STRAINED CATIONIC HETEROCYCLES AND OTHER NOVEL PHOSPHAALKENE-DERIVED SPECIES

by

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Abstract

This thesis outlines the results from three projects undertaken as part of my Ph.D. studies, with Chapter 1 serving as a general introduction and Chapter 5 serving to summarize the thesis.

Chapter 2 details a Lewis acid-mediated methodology for preparing phosphaalkenes from silyl phosphines [$RP(SiMe_3)_2$; R = alkyl, aryl, silyl] and aldehydes or ketones. The scope of this methodology was explored and phosphaalkenes *t*BuP=CH*t*Bu (**1**), AdP=CH*t*Bu (**2**), MesP=CH*t*Bu (**3**) and MesP=CPh_2 (**4**) were prepared on preparative scales. For phosphaalkene **1**, this reduced its synthesis from 11 weeks to less than one hour. Additionally, $AlCl_3$ and $GaCl_3$ adducts of phosphaalkenes **1** and **2** were synthesized and characterized by X-ray crystallography.

In Chapter 3, the reactions of phosphaalkenes **1** and **2** with potential cationic initiators are discussed. For both phosphaalkenes, treatment with substoichiometric HOTf affords rare diphosphiranium cations. Mechanistic studies reveal that this process proceeds via phosphenium triflate intermediates. Unexpectedly, treatment with the related MeOTf affords diphosphetanium cations via methylenephosphonium intermediates. Additionally, it was found that the diphosphetanium cation formed from phosphaalkene **1** would react with two additional equivalents of MeOTf to afford an unprecedented dicationic diphosphetanium.

Finally, Chapter 4 describes the abnormal reaction of IMes, a N-heterocyclic carbene (NHC), with phosphaalkenes to afford novel 4-phosphino-2-carbenes. Interestingly, DFT calculations of plausible reaction intermediates suggest the reactions proceed via free abnormal NHCs (*a*NHCs). The phosphino-functionalized NHC (**5**),

derived from the reaction of IMes with $MesP{=}CPh_2$, was used to study the coordination properties of this novel class of ligands. Treating carbene **5** with substoichiometric (tht)AuCl (0.5 equiv) affords a biscarbene complex, indicating that AuCl is preferentially coordinated by the carbene functionality. *P*-coordination of AuCl occurs when carbene **5** is treated with additional equivalents of AuCl, confirming the bifunctional nature of this ligand. Additionally, rhodium and iridium complexes of the type $(NHC)M(CO)_2Cl$ (M = Rh, Ir) were prepared and CO stretching frequencies of these complexes suggest that carbene **5** has similar donor properties as IMes.

Preface

Sections of this work have been published previously. In Chapter 1, sections 1.3.2 and 1.3.3, introductions to low-valent phosphorus chemistry and phosphaalkene polymers, respectively, are expansions of topics discussed in a Perspectives article published in *Dalton Transactions*. The Perspective reviewed work done by our group related to phosphaalkene supported catalysis, addition polymerization of P=C bonds and conjugated polymers containing P=C bonds, and was prepared jointly with Julien Dugal-Tessier, a fellow student, and Prof. Derek P. Gates (Bates, J.I.; Dugal-Tessier, J.; Gates, D.G. *Dalton Trans.* **2010**, *39*, 3151).

The information presented in Chapter 2 has been published in the *New Journal of Chemistry*. I performed all synthetic work described. Brian O. Patrick collected the X-ray data for compound **2.13** and solved its structure. I completed the X-ray data collection and structural solutions for the other compounds. Prof. Derek P. Gates and I prepared the manuscript jointly (Bates, J.I.; Patrick, B.O.; Gates, D.G. *New J. Chem.* **2010**, *34*, 1660).

The work presented in Chapter 3 will be submitted as a full paper prepared with Prof. Derek P. Gates. All synthetic and X-ray crystallographic work was completed by me. Preliminary results, namely the preparation and molecular structures of compounds **3.6a** and **3.8b**, were disclosed previously in a communication published in the *Journal of the American Chemical Society* (Bates, J.I.; Gates, D.P. *J. Am. Chem. Soc.* **2006**, *128*, 15998).

The work presented in Chapter 4 will be submitted as a full paper prepared with Prof. Pierre Kennepohl and Prof. Derek P. Gates. All synthetic and X-ray crystallographic work was completed by me. Computational models were prepared and

calculations performed by me, with Prof. Pierre Kennepohl being consulted extensively in the interpretation of the results. Preliminary results were communicated as a communication in *Angewandte Chemie International Edition* (Bates, J.I.; Kennepohl, P.; Gates, D.G. *Angew. Chem. Int. Ed.* **2009**, *48*, 9844). These results include the synthesis and molecular structures of compounds **4.3** and **4.9** and some preliminary computational work.

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List of Symbols and Abbreviations

Ad = adamantyl

ATR = attenuated total reflectance

m-CPBA = *m*-chloroperoxybenzoic acid

CCDC = Cambridge Crystallographic Data Centre

cod = cyclooctadiene

δ = chemical shift

δ^+,δ^- = partial positive and negative charges, respectively

Δ = heat or difference

DNA = deoxyribonucleic acid

E = an electrophile or a generic element

E = *entgegen* (configurational)

EI = electron-impact

fwhh = full-width at half-height

GOF = goodness of fit

GPC = Gel Permeation Chromatography

$\{^1H\}$ = proton decoupled (spectroscopy)

η = hapto

h = hour

I*t*Bu = *N*,*N*'-di-*tert*-butylimidazol-2-ylidene

IH = imidazol-2-ylidene

IMe = *N*,*N*'-dimethylimidazol-2-ylidene

IMes = *N*,*N*'-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene

IPr = IDipp = *N*,*N*'-bis(2,6-di-*iso*-propylphenyl)imidazol-2-ylidene

init. = initiator

IR = infrared

J = coupling constant (spectroscopy)

Kα = spectral line

lit. = literature

μ = absorption coefficient (crystallography)

m = multiplet (spectroscopy)

M = Molar (mol L^{-1}) or a generic metal

M_n = number-average molecular weight

M_w = weight-average molecular weight

m/z = mass-to-charge ratio

MeCN = acetonitrile

Mes = Mesityl = 2,4,6-trimethylphenyl

Mes* = Supermesityl = 2,4,6-tri-*tert*-butylphenyl

MS = mass spectrometry

MW = molecular weight

NHC = N-heterocyclic carbene

NMR = Nuclear Magnetic Resonance

n = principal quantum number

Nu = nucleophile

ORTEP = Oak Ridge Thermal Ellipsoid Plot Program (crystallography)

OTf = triflate = $-SO_3CF_3$

PDI = polydispersity index

$\%V_{bur}$ = percentage buried volume

ppm = parts per million

PMP = poly(methylenephosphine)

PPP = poly(phenylenephosphaalkene)

PPV = poly(phenylenevinylene)

PS = polystyrene

Py = pyridyl = $-C_5H_5N$

R, R', or R" = Side group

R = residual factor (crystallography)

R = *rectus* (configurational)

refln = reflections

R.T. = Room temperature, 25 °C

S = *sinister* (configurational)

T or Temp. = Temperature

THF = tetrahydrofuran

tht = tetrahydrothiophene

UBC = The University of British Columbia

UV = ultraviolet

VAZO 88 = 1,1'-Azobis(cyclohexanecarbonitrile)

X = halide, counterion or leaving group

Z = number of repeating units in the unit cell (crystallography)

Z = *zusammen* (configurational)

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While I have many “mommies”, I have one Mom. This is for you!

Chapter 1: Introduction

"Just think of the differences today. A young person gets interested in chemistry and is given a chemical set. But it doesn't contain potassium cyanide. It doesn't even contain copper sulfate or anything else interesting because all the interesting chemicals are considered dangerous substances. Therefore, these budding young chemists don't get a chance to do anything engrossing with their chemistry sets. As I look back, I think it is pretty remarkable that Mr. Ziegler, this friend of the family, would have so easily turned over one-third of an ounce of potassium cyanide to me, an eleven-year-old boy."

– Linus Pauling[1]

1.1 Introduction

Given the ubiquitous nature of chemicals in our daily lives – the chemically treated water for our morning showers, the vehicles and fuel used for our commutes to work, the computers and liquid crystal displays (LCDs) used to do our work, the monosodium glutamate (MSG) added to our take out Chinese dinners, and the last decaffeinated coffees before the return to our beds – it seems appropriate, in this the International Year of Chemistry (2011), to begin with a question: what is chemistry?

*A version of this chapter has been published. Joshua I. Bates, Julien Dugal-Tessier and Derek P. Gates, "Phospha-organic chemistry: from molecules to polymers" *Dalton Trans.*, **2010**, 3151-5159.

Raymond Chang offers a simple, yet encompassing, answer in his defining chemistry as "the study of matter and the changes it undergoes."[2] However, for most people, chemist or not, the question presumably brings the periodic table to mind. A powerful symbol, the periodic table is also an incredibly powerful tool for predicting the chemistry of the elements.

Arguably, the most thoroughly studied element on the periodic table is carbon, with an entire branch of chemistry, organic chemistry, being devoted to it and its compounds. As a consequence of this focused study, the chemistry of carbon is well known and, generally, quite predictable. Among its many fascinating properties, carbon readily catenates, that is forms long chain-like structures comprising covalently bonded carbon atoms, and forms multiple-bonds, with both itself and other heteroatoms (in particular N, O, and S). Indeed, synthetic chemists take advantage of this combination of chemical traits to prepare various organic compounds ranging from drugs to plastics.

The complement to organic chemistry is inorganic chemistry, or the study of everything "that is not organic." Although the distinction between these two classical branches of synthetic chemistry is slowly blurring, particularly with the emergence of organometallic chemistry, their differentiation remains as an artifact of alchemical belief in vitalism: that organic compounds (those extracted from animal or vegetable sources) were fundamentally different from inorganic compounds (those obtained from the mineral world), where the latter lacked some sort of "vital essence" of life.[3] It is not without irony that the birth of modern organic chemistry, and purported death of vitalism, is often attributed to the *inorganic* synthesis of urea by Friedrich Wöhler using silver isocyanate and ammonium chloride.[4]

While organic chemistry may have had an inorganic birth, the rapid maturation of the field has allowed the child to become the teacher in that, one of the central themes of organometallic and inorganic chemistry is the generalization of the chemistry of carbon to other elements. In particular, the formation of multiple-bonds between elements with principle quantum number ≥3 is of current interest[5, 6] and is discussed in more detail in section 1.2. The obvious extension would be to silicon, which also possesses four valence electrons and sits just below carbon on the periodic table. Although examples of compounds containing multiple bonds between heavier atoms such as C=Si,[7, 8] Si=Si[9] and Si≡Si[10] are now known, it is the element phosphorus, diagonally related to carbon, which has been dubbed the "carbon-copy."[11, 12] A discussion of phosphorus and some aspects of its chemistry are presented in section 1.3.

The preceding is not meant to suggest that organic chemistry has nothing to benefit from advances in inorganic chemistry. On the contrary, as evidenced by the awarding of three Nobel prizes in the past 10 years for aspects of organometallic chemistry applied to organic chemistry: catalytic asymmetric hydrogenation (2001), metathesis (2005), and palladium catalyzed cross-coupling (2010) reactions. Nor is this only a recent trend, as illustrated by the awarding of the 1979 Nobel Prize for Chemistry to Herbert C. Brown and Georg Wittig "for their development of the use of boron- and phosphorus-containing compounds, respectively, into important reagents in organic synthesis" or the 1912 prizes to Victor Grignard "for the discovery of the Grignard reagent" and Paul Sabatier 'for his method of hydrogenating organic compounds in the presence of finely disintegrated metals." Clearly, some of the developments in carbon chemistry fall under domains of both organic and inorganic chemistry.

1.2 Heavier Main Group Element Multiple Bonds

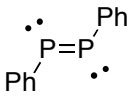
As alluded to above, the literature is full of examples of compounds containing multiple-bonds between C and the elements C, N, O and, to some extent, S. It is worth noting however that, with the exceptions of those based on N-N, O-O, and combinations thereof, all π-bonds are weaker than their corresponding σ-bonds (Table 1.1).[13] The prevalence of organic multiple bonds, as opposed to heavier inorganic element multiple-bonds (n ≥3), can be attributed to several factors such as: (a) that these lighter elements readily hybridize; (b) that 2p orbitals are smaller and less diffuse, enabling improved overlap for the formation of π bonds; and (c) that, lacking available d-orbitals, even small substituents can provide effective kinetic stabilization.

Table 1.1 Selected Homonuclear Bond Strengths (kJ mol^{-1}) of Main Group Elements

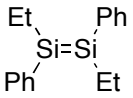
	13	14	15	16	17
	B	C	N	O	F
σ	293 ± 21	346	167	142	155
π		256 ± 21	387 ± 13	352 ± 1	
	Al	Si	P	S	Cl
σ	133	222	201	226	240
π		103	140 ± 8	199 ± 7	
	Ga	Ge	As	Se	Br
σ	113 ± 17	188	146	172	190
π		84 ± 21	117 ± 21	100	
			Sb	Te	I
σ			121	126	149
π			87 ± 7	92 ± 8	

Early reports involving multiple-bonding between heavier elements, such as that of phosphobenzene (**1.1**) by Kohler and Michaelis[14] and of a disilene (**1.2**) by Kipping,[15] were later proved to be false and that the products were, rather, oligomeric or

polymeric.[16, 17] Such early failures led to the so-called "double-bond rule," which states that chemical elements with a principal quantum number greater than two do not form multiple bonds with themselves or with other elements.[18-21]

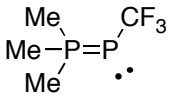


1.1



1.2

Widely cited regarding this topic is Dasent's book *Non Existent Compounds – Compounds of Low Stability*, which is "about compounds whose structures do not offend the simpler rules of valence, but which nevertheless are characterized by a low stability."[22] It should be noted, however, that the author did not imply that these unknown compounds could not be prepared in the future; rather, he discussed the factors that might explain the low-stability of these compounds. Interestingly, it is around this time that new transient species containing genuine multiple-bonds, such as **1.3**,[23] **1.4**,[24] and **1.5**,[25-27] were detected.



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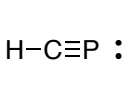

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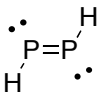
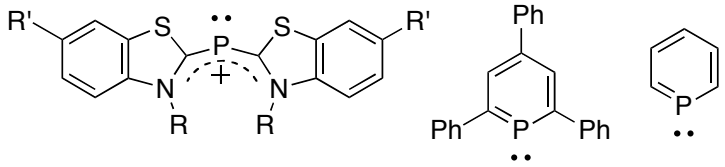


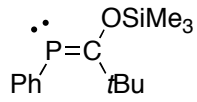
1.5

Although initially met with some skepticism, due to the influence of the "double-bond rule," these early results paved the way for other pioneering discoveries. In 1964, Dimroth and Hoffman reported the phosphamethine cation **1.6**.[28] This was followed by the preparation of 2,4,6-triphenylphosphabenzene (**1.7**) by Märkl in 1966[29] and the preparation of the parent phosphabenzene (**1.8**) by Ashe in 1971.[30] The relative stability of these species can be attributed primarily to the thermodynamic stabilization of the P=C bond through π-delocalization.



1.6 **1.7** **1.8**

An alternative kinetic stabilization strategy, that is the use of sterically demanding substituents, enabled Becker to prepare the first acyclic phosphaalkene (**1.9**), a compound containing a localized P=C bond, in 1976.[31] In 1981, this approach was employed in the synthesis of a number of other firsts: Becker – P≡C (**1.10**),[32] Yoshifuji – P=P (**1.11**),[33] West – Si=Si (**1.12**),[9] and Brook – Si=C (**1.13**).[7]



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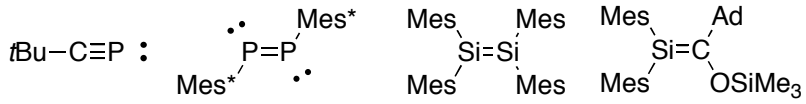


1.10 **1.11** **1.12** **1.13**

It should be noted that, in addition to kinetic stabilization, the use of sterically demanding substituents could have a significant thermodynamic stabilizing effect as well. Calculations performed by Burford et al.[34] suggest that the cyclodimerization of 1,2-substituted olefins [R(H)C=C(H)R] is strongly exothermic when the substituents are small (R = H, Me; $\Delta E \approx -84$ kJ mol^{-1}), but becomes increasingly endothermic as the size of the substituents increases (Figure 1.1): R = *t*Bu, $\Delta E = -7$ kJ mol^{-1}; R = Mes, $\Delta E = +68$ kJ mol^{-1}; R = Mes*, $\Delta E = +395$ kJ mol^{-1} (Mes* = 2,4,6-tri-*tert*-butylphenyl). This relative destabilization can be attributed to steric interactions that are more pronounced in the cyclic systems where the nature of the bonding forces the substituents closer together. Therefore it is not surpring that, as compared to the cyclobutane systems, the relative

stability of tetra-substituted alkenes is increased dramatically ($Mes_2C{=}CMes_2$: ΔE = +1873 kJ mol^{-1}). Due to the longer Si-Si bonds which keep the substituents further apart, the destabilizing effect is smaller, but not insignificant, when comparing the stability of species such as $Mes_2Si{=}SiMes_2$ with their corresponding cyclotetrasilanes (ΔE = +487 kJ mol^{-1}).

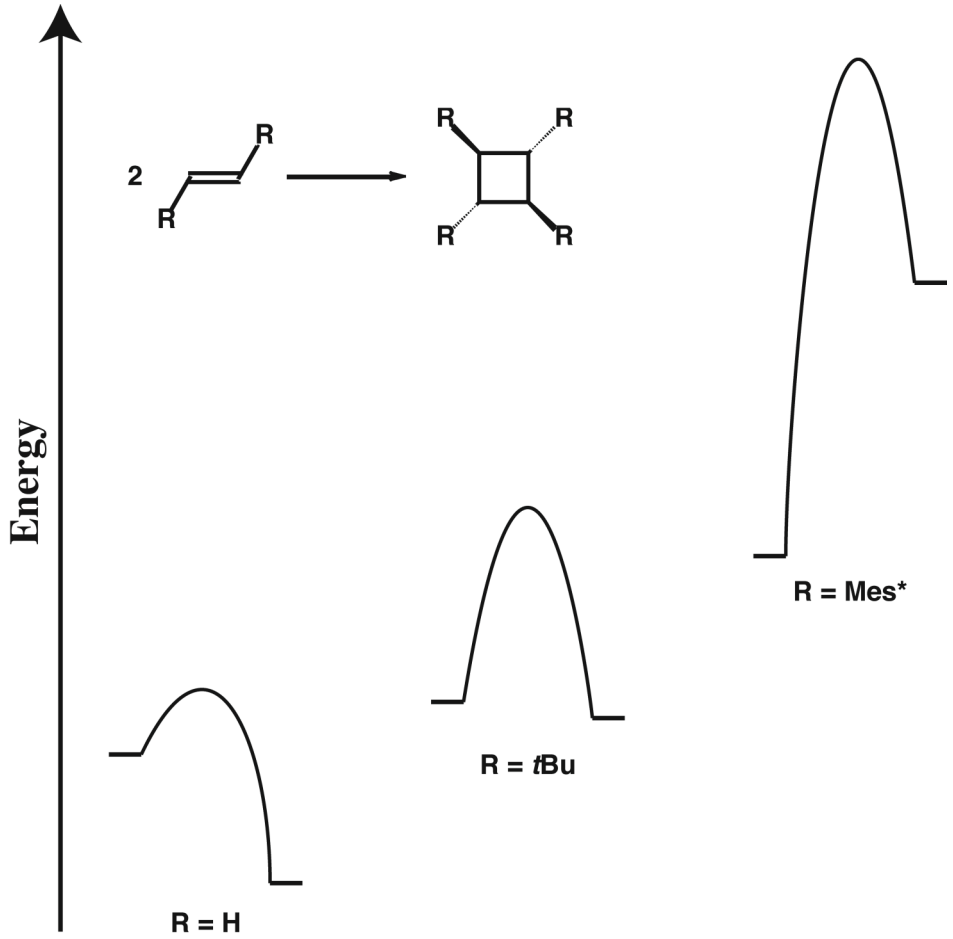


Figure 1.1 Qualitative energetic comparisons for the cyclodimerization of ethene and ethenes 1,2-substituted by *t*Bu and Mes*.

The topic of heavier main group multiple bonds has attracted, and continues to attract, significant interest since these first few examples. In 1999, Philip Power wrote a review, entitled "π-Bonding and the Lone Pair Effect in Multiple Bonds between Heavier Main Group Elements."[6] However, in order to limit his review to a manageable size,

some 680 references describing the state-of-the-art over the past 40 years, several limitations to the scope of the review were implemented: (a) only compounds in which multiple bonds occurs between elements of group 13-16 were considered; (b) compounds for which the multiple bond is an intricate part of a ring structure were not considered; (c) and hypervalent multiply bonded systems, such as phosphine oxides and ylides, were not considered. In what is essentially an update of his extensive review, Power, along with Roland Fischer, have included nearly 400 additional references that were published since 2000.[5]

Among the many fascinating compounds discussed, the complete series of heavy alkyne analogues R-E≡E-R (E = Si,[10] Ge,[35] Sn,[36] Pb[37]) are now known. In contrast with the linear alkynes, all the heavier alkyne analogues exhibits a trans-bent geometry that is indicative of non-bonding electron density present on the tetrel (group 14) atoms. In the case of the heaviest tetrel, plumbynes are better though of as two Pb atoms, each possessing a non-bonding lone pair of electrons, joined by a single bond.

1.3 Phosphorus – The 13th Element

1.3.1 A Brief History of Phosphorus and its Chemistry

An essential component of all life on Earth as we know it (see below), phosphorus enjoys one of the most intriguing histories of all the known elements.[38] The alchemist Hennig Brandt, who was working in Hamburg, Germany, discovered phosphorus in 1669.[39] It is from his attempt to isolate gold by distilling putrefied urine that Brandt was able to isolate small amounts of a white, waxy substance that glows in the dark upon exposure to air. In 1680, Robert Boyle improved the process for isolating this material,

which he named "aerial noctiluca." We now know this substance to be white phosphorus (named for the Greek phos, light, and phorus, bringing), P_4, the most common allotrope of this element's many allotropes.[40] It is interesting to note that phosphorus was soon after detected in plants (Albino – 1688), but not detected in bones (Gahn and Scheele – 1769) or in minerals (Gahn – 1779) until much later. In this, phosphorus is probably unique as the only element to be first discovered from animal, then vegetable and, finally, mineral sources.[40]

In 1830, the Frenchman Charles Sauria revolutionized the match industry when he introduced white phosphorus to matches. This instant source of fire was an incredible boon, however, the use of white phosphorus was not without consequence. For the end user, these matches presented, ironically, a fire risk in that they were prone to igniting accidentally and, in turn, lighting the unsuspecting user on fire. For the matchmakers, it soon became apparent that white phosphorus is highly toxic. While acute exposure can cause a rapid death, chronic exposure to white phosphorus leads to a horrible condition known as "phossy-jaw" and, eventually, death caused by organ failure. Given the dangers of white phosphorus to both the end user and the manufacturer, there was great interest in replacing white phosphorus in matches. The discovery of red phosphorus, which is neither spontaneously flammable nor poisonous, by Schrötter in 1844 led to the development of safety matches. Near the turn of the century, Sevene and Cahen in France developed strike-anywhere matches, in whom the phosphorus ignition source is phosphorus sesquisulfide.

The practice of using phosphate fertilizers began in the mid-19th century with the realization that phosphorus is essential to life. Today all fertilizers contain phosphorus

and the majority of the world's ~150 million ton production of phosphate rock goes to this purpose. Following World War II, the use of phosphorus in detergents, in particular sodium tripolyphosphate ($Na_3P_3O_{10}$), became popular due its water softening properties; however, due to concern over eutrophication, the use of phosphate detergents has been on the decline since the 1970s. Interestingly, while the phosphates certainly did encourage algae to flourish, their bad reputation in this regard was undeserved. It has since been reallized that the real culprits for the observed eutrophication were heavy metal and pesticide pollutants, which killed off the zooplankton, the organisms which feed on the algae, and allowed the uncontrolled plant growth. Sadly, the element also has a dark side that has been exploited in its use in incendiary weapons and in terrifying nerve agents.

While it was well established that phosphorus was essential to life, it was not until 1929 that Fiske and Subarow discovered adenosine triphosphate (ATP), the energy source of biological cells.[41] The synthesis of ATP by Todd[42] earned him a Nobel Prize in 1957. For their discovery of the double helix structure of nucleic acids, a key component of which is the polyphosphate ester backbone, Crick, Watson and Wilkins were awarded the 1962 Nobel Prize in Chemistry.

It is not, however, only in the areas of biology and biochemistry for which the study of phosphorus has been recognized by the awarding of a Nobel Prize. As mentioned in the preceding section, Wittig shared the 1979 Nobel Prize in Chemistry for his development phosphorus-based olefination reagents. The study of phosphorus compounds has also contributed to the development of new theories related to bonding, such as the concept of "pseudo-rotation" introduced by Barry in 1960 to rationalize the equivalence, on the NMR-timescale, of the five fluorine atoms in PF_5.[43]

By now, the importance of phosphorus, both to chemistry and to life, should be evident. The following section deals with the chemistry of low-coordinate phosphorus, a topic that has recently garnered significant interest.

1.3.2 Low-Coordinate Phosphorus

The modern study of phosphorus spans the diverse areas of inorganic, organic, biological and materials chemistry. To a synthetic chemist, perhaps the best-known class of phosphorus compounds is phosphines with their ubiquitous use in coordination chemistry and catalysis. Given that the chemistry of phosphines resembles that of amines, one might expect in general that the chemistry of phosphorus would parallel that of nitrogen; however, in low-coordination environments phosphorus more closely mimics carbon (Figure 1.2).[44] So extensive is this parallel that this subfield of organophosphorus chemistry has been termed "phospha-organic" and has led, as mentioned previously, to phosphorus being coined the "carbon copy".[11, 12]

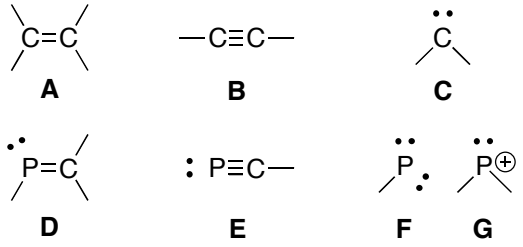


Figure 1.2 Common low-coordinate carbon species and their isolobal phosphorus analogues: phosphaalkenes (**D**), phosphaalkynes (**E**), phosphinidenes (**F**) and phospheniums (**G**)

Perhaps most illustrative of the phosphorus-carbon analogy are phosphaalkenes (**D**), species containing a formal (3p-2p) π bond between P and C. Although P=C π bonds are calculated to be somewhat weaker than C=C π bonds (180 kJ mol^{-1} vs. 272 kJ mol^{-1}),[45, 46] UV photoelectron spectroscopy indicates ethylene and phosphaethylene

($HP=CH_2$) have similar frontier molecular orbitals: C=C π bond (-10.5 eV) versus P=C π bond (-10.3 eV), with the phosphorus lone pair being slightly lower in energy (-10.7 eV).[47] Moreover, the conjugative properties of both π bonds are similar,[48] reflecting the essentially apolar nature of the P=C bond.[49]

By analogy to the synthesis of C=C bonds, a variety of methodologies for preparing P=C bonds have been developed (Figure 1.3). The first acyclic phosphaalkenes were prepared by the Becker reaction (**i**), a keto-enol tautomerization related to the Brook rearrangement.[31] Related condensation strategies take advantage of the oxophilicity of silicon, both the normal (**ii**)[50] and base-catalyzed (**iii**)[51] phospha-variants of the Peterson-olefination reaction, and of phosphorus, variants of the phospha-Wittig reaction (**iv**).[52-56] Similar to the phospha-Wittig reagents, terminal phosphinidene complexes have also been exploited as a source of nucleophilic phosphorus, with the departing metal complex acting an oxygen-scavenger (**v**).[57, 58] For a few highly stabilized phosphaalkenes, the phosphaalkenes can be prepared from the direct condensation of a primary phosphine with an appropriate carbonyl derivative (**vi** and **vii**).[59, 60] Finally, a variety of base-mediated processes, such as 1,2-eliminations (**viii**),[61-67] keto-enol type tautomerizations (**ix**),[68-70] and a purported carbene-insertion reaction (**x**),[71, 72] have also been used in the preparation of phosphaalkenes.

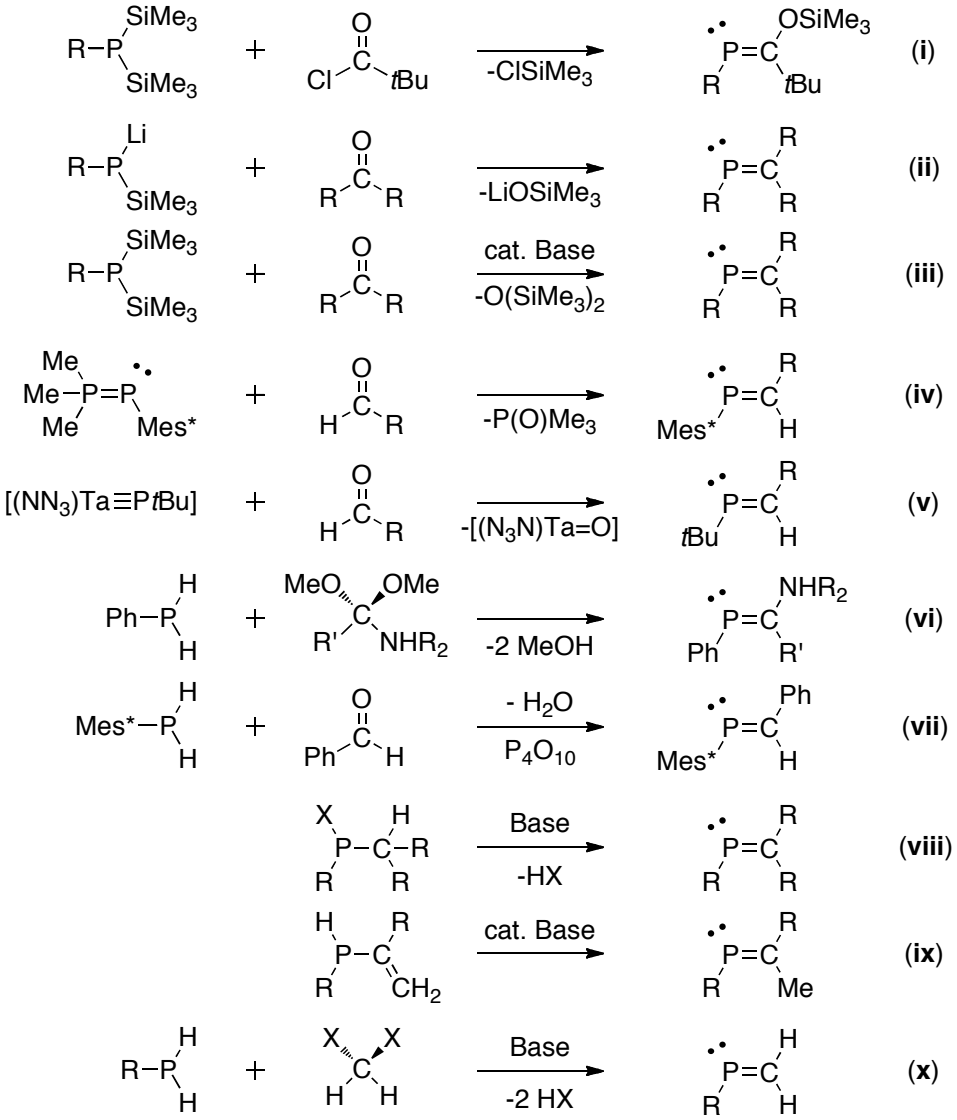


Figure 1.3 Common synthetic strategies for preparing phosphaalkenes.

