, J_{DF} = 1.25 Hz), 5.72 (1H, ddd, H_G, J_{GD} = 9.5 Hz, J_{GF} = 5.5 Hz, J_{GB} = 2.5 Hz), 6.96-7.05 (3H, m), 7.32 (2H, m); Minor isomer **123** δ (C_7D_8, 400 MHz, ^1H NMR): 1.53 (1H, dddd, H_C, J_{CE} = 14.5 Hz, J_{CA} = 7.5 Hz, J_{CF} = 5 Hz, J_{CB} = 1 Hz), 1.92 (1H, ddd, H_E, J_{EC} = 14.5 Hz, J_{EF} = 4.5 Hz, J_{EA} = 4.0 Hz), 2.29 (1H, ddd, H_A, J_{AB} = 10 Hz, J_{AC} = 7.5 Hz, J_{AE} = 4 Hz), 2.77 (1H, dddd, H_B, J_{BA} = 10 Hz, J_{BD} = 5.5 Hz, J_{BG} = 2 Hz, J_{BC} = 1 Hz), 3.35 (1H, dddd, H_F, J_{FG} = 5.5 Hz, J_{FC} = 5 Hz, J_{FE} = 4.5 Hz, J_{FD} = 1 Hz), 5.49 (1H, ddd, H_D, J_{DG} = 9.5 Hz, J_{DB} = 5.5 Hz, J_{DF} = 1 Hz), 5.79 (1H, ddd, H_G, J_{GD} = 9.5 Hz, J_{GF} = 5.5 Hz, J_{GB} = 2 Hz), 6.96-7.05 (3H, m), 7.47 (2H, m); *m/e* (relative intensity): 51 (33.9), 77 (100), 78 (57.7), 79 (56.1), 123 (50.3), 129 (20.5), 154 (29.2), 155 (29.1), 157 (39.8), 158 (54.4), 195 (22.6) and 308 (M^+, 68.2). *Exact Mass* calcd. for $C_{14}H_{12}O_3{}^{80}Se$: 307.9951; found: 307.9946.

Diels-Alder adducts of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** and maleic anhydride **114** and **115**



114



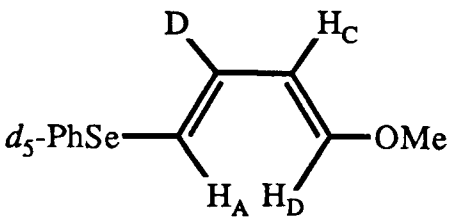
115

To a pale yellow solution of 1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (117 mg, 0.49 mmol) in 2 mL of toluene was added maleic anhydride (48 mg, 0.49 mmol). The solution immediately turned bright yellow, and was transferred to a reactor bomb and heated in the dark for 20 h at 80°C. On cooling to room temperature a white solid precipitated; the solid was collected by filtration and washed with a 1:1 mixture of toluene and hexanes to yield **114** (142 mg, 86%); IR (Nujol): 1858, 1777, 1220, 1040, 925, 784, 756 and 697 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.29 (3H, s, OMe), 3.38 (1H, dd, H_A , J_{AB} = 11 Hz, J_{AC} = 5 Hz), 3.79 (1H, dd, H_B, J_{BA} = 11 Hz, J_{BD} = 8.5 Hz), 3.90 (1H, dd, H_D, J_{DB} = 8.5 Hz, J_{DF} = 7.5 Hz), 4.29 (1H, dd, H_C, J_{CE} = 5.5 Hz, J_{CA} = 5 Hz), 6.09 (1H, dd, H_E, J_{EF} = 9 Hz, J_{EC} = 5.5 Hz), 6.56 (1H, dd, H_F, J_{FE} = 9 Hz, J_{FD} = 7.5 Hz), 7.30 (3H, m), 7.71 (2H, m). *Anal.* calcd. for $C_{15}H_{15}O_4Se$: C 53.42, H 4.22; found: C 53.62, H 4.22.

To a pale yellow solution of 1-(phenylseleno)-4-methoxy-1,3-butadiene **88b** (155 mg, 0.65 mmol) in 2 mL of toluene was added maleic anhydride (64 mg, 0.65 mmol). The solution immediately turned bright yellow, and was transferred to a reactor bomb and heated under light from a 275 W sunlamp (positioned 30 cm from the bomb) for 20 h at 80°C. Hexanes was added dropwise to the rapidly stirred bright yellow solution, resulting in precipitation of a white solid (19 mg - shown to be **114** by ^1H NMR spectroscopy). On evaporation a yellow oil was obtained, which was washed thoroughly with hexanes (to remove

