Addition-Transfer Reactions of Zirconium Alkyne Complexes

by

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Abstract

A unique type of reaction, namely the addition-transfer process, has been developed. This reaction transforms the zirconium alkyne complexes, $Cp_2Zr(\eta^2$-alkyne)(PMe_3), to 2-diphenylphosphino and 2-trimethylstannyl alkenyl zirconium compounds by reaction with Ph_2PCl and Me_3SnCl respectively. In the former process, the Ph_2P group is found to be cis to the Cp_2ZrCl group whereas, in the latter case, the Me_3Sn and the Cp_2ZrCl moieties are trans to one another. This reaction was also used to synthesize dienyl zirconium compounds having Ph_2P substitutions on the diene. Preliminary mechanistic proposals suggest that the Ph_2PCl is reacting via a four-centre pathway involving the P-Cl bond and one of the Zr-C bonds of the zirconium alkyne complex; whereas Me_3SnCl reacts via a transition state similar to a π-complex.

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List of Abbreviations

Å	Angstrom units, 10^{-8}cm
^{t}Bu	tertiary-butyl group, $-C(CH_3)_3$
C	Celsius
Cp^-	η^5-cyclopentadienyl ligand, $C_5H_5^-$
d	doublet
d	deuterated
δ	chemical shift
Et	ethyl group, $-CH_2CH_3$
Hz	Hertz, cycles seconds^{-1}
g	gram
J	coupling constant
L	ligand
m	multiplet
M	Molar
Me	methyl
MHz	megaHertz
min	minute
mL	millilitre
mm	millimetre
mmol	millimole
NBS	N-bromosuccinimide
N-PSP	N-(phenylseleno)phthalimide
N-PTP	N-(phenylthio)phthalimide
NMR	nuclear magnetic resonance
NOEDIFF	nuclear Overhauser effect difference

Ph	phenyl
ppm	parts per million
R	alkyl group
R. T.	room temperature
s	singlet
tert	tertiary
THF	tetrahydrofuran
TMS	tetramethylsilane

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For Shanthini, whose love and support have sustained me throughout this work.

CHAPTER 1

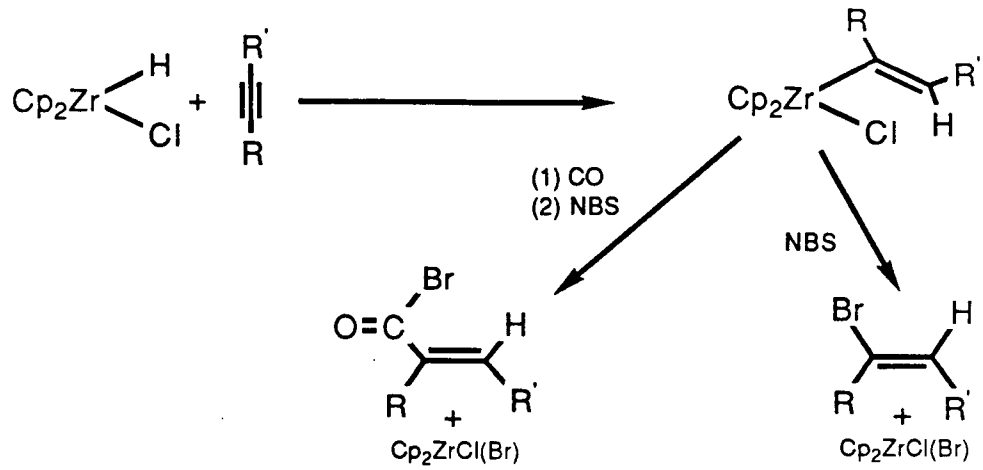
INTRODUCTION

1.1 General

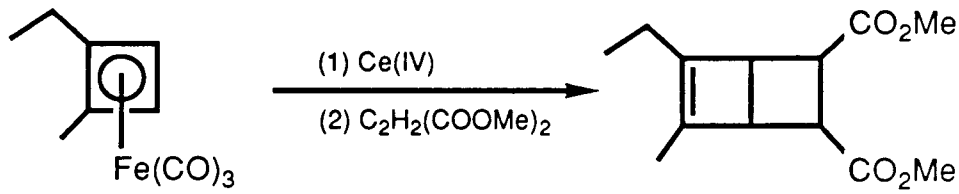
During the past few decades, numerous new classes of organometallic transition metal complexes have been synthesized.[1] Greater understanding of their reactivity and structural aspects has led to the development of new synthetic methods in organic chemistry and to a better understanding of catalytic processes. The observed chemoselectivity, regioselectivity and stereoselectivity in these reactions has attracted many organic chemists to involve such reactions in organic synthesis. In this respect, many organotransition metal complexes have been used as catalytic and stoichiometric reagents.[2] The following examples show some of the variety of such applications in organic synthesis (Scheme 1).

The use of transition metal alkyne complexes in organic synthesis has been investigated by many researchers in recent years.[1,2] The reactivity of the alkyne upon coordination to a transition metal has enabled the development of useful synthetic transformations. Coupling reactions of such alkynes have provided ways to synthesize metallacycles and cyclic organic compounds. In this chapter we will discuss synthetic aspects of zirconium alkyne complexes and their applications in organic synthesis. Transmetallation and transfer reactions of organozirconium compounds are briefly presented for comparison with the new reactions which have been developed in our laboratory.

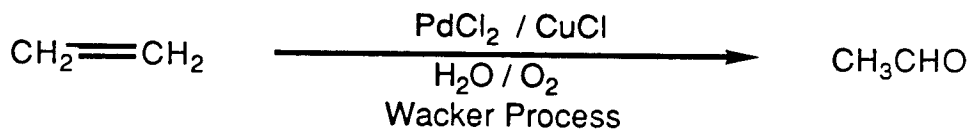
(i) Formation of Acryloyl and Alkenyl Halides



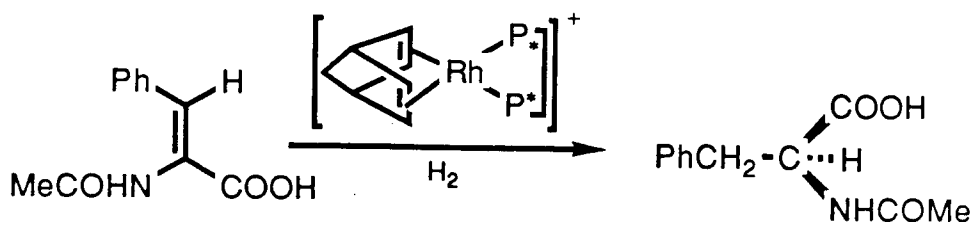
(ii) Protecting and Stabilizing Reagents



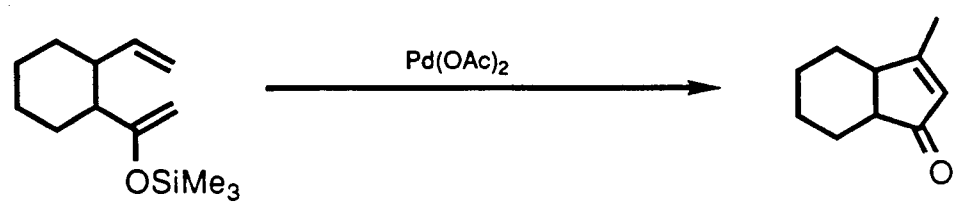
(iii) Oxidation Reactions



(iv) Asymmetric Hydrogenation



(v) Cyclization Reaction



Scheme 1

1.2 Transition Metal Alkyne Complexes

Metal alkyne complexes have been reported for nearly all the transition elements.[3] Studies of alkyne complexes in the past have led to the discovery of some novel reactivity patterns and interesting structural features. Alkynes have two bonding and two antibonding π-molecular orbitals which can interact with metal d-orbitals to give mononuclear and alkyne bridged polynuclear complexes. Upon coordination the acetylenic carbon-carbon bond distance increases from 1.20Å in the free alkyne to 1.24-1.40Å, and the linear R-C-C bond angle decreases to 168°-140°.[4a] Based on these structural aspects, metal alkyne complexes are usually drawn as metallacyclopropene complexes.

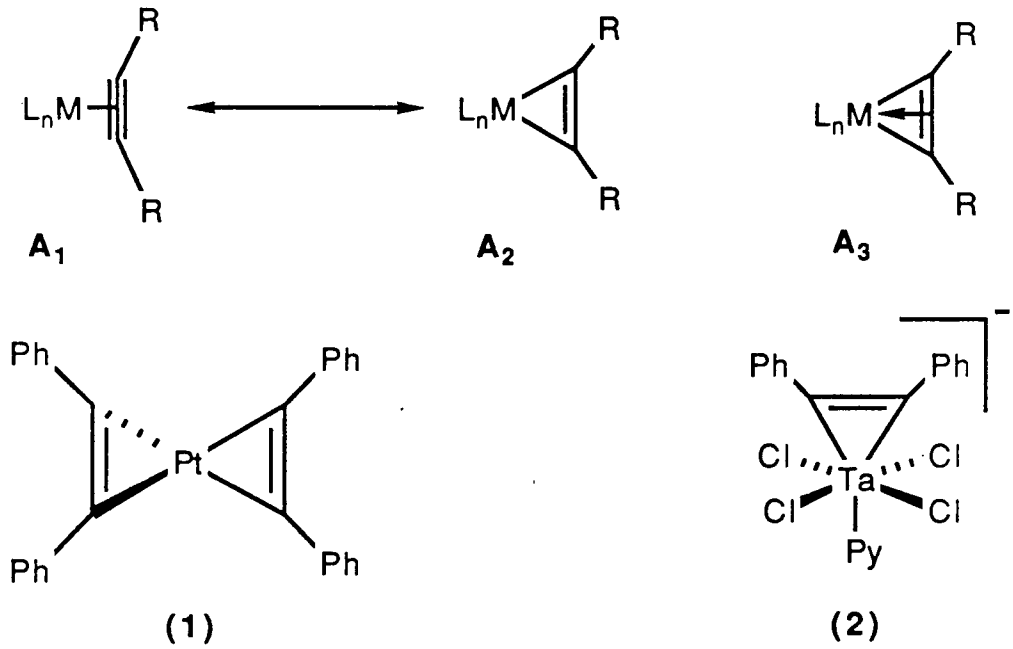


Figure 1. Valence bond structures and examples of mononuclear alkyne complexes.

The valence bond structures A_1 and A_2 represents the π and σ limiting formulations of a mononuclear alkyne complex. In A_2 the alkyne acts as a four-electron donor. The carbon-carbon bond distances in these complexes are usually in

the range of 1.27-1.29Å (Structure **1** in Figure 1). In some electron-deficient transition metal complexes longer carbon-carbon bond distances seem to suggest a σ, π type interaction as shown in the valence bond structure A_3, where the alkyne acts as a six-electron donor (Structure **2** Figure 1).[4a]

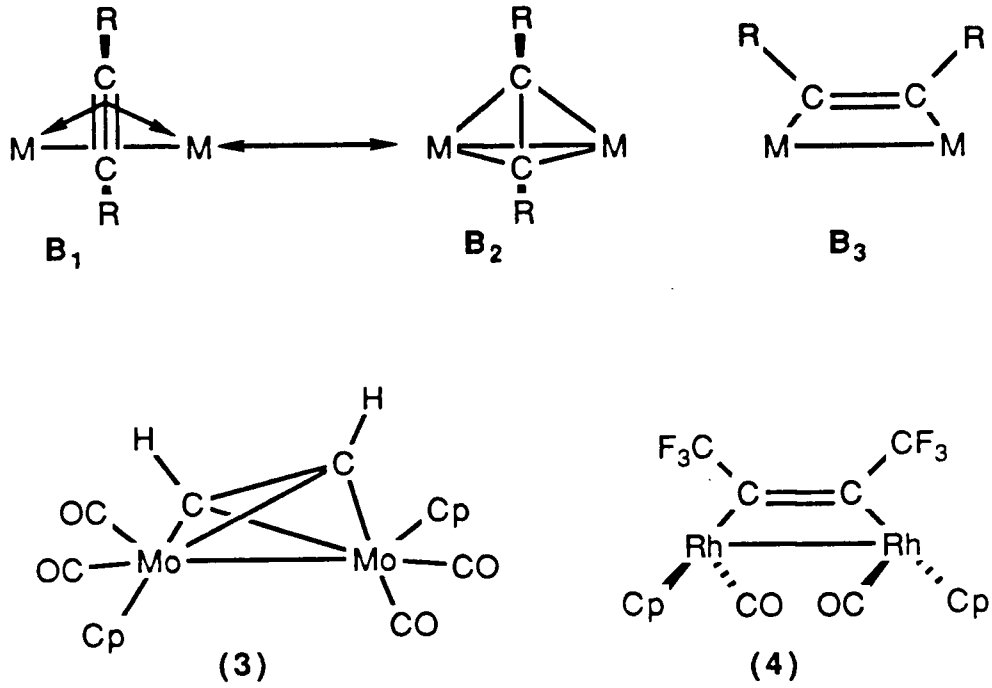


Figure 2. Valence bond structures and examples of binuclear alkyne complexes.

In the case of binuclear complexes containing one alkyne, the alkyne could either bridge along the metal-metal bond axis or perpendicular to the bond axis. In the former case, the alkyne acts as a two electron donor (to each metal) and this is represented in B_3 (Figure 2). In the latter case the alkyne is a four electron donor (in resonence form B_1) and this is represented by the two limiting valence bond structures B_1 and B_2 (Figure 2). In such complexes the carbon-carbon bond distances are in the range of 1.32-1.34Å (Structure **3** in Figure 2).[4a]

A simple orbital description of metal-alkyne bonding in a mononuclear complex is shown in Figure 3. Essentially the bonding involves the donation of electrons from the π-bonding orbitals of the alkyne into a metal orbital of suitable symmetry, and back-donation of electrons from appropriate filled metal orbitals into the π-antibonding orbitals of the alkyne. Such interactions will give rise to the metallacyclopropene valence-bond structure **A**$_2$.[4b]

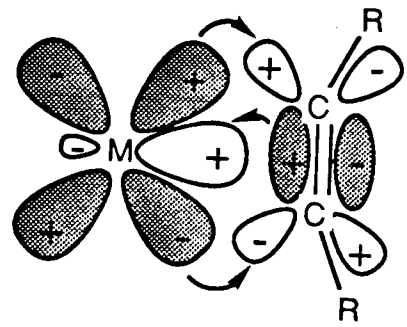
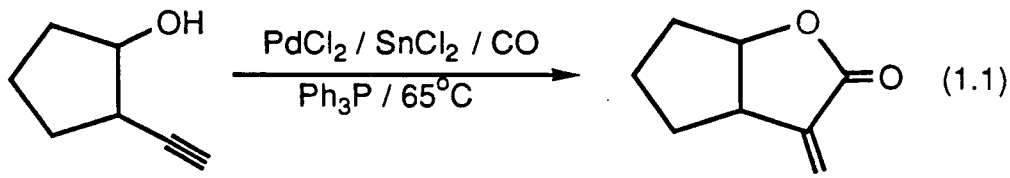
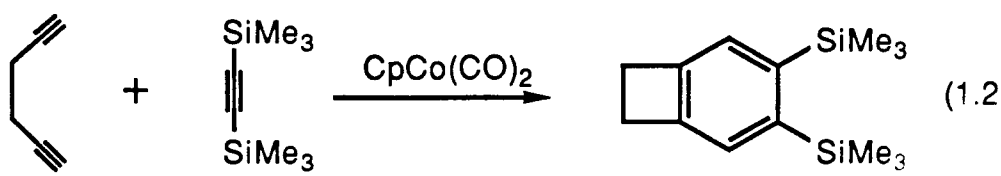
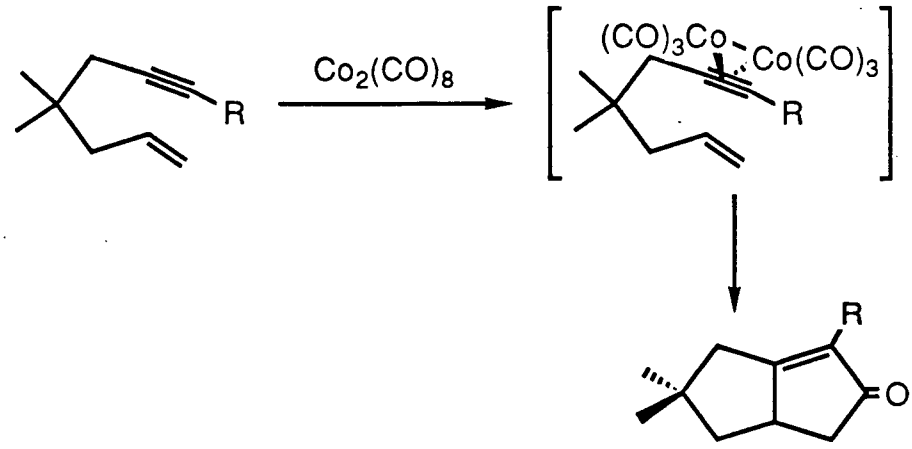


Figure 3. A qualitative orbital description of metal-alkyne bonding.