Phosphaalkene can also undergo a variety of olefin-like reactions (Figure 1.4). These include 1,2-addition reactions with small molecules such as HX (**xii**), to afford normal X-P-C-H[73] or inverse H-P-C-X[74] products, or a variety of [n+2] cycloaddition reactions, such as Diels-Alder chemistry (**xiii**).[75, 76] Additionally, if the lone pair is protected by coordination to a transition metal, the P=C bond can be hydrogenated (**xiv**)[77] or epoxidized (**xv**).[78] Although examples of η^2-binding of phosphaalkenes to transition metals are known, complexes involving η^1 coordination through the lone pair

are more common. Interestingly, these coordination motifs can exist in equilibrium (**xvi**). This is a consequence of the small energy difference between the molecular orbitals.

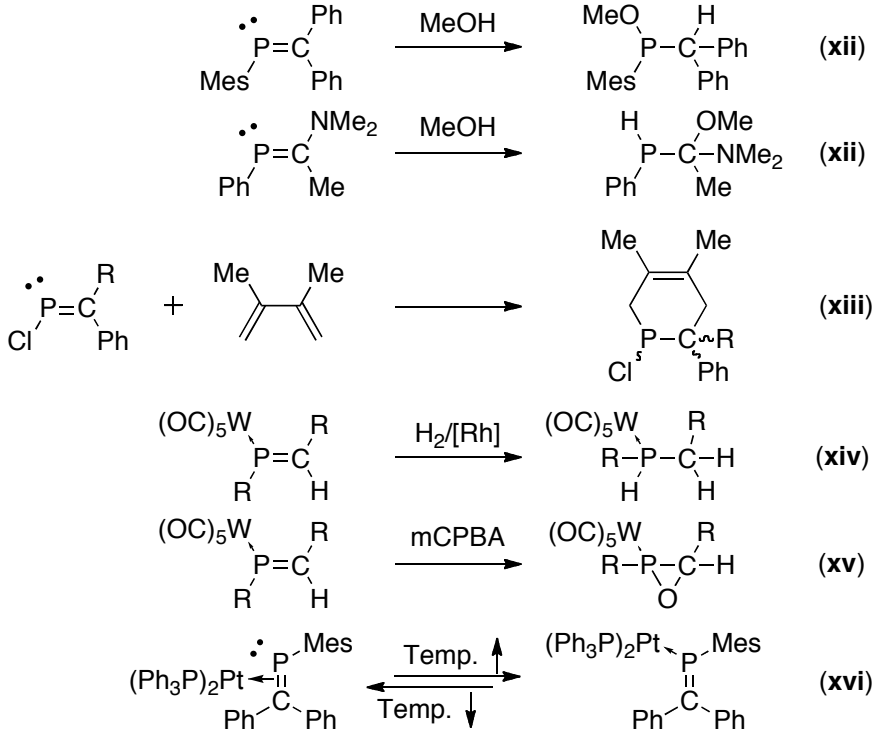
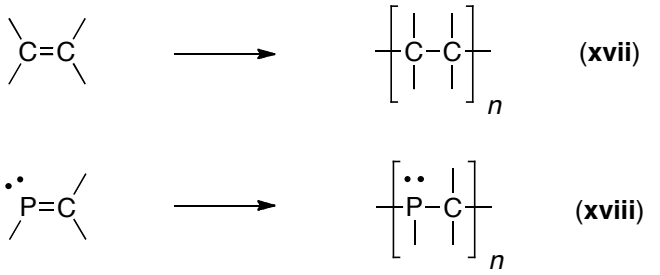


Figure 1.4 Examples of phosphaalkenes exhibiting olefin-like reactivity

Inspired by the known parallels between the chemistry of P=C and C=C bonds, we in the Gates research group are intrigued by the possibility of extending addition polymerization, the methodology of choice in the polymerization of olefins, to inorganic systems. As is the case for polyolefins, the properties of these novel materials would reflect the functionality of the monomers, which may in turn exhibit interesting molecular chemistry. The following section will highlight recent work by the Gates group in the area of phosphaalkene polymers.

1.3.3 Phosphaalkene Polymers

There is a growing interest in macromolecular systems incorporating inorganic elements due to their unique functionality and properties that are unattainable from traditional organic frameworks.[79, 80] The most successful routes to inorganic polymers involve ring opening and condensation polymerization. Given the generality and versatility of addition polymerization to prepare polyolefins (**xvii**), it would be desirable to apply addition polymerization methodologies to the growing number of unsaturated systems featuring inorganic elements, such as phosphaalkenes (**xviii**) (Scheme 1.1).

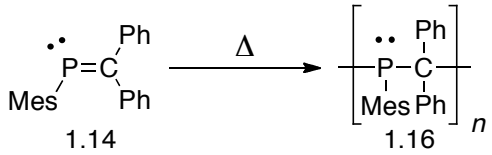


Scheme 1.1 P=C/C=C analogy applied to addition polymerization

The addition polymerization of alkenes is driven by the exothermic formation of two σ bonds in the polymer from the σ + π bonds of the monomer (e.g. ΔH°_p = -80 kJ mol^{-1} for ethylene). Similarly, calculations for phosphaethylene, HP=CH$_2$, give a ΔH°_p of -70 kJ mol^{-1}, suggesting the polymerization of phosphaalkenes is thermodynamically favorable. This notion is also consistent with the results of early efforts to prepare simple low-coordinate phosphorus compounds, such as the preparation of phosphaethylene,[62] phosphaacetylene,[24] and many others multiply-bonded phosphorus compounds[61, 65, 69, 81-84] were often plagued by "polymeric" byproducts. Although these species were poorly, if at all, characterized, they serve as a starting point for further work.

Within this context, the key difference between ethylene and phosphaethylene lies in the kinetic stability of the former, which permits the isolation, purification, and deliberate initiation of the monomer to prepare polymers of high molecular weight. Although phosphaalkenes can be rendered isolable through the use of bulky substituents, which provide both kinetic and thermodynamic stabilization, too much steric hindrance may prevent polymerization as is the case for hindered olefins.[34]

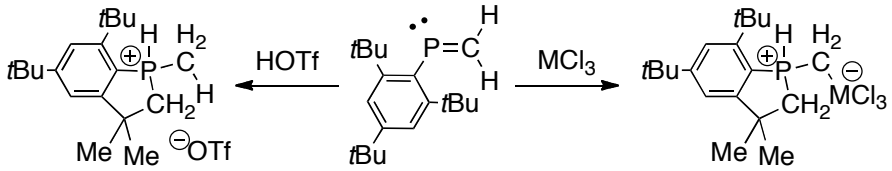
With these challenges in mind, early studies by the Gates group focused initially on two potential monomers: MesP=CPh_2 (**1.14**) and Mes*P=CH_2 (**1.15**). Surprisingly, purification of **1.14** by vacuum distillation afforded, in addition to pure phosphaalkene, a gummy residue from which poly(methylenephosphine) **1.16** was isolated as a colorless solid (Scheme 1.2): M_n of 11500 g/mol (vs. polystyrene) and a PDI of 1.25.[85] Significantly, although the mechanism of polymerization was not immediately evident, the fact that purified phosphaalkene **1.14** does not polymerize upon redistillation suggests that an impurity may be serving as the polymerization initiator.



1.14 1.16

Scheme 1.2 Thermal polymerization of phosphaalkene **1.14**

To assess the possible cationic polymerization of P=C bonds, phosphaalkenes were treated with protic (HOTf) and Lewis acids (MCl_3: M = Al, Ga, In). In each case, the reactions of phosphaalkene **1.15** with stoichiometric cationic initiator afforded products consistent with the insertion of a phosphenium (**G**) into a C-H bond of an *o*-^{t}Bu group on the Mes* substituent (Scheme 1.3).[86, 87] Such insertions are fairly common in the chemistry of low-coordinate phosphorus compounds bearing Mes* substituent.[88-96]



1.15

Scheme 1.3 Reaction of phossphaalkene **1.15** with protic and Lewis acids

Significantly, treating concentrated solutions of **1.15** with substoichiometric $GaCl_3$ or HOTf afforded, respectively, the linear dimer **1.17** (Figure 1.5) and oligomers up to six repeat units.[87] Importantly, this represents the first step in the putative cationic polymerization of a P=C bond.

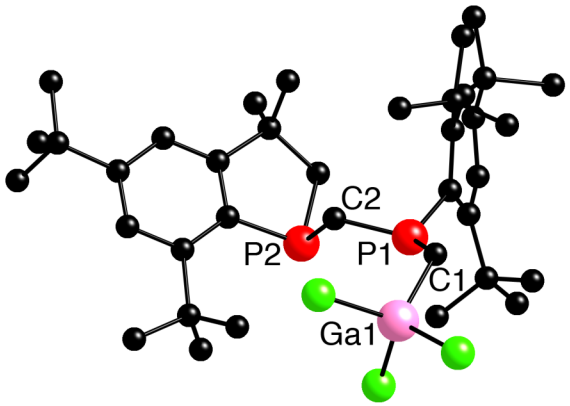
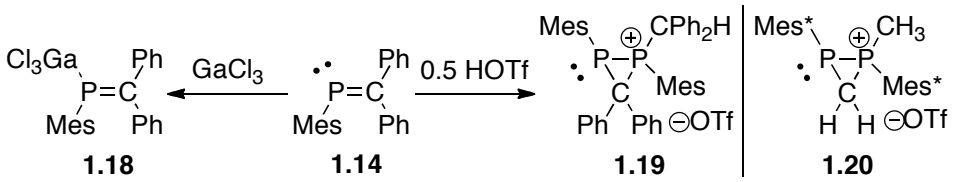


Figure 1.5 Molecular structure of the linear dimer **1.17**.

In contrast to the C-H activation observed when Mes*-substituted **1.15** was treated with $GaCl_3$ and HOTf, Mes-substituted **1.14** reacts differently (Scheme 1.4). [87] Regardless of concentration or stoichiometry, the sole product of the reaction of **1.14** with $GaCl_3$ is the η^1 adduct **1.18**, a rare example of a coordination complex between a phosphaalkene and a main-group metal.[97, 98] By comparison to the ^{31}P NMR spectrum of diphosphiranium **1.20**, the reaction of phosphaalkene **1.14** with HOTf suggests the formation of the diphosphiranium **1.19**.



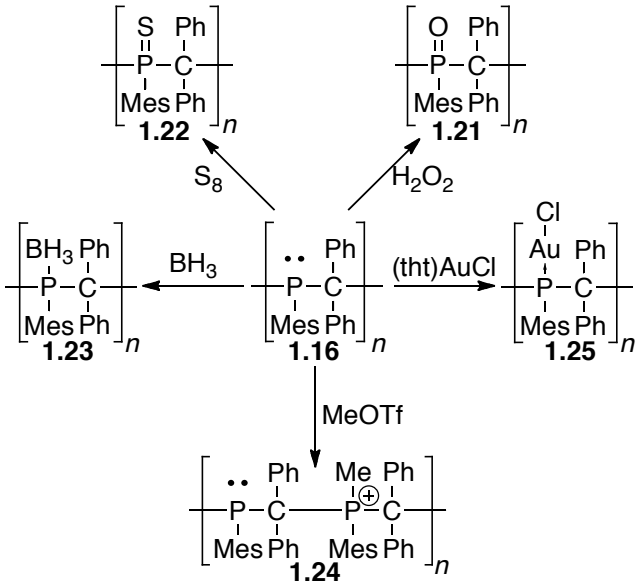
Scheme 1.4 Reaction of phosphaalkene **1.14** with protic and Lewis acids

The formation of diphosphiranium **1.19** illustrates that diphosphiranium cations are accessible via the cationic cyclodimerization of phosphaalkenes; however, it was not possible to crystallize this compound. These highly strained ring motifs exhibit interesting bonding and structural characteristics and are potential building blocks for more sophisticated organo-phosphorus compounds.[99-101]

Given that cationic initiators afforded only novel molecular or oligomeric species, either an anionic or a radical impurity was suspected as being responsible for initiating the thermal polymerization of phosphaalkene **1.14** (Scheme 1.2). The reactions of **1.14** with MeLi and VAZO 88 [1,1'-azobis(cyclohexanecarbonitrile)] were investigated. Using 5 mol% of either initiator and heating reaction mixture to 140 °C afforded polymers (MeLi: M_n = 6200; PDI = 1.29 and VAZO 88: M_n = 5700; PDI =1.10) that were indistinguishable from polymer **1.16** obtained from the thermal polymerization.[85]

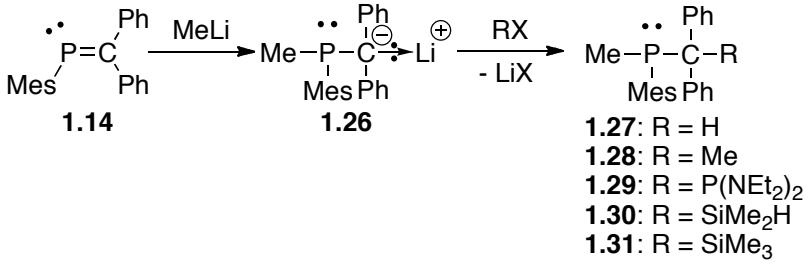
The presence of alternating phosphorus and carbon atoms within the backbone of poly(methylenephosphine)s offer the prospect of phosphine functionality within a macromolecular framework (Scheme 1.5). Air- and moisture-stable polymers **1.21** and **1.22** can be prepared, respectively, by oxidation with H_2O_2 or elemental sulfur.[102] The air-sensitive nature of the phosphine moiety in polymer **1.16** can be protected by coordination of BH_3 (**1.23**).[103] Ionomer **1.24**, with phosphonium content up to 50%, can be prepared by methylation of polymer **1.16** with MeOTf.[103] The phosphine

functionality can also be used to coordinate transition metals, as demonstrated by the gold(I) containing polymer **1.25**.[103, 104]



Scheme 1.5 Functionalization of PMP **1.16**

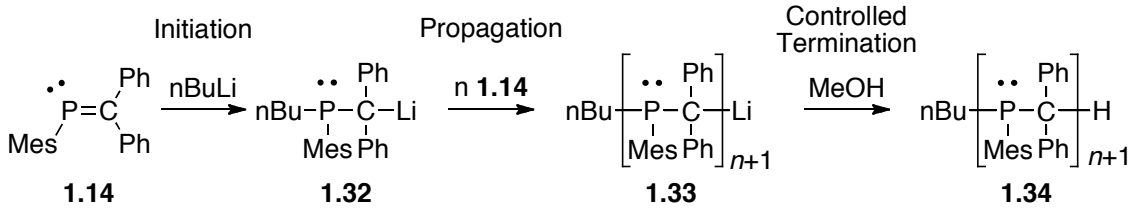
Mechanistic studies into the anionic polymerization of phosphaalkene **1.14** revealed that the initiation step involves a nucleophilic attack at the phosphorus atom, generating the carbanion intermediate **1.26** (Scheme 1.6). Subsequent quenching of **1.26** with a variety of electrophiles affords model compounds **1.27-1.31**. These studies suggest it may be possible to introduce end-functionalities and access telechelic polymers.[105]



Scheme 1.6 Preparation of model compounds

Interestingly, the addition of phosphaalkene **1.14** to solutions of the initiated species **1.21** afforded oligomers at ambient temperatures, thus indicating that high temperatures were not necessary for propagation.[106] This result paved the way for

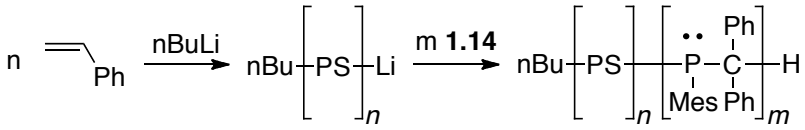
establishing the first ambient-temperature living anionic polymerization of a phosphaalkene (Scheme 1.7).[107] Using living anionic methods of initiation, controlled molecular weight polymers with lengths (*n*) of 25, 33, 50 and 100 could be obtained.



1.14 **1.32** **1.33** **1.34**

Scheme 1.7 Living anionic polymerization of phosphaalkene **1.14**

Remarkably, the living polymerization of phosphaalkene **1.14** could be initiated using living polystyrene (Scheme 1.8) to afford polystyrene-*block*-poly(methylenephosphine) **1.35** (*n* = 100, *m* = 28 and *n* = 100, *m* = 50).[107] Related random copolymers of phosphaalkene **1.14** and styrene can be prepared using radical initiators. Notably, these random copolymers have been shown to be effective macromolecular supports for palladium catalyzed Suzuki-Miyaura cross-coupling reactions.[108] Moreover, the macromolecular catalysts could be precipitated using non-polar solvents, facilitating the convenient separation of the product from the catalysts and allowing the latter to recovered and reused without the need for chromatography.

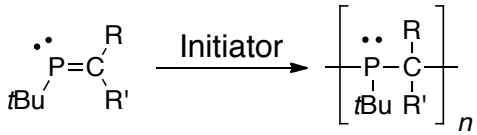


1.35

Scheme 1.8 Block copolyermization of styrene and phosphaalkene **1.14**

1.4 Outline of this Thesis

Upon joining the Gates group in 2004, my initial project was to extend the P=C/C=C analogy[11, 12] to the synthesis of new poly(methylenephosphine) polymers and copolymers[85, 108] bearing bulky *P*-alkyl substituents (e.g. *t*Bu or Ad) (Scheme 1.9). In light of Fu and coworkers discovery that electron-rich tertiary phosphines bearing bulky alkyl-substituents (e.g. P*t*Bu$_3$) are able to promote the palladium-mediated Suzuki-Miyaura cross-coupling of aryl chlorides,[109, 110] these new functional macromolecules could potentially be very interesting polymeric supports for palladium catalyzed reactions.



Scheme 1.9 General polymerization of tBu-P-substitutend phosphaalkenes

Before such polymerization studies could begin, however, suitable phosphaalkene monomers would have to be synthesized. Although a number of *t*Bu-P substituted phosphaalkenes are known, all but one have heteroatom substituents (i.e. not H nor C) on the P=*C* carbon [e.g. *t*BuP=C(SiMe$_3$)$_2$ or *t*BuP=C(NMe$_2$)$_2$][71, 111] or are protected by coordination of the phosphorus lone pair to a transition metal [*t*Bu(W(CO)$_5$)P=CMe$_2$].[112] The single exception is the phosphaalkene *t*BuP=CH*t*Bu (**1.36**), however its preparation was reported as requiring either extended reaction times (~11 weeks)[97] or exotic reagents.[57, 112] Clearly alternative synthetic strategies would be desirable. With the notable exception of the acid-catalyzed dehydration of alcohols, most methods for preparing C=C bonds or P=C bonds, as illustrated in Figure 1.4, are either base-mediated (e.g. dehydrohalogenation) or employ highly nucleophilic sources of carbon/phosphorus

(e.g. Wittig and phospha-Wittig reagents). Chapter 2 describes efforts to develop a Lewis-acid mediated methodology for the preparation of P=C bonds. This new method provides a convenient means for accessing alkyl-P-substituted phosphaalkenes such as **1.36**, for which the reaction time was reduced from ~11 weeks to less than one hour.

Having developed a convenient method for preparing phosphaalkene **1.36**, the potential cationic polymerization of this electron-rich monomer was explored. As was observed for phosphaalkenes **1.14** and **1.15**, treating phosphaalkene **1.36** with electrophilic initiators leads to the formation of heterocyclic dimers, including the first crystallographically characterized diphosphiranium cation (see Scheme 1.4). Unexpectedly, however, the nature of the observed dimeric products depends on the initiator used, where the use of related HOTf and MeOTf led to the formation of anticipated three- and unanticipated four-membered rings, respectively. The products and mechanistic insights into their formation are discussed in Chapter 3.

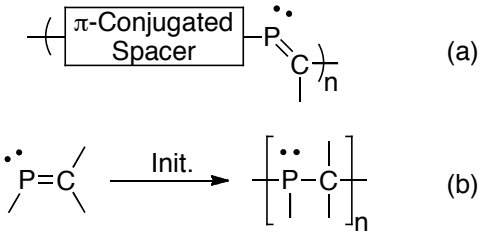
Changing gears slightly, Chapter 4 describes efforts to use N-heterocyclic carbenes (NHCs) as nucleophilic initiators for the polymerization of phosphaalkenes. Whereas transient electrophilic carbenes are known to react with phosphaalkenes to afford phosphiranes, three-membered neutral heterocycles containing one phosphorus atom in the ring, the reaction of NHCs with phosphaalkenes was unknown.[113] Surprisingly, instead of polymers, unprecedented 4-phosphino-substituted NHCs were obtained.[114] Additionally, this chapter includes experimental studies into the coordination chemistry of these novel bifunctional ligands and computational studies into potential mechanisms for these unanticipated reactions.

Finally, Chapter 5 summarizes the findings of this thesis and proposes future directions for this work.

Chapter 2: A Lewis Acid-Mediated Synthesis of P-Alkyl-Substituted Phosphaalkenes

2.1 Introduction

Possessing a formal (3p–2p)π bond between phosphorus and carbon, the chemistry of phosphaalkenes ($RP=CR_2$) often more closely resembles that of olefins ($R_2C=CR_2$) than imines ($RN=CR_2$).[11, 12, 44] Although the P=C/C=C analogy is common in molecular chemistry, there has recently been considerable interest in extending this analogy to polymer science.[115] Examples include the development of π-conjugated polymers containing P=C bonds[116-119] and the addition polymerization of P=C bonds to afford poly(methylenephosphine)s, PMPs (Scheme 2.1).[85, 104, 107, 108, 120, 121]



Scheme 2.1 Examples illustrating the use of P=C bonds in polymer science: (a) π-conjugated polymers; (b) addition polymerization of P=C bonds.

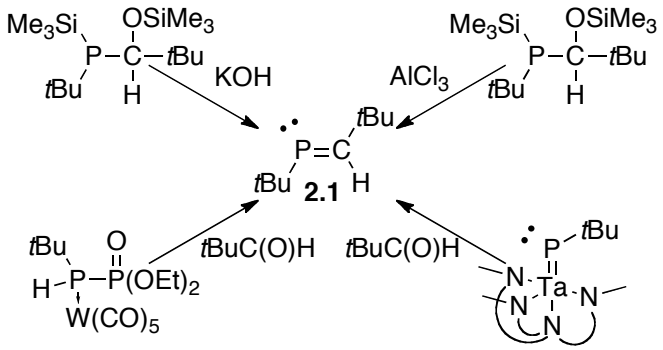
*A version of this chapter has been published. Joshua I. Bates, Brian O. Patrick and Derek P. Gates, "A Lewis acid-mediated synthesis of P-alkyl-substituted phosphaalkenes," *New J. Chem.*, **2010**, 1660-1666. Copyright 2010 Royal Society of Chemistry.

We have been interested in exploring substituent-effects in the polymerization of phosphaalkene monomers as a means of evaluating the scope of this new reaction. Moreover, the ability to vary substituents is critical to gaining an understanding of structure–property relationships in PMPs and to tune the donor properties of these macromolecular ligands. Such studies require access to simple and convenient methods to prepare isolable phosphaalkenes bearing a variety of different substituents.

Although many methods for the assembly of P=C bonds are known, the phospha-Peterson[32, 50, 122-129] reaction is attractive due to its versatility as a route to Mes–P-substituted phosphaalkenes.[51, 130] The reaction involves treating ketones or aldehydes with either $RP(SiMe_3)_2$ and a catalyst (e.g. KOH) or $RP(SiMe_3)Li$ alone. While this method is very effective for the preparation of *P*-aryl-substituted phosphaalkenes, it is less suitable when *P*-alkyl-substituents are desired due to the difficulty in generating the alkylsilylphosphide intermediates.[51] For example, the preparation of *t*BuP=CH*t*Bu (**2.1**) from $tBuP(SiMe_3)_2$ and *t*BuC(O)H using KOH as a catalyst requires ca. 11 weeks.[97]

We were intrigued with compound **2.1** because it is a rather rare example of an isolable *P*-alkyl-substituted phosphaalkene and is a precursor to novel P_2C and P_2C_2 heterocycles.[131] Clearly, a less time-consuming route to that described above is desirable. Alternative phospha-Wittig strategies to **2.1** or **2.1**·$W(CO)_5$ are known (Scheme 2.2).[57, 112] We also noted that treating $tBuP(SiMe_3)CH(OSiMe_3)tBu$, derived from $tBuP(SiMe_3)_2$ and *t*BuC(O)H, with $AlCl_3$ afforded high yields of **2.1** (86%).[97] Strikingly, no timeframe is specified for this reaction nor was the direct reaction of $tBuP(SiMe_3)_2$ and *t*BuC(O)H in the presence of $AlCl_3$ mentioned. Interestingly, recent work has shown that Lewis acids can catalyze the coupling of silylphosphines and aldehydes to give α-

siloxyalkylphosphines.[132] If such an acid mediated approach could be applied to the synthesis of **2.1**, it may provide a convenient route to *P*-alkyl-substituted phosphaalkenes for further study.



Scheme 2.2 Known synthetic routes to the *t*Bu-P-substituted phosphaalkene **2.1** or **2.1**·$W(CO)_5$

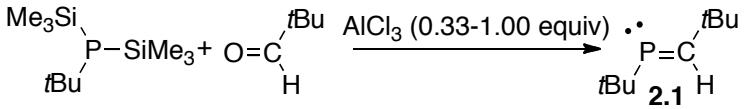
Herein, we report a simple one-pot synthesis of phosphaalkenes from $RP(SiMe_3)_2$, a ketone or aldehyde, and $AlCl_3$. In addition, the preparation and molecular structures of the phosphaalkene–Lewis acid adducts, (Cl_3Al)*t*BuP=CH*t*Bu, (Cl_3Ga)*t*BuP=CH*t*Bu and (Cl_3Ga)AdP=CH*t*Bu (Ad = 1-adamantyl), are also reported.

2.2 Results and Discussion

To assess the feasibility of a Lewis acid-mediated synthesis of phosphaalkenes, an equimolar mixture of *t*BuP$(SiMe_3)_2$ and *t*BuC(O)H in dichloromethane was treated with $AlCl_3$ (1 equiv.). Analysis by ^{31}P NMR spectroscopy of an aliquot removed from the reaction mixture revealed that the signal assigned to *t*BuP$(SiMe_3)_2$ (δ = 108) was replaced by a new signal assigned to **2.1** (δ = 273).[97] The separation of **2.1** from the side-products, Me_3SiCl and $[Cl_2AlOSiMe_3]_2$, may be accomplished through the use of reduced pressures to first remove the solvent and Me_3SiCl (25 °C, 200 mmHg). Subsequently, the phosphaalkene **2.1** can be distilled (bp = 75 °C, 60 mmHg). This separation must be

performed carefully in order to avoid contamination of **2.1** with volatile $[Cl_2AlOSiMe_3]_2$. The liquid product **2.1** is isolated in 80% yield and its purity was confirmed by NMR spectroscopy and elemental analysis.

Given the difficulty in separating $[Cl_2AlOSiMe_3]_2$ from **2.1**, we sought methods to minimize the production of Al-containing species. Thus, *t*BuP$(SiMe_3)_2$ and *t*BuC(O)H in dichloromethane were treated with substoichiometric amounts of $AlCl_3$. Monitoring by ^{31}P NMR spectroscopy revealed that *t*BuP$(SiMe_3)_2$ could be transformed quantitatively to **2.1** in the presence of 0.5 to 1.0 equiv. of $AlCl_3$ (Scheme 2.3). The reaction times were substantially longer when less $AlCl_3$ is used. When 0.8 equiv. $AlCl_3$ was employed, the isolated yield of **2.1** was ca. 70–80%. When 0.33 equiv. of $AlCl_3$ was employed, a 2:1 mixture of product **2.1** and intermediate, *t*BuP$(SiMe_3)$CH$(OSiMe_3)$*t*Bu, were observed. Although it appears possible to use reduced quantities of $AlCl_3$, in the following studies stoichiometric quantities were employed since this gives the most rapid reaction.

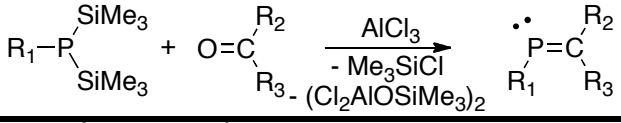


Scheme 2.3 Formation of 2.1 using substoichiometric $AlCl_3$

To assess the generality of the $AlCl_3$-mediated synthesis of phosphaalkenes, we performed a series of NMR scale reactions involving the mixing of equimolar quantities of $R^1P(SiMe_3)_2$ (R^1 = *t*Bu, Ad, Mes), aldehyde/ketone and $AlCl_3$ in CH_2Cl_2. In most instances, the phosphaalkene product is rapidly and quantitatively formed as suggested by ^{31}P NMR spectroscopy (Table 2.1). Although phosphaalkene **2.2** initially forms cleanly, the previously reported 1,2-diphosphetane is observed on standing.[133] In the case of the extremely hindered 2,2,4,4-tetramethylpentan-3-one, its reaction with *t*BuP$(SiMe_3)_2$ to form **2.3** required prolonged heating (100 °C for 12 h). Although the C–Me

phosphaalkene **2.5** could be detected by ^{31}P NMR spectroscopy, this species was present in low quantities (ca. 25% of total P). Given that *t*BuPH$_2$ was present in the reaction mixture (δ = 80, t), it is likely that the readily enolizable ketone, *t*BuC(O)Me, provided acidic protons for reaction with *t*BuP(SiMe$_3$)$_2$. Interestingly, this methodology is amenable to the preparation of a P-silyl-phosphaalkene as illustrated by the quantitative formation of **2.9** from P(SiMe$_3$)$_3$ and pivaldehyde.