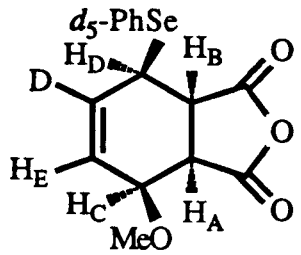
Ph_2Se_2), leaving a pale yellow oil **115** (149 mg, 68%); IR (film): 1874, 1785, 1480, 1438, 1226, 936, 740 and 690 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 2.32 (1H, ddd, H_B, J_{BA} = 9.5 Hz, J_{BD} = 4 Hz, J_{BF} = 2.5 Hz), 2.52 (3H, s, OMe), 3.27 (1H, dd, H_A, J_{AB} = 9.5 Hz, J_{AC} = 4 Hz), 3.49 (1H, ddd, H_E, J_{EF} = 5.5 Hz, J_{EC} = 3 Hz, J_{ED} = 0.75 Hz), 3.80 (1H, ddd, H_C, J_{CA} = 4.5 Hz, J_{CE} = 3 Hz, J_{CF} = 1.25 Hz), 5.54 (1H, dddd, H_F, J_{FD} = 10 Hz, J_{FE} = 5.5 Hz, J_{FB} = 2.5 Hz, J_{FC} = 1.25 Hz), 5.67 (1H, ddd, H_D, J_{DF} = 10 Hz, J_{DB} = 4 Hz, J_{DE} = 0.75 Hz), 6.86-6.97 (3H, m), 7.29 (2H, m); *m/e* (relative intensity): 50 (20.4), 77 (41.7), 148 (31.4), 171 (100) 156 (29.9), 158 (59.9) and 338 (M^+, 10.3). *Exact Mass* calcd. for $C_{15}H_{15}O_4{}^{80}Se$: 338.0057; found: 338.0060.

(*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-d_5-2-*d* **88**-d_6



As outlined in general procedure 5, (*E*,*E*)-chlorobis(h^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* **55**-d_1 (75 mg, 0.22 mmol) was reacted with *N*-PSP-d_5 (68 mg, 0.22 mmol) to yield a pale yellow oil **88**-d_6 (47 mg, 87%); IR (film): 2274, 1628, 1543, 1458, 1338, 1213, 1110, 928 and 640 cm^{-1}; ^1H NMR was identical to **88**-d_1 with the absence of the aromatic resonances; *m/e* (relative intensity): 54 (35.0), 82 (41.4), 83 (20.8), 121 (27.3), 123 (33.6), 133 (25.8), 134 (21.0), 135 (34.4), 149 (21.5), 160 (21.2), 162 (40.2), 164 (66.6), 165 (27.2), 166 (100) and 246 (M^+, 73.7). *Exact Mass* calcd. for $C_{11}H_6{}^2H_6O^{80}Se$: 246.0430; found: 246.0425.

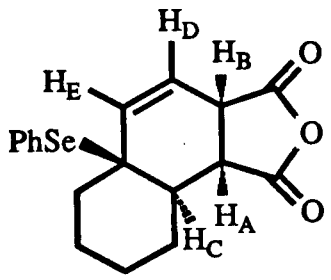
Diels-Alder adduct of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene-d_5-2-*d* **88**-d_6 and maleic anhydride **114**-d_6



143-d_6

The preparation of **114**-d_6 was as described above for **114**. To a solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene-d_5-2-*d* **88**-d_6 (160 mg, 0.65 mmol) in 2 mL of toluene was added maleic anhydride (64 mg, 0.65 mmol). Workup provided a white solid **114**-d_6 (187 mg, 84%); IR (Nujol): 2287, 1859, 1778, 1229, 1087, 938, 841, 768 and 683 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 3.29 (3H, s, OMe), 3.38 (1H, dd, H_A, J_{AB} = 11 Hz, J_{AC} = 5 Hz, 3.79 (1H, dd, H_B, J_{BA} = 11 Hz, J_{BD} = 8.5 Hz), 3.90 (1H, d, H_D, J_{DB} = 8.5 Hz), 4.29 (1H, dd, H_C, J_{CE} = 5.5 Hz, J_{CA} = 5 Hz), 6.09 (1H, d, H_E, J_{EC} = 5.5 Hz); *m/e* (relative intensity): 83 (100), 105 (36.7), 110 (14.9), 149 (15.6), 161 (25.2), 162 (18.8), 163 (48.4), 181 (14.7) and 344 (M^+, 6.5). *Exact Mass* calcd. for $C_{15}H_8{}^2H_6O_4{}^{80}Se$: 344.0434; found: 344.0435.