Although many transition metals react with alkynes, only a few form complexes with appropriate reactivity and stability to be applied in organic synthesis. $PdCl_2$, combined with other reagents has been used for the cyclocarbonylation of acetylenic alcohols (equation 1.1).[5] $CpCoL_2$ has been an efficient catalyst for the







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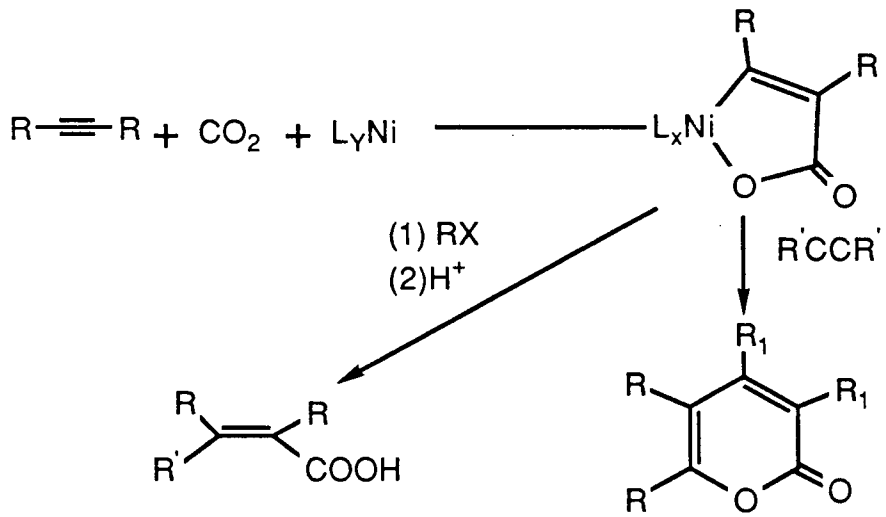

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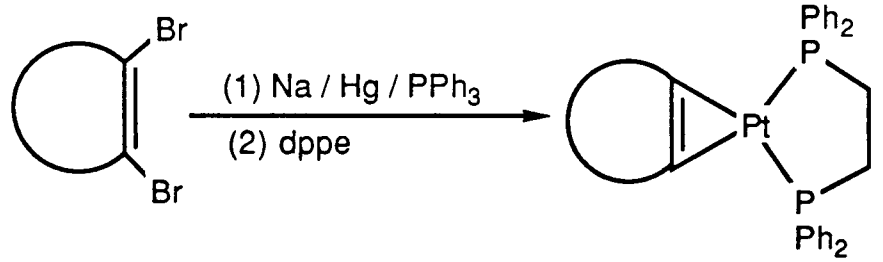


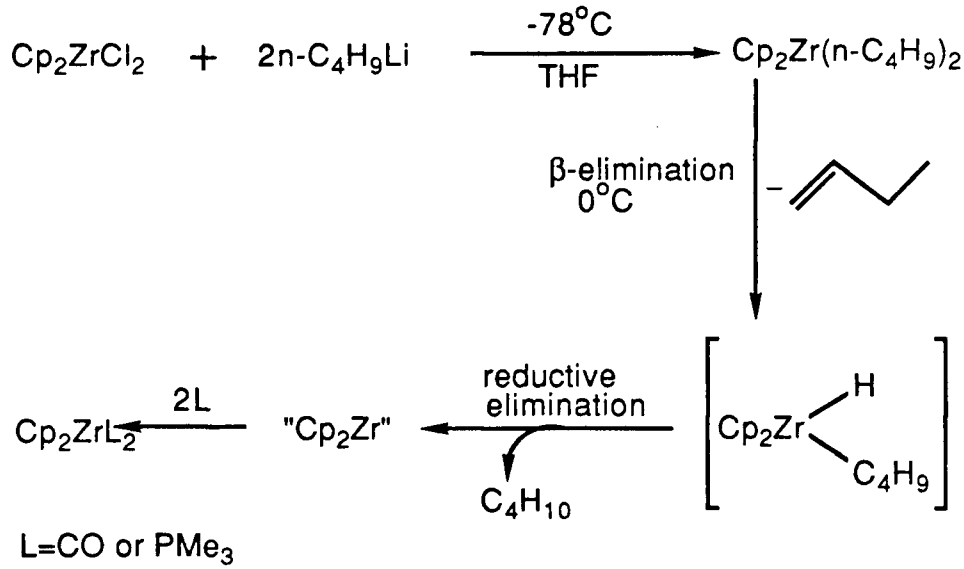
(1.5)

cyclotrimerization of alkynes to give aromatic compounds (equation 1.2).[6] $Co_2(CO)_8$ has been used as a protecting group for alkynes and for cyclizing alkyne units with an olefinic unit to give cyclic ketones (equation 1.3).[7] Reactions involving Ni(0) complexes with an alkyne and CO_2 give highly reactive metallacycles containing the alkyne and CO_2 coupled unit (equation 1.4).[8] Furthermore, transition metals have

been used to stabilize highly reactive unstable alkynes which are generated in situ (equation 1.5).[9]

1.3 Zirconium Alkyne Complexes

Most of the known organozirconium complexes are formally d^0, 16-electron, Zr(IV) species with only one empty orbital and no lone pair of electrons. The absence of d-electrons suggests that a Zr(IV) species would not be capable of stabilizing π-acceptors and σ-donors via backbonding. In contrast, the hypothetical "Cp_2Zr" zirconocene fragment is a d^2, 14-electron Zr(II) species. Such an intermediate with two empty orbitals and a pair of unshared electrons would be ideal for interacting with π-acceptor type ligand (refer to Figure 3).

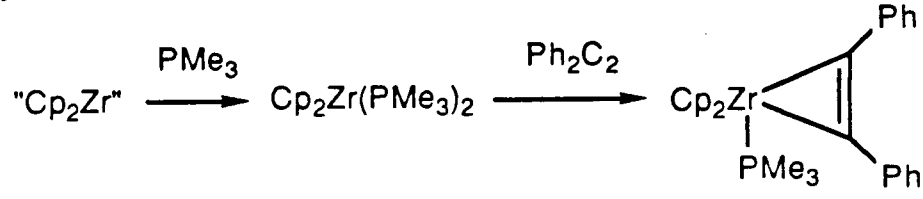


Scheme 2

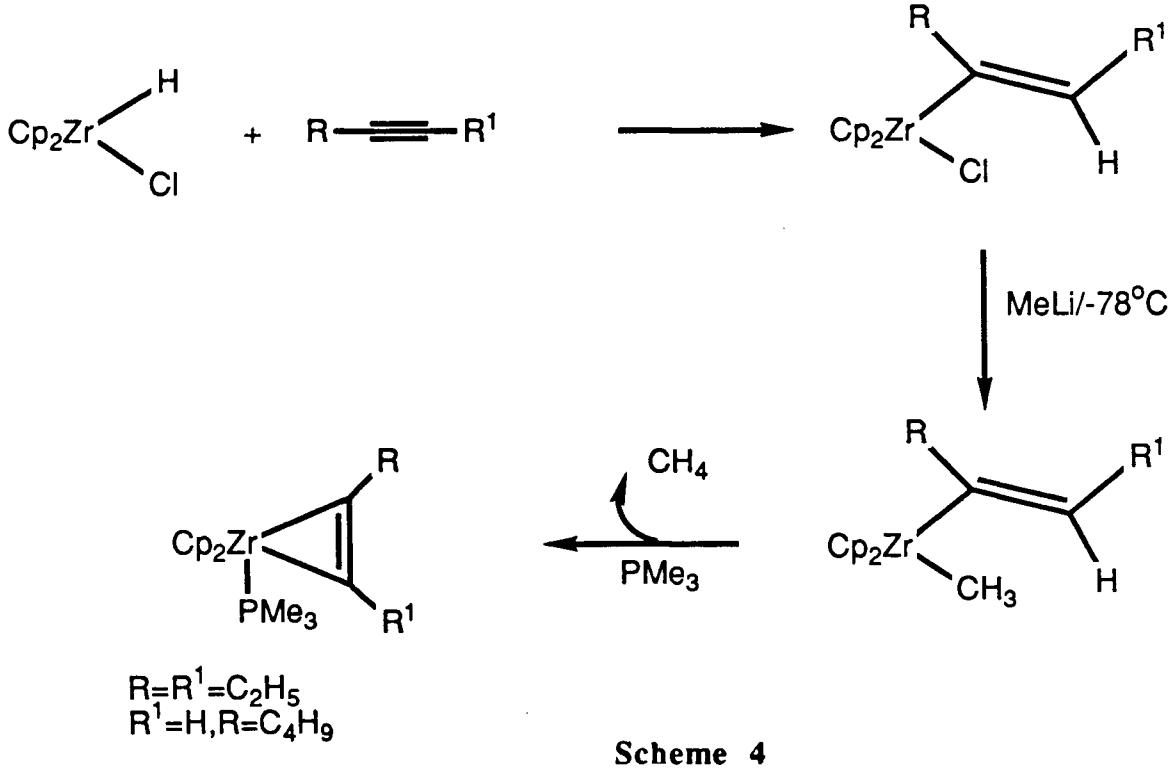
Based on the above rationale, it would be possible to make zirconium alkyne complexes by generating "Cp_2Zr" in situ or as stable adducts with σ-donor ligands, and reacting them with the appropriate alkyne. However attempts to generate

"Cp_2Zr" species using metals as reducing agents have resulted in the formation of Zr(III) compounds.[10] Negishi and coworkers have successfully generated "Cp_2Zr" in situ by reducing Cp_2ZrCl_2 with two equivalents of BuLi. The reactive "Cp_2Zr" intermediate was immediately trapped with PMe_3 or CO to give $Cp_2Zr(PMe_3)_2$ and $Cp_2Zr(CO)_2$ respectively. Formation of n-butane and but-1-ene during the reaction suggest a pathway involving β-hydride elimination followed by reductive elimination to give "Cp_2Zr" species (Scheme 2).[11]

The "Cp_2Zr" species, or its stable adduct Cp_2ZrL_2, has been shown to undergo substitution with alkynes and alkenes to generate the corresponding three-membered metallacycles (Scheme 3).[12]

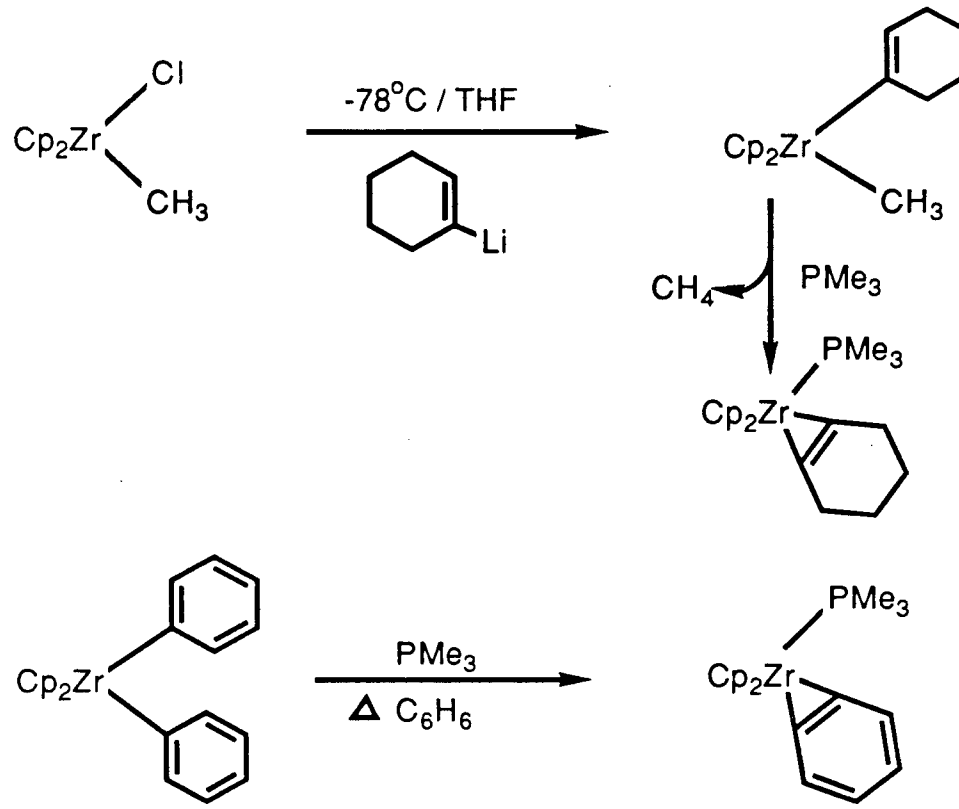


Scheme 3



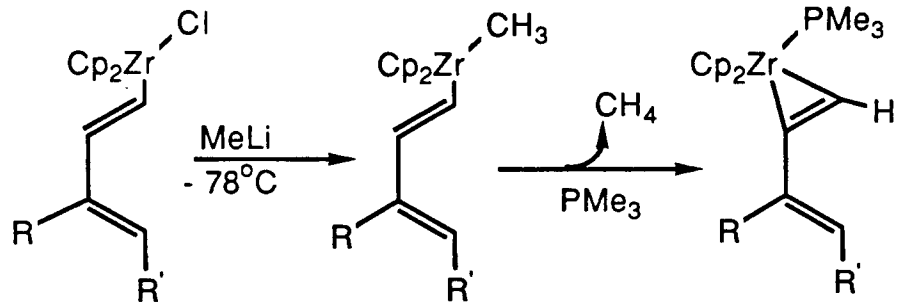
$R=R^1=C_2H_5$
$R^1=H, R=C_4H_9$

Scheme 4



Scheme 5

Recently Buchwald and coworkers have shown that zirconium alkyne complexes can be made from the corresponding $Cp_2Zr(CH_3)$(alkenyl) complexes (Scheme 4).[13] In an analogous manner, small cyclic alkyne and benzyne complexes of



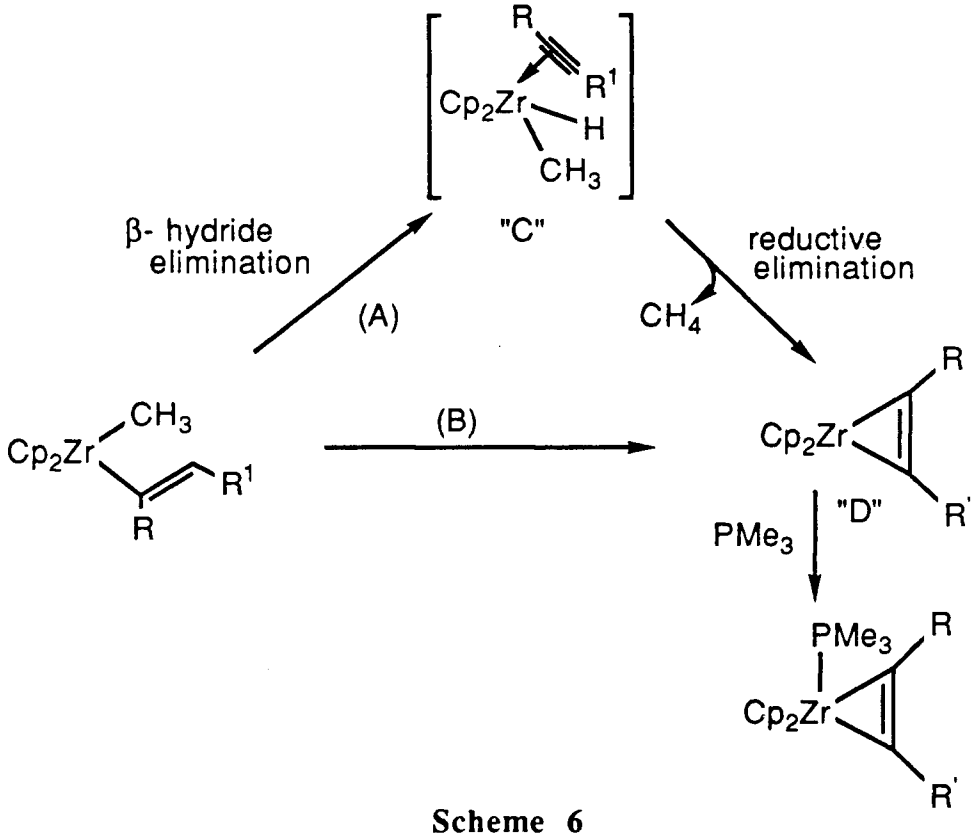
(1.6)

(a) R=H,R^1 = OMe

(b) R R^1 = $-(CH_2)_4-$

zirconium have also been made (Scheme 5).[14] The synthetic methodology mentioned has been successfully extended in our laboratory to the synthesis of zirconium alkyne complexes of enynes (equation 1.6).[15]

The crystal structures of zirconium alkyne complexes $Cp_2Zr(\eta^2$-cyclohexyne)(PMe_3) and $Cp_2Zr(\eta^2$-1-hexyne$)(PMe_3)$ have been determined.[13,14] For the former, the carbon-carbon triple-bond distance and the R-C-C bond angles of these complexes are found to be 1.295Å, 126.0°, 125.2°. For the latter, these parameters are 1.286Å and 135.8° respectively. These values clearly suggest that these alkyne complexes would be best represented by the valence bond structure A, (Figure 1)



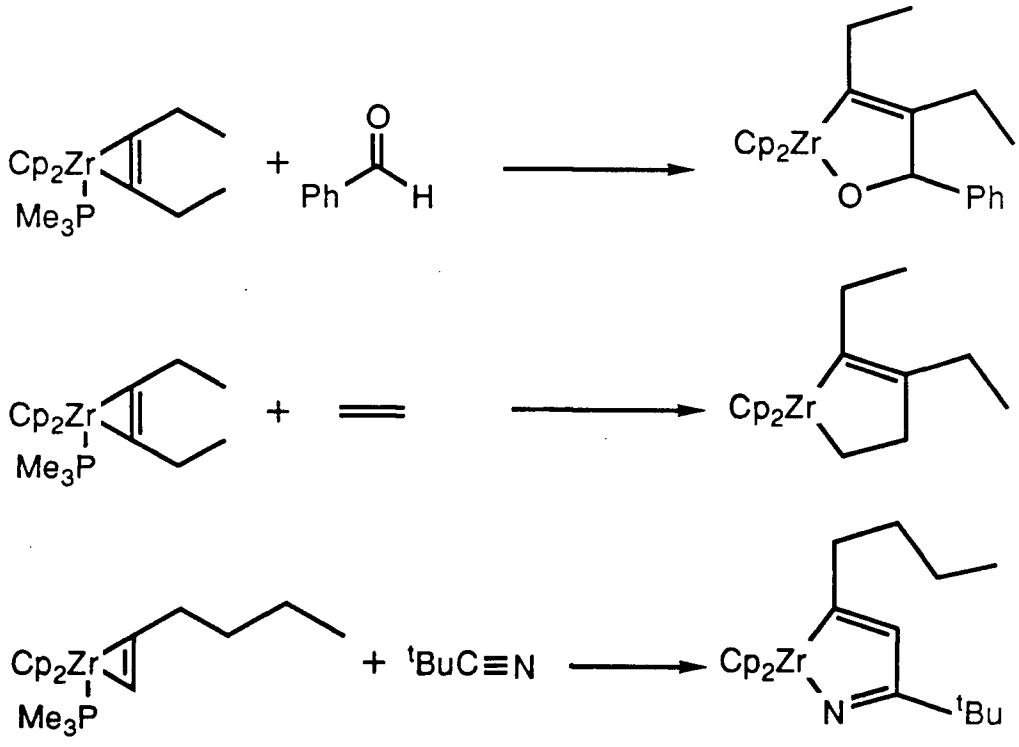
Scheme 6

Scheme 6 shows the most likely pathway for the formation of alkyne complexes from the corresponding alkenyl methyl zirconocene complexes.[14] Pathway A involves a β-hydride elimination to form intermediate "C" followed by reductive elimination of

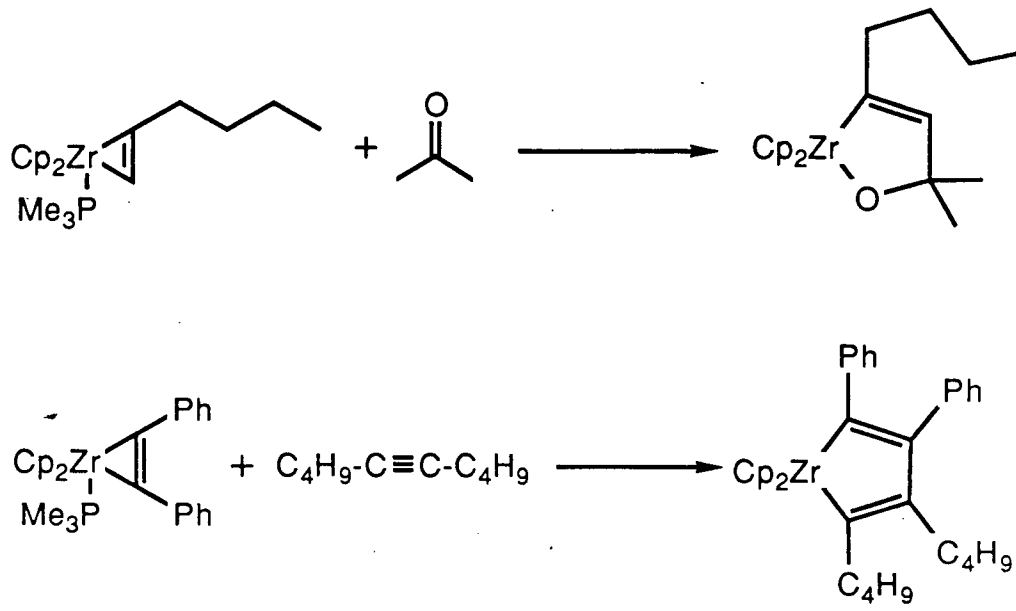
methane to give "D". The alternate mechanism, shown in B, involves C-H activation leading to the simultaneous production of methane and "D".[16] Kinetic isotope effects and substitution effects on analogous zirconium complexes favour a pathway similar to C-H activation or cyclometallation.[16] Further, it has been suggested that an intermediate of type "C" is very unlikely in the case of benzyne and cyclic alkyne complexes where stabilization through backbonding is a crucial factor.[17]

1.4 Reactivity of Zirconium Alkyne Complexes

The zirconium alkyne complexes have been shown to undergo insertion reactions with various alkynes, nitriles, aldehydes, ketones and ethylene (Scheme 7).[13] The facility of these reactions can be attributed to the favourable ring expansion of the highly strained cyclopropene to a less strained five-membered metallacycle.