Table 2.1 Selected ^{31}P NMR data (CH_2Cl_2) for phosphaalkenes prepared following $AlCl_3$-mediated procedure.

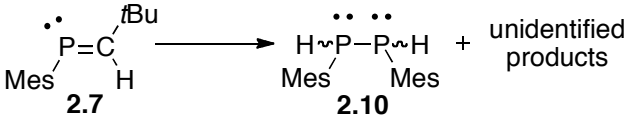


R^1	R^2	R^3	Product	^{31}P NMR (δ)
*t*Bu	*t*Bu	H	**2.1**	273
*t*Bu	Ph	Ph	**2.2**	292
*t*Bu	*t*Bu	*t*Bu	**2.3**	295
*t*Bu	*t*Bu	Ph	**2.4**	277
*t*Bu	*t*Bu	Me	**2.5**	270
Ad	*t*Bu	H	**2.6**	268
Mes	*t*Bu	H	**2.7**	224
Mes	Ph	Ph	**2.8**	234
SiMe$_3$	*t*Bu	H	**2.9**	240

In addition to **2.1**, three other phosphaalkenes have been isolated on a preparative scale (**2.6**, **2.7** and **2.8**) following this new methodology. The procedure described above for **2.1** was followed in each case and analysis of the reaction mixtures by ^{31}P NMR spectroscopy suggested quantitative conversion of RP(SiMe$_3$)$_2$ to phosphaalkene. The separation of the heavier phosphaalkenes from the aluminum-containing byproduct proved impossible by fractional distillation due to the very similar volatility of these compounds. Instead, [$Cl_2AlOSiMe_3$]$_2$ can be removed by extracting a solution of the crude product with a degassed mixture of aqueous NaOH (~5 M) and hexanes. The use of hexanes is critical to keep salts out of the organic layer. Remarkably, the organic layer

contained the unhydrolyzed phosphaalkene product free from Al-containing impurities. Final purification was accomplished through vacuum sublimation (**2.6**), distillation (**2.7**) or recrystallization from hexanes (**2.8**). To our knowledge, the only other isolable P–Ad substituted phosphaalkene is the Becker phosphaalkene, AdP=C(*t*Bu)OSiMe$_3$.[134] We have previously observed AdP=CPh$_2$ by ^{31}P NMR spectroscopy (δ = 286); however, only the head-to-head dimeric 1,2-diphosphetane, [AdP–CPh$_2$]$_2$, could be isolated.[51]

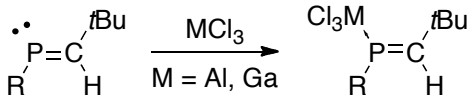
Although, pure **2.7** can be isolated as a colorless oil, after several days in a sealed vial under inert atmosphere, colorless crystals precipitate from the oil. Surprisingly, these crystals were determined to be the diphosphine **2.10** after analysis using NMR spectroscopy and X-ray diffraction (Scheme 2.4). Compound **2.10** had previously been isolated and crystallographically characterized from the reaction of LiPHMes and 1,2-dibromoethane,[135] and has been detected in solution in several other instances.[136-142] Whether this transformation is caused by the presence of a trace impurity or is a consequence of some inherent instability of **2.7** has not been ascertained. However, it should be noted that the analogous crystals of **2.10** are isolated each time **2.7** is prepared.



Scheme 2.4 Decomposition of phosphaalkene **2.7** to afford diphosphine **2.10**

As a means to probe their reactivity and to structurally characterize P-alkyl phosphaalkenes, the potential formation of adducts of **2.1** and **2.6** with group 13 Lewis acids was explored. We have previously reported that treating **2.8** with group 13 Lewis acids affords the simple P-adduct (Cl$_3$Ga)MesP=CPh$_2$ (**2.11**).[87] In contrast, evidence of *C*-addition of GaCl$_3$ was observed with bulkier Mes*P=CH$_2$ (Mes* = 2,4,6-tri-tert-butylphenyl) to afford fleeting phosphenium zwitterion Mes*P–CH$_2$GaCl$_3$.[87] Therefore,

an investigation of the reactions of **2.1** and **2.6** with $GaCl_3$ and $AlCl_3$ was conducted (Scheme 2.5). Prior studies had shown that the reaction of **2.1** with sources of H^+ or Me^+ affords novel diphosphiranium or diphosphetanium cations, respectively.[131]



2.1 R = *t*Bu
2.6 R = Ad

2.12 R = *t*Bu, M = Al
2.13 R = *t*Bu, M = Ga
2.14 R = Ad, M = Ga

Scheme 2.5 Formation of Lewis-adducts **2.12 – 2.14**

Analysis of a solution of phosphaalkene **2.1** and $AlCl_3$ (1 equiv.) in CH_2Cl_2 by ^{31}P NMR spectroscopy revealed that the signal for **2.1** (δ = 273) was not present and a new singlet resonance was observed (δ = 199.8). The chemical shift is consistent with that reported previously for (Cl_3Al)*t*BuP=CH*t*Bu (**2.12**) (δ = 200.5 in C_7D_8).[97] Furthermore, the ^1H and ^{13}C NMR spectra of crystals obtained from the reaction solution were also consistent with adduct formation. Analysis of the crystals by X-ray diffraction confirmed the adduct formation and the *trans* arrangement of the *t*Bu substituents in **2.12** (Figure 2.1). Perhaps this indicates that the bulky alkyl substituent imposes a larger steric demand than the Lewis acid. Similarly, the new adducts *Z*-(Cl_3Ga)*t*BuP=CH*t*Bu (**2.13**) and *Z*-(Cl_3Ga)AdP=CH*t*Bu (**2.14**) were isolated and crystallographically characterized (Figures 2.2 and 2.3, respectively).

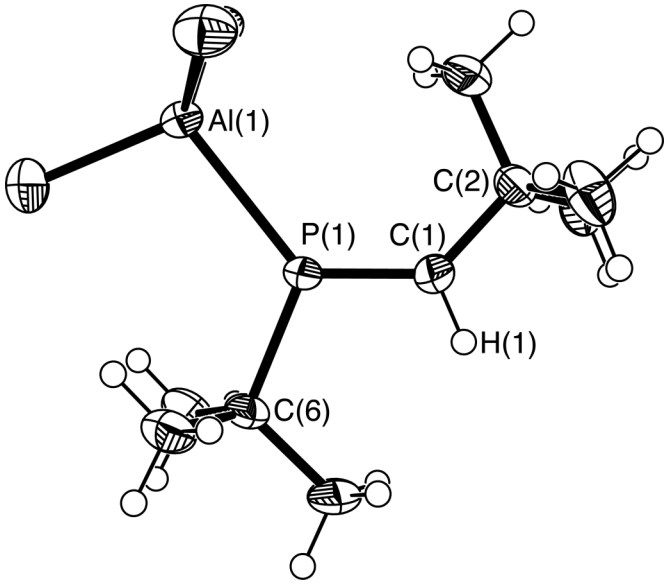


Figure 2.1 The solid-state molecular structure of **2.12**. Displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows. P(1)-C(1) 1.652(3), P(1)-C(6) 1.866(3), P(1)-Al(1) 2.4516(11), C(1)-C(2) 1.502(4), C(6)-P(1)-C(1) 111.96(14), C(1)-P(1)-Al(1) 128.52(11), C(6)-P(1)-Al(1) 119.46(10), P(1)-C(1)-C(2) 132.5(2), C(6)-P(1)-C(1)-C(2) 179.2(3).

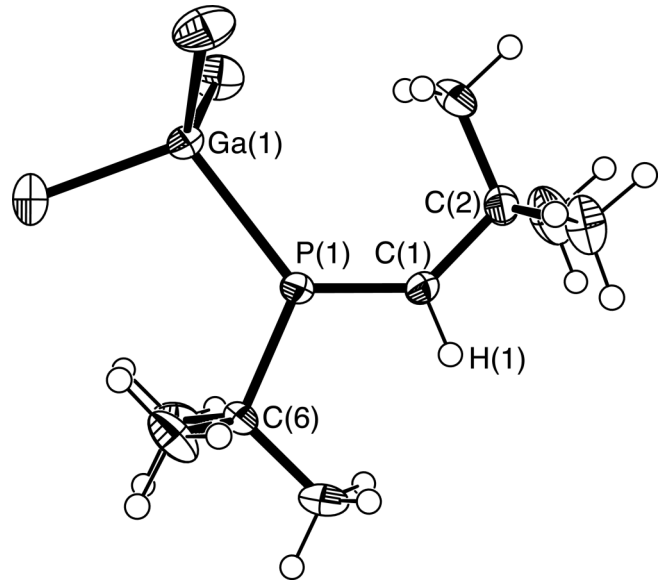


Figure 2.2 The solid-state molecular structure of **2.13**. Displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows. P(1)-C(1) 1.655(3), P(1)-C(6) 1.862(2), P(1)-Ga(1) 2.4164(7), C(1)-C(2) 1.502(3), C(6)-P(1)-C(1) 113.30(12), C(1)-P(1)-Ga(1) 127.77(9), C(6)-P(1)-Ga(1) 118.84(8), P(1)-C(1)-C(2) 132.7(2), C(6)-P(1)-C(1)-C(2) 179.2(2).

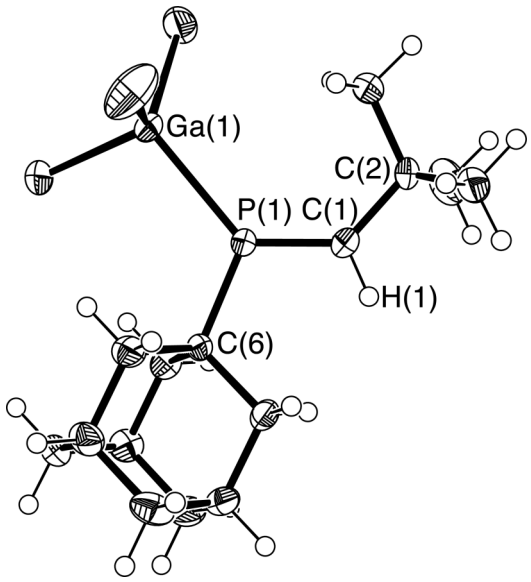


Figure 2.3 ORTEP view of a molecule of **2.14**. Displacement ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows. P(1)-C(1) 1.647(4), P(1)-C(6) 1.842(3), P(1)-Ga(1) 2.4178(10), C(1)-C(12) 1.503(5), C(6)-P(1)-C(1) 112.56(17), C(1)-P(1)-Ga(1) 129.74(14), C(2)-P(1)-Ga(1) 117.30(11), P(1)-C(1)-C(12) 131.7(3), C(6)-P(1)-C(1)-C(2) 179.8(4).

Interestingly, the $^{31}P\{^{1}H\}$ NMR spectra (300 MHz, 298 K) of the Ga and Al adducts show very broad resonances. For example, the full width at half-height (fwhh) for **2.13** (233 Hz) is much larger than that for uncomplexed **2.1** (9 Hz). We speculate that a fluxional process, such as equilibration between coordinated and free phosphaalkene, may be taking place in solution. Evidence for weak binding of Lewis acids to **2.1** has been alluded to previously since $AlCl_3$ is readily displaced from **2.12** in the presence of Et_2O.[97]

There are very few other η^1 complexes of phosphaalkenes to *p*-block metals. We have previously reported the molecular structure of **2.11** and detected $(Cl_3Ga)Mes^*P\text{-}CH_2$ at low-temperature (-80 °C). It has also been reported that the inversely polarized phosphaalkene $[Cp^*(CO)_2Fe]P=C(NMe_2)_2$ will form η^1 complexes with MMe_3 (M = Al, Ga, In); however, crystallographic analysis revealed significant pyramidalization of the phosphorus atoms (~340°) and lengthening of the P–C bonds suggests little double bond

character in these species.[98] In **2.12**, **2.13**, and **2.14** the sum of the angles at phosphorus are 360°, consistent with retention of the P=C bond upon complexation.

Analysis of the metrical parameters reveals that the P=C bond lengths in **2.12** [1.652(3) Å], **2.13** [1.655(3) Å] and **2.14** [1.647(4) Å] are similar in length. These P=C bond lengths lie at shorter end of the range associated with P=C bonds (1.61–1.71 Å),[44] but are comparable to $(CO)_5W[CH_2CH_2C(1\text{-cyclohexene})]P{=}CH\textit{t}Bu$ (1.649 Å)[143] and $(CO)_5W(\textit{t}Bu)P{=}CH\textit{i}Pr$ (1.652 Å),[112] and are consistent with the retention of multiple-bond character upon adduct formation. The P=C bond length in **2.11** [1.687(3) Å] is slightly longer than that for **2.13** and **2.14**, which likely results from π-delocalization between the P=C bond and the aryl moiety in the former.

The $P–C_{alkyl}$ bond lengths in **2.12** [1.866(3) Å], **2.13** [1.862(2) Å] and **2.14** [1.842(3) Å] lie towards the shorter end of the range typical of $P–C_{alkyl}$ bonds (range: 1.85–1.90).[144] Interestingly, the $P–C_{\textit{t}Bu}$ bonds are significantly longer than the $P–C_{Ad}$ bond. Presumably this reflects the lower steric demand of the cyclic Ad substituent. The P–Ga bond lengths in **2.13** [2.4164(7) Å] and **2.14** [2.4178(10) Å] are comparable to that in **2.11** [2.3938(7) Å] and are typical of P–Ga bonds.

2.3 Conclusions

The $AlCl_3$-mediated reaction of bis(silyl)phosphines and aldehydes or ketones provides a useful one-pot route to phosphaalkenes. The acid-mediated method is preferable to base-mediated routes when the preparation of P–alkyl-substituted phosphaalkenes is desired. A series of phosphaalkenes bearing P–*t*Bu and P–Ad substituents have been prepared and isolated following this new methodology. The

adducts *Z*–(Cl_3Ga)*t*BuP=CH*t*Bu (**2.13**), *Z*–(Cl_3Al)*t*BuP=CH*t*Bu (**2.12**), and *Z*–(Cl_3Ga)AdP=CH*t*Bu (**2.14**) are rare examples of phosphaalkene complexes of a group 13 Lewis acid and provide a means to investigate the structural features of *P*–alkyl-substituted phosphaalkenes.

2.4 Experimental

2.4.1 Materials and General Procedures

All manipulations were performed under an atmosphere of nitrogen. Hexanes, dichloromethane and diethyl ether were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. Distilled water was degassed prior to use. C_6D_6 was stored over molecular sieves before use and ampules of CD_2Cl_2 were used as received from CIL. Benzophenone (Aldrich) was sublimed before use. Pivaldehyde, 3,3-dimethylbutan-2-one and $AlCl_3$ were used as received from Aldrich. NaOH and anhydrous $MgSO_4$ were purchased from Fisher and used as received. 2,2,4,4-Tetra-methylpentan-3-one,[145] 2,2-dimethyl-1-phenylpropan-1-one,[146] *t*BuP($SiMe_3$)$_2$,[147] AdP($SiMe_3$)$_2$,[51, 148] MesP($SiMe_3$)$_2$[147] and P($SiMe_3$)$_3$[149] were prepared following literature procedures. ^{1}H, ^{31}P and ^{13}C{^{1}H} NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. Chemical shifts are reported relative to residual C_6HD_5 or $CHDCl_2$ (δ = 7.16 or 5.32 for ^{1}H, respectively), 85% H_3PO_4 as an external standard (δ = 0.0 for ^{31}P), and C_6D_6 or CD_2Cl_2 (δ = 128 or 53.8 for ^{13}C, respectively). Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV).

2.4.2. General Procedure for NMR Scale Reactions

To a small vial charged with $AlCl_3$ (33 mg, 0.25 mmol), dichloromethane (~2 mL) and a small magnetic stir-bar was added a solution of $RP(SiMe_3)_2$ (0.25 mmol) and aldehyde/ ketone (0.25 mmol) in dichloromethane (~2 mL). The mixture was stirred for 10 min and then an aliquot removed and analyzed by ^{31}P NMR spectroscopy. The presence of phosphaalkene is indicated by a diagnostic signal in the respective NMR spectra ($\delta > 200$).

2.4.3. Preparation of *t*BuP=CH*t*Bu (2.1)

To a suspension of $AlCl_3$ (5.6 g, 42 mmol) in dichloromethane (100 mL) was added a mixture of *t*BuP$(SiMe_3)_2$ (10.0 g, 43 mmol) and pivaldehyde (3.8 g, 44 mmol) in dichloromethane (50 mL). The resulting mixture was stirred until quantitative conversion to **2.1** was observed from ^{31}P NMR spectroscopy (~30 min). Volatiles (dichloromethane and $ClSiMe_3$) were removed at reduced pressure (200 Torr). A reduced pressure distillation (75 °C/60 Torr) affords **2.1** as a pale yellow oil (5.4 g, 80%).

^{31}P, ^{1}H and ^{13}C NMR spectra confirmed the formation of **2.1**: $^{31}P\{^{1}H\}$ NMR (C_6D_6) $\delta = 275.7$, lit. ($CDCl_3$) $\delta = 278.2$.[97] Found: C, 68.14; H, 12.03%. $C_9H_{11}P$ requires C, 68.32; H, 12.10%.

2.4.4 Preparation of AdP=CH*t*Bu (2.6)

To a suspension of $AlCl_3$ (4.3 g, 32 mmol) in dichloromethane (100 mL) was added a mixture of AdP$(SiMe_3)_2$ (10.0 g, 32 mmol) and pivaldehyde (2.8 g, 33 mmol) in dichloromethane (50 mL). The resulting mixture was stirred for 1 h and then the volatiles (dichloromethane and $ClSiMe_3$) were removed at reduced pressure (200 Torr). The crude product was dissolved in diethyl ether (100 mL) and added dropwise to a stirred mixture

of degassed 5 M NaOH(aq.) (200 mL) and hexanes (100 mL). The organic fraction was separated and the aqueous fraction washed with hexanes (3 x 30 mL). The combined organic fractions were dried with anhydrous $MgSO_4$, filtered, and evaporated to dryness. The crude solid was vacuum distilled and sublimed (100 °C/2 mmHg) to afford an analytically pure colorless solid (4.3 g, 57%).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = 268.4. ^1H NMR (CD_2Cl_2) δ = 8.65 (d, $^2J_{PH}$ = 24.9 Hz, 1H), 1.98 (m, 3H), 1.80 (m, 6H), 1.75 (m, 6H), 1.13 (d, $^4J_{PH}$ = 1.8 Hz, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ = 194.6 (d, $^1J_{PC}$ = 46.2 Hz), 42.6 (d, $^2J_{PC}$ = 8.4 Hz), 38.4 (d, $^2J_{PC}$ = 11.8 Hz), 37.3, 36.1 (d, $^1J_{PC}$ = 34.0 Hz), 31.2 (d, $^3J_{PC}$ = 12.9 Hz), 29.7 (d, $^3J_{PC}$ = 6.6 Hz). MS (EI): *m/z* [%] 135, 136 [100, 15, Ad^+], 236, 237 [18, 3, M^+]. Found: C, 76.56; H, 10.89%. $C_{15}H_{25}P$ requires C, 76.23; H, 10.66%.

2.4.5 Preparation of MesP=CH*t*Bu (2.7)

To a suspension of $AlCl_3$ (1.7 g, 13 mmol) in dichloromethane (40 mL) was added a mixture of $MesP(SiMe_3)_2$ (4.0 g, 13 mmol) and pivaldehyde (1.1 g, 13 mmol) in dichloromethane (25 mL). The resulting mixture was stirred for 1 h and then the volatiles (dichloromethane and $ClSiMe_3$) were removed at reduced pressure (200 Torr). The crude product was dissolved in diethyl ether (100 mL) and added dropwise to a stirred mixture of degassed 5 M NaOH(aq.) (200 mL) and hexanes (100 mL). The organic fraction was separated and the aqueous fraction washed with hexanes (3 x 30 mL). The combined organic fractions were dried with anhydrous $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by vacuum distillation (1.9 g, 63%).

^{31}P and ^1H NMR spectra confirmed the formation of **2.7**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = 224.6, lit. (C_6D_6) δ = 228.4.[150, 151]

After several days, crystals of **2.10** precipitate from the liquid **2.7**. **2.10**: $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ = -111.9 (60%), -119.1 (40%), lit. (C_6D_6) δ = -109.9 (60%), -117.1 (40%).[135]

2.4.6 Preparation of $MesP=CPh_2$ (2.8)

To a suspension of $AlCl_3$ (2.2 g, 17 mmol) in dichloromethane (50 mL) was added a mixture of $MesP(SiMe_3)_2$ (5.0 g, 16 mmol) and benzophenone (3.1 g, 17 mmol) in dichloromethane (50 mL). The resulting mixture was stirred for 1 h and then the volatiles (dichloromethane and $ClSiMe_3$) were removed in vacuo. The crude product was dissolved in diethyl ether (100 mL) and added dropwise to a stirred mixture of degassed 5 M NaOH(aq.) (200 mL) and hexanes (100 mL). The organic fraction was separated and the aqueous fraction washed with hexanes (3 x 30 mL). The combined organic fractions were dried with anhydrous $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by vacuum distillation and then recrystallization from hexanes to afford yellow crystals of **2.8** (4.1 g, 76%).

^{31}P, ^{1}H and ^{13}C NMR spectra confirmed the formation of **2.8**: $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ = 234.6, lit. ($CDCl_3$) δ = 233.[63] Found: C, 83.17; H, 6.62%. $C_{22}H_{21}P$ requires C, 83.52; H, 6.69%.

2.4.7 Preparation of *Z*–(Cl_3Al)*t*BuP=CH*t*Bu (2.12)

To a solution of $AlCl_3$ (0.266 g, 2 mmol) in dichloromethane (2 mL) was added a solution of **2.1** (0.316 g, 2 mmol) in dichloromethane (1 mL). Upon the reaction mixture was layered 1 mL of hexanes. The mixture was stored at -40 °C for 24 h at which point crystals of **2.12** suitable for X-ray crystallography were harvested (0.25 g, 43%).

^{31}P and ^{1}H spectra confirmed the formation of **2.12**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 198.6, lit. (C_7D_8) δ = 200.5.[97]

2.4.8 Preparation of *Z*–(Cl_3Ga)*t*BuP=CH*t*Bu (2.13)

To a solution of $GaCl_3$ (0.350 g, 2 mmol) in dichloromethane (2 mL) was added a solution of **2.1** (0.316 g, 2 mmol) in dichloromethane (1 mL). Upon the reaction mixture was layered 1 mL of hexanes. The mixture was stored at -40 °C for 24 h at which point crystals of **2.13** suitable for X-ray crystallography were collected (0.48 g, 72%).

^{31}P{^{1}H} NMR (CD_2Cl_2) δ = 194.4; ^{1}H NMR (CD_2Cl_2) δ = 8.74 (d, $^{2}J_{PH}$ = 24.3 Hz, 1H), 1.60 (d, $^{3}J_{PH}$ = 16.8, 9H), 1.38 (d, $^{4}J_{PH}$ = 1.8 Hz, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ = 190.8 (d, $^{1}J_{PC}$ = 20.6 Hz), 40.9, 40.7 (d, $^{1}J_{PC}$ = 4.9 Hz), 31.5 (d, $^{2}J_{PC}$ = 12.9 Hz), 29.9. Found: C, 32.40; H, 5.89%. $C_9H_{19}PGaCl_3$ requires C, 31.82; H, 5.73%.

2.4.9 Preparation of *Z*–(Cl_3Ga)AdP=CH*t*Bu (2.14)

To a solution of $GaCl_3$ (0.200 g, 1.1 mmol) in dichloromethane (1 mL) was added a solution of **2.6** (0.260 g, 1.1 mmol) in dichloromethane (1 mL). The mixture layered with hexanes (2 mL) and was stored at -40 °C for 24 h from which crystals of **2.14** suitable for X-ray crystallography were grown (0.34 g, 75%).

^{31}P{^{1}H} NMR (CD_2Cl_2) δ = 189.3; ^{1}H NMR (CD_2Cl_2) δ = 8.60 (d, $^{2}J_{PH}$ = 23.7 Hz, 1H), 2.24 (m, 6H), 2.15 (m, 3H), 1.81 (m, 6H), 1.37 (d, $^{4}J_{PH}$ = 1.8, 9H). ^{13}C{^{1}H} (CD_2Cl_2) δ = 189.8 (d, $^{1}J_{PC}$ = 24.1 Hz), 45.1, 41.0, 40.5, 36.1, 31.5 (d, $^{3}J_{PC}$ = 9.6 Hz), 29.4 (d, $^{3}J_{PC}$ = 7.1 Hz). Found: C, 43.67; H, 5.95%. $C_{15}H_{25}PGaCl_3$ requires C, 43.68; H, 6.11%.

2.4.10 X-Ray Crystallography

Crystals suitable for diffraction were immersed in Paratone-N oil and mounted on a glass fiber. Data for **2.13** were collected on a Bruker X8 APEX diffractometer and for both **2.12** and **2.14** on a Bruker X8 APEX II diffractometer with graphite-monochromated MoKα radiation. Data were collected and integrated using the Bruker SAINT[152] software package and corrected for absorption effects using SADABS[153] (**2.12**) or TWINABS[154] (**2.13** and **2.14**). **2.13** crystallizes as a two-component twin with the two components (major : minor ≈ 3 : 1) related by a 180° rotation about the (0 0 1) reciprocal axis. **2.14** crystallizes as a two-component twin with the two components (major : minor ≈ 2 : 1) related by a 180° rotation about the (1 0 0) reciprocal axis. All data sets were corrected for Lorentz and polarization effects. All structures were solved by direct methods[155] and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXTL[156] crystallographic software package from Bruker-AXS. H-atoms were included in calculated positions (riding model). Compounds **2.12** and **2.13** are isomorphous and were refined using the same origin (Table 2.2).

Table 2.2 Crystallographic data for **2.12**, **2.13** and **2.14**.

	2.12	**2.13**	**2.14**
Formula	$C_9H_{19}PAlCl_3$	$C_9H_{19}PgaCl_3$	$C_{15}H_{25}PGaCl_3$
Fw	291.54	334.28	412.39
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Color	Colorless	Colorless	Colorless
a (Å)	11.0934(8)	11.0971(14)	10.5923(11)
b (Å)	8.8646(6)	8.8556(12)	15.9466(17)
c (Å)	16.1716(11)	16.184(2)	11.3326(13)
α (deg)	90	90	90
β (deg)	108.143(2)	108.247(5)	107.238(5)
γ (deg)	90	90	90
V (Å^3)	1511.23(18)	1510.5(3)	1828.2(3)
T (K)	173(2)	173(2)	100(2)
Z	4	4	4
μ (Mo Kα) (cm^{-1})	7.38	24.26	20.21
cryst size (mm^3)	0.4 × 0.2 × 0.1	0.15 × 0.15 × 0.10	1.0 × 0.5 × 0.3
calcd density (Mg m^{-3})	1.281	1.470	1.498
2θ (max) (deg)	55.8	56.0	56.4
no. of reflns	18581	32228	39679
no. of unique data	3626	6868	7795
R(int)	0.0366	0.0505	0.0880
Refln/param ratio	27.26	51.25	42.14
R1[a]	0.0484; $I > 2\sigma(I)$	0.0377; $I > 2\sigma(I)$	0.0572; $I > 2\sigma(I)$
wR2 (all data)[b]	0.1324	0.0887	0.1350
GOF	1.154	1.097	1.077

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2\ [\text{all data}]) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Chapter 3: Cyclic Phosphorus Cations: Different Fates for the Electrophile-Initiated Reaction of Phosphaalkenes

3.1 Introduction

Three-membered heterocycles such as oxiranes and aziridines, first discovered in 1859[157] and 1888[158], respectively, are currently produced in the millions of tons and used to prepare other value-added products ranging from polymers to pharmaceuticals. In addition to their industrial importance, these cyclic species are also of fundamental interest due to the strained nature of their bonding. Although a much younger field – the first phosphiranes were not discovered until 1963, more than 80 years later than their lighter congeners[159] – the study of three-membered phosphorus heterocycles has nevertheless received considerable attention due to their novel structures, bonding and utility as building blocks in organophosphorus chemistry.[160-162] Moreover, because phosphorus heterocycles often behave differently or have no isolable counterparts in nitrogen chemistry, they illustrate the striking differences between the chemistry of the first and second periods and provide a unique opportunity to expand upon our knowledge of chemical bonding (Figure 3.1).[113]

*A version of this chapter has been published. Joshua I. Bates and Derek P. Gates, "Diphosphiranium (P_2C) or Diphosphetanium (P_2C_2) Cyclic Cations: Different Fates for the Electrophile-Initiated Cyclodimerization of a Phosphaalkene," *J. Am. Chem. Soc.*, **2006**, *128*, 15998-15999.

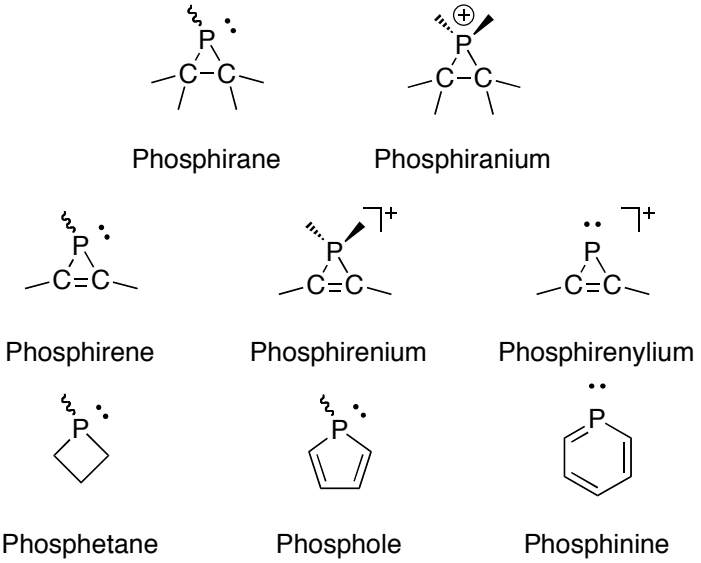
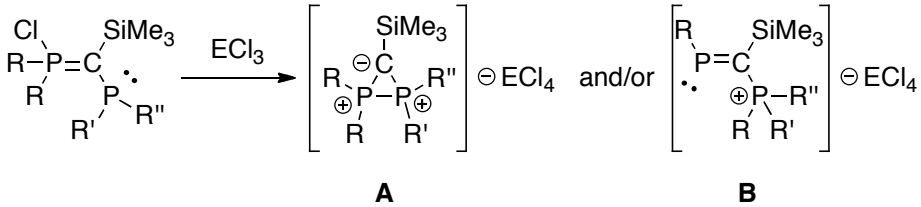


Figure 3.1 Representative examples of phosphorus-based heterocycles.