Diels-Alder adduct of (*E*)-1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d** and maleic anhydride **124** and **125**



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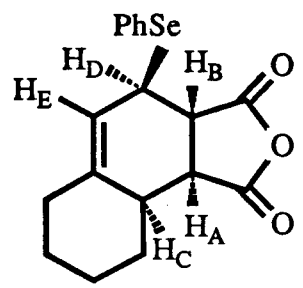


124

To a colorless solution of (*E*)-1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d** (81 mg, 0.31 mmol) in 2 mL of toluene was added maleic anhydride (30 mg, 0.31 mmol). The solution immediately turned bright yellow, and was transferred to a reactor bomb and heated in the dark for 55 h at 60°C. Evaporation of the pale yellow solution gave a yellow oil . Crystallization from a toluene/hexanes mixture at -30°C gave a white solid **124** (87 mg, 78%); IR (Nujol): 1860, 1776, 1224, 1011, 933, 902, 793 and 740 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.97 (2H, m), 1.30 (1H, m), 1.42 (1H, m), 1.56 (2H, m), 1.80 (1H, m), 1.91 (1H, m), 2.39 (1H, m), 2.42 (1H, dd, H_A, J_{AD} = 10.5 Hz, J_{AB} = 9 Hz), 2.77 (1H, dd, H_B J_{BA} = 9 Hz, J_{BC} = 5.5 Hz), 3.74 (1H, dddd, H_C, $J_{CB} = J_{CE}$ = 5.5 Hz, $J_{CD} = J$ = 1.5 Hz), 5.47 (1H, ddd, H_E, J_{EC} = 5.5 Hz, $J_{ED} = J$ = 1.5 Hz), 6.99 (3H, m), 7.55 (2H, m). *Anal.* calcd. for $C_{18}H_{17}O_3Se$: C 59.84, H 5.02; found: C 59.90, H 5.00.

As described above, (*E*)-1-phenylseleno-[2-(1-cyclohexen-1-yl)ethene] **88d** (208 mg, 0.79 mmol) in 2 mL of toluene containing maleic anhydride (77 mg, 0.79 mmol) were heated in the dark at 110°C for 18 h. Crystallization from toluene/hexanes yielded a white solid **125** (223 mg, 78%); IR (Nujol): 1851, 1778, 1210, 1020, 936, 793, 740 and 693 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR): 1.32 (2H, m), 1.71 (1H, m), 1.95 (2H, m), 1.97 (1H, m, H_D), 1.98 (1H, m), 2.17 (2H, m), 3.22 (1H, dd, H_B, J_{BA} = 10 Hz, J_{BD} = 7.5 Hz), 3.82 (1H, ddd, H_A, J_{AB} = 10 Hz, J_{AC} = 6 Hz, J_{AE} = 1.75 Hz), 5.39 (1H, dd, H_E, J_{EC} = 9.5 Hz, J_{EA} = 1.75 Hz), 5.61 (1H, dd, H_C, J_{CE} = 9.5 Hz, J_{CA} = 6 Hz), 7.23-7.35 (3H, m), 7.47 (2H, m). *Anal.* calcd. for $C_{18}H_{17}O_3Se$: C 59.84, H 5.02; found: C 59.99, H 5.08.

Effect of Ph_2Se_2-d_{10} and AIBN on the 1,3-rearrangement of **114**

To a solution of **114** (30 mg, 0.09 mmol) in 0.5 mL of C_6D_6 was added Ph_2Se_2-d_{10} (7 mg, 25 mol %) or AIBN (4 mg, 25 mol %). The mixtures were sealed in 5 mm NMR tubes and heated at 80°C in the dark for 20 h. For Ph_2Se_2-d_{10}, 5% conversion of **114** to **115** was observed by ^1H NMR spectroscopy, while AIBN gave only 15% conversion.

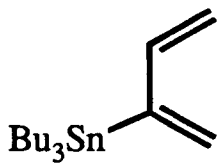
Crossover Experiment on the photochemical 1,3-rearrangement of **114** to **115**

A known ratio (approximately 1:1) of **114** (25 mg, 0.07 mmol) and **114**-d_6 (25 mg, 0.07 mmol) dissolved in 0.5 mL of $CDCl_3$ was photolyzed with fluorescent light (at 29°C) in a 5 mm NMR tube. Analysis for crossover products was obtained by low resolution mass spectrometry. See pp 130-133 for a discussion of the results.

6.6 Preparation and Diels-Alder Reactivity of 2-(Trialkylstannyl)-1,3-butadienes and 2-(Phenylseleno)-1,3-butadiene.

6.6.1 Synthesis and Cycloaddition Reactions of 2-(Phenylseleno)-1,3-butadiene and 2-(Trialkyl)-1,3-butadienes.

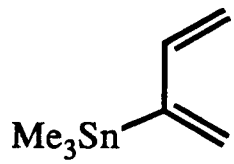
1,3-Butadienyl-2-tributylstannane **128a**



Tributyltin chloride (14.64 g, 45 mmol) dissolved in 25 mL of THF was added dropwise, at room temperature, to a stirred solution of Grignard reagent **24** (75 mL, 45 mmol; 0.6 M solution in THF) under nitrogen. The mixture was stirred at room temperature for a further 6 h, when 10 mL of water was added to decompose any unreacted Grignard reagent. At this stage, most of the THF was evaporated leaving a white slurry which was extracted with 3 x 100 mL portions of diethyl ether (Et_2O). The Et_2O layer was washed with 2 x 100 mL portions of aqueous 2 M potassium fluoride to remove any unreacted Bu_3SnCl. Finally the organic layer was washed with 2 x 100 mL of water and dried over anhydrous $MgSO_4$. Evaporation of the solvent and distillation under vacuum yielded one fraction (40-50°C/10^{-3} Torr; 1 Torr = 133.3 Pa) of a colorless liquid **128a** (10.9 g, 71%).