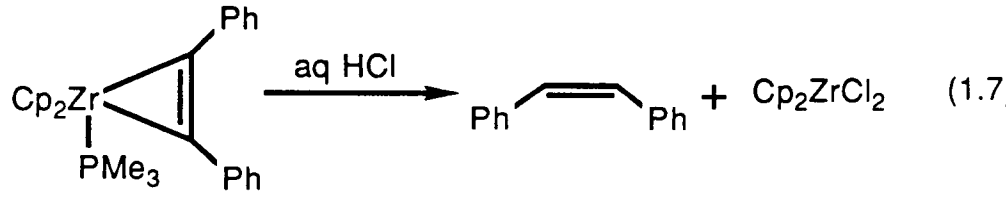


Scheme 7 (continued)



Scheme 7

Negishi and coworkers have successfully utilized the ring expansion reaction in an intramolecular fashion to synthesize organic compounds from enynes (Scheme 8).[18]



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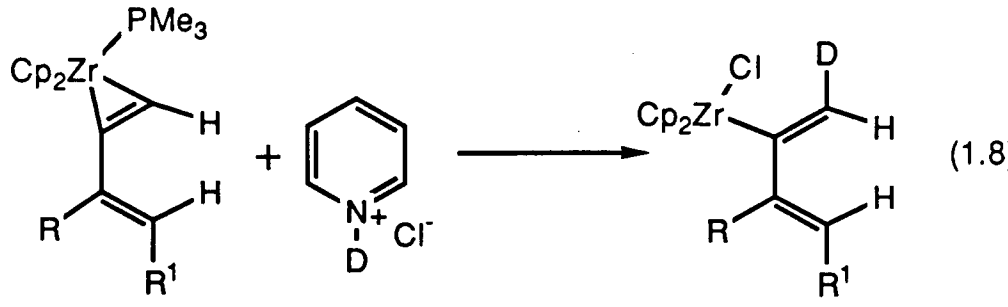


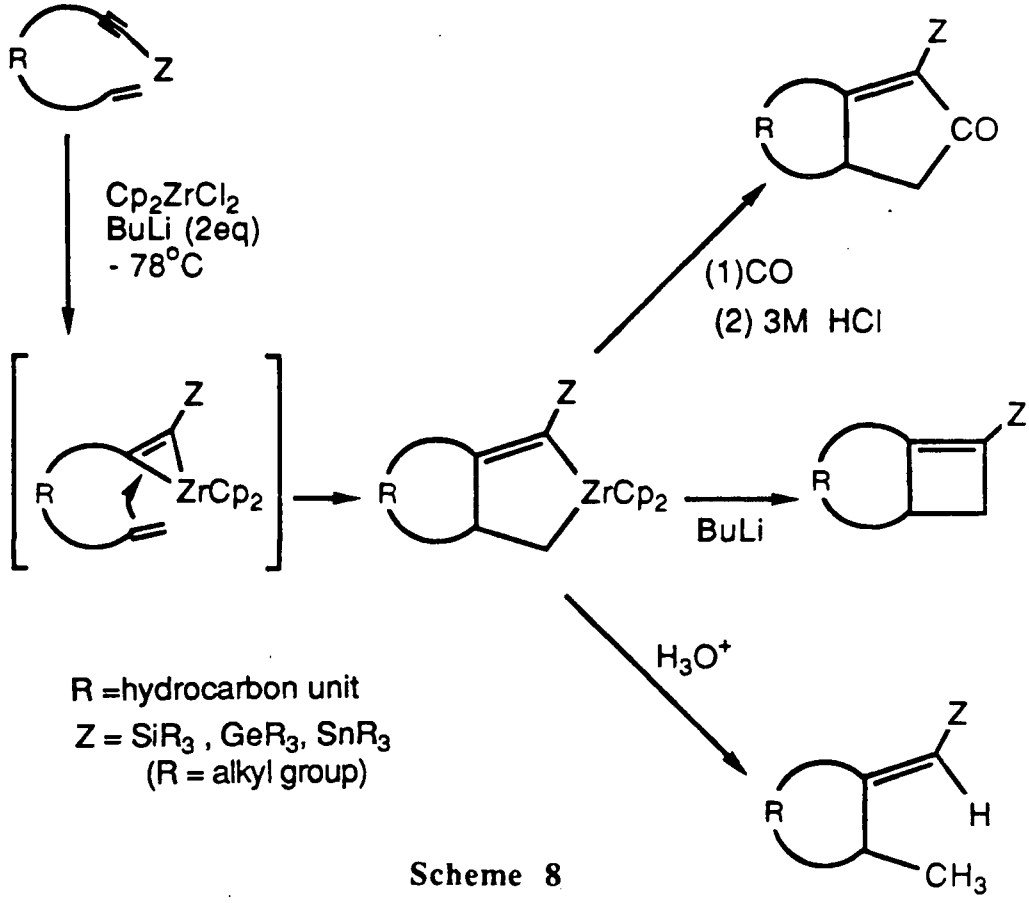
(1.8)

(a) R=H,R^1 = OMe

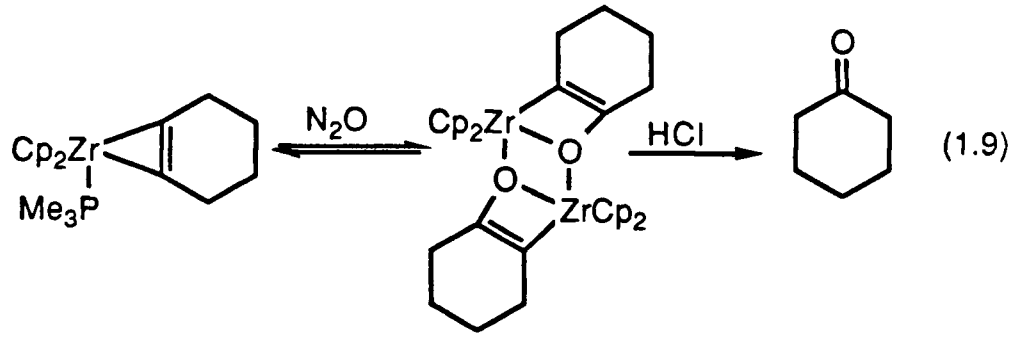
(b) R R^1 = -$(CH_2)_4$-

Protonolysis of the zirconium cyclopropene complex of diphenyl acetylene

resulted in the formation of cis-alkene and Cp_2ZrCl_2 (equation 1.7).[19] An interesting extension of this reaction is the controlled proto ıolysis using one equivalent of pyridinium hydrochloride to selectively cleave one of the zirconium-carbon bonds of the metallacyclopropene ring (equation 1.8).[15]



Scheme 8



(1.9)

Reaction of N_2O with zirconium cyclohexyne complexes resulted in an unprecedented oxametallacyclobutene derivative of zirconocene. Treating this with acid resulted in the formation of cyclohexanone and Cp_2ZrCl_2 (equation 1.9).[20]

1.5 Transmetallation Reactions

Transmetallation reactions involve the transfer of an organic moiety from one metal to another. Experimentally it is observed that the transmetallation of a σ-bonded organic moiety from certain zirconium complexes to a Lewis acidic metal halide is viable.[21] However, the scope of a thermodynamically favourable transmetallation process may be limited due to kinetic barriers. A mechanism involving a four-centre transition state requiring the availability of an empty orbital on each metal has been proposed by Negishi and Takahashi (Figure 4).[22] It is important to note that this mechanism predicts the transfer of the organic group with retention of configuration.

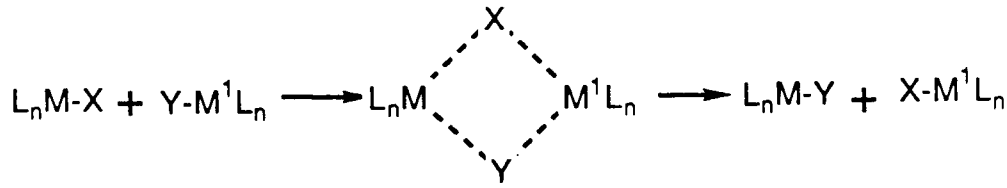


Figure 4. The proposed transition state for the transmetallation reaction.

One of the extensively investigated reactions in this respect is the reaction involving haloaluminum compounds.[23] Mechanistic investigation carried out with stereospecifically labelled dideuteroorganozirconium complexes and $AlCl_3$ have been shown to proceed with retention of configuration (Figure 5).[23] It is also interesting to note the reaction of Cp_2ZrCl_2 with alkyl aluminates has resulted in the transfer of the

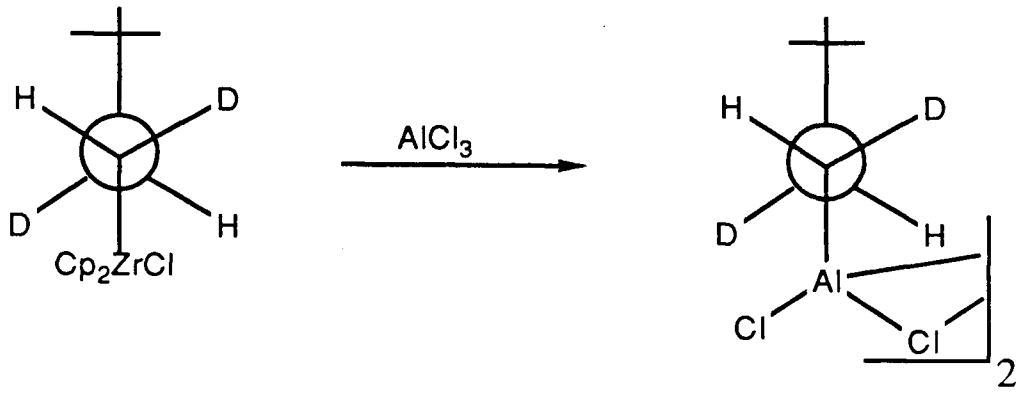
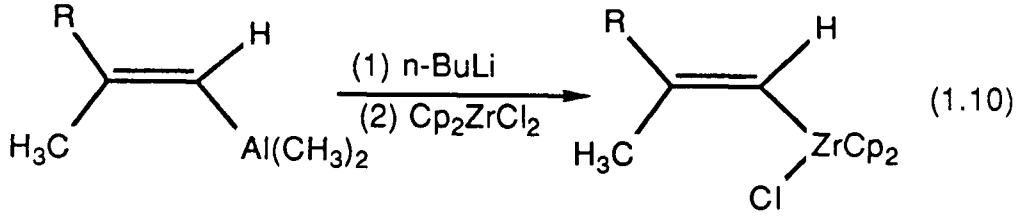


Figure 5. A Newman projection showing the transfer of an alkyl group with retention of configuration.

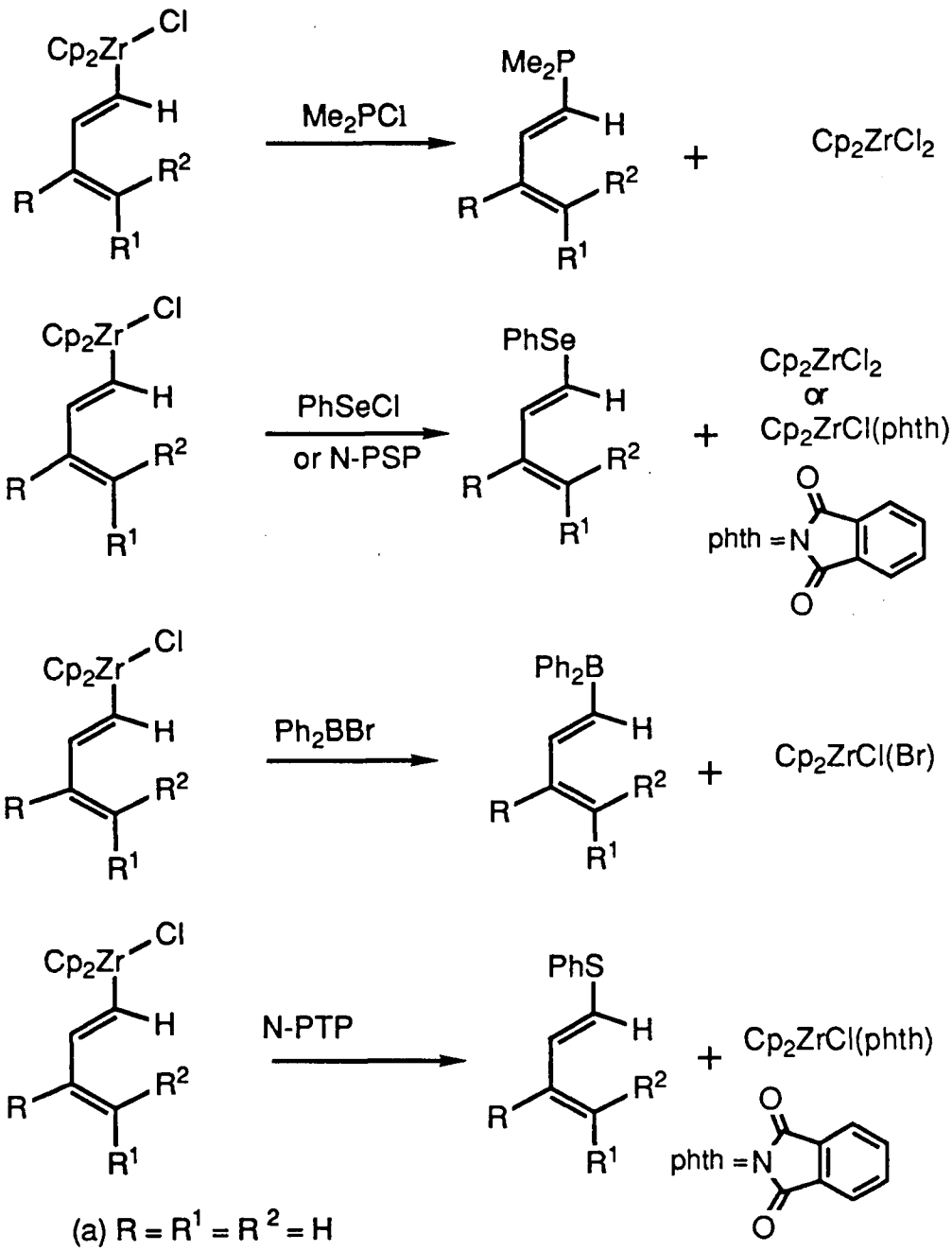
organic moiety from aluminum to zirconium (equation 1.10).[24] Transmetallation reactions with the Lewis acidic metal halides $ZnCl_2$, CuCl, and $PdCl_2$ have also been reported.[25]



(1.10)

1.6 Transfer Reactions

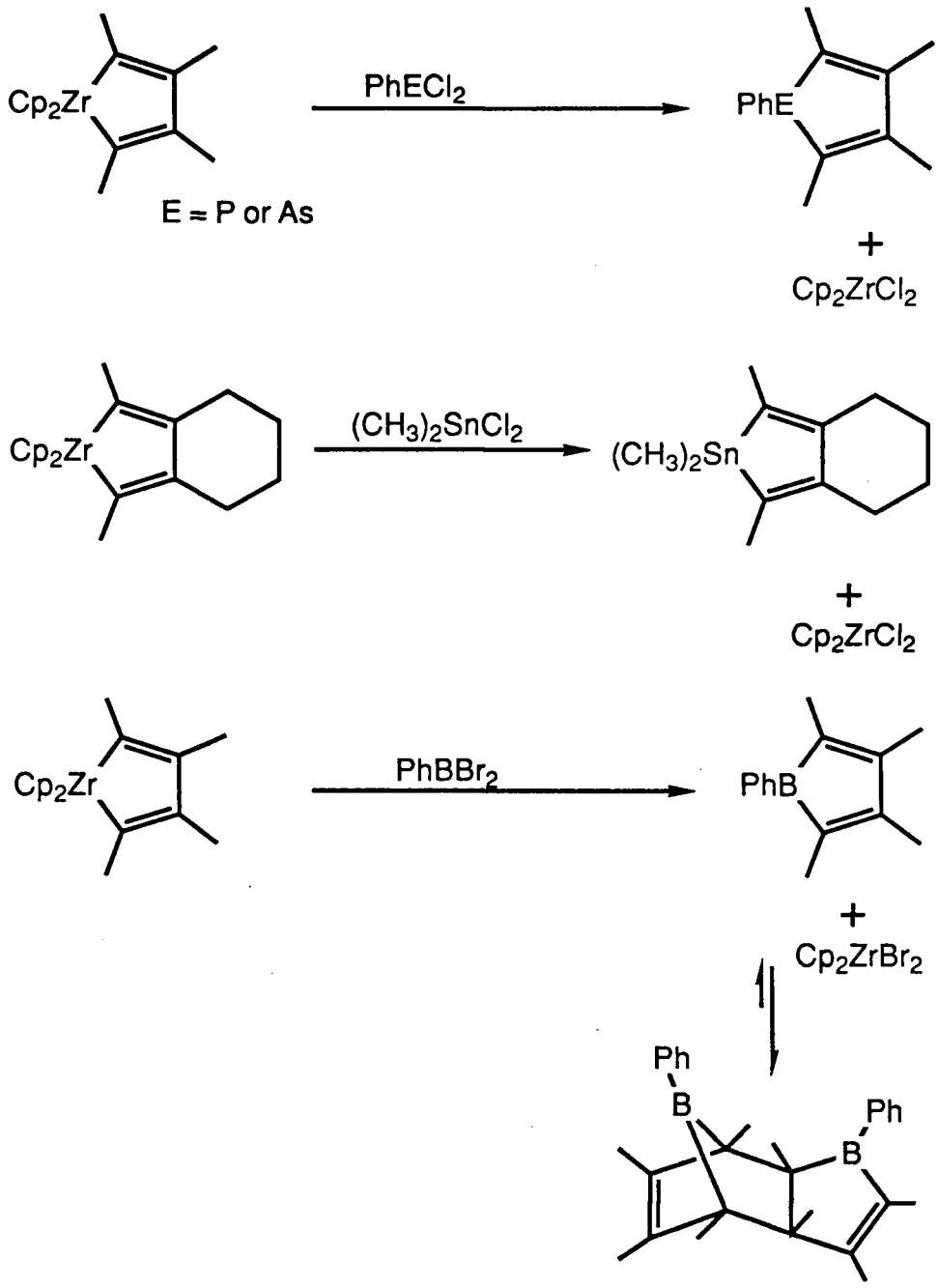
Transfer reactions, as opposed to transmetallations, involve transfer of an organic moiety from a metal to a non-metal derivative. Such transfer reactions have been extremely useful in the synthesis of heterosubstituted dienes.[26] It is important to note that the dienyl moiety is transferred stereoselectively from zirconium to the hetero-atom of the organometalloid (Scheme 9).