A dramatic illustration of the difference between the chemistry of nitrogen and phosphorus is provided by the pioneering investigations of bisphosphinocarbenium ions $(P_2CR_5)^+$.[99, 100] In an effort to prepare the phosphorus analogues of amidinium ions (Figure 3.2, **C**) via the abstraction of chloride from *C*-phosphino-*P*-chloro phosphorus ylides (Scheme 3.1), Bertrand and coworkers determined that a subtle steric balance dictates whether one obtains an acyclic *C*-phosphoniophosphaalkene (**B**) or a symmetric diphosphiranium cation (**A**). Remarkably, the "carbenium" (i.e. cationic) carbon atom in the symmetrical diphosphiranium (**A**) draws so much electron density from its phosphorus and silicon neighbours that it is formally and effectively anionic![100]



Scheme 3.1 Reactions of *C*-phosphino-*P*-chloro phosphorus ylides with chloride abstracting reagents

Computational studies on the parent system, $(P_2CH_5)^+$, located five local minima on the potential energy surface (Figure 3.2).[101] Significantly, none of these reflect the structure of amidinium ions, which adopt an acyclic and planar N—C—N framework exclusively (the unknown cyclic valence isomer **D** is calculated to be 129.2 kcal mol^{-1} higher in energy than **C**).[100] Among the calculated local minima, the closest structural analogues to the amidinium ion are the bis(phosphanyl) carbenium (**G**) and the *C*-phosphinomethylenephosphonium (**H**)[163] ions, however, in contrast to the planar nitrogen system, both exhibit significantly pyramidalized phosphorus centers. Interestingly, the isolation of an asymmetric diphosphiranium ion (**E**), which the calculations suggest being lower in energy than either structural isomers **F** (4.5 kcal mol^{-1}) or **I** (47.1 kcal mol^{-1})[101] for which derivatives have been crystallographically characterized,[99, 100] remains an elusive goal. Although it could not be isolated, spectroscopic evidence for structure-type **E** was first obtained from the *P*-methylation of diphosphirane $(Mes^*P)_2CH_2$ (Mes* = 2,4,6-tri-*tert*-butylphenyl).[101] In contrast, the analogous asymmetric diaziridinium cation has only been postulated as an intermediate,[164, 165] further emphasizing the difference between the chemistry of phosphorus and nitrogen.

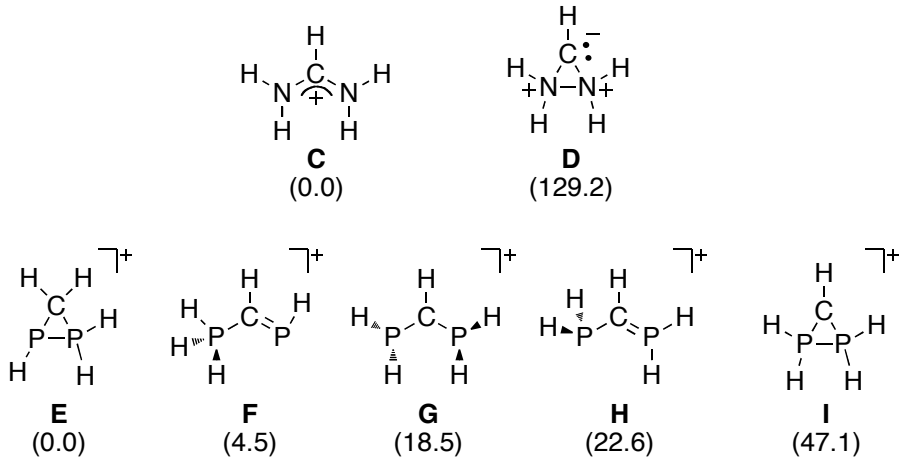
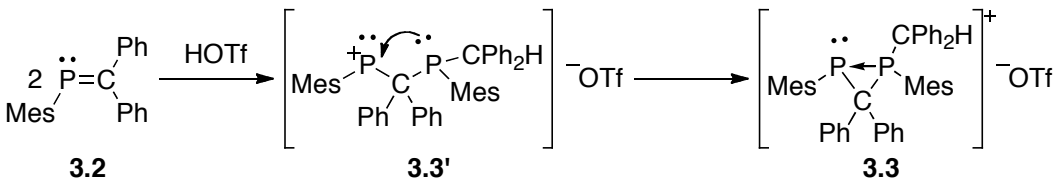


Figure 3.2 Top: Structures and relative energies (kcal mol^{-1}) of $(N_2CH_5)^+$ ions **C** and **D**. Bottom: Structures and relative energies (kcal mol^{-1}) of structural isomers **E-I** on the $(P_2CH_5)^+$ potential energy surface.

As part of our ongoing efforts to study the addition polymerization of phosphaalkenes,[85, 103-105, 107, 108, 115, 120, 121, 166] our group recently reported the spectroscopic detection of asymmetric diphosphiranium ions formed from the reaction of phosphaalkenes [Mes*P=CH_2 (**3.1**) or MesP=CPh_2 (**3.2**)] with in situ generated phosphenium ions.[87] We propose that, following linear dimerization, the acyclic 3-phosphino-1-phosphenium ion cyclizes via the formation of an intramolecular phosphine-phosphenium adduct such as **3.3** (Scheme 3.2). This is analogous to the intra- and inter-molecular coordination chemistry of phosphines with phosphenium ions that Burford and coworkers have exploited to systematically develop a series of novel cyclic and acyclic catena-phosphorus cations.[167-169] Unfortunately, attempts to isolate pure materials from our cyclodimerization reaction mixtures were unsuccessful.[87]

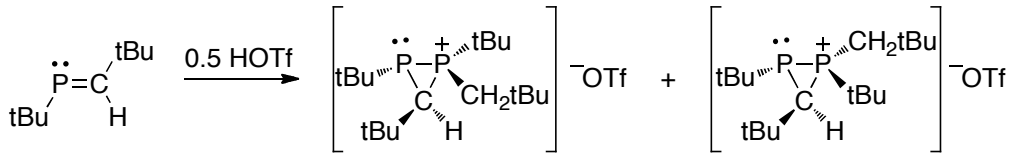


Scheme 3.2 HOTf initiated cyclodimerization of phosphaalkene **3.2**

Hypothesizing that bulky and electron-rich substituents, such as *tert*-butyl or adamantyl (Ad), might effectively stabilize and allow for the isolation of a species containing the highly reactive and electron-deficient P_2C-framework found in **E**, we studied the reactivity of phosphaalkenes *t*BuP=CH*t*Bu (**3.4**) and AdP=CH*t*Bu (**3.5**) with cationic initiators. Herein, we report the first crystallographically characterized asymmetric diphosphiranium salts and the unexpected synthesis of unprecedented mono- and di-cationic diphosphetanium ions.[131] Importantly, we have demonstrated that the reaction of phosphaalkenes with electrophiles provides an effective route to novel phosphorus heterocycles.

3.2 Results and Discussion

To test the hypothesis of the stabilizing effects of bulky alkyl substituents, a colorless CH_2Cl_2 solution of phosphaalkene **3.4** was treated with a CH_2Cl_2 solution of HOTf (0.5 equiv) and, subsequently, analyzed the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 3.3). The spectrum revealed that **3.4** ($\delta = 274$) was entirely consumed and was replaced by signals assigned to two products containing direct P-P bonds (**3.6b**: $\delta = -35.8, -119.8$; $J_{PP} = 248$ Hz; 40%; **3.6a**: $\delta = -44.2, -49.9$; $J_{PP} = 260$ Hz; 60%). Following removal of solvent, the $^{31}P\{^1H\}$ spectrum of the crude product was consistent with that of the reaction mixture (Figure 3.3). In contrast to previous investigations, no additional products were observed in the reaction of **3.4** with HOTf.[87]



3.4 **3.6a** (major) **3.6b** (minor)

Scheme 3.3 HOTf initiated cyclodimerization of phosphaalkene **3.4**

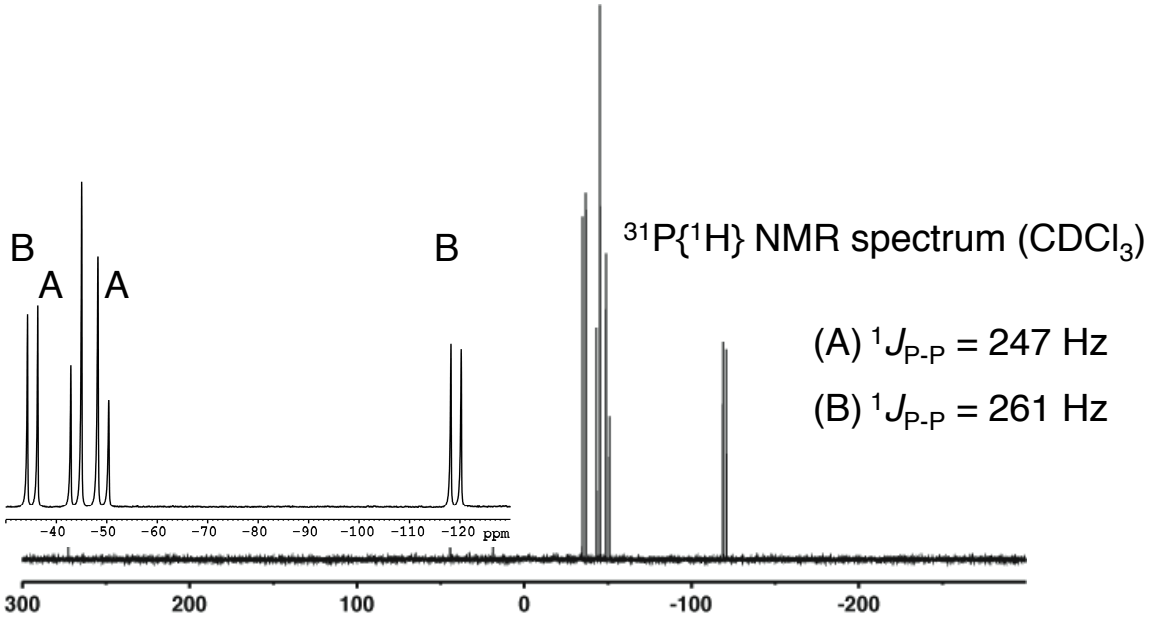


Figure 3.3 $^{31}P\{^{1}H\}$ NMR spectrum (in $CDCl_3$) of crude product obtained from reaction of phosphaalkene **3.4** and substoichiometric HOTf

The product mixture was stable in solution and as a colourless powder and, consequently, single crystals of the major species could be obtained from a concentrated toluene/hexanes solution. While the same relative product ratio is obtained, further studies found Et_2O to be a better solvent for the reaction since the major species crystallizes reliably from Et_2O at -30 °C (overall isolated yield ≈ 40%). The molecular structure confirms the identity of the major product as the unsymmetrical diphosphiranium **3.6a** (Figure 3.4). Although the minor product has not yet been isolated, its proton assignment was extracted from the ^{1}H NMR spectrum of the mixture and is consistent with the structure of **3.6b**. Interestingly, only two, out of a potential four, diastereomeric pairs are observed. This suggests the cyclodimerization might be occuring

in a step-wise fashion, where a phosphenium triflate, formed from the reaction of HOTf with the first equivalent of phosphaalkene,[170] reacts with the second equivalent of phosphaalkene with retention of the *E*-stereochemistry.

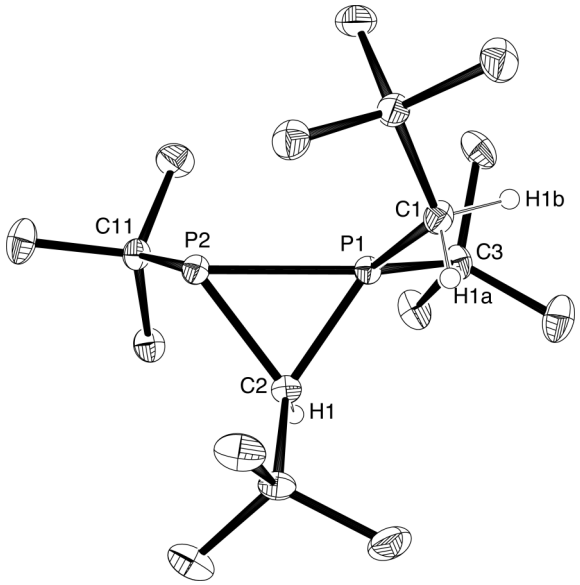
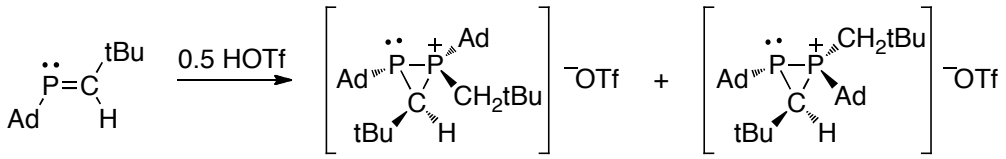


Figure 3.4 ORTEP of **3.6a** (thermal ellipsoids set at 30% probability). The triflate anion and all hydrogen atoms except H1, H1a, and H1b are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-P(2) 2.164(1), P(1)-C(1) 1.836(1), P(1)-C(2) 1.815(1), P(1)-C(3) 1.865(2), P(2)-C(2) 1.888(1), P(2)-C(11) 1.890(1); P(2)-P(1)-C(2) 55.8 (1), P(1)-P(2)-C(2) 52.7(1), P(1)-C(2)-P(2) 71.5(1).

In an attempt to explore the generality of this new reaction, a solution of phosphaalkene **3.5** was treated with HOTf (0.5 equiv) in CH_2Cl_2 solution (Scheme 3.4). Analogously to the reaction of phosphaalkene **3.4** with HOTf, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture revealed that phosphaalkene **3.5** was completely consumed and replaced by two new species, tentatively assigned to **3.7a** and **3.7b**, containing direct P-P bonds (δ = -36.3, -127.1; $^1J_{PP}$ = 250 Hz; 40%; δ = -48.2, -54.1; $^1J_{PP}$ = 256 Hz; 60%).



3.5 **3.7a** (major) **3.7b** (minor)

Scheme 3.4 HOTf initiated cyclodimerization of phosphaalkene **3.5**

Although the mixture of **3.7a** and **3.7b** is stable in a CH_2Cl_2 solution and as a powder, different solvent combinations involving CH_2Cl_2, toluene, Et_2O and hexanes failed to afford crystals of either product. However, when acetonitrile is used as a co-solvent with CH_2Cl_2 and hexanes, slow evaporation of the solvent afforded crystals of **3.7a**·HOTf suitable for X-ray crystallographic analysis (Figure 3.5). Interestingly, while this confirms the formation of the diphosphiranium cation **3.7a**, the ^{31}P NMR spectrum of the redesolved crystals revealed only a singlet at –52.3 ppm. This indicates both phosphorus atoms are equivalent, at least on the NMR time-scale; the reason for this, however, is unclear and requires further investigation.

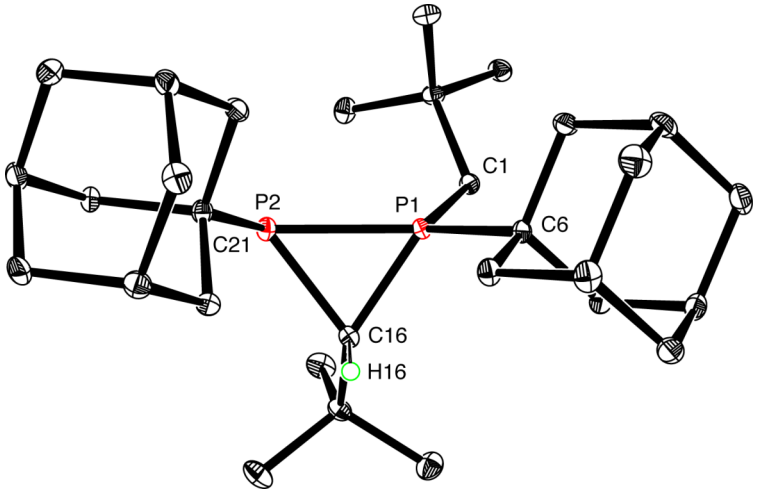
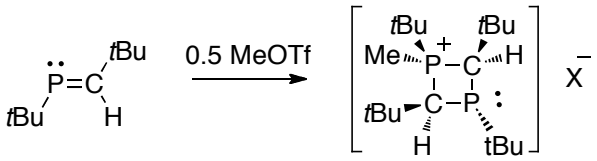


Figure 3.5 ORTEP of **3.7a**·HOTf (thermal ellipsoids set at 30% probability). Both triflate anions and all hydrogen atoms except H(16) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-P(2) 2.161(1), P(1)-C(1) 1.843(2), P(1)-C(16) 1.815(2), P(1)-C(6) 1.866(2), P(2)-C(16) 1.892(2), P(2)-C(21) 1.875(2); P2-P1-C2 56.0 (1), P1-P2-C2 52.7(1), P1-C2-P2 71.3(1).

To our knowledge, compounds **3.6a** and **3.7a** are the first crystallographically characterized asymmetric diphosphiranium cations (**E**) bearing only carbon or hydrogen ring-substituents and each was isolated as the single diastereomeric pair observed. Mathey, Regitz and coworkers reported an $Al_2P_3C_3$ cage compound that formally contains a diphosphiranium moiety; however, the carbon atom bears a zwitterionic Al substituent.[171] The P-P bond lengths in **3.6a** [2.1637(5) Å] and **3.7a** [2.1608(7) Å] are shorter than the typical P-P single bonds (2.25 Å),[144] but similar to the P-P^+ bonds observed in [(*t*BuP)$_3$Me]OTf [2.1465(6) and 2.1652(6) Å].[168] The P-C bond lengths in both compounds are typical of P-C bonds (1.85-1.95 Å),[144] with slightly shorter bond lengths observed at the phosphonium centers than at the phosphine centers.[168] Interestingly, the former P=C bonds [**3.6a**: P(2)-C(2) 1.888(1) Å and **3.7a**: P(2)-C(16) 1.892(2) Å] are significantly longer than the new *C*-phosphonium bonds [**3.6a**: P(1)-C(2) 1.815(1) Å and **3.7a**: P(1)-C(16) 1.815(2) Å] and both are distinctly single bonds [cf., ($GaCl_3$)*t*BuP=CH*t*Bu: P=C 1.655(3) Å].[172] This is in contrast to the P-P (2.120(1) Å) and P-C (1.710(3) and 1.731(3) Å) bonds observed in the symmetrical diphosphiranium cation (**A** or **I**), derived from the *C*-phosphino-*P*-chloro phosphorus ylides, which exhibit a certain degree of delocalized multiple-bond character.[99, 100] The small endocyclic bond angles [**3.6a**: P(2)-P(1)-C(2) 55.8(1)°; P(1)-P(2)-C(2) 52.7(1)°; P(1)-C(2)-P(2) 71.5(1)° and **3.7a**: P(2)-P(1)-C(16) 56.0(1)°; P(1)-P(2)-C(16) 52.7(1)°; P(1)-C(16)-P(2) 71.3(1)°] reflect the strain in the P_2C rings.

Having established that HOTf can promote the cyclodimerization of P=C bonds, MeOTf was considered as another potential cationic initiator (Scheme 3.5). Surprisingly, after treating phosphaalkene **3.4** with MeOTf (0.5 equiv) in CH_2Cl_2, a single product, in

contrast with that described in Schemes 3.3 and 3.4, was detected in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture (δ = 61.6, 18.1; $^{2}J_{PP}$ = 15 Hz) (Figure 3.6). Moreover, this product is air- and moisture-stable, and its ^{1}H NMR spectrum shows a doublet resonance consistent with a P-CH_3 group (δ = 2.30; $^{2}J_{PH}$ = 11 Hz).



3.4 **3.8a**: X = OTf
3.8b: X = I

Scheme 3.5 MeOTf initiated cyclodimerization of phosphaalkene **3.4**

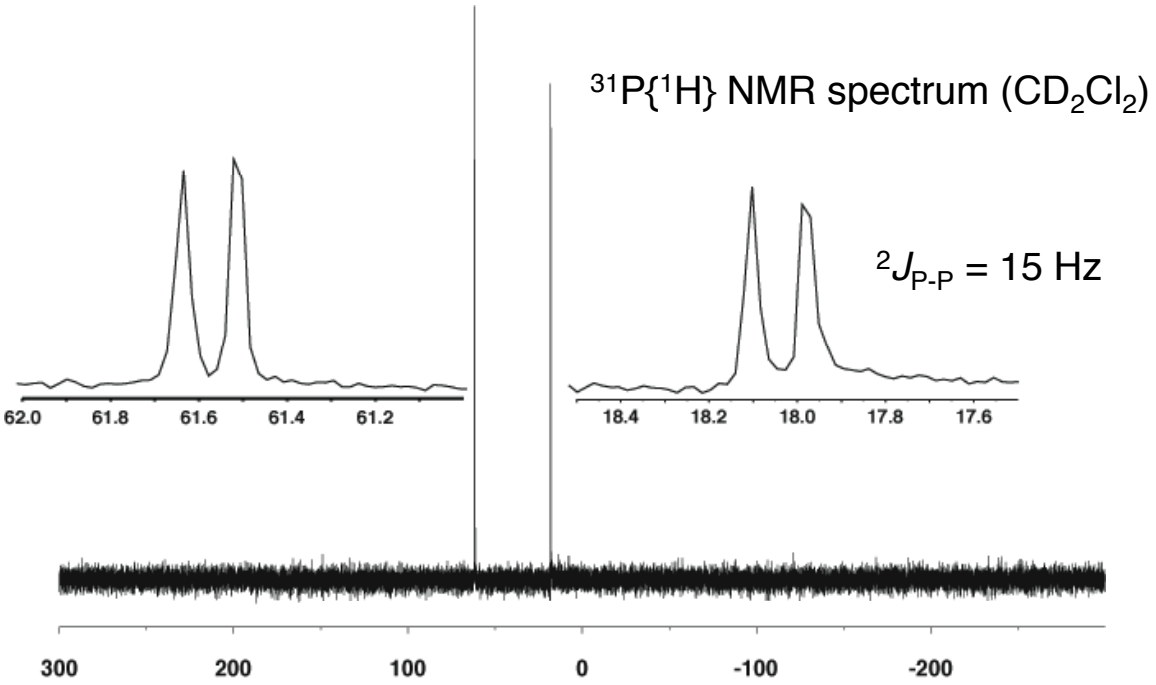


Figure 3.6 $^{31}P\{^{1}H\}$ NMR spectrum (in CD_2Cl_2) of crude product obtained from reaction of phosphaalkene **3.4** and substoichiometric MeOTf

These observations are in contrast to those observed for air- and moisture-sensitive diphosphiranium **3.6** and, although consistent with a dimer, suggest that Me^{+} interacts with the P rather than the C in phosphaalkene **3.4**. After exchange of the triflate in **3.8a** with iodide, by washing repeatedly with saturated KI(aq), X-ray crystallography

revealed that the product was a 1,3-diphosphetanium salt (**3.8b**) containing a P_2C_2 ring (Figure 3.7).

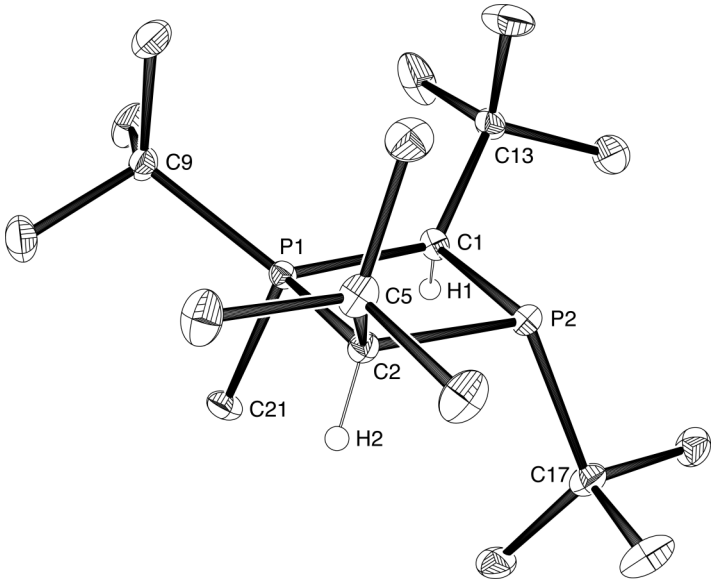
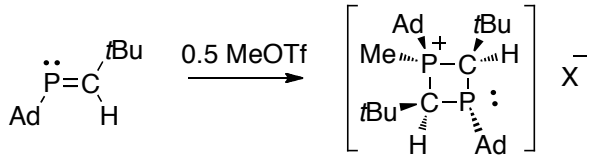


Figure 3.7 ORTEP of **3.8b** (thermal ellipsoids set at 30% probability). The iodide atom and all hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.858(2), P(1)-C(2) 1.859(2), P(1)-C(9) 1.883(2), P(1)-C(21) 1.810(2), P(2)-C(1) 1.905(2), P(2)-C(2) 1.900(3), P(2)-C(17) 1.891(2); C(1)-P(1)-C(2) 91.3 (1), P(1)-C(1)-P(2) 90.0(1), C(1)-P(2)-C(2) 88.6(1), P(1)-C(2)-P(2) 90.1(1), P(1)-C(1)-C(13) 130.2(2), P(1)-C(2)-C(5) 127.6(2), P(2)-C(1)-C(13) 113.8(2), P(2)-C(2)-C(5) 113.4(2), P(1)-C(1)-P(2)-C(2) 2.4(1).

In an analogous fashion, treating phosphaalkene **3.5** with MeOTf (0.5 equiv) also affords a diphosphetanium cation (Scheme 3.6). Similarly, the cation is air- and moisture-stable and the structure of **3.9b**, depicted in Figure 3.8, was obtained by X-ray crystallographic analysis following exchange of the triflate counter anion for iodide using saturated KI(aq).



3.5 **3.9a**: X = OTf
3.9b: X = I

Scheme 3.6 MeOTf initiated cyclodimerization of phosphaalkene **3.5**

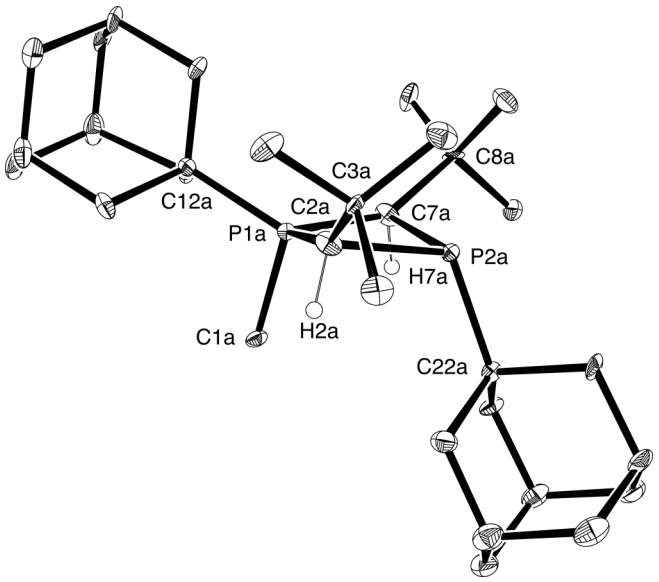


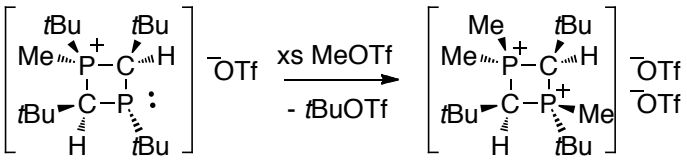
Figure 3.8 ORTEP of **3.9b** (thermal ellipsoids set at 30% probability). The iodide anion and all hydrogen atoms except H2a and H7a are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1a-C1a 1.774(9), P1a-C12a 1.86(2), P1a-C2a 1.778(4), P1a-C7a 1.762(4), P2a-C2a 1.958(4), P2a-C7a 1.987(5), P2a-C22a 1.87(2); C2a-P1a-C7a 96.7(2), P1a-C2a-P2a 88.7(2), C2a-P2a-C7a 84.2(2), P1a-C7a-P2a 88.2(2), P1a-C2a-C3a 152.9(6), P1a-C7a-C8a 151.0(8), P2a-C2a-C3a 99.0(5), P2a-C7a-C8a 101.0(9), P1a-C2a-P2a-C7a 10.9(2).

Salts **3.8b** and **3.9b** represent the first structurally characterized examples of simple 1,3-diphosphetanium cations.[173-175] For **3.8b**, aside from a shorter P-Me bond (1.810(2) Å), most of the P-C bond lengths are typical of P-C bonds (1.85-1.95 Å).[144] As might be anticipated, the endocyclic *C*-phosphonium bonds [P(1)-C(1) 1.858(2) and P(1)-C(2) 1.859(2) Å] are a little shorter than the endocyclic *C*-phosphino bonds [P(2)-C(1) 1.905(2) and P(2)-C(2) 1.900(3) Å].[168] Interestingly, the P_2C_2 ring in diphosphetanium **3.8b** is nearly planar (avg dihedral angle ~3°) and the ring itself is a slightly distorted square (sum of internal angles is 359.8(4)°), with individual angles being ~90°. The observed planarity and square-like shape of the P_2C_2 ring in **3.8b** contrasts with the puckered structures often observed for neutral diphosphetanes [cf $(-PCF_3-CF_2-)_2$: ring dihedral angle 35.4° and C-P-C angle 77.6°].[113] Due to disorder in the structure of **3.9b**, any comparisons with the structure of **3.8b** must be made cautiously; nevertheless, the

structure of **3.9b** clearly illustrates that the product of the reaction of phosphaalkene **3.5** with MeOTf is also a diphosphetanium salt.

Given that the chemistry of neutral phosphetanes and of cationic phosphetanium ions are reasonably well developed,[113] it is perhaps surprising to note that alkylation of simple 1,3-diphosphetanes has not been reported.[173-175] Although ring strain reduces the basicity of cyclic phosphines significantly,[113] studies on tetra-*tert*-butyltetraphosphacubane, which formally comprises six P_2C_2 units as the faces of a cube, show that it can be alkylated or protonated using strong electrophiles such as HOTf or MeOTf to afford polycyclic diphosphetaniums cations.[173] Interestingly, the cubane compound can be doubly protonated using Magic Acid ($FSO_3H{\cdot}SbF_5$) in SO_2; however, despite the availability of three P lone pairs, attempts to doubly alkylate using excess alkylating agent were unsuccessful. Therefore, it is surprising to observe that **3.8a** reacts with MeOTf in CH_2Cl_2.