Spectroscopic data for **128a** were consistent with those reported in the literature.[97a]

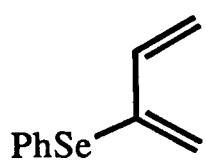
1,3-Butadienyl-2-trimethylstannane **128b**



Trimethyltin chloride (6.0 g, 30 mmol) dissolved in 25 mL of THF was added dropwise, at room temperature, to a solution of Grignard reagent **24** (50 mL, 30 mmol; 0.6 M in THF) under nitrogen. The mixture was stirred at room temperature for a further 6 h. The workup was identical to that described for **128a**. Distillation, at reduced pressure, yielded **128b** (4.35 g, 65%) as a colorless liquid, distilling at 42°C/11 Torr.

Spectroscopic data for this compound were identical to those reported in the literature.[98]

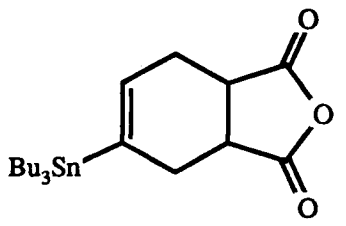
2-(Phenylseleno)-1,3-butadiene **129**



Phenylselenenyl chloride (PhSeCl) (4.78 g, 25 mmol) dissolved in 25 mL of THF was added dropwise, at room temperature, to a stirred solution of Grignard reagent **24** (100 ml, 25 mmol; 0.25 M in THF) under nitrogen. The deep red color of the PhSeCl discharged immediately on addition to **24**; the reaction was then stirred at room temperature for a further hour. The workup was identical to that described for **128a**, with the omission of the aqueous

KF washings. After drying the organic layer over $MgSO_4$, evaporation of the solvent yielded a yellow oil. Distillation of the latter under vacuum (10^{-3} Torr) gave a pale yellow oil **129** (3.66 g, 70%); IR (film): 1620, 1572, 1477, 1439, 1214, 914 and 735 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 5.00 (1H, d, J = 10.5 Hz), 5.34 (1H, m), 5.53 (1H, m), 5.62 (1H, d, J = 17 Hz), 6.24 (1H, dd, J = 10.5 Hz, 17 Hz), 6.94 (3H, m) and 7.44 (2H, m). *Anal.* calcd. for $C_{10}H_{10}Se$: C 57.43, H 4.82; found: C 57.66, H 4.81.

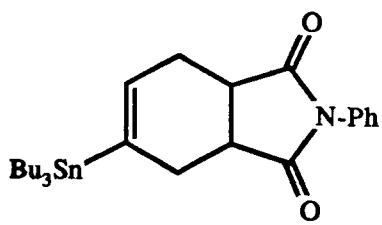
Diels-Alder adduct of **128a** with maleic anhydride **131**



A solution of **128a** (500 mg, 1.46 mmol) and maleic anhydride (143 mg, 1.46 mmol) in 2 mL of toluene was stirred at room temperature under nitrogen for 48 h. The solvent was evaporated and the residue was purified directly by column chromatography on silica (eluent: ether/petroleum ether 1:2) yielding **131** (482 mg, 75%) as a white solid.

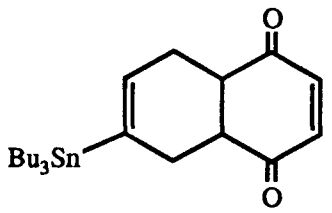
Spectroscopic data for **131** were identical to that reported in the literature.[97a]

Diels-Alder adduct of **128a** with *N*-phenylmaleimide **132**



A solution of **128a** (500 mg, 1.46 mmol) and *N*-phenylmaleimide (252 mg, 1.46 mmol) in 3 mL of toluene was refluxed for 8 h. The solvent was evaporated and the residue was subjected to column chromatography on silica (eluent: ether/petroleum ether 1:3) which yielded **132** (675 mg, 90%) as a yellow oil; IR (film): 1779, 1712, 1499, 1456, 1378, 1190, 1171 and 690 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.90 (15H, m), 1.29 (6H, m), 1.48 (6H, m), 1.84 (1H, m), 1.99 (1H, m), 2.53 (2H, m), 2.63 (1H, dd, J = 6 Hz, 15 Hz), 2.85 (1H, d, J = 15 Hz), 6.01 (1H, m), 7.00 (1H, m), 7.15 (2H, m) 7.41 (2H, m). *Anal.* calcd. for $C_{26}H_{39}NO_2Sn$: C 60.49, H 7.61, N 2.71; found: C 60.60, H 7.79, N 2.60.