(a) $R = R^1 = R^2 = H$
(b) $R = R^1 = H$, $R^2 = OMe$
(c) $R = R^2 = H$, $R^1 = OMe$
(d) $R\,\underline{\quad}\,R^1 = -(CH_2)_4-$, $R^2 = H$

Scheme 9

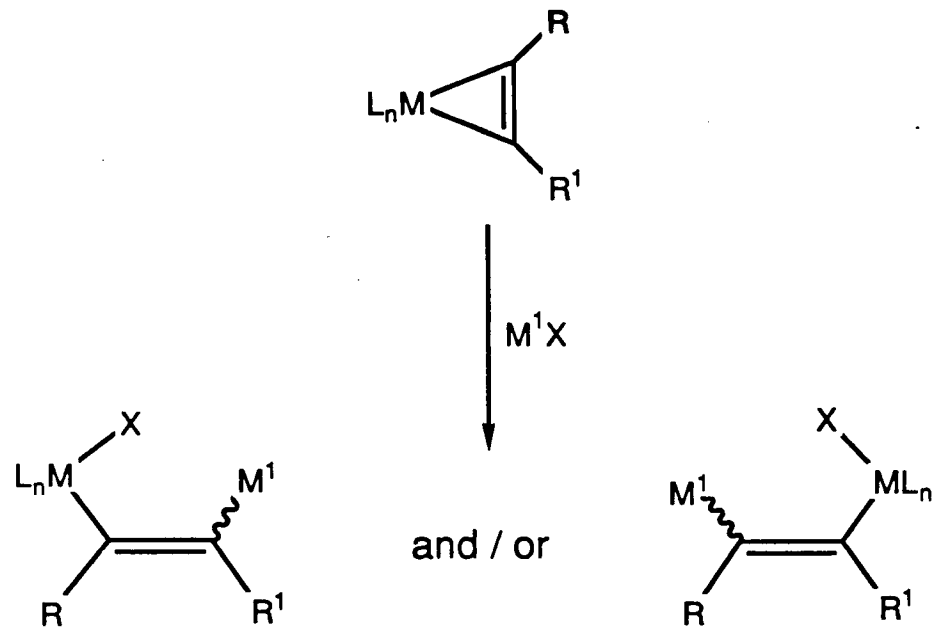
In a similar fashion, five-membered ring metallacycles of zirconium undergo transfer reactions to give five-membered ring heterocycles (Scheme 10).[27]



Scheme 10

1.7 Addition-Transfer Reactions

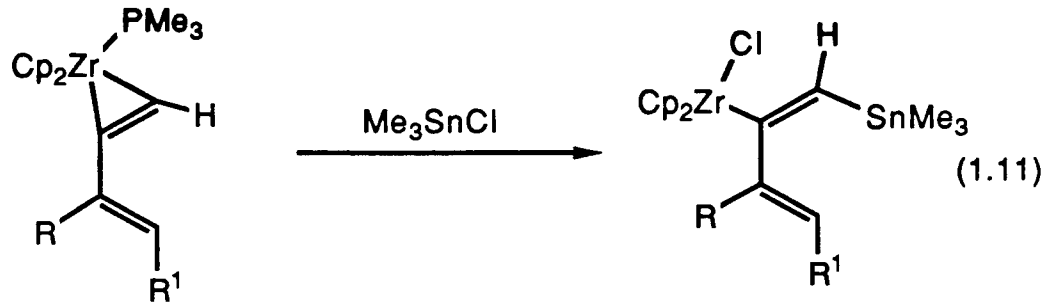
The reaction of Me_3SnCl with zirconium alkyne complexes has shown a unique type of reactivity.[15] Scheme 11 shows the general case of such a reaction of an alkyne complex with M^1-X (M^1 = metal or metalloid compound, X = halide).



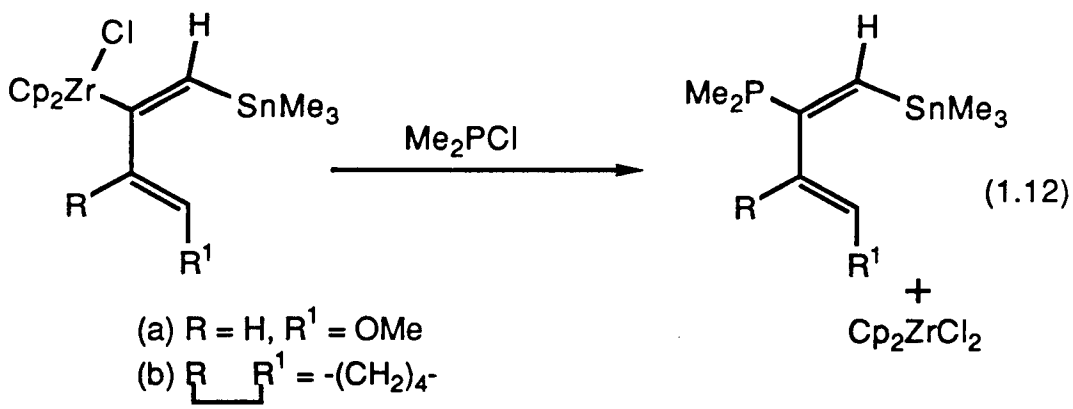
Scheme 11

Upon examination of the reactants and the products, it is obvious that this is not a simple transmetallation or transfer process since the organic fragment is still bound to the metal M. The regioisomeric products are a result of the fact that either of the metal-carbon bonds of the alkyne complex can, in principle, be cleaved. Consideration of the general structure of the products shows that the M^1-X bond adds across one of the metal-carbon bonds (M-C) resulting in the transfer of X to the metal

M and M^1 to one end of the alkyne. Based on the above description, we will refer to such transformations as addition-transfer reactions.



(1.11)



(1.12)

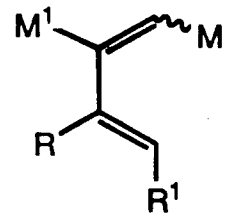
(a) R = H, R^1 = OMe

(b) R R^1 = $-(CH_2)_4-$

The only known addition-transfer reaction involving a zirconium alkyne complex of an enyne and Me_3SnCl is shown in equation 1.11.[15] Furthermore, the "Cp_2ZrCl" moiety of the product in equation 1.11 can subsequently undergo a transfer reaction with Me_2PCl (equation 1.12).[15] These two reactions clearly illustrate the differences between the addition-transfer reaction and transfer reaction.

In general, the addition-transfer reaction provides a synthetic route to hetero-substituted dienes of the type shown in Figure 6. Based on this we investigated the reactivity of zirconium alkyne complexes with Ph_2PCl. We also studied the effect of alkyl and aryl substitutions on the alkyne and the resulting stereochemistry of the

products. The following chapters present the results of these investigations and the proposed mechanisms for the addition-transfer reaction.



M, M^1 = organotransition metal group (eg Cp_2ZrCl) or organo metalloid (eg Me_3Sn)

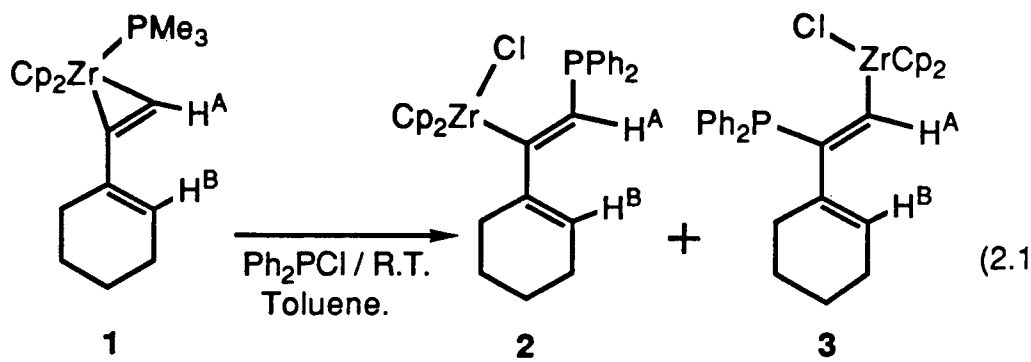
Figure 6. The structure of a 1,2-disubstituted diene resulting from the addition-transfer reaction.

CHAPTER 2

RESULTS AND DISCUSSION

2.1 Synthesis of Chlorobis(η^5-cyclopentadienyl)(diphenylphosphino-1,3-dienyl)zirconium(IV)

As mentioned in the previous chapter, the addition-transfer reaction coupled with a transfer reaction yields 1-stannyl-2-phosphino-1,3-dienes (equations 1.11, 1.12). The observed stereochemistry in this case has the stannyl and the phosphinyl groups trans to one another. With a view to further utilize and develop the addition-transfer reactions, we investigated the reactivity of zirconium alkyne complexes with Ph_2PCl. The enyne complex **1** reacts smoothly with 1 equivalent of Ph_2PCl at room temperature to give a major product **2** and a minor product **3** in ≈ 4:1 ratio (equation 2.1). Figure 7 shows the ^1H NMR spectrum of the products **2** and **3**.



(2.1)

The stereochemistry of the major product **2** was determined by NOEDIFF experiments. The observed enhancements on irradiating the resonances of protons

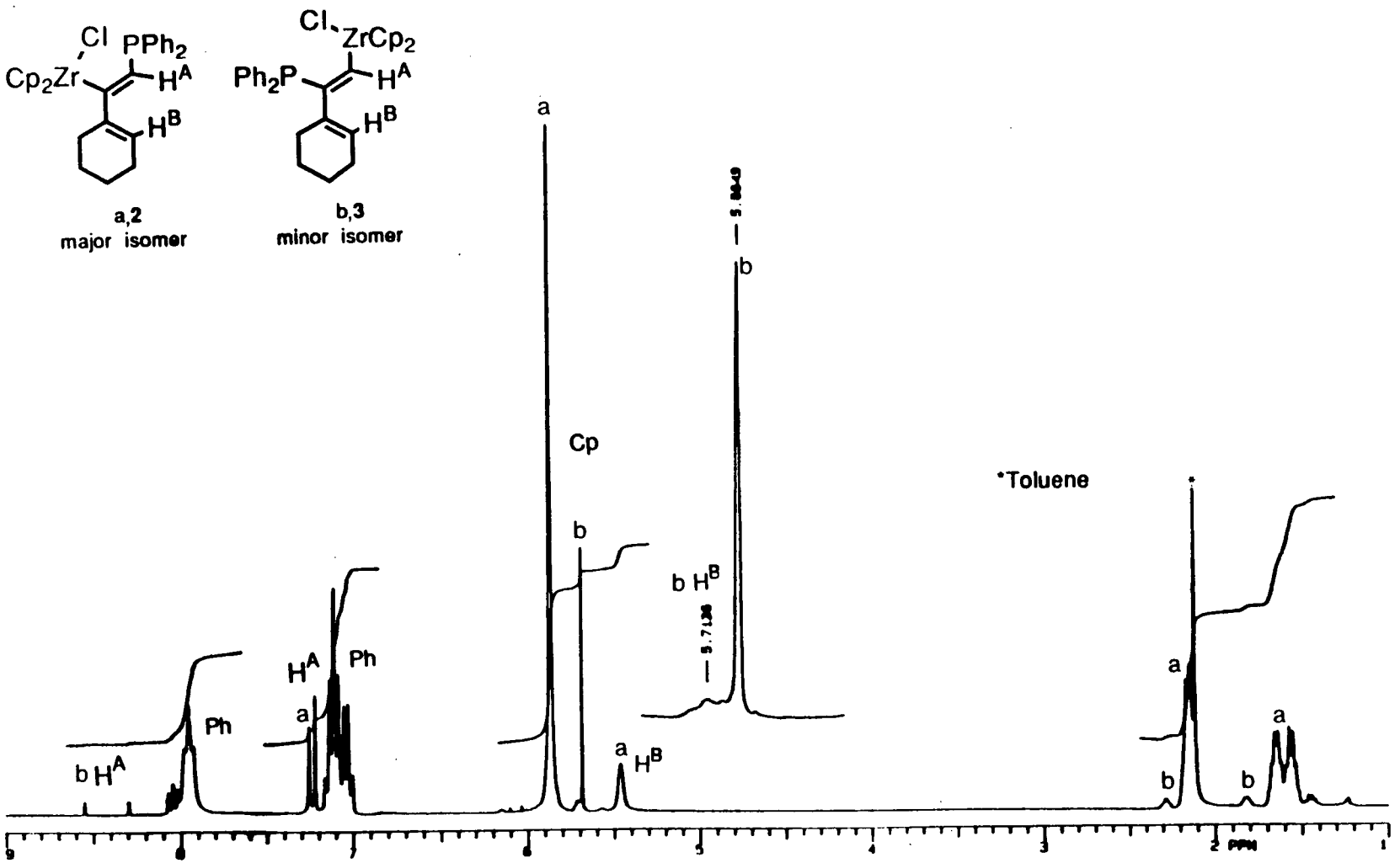


Figure 7. 300 MHz ^{1}H NMR spectrum of compounds **2** and **3** in C_7D_8.

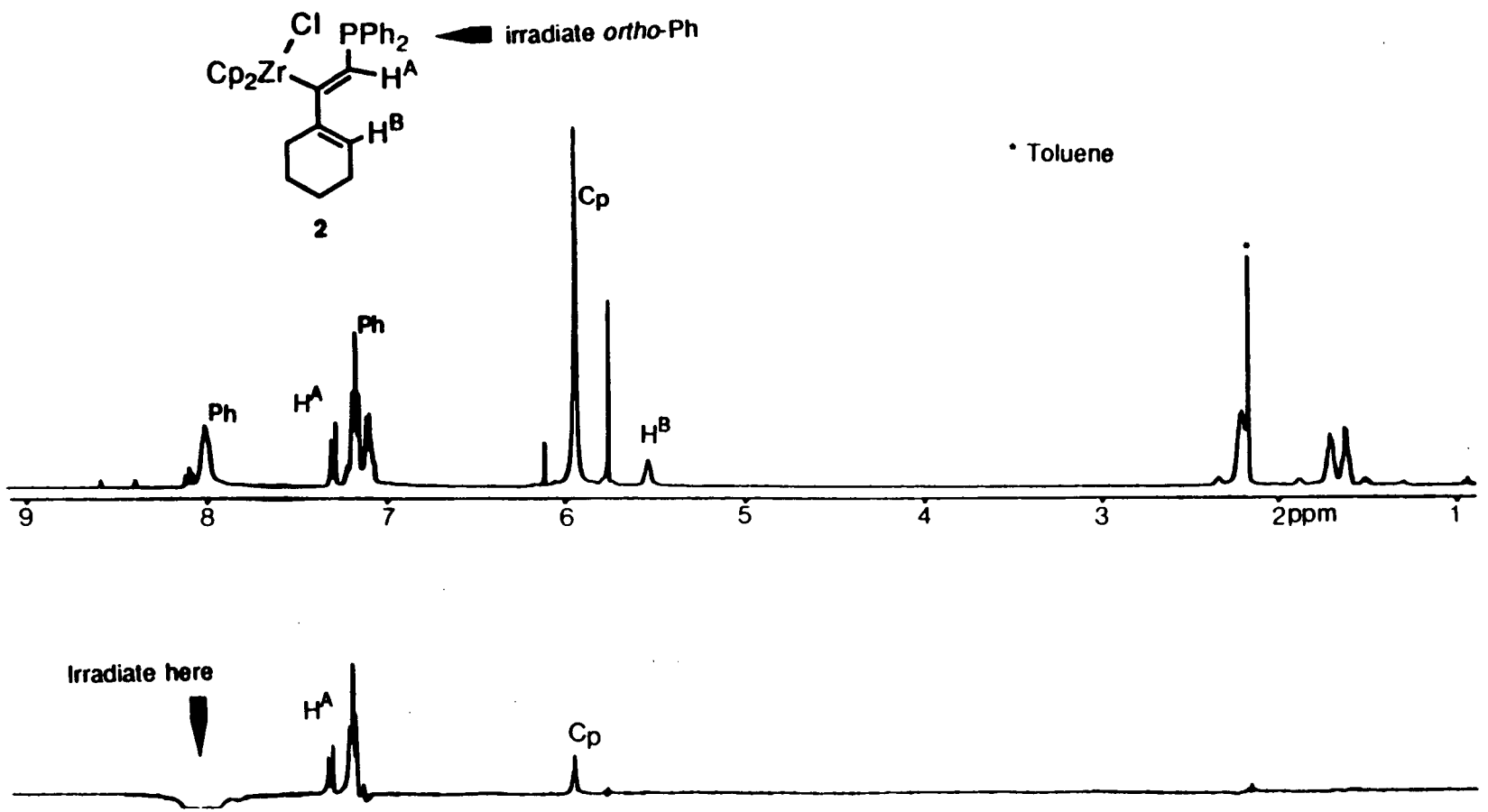
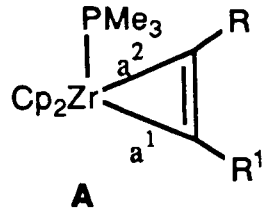


Figure 8. 400 MHz ^{1}H NMR spectrum and NOEDIFF spectrum of compound **2** in C_7D_8.