While several unidentified diphosphorus species were observed in the $^{31}P\{^1H\}$ NMR spectrum of an aliquot of the reaction mixture, using excess MeOTf (~5 equiv) allowed for isolation of colorless crystals that are only sparingly soluble in CH_2Cl_2, but dissolve readily in the more polar MeCN (Scheme 3.7). The ^{31}P NMR spectrum of the crystals revealed two signals (δ = 74.9, 55.3; $^2J_{PP}$ = 16 Hz), consistent with the methylation of the phosphine functionality of **3.8a** and the formation of a dication. Remarkably, however, the ^1H NMR spectrum revealed not the expected two *P*-Me and two *P*-*t*Bu but, rather, three *P*-Me and only one *P*-*t*Bu resonances. The formation of the 1,3-diphosphetanium dication **3.10** was confirmed by X-ray crystallographic analysis and its molecular structure is depicted in Figure 3.9.



3.8a **3.10**

Scheme 3.7 Formation of dicationic diphosphetanium **3.10**

Similarly to the structure of the mono-cationic **3.8b**, the P-C bond lengths are all typical with the exception of the short P-Me bonds [P(1)-C(1) 1.793(4), P(1)-C(2) 1.791(4) and P(2)-C(8) 1.781(4) Å]. Notably, there is no significant difference between the endocyclic bonds to either phosphonium center. Although the endocyclic angles are all ~90°, the P_2C_2 ring of **3.10** is more puckered (dihedral angle 13.9°) and its square shape more distorted (sum of internal angles is 356.6(8)°) than that of **3.8b**. The smaller P(1)-C-C_{tBu} angles (**3.8b**: ~130° versus **3.10**: ~123°) suggest a reduced steric influence of Me (Me_2P^+) versus *t*Bu (Me*t*BuP^+) on the *C*-tBu substituents.

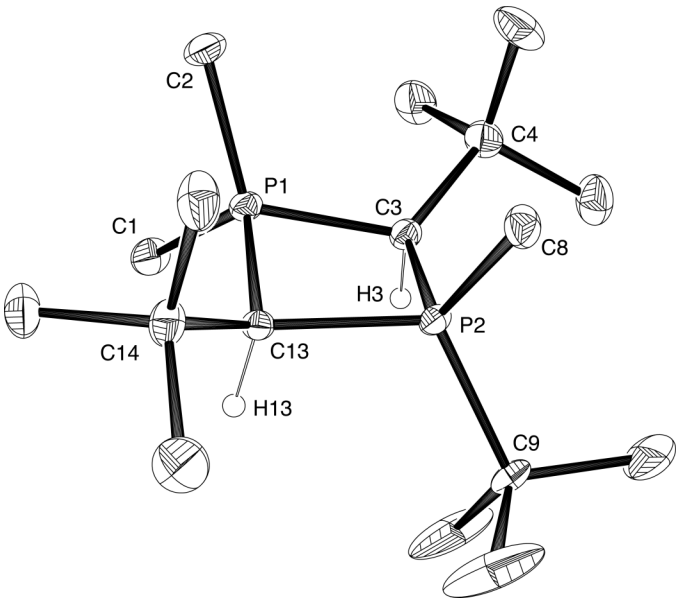
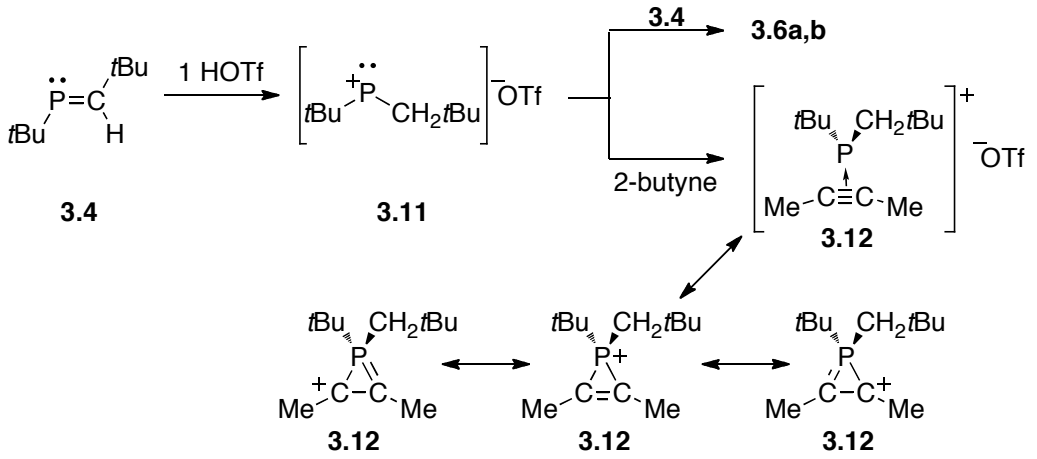


Figure 3.9 ORTEP of **3.10** (thermal ellipsoids set at 30% probability). The dichloromethane atoms, the triflate atoms and all hydrogen atoms except H(3) and H(13) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.793(4), P(1)-C(2) 1.791(4), P(1)-C(3) 1.846(4), P(1)-C(13) 1.840(4), P(2)-C(3) 1.859(4), P(2)-C(8) 1.781(4), P(2)-C(9) 1.856(4), P(2)-C(13) 1.857(3); C(1)-P(1)-C(2) 109.4(2), C(3)-P(1)-C(13) 88.5(2), C(3)-P(2)-C(13) 87.6(2), C(8)-P(2)-C(9) 110.6(2), P(1)-C(3)-P(2) 90.1(2), P(1)-C(13)-P(2) 90.4(2), P(1)-C(3)-C(4) 123.1(3), P(2)-C(3)-C(4) 127.7(3), P(1)-C(13)-C(14) 122.0(3), P(2)-C(13)-C(14) 128.3(3), P(1)-C(3)-P(2)-C(13) 13.9(2).

Once the nature of the products of the reactions had been established, we undertook preliminary investigations to spectroscopically identify intermediates in these unexpected reactions. ^{31}P NMR spectra of reaction mixtures containing phosphaalkene **3.4** and HOTf (1:1) showed quantitative formation of a new signal (δ = 210), which was assigned to phosphenium triflate **3.11** (there is likely some coordination of the phosphenium by triflate).[170] Further evidence that **3.11** is an intermediate in the formation of diphosphiranium **3.6** from phosphaalkene **3.4** and HOTf was obtained by treating in situ generated **3.11** with **3.4** (1:1) to obtain, based on ^{31}P NMR spectroscopy, **3.6a,b** quantitatively (Scheme 3.8). Although **3.11** could not be isolated, it is stable in solution for several days and is readily trapped by 2-butyne to give the phosphirenium **3.12**.



Scheme 3.8 Trapping of phosphenium triflate intermediate **3.11** and relevant resonance structures for phosphirenium **3.12**

As is typical for phosphirenium ions, the ^{31}P NMR spectrum of compound **3.12** exhibits a single high field resonance (δ = -86.3).[176] The structure of **3.12**, obtained by X-ray crystallographic analysis, is depicted in Figure 3.10. While both exocyclic P-C bonds are typical of single bonds [P(1)-C(1) 1.842(2) and P(1)-C(5) 1.796(2) Å], the endocyclic bonds are significantly shorter [P(1)-C(10) 1.740(2) and P(1)-C(11) 1.736(2) Å]. This observation is consistent with partial multiple-bond character between the P atom and the endocyclic C atoms, which suggests a degree of non-classic 2π Hückel aromaticity, involving the π electrons from the C=C bond and either empty *d*- or σ*-orbitals at P, is present in the ring.[113]

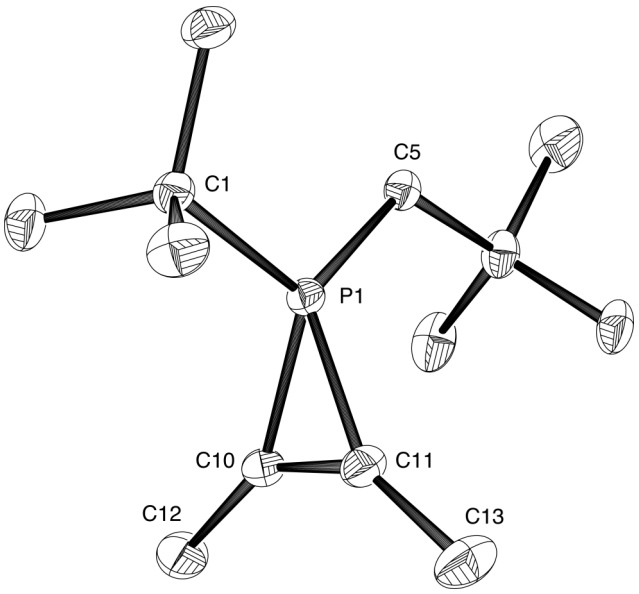
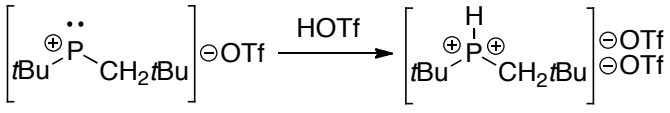


Figure 3.10. ORTEP of **3.12** (thermal ellipsoids set at 30% probability). The triflate atoms and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.842(2), P(1)-C(5) 1.796(2), P(1)-C(10) 1.740(2), P(1)-C(11) 1.736(2), C(10)-C(11) 1.315(3); C(10)-P(1)-C(11) 44.5(1), P(1)-C(10)-C(11) 67.6(1), P(1)-C(11)-C(10) 67.9(1).

While it is clear that phosphenium **3.11** is highly electrophilic, it is also weakly nucleophilic as evidenced by the protonation of the phosphorus lone pair (**3.13**: $\delta_P = 96.2$; $^1J_{PH} = 527$ Hz) by a second equivalent of HOTf (Scheme 3.9). Although it is clear that strong anion-cation interactions must be present in solution, the phosphorus atom in **3.13** is formally dicationic. Such highly charged species are of current interest for their potential as powerful reagents for a variety of stoichiometric or catalytic reactions.[177-185] As might be expected, compound **3.13** is very acidic and is readily deprotonated by even weakly basic solvents such as toluene or Et_2O.



3.11 **3.13**

Scheme 3.9 Protonation of phosphenium triflate **3.11**

Anticipating that a P-Me substituent would be much less labile than a P-H substituent, phosphenium **3.11** was treated with MeOTf. The reaction resulted in a complex mixture of phosphorus containing products, from which complex **3.14** was obtained as a crystalline solid in very low yield (<1%). Although it could not be characterized spectroscopically, the structure of **3.14**, depicted in Figure 3.11, was obtained by X-ray crystallography and its details are included due to its novelty.

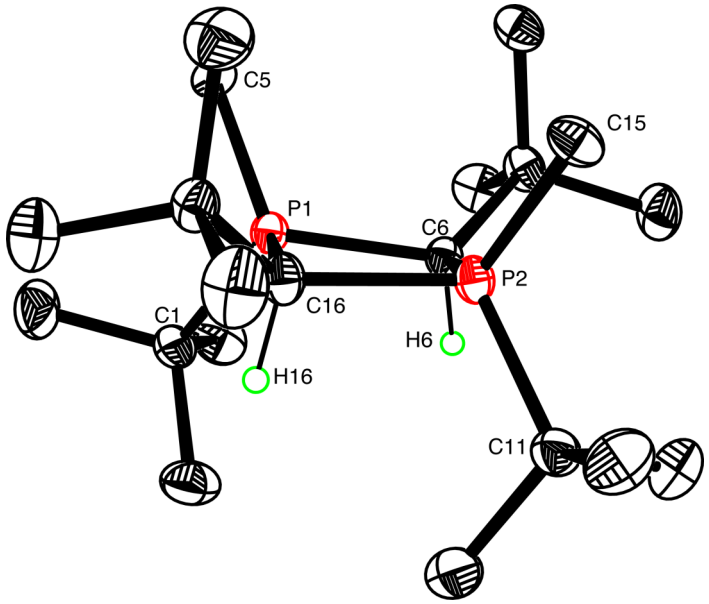
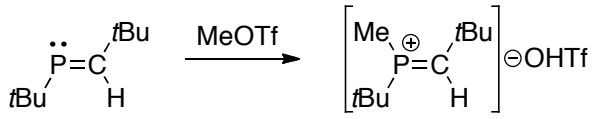


Figure 3.11 ORTEP of **3.14** (thermal ellipsoids set at 30% probability). The triflate atoms and all hydrogen atoms except H(6) and H(16) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.857(3), P(1)-C(5) 1.774(4), P(1)-C(6) 1.848(3), P(1)-C(16) 1.852(3), P(2)-C(6) 1.862(3), P(2)-C(11) 1.856(4), P(2)-C(15) 1.780(3), P(2)-C(16) 1.854(3); C(6)-P(1)-C(16) 88.9(1), C(6)-P(2)-C(16) 88.4(1), P(1)-C(6)-P(2) 90.7(1), P(1)-C(16)-P(2) 90.9(2), P(1)-C(6)-P(2)-C(16) 7.7(2).

As has been the trend for the diphosphetaniums discussed above, the P-Me bonds are short [P(1)-C(5) 1.774(4) and P(2)-C(15) 1.780(3) Å] whilst the other P-C bonds are more typical (1.848(3)-1.862(3) Å]. The ring structure of **3.14** appears to be intermediate between those of **3.8b** and **3.10**, with the sum of internals angles being 358.9(5)° and the dihedral angle being 7.7(2)°, consistent with **3.14** being intermediate in terms of sterics, four *tert*-butyl substituents but only two on each side.

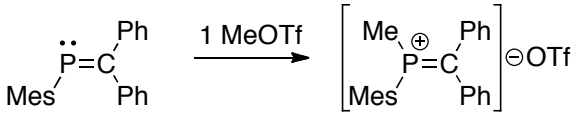
Having established the intermediacy of phosphenium **3.11** in the formation of diphosphiranium **3.6**, we next considered the mechanism for the formation of **3.8a** from phosphaalkene **3.4** and MeOTf. Speculating that the phosphaalkene must initially be methylated at P to afford a rare methylenephosphonium ion **3.15**, phosphaalkene **3.4** was treated with MeOTf (1:5) and studied by NMR spectroscopy (Scheme 3.10).[186-189] The role of the excess MeOTf is to maximize the formation of **3.15** and minimize the exposure of this highly reactive intermediate to unmethylated **3.4**. The signals observed in the ^{31}P and ^{13}C NMR spectra of the reaction mixture are consistent with the formation of **3.15** as the major product (^{31}P: $\delta = 176$; $^{13}C\{^1H\}$: $\delta_{P=C} = 153$; $^1J_{PC} = 98$ Hz) with **3.8a** present as well.



3.4 **3.15**

Scheme 3.10 Formation of methylenephosphonium **3.15** via methylation of phosphaalkene **3.4**

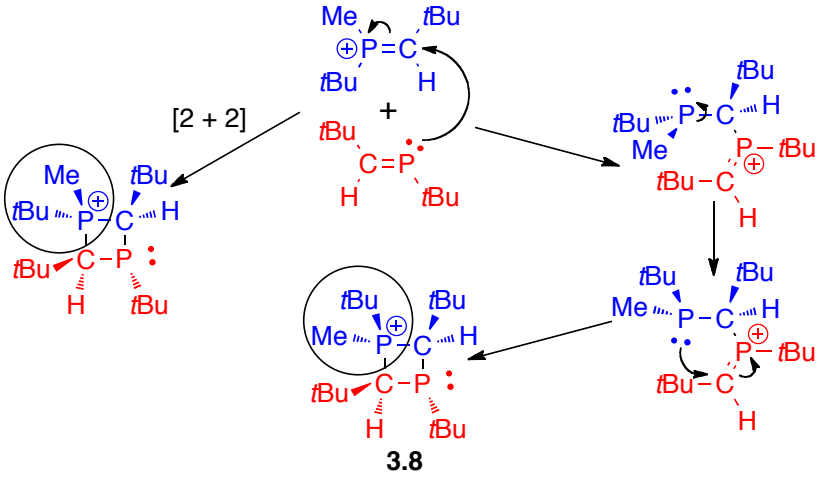
Although the reaction between phosphaalkene **3.2** and MeOTf requires heating to proceed, the ^{31}P and ^{13}C NMR spectra (^{31}P: $\delta = 176$; $^{13}C\{^1H\}$: $\delta_{P=C} = 153$; $^1J_{PC} = 98$ Hz) of the reaction mixture are consistent with the formation of the methylenephosphonium ion **3.16** (Scheme 3.11). Notably, addition of either phosphaalkene **3.2** or **3.4** to a solution of **3.16** did not lead to any further reaction.



3.2 **3.16**

Scheme 3.11 Formation of methylenephosphonium **3.15** via methylation of phosphaalkene **3.2**

On the basis of the arrangement of the *t*Bu substituents in **3.8b**, we postulate that the reaction must follow a stepwise rather than a concerted reaction mechanism (Scheme 3.12). A concerted [2 + 2] cycloaddition of **3.4** to **3.15** would necessitate a *trans*-configuration of the *t*Bu substituents in **3.8a**. In contrast, the stepwise addition of **3.4** to **3.15** could afford intermediate [*t*Bu(Me)P-CH(*t*Bu)-P(*t*Bu)-CH(*t*Bu)]OTf, which, after a necessary rotation of CH(*t*Bu) to enable ring closure, gives the observed arrangement of *t*Bu groups in **3.8** (3 above, 1 below the P_2C_2 plane). The reason for the umpolung-like reactivity of the P=C bond when Me^+ is used as the electrophile in place of H^+ is not certain, but may reflect a kinetic preference for addition of electrophiles to the P lone pair, rather than the P=C bond. Subsequently, the lability of the resulting P-H bond could allow for the transfer of the proton to the C and, thus, the formation of a thermodynamically more stable phosphenium triflate.



Scheme 3.12 Proposed step-wise mechanism for the formation of **3.8** (triflate counter anion not shown)

3.3 Conclusions

In summary, I have demonstrated that phosphaalkenes, when treated with HOTf, are convenient precursors to diphosphiranium cations, which are highly strained phosphorus heterocycles that have no isolable counterparts in nitrogen chemistry. Surprisingly, treating phosphaalkenes with the related MeOTf affords not 3-membered diphosphiranium rings but, rather, 4-membered diphosphetanium cations. These heterocycles result from two distinct cationic phosphorus intermediates, phosphenium and methylenephosphonium cations, and illustrates the unanticipated umpolung reactivity of phosphaalkenes. Additionally, the possibility to use these heterocycles as dormant ring-closed forms of the propagating species in the cationic polymerization of phosphaalkenes is of considerable interest.

3.4 Experimental

3.4.1 General Considerations.

Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen. Hexanes, dichloromethane and toluene were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. C_6D_6 was stored over molecular sieves (4Å) before use and ampules of CD_2Cl_2 were used as received from CIL. HOTf and MeOTf were used as received from Aldrich. Phosphaalkenes *t*BuP=CH*t*Bu, AdP=CH*t*Bu and MesP=CPh_2 were prepared following literature procedures.[172] ^{31}P, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers with chemical shifts (δ) in parts per million (ppm). Chemical shifts are referenced and reported relative to 85% H_3PO_4 as an external standard (δ = 0.0 for ^{31}P) or referenced to TMS and measured relative to residual

solvent peak (C_6HD_5 or $CHDCl_2$: δ = 7.16 or 5.32 for ^1H, respectively; C_6D_6 or CD_2Cl_2: δ = 128 or 53.8 for ^{13}C, respectively). Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV).

3.4.2 Preparation of Diphosphiranium 3.6

A solution of **3.4** (0.506 g, 3.20 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a stirred solution of HOTf (0.238 g, 1.59 mmol) in CH_2Cl_2 (3 mL) at 25 °C. After the mixture was stirred for 20 min, the solvent was removed in vacuo, yielding a colourless powder. The powder is dissolved in 1 mL of CH_2Cl_2 and precipitated with 20 mL of hexanes twice to remove impurities. Residual solvent was removed in vacuo. A sample of powder dissolved in $CDCl_3$ and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy was consistent with a mixture of two compounds, both containing two phosphorus atoms (**3.6b**: δ = -35.8, -119.8; J_{PP} = 248 Hz; **3.6a**: δ = -44.2, -49.9; J_{PP} = 260 Hz) in roughly a 2:3 ratio. Crude yield: 0.500 g (67%). Crystals of **3.6a** suitable for X-ray crystallography were obtained.

3.6a: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = -46.6 (d, J_{PP} = 261 Hz), -50.7 (d, J_{PP} = 261 Hz). ^1H NMR (CD_2Cl_2): δ = 2.83 (dd, J_{PH} = 4 Hz, J_{PH} = 7Hz, 1H), 2.58 (ddd, J_{PH} = 7 Hz, J_{PH} = 11 Hz, J_{HH} = 16 Hz, 1H), 2.28 (dd, J_{PH} = 14 Hz, J_{HH} = 16 Hz, 1H), 1.63 (dd, J_{PH} = 1 Hz, J_{PH} = 20 Hz, 9H), 1.43 (dd, J_{PH} = 3 Hz, J_{PH} = 16 Hz, 9H), 1.26 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 40.3 (dd, J_{PC} = 5 Hz, J_{PC} = 8 Hz), 36.9 (dd, J_{PC} = 10 Hz, J_{PC} = 42 Hz), 34.3 (dd, J_{PC} = 10 Hz, J_{PC} = 49 Hz), 34.0 (dd, J_{PC} = 4 Hz, J_{PC} = 12 Hz), 33.5 (dd, J_{PC} = 2 Hz, J_{PC} = 4 Hz), 32.2 (dd, J_{PC} = 10 Hz, J_{PC} = 18 Hz), 31.9 (dd, J_{PC} = 6 Hz, J_{PC} = 8 Hz), 31.2 (dd, J_{PC} = 8 Hz, J_{PC} = 17 Hz), 31.2 (dd, J_{PC} = 5 Hz, J_{PC} = 6 Hz), 30.0 (dd, J_{PC} = 1 Hz, J_{PC} = 2 Hz).

3.6b: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = -35.8 (d, J_{PP} = 248 Hz), -119.8 (d, J_{PP} = 248 Hz). ^{1}H NMR (CD_2Cl_2): δ = 3.19 (dd, J_{PH} = 2 Hz, J_{PH} = 10 Hz, 1H), 3.17 (dd, J_{PH} = 7 Hz, J_{HH} = 16Hz, 1H), 2.23 (dd, J_{HH} = 16 Hz, J_{PH} = 17 Hz, 1H), 1.55 (dd, J_{PH} = 2 Hz, J_{PH} = 22 Hz, 9H), 1.31 (d, J_{PH} = 1 Hz, 9H), 1.30 (dd, J_{PH} = 1 Hz, J_{PH} = 16 Hz, 9H), 1.24 (s, 9H).

3.4.3 Preparation of Diphosphiranium 3.7

A solution of **3.5** (0.236 g, 1.0 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a stirred solution of HOTf (0.075 g, 0.50 mmol) in CH_2Cl_2 (2 mL) at 25 °C. After the mixture was stirred for an hour, an aliquot was removed and the ^{31}P NMR spectroscopy was consistent with a mixture of two compounds, both containing two phosphorus atoms (**3.7b**: δ = -36.3, - 127.1; J_{PP} = 250 Hz; **3.7a**: δ = -48.2, -54.1; J_{PP} = 256 Hz) in roughly a 2:3 ratio. Crude yield: 0.275 g (88%). Crystals of **3.7a**·HOTf suitable for X-ray crystallography were obtained.

3.4.4 Preparation of Diphosphetanium 3.8a

A solution of **3.4** (0.200 g, 1.27 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a stirred solution of MeOTf (0.104 g, 0.63 mmol) in CH_2Cl_2 (0.5 mL) at 25 °C. After the mixture was stirred for 1 hour, the volatiles were removed in vacuo, yielding a colorless powder. Solid is washed with 5 mL of hexanes and filtered dry. Yield: 0.210 g (69%).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = 61.6 (d, $^{2}J_{PP}$ = 15 Hz), 18.1 (d, $^{2}J_{PP}$ = 15 Hz).

3.4.5 Preparation of Diphosphetanium 3.8b

A solution of **3.8a** (0.100 g, 0.21 mmol) in CH_2Cl_2 (10 mL) was treated with saturated aqueous solutions of KI. The organic fractions are collected and dried using $MgSO_4$ and filtered to remove insoluble material. The solvent is removed in vacuo to yield a pale yellow powder. The product was recrystallized by slow evaporation of a

concentrated CH_2Cl_2 solution to yield crystals suitable for X-ray diffraction. Yield = 0.035g (38%).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 61.8 (d, $^2J_{PP}$ = 15 Hz), 20.9 (d, $^2J_{PP}$ = 15 Hz). ^1H NMR (CD_2Cl_2): δ = 3.51 (dd, J_{PH} = 1 Hz, J_{PH} = 19 Hz), 2.56 (d, J_{PH} = 11 Hz), 1.60 (d, J_{PH} = 17 Hz), 1.35 (d, J_{PH} = 14 Hz), 1.26 (dd, J_{PH} = 1 Hz, J_{PH} = 1 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 49.6 (dd, J_{PC} = 23 Hz, J_{PC} = 25 Hz), 39.7 (dd, J_{PC} = 3 Hz, J_{PC} = 7 Hz), 35.5 (dd, J_{PC} = 4 Hz, J_{PC} = 21 Hz), 32.2 (dd, J_{PC} = 5 Hz, J_{PC} = 36 Hz), 31.2 (dd, J_{PC} = 7 Hz, J_{PC} = 9 Hz), 30.8 (dd, J_{PC} = 1 Hz, J_{PC} = 16 Hz), 28.6 (dd, J_{PC} = 1 Hz, J_{PC} = 4 Hz), 15.1 (d, J_{PC} = 45 Hz). Anal. Calcd. for $C_{19}H_{41}P_2I$: C, 49.78; H, 9.02. Found: C, 50.16; H, 9.27.

3.4.6 Preparation of Diphosphetanium 3.9a

A solution of **3.5** (0.236 g, 1.00 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a stirred solution of MeOTf (0.85 g, 0.52 mmol) in CH_2Cl_2 (0.5 mL) at 25 °C. After the mixture was stirred for 1 hour, the volatiles were removed in vacuo, yielding a colorless powder. Solid is washed with 5 mL of hexanes and filtered dry. Yield: 0.280 g (88%).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 58.4 (d, $^2J_{PP}$ = 15 Hz), 20.6 (d, $^2J_{PP}$ = 15 Hz).

3.4.7 Preparation of Diphosphetanium 3.9b

A solution of **3.9a** (0.200 g, 0.31 mmol) in CH_2Cl_2 (10 mL) was treated with saturated aqueous solutions of KI. The organic fractions are collected and dried using $MgSO_4$ and filtered to remove insoluble material. The solvent is removed in vacuo to yield a pale yellow powder. The product was recrystallized by slow evaporation of a concentrated CH_2Cl_2 solution to yield crystals suitable for X-ray diffraction. Yield = 0.110 g (58%).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 58.7 (d, $^{2}J_{PP}$ = 16 Hz), 21.0 (d, $^{2}J_{PP}$ = 16 Hz). ^{1}H NMR ($CDCl_3$): δ = 3.49 (d, J_{PH} = 18 Hz, 2H), 2.64 (d, J_{PH} = 10 Hz), 2.24 (m, 6H), 2.21 (br s, 3H), 2.10 (br s, 3H), 1.90 (m, 6H), 1.79 (m, 6H), 1.75 (m, 6H), 1.26 (s, 18H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 47.9 (dd, J_{PC} = 23 Hz, J_{PC} = 23 Hz), 45.4 (dd, J_{PC} = 3 Hz, J_{PC} = 3 Hz), 41.6 (d, J_{PC} = 13 Hz), 36.8, 36.2, 35.7, 35.2 (dd, J_{PC} = 4 Hz, J_{PC} = 21 Hz), 34.9 (dd, J_{PC} = 4 Hz, J_{PC} = 37 Hz), 31.5 (dd, J_{PC} = 8 Hz, J_{PC} = 8 Hz), 28.9 (d, J_{PC} = 9 Hz), 28.2 (d, J_{PC} = 10 Hz), 13.0 (d, J_{PC} = 46 Hz).

3.4.8 Preparation of Diphosphetanium 3.10

A solution of **3.8a** (0.350 g, 0.73 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a stirred solution of MeOTf (0.600 g, 3.66 mmol) in CH_2Cl_2 (2 mL) at 25 °C. The mixture was stirred for over-night and then placed in a freezer (-30 °C) to afford colorless crystals suitable for X-ray diffraction. Yield: 0.260 g (61%).

$^{31}P\{^{1}H\}$ NMR (CD_3CN): δ = 74.9 (d, $^{2}J_{PP}$ = 16 Hz), 55.3 (d, $^{2}J_{PP}$ = 16 Hz). ^{1}H NMR (CD_3CN): δ = 4.49 (dd, J_{PH} = 19 Hz, J_{PH} = 22 Hz, 2H), 2.81 (d, J_{PH} = 14 Hz, 3H), 2.68 (d, J_{PH} = 13 Hz, 3H), 2.56 (d, J_{PH} = 14 Hz, 3H), 1.56 (d, J_{PH} = 20 Hz, 9H), 1.31 (s, 18H). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ = 122.0 (q, J_{FC} = 319 Hz), 44.5 (dd, J_{PC} = 29 Hz, J_{PC} = 38 Hz), 37.9 (dd, J_{PC} = 3 Hz, J_{PC} = 4 Hz), 37.8 (dd, J_{PC} = 10 Hz, J_{PC} = 24 Hz), 31.3 (dd, J_{PC} = 5 Hz, J_{PC} = 6 Hz), 26.6 (d, J_{PC} = 2 Hz), 16.7 (dd, J_{PC} = 9 Hz, J_{PC} = 39 Hz), 10.5 (d, J_{PC} = 37 Hz), 5.6 (d, J_{PC} = 30 Hz).

3.4.9 Preparation of Phosphenium 3.11

A solution of **3.4** (0.100 g, 0.63 mmol) in C_6D_6 (1 mL) was added dropwise to a stirred solution of HOTf (0.95 g, 0.63 mmol) in C_6D_6 (1 mL) at 25 °C. After the mixture was stirred for 15 min, an aliquot (0.5 mL) was removed and analyzed by NMR.