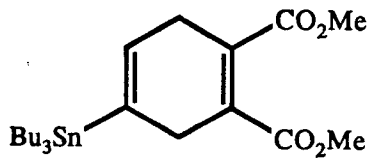
Diels-Alder adduct of **128a** with *p*-benzoquinone **133**



A solution of **128a** (500 mg, 1.46 mmol) and *p*-benzoquinone (158 mg, 1.46 mmol) in 3 mL of toluene was refluxed under nitrogen for 5 h. The solvent was evaporated and the residue was purified by column chromatography on silica (eluent: dichloromethane) to give **133** as a yellow oil (453 mg, 69%); IR (film): 1684, 1602, 1260, 1090 and 850 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.90 (15H, m), 1.32 (6H, m), 1.32 (6H, m), 1.54 (6H, m), 1.84 (1H, m), 2.17 (1H, m), 2.39 (1H, m) 2.57 (1H, m), 2.63 (1H, m), 2.70 (1H, m), 5.72 (1H, m), 6.05 (2H, s). From the chromatography of **136** a white solid (53 mg, 8%) was obtained. Spectroscopic data, as follows, indicated that this solid was the hydroquinone of **133**; IR (Nujol): 3286, 1625, 1595, 1311, 1242, 992, 807 and 743 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.93 (9H, t, J = 7 Hz), 0.99 (6H, t, J = 8 Hz), 1.37 (6H, m), 1.58 (6H,

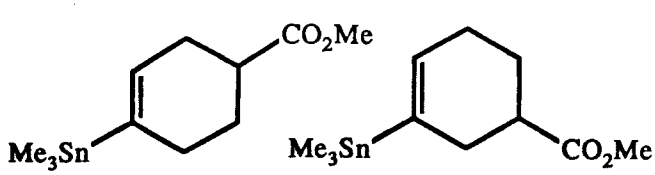
m), 3.27 (2H, m), 3.63 (2H, m), 3.83 (2H, b s, δ was concentration dependent and signal disappeared on D_2O exchange). 6.06 (1H, m), 6.10 (1H, d, J = 8.5 Hz), 6.22 (1H, d, J = 8.5 Hz); *m/e* (relative intensity): 56 (93.1), 147 (70.0), 161 (100), 281 (13.4), 338 (6.4), 395 (14.3). *Exact Mass* calcd. for $C_{18}H_{27}O_2{}^{120}Sn$ $(M\text{- n-Bu})^+$: 395.1033; found: 395.1027.

Diels-Alder adduct of **128a** with dimethyl acetylenedicarboxylate **134**



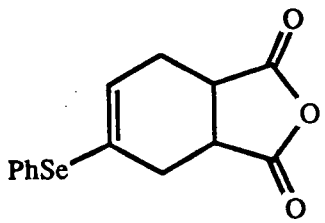
A solution of **128a** (500 mg, 1.46 mmol) and dimethyl acetylenedicarboxylate (207 mg, 1.46 mmol) in 3 mL of toluene was refluxed overnight under nitrogen. The solvent was evaporated and the residue was purified by column chromatography on silica (eluent: ether/petroleum ether 1:7) to give **134** (503 mg, 71%) as a colorless liquid; IR (film): 1736, 1726, 1668, 1618, 1434, 1261 and 1065 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.91 (15H, m), 1.32 (6H, m), 1.51 (6H, m), 2.93 (2H, m), 3.27 (2H, m), 3.42 (3H, s), 3.45 (3H, m), 5.63 (1H, m). *Anal.* calcd. for $C_{22}H_{38}O_4Sn$: C 54.46, H 7.89; found: C 54.61, H 7.87.

Diels-Alder adduct of **128b** with methyl acrylate **135a/135b**



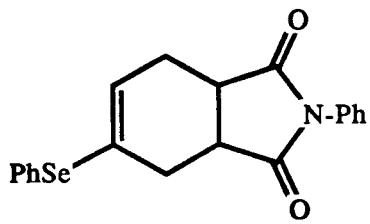
A solution of **128b** (1.73 g, 7.98 mmol) and methyl acrylate (3.43 g, 39.92 mmol) in 10 mL of toluene was refluxed overnight under nitrogen. The solvent and excess methyl acrylate were evaporated and the residue was subjected to column chromatography on silica (eluent: ether/petroleum ether 1:20) yielding **135a/135b** (1.74 g, 72%). Capillary GLC and ^{1}H NMR indicated that the regioisomers **135a/135b** were present in a 2:1 ratio. The following data were obtained for this mixture; IR (film): 1737, 1618, 1437, 1166 and 767 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR): 0.07 (9H, s), 1.67-2.54 (7H, m), 3.36 and 3.37 (3H, 2 singlets; **135a** and **135b**, respectively), 5.75 (1H, m). *Anal.* calcd. for $C_{11}H_{20}O_2Sn$: C 43.61, H 6.65; found: C 43.91, H 6.80.