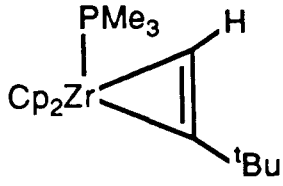
H^A, H^B, the *ortho* protons of the phenyl rings on phosphorus and the protons of the cyclopentadienyl ligand, are all consistent with the stereochemistry shown. Figure 8 shows one such NOEDIFF experiment spectrum where the irradiation of the *ortho* protons of the phenyl rings resulted in the enhancement of the protons on the Cp rings and H_A. Since the stereoisomers **2** and **3** were not readily separable, NOEDIFF experiments on the minor isomer were not carried out. The trans stereochemistry assigned for the minor compound **3** is based on the very large phosphorus-proton coupling constant, $^3J_{P\text{-}H^A}$ = 76.1 Hz, relative to $^2J_{P\text{-}H^A}$ = 10.1 Hz in the major compound **2**; the larger phosphorus coupling in **3** is typical for a trans relationship of the Ph_2P group and H^A, while the small coupling is consistent with a geminal disposition of the Ph_2P moiety and H^A in **2**. Thus, the stereochemistry of the products resulting from the addition-transfer reaction is dependent upon whether Me_3SnCl or Ph_2PCl is used. It is interesting that in the case of Ph_2PCl both possible cis isomers were formed, whereas for Me_3SnCl only a single trans isomer is produced. This observation prompted us to investigate the reactivity of a range of substituted zirconium alkyne complexes towards these reagents in an attempt to understand the mechanism and the stereoselectivity of these reactions.

2.2 Synthesis of Zirconium Alkyne Complexes

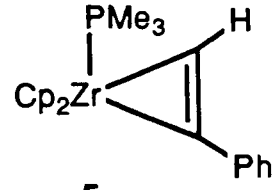
Figure 9 shows the three alkyne complexes (**4-6**) we chose to synthesize. The choice of substituents was based on the varying steric and electronic influences they might exert during the reaction. In complex **4**, the *tert*-butyl group imposes steric crowding on one side, a^1, of the cyclopropene ring with minimal effect on side a^2 (structure A, Figure 9). In compound **5**, having a phenyl group, the side a^1 of the ring



A



4



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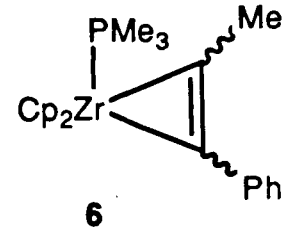


6

Figure 9. The alkyne complexes synthesized to study the steric and electronic effects of addition-transfer reactions.

is less sterically crowded than in **4**. Compound **6** is an internal alkyne complex and therefore will have steric crowding on both sides a^1 and a^2 of the ring. Also, in compounds **5** and **6**, the phenyl substituent might be expected to have a different electronic influence than that of an alkyl group.

The alkyne complexes were prepared using procedures similar to those employed by Buchwald (Scheme 4, Chapter 1). The zirconium alkenyl complexes were synthesized via hydrozirconation of the corresponding alkynes and could be isolated in good yields.[28] Subsequent reaction of these alkenyl complexes with MeLi in THF at -78^{0}C gave the unstable alkenyl(methyl)zirconocene complexes which were immediately extracted with toluene, filtered and then stirred with excess PMe_3 for 36 hours to obtain the corresponding alkyne complexes. Figure 10 shows the ^{1}H NMR of the methyl-phenyl-alkyne complex **6** and, as can be seen by the two sets of resonances, both possible isomers, **6a** and **6b,** in an approximately 2:1 ratio are formed. Compounds **4** and **5** gave only a single isomer in which the terminal carbon points directly towards the PMe_3 group.

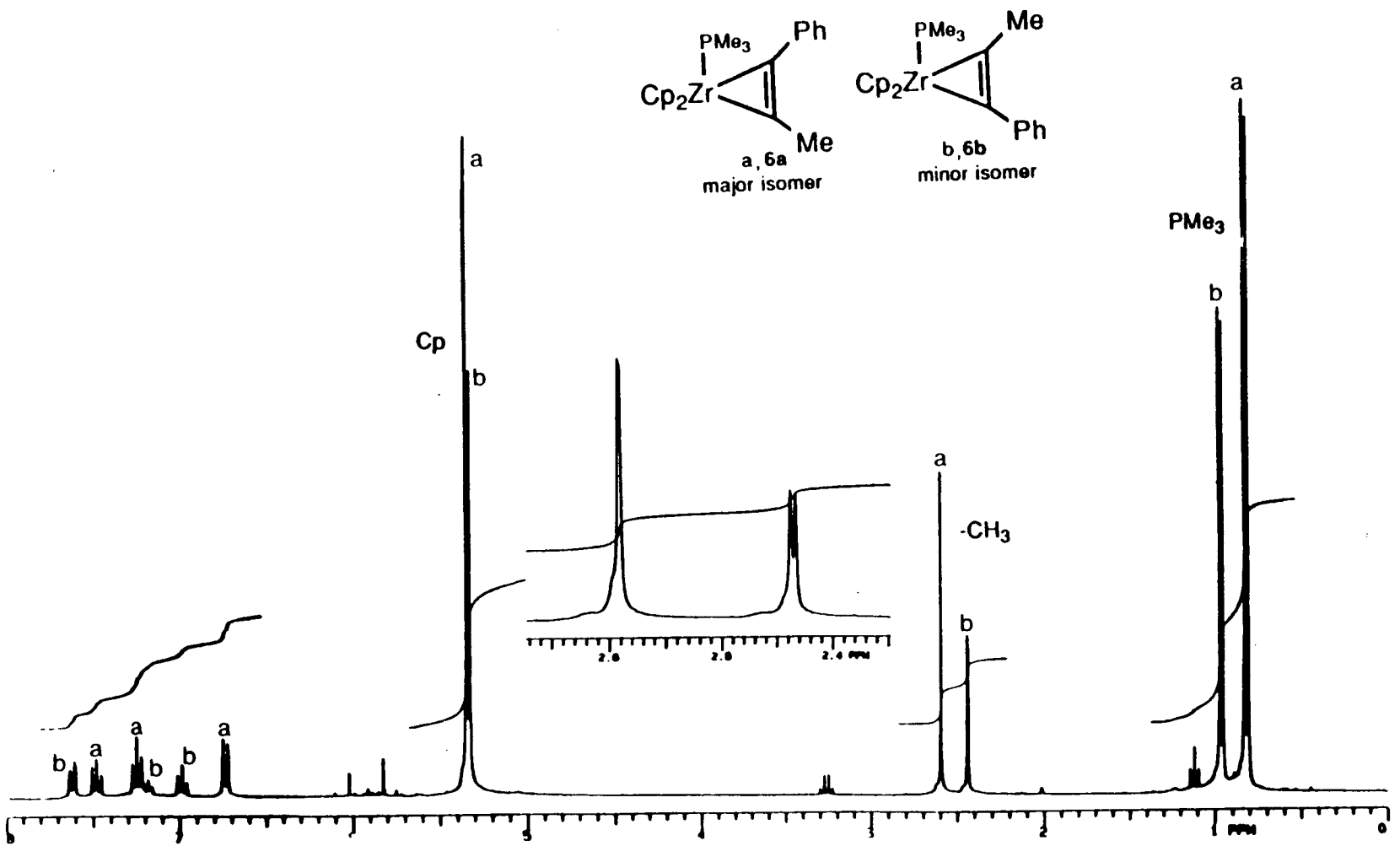
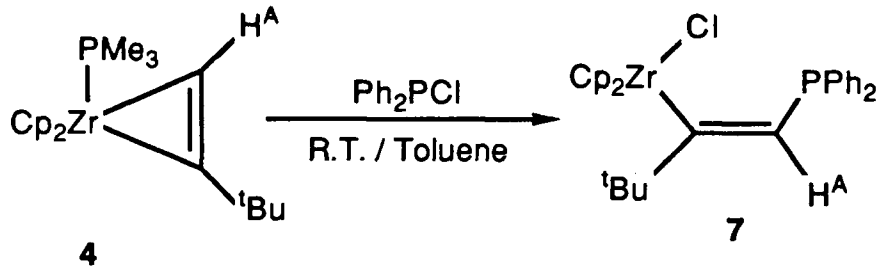


Figure 10. 300 MHz ^{1}H NMR spectrum of compounds **6a** and **6b**.in C_6D_6.

2.3 Reactions of Zirconium Alkyne Complexes (4-6) with Ph_2PCl

All the reactions were carried out using one equivalent of Ph_2PCl in toluene at room temperature. From the reaction with the *tert*-butyl alkyne complex **4,** there is obtained a single product **7** (equation 2.2). The stereochemistry of the product was assigned from the results obtained from NOEDIFF experiments. Irradiating the *tert*-butyl group resonances resulted in an enhancement of H^A and the protons of the Cp ring. Further, irradiation of the *ortho* protons of the phenyls on phosphorus enhanced H^A and the Cp's. Also the coupling constant $^2J_{P\text{-}H^A}$ = 10.1 Hz, was comparable with that observed in compound **2**, consistent with the assigned stereochemistry.



4 **7** (2.2)

From the phenyl alkyne complex **5** was isolated a pale pink crystalline material consisting of a mixture of two compounds **8** and **9** in ≈ 5:1 ratio (equation 2.3). NOEDIFF experiments involving the irradiation of the Cp's and the *ortho* protons of the phenyl rings on phosphorus gave enhancements which were consistent with the proposed stereochemistry (Figure 11). Also NOEDIFF experiments were useful in locating the peak corresponding to H^A. The coupling constant, $^2J_{P\text{-}H^A}$ = 10.7 Hz, was consistent with what was observed in compounds **2** and **7.** The assignment of the stereochemistry of the minor isomer was based on the coupling constant $^3J_{P\text{-}H^A}$ = 74.8 Hz, which is similar to that observed in compound **3**, and indicates trans, vicinal

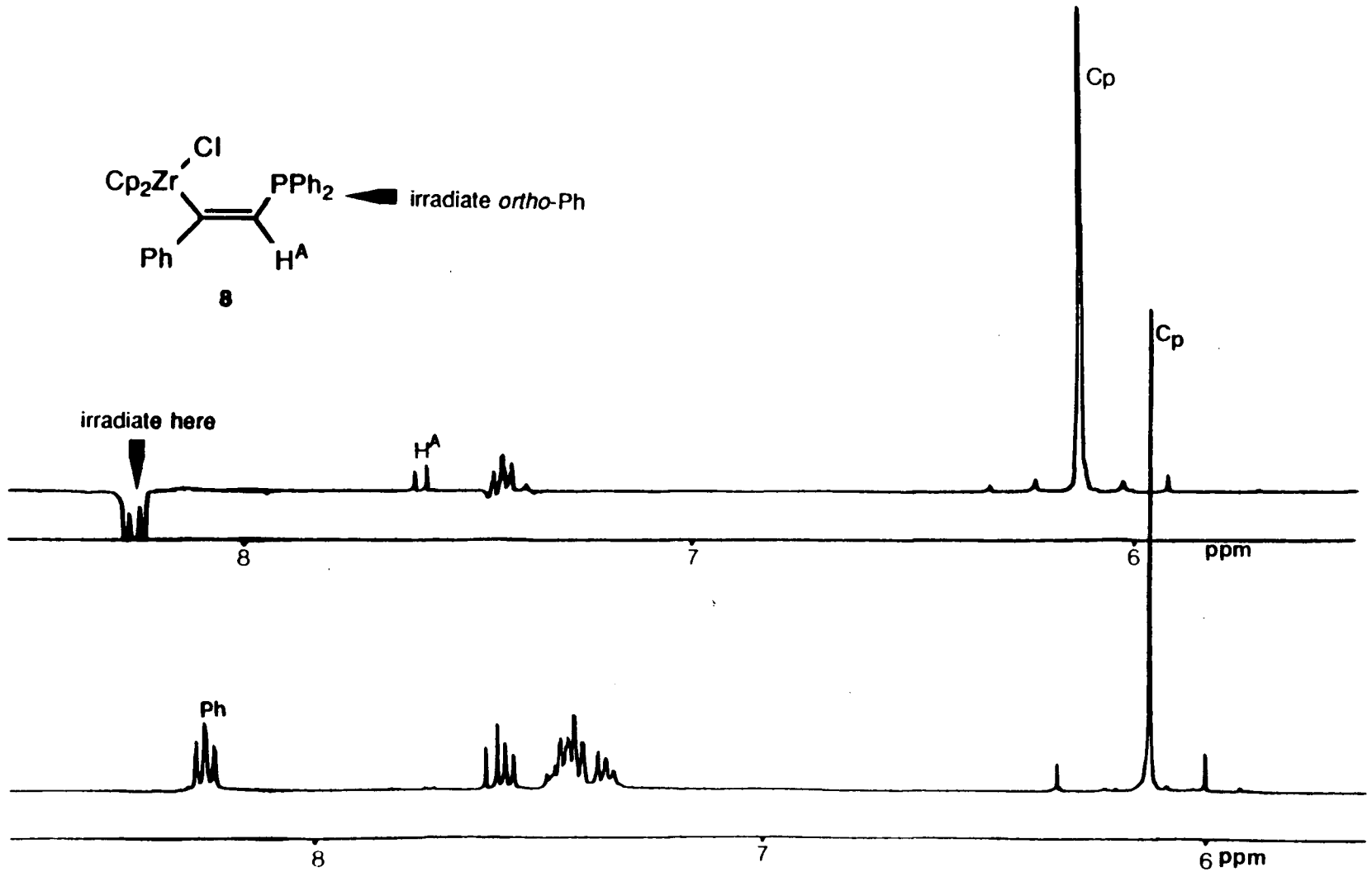
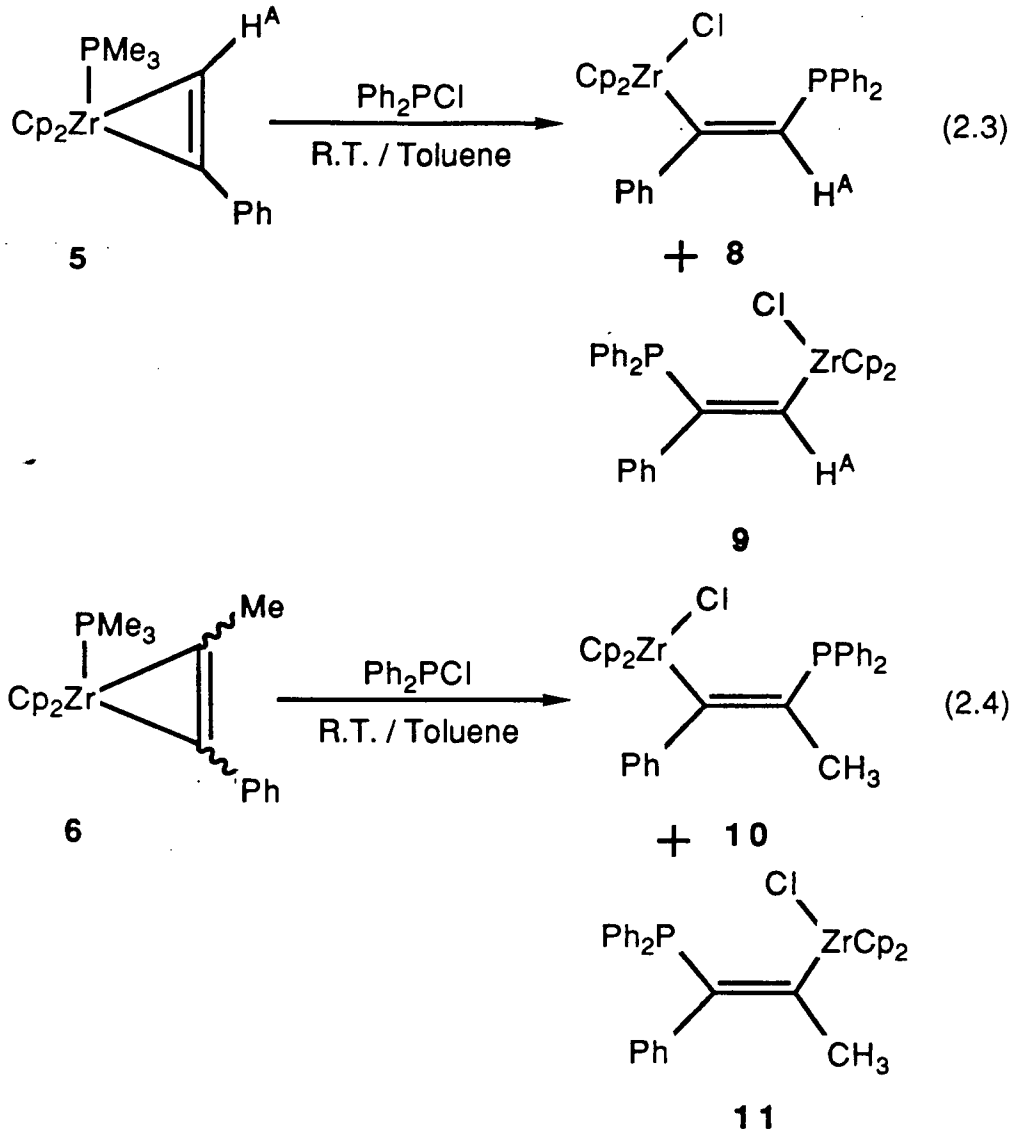


Figure 11. 400 MHz ^{1}H NMR spectrum and NOEDIFF spectrum of compound **8** in C_6D_6.



(2.3)

(2.4)

relationship between phosphorus and H^A. In addition, the chemical shift differences between the Cp resonances and ^{31}P resonances of the two isomers **8** and **9** were similar to the differences observed in **2** and **3**.

Attempts to crystallize the products from the reaction with methyl-phenyl alkyne complex **6** were not successful. The white powder, obtained by precipitation from a crude solution in toluene with excess hexanes, consisted of two compounds in ≈1:1 ratio. The chemical shift of the ^{31}P resonances and those of the Cp's in the ^{1}H NMR of these compounds were comparable with other compounds. Based on these

results the stereochemistry of the two products were assigned as shown in **10** and **11** (equation 2.4).

2.4 Mechanism for the Addition-Transfer Reaction Involving Ph_2PCl

The proposed mechanism for the addition-transfer reaction involving Ph_2PCl is shown in Figure 12. Initial dissociation of PMe_3, followed by the coordination of the Ph_2PCl via the lone pair of electrons of the phosphorus will give the two possible intermediates, $\mathbf{B^1}$ and $\mathbf{B^2}$. Rearrangement of these intermediates, by shifting the donor atom from phosphorus to chlorine, leads to the formation of transition states $\mathbf{C^1}$ and $\mathbf{C^2}$. As discussed in Chapter 1, such four-centred transition states have been proposed for the stereospecific transfer of alkenyl groups from zirconium to aluminum (Figure 4, Chapter 1). A similar transition state has also been proposed for the electrophilic cleavage of zirconium alkyl complexes with Br_2.[29] The proposed four-centred transition states, $\mathbf{C^1}$ and $\mathbf{C^2}$, are similar to these and involve the P-Cl bond and one of the zirconium carbon bonds of the metallacyclopropene ring. As shown in Figure 12, the appropriate bond breaking and bond forming steps for $\mathbf{C^1}$ and $\mathbf{C^2}$ would lead to the formation of $\mathbf{D^1}$ and $\mathbf{D^2}$ respectively, where the Cp_2ZrCl moiety and the Ph_2P moiety are cis related. If the formation of $\mathbf{C^1}$ and $\mathbf{C^2}$ is kinetically controlled, their relative amounts will depend upon the relative bulkiness of the "R" groups. This mechanism is consistent with the observed product ratios in both the terminal and internal alkyne complexes.