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 210. ^{1}H NMR (C_6D_6): δ = 1.55 (bs, 2H), 1.04 (d, J_{PH} = 1 Hz, 9H), 0.92 (d, J_{PH} = 14 Hz, 9H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 119.6 (quartet, J_{FC} = 318 Hz), 45.8 (d, J_{PC} = 37 Hz), 34.0 (d, J_{PC} = 24 Hz), 30.9 (d, J_{PC} = 8 Hz), 30.7 (d, J_{PC} = 16 Hz), 24.5 (d, J_{PC} = 17 Hz).

3.4.10 Preparation of Phosphirenium 3.12

A solution of **3.11** was prepared by dropwise addition of a solution of phosphaalkene **3.4** (0.158 g, 1.00 mmol) in CH_2Cl_2 (2 mL) to a stirred solution of HOTf (0.150 g, 1.00 mmol) in CH_2Cl_2 (2 mL) at 25 °C. After an hour, a solution of 2-butyne (0.100 g, 1.85 mmol) in CH_2Cl_2 (2 mL) was added to the mixture. Slow evaporation of the solvent afforded colourless crystals suitable for X-ray crystallography. Yield: 0.250 g (69%).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ = -86.3. ^{1}H NMR (CD_2Cl_2): δ = 2.61 (d, J_{PH} = 10 Hz, 2H), 2.45 (d, J_{PH} = 14 Hz, 6H), 1.31 (d, J_{PH} = 21 Hz, 9H), 1.01 (d, J_{PH} = 1 Hz, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 131.5 (d, $^{1}J_{PC}$ = 3 Hz), 121.4 (q, $^{1}J_{FC}$ = 321 Hz), 36.1 (d, $^{1}J_{PC}$ = 38 Hz), 31.4 (d, $^{2}J_{PC}$ = 7 Hz), 31.2 (d, $^{1}J_{PC}$ = 25 Hz), 30.5 (d, $^{2}J_{PC}$ = 8 Hz), 26.8, 11.5 (d, $^{2}J_{PC}$ = 3 Hz).

3.4.11 Preparation of Methylenephosphonium 3.15

A solution of **3.4** (0.100 g, 0.63 mmol) in C_6D_6 (1 mL) was added dropwise to a stirred solution of MeOTf (0.520 g, 3.15 mmol) in C_6D_6 (2 mL) at 25 °C. After the mixture was stirred for 30 min, an aliquot (0.5 mL) was removed and analyzed by NMR.

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 176. ^{1}H NMR (C_6D_6): δ = 7.21 (d, J_{PH} = 11 Hz, 1H), 2.37 (d, J_{PH} = 23 Hz, 3H), 1.28 (d, J_{PH} = 20 Hz, 9H), 1.15 (d, J_{PH} = 1 Hz, 9H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 152.7 (d, J_{PC} = 98 Hz), 122.1 (quartet, J_{FC} = 322 Hz), 40.0 (d, J_{PC} = 39

Hz), 39.3 (d, J_{PC} = 13 Hz), 30.5 (d, J_{PC} = 16 Hz), 28.0 (d, J_{PC} = 2 Hz), 7.5 (d, J_{PC} = 35 Hz).

3.4.12 Preparation of Methylenephosphonium 3.16

A solution of **3.2** (0.100 g, 0.32 mmol) in CD_2Cl_2 (0.5 mL) was added to a solution of MeOTf (0.130 g, 0.79 mmol) in CD_2Cl_2 (0.5 mL) in a bomb equipped with a magnetic stir-bar. The mixture was heated with stirring at 80 °C for 1 hour. Upon cooling, the mixture was analyzed by NMR.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ = 112.5. ^1H NMR (C_6D_6): δ = 7.69-7.04 (m, 12H), 2.86 (d, J_{PH} = 26 Hz, 3H), 2.56 (d, J_{PH} = 3 Hz, 6H), 2.36 (d, J_{PH} = 2 Hz, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 176.2 (d, J_{PC} = 97 Hz), 148.0 (d, J_{PC} = 4 Hz), 144.5 (d, J_{PC} = 6 Hz), 136.9 (d, J_{PC} = 3 Hz), 135.7 (d, J_{PC} = 2 Hz), 133.4 (d, J_{PC} = 6 Hz), 133.2 (d, J_{PC} = 5 Hz), 131.4, 131.2, 130.9, 130.8 (2C), 130.6, 130.4, 130.2 (2C), 129.8, 129.7, 121.5 (quartet, J_{FC} = 321 Hz), 117.4 (d, J_{PC} = 85 Hz), 23.3 (d, J_{PC} = 6 Hz), 21.8 (d, J_{PC} = 1 Hz), 11.9 (d, J_{PC} = 48 Hz).

3.4.13 X-Ray Crystallography

All single crystals were immersed in oil and mounted on a glass fiber. Data were collected at 173±0.1K on a Bruker X8 APEX 2 diffractomer with graphite-monochromated Mo Kα radiation. Data was collected and integrated using the Bruker SAINT[152] software package and corrected for absorption effect TWINABS[154] (for 4.14) and SADABS[153] (for all others). All data sets were corrected for Lorentz and polarization effects. All structures were solved by direct methods[155] and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms

using the SHELXTL[156] crystallographic software package from Bruker-AXS. All data sets were corrected for Lorentz and polarization effects. Additional crystal data and details of the data collection and structure refinement are given in Table 3.1.

The crystals of **3.5a**, **3.8b**, **3.12** and **3.14** presented no crystallographic complications. The structure of **3.9b** and **3.10** exhibited some disorder. For **3.9b**, there are two overlapping cations, each contributing 50% to the total electron desity attributed to the ring. The two cations relate via a psuedo-mirror plane that passes through the cyclic carbon atoms at ~60° to the mean plane of the ring, which results in the phosphino-Ad from one moiety to overlap with the phosphonium-Ad of the second and vice versa. In **3.10**, one of the four triflate-anions is disordered. The crystal of **3.8b** was a racemic twin with each component crystallizing as a single enantiomer. The twin components were present in a 3:2 ratio, where the minor component is related to the major component by a 180° rotation about the (1 0 0) direct axis. That the ratio of the two components is not 0.5 presumably reflects the composition of the selected crystal and does not reflect the composition of the bulk, which is expected to be a racemate.

Table 3.1. Crystallographic Data for Compounds **3.6a**, **3.7a**, **3.8b**, **3.9b**, **3.10**, **3.12**, **3.14.**

	3.6a	**3.7a**·HOTf	**3.8b**	**3.9b**
Formula	$C_{19}H_{39}F_3O_3P_2S$	$C_{32}H_{52}F_6O_6P_2S_2$	$C_{19}H_{41}IP_2$	$C_{31}H_{53}IP_2$
FW	466.50	772.80	4458.36	614.57
cryst syst	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/n$	$P2_1$	$Pca2_1$	$P2_1/n$
a (Å)	8.608(1)	10.600(1)	19.631(1)	13.232(1)
b (Å)	21.465(1)	17.169(1)	9.746(1)	12.130(1)
c (Å)	13.806(1)	11.212(1)	23.632(1)	18.335(1)
α (deg)	90	90	90	90
β (deg)	102.656(2)	118.210(2)	90	90.057(2)
γ (deg)	90	90	90	90
V (Å^3)	2489.1(2)	1798.0(1)	4521.5(3)	2942.8(2)
T (K)	173	173	173	173
μ(Mo Kα) (cm^{-1})	2.97	3.10	15.56	12.15
cryst size (mm^3)	0.5 × 0.35 × 0.1	0.35 × 0.25 × 0.25	0.5 × 0.5 × 0.2	0.8 × 0.2 × 0.1
Calcd density (Mg m^{-3})	1.245	1.427	1.347	1.387
2θ(max) (deg)	55.6	55.8	55.6	56.0
no. of reflns	31780	29398	31854	28106
no. of unique data	5915	7760	10524	6809
R(int)	0.0349	0.0194	0.0282	0.0250
refln/param ratio	21.35	17.45	23.97	11.35
R1[a] ($I > 2\sigma(I)$)	0.0338	0.0234	0.0235	0.0471
wR2 (all data)[b]	0.0897	0.0586	0.0507	0.1037
GOF	1.046	1.046	1.018	1.573
	3.10	**3.12**	**3.14**	
Formula	$C_{39}H_{78}Cl_2F_{12}O_{12}P_4S_4$	$C_{14}H_{26}F_3O_3PS$	$C_{22}H_{44}F_6O_6P_2S_2$	
Fw	1290.09	362.38	644.63	
cryst syst	Monoclinic	Monoclinic	Monoclinic	
space group	Cc	$P2_1/n$	$P2_1/n$	
a (Å)	20.876(3)	8.752(1)	11.383(1)	
b (Å)	18.823(2)	16.218(1)	13.746(1)	
c (Å)	16.796(2)	12.982(1)	19.378(1)	
α (deg)	90	90	90	
β (deg)	109.847(6)	92.657(3)	96.784(1)	
γ (deg)	90	90	90	
V (Å^3)	6208(2)	1840.62(2)	3010.98(12)	
T (K)	173	173	173	
μ(Mo Kα) (cm^{-1})	4.27	2.98	3.54	
cryst size (mm^3)	0.3 × 0.25 × 0.25	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2	
Calcd density (Mg m^{-3})	1.380	1.308	1.422	
2θ(max) (deg)	55.6	56.0	55.8	
no. of reflns	29244	32301	22468	
no. of unique data	13644	4449	6859	
R(int)	0.0366	0.0595	0.0303	
refln/param ratio	18.98	14.68	19.21	
R1[a] ($I > 2\sigma(I)$)	0.0529	0.0417	0.0670	
wR2 (all data)[b]	0.1243	0.1052	0.2008	
GOF	1.016	1.016	1.029	

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2(F^2\ [\text{all data}]) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Chapter 4: Abnormal Reactivity and Formation of 4-Phosphino-Carbenes and Their Metal Complexes

4.1 Introduction

Historically, neutral divalent carbon species (carbenes) were known as important reactive intermediates and perceived to be too reactive and short-lived to be isolated.[190-192] Therefore, the development of "bottleable" uncomplexed carbenes represents a landmark achievement[193, 194] and has prompted a surge of interest in the study of the properties and reactivity of these once-elusive species.[195-206] Perhaps the most widely studied are the N-heterocyclic carbenes (NHCs) in which the divalent carbon moieties are flanked by one or two π-donor nitrogen atoms within a five-membered heterocycle; however, a variety of other cyclic motifs are also known (Figure 4.1).

*A version of this chapter has been published. Joshua I. Bates, Pierre Kennepohl and Derek P. Gates, "Abnormal Reactivity of an N-Heterocyclic Carbene (NHC) with a Phosphaalkene: A Route to a 4-Phosphino-Substituted NHC," *Angew. Chem. Int. Ed.*, **2009**, 9844-9847.

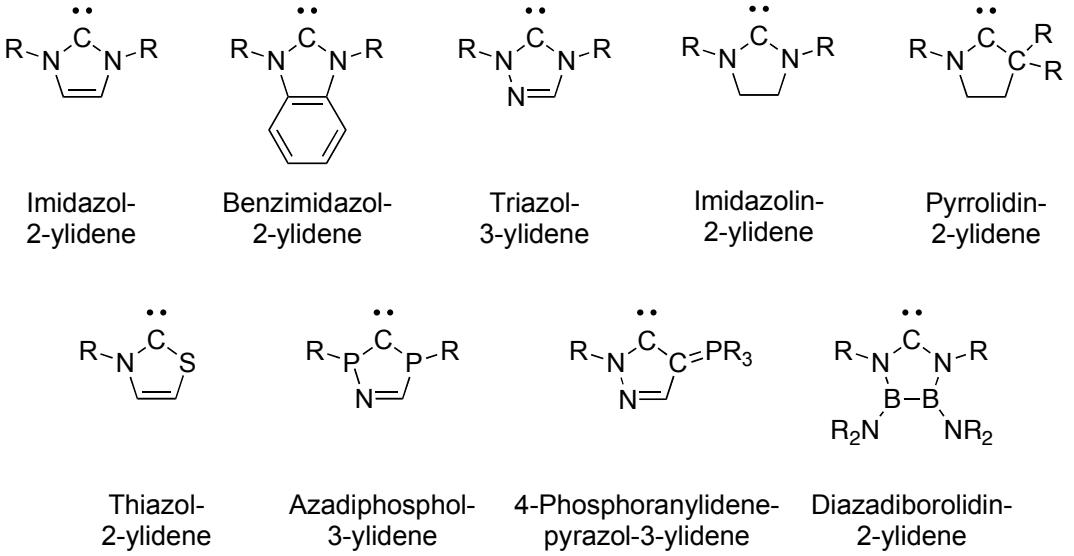
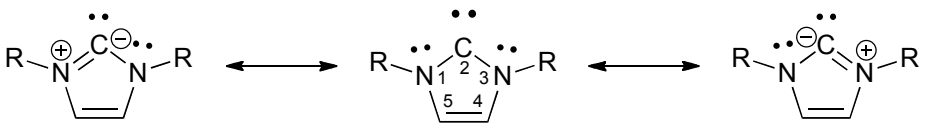


Figure 4.1 Representative examples of NHCs and other 5-membered heterocyclic carbenes.

Although sterically demanding substituents (R) certainly play a supportive role, the remarkable stability of these NHCs is largely due to the mesomeric interactions of the nitrogen lone pairs with the empty *p* orbital of the sp^2 hybridized carbene (Figure 4.2). Resonance structures, such as **B**, also explain nicely why imidazol-2-ylidenes (**A**) are such strongly σ-donating and weakly π-accepting nucleophiles. As a consequence, they are excellent ligands for *d*-block metals. Indeed, much of the interest in NHCs has been driven by the fact that their metal complexes are highly effective in catalyzing organic transformations. Although not as extensively studied, the role of NHCs in organocatalysis[207, 208] and in *p*-block chemistry[197, 209-221] has recently been the subject of increased attention.



B **A** **B**

Figure 4.2 An illustration of the mesomeric interactions that stabilize NHCs.

One general characteristic of NHCs is their tendency to bind electrophiles at the most reactive site, namely, the 2-position of the ring (**A**).[222] However, in 2001, Crabtree and co-workers reported the structure of an Ir-complex in which the NHC ligand was bound the "wrong way" (Figure 4.3: Top, **C**).[223] Since that remarkable discovery, the chemistry of these so-called abnormal NHCs (*a*NHCs), for which the reactions occur at the 4- or 5-positions, has been reasonably well established for *d*- and *f*-block elements.[224-228] Notably, Bertrand and coworkers have recently succeeded in crystallizing metal-free examples of an *a*NHCs (**D**),[229] a mesoionic carbene (**E**),[230] and a bent allene (**F**)[231, 232] and Robinson and coworkers have prepared the first anionic N-heterocyclic dicarbene (**G**),[233] containing both normal (C2) and abnormal (C4) carbene centers in the same imidazole ring (Figure 4.3: Bottom). Interestingly, the lithium salt of this dicarbene is polymeric in the solid state.

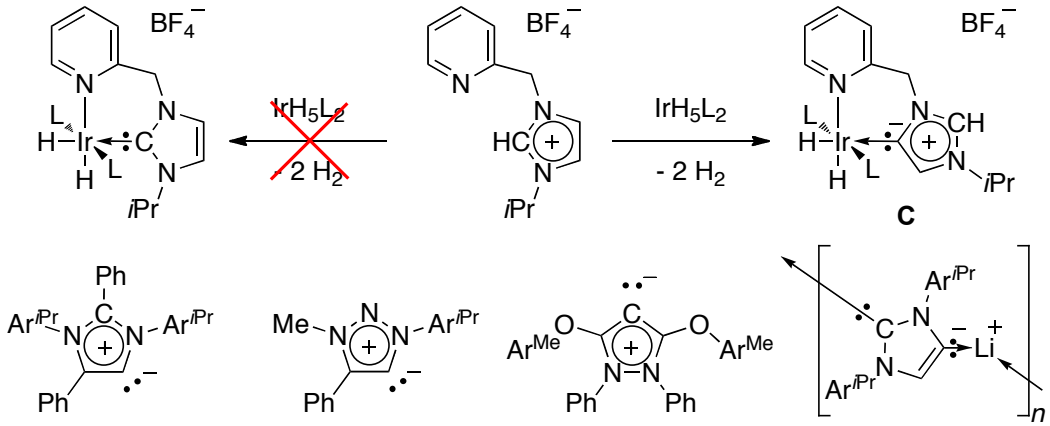
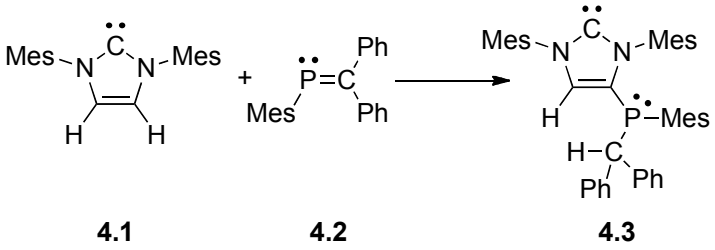


Figure 4.3 Top: First reported example of an *a*NHC metal complex (**C**). Bottom: First examples of isolable an *a*NHC (**D**), a mesoionic carbene (**E**), a bent allene (**F**) and an anionic N-heterocyclic dicarbene (**G**).

In contrast, abnormal reactions of NHCs with *p*-block elements are rarely observed, unless the 2-position is blocked or bound to a metal.[234-239] Recently, we

reported the unexpected abnormal reaction of the NHC 1,3-dimesitylimidazol-2-ylidene (IMes, **4.1**) with the phosphaalkene MesP=CPh_2 (**4.2**), affording the unprecedented bifunctional 4-phosphino-2-carbene (**4.3**) (Scheme 4.1).[114] Bertrand and co-workers and Roesky and co-workers have since reported that stable C2-bound NHC complexes of *p*-block elements are suitable precursors for heteroatom functionalized NHCs similar to **4.3**.[240, 241] The prospect of directly functionalizing a free NHC at the 4- and 5-positions with *p*-block moieties is exciting as it could enable the synthesis of ligands with unique electronic and coordination properties.



4.1 **4.2** **4.3**

Scheme 4.1 Formation of NHC **4.3** from IMes and phosphaalkene **4.2**

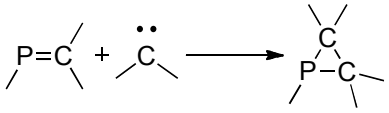
Herein, we report the abnormal reaction of unprotected NHCs with phosphaalkenes. Additionally, the preparation and structures of several transition-metal complexes is reported to illustrate the bifunctionality of these novel ligands.

4.2 Results and Discussion

4.2.1 Abnormal Reactivity of NHCs with Phosphaalkenes

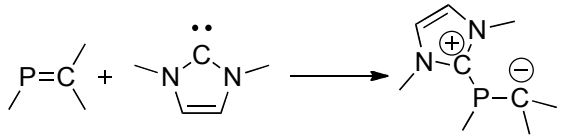
Our interest in the addition polymerization reactions of P=C bonds[85, 107, 108, 115, 121, 166] prompted us to investigate the reactions of phosphaalkenes with potential polymerization initiators. Recently, we have reported that treating *t*BuP=CH*t*Bu (2 equiv) with trifluoromethanesulfonic acid affords a cyclic dimer, an asymmetric

diphosphiranium cation, which may be envisaged as an intramolecularly stabilized phosphenium ion (R_2P^+).[131] These ions, which are putatively involved in the cationic polymerization of P=C bonds,[87] are isovalent with carbenes (R_2C). Analogously, phosphaalkenes are known to react with fleeting electrophilic carbenes to afford phosphiranes, neutral PC_2 heterocycles (Scheme 4.2);[113, 160, 242] however, reactions of phosphaalkenes with NHCs have not been reported.[243]



Scheme 4.2 Generic cyclopropanation reaction of a phosphaalkene with an electrophilic carbene

As an alternative to a cyclopropanation reaction, we postulated that the nucleophilic addition of an NHC across the P=C bond might generate a zwitterionic species (Scheme 4.3), in much the same way that has been observed for the anionic polymerization of phosphaalkenes. Indeed, some multiple-bond-containing phosphorus compounds, such as phosphaalkynes[244-247] and iminophosphines,[248, 249] are known to react in this way with NHCs. In the case of phosphaalkynes, subsequent cyclizations are often observed. Recently it has been shown that zwitterionic polymerizations[250, 251] of lactide can afford cyclic polymers.[252-258] Therefore the potential to prepare cyclic poly(methylenephosphine)s[106] using NHCs as initiators is an intriguing possibility.



Scheme 4.3 Putative initiation of a zwitterionic polymerization of a phosphaalkene using a NHC as an initiator

To examine the reaction of a phosphaalkene with an NHC, IMes (**4.1**) and $MesP{=}CPh_2$ (**4.2**) were dissolved in THF and heated at 70 °C overnight (Scheme 4.1).

Mass spectrometry of the crude isolated product revealed a parent mass of 620 g mol^{-1}, which, being the sum of IMes (MW = 304 g mol^{-1}) and phosphaalkene **4.2** (MW = 316 g mol^{-1}), suggested that a carbene-phosphaalkene adduct had been formed. Analysis of the product's ^{31}P NMR spectrum in C_6D_6 revealed the phosphaalkene starting material (δ = 234 ppm) was no longer present and had been replaced by a single resonance (δ = -37.7 ppm) (Table 4.1).

Table 4.1 ^{31}P and $^{13}C\{^1H\}$ NMR chemical shifts new compounds reported in this chapter and selected known compounds for comparison purposes.

	^{31}P (ppm)	$^{13}C\{^1H\}$ (ppm)	Reference
4.3[a]	-37.9	220.3 ($^3J_{PC}$ = 5 Hz, NCN)	This work
4.5[a]	-37.4	220.4 (NCN)	This work
4.7[a]	-33.7, -35.3	N/A	This work
4.12[b]	-36.4	175.2 (NCN)	This work
4.9[c]	-0.14	177.6 (NCN)	This work
4.10[c]	-37.8	186.5 (NCN)	This work
IMes·AuCl[d]		173.4 (NCN)	[259]
4.13[c]	-38.4 (major), -39.1 (minor)	186.2 ($^1J_{RhC}$ = 51 Hz, major NCN), 185.5 ($^1J_{RhC}$ = 50 Hz, minor NCN)	This work
4.15[c]	-38.6	183.4 ($^1J_{RhC}$ = 74 Hz, NCN)	This work
$IMesRh(CO)_2Cl$[d]		182.8 ($^1J_{RhC}$ = 74 Hz, NCN)	[260]
4.14[c]	-38.5 (major), -39.3 (minor)	183.7 (major NCN), 182.8 (minor NCN)	This work
4.16[c]	-38.8	177.1 (NCN)	This work
$[Ir(1)(CO)_2Cl]$[d]		176.1 (NCN)	[261]

[a] In C_6D_6; [b] In THF; [c] In CD_2Cl_2; [d] In $CDCl_3$

At first glance, this chemical shift, similar to that observed for $Mes(Me)P\text{-}CPh_2Li$ (δ = -44.3),[105] suggests that a zwitterionic species was formed (Scheme 4.3). However, close examination of the ^1H NMR spectrum ruled out this possibility (Figure 4.4).

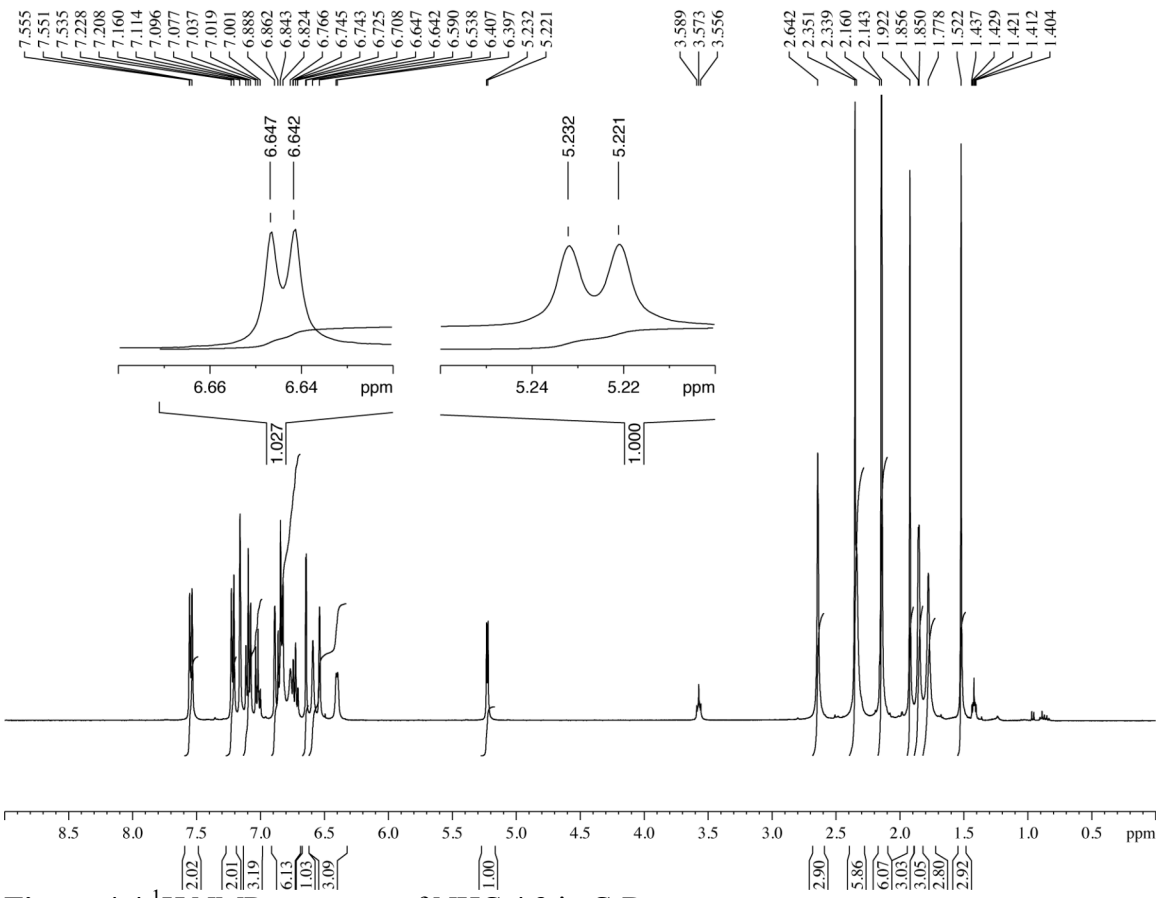


Figure 4.4 ^{1}H NMR spectrum of NHC **4.3** in C_6D_6.

The signal assigned to the vinylic protons of the C_3N_2 ring (δ = 6.64, J_{PH} = 2.0 Hz) integrated for one hydrogen atom, rather than the expected two hydrogen atoms, and a new signal (δ = 5.23, J_{PH} = 4.4 Hz) was observed that was consistent with a proton in a C*H*Ph_2 environment. These results suggest that a proton had been transferred from the heterocycle to the P*C*Ph_2 moiety. Further evidence for the transfer of a proton from the NHC backbone to a benzylic carbon is found in the mass spectrum, where one of the major fragments is $CHPh_2^+$, *m/z* = 167 g mol^{-1}, which is typical of the fragmentation of species such as Mes(R)P-$CHPh_2$ [R = Me, Bu].[105] Perhaps most enlightening was the doublet resonance at δ = 220.3 ppm ($^{3}J_{PC}$ = 4.5 Hz) observed in the ^{13}C NMR spectrum (Figure 4.5).

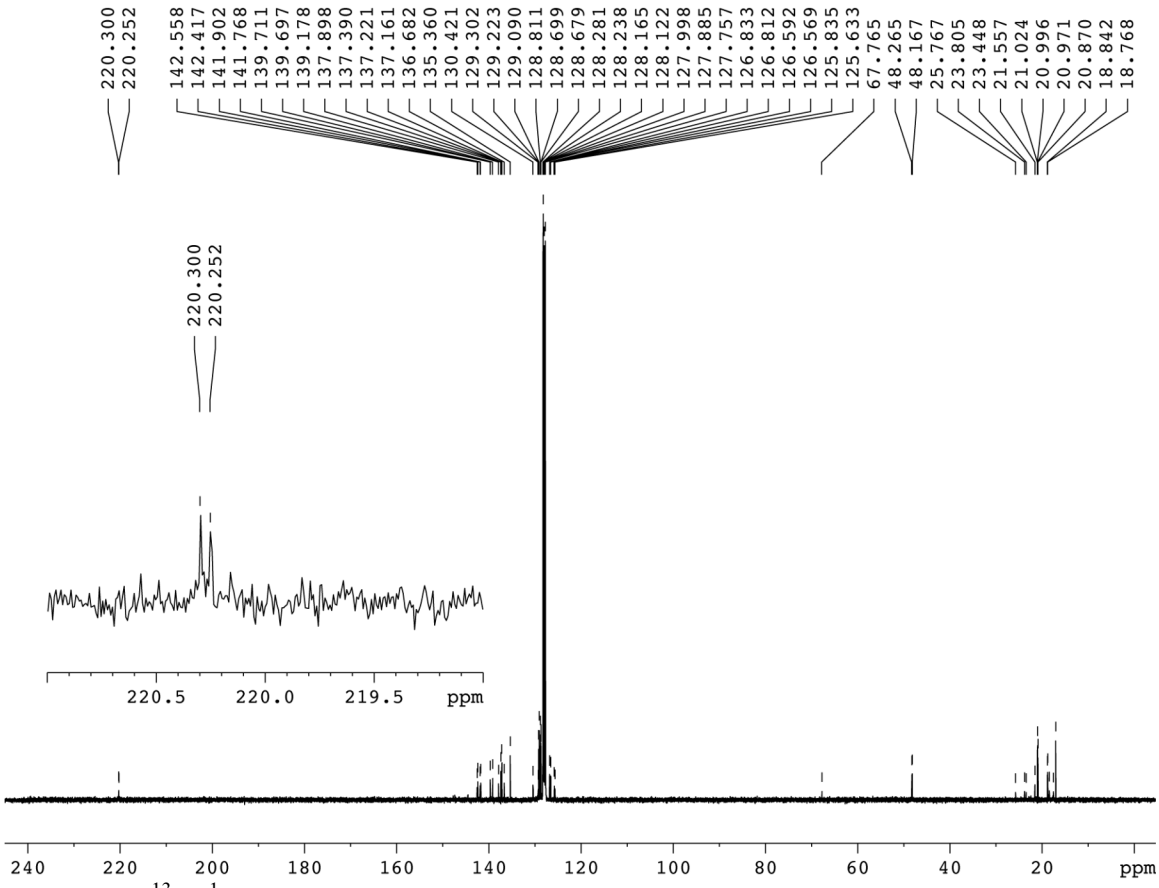


Figure 4.5 $^{13}C\{^{1}H\}$ NMR spectrum of NHC **4.3** in C_6D_6.