Diels-Alder adduct of **129** with maleic anhydride **137**



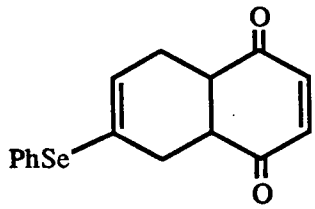
A solution of **129** (750 mg, 3.59 mmol) and maleic anhydride (351 mg, 3.59 mmol) in 3 mL of toluene was stirred at room temperature for 48 h, under nitrogen. White crystals gradually deposited from solution. Low temperature recrystallization of this material (from ether/petroleum ether) yielded pure **137** (771 mg, 70%); IR (Nujol): 1845, 1780, 1245, 1010 and 942 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR): 1.42 (1H, m), 1.76 (1H, m), 2.04 (1H, m), 2.11 (2H, m), 2.37 (1H, m), 5.61 (1H, m), 6.97 (3H, m), 7.33 (2H, m). *Anal.* calcd. for $C_{14}H_{12}O_3Se$: C 54.74, H 3.94; found: C 54.56, H 3.92.

Diels-Alder adduct of **129** with *N*-phenylmaleimide **138**



A solution of **129** (1.00 g, 4.78 mmol) and *N*-phenylmaleimide (829 mg, 4.78 mmol) in 3 mL of toluene was refluxed for 8 h under nitrogen. The solvent was evaporated and the residue was subjected to chromatography on silica (eluent: ether/petroleum ether 1:3) to give a yellow oil **138** (1.39 g, 76%); IR (film): 1960, 1882, 1782, 1715, 1597, 1575, 1384, 1180 and 745 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.75 (1H, m), 2.08 (1H, m), 2.40 (2H, m), 2.49 (1H, m), 2.78 (1H, m), 5.92 (1H, m), 6.98-7.50 (10H, m). *Anal.* calcd. for $C_{20}H_{17}NO_2Se$: C 62.83, H 4.48, N 3.66; found: C 62.91, H 4.63, N 3.80.

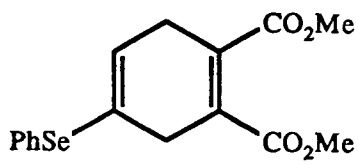
Diels-Alder adduct of **129** with *p*-benzoquinone **139**



A solution of **129** (657 mg, 3.14 mmol) and *p*-benzoquinone (340 mg, 3.14 mmol) in 2 mL of toluene was refluxed for 2 h under nitrogen. Upon cooling the reaction to room temperature a white solid deposited. After evaporation of the bulk of the solvent, the residue was dissolved in CH_2Cl_2 and passed through a short column (4 cm x 2 cm) of silica. Removal of the solvent and recrystallization from toluene/petroleum ether yielded white crystals of **139**

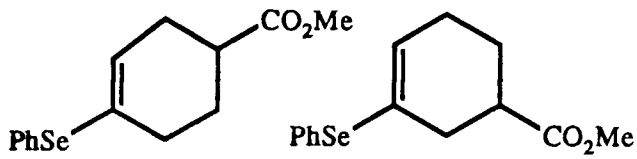
(638 mg, 64%); IR (KBr): 1676, 1598, 1577, 1475, 1435, 1263, 737 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 1.68 (1H, m), 2.05 (1H, m), 2.17 (1H, m), 2.41 (2H, m), 2,59 (1H, m), 5.87 (1H, m), 5.92 (1H, s), 5.93 (1H, s), 7.00 (3H, m) and 7.47 (2H, m). *Anal.* calcd. for $C_{16}H_{14}O_2Se$: C 60.58, H 4.45; found: C 60.56, H 4.52. Purification of **139** using long columns of silica (>10 cm x 2 cm) led to significant decomposition, as well as formation of small quantities (generally < 3%) of the corresponding hydroquinone. ^1H NMR data of the latter is as follows; δ (C_6H_6, 400 MHz): 3.21 (2H, m), 3.58 (2H, m), 3.77 and 3.90 (2 broad singlets, δ was concentration dependent; signals disappeared on D_2O exchange), 6.08 (1H, d, J = 8.5 Hz), 6.13 (1H, d, J = 8.5 Hz), 6.20 (1H, m), 6.93 (3H, m), 7.46 (2H, m).

Diels-Alder adduct of **129** with dimethyl acetylenedicarboxylate **140**



A solution of **129** (1.00 g, 4.78 mmol) and dimethyl acetylenedicarboxylate (680 mg, 4.78 mmol) in 3 mL of toluene was refluxed overnight under nitrogen. The solvent was evaporated and the residue directly subjected to column chromatography on silica (eluent: ether/petroleum ether 1:7), which yielded a yellow oil **140** (1.36 g, 81%); IR (film): 1731, 1669, 1640, 1578, 1434, 1263, 1064, 742 and 689 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 2.78 (2H, m), 3.16 (2H, m), 3.27 (3H, s), 3.41 (3H, s), 5.80 (1H, m), 6.96 (3H, m), 7.42 (2H, m). *Anal.* calcd. for $C_{16}H_{16}O_4Se$: C 54.71, H 4.59; found: C 55.00, H 4.67.