It is important to note that in the synthesis of complexes **4** and **5**, only a single product is formed; PMe_3 being coordinated to the least-hindered site. Substitution of a methyl group for hydrogen leads to the formation of both possible isomers, **6a** and, **6b** in ≈2:1 ratio (Figure 10). This seems to suggest that in complex **6**, the steric environment on either side of the metallacyclopropene ring is comparable; whereas in

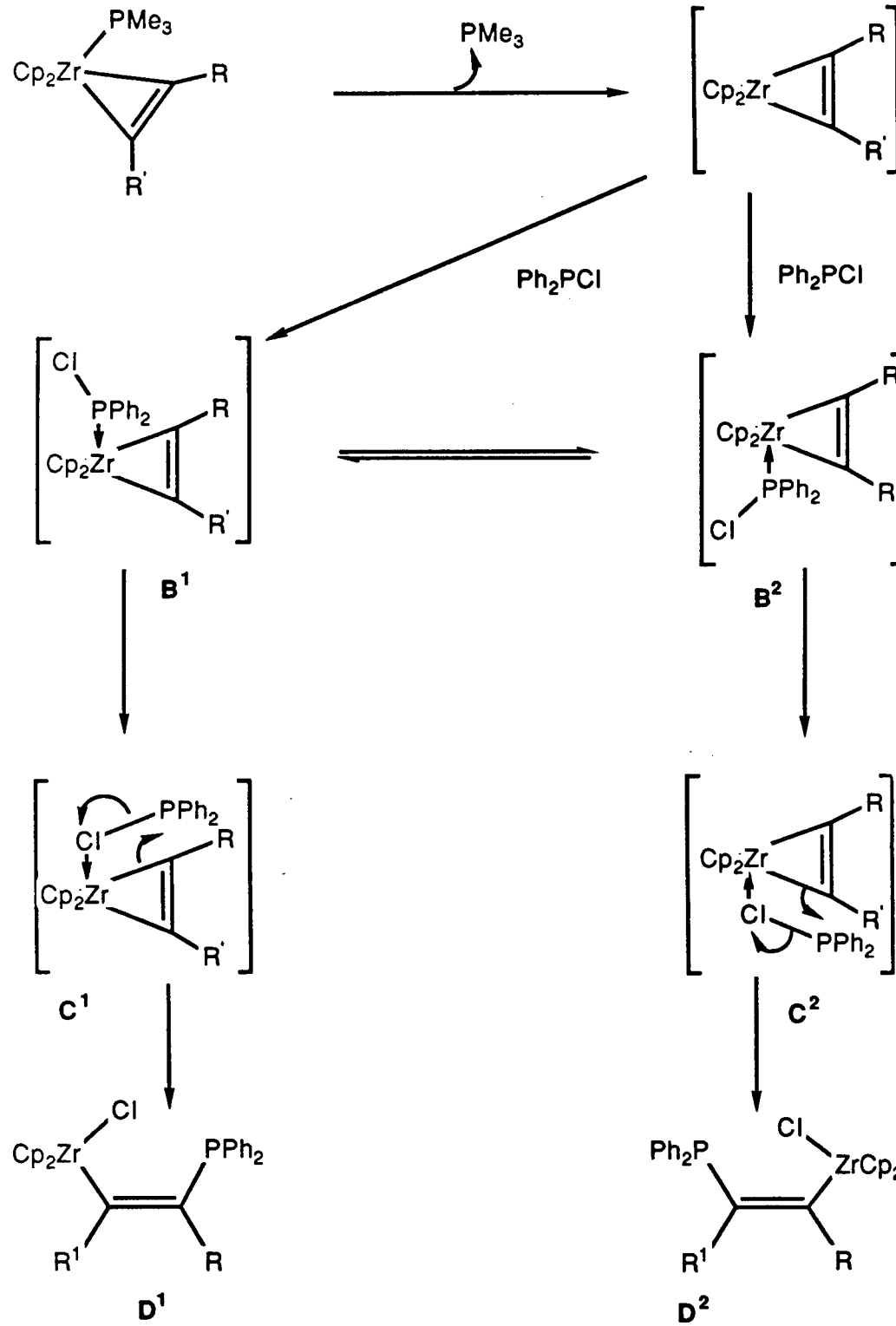
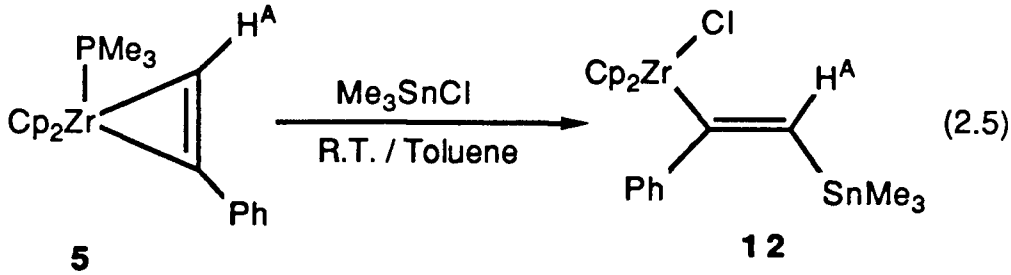


Figure 12. The proposed mechanism for the addition transfer-reaction involving Ph_2PCl.

complexes **4** and **5** they are quite different. Therefore, when the internal alkyne complex **6** reacts with Ph_2PCl the intermediates $\mathbf{B^1}$ and $\mathbf{B^2}$ will be formed in ≈ 2:1 ratio. Since the ratio of the products $\mathbf{D^1}$ and $\mathbf{D^2}$ are equal, the transition states $\mathbf{C^1}$ and $\mathbf{C^2}$ will be of equal energy. The above rationale suggests that intermediates $\mathbf{B^1}$ and $\mathbf{B^2}$ are in equilibrium and that the minor intermediate, having a higher energy, reacts faster than the major intermediate.

2.5 Reactions of Zirconium Alkyne Complexes (4-6) with Me_3SnCl

All reactions involving complexes **4-6** were carried out with one equivalent of Me_3SnCl in toluene at room temperature, similar to that described above for Ph_2PCl. From the reaction with the phenyl alkyne complex **5** there was obtained a single product **12** (equation 2.5). The stereochemistry of the product was assigned by NOEDIFF experiments. Sequential irradiation of the resonances due to the protons of the Cp rings, the Me_3Sn, *ortho* protons of the phenyl group and H^A resulted in the enhancement of resonances consistent with the proposed stereochemistry. The analysis of the ^1H NMR spectrum shows a coupling of 46.9 Hz from $^{117/119}Sn$ to $^1H^A$ which strongly suggests that the Me_3Sn group and H^A are geminal.[30] The ^1H NMR spectrum of the compound **12** is shown in Figure 13.



5 **12** (2.5)

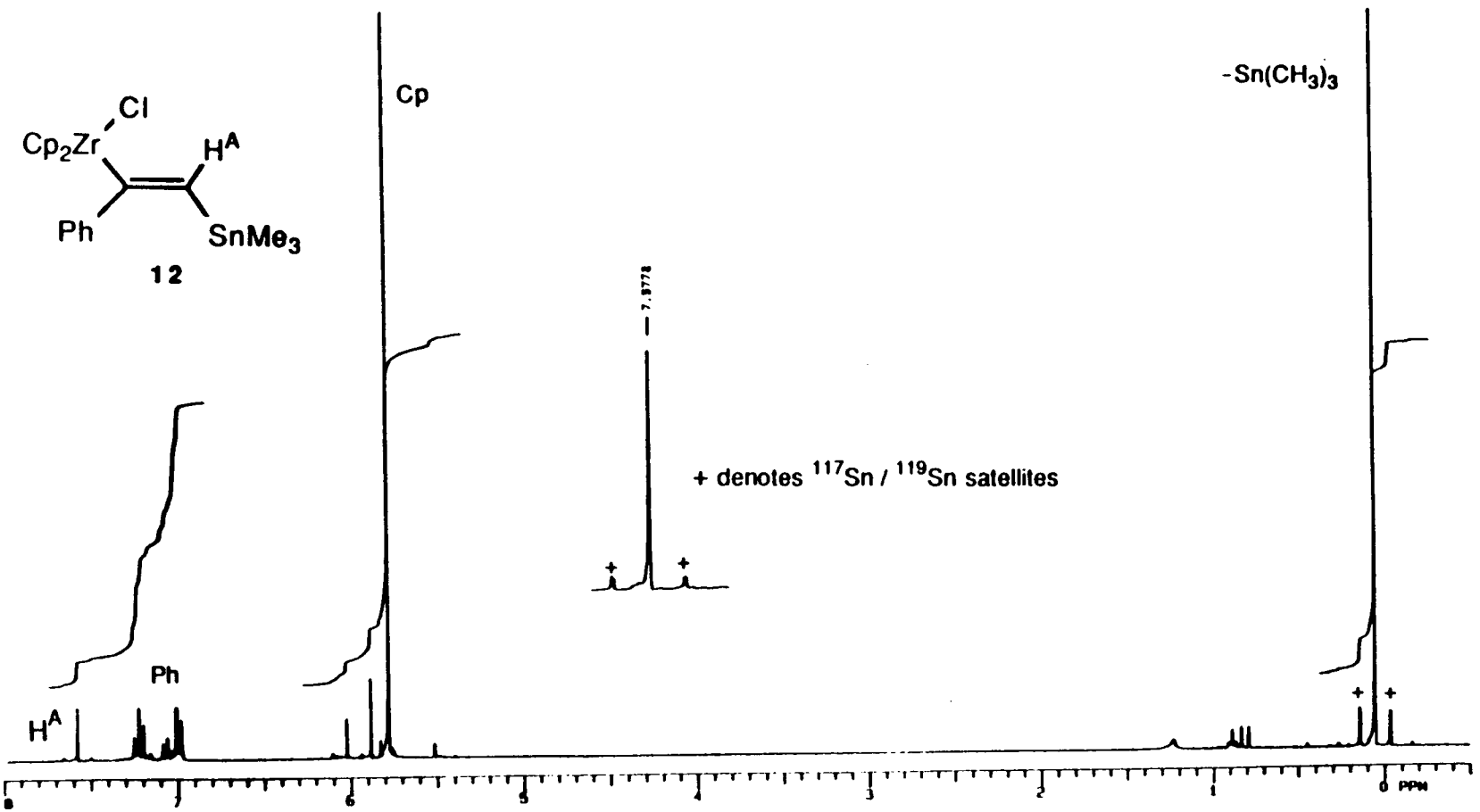
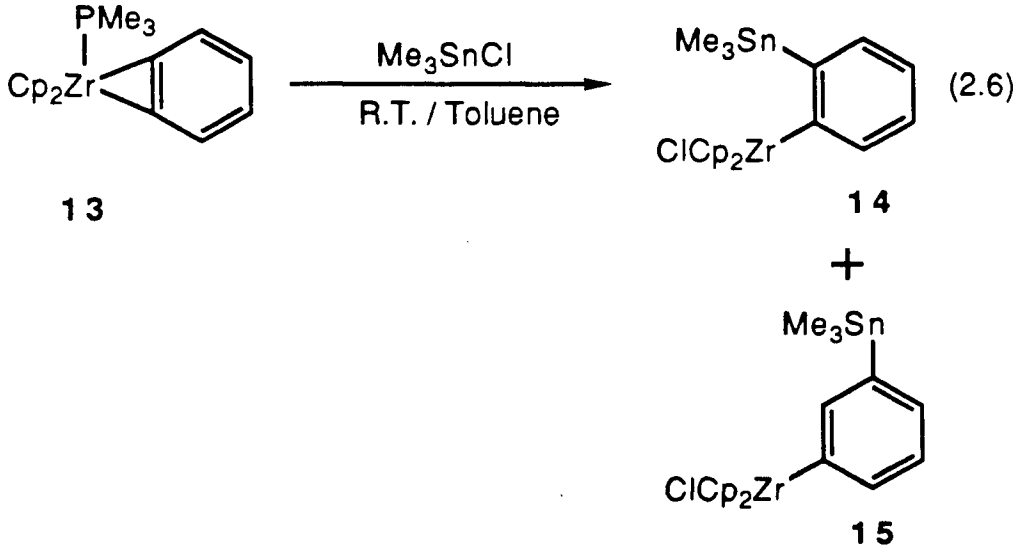


Figure 13. 300 MHz ^{1}H NMR spectrum of compound **12** in C_6D_6.

The reaction of the *tert*-butyl alkyne complex **4** with Me_3SnCl leads to a range of unidentifiable products. In the case of the methyl-phenyl alkyne complex **6**, no reaction occurred even after 36 hours. A ^1H NMR spectrum of the reaction mixture showed that the reactants remained intact.

2.6 Reaction of Cp_2Zr(benzyne)(PMe_3) Complex with Me_3SnCl



In order to block the formation of the product having the organotin moiety trans to the zirconocene fragment, the benzyne complex **13** was examined in the reaction with Me_3SnCl. The reaction of one equivalent of benzyne complex **13** with Me_3SnCl gave a white crystalline material consisting of two compounds **14** and **15** in ≈ 4:1 ratio (equation 2.6). The ^1H NMR spectrum of the products is shown in Figure 14. The two sets of doublets and two sets of triplets of equal intensity in the phenyl region clearly indicate the stereochemistry of the major isomer **14**. The other three broad signals in a 1:2:1 ratio could be due to a 1,3-disubstituted phenyl ring (compound **15**), although the origin of the material is unknown at this time. The appearance of ^1H-

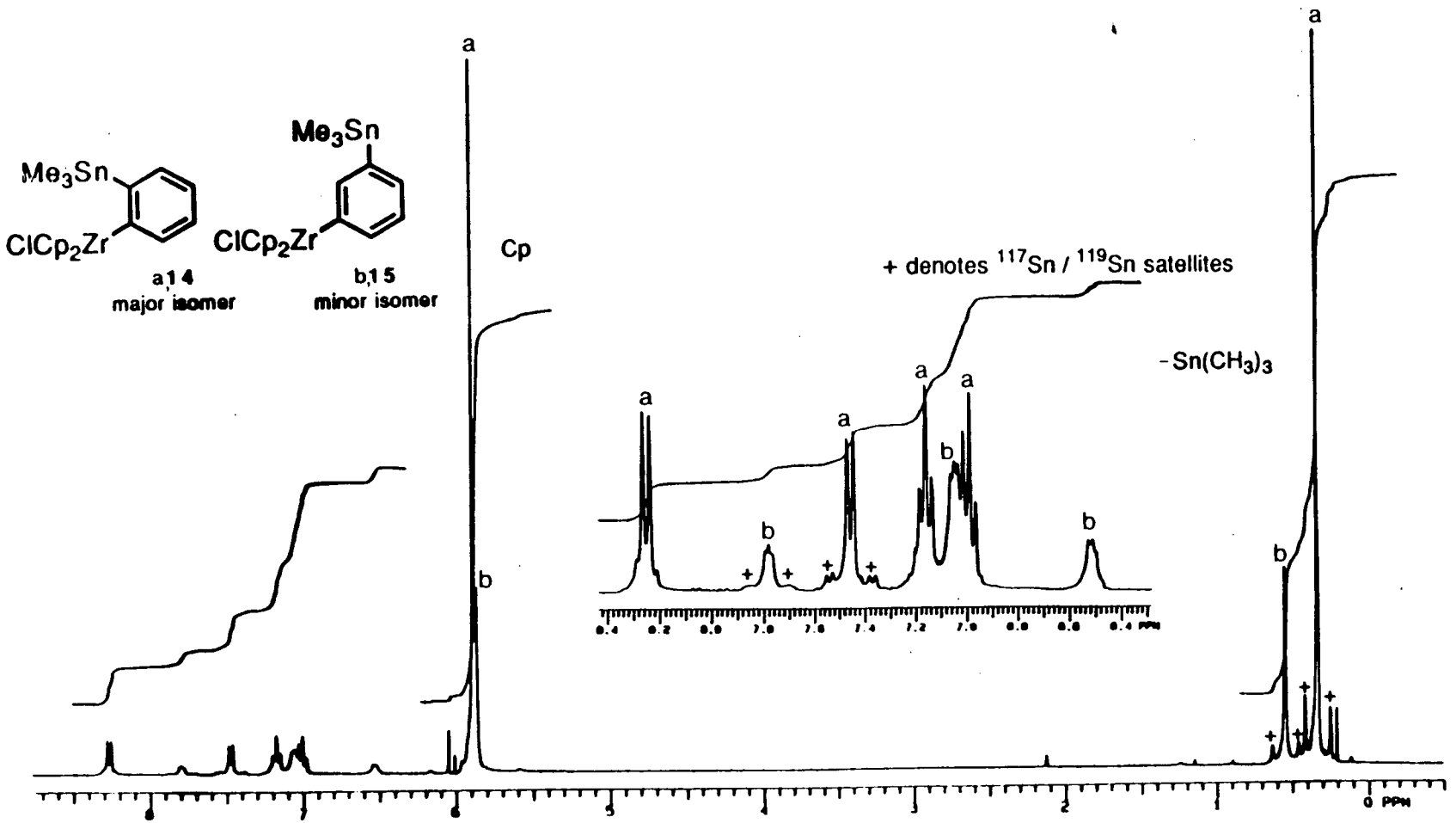


Figure 14. 300 MHz ^{1}H NMR spectrum of compound **14** and **15** in C_6D_6.

$^{117/119}$Sn satellites for the two peaks at 7.45 ppm and 7.78 ppm indicates that they are *ortho* to the Me_3Sn group.