Remarkably, this downfield signal, aside from being a doublet, is identical to that of IMes ($\delta = 220.3$)[262] and suggests that the carbenic functionality is still present after the reaction. The presence of a carbene moiety in the product (Scheme 4.1) was confirmed by X-ray crystallographic analysis and the molecular structure of NHC **4.3** is shown in Figure 4.6 (discussed below).

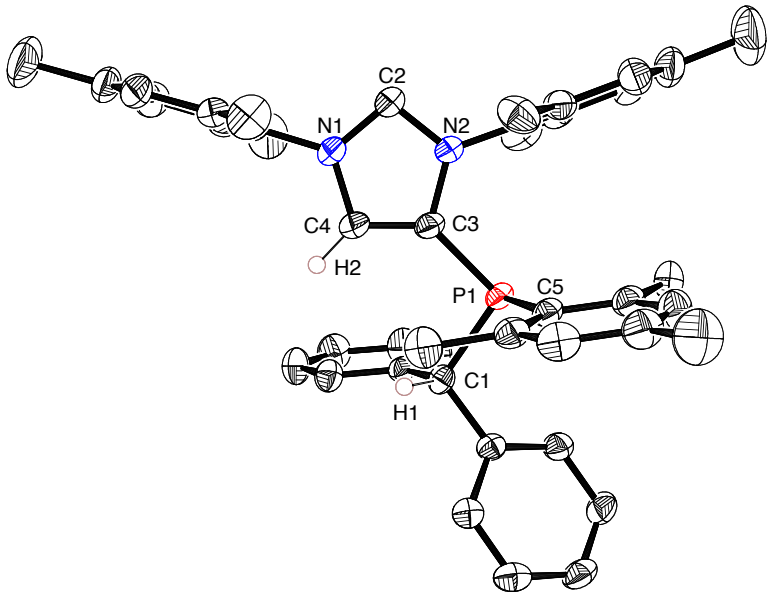


Figure 4.6. Molecular structure of **4.3**·½C_6H_6 (thermal ellipsoids set at 50% probability). The partial benzene atoms and all hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.869(2), P(1)-C(3) 1.816(2), P(1)-C(5) 1.846(2), C(2)-N(1) 1.363(2), C(2)-N(2) 1.366(3), C(4)-N(1) 1.388(2), C(3)-N(2) 1.406(2), C(3)-C(4) 1.349(3); N(1)-C(2)-N(2) 101.2(2), C(3)-C(4)-N(1) 107.2(2), C(4)-C(3)-N(2) 104.4(2).

Compound **4.3**, derived from the formal insertion of the P=C bond into the C-H bond at the 4-position of IMes, is the first NHC bearing a phosphino-substituent at the backbone and represents a rare example of an imidazol-2-ylidene where the C4 and C5 substituents are not an H, alkyl or aryl group (Figure 4.7): quinone annulated **H**,[263] N-heterocycle annulated **I** and **J**,[264-267] oxazoline derived **K** and **L**,[268-270] dihalogenated **M**,[234, 271, 272] deuterated **N**,[235] silylated **O**[273] and **P**,[240] and step-wise functionalized derivatives **Q** and **R**.[241] Interestingly, the nature of the backbone substituents can have a dramatic influence on the reactivity of the carbene. For example, the donor properties of heterocyclic derivatives **H** can be tuned electrochemically[274, 275] and the remarkably stable dihalogenated derivatives **M** can be handled in air.[234] Whereas derivatives **H-L** are synthesized from precursors already bearing the desired backbone functional group, derivatives **M-R** are examples where new functionality has been introduced to existing

free NHCs with retention of the carbene moiety. Indeed, the elegant work of Bertrand and co-workers has recently shown that the C4- and C5-positions can be functionalized subsequently and with different substituents (**Q** and **R**).[241] Taken together, these methods for modifying the carbene backbone opens the exciting possibility of tuning existing electronic properties of and introducing new functionality to NHCs.

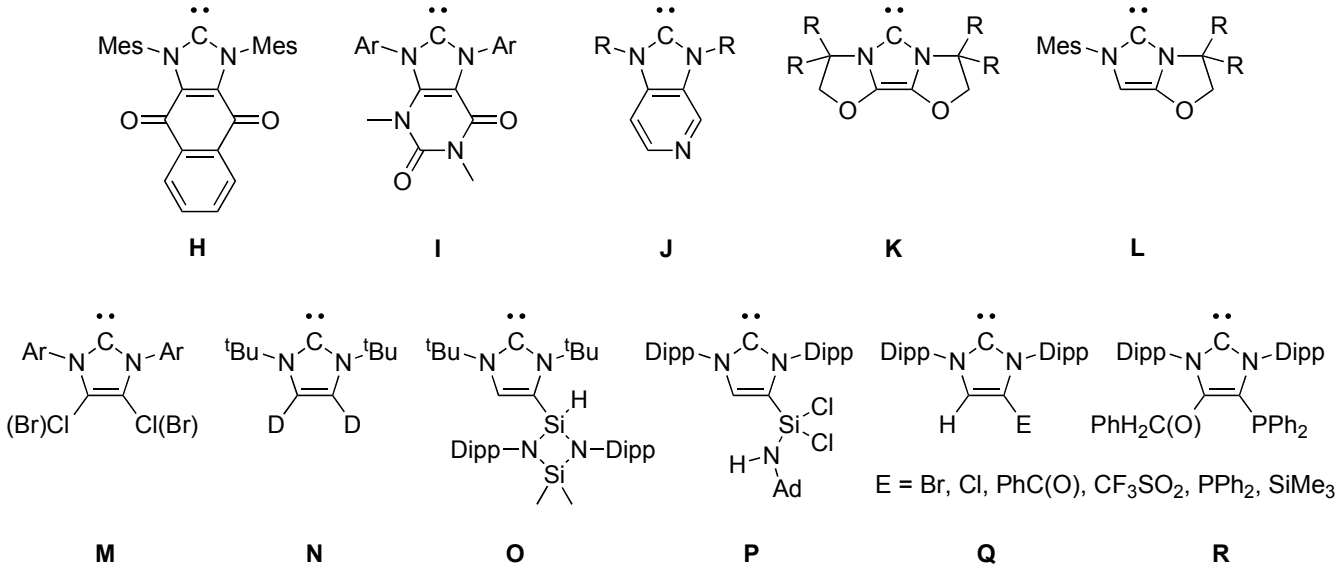
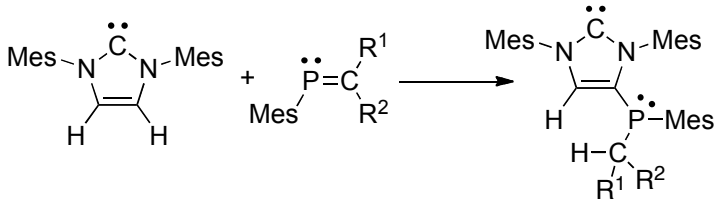


Figure 4.7 Representative examples of the known imidazol-2-ylidene derivatives **H**-**R** which feature C4 and/or C5 substituents that differ from H, alkyl, and aryl groups.

To test the scope of this new reaction, we treated phosphaalkenes MesP=C(4-$C_6H_4F)_2$ (**4.4**) and MesP=CPh(2-Py) (**4.6**) with IMes to afford NHC's **4.5** and **4.7** (Scheme 4.4), respectively. The latter (**4.7**) is composed of an equal mixture of diastereomers. In striking contrast to the reaction of NHC **4.1** with phosphaalkene **4.2**, which requires elevated temperatures (70 °C), the reaction with the electrophilic phosphaalkene **4.4** occurs at ambient temperatures.



4.1 **4.4: $R^1 = R^2 = 4\text{-}C_6H_4F$** **4.5: $R^1 = R^2 = 4\text{-}C_6H_4F$**
4.6: R^1 = Ph; R^2 = 2-Py **4.7: R^1 = Ph; R^2 = 2-Py**

Scheme 4.4 Formation of NHCs **4.5** and **4.7** from IMes and phosphaalkenes **4.4** and **4.6**

Both NHCs **4.5** (δ = -37.4) and **4.7** (δ = -33.7, -35.3) exhibit ^{31}P NMR chemical shifts similar to that observed for NHC **4.3**. Likewise, NHC **4.5** also exhibits a resonance in the $^{13}C\{^1H\}$ NMR spectrum (δ = 220.4) consistent with the presence of a carbene functionality; however, despite several attempts, we were unable to detect signals for the diastereomeric carbene centers in **4.7** due to poor solubility and slow relaxation times. The molecular structures of both NHCs **4.5** and **4.7** (Figures 4.8 and 4.9, respectively) were confirmed by X-ray crystallographic analysis (discussed below). Efforts to extend the reaction to the bulky I*t*Bu gave ~50% conversion of phosphaalkene **4.2** to product (δ = -32.3), as determined by ^{31}P NMR spectroscopy, after three weeks at 100 °C.

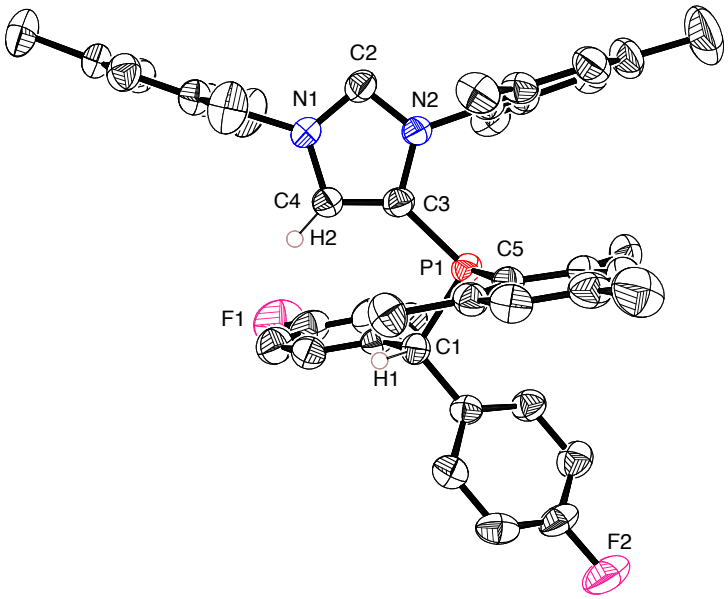


Figure 4.8 Molecular structure of **4.5**·½THF (thermal ellipsoids set at 50% probability). The partial THF atoms and all hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.867(3), P(1)-C(3) 1.821(3), P(1)-C(5) 1.838(3), C(2)-N(1) 1.367(3), C(2)-N(2) 1.365(3), C(4)-N(1) 1.390(3), C(3)-N(2) 1.403(3), C(3)-C(4) 1.352(4); N(1)-C(2)-N(2) 101.3(2), C(3)-C(4)-N(1) 107.4(3), C(4)-C(3)-N(2) 104.3(2).

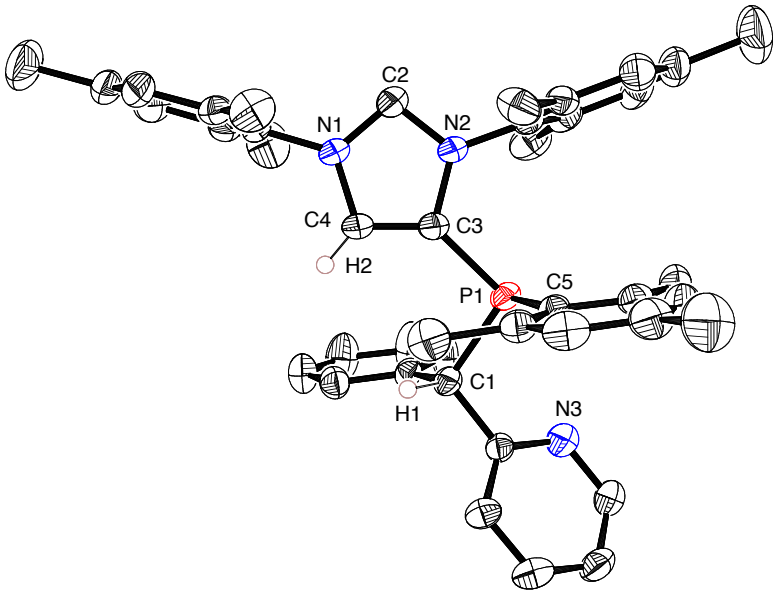


Figure 4.9 Molecular structure of **4.7**·½C_6H_6 (thermal ellipsoids set at 50% probability). The partial benzene atoms and all hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.862(3), P(1)-C(3) 1.810(3), P(1)-C(5) 1.836(3), C(2)-N(1) 1.359(4), C(2)-N(2) 1.368(3), C(4)-N(1) 1.388(4), C(3)-N(2) 1.402(4), C(3)-C(4) 1.346(4); N(1)-C(2)-N(2) 101.1(2), C(3)-C(4)-N(1) 107.4(3), C(4)-C(3)-N(2) 104.2(3).

Important metrical parameters for NHC **4.3**, **4.5**, and **4.7** are tabulated in Table 4.2 and, for comparison, the metrical parameters are also provided for IMes, IDipp and other related substituted NHCs. Interestingly, the presence of the bulky substituents at the C4-position, either phosphino or silyl, induce similar slight perturbations upon the bond lengths and angles in the NHC heterocycles compared to the respective parent NHCs. Therefore, the differences between the parent and substituted NHCs will be discussed by comparing NHC **4.3** with unsubstituted IMes.[262] For example, the C(4)-C(3)-C(2) angle in **4.3** (104.4(2)°) is smaller than in IMes (106.5(3)°); this is accompanied by an expansion of the exocyclic angles at C(3). Furthermore, the N(2)-C(3) and C(3)-C(4) bond lengths in **4.3** are slightly elongated with respect to those in IMes (1.406(2) Å versus 1.378(4) Å and 1.331(5) Å versus 1.349(3) Å, respectively). Surprisingly, despite the significant steric congestion, the P-C bonds lengths in **4.3** (1.816-1.869 Å) are at the shorter end of the typical range for P-C bonds (1.85-1.90 Å) and are even slightly shorter than those observed in Mes(Me)P-$CHPh_2$ (1.840-1.882 Å),[105] where the bulky imidazole-substituent in **4.3** has been replaced with a methyl group.

Table 4.2 Selected bond distances (Å) and angles (°) for **4.3**, **4.5**, **4.7** and related compounds.

	IMes	**4.3**	**4.5**	**4.7**	IDipp	**Q**[a]	**P**[a]
Bond distances (Å)							
N(1)-C(2)	1.365(4)	1.363(2)	1.367(3)	1.359(4)	1.365(3)	1.371(2)	1.366(2)
C(2)-N(2)	1.371(4)	1.366(3)	1.365(3)	1.368(3)	1.369(3)	1.370(2)	1.372(2)
N(2)-C(3)	1.378(4)	1.406(2)	1.403(3)	1.402(4)	1.394(3)	1.407(1)	1.413(2)
C(3)-C(4)	1.331(5)	1.349(3)	1.352(4)	1.346(4)	1.335(3)	1.351(2)	1.357(2)
C(4)-N(1)	1.381(4)	1.388(2)	1.390(3)	1.388(4)	1.394(3)	1.385(2)	1.381(2)
Bond angles (°)							
C(2)-N(1)-C(4)	112.8(3)	113.1(2)	112.8(2)	113.1(2)	113.0(2)	113.1(1)	113.1(1)
N(1)-C(2)-N(2)	101.4(2)	101.2(2)	101.3(2)	101.2(2)	101.4(2)	101.3(1)	101.4(1)
C(2)-N(2)-C(3)	112.8(3)	114.1(2)	114.2(2)	114.2(2)	113.0(2)	113.6(1)	113.9(1)
N(2)-C(3)-C(4)	106.5(3)	104.4(2)	104.3(2)	104.2(3)	106.2(2)	104.7(1)	104.0(1)
N(1)-C(4)-C(3)	106.5(3)	107.2(2)	107.4(3)	107.4(3)	106.3(2)	107.2(1)	107.6(1)
Reference	[262]	This work	This work	This work	[276]	[241]	[240]

[a] Compound numbers refer to structures in Figure 4, where both are derivatives of IDipp and the 4-substituents in **Q** is $–PPh_2$ and in **P** is $–SiCl_2$(NHAd).

4.2.2 Computational Investigation of Plausible Mechanisms for Abnormal Reactivity

While it is reasonably well established that NHCs may react at the 4- and 5-positions, such behavior is still relatively rare and, in general, the mechanism for forming *a*NHC-adducts remains uncertain.[225-228] Surprised by this unexpected abnormal reaction of an NHC with a phosphaalkene, we evaluated three plausible mechanistic pathways for the formation of these 4-phosphino-substituted NHCs by DFT calculations (Figure 4.10).[277][278-282]

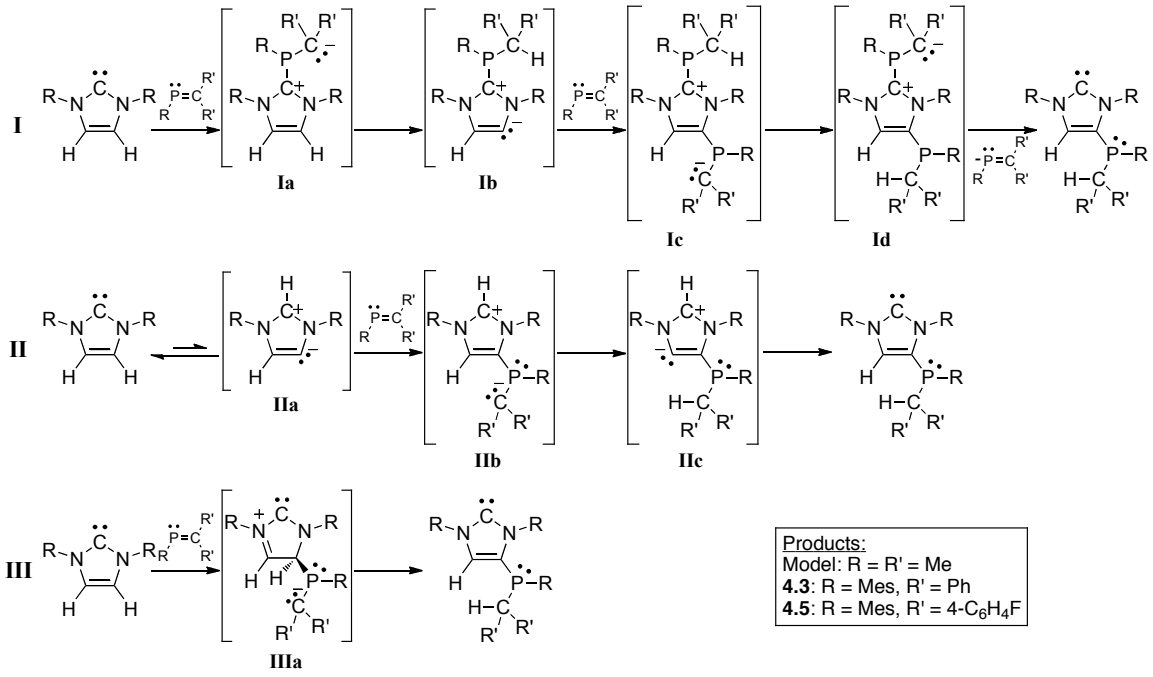


Figure 4.10 Postulated mechanisms (Top: Mechanism **I**; Middle: Mechanism **II**; Bottom: Mechanism **III**) for the formation of 4-phosphino-substituted NHCs. For model system, R = R' = Me. For formation of **4.3**, R = Mes, R' = Ph. For formation of **4.5**, R = Mes, R' = 4-C_6H_4F.

The first mechanism (**I**) involves initial nucleophilic addition of the NHC's C2 carbon to the P=C bond of the phosphaalkene to afford a zwitterionic intermediate (**Ia**). The N-heterocycle is now formally an imidazolium cation and, as such, its backbone protons are now relatively acidic ($pk_a \approx 33$)[283, 284] and susceptable to deprotonation by a

strong base, such as the carbanion moiety present on a second equivalent of intermediate **Ia**. Although the formation of the observed product from intermediate **Ib** can be envisaged as a simple rearrangement, such an intramolecular transformation seems highly improbable. Instead, the *a*NHC functionality in **Ib** can react with a second phosphaalkene to generate a third zwitterionic intermediate (**Ic**). Subsequently, a proton transfer would afford **Id** and, finally, elimination of the phosphaalkene from the 2-position would afford the observed product. This mechanism is similar to that proposed first by Arduengo[234] for the chlorination of both C4 and C5 (H) and more recently by Bertrand[229, 241] (**Q** and **R**) and Roesky[240] (**P**) for the selective substitution of either C4 or C5.

The second mechanism (**II**) involves isomerization of the NHC to its *a*NHC isomer (**IIa**) prior to addition across the P=C bond. Having directly established the non-hydrogen atom skeleton (**IIb**), the observed product could be obtained by subsequent intramolecular proton transfers. Carty and coworkers have suggested a similar mechanism might be involved in the formation of an *a*NHC-adduct they obtained from the reaction of an electrophilic phosphinidene with I*t*Bu.[236]

The third mechanism (**III**) involves the direct nucleophilic addition of an enamine resonance form of an NHC (a formal positive charge on the N1 nitrogen atom and a formal negative charge on the C4 carbon atom) to the P=C bond of the phosphaalkene to afford a zwitterionic intermediate (**IIIa**). Transfer of the proton from the heterocycle to the formal carbanion unit would yield the 4-phosphino-2-carbene. This electrophilic aromatic substitution-type mechanism appears to be involved in the reported deuteration of I*t*Bu at the 4- and 5-positions by DMSO-d_6.[235]

Preliminary calculations were conducted on a model system (R = R' = Me; product being 4-phosphino-2-carbene **4.8**) to assess the feasibility of the proposed mechanisms. All calculations were performed using optimized geometries and the results of the DFT calculations, modelled in the gas phase and in the dielectric of THF, are depicted in Figure 4.11 (mechanism **I**) and Figure 4.12 (mechanism **II**). Calculations upon the model system, and upon the full experimental system (R = Mes; R' = Ph) discussed below, did not lead to a stable geometry for the postulated zwitterionic intermediate **IIIa**. Specifically, the newly formed P-C bond breaks and the fragments then separate with reformation of the original NHC and phosphaalkene. Therefore, this mechanism was not considered further.

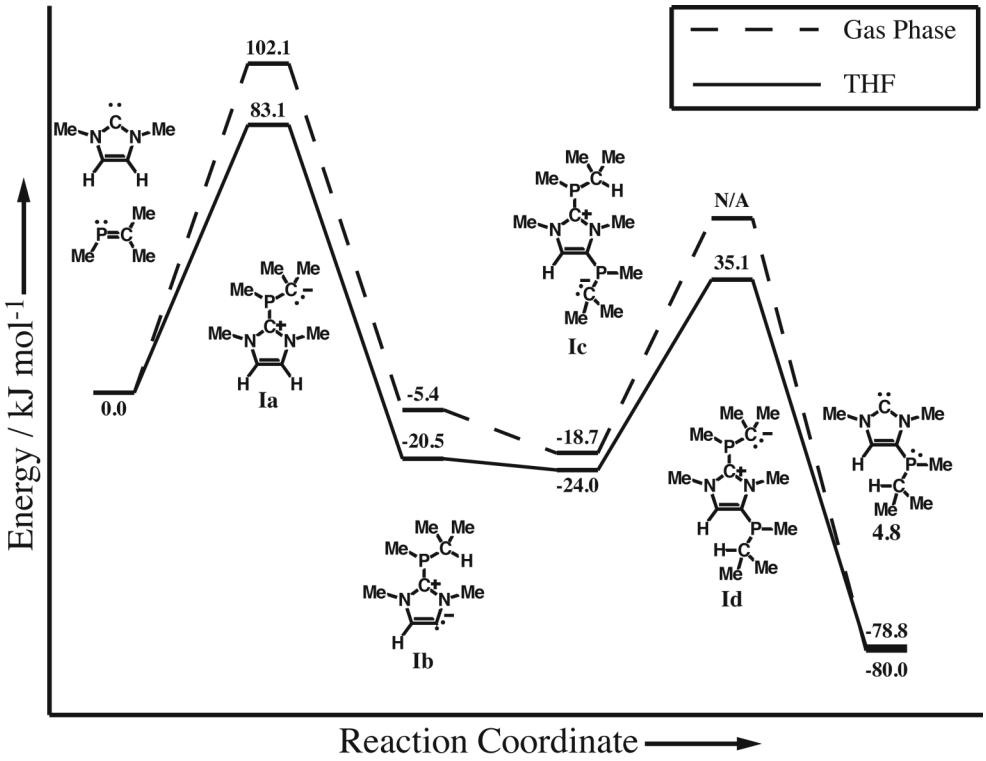


Figure 4.11 Results of DFT calculations (----- gas phase, —— THF) for the model reaction between IMe and MeP=CMe_2 to afford **4.8** following the postulated mechanism **I**. The structures and total energy of each intermediate are given. Note that gas phase calculations of intermediate **Id** did not lead to a stable geometry. Transition states have not been calculated.

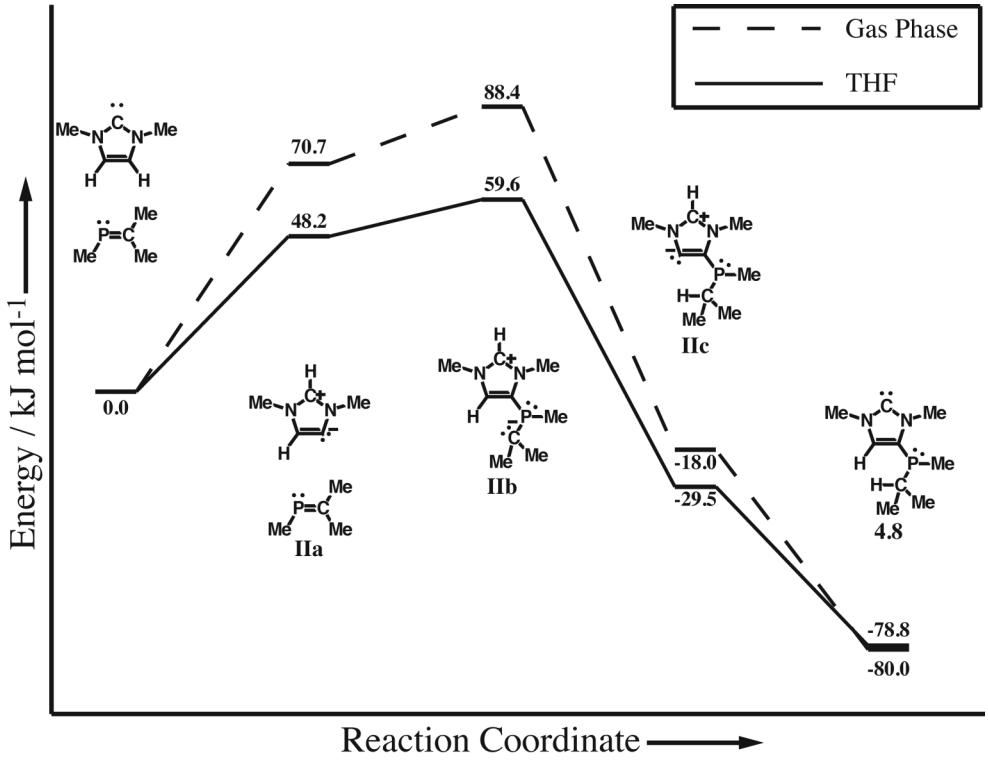


Figure 4.12 Results of DFT calculations (----- gas phase, —— THF) for the model reaction between IMe and $MeP{=}CMe_2$ to afford **4.8** following the postulated mechanism **II**. The structures and total energy of each intermediate are given. Transition states have not been calculated.

Although it appears to have little effect on the energetics of the overall reaction [Formation of **4.8**: Gas Phase – ΔE_{rxn} = -80.0 kJ mol^{-1} vs THF – ΔE_{rxn} = -78.8 kJ mol^{-1}), as might be anticipated, the zwitterionic intermediates modeled in the dielectric field of THF for both mechanistic pathways are significantly stabilized as compared to those modeled in the gas phase. It should be noted that gas phase calculations on intermediate **Id** did not lead to a stable geometry. Like the calculations on intermediate **IIIa** where the C4-P bond breaks, the C2-P bond in **Id** fragments with release of phosphaalkene and carbene **4.8**. The difference in energy between the starting reagents and the product of ~80 kJ mol^{-1}, which agrees well with rough calculations based on calculated bond dissociation energy for phosphorus-carbon bonds ($E_{\sigma+\pi}$ = 482 kJ mol^{-1}; E_{σ} = 276 kJ mol^{-1}; $\Delta H°_{rxn}$ = -70 kJ mol^{-1}),[46] suggests that the overall reaction is exothermic. For both

postulated mechanisms, the highest energy intermediates (**Ia** and **IIb**) follow nucleophilic addition of the carbene to the P=C bond and reflects the localized build up of negative charge. Interestingly, intermediate **IIb** is slightly lower in energy, illustrating the stronger donor properties of *a*NHCs.

While the energy difference between the normal and abnormal carbene (**IIa**) remains large in THF (ΔE = 48.2 kJ mol^{-1}), it is somewhat lower than the difference calculated in the gas phase (ΔE = 70.7 kJ mol^{-1}). Related comparisons of the normal and abnormal isomers of IH, IMe, I*t*Bu and IMes are tabulated in Table 4.3. These results agree with previous gas phase calculations for the parent carbene (IH: ΔE = 84 kJ mol^{-1} and ΔE = 73 kJ mol^{-1}).[285, 286] Intriguingly, this suggests that abnormal carbene behavior might be more prevalent in high dielectric solvents and may explain the apparent direct formation of *a*NHC metal-[287-290] and main group-adducts[236-239, 273] from free normal carbenes.

Table 4.3 Energetic comparisons of normal and abnormal NHCs.

	Energy (kJ mol^{-1})[a]	
	Gas Phase	THF
*a*IH	72.3	49.4
*a*IMe	70.7	48.2
*a*ItBu	61.2	30.6
*a*IMes	60.6	51.7

[a] Tabulated energies determined energy difference of geometry optimized structures.

Having identified reasonable intermediates for mechanisms **I** and **II**, the calculations were repeated for the reaction of NHC **4.1** with phosphaalkene **4.2** to afford 4-phosphino-NHC **4.3** (Figure 4.13). Additionally, intrigued by the room temperature reaction of carbene **4.1** with phosphaalkene **4.4** (R = Mes; R' = ArF = 4-C_6H_4F), I performed similar calculations to investigate how the fluorine atoms might be influencing the reactivity so significantly (Figure 4.14). Both sets of calculations were modeled in the

dielectric field of THF and the optimized geometries for **4.1**, **4.2**, **4.3**, **4.4** and **4.5** were in general agreement with the molecular structures obtained from X-ray crystallography.