Diels-Alder adduct of **129** with methyl acrylate **141a/141b**



A solution of **129** (1.30 g, 6.22 mmol) and methyl acrylate (1.60 g, 18.66 mmol) in 3 mL of toluene was refluxed overnight under nitrogen. The solvent was evaporated and the resulting yellow liquid was distilled, under vacuum (10^{-3} Torr), to yield a pale yellow liquid (1.65 g, 90%). All data reported are for the 4:1 mixture of *para*:*meta* regioisomers **141a/141b**; the ratio having been determined by ^{1}H NMR and capillary GLC; IR (film): 1738, 1578, 1475, 1437, 1169,1020, 738 and 692 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR): 1.46-2.71 (7H, m), 3.23 and 3.30 (3H, 2 singlets; **141a** and **141b**, respectively), 6.00 and 6.03 (1H, 2 multiplets), 6.97 (3H, m), 7.44 and 7.47 (2H, 2 multiplets). *Anal.* calcd. for $C_{14}H_{16}O_2Se$: C 56.96, H 5.46; found: C 56.71, H 5.49.

Reaction of **128b** with PhSeCl

To a solution of **128b** (200 mg, 0.92 mmol) in 1 mL of toluene was added, dropwise, a toluene solution of phenylselenenyl chloride (176 mg, 0.92 mmol). On addition, the deep red color of the PhSeCl discharged immediately. The mixture was stirred overnight at room temperature, after which 75 mg of KF and 3 mL of of THF were added to destroy the Me_3SnCl by-product. After a further 2 h at room temperature, the resulting slurry was filtered through a short column of basic alumina. Evaporation of the solvent yielded a pale yellow oil

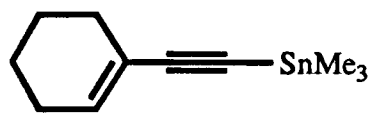
(164 mg, 85%); spectroscopic data for which were identical to that reported for the phenylseleno diene **129.**

Reaction of **135a/135b** with PhSeCl

To a solution of **135a/135b** (2:1 *para:meta*) (150 mg, 0.50 mmol) in 1 mL of toluene was added a solution of phenylselenenyl chloride (95 mg, 0.05 mmol). The mixture was stirred overnight at room temperature during which time the deep red color of the mixture had changed to a bright yellow. The reaction workup was identical to that described in the above reaction. A yellow oil was isolated whose spectroscopic data were consistent with those for **141a/141b**, with the exception that ^{1}H NMR and capillary GLC indicated a *para:meta* ratio of 2:1.

6.6.2 Attempted Syntheses of Type B' 1,3-Dienes where ML_n is Cp_2ZrCl.

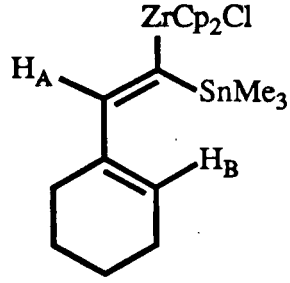
(1-Cyclohexenylethynyl)trimethylstannane **143**



To a stirred solution of 1-ethynylcyclohexene **51d** (5.0 g, 47.2 mmol) in 100 mL of THF was added, dropwise, methyllithium (37 mL, 51.9 mmol, 1.4 M in THF) at -78°C. After

stirring at this temperature for 30 min, the mixture was warmed to -20°C and stirred for 30 min. A solution of trimethyltin chloride (10.35 g, 51.9 mmol) in 25 mL of THF was added slowly and the reaction was stirred for 30 min at -20°C. The reaction was warmed to room temperature and stirred for 1 h . The solution was extracted with 3 x 100 mL of aqueous potassium fluoride to remove the excess Me_3SnCl. Extraction with 3 x 100 mL portions of Et_2O, followed by washing of the organic layer with 2 x 100 mL of water and subsequent drying over $MgSO_4$ gave, after evaporation of the solvent, a yellow oil. Distillation, at reduced pressure (75°C/12 Torr), yielded a colorless liquid **143** (8.0 g, 63%); IR (film): 3027, 2928, 2858, 2127, 1436, 1348, 1154, 1043, 918 and 768 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.15 (9H, s, J_{HSn} = 58 Hz), 1.40 (4H, m), 1.80 (2H, m), 2.33 (2H, m), 6.22 (1H, m). *Anal.* calcd. for $C_{11}H_{18}Sn$: C 49.12, H 6.75; found: 48.90, H 6.80.