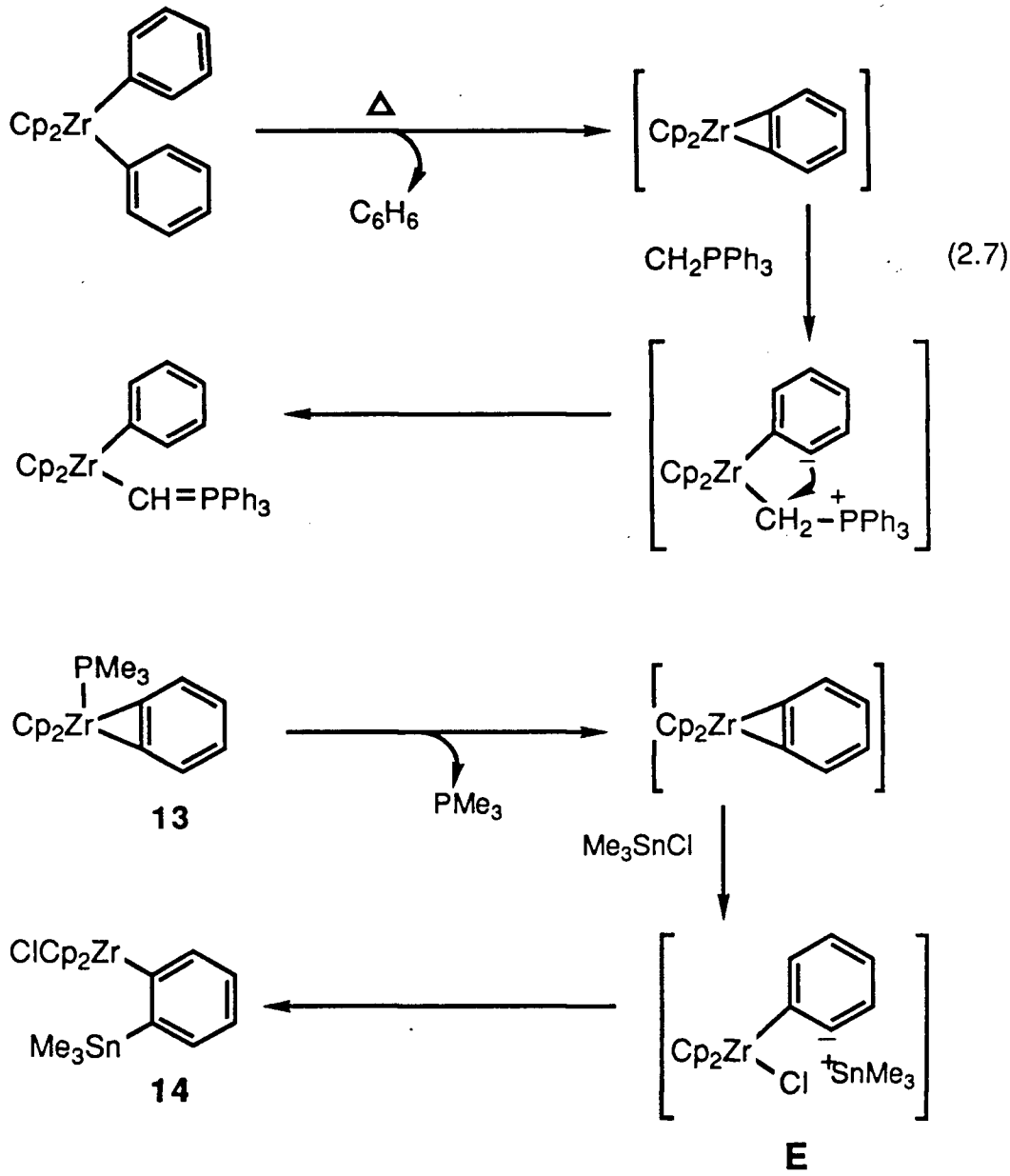


Figure 15. The proposed mechanism for the formation of compound **14**.

Figure 15 shows the possible pathway leading to the formation of the major isomer **14**. A zwitterionic intermediate has been proposed for the reaction of zirconium benzyne complexes with ylids[31] (equation 2.7). By comparison to this the

intermediate **E** would likely be a tight ion pair. The occurrence of these reactions in a nonpolar solvent like toluene supports this contention.

2.7 Mechanism for the Addition-Transfer Reaction Involving Me_3SnCl

Compared to the reactivity of Ph_2PCl, Me_3SnCl gives a single product with the Cp_2ZrCl and the Me_3Sn moieties being trans related. A four-centred mechanism similar to that proposed for the Ph_2PCl reaction cannot lead to the observed trans stereochemistry. The lack of a lone pair of electrons on tin, as found for phosphorus, would be a possible reason for the observed difference in reactivity. The proposed mechanism for the addition-transfer reaction involving Me_3SnCl is shown in Figure 16. The heterolytic cleavage of the Sn-Cl bond, followed by the addition of the Me_3Sn^+ across the double bond of the metallacyclopropene, leads to the formation of the transition state **F**. The appropriate bond breaking and bond forming reaction of the π-complex **F** would lead to the formation of product **G**, where the Me_3Sn moiety and the Cp_2ZrCl moiety are trans related. The Newman projection of the transition state **F** is shown in $\mathbf{F^1}$. Because $\mathbf{F^1}$ can only have the eclipsed conformation, the energy of this transition state will greatly depend upon the nonbonded interaction between R^1 and R. This may well explain why the internal alkyne complex **6** does not take part in the reaction. The dissociation of PMe_3 is invoked as the first step even though the coordination of the Cl is not initially important to the formation of **F**. However, such a dissociation was thought necessary for the formation of the transition state **F** which might otherwise be sterically crowded. Further, the PMe_3 might play a role in promoting the heterolytic cleavage of the Sn-Cl bond via formation of a transient five coordinate adduct such as $(Me_3SnCl)(PMe_3)$.[32a] A pyridine adduct, $(Me_3SnCl)(NC_5H_5)$, similar to the PMe_3 adduct has been proposed.[32]

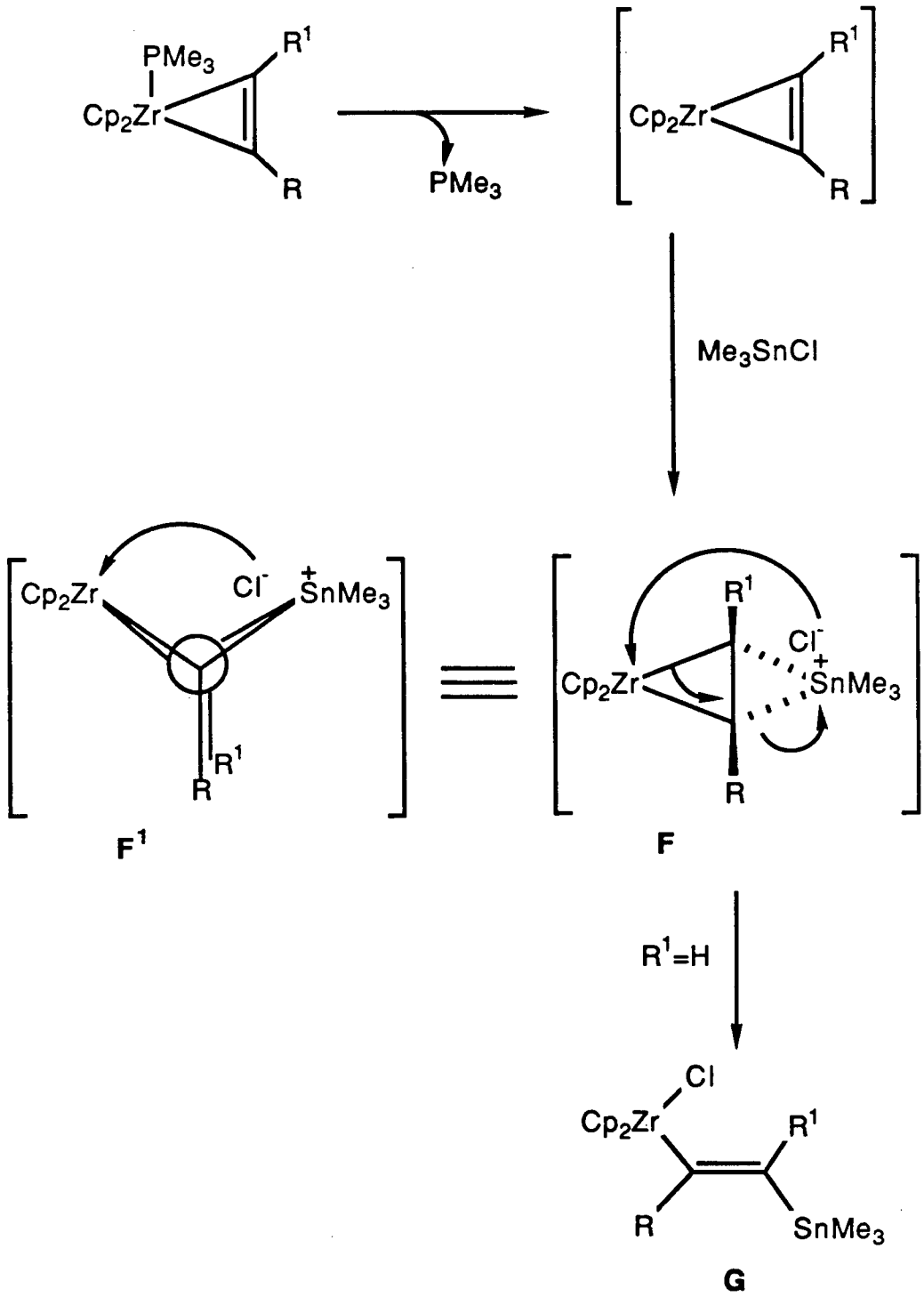


Figure 16. The proposed mechanism for the addition-transfer reaction involving Me_3SnCl.

2.8 Conclusions and Suggestions for Future Work

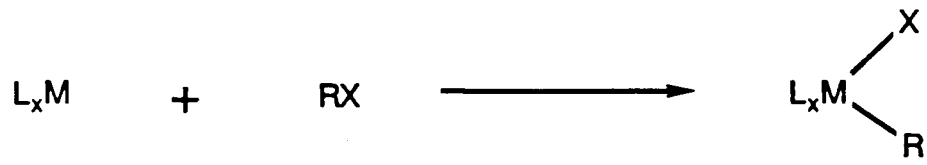
Addition-transfer reactions involving Ph_2PCl were successfully used in the synthesis of 1-phosphinyl and 2-phosphinyl substituted 1,3-dienyl-zirconium complexes. Reacting Ph_2PCl with three different types of alkyne complexes have revealed that the regioselectivity of these reactions increases dramatically with the increase in steric bulk of the substituents on the alkyne. In the case of the *tert*-butyl alkyne complex, 100% regioselectivity was observed. Furthermore, all the reactions with Ph_2PCl gave the products with cis stereochemistry.

The addition-transfer reactions with Me_3SnCl have shown the reaction to be chemoselective towards some terminal alkyne complexes, where the Me_3SnCl reacts exclusively at the least hindered site and always gives the trans product. With a benzyne zirconium complex, an *ortho* disposition is found as expected.

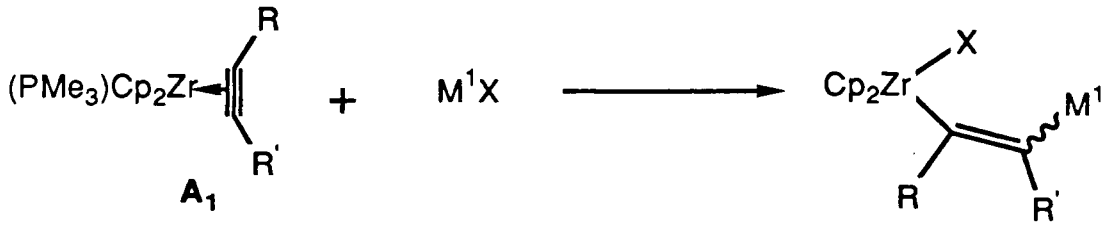
Addition-transfer reactions are quite different to simple transfer or transmetallation reactions in that the stereochemistry of the latter always proceed with retention of configuration of the organic group regardless of the choice of metal or metalloid.

The well-known process of oxidative addition[1] can be compared to the addition-transfer reaction if one considers the η^2-alkyne resonance form of the alkyne complexes rather than the metallacyclopropene resonance form. In the case of a simple oxidative addition reaction of a metal complex L_nM (where M is in the formal zero oxidation state) with an organic halide RX, the metal increases its formal oxidation state to M(II) (Scheme 12). Also this process involves the cleaving of the R-X bond to form the M-X and the M-R bonds. The addition-transfer reaction can be related to this process since zirconium increases its formal oxidation state from Zr(II) to Zr(IV). However, instead of forming a Zr-M^1 bond, the group M^1 is transferred to

(i) oxidative addition



(ii) addition-transfer



Scheme 12

the other end of the alkene to which the zirconium is attached. This discussion emphasizes the uniqueness of this addition-transfer reaction.

Our objective in the future is to extend the addition-transfer reaction to other organometalloid reagents containing selenium, sulphur and boron. We are also interested in probing the stereoselectivity of this reaction in an effort to generate a new method of synthesizing highly functionalized alkenes and dienes.

CHAPTER 3

EXPERIMENTAL

3.1 General Information

All manipulations were performed under purified nitrogen[33] 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 purified 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.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Varian XL-300 spectrometer (at 300 MHz). All NOEDIFF experiments were carried out on a Bruker WH-400 spectrometer (at 400 MHz). The compounds were run as solutions of benzene-d_6 (C_6D_6) or toluene-d_8 (C_7D_8) and the signal positions were given on the δ scale in ppm with reference to C_6D_5H at 7.15 ppm and $C_6D_5CD_2H$ at 2.09 ppm, respectively.[34] ^{13}C NMR spectra were run at 75.4 MHz on a Varian XL-300 spectrometer and the peaks are referenced to C_6D_6 at 128.0 ppm or to the methyl carbon of C_7D_8 at 20.4 ppm. The ^{31}P NMR spectra were also run on the same instrument (at 121.4 MHz) and the signal positions were recorded relative to the external reference of $P(OMe)_3$ at 141.0 ppm. The proton-tin coupling constants (J_{H-Sn}) are given as an average of the ^{117}Sn and ^{119}Sn values. The observed integral values for the η^5-cyclopentadienyl ligand Cp, were consistently less than the

expected. A similar trend has been previously reported and is believed to result from a long spin-lattice relaxation time for the Cp ligand.[35]

The NMR solvents C_6D_6 and C_7D_8 were purchased from MSD Isotopes. These solvents were dried overnight with activated 4Å molecular sieves, vacuum transferred into a reactor bomb, "freeze-pump-thawed" three times and stored in the glovebox. Hexanes and THF were predried over CaH_2 followed by distillation from sodium-benzophenone ketyl. Diethyl ether and toluene were distilled from sodium-benzophenone ketyl.

Microanalyses were performed by Mr. P. Borda of this department. The products resulting from the addition-transfer reactions of Ph_2PCl seem to crystallize with a fractional amount of toluene. Therefore, during the calculations of carbon and hydrogen percentages, the amount of toluene present in these compounds was also taken into account. Pumping on the samples under vacuum for 15 hours was not successful in complete solvent removal. Fractional amounts of solvent present in the dried samples was confirmed by ^1H NMR spectroscopy.

Methyllithium (1.4 M solution) in Et_2O, bis(η^5-cyclopentadienyl)-zirconium(IV)dichloride (Cp_2ZrCl_2), trimethyltin chloride (Me_3SnCl), chloro-diphenylphosphine (Ph_2PCl), 3,3-dimethyl-1-butyne (*tert*-butylacetylene), 1-phenylpropyne (methylphenylacetylene), and 1-phenylethyne (phenylacetylene) were purchased from Aldrich Chemical Co., Inc.. The white residues present in the commercial MeLi were removed by filtration through Celite and the solvent (Et_2O) was evaporated. The resulting powder was redissolved in a 9:1 mixture of Et_2O:THF and was standardized against diphenylacetic acid in THF. This solution was stored in a reactor bomb at -10^{0}C.

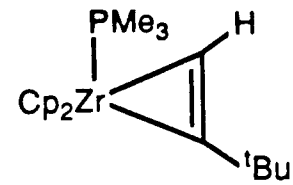
Chloro(alkenyl)bis(η^5-cyclopentadienyl)zirconium(IV) complexes,[36] (trimethylphosphine)(benzyne)bis(η^5-cyclopentadienyl)zirconium(II),[14] chlorobis(η^5-

cyclopentadienyl)hydridozirconium(IV),[37] lithium tri-*tert*-butoxyaluminohydride[38] and 1-ethynylcyclohexene[39] were prepared by literature procedures.

3.2 General Procedure 1: Synthesis of (trimethylphosphine)(η^2-alkyne) bis(η^5-cyclopentadienyl)zirconium(II) Complexes

The Cp_2Zr(alkenyl)Cl complex was dissolved in THF and transferred into a reactor bomb. The reactor bomb was then attached to a vacuum line and the contents were cooled to -78^{0}C. To the cooled solution, 1 equivalent of 0.38 M MeLi solution was syringed in slowly under a strong flow of argon. After stirring the resulting solution for 15 min at -78^{0}C, it was allowed to warm up to R.T. and stirred for 30 min. The solvent (THF) was then removed under vacuum and the residue was extracted with toluene. The undissolved LiCl was removed by filtration through a layer of Celite. The clear solution was concentrated and transferred into another reactor bomb to which an excess of PMe_3 (10 equivalents) was added and stirred for 36 hours at R.T.. Evaporation of the solvent results in an oily material consisting of >80% (by NMR) of the zirconium alkyne complex.

3.2.1 Synthesis of (η^5-C_5H_5)$_2$Zr(η^2-^{t}BuC≡CH)(PMe_3)



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The following reagents were used as described in general procedure 1. Chloro[(E)2-*tert*-butylethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) (0.85 g, 2.5

mmol) dissolved in THF (10 mL), 6.58 mL of 0.38 M MeLi and 2.0 mL (>10 equivalents) of PMe_3 were used. Evaporation of toluene at the end of the procedure gave a red, oily material which was dissolved in hexanes. Cooling this solution at -20^0C overnight gave a yellow crystalline product (0.8g, 84%).

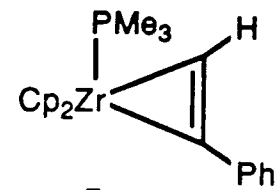
^{1}H NMR: δ (C_6D_6, 300 MHz): 0.95 (9H, d, PMe_3, J_{P-H} = 5.3 Hz), 1.48 (9H, s, *tert*-butyl), 5.33 (10H, d, Cp, J_{P-H} = 1.7 Hz), 7.54 (H^A, d, J_{P-H^A} = 4.9 Hz)

^{31}P NMR: δ (C_6D_6, 121.5 MHz): -0.64 (s).

^{13}C NMR: δ (C_6D_6, 75.4 MHz): 16.93 (d, J_{P-C} = 17.7 Hz), 32.96 (s), 38.47 (s), 102.19 (Cp, s), 134.38 (d, J_{P-C} = 30.6 Hz), 196.92 (d, J_{P-C} = 9.8 Hz).

Anal. Calcd. for $C_{19}H_{29}PZr$: C 60.11, H 7.70. Found: C 60.24, H 7.90.

3.2.2 Synthesis of $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}PhC{\equiv}CH)(PMe_3)$



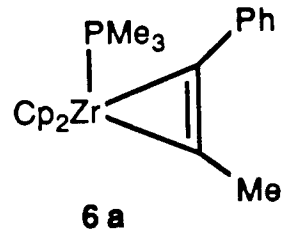
5

The following reagents were used as described in procedure 1. Chloro[(E) 2-phenylethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) (1.01 g, 2.81 mmol) dissolved in THF (20 mL), 7.3 mL of 0.38 M MeLi and 2.2 mL (>10 equivalents) of PMe_3 were used. Evaporation of toluene at the end of the procedure gave a red, oily material which, after washing with hexanes and drying, gave a red powder in 85% purity (0.97g, 86%). Thus far this compound has not been isolated in crystalline form.

^{1}H NMR: δ (C_6D_6, 300 MHz): 0.96 (9H, d, PMe_3, J_{P-H} = 5.9 Hz), 5.31 (10H, d, Cp, J_{P-H} = 1.7 Hz), 7.23 (1H, t, *para*-Ph), 7.48 (2H, t, *meta*-Ph), 7.86 (2H, d, *ortho*-Ph), 8.05 (1H, d, H^A, J_{P-H^A} = 3.8 Hz).

^{31}P NMR: δ (C_6D_6, 121.5 MHz): 0.56 (s).

3.2.3 Synthesis of $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}PhC{\equiv}CMe)(PMe_3)$



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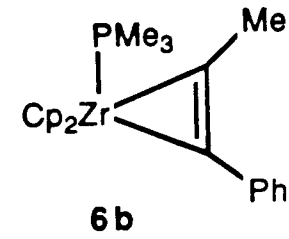


6 b

The following reagents were used as described in general procedure 1. Chloro[(E) 2-phenyl-1-methylethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) and Chloro[(E) 2-methyl-1-phenylethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) (in ≈4:1 ratio) (0.77 g, 2.06 mmol) dissolved in THF (10 mL), 5.4 mL of 0.38 M MeLi and 1.5 mL (> 10equivalents) of PMe_3 were used. Evaporation of toluene at the end of the procedure gave a brownish oil. Attempts to crystallize with a ≈4:1 mixture of Et_2O:hexanes gave a white powder in 90% purity (0.74 g, 87%). The ratios of the isomers **6a** (major) : **6b** (minor) was found to be ≈2:1 by ^{31}P NMR.

^{1}H NMR: δ (C_6D_6, 300 MHz): Major isomer: 0.81 (9H, d, PMe_3, $J_{P\text{-}H}$ = 5.8 Hz), 2.59 (3H, d, Me, $J_{P\text{-}H}$ = 0.4 Hz), 5.34 (10H, d, Cp, $J_{P\text{-}H}$ = 1.6 Hz), 6.73 (2H, d, *ortho*-Ph), 7.24 (2H, t, *meta*-Ph), 7.48 (1H, t, *para*-Ph); Minor isomer: 0.96 (9H, d, PMe_3, $J_{P\text{-}H}$ = 5.9 Hz), 2.44 (3H, d, Me, $J_{P\text{-}H}$ = 1.3 Hz), 5.32 (10H, d, J_P = 1.7 Hz), 6.98 (2H, t, *meta*-Ph), 7.17 (1H, t, *para*-Ph), 7.61 (2H, d, *ortho*-Ph).

^{31}P NMR: δ (C_6D_6, 121.5 MHz): Major isomer: -3.58 (s); Minor isomer: -0.30 (s).

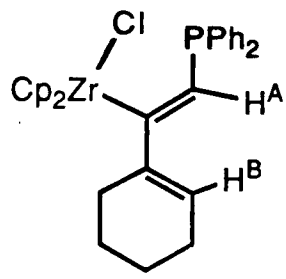
NOEDIFF experiments: (C_6D_6, 400 MHz):

Resonance subjected to irradiation (δ)	Observed enhancements (δ)
Major isomer	
0.81 (P*Me*$_3$)	5.34 (C_5H_5)
	6.73 (*ortho*-Ph)
2.59 (*Me*)	5.34 (C_5H_5)
	6.73 (*ortho*-Ph)
Minor isomer	
0.96 (P*Me*$_3$)	5.32 (C_5H_5)
	2.44 (*Me*)
2.44 (*Me*)	0.96 (*Me*)
	7.16 (*ortho*-Ph)

3.3 General Procedure 2 : Addition-Transfer Reactions of Ph_2PCl and $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-alkyne})(PMe_3)$

The $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-alkyne})(PMe_3)$ complex was dissolved in toluene and transferred into a reactor bomb. One equivalent of Ph_2PCl, dissolved in toluene, was added to the contents in the reactor bomb and stirred for 6 hours at R.T. The white precipitate (Cp_2ZrCl_2) was removed by filtration through a layer of Celite. The product was crystallized from toluene and hexanes at -20^{0}C.

3.3.1 Synthesis of (Z)-Chloro[2-diphenylphosphino-1-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) and Chloro[(Z) 2-diphenylphosphino-(E)2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV)



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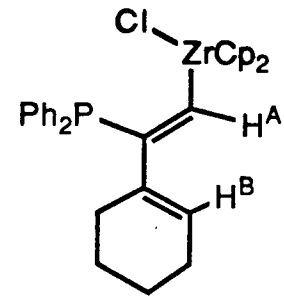

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The cyclohexenyl enyne complex (η^5-$C_5H_5)_2Zr(HC{\equiv}CC_6H_9)(PMe_3)$ **1** (0.366 g, 0.91 mmol) was dissolved in toluene (≈10 mL) and Ph_2PCl (0.2 g, 0.91 mmol), dissolved in (≈5 mL) toluene, was added. Workup gave a white crystalline product (0.41 g, 82%). The ratios of the isomers **2** (major) : **3** (minor) was found to be 4:1 by ^{31}P NMR.

^{1}H NMR: δ (C_7D_8, 300 MHz): Major isomer: 1.60 (4H, m), 2.15 (4H, m), 5.46 (H^B, m), 5.86 (10H, s, Cp), 7.07 (6H, m, Ph) 7.23 (H^A, d, $J_{P\text{-}H^A}$ = 10.1 Hz), 7.95 (4H, m, Ph); Minor isomer: 1.45 (4H, m), 1.82 (2H, m), 2.28 (2H, m), 5.68 (10H, s, Cp), 5.71 (H^B, m), 8.37 (H^A, d, $J_{P\text{-}H^A}$ = 76.1 Hz).

^{31}P NMR: δ (C_7D_8, 121.5 MHz): Major isomer: -58.38 (s); Minor isomer: -40.09 (s).

^{13}C NMR: δ (C_7D_8, 75.4 MHz): Major isomer: 22.69 (s), 23.62 (s), 26.46 (s), 28.23 (s), 111.0 (s, Cp), 119.92 (d, $J_{P\text{-}C}$ = 46.8 Hz), 128.67 (d, $J_{P\text{-}C}$ = 7.9 Hz), 129.44 (s), 132.31 (d, $J_{P\text{-}C}$ = 9.4 Hz); Minor isomer: 21.39 (s), 23.13 (s),

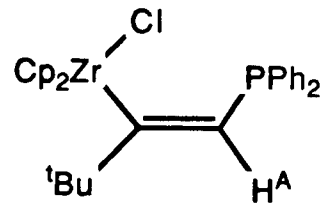
28.48 (s), 25.63 (s), 110.72 (s, Cp), 128.49 (d, J_{P-C} = 2.9 Hz), 129.76 (s), 132.69 (d, J_{P-C} = 10.2 Hz).

Anal. Calcd. for $C_{30}H_{30}ClPZr.0.4C_7H_8$: C 67.33, H 5.72. Found: C 67.29, H 5.71.

NOEDIFF experiments: (C_7D_8, 400 MHz):

Resonance subjected to irradiation (δ)	Observed enhancements (δ)
5.46 (*H*^{B})	2.15 (cyclohexene -C*H*$_2$-)
	5.86 (C$_5$*H*$_5$)
	7.23 (*H*^{A})
5.86 (C$_5$*H*$_5$)	5.46 (*H*^{B})
	7.95 (*ortho*-P*Ph*$_2$)
7.95 (*ortho*-P*Ph*$_2$)	5.86 (C$_5$*H*$_5$)
	7.07 (*meta*-P*Ph*$_2$)
	7.23 (*H*^{A})
7.23 (*H*^{A})	2.15 (cyclohexen -C*H*$_2$-)
	5.46 (*H*^{B})
	7.95 (*ortho*-P*Ph*$_2$)

3.3.2 Synthesis of (Z)-Chloro(2-diphenylphosphino-1-*tert*-butylethenyl) bis(η^5-cyclopentadienyl)zirconium(IV)



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$(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}^tBuC{\equiv}CH)(PMe_3)$ **4** (0.15 g, 0.4 mmol) was dissolved in toluene (≈5 mL) and Ph_2PCl (0.09 g, 0.4 mmol), dissolved in (≈2 mL) toluene, was added. Workup gave a white crystalline product (0.17 g, 82%).

^{1}H NMR: δ (C_6D_6, 300 MHz): 1.13 (9H, s, C*Me*$_3$), 5.87 (10H, s, Cp), 7.07 (6H, m, Ph), 7.35 (H^A, d, $J_{P\text{-}H^A}$ = 10.1 Hz), 7.95 (4H, m, Ph).

^{31}P NMR: δ (C_6D_6, 121.5 MHz): -63.77 Hz.

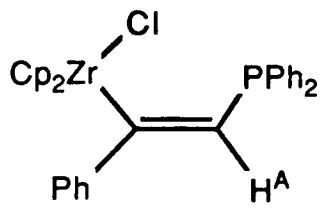
^{13}C NMR: δ (C_6D_6, 75.4 MHz): 32.71 (s, C(*C*H$_3$)), 43.49 (s, *tert*-C), 110.61 (s, *C*$_5$H$_5$), 121.96 (d, $J_{P\text{-}C}$ = 49.1 Hz), 128.59 (d, $J_{P\text{-}C}$ = 8.2 Hz), 129.38 (s), 132.34 (d, $J_{P\text{-}C}$ = 9.1 Hz). 136.94 (d, $J_{P\text{-}C}$ = 24.3 Hz).

Anal. Calcd. for $C_{28}H_{30}ClPZr.0.2C_7H_8$: C 65.08, H 5.87. Found: C 65.29, H 6.14.

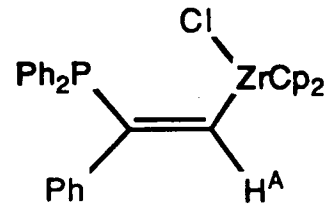
NOEDIFF experiments: (C_6D_6, 400 MHz):

Resonance subjected to irradiation (δ)	Observed enhancements (δ)
1.13 (C*Me*$_3$)	5.87 (C$_5$*H*$_5$)
	7.35 (*H*^{A})
5.87 (C$_5$*H*$_5$)	1.13 (C*Me*$_3$)
	7.95 (*ortho*-P*Ph*$_2$)

3.3.3 Synthesis of (Z)-Chloro(2-diphenylphosphino-1-phenylethenyl)bis(η^5-cyclopentadienyl)zirconium(IV) and Chloro[(Z)-2-diphenylphosphino-(E)2-phenylethenyl)bis(η^5-cyclopentadienyl)zirconium(IV)



8



9

(η^5-C_5H_5)$_2$Zr(η^2-PhC≡CH)(PMe$_3$) **5** (0.607 g, 1.53 mmol) was dissolved in toluene (≈10 mL) and Ph_2PCl (0.337 g, 1.53 mmol), dissolved in (≈5 mL) toluene, was added. Workup gave a white crystalline product (0.63 g, 76%). The ratio of the isomers **8** (major) : **9** (minor) was found to be 83:17 by ^{31}P NMR.

^{1}H NMR: δ (C_6D_6, 300 MHz): Major isomer: 6.12 (10H, s, Cp), 7.14 (9H, m), 7.57 (2H, m), 7.59 (H^A, d, $J_{P\text{-}H^A}$ =10.7 Hz), 8.24 (4H, m, *ortho*-P*Ph*$_2$); Minor isomer: 5.99 (10H, s, Cp), 9.33 (H^A, d, $J_{P\text{-}H^A}$ = 74.8 Hz).

^{31}P NMR: δ (C_6D_6, 121.5 MHz): Major isomer: -55.52 (s); Minor isomer: -38.88 (s).

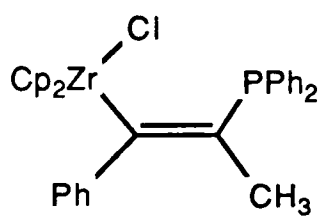
^{13}C NMR: δ (C_6D_6, 75.4 MHz): 110.10 (s, Cp of major isomer), 114.12 (s, Cp of minor isomer), 125.32 (s), 126.45 (s), 128.55 (s), 128.75 (d, $J_{P\text{-}C}$ = 8.1 Hz), 129.59 (s), 132.32 (d, $J_{P\text{-}C}$ = 9.6 Hz).

Anal. Calcd. for $C_{30}H_{26}ClPZr.0.4C_7H_8$: C 67.80, H 5.07. Found: C 67.68, H 4.99.

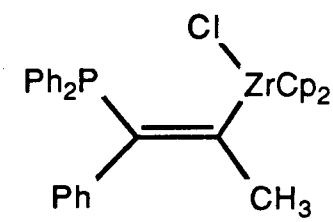
NOEDIFF experiments: (C_6D_6, 400 MHz):

Resonance subjected to irradiation (δ)	Observed enhancements (δ)
6.12 (C_5H_5)	8.24 (*ortho*-PPh_2)
	7.43 (*ortho*-Ph)
8.24 (*ortho*-PPh_2)	6.12 (C_5H_5)
	7.43 (*meta*-Ph)
	7.59 (H^A)

3.3.4 Synthesis of Chloro[(E)2-methyl-1-phenyl-(Z)2-diphenylphosphinoethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) and Chloro-[1-methyl-(E)2-phenyl-(Z)2-diphenylphosphinoethenyl)bis(η^5-cyclopentadienyl)zirconium(IV)



10



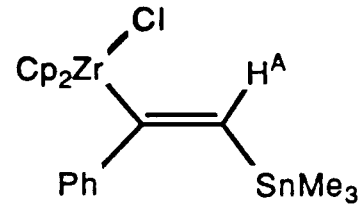
11

(η^5-C_5H_5)$_2$Zr(η^2-PhC≡CMe)(PMe_3) **6** (0.135g , 0.32 mmol) was dissolved in toluene (≈5 mL) and Ph_2PCl (0.072 g, 0.32 mmol), dissolved in (≈5 mL) toluene, was added. Attempts to crystallize the product were not successful. Adding excess of hexanes to the toluene solution gave a white powder (0.11 g, 62%) containing >70% of the product. The ratio of the two products, **10** and **11**, was found to be 56:44 by ^{31}P NMR.

^{1}H NMR: δ (C_6D_6, 300 MHz): 1.73 (3H, d, Me, J_{P-H} = 7.6 Hz), 1.97 (3H, d, J_{P-H} = 3.9 Hz), 5.79 (s, Cp), 5.80 (s, Cp); Phenyl resonances of both isomers: 6.92 (m), 7.08 (m), 7.24 (m), 7.86 (m).

^{31}P NMR: δ (C_6D_6, 121.5 MHz): Major isomer: -39.41 (s); Minor isomer: -39.16 (s).

3.4 Synthesis of (Z)-Chloro(1-phenyl-2-trimethylstannylethenyl)bis-(η^5-cyclopentadienyl)zirconium(IV).



12

(η^5-C_5H_5)$_2$Zr(η^2-PhC≡CH)(PMe_3) **5** (0.567 g, 1.42 mmol) was dissolved in (≈10 mL) toluene and Me_3SnCl (0.283 g, 1.42 mmol) was added. The resulting mixture was transferred into a reactor bomb and stirred for 36 hours at room temperature. Removing the solvent (toluene) under vacuum gave an orange oil. Extracting the oil with ≈35mL of hexanes and cooling it at -20^{0}C overnight gave a yellow crystalline product **12** (0.57 g, 77%).

^{1}H NMR: δ (C_6D_6, 300 MHz): 0.05 (9H, s, SnMe3, $J_{H\text{-}Sn}$ = 53.4 Hz), 5.77 (10H, s, Cp), 6.99 (2H, d, *ortho*-Ph), 7.06 (1H, t, *para*-Ph), 7.22 (2H, t, *meta*-Ph), 7.58 (H^A, s, $J_{H\text{-}Sn}$ = 46.9 Hz).

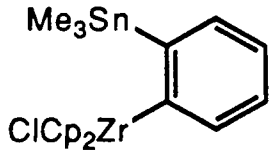
^{13}C NMR: δ (C_6D_6, 75.4 MHz): -7.27 (s, $SnMe_3$, $J_{C\text{-}Sn}$ = 322.4 Hz), 106.91 (s, $J_{C\text{-}Sn}$ = 307.3 Hz), 112.06 (s, Cp), 124.85 (s), 125.87 (s), 128.58 (s), 150.35 (s), 223.13 (s).

Anal. Calcd. for $C_{21}H_{25}ClSnZr$: C 48.25, H 4.82. Found: C 48.59, H 5.08.

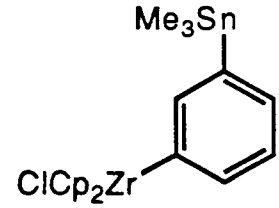
NOEDIFF experiments: (C_6D_6, 400 MHz):

Resonance subjected to irradiation (δ)	Observed enhancements (δ)
0.05 (Sn*Me*$_3$)	6.99 (*ortho*-Ph)
	7.58 (H^A)
5.77 (C_5H_5)	6.99 (*ortho*-Ph)
	7.58 (H^A)
6.99 (*ortho*-Ph)	0.05 (Sn*Me*$_3$)
	5.77 (C_5H_5)
7.58 (H^A)	0.05 (Sn*Me*$_3$)
	5.71 (C_5H_5)

3.5 Synthesis of Chloro(2-trimethylstannylphenyl)bis(η^5-cyclopentadienyl)zirconium(IV) and Chloro(3-trimethylstannylphenyl)bis(η^5-cyclopentadienyl)zirconium(IV)



14



15

$(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}C_6H_4)(PMe_3)$ **13** (0.17 g. 0.46 mmol) was dissolved in (≈10 mL) toluene and Me_3SnCl (0.09 g, 0.46 mmol) was added. The resulting mixture was transferred into a reactor bomb and stirred for 36 hours at room temperature. Removing the solvent (toluene) under vacuum gave a colorless oil. Dissolving the oil in a solvent mixture containing toluene and hexanes and cooling at -20^{0}C overnight gave a white crystalline product (0.15 g, 63%). The ratios of isomers **14** (major): **15** (minor) was found to be 4:1 by ^{1}H NMR.

^{1}H NMR: δ (C_6D_6, 300 MHz): Major isomer: 0.31 (9H, s, Sn*Me*$_3$, $J_{H\text{-}Sn}$ = 49.6 Hz), 5.87 (10H, s, Cp), 6.99 (1H, t, $J_{H\text{-}H}$ = 7.2 Hz), 7.16 (1H, t, $J_{H\text{-}H}$ = 7.6 Hz), 7.45 (1H, d, $J_{H\text{-}H}$ = 7.2 Hz, $J_{H\text{-}Sn}$ = 51.0 Hz), 8.25 (1H, d, $J_{H\text{-}H}$ = 7.6 Hz); Minor isomer: 0.05 (s, Sn*Me*$_3$, $J_{H\text{-}Sn}$ = 53.0 Hz), 5.84 (10H, s, Cp), 6.52 (1H, m), 7.04 (2H, m), 7.78 (1H, m, $J_{H\text{-}Sn}$ = 50.4 Hz).

^{13}C NMR: δ (C_6D_6, 75.4 MHz): Major isomer: -6.07 (s, Sn*Me*$_3$), 112.78 (s, Cp); Minor isomer: -4.16 (s, Sn*Me*$_3$)114.06 (s, C_5H_5).

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