(*E*)-1-Trimethylstannyl-1-chlorobis(η^5-cyclopentadienyl)-[2-(1-Cyclohexen-1-yl)ethenyl]zirconium(IV) **144**

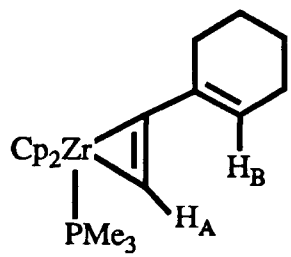


To a stirred solution of (1-cyclohexenylethynyl)trimethylstannane (500 mg, 1.86 mmol) in 20 mL of toluene was added, at room temperature in the dark, in three portions $Cp_2ZrCl(H)$ **1** (528 mg, 2.05 mmol). After 3 h the resulting orange homogeneous solution was evaporated. Analysis of the crude oil, by ^1H NMR, showed the presence of two isomers in the ratio 95:5. Crystallization of the oil from toluene/hexanes gave yellow crystals **144** (714 mg, 73%); IR (Nujol): 1556, 1016, 919, 807, 758 and 608 cm^{-1}; δ (C_6D_6, 400 MHz,

^{1}H NMR): 0.31 (9H, s, J_{HSn} = 49 Hz), 1.40-1.56 (4H, m), 1.99 (4H, m), 5.67 (1H, m, H_C), 5.86 (10H, s, Cp), 7.42 (1H, b s, H_A, J_{HSn} = 230 Hz). *Anal.* calcd. for $C_{21}H_{29}ClSnZr$: C 47.88, H 5.55, Cl 6.73; found: C 48.10, H5.70, Cl 6.95.

(Trimethylphosphine)[2-(1-cyclohexen-1-yl)-η^2-ethynyl]bis(η^5-cyclopentadienyl)zirconium(II)

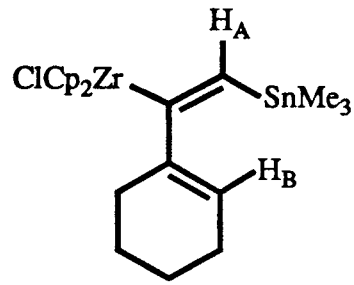
146



To a solution of (*E*)-chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) **55d** (1.0 g, 2.75 mmol) in 5 mL of toluene at -78°C was added methyllithium (1.96 mL, 2.75 mmol, 1.4 M). The reaction was stirred at this temperature for 30 min, after which it was slowly allowed to warm to room temperature. On warming, the pale yellow homogeneous solution became cloudy and darkened to an orange-red slurry. On reaching room temperature the solvent was evaporated and the product extracted with ~10:1 hexanes:toluene and filtered through Celite® to give (*E*)-[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)(methyl)zirconium(IV) (0.89 g, 94%); IR (Nujol): 1627, 1593, 1418, 1283, 1009, 951, 780, 743 and 666 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR): 0.08 (3H, s, Me), 1.52 (2H, m), 1.60 (2H, m), 2.07 (2H, m), 2.14 (4H, m), 5.73 (1H, m, H_C), 5.80 (10H, s, Cp), 6.47 (1H, d, H_B, J_{BA} = 19 Hz), 6.94 (1H, d, H_A, J_{AB} = 19 Hz); the thermal instability of this compound did not allow for further analysis. Due to this instability, (0.89 g, 2.60 mmol) was immediately reacted with PMe_3 (1.98 g, 26.0 mmol) in 2 mL of toluene for 3 days at room temperature in the dark. Evaporation of the volatiles and

crystallization of the orange-red oil from toluene/hexanes gave orange crystals of **148** (687 mg, 66%); IP (Nujol): 1627, 1593, 1418, 1283, 1009, 951, 780, 743 and 666 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.97 (9H, d, J_{HP} = 6 Hz), 1.80 (2H, m), 1.90 (2H, m), 2.53 (2H, m), 2.75 (2H, m), 5.42 (10H, d, Cp, J_{HP} = 1.5 Hz), 6.33 (1H, m, H_B), 7.51 (1H, d, H_A, J_{AP} = 4 Hz); δ (C_6D_6, 121.5 MHz, $^{31}P\{^1H\}$ NMR): 1.0 (s). *Anal.* calcd. for $C_{21}H_{29}PZr$: C 62.49, H 7.24; found: C 62.31, H 7.38.

(*E*)-[2-(1-Cyclohexen-1-yl)ethenyl]-1-trimethylstannyl-2-chlorobis(η^5-cyclopentadienyl)zirconium(IV) **148**



To a solution of **147** (100 mg, 0.25 mmol) in 1.5 mL of toluene was added Me_3SnCl (99 mg, 0.50 mmol). The mixture was stirred at room temperature for 3 h, resulting in a color change from orange to yellow. Evaporation of the volatiles followed by crystallization from toluene/hexanes gave yellow crystals **148** (97 mg, 74%); IR (Nujol): 1620, 1340, 924, 805, 769 and 727 cm^{-1}; δ (C_6D_6, 400 MHz, ^1H NMR): 0.23 (9H, s, J_{HSn} = 53 Hz), 1.55 (2H, m), 1.63 (2H, m), 1.98 (2H, m), 2.11 (2H, m), 5.28 (1H, m, H_B), 5.78 (10H, s, Cp), 7.22 (1H, s, H_A, J_{ASn} = 43 Hz). *Anal.* calcd. for $C_{21}H_{29}ClSnZr$: C 47.88, H 5.55; found: C 48.20, H 5.74.

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