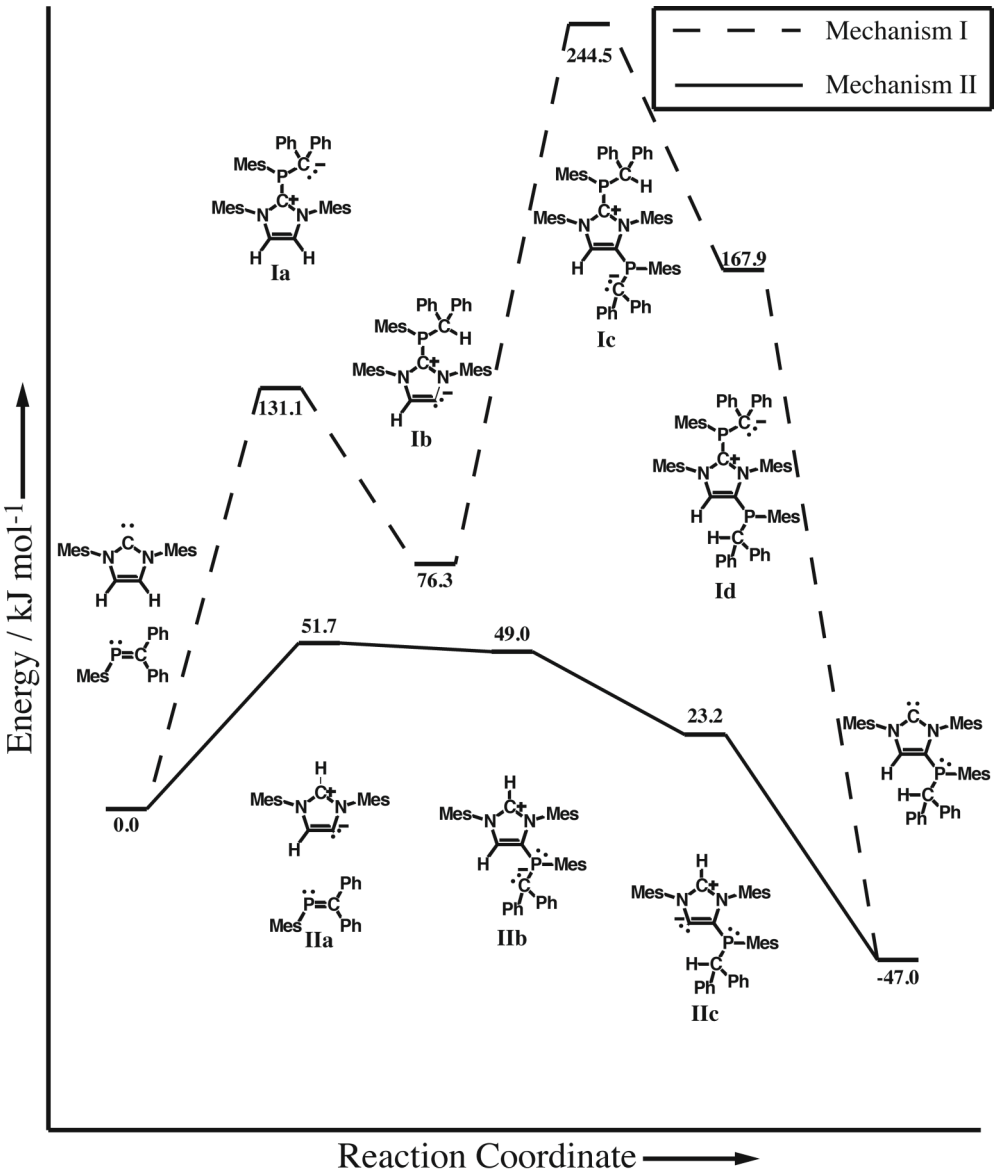


Figure 4.13 Results of DFT calculations, modeled in the dielectric field of THF, showing two plausible mechanistic pathways (----- Mechanism **I**, —— Mechanism **II**) for the reaction between IMes (**4.1**) and $MesP{=}CPh_2$ (**4.2**) to afford 4-phosphino-2-carbene (**4.3**). The structures and total energy of each intermediate are given. Transition states have not been calculated.

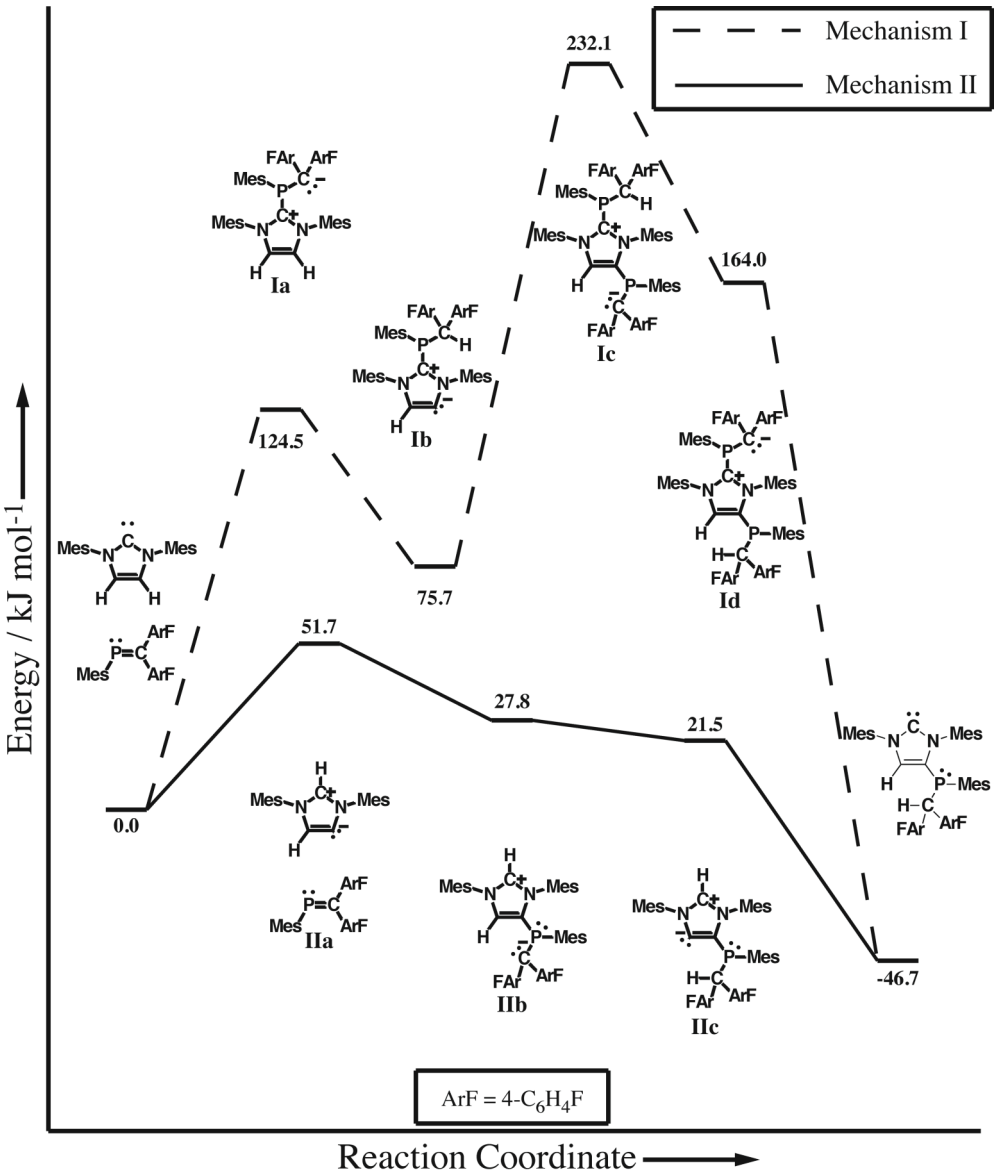


Figure 4.14 Results of DFT calculations, modeled in the dielectric field of THF, showing two plausible mechanistic pathways (----- Mechanism **I**, —— Mechanism **II**) for the reaction between IMes (**4.1**) and MesP=C(4-C_6H_4F)$_2$ (**4.4**) to afford 4-phosphino-2-carbene (**4.5**). The structures and total energy of each intermediate are given. Transition states have not been calculated.

Although the formation of both **4.3** and **4.5** in THF are still energetically favorable by ~47 kJ mol^{-1}, the reactions are less favored than those of the model system (~80 kJ mol^{-1}). Although electronic differences cannot be discounted (see below), presumably this relative energy difference (~33 kJ mol^{-1}) reflects the significant steric interactions present in the full systems where the methyl groups have been replaced by

larger aryl-substituents (Table 4.4). This notion is further supported by comparing the energies for intermediate **Ia** and **Id** of the full system (R' = Ph), where replacing the proton at C4 by the phosphorus functionality increases the relative energy of the system by 36.8 kJ mol^{-1}. For *a*NHC intermediates **Ib** and **IIc**, the differences between the full (R = Mes; R' = Ph) and model (R = R' = Me) systems are ΔE(**Ib**) = 96.8 kJ mol^{-1} and ΔE(**IIc**) = 52.7 kJ mol^{-1}. While this further illustrates the steric differences between the model and full systems, the Δ(ΔE) = 44.1 kJ mol^{-1} reveals that C2-substitution is significantly less favored with larger phosphino-substituents. A similar conclusion can be drawn by direct comparison of intermediates **Ib** and **IIc** for the full system (ΔE = 53.1 kJ mol^{-1}). These results clearly illustrate the challenge associated with accomodating the large phosphino-substituent on the imidazole-framework, especially when positioned between the two flanking *N*-mesityl substituents on IMes.

Table 4.4 Energy comparisons between full and model systems modelled in THF.

	Energy (kJ mol^{-1})				
	Model	Full (R' = Ph)	ΔE (Ph)	Full (R' = ArF)	ΔE (ArF)
Ia	83.1	131.1	48.0	124.5	41.4
Ib	-20.5	76.3	96.8	75.7	96.2
Ic	-24.0	244.5	268.5	232.1	256.1
Id	35.1	167.9	132.8	164.0	128.9
IIb	59.6	49.0	-10.6	27.8	-31.8
IIc	-29.5	23.2	52.7	21.5	51
Product	-78.8	-47.0	31.8	-46.7	32.1

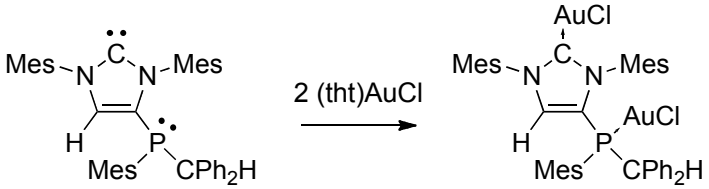
In contrast, replacing the C-Me by C-Ph substituents contributes a significant stabilizing effect upon the intermediates **Ia** and **IIb** which result from addition of the carbene to the P=C bond. Assuming no electronic differences and the respective steric contributions of 96.8 kJ mol^{-1} (**Ib**: C2-substitution) and 52.7 kJ mol^{-1} (**IIc**: C4-

substitution) discussed in the previous paragraph, the expected energies [E(expected) = E(model) + E(steric)] for intermediates **Ia** and **IIb** for the full system would be 179.9 kJ mol^{-1} and 112.3 kJ mol^{-1}, respectively. Approximating the relative ability of the C-aryl substituents to stabilize the build up of negative charge at the carbon atom as the difference between the expected and observed energy values, the phenyl substituents stabilize the built up charge in intermediate **Ia** by 48.8 kJ mol^{-1} and **IIb** by 63.3 kJ mol^{-1}. As might be anticipated, the fluorinated aryl substituents are even more effective at stabilizing the build up of negative charge (**Ia**: 55.4 kJ mol^{-1} and IIb: 84.5 kJ mol^{-1}) Interestingly, the stabilizing effect is much larger for the *a*NHC-adduct rather than NHC-adduct (Δ**Ia**: $\Delta(\Delta E)$ = 6.5 kJ mol^{-1} versus Δ**IIb**: $\Delta(\Delta E)$ = 21.2 kJ mol^{-1}) and presumably reflects the stronger donor properties of *a*NHCs which push additional electron density towards the electron deficient fluorine atoms.

As can be clearly seen in Figures 4.13 and 4.14, all intermediates which follow mechanism **II** are considerably more energetically favorable than those which follow mechanism **I**. Furthermore, the correlation between the observed room temperature reaction of **4.1** and **4.4** with the calculated stabilizing effects of the fluorinated aryl groups, significant only for the formation of intermediates **Ia** and **IIb**, suggests that the nucleophilic addition of the carbene to the P=C bond may be the rate limiting step. Therefore, I speculate that the reaction proceeds along mechanism **II**, although measurement of the reaction kinetics and/or calculations of the transition states are necessary to confirm this hypothesis.

4.2.3 Transition-metal Complexes of NHC 4.3: Bifunctionality and Donor Properties.

Interested in the donor properties of these potentially bifunctional non-chelating ligands, we initially investigated the coordinating properties of NHC **4.3** with gold(I), a metal ion that binds readily to both carbenes and phosphines. Treating a THF solution of NHC **4.3** with two equivalents of [(tht)AuCl] (tht = tetrahydrothiophene) afforded the digold complex **4.9** in moderate isolated yield (55%) (Scheme 4.5).



4.3 **4.9**

Scheme 4.5 Formation of digold complex **4.9**

Both the downfield shift of the phosphine resonance (**4.9**: δ_P = -0.1 versus **4.3**: δ_P = -37.9) and upfield shift of the carbene resonance (**4.9**: δ_C = 177.6 versus **4.3**: δ_C = 220.3) are consistent with those observed upon coordination of AuCl by related Mes(Me)P-CPh_2H [Mes(Me)(AuCl)P-CPh_2H: δ_P = 16.0 versus Mes(Me)P-CPh_2H: δ_P = -23.0) and IMes (IMes·AuCl: δ_C = 173.4 versus IMes: δ_C = 220.3). The coordination of two AuCl moieties was confirmed by X-ray crystallographic analysis (discussed below) and the molecular structure of **4.9** is shown in Figure 4.15.

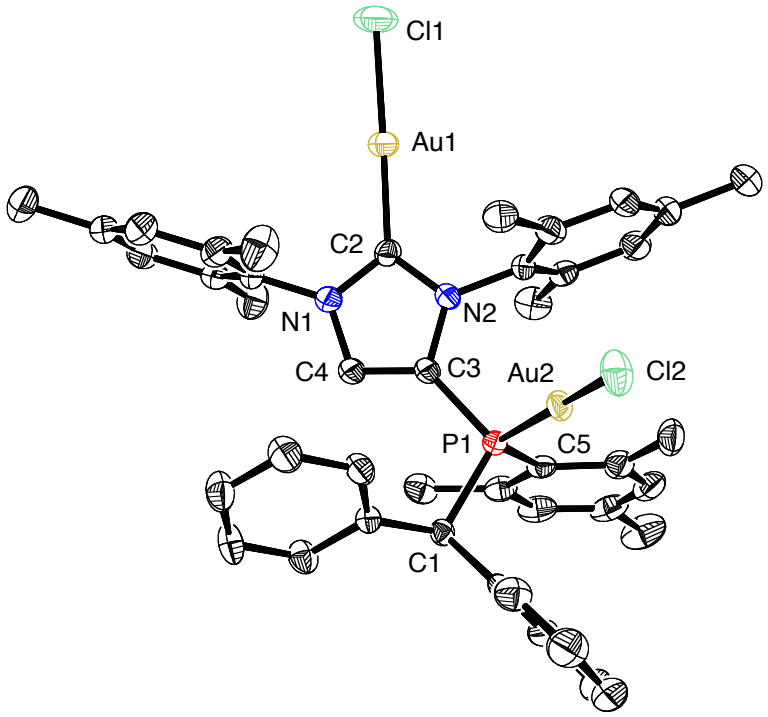
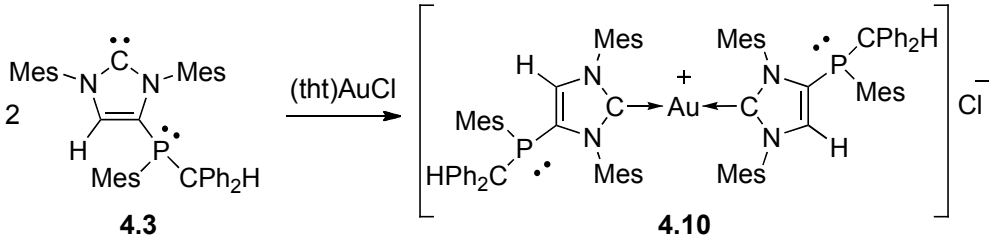


Figure 4.15 Molecular structure of **4.9**·CH_2Cl_2 (thermal ellipsoids set at 50% probability). The dichloromethane atoms and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.882(5), P(1)-C(3) 1.817(6), P(1)-C(5) 1.826(5), C(2)-N(1) 1.360(7), C(2)-N(2) 1.345(6), C(4)-N(1) 1.376(7), C(3)-N(2) 1.397(7), C(3)-C(4) 1.354(7), C(2)-Au(1) 1.971(5), P(1)-Au(2) 2.238(1), Au(1)-Cl(1) 2.266(2), Au(2)-Cl(2) 2.284(1); N(1)-C(2)-N(2) 105.1(5), C(3)-C(4)-N(1) 108.0(5), C(4)-C(3)-N(2) 105.2(5), C(2)-Au(1)-Cl(1) 176.9(2), P(1)-Au(2)-Cl(2) 171.9(1), N(1)-C(4)-C(3)-P(1) 170.2(4).

Changing the reaction stoichiometry, addition of [(tht)AuCl] to a THF solution of two equivalents of NHC **4.3** affords, within minutes, a colorless precipitate which is soluble in methylene chloride and chloroform (Scheme 4.6).



Scheme 4.6 Formation of dicarbene complex **4.10**

Analysis of the supernatent solution by ^{31}P NMR spectroscopy indicated that no phosphorus species remained in solution, suggesting that both carbene donors are present

in the product. The coordination of two carbenes to a single Au(I) center was confirmed by X-ray crystallographic analysis (discussed below) and the molecular structure of **4.10** is shown in Figure 4.16. Although the related $[(IMes)_2Au]^+$ cation has been detected by mass spectrometry,[291] other $[(NHC)_2Au]X$ salts have been isolated and characterized.[292] Interestingly, only a single resonance in the ^{31}P NMR spectrum (δ = -37.8) and a single carbene resonance in the $^{13}C\{^1H\}$ NMR spectrum (δ = 186.5) were observed for the product. Consistent with both NHCs binding to the gold atom via the C- rather than P-lone pair of electrons, this suggests that only a single diastereomer is present. X-ray crystallography determined this to be the R,R and S,S enantiomeric pair and not the meso isomer. Although the phosphine functionality is remote from the carbene center, presumably the stereochemical information is transferred through steric interactions between the bulky phosphine and the flanking *N*-mesityl substituents.

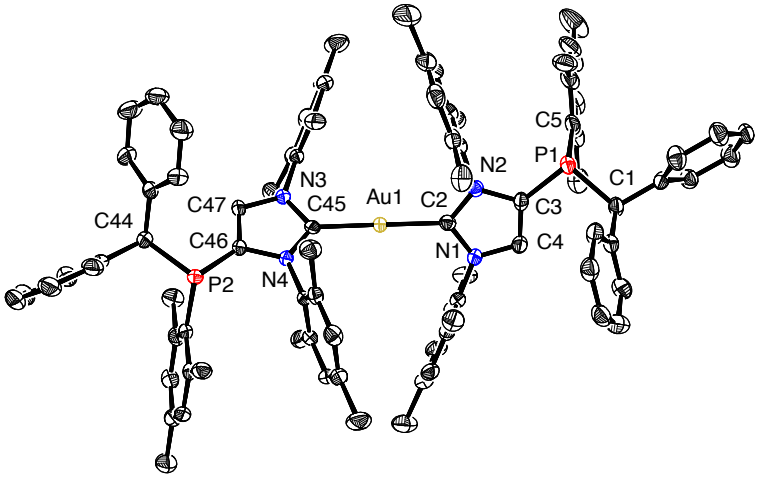
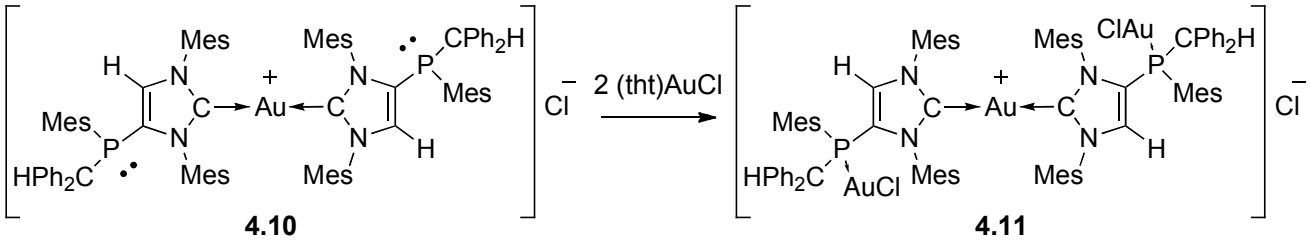


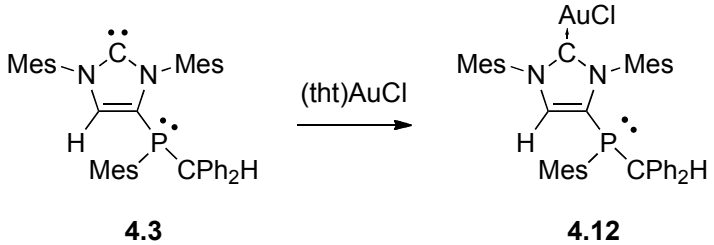
Figure 4.16 Molecular structure of **4.10**·$3CH_2Cl_2$·H_2O (thermal ellipsoids set at 50% probability). The dichloromethane, water and all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(1) 1.877(5), P(1)-C(3) 1.821(5), P(1)-C(5) 1.848(5), C(2)-N(1) 1.351(6), C(2)-N(2) 1.347(6), C(4)-N(1) 1.388(6), C(3)-N(2) 1.401(6), C(3)-C(4) 1.347(7), C(2)-Au(1) 2.010(4), P(2)-C(44) 1.869(5), P(2)-C(46) 1.815(5), P(2)-C(48) 1.845(5), C(45)-N(3) 1.350(6), C(45)-N(4) 1.344(6), C(47)-N(3) 1.387(6), C(46)-N(4) 1.408(5), C(46)-C(47) 1.365(6), C(45)-Au(1) 2.007(4); N(1)-C(2)-N(2) 105.2(4), C(3)-C(4)-N(1) 107.7(4), C(4)-C(3)-N(2) 105.5(4), C(2)-Au(1)-C(45) 177.8(2), N(3)-C(45)-N(4) 105.0(4), C(46)-C(47)-N(3) 107.1(4), C(47)-C(46)-N(4) 105.0(4).

Intriguingly, a preliminary NMR-scale investigation revealed that complex **4.10**, with its two free phosphine functionalities, will react with two additional equivalent of (tht)AuCl (Scheme 4.7). Two resonances (δ = 0.6 and δ = 0.5) are observed in the ^{31}P NMR spectrum of the reaction mixture, suggesting that both phosphine functionalities are now coordinated to AuCl (**4.11**), albeit in slightly different chemical environments, and hinting at the possibility of preparing coordination polymers or other large organometalic structures using complex **4.10** as a building block.



Scheme 4.7 Formation of trigold complex **4.11**

Upon mixing of stoichiometric (1:1) THF solutions of NHC **4.3** and of (tht)AuCl, a new signal, shifted slightly downfield from the signal attributed to **4.3** (δ = -36.4 versus δ = -37.3 in THF), was observed in the ^{31}P NMR spectrum of the reaction mixture. In contrast, the resonance in the ^{13}C{^{1}H} NMR spectrum assigned to the carbenic carbon (δ = 175.2 in THF), similar to that observed for complex **4.9** (δ = 173.4), is shifted significantly upfield from that of the free carbene (δ = 220.3 ppm). These results are consistent with the formation of complex **4.12** (Scheme 4.8) and support the hypothesis that the complexation of gold occurs first at the carbene center.



Scheme 4.8 Formation of monogold complex **4.12**

Interestingly, complex **4.12** is initially soluble in THF, much like the neutral complex **4.9**, however, over the course of a couple of hours, a colourless powder precipitates from solution, much like ionic complex **4.10**. This hints at the possible formation of a coordination oligomer/polymer, where the phosphine functionality displaces the Cl from the Au(I) of a second complex **4.12**. The crude product, again like complex **4.10**, is soluble in chlorinated solvents; however, the species present in solution exhibits a single sharp resonance (δ = -36.8 in $CDCl_3$) in the ^{31}P NMR spectrum, which indicates, at least upon dissolution in chlorinated solvent, that the product is monomeric. Efforts to grow crystals to study the product in the solid state by X-ray crystallography are ongoing.

Selected bonds lengths and angles for complexes **4.9** and **4.10**, and for related species for comparison purposes, are shown in Table 4.5. It has been shown previously that coordination of AuCl by IMes induces several small but significant structural changes to the structure of the heterocycle. Specifically, the C(2)-N(1) and C(2)-N(2) bonds (IMes: 1.365(4) and 1.371(4) Å; IMes·AuCl: 1.337(4) Å) and the C(2)-N(1)-C(4) and C(2)-N(2)-C(3) angles (IMes: 2 x 112.8(3)°; IMes·AuCl: 2 x 110.1(2)°) contract while the C(3)-C(4) bond (IMes: 1.331(5) Å; IMes·AuCl: 1.365(4) Å) and N(1)-C(2)-N(2) angle (IMes: 101.4(2)°; IMes·AuCl: 106.9(4)°) expand. Complexes **4.9** and **4.10** appear to exhibit similar changes to their heterocyclic structures, as compared to free NHC **4.3**, upon coordination of Au(I); however, due to larger ESD's, the comparison of the bond lengths remains qualitative. The C-Au bonds in both **4.9** (1.971(5) Å) and **4.10** (2.007(4) Å and 2.010(4) Å) are similar to that observed in IMes·AuCl (1.999(5) Å). The L-Au-Cl angles in **4.9** (C(2)-Au(1)-Cl(1): 176.9(2)°; P(1)-Au(2)-Cl(2): 171.9(1)°) and the

C-Au-C angle in **4.10** (C(2)-Au(1)-C(45): 177.8(2)°) deviate significantly from linearity; however, similar distortions are known for other bulky and/or asymmetric carbenes[259] and phosphines.[104, 293] Compared to the symmetrical IMes·AuCl (N(1)-C(2)-Au(1) = N(2)-C(2)-Au(1) = 126.5(2)°), the asymmetry of NHC **4.3** ligand is evident from the Au atoms being bent away from the phosphino-substituted side of the rings in both **4.9** (N(1)-C(2)-Au(1): 125.9(4)°; N(2)-C(2)-Au(1): 128.7(4)°) and **4.10** (N(1)-C(2)-Au(1): 126.4(3)° and N(3)-C(45)-Au(1): 126.9(3)°; N(2)-C(2)-Au(1): 128.2(3)° and N(4)-C(45)-Au(1): 128.1(3)°). Presumably this distortion is responsible for the apparent diastereoselectivity observed in the formation of **4.10**. The P(1)-Au(2) (2.238(1) Å) and Au(2)-Cl(2) (2.284(1) Å) bonds in **4.9** are both shorter than those found in the related Mes(Me)(AuCl)P-CPh_2H [P-Au: 2.257(1) Å; Au-Cl: 2.305(1) Å],[104] but within the range observed in other phosphine-AuCl complexes [P–Au: 2.21–2.26 Å; Au–Cl: 2.23–2.31 Å].[294-297]

Table 4.5 Selected bond distances (Å) and angles (°) for complexes **4.9** and **4.10** and related species.

	IMes	IMes·AuCl	**4.3**	**4.9**	**4.10**
Bond distances (Å)					
N(1)-C(2)	1.365(4)	1.337(4)	1.363(2)	1.360(7)	1.351(8)
C(2)-N(2)	1.371(4)	1.337(4)	1.366(3)	1.345(6)	1.346(8)
N(2)-C(3)	1.378(4)	1.388(3)	1.406(2)	1.397(7)	1.405(8)
C(3)-C(4)	1.331(5)	1.365(4)	1.349(3)	1.354(7)	1.356(9)
C(4)-N(1)	1.381(4)	1.388(3)	1.388(2)	1.376(7)	1.388(8)
C(2)-Au(1)		1.999(5)		1.971(5)	2.009(6)
Au(1)-Cl(1)		2.276(1)		2.266(2)	
Bond Angles (°)					
C(2)-N(1)-C(4)	112.8(3)	110.1(2)	113.1(2)	110.2(4)	110.9(6)
N(1)-C(2)-N(2)	101.4(2)	106.9(4)	101.2(2)	105.1(5)	105.1(6)
C(2)-N(2)-C(3)	112.8(3)	110.1(2)	114.1(2)	111.5(4)	111.5(6)
N(2)-C(3)-C(4)	106.5(3)	106.4(1)	104.4(2)	105.2(5)	105.3(6)
N(1)-C(4)-C(3)	106.5(3)	106.4(1)	107.2(2)	108.0(5)	107.4(6)
N(1)-C(2)-Au(1)		126.5(2)		125.9(4)	126.7(4)
N(2)-C(2)-Au(1)		126.5(2)		128.7(4)	128.2(4)
Reference	[262]	[259]	This work	This work	This work

Recently, Nolan, Cavallo, and coworkers have developed the "buried volume" method as a means of measuring and comparing the steric demand of NHC ligands.[298] In contrast with other methods for measuring the steric properties of a ligand, such as the Tolman's cone angle which has been extremely effective for comparison of phosphines,[299] the buried volume method is not limited to a certain class of ligands and, as such, is suitable for comparing all kinds of ligands, such as mono- or multi-dentate phosphine-, NHC- or cyclopentadienyl-based ligands, with a single parameter $\%V_{bur}$. In an exhaustive study, Clavier and Nolan have examined the buried volume of many NHCs and phosphines that form complexes with coinage metals and determined that those complexes with a linear geometry at the metal, such as the Au(I) complexes described above, are ideal for comparison due to the minimization of the steric influence of additional spectator ligands on the metal center.[300] Using the Samb*V*ca program,[298, 301] the $\%V_{bur}$ was determined for NHC **4.3** and related ligands and the results are tabulated in Table 4.6.

Table 4.6 $\%V_{bur}$ and cone angles for NHC 4.3 and related species based on their complexes with AuCl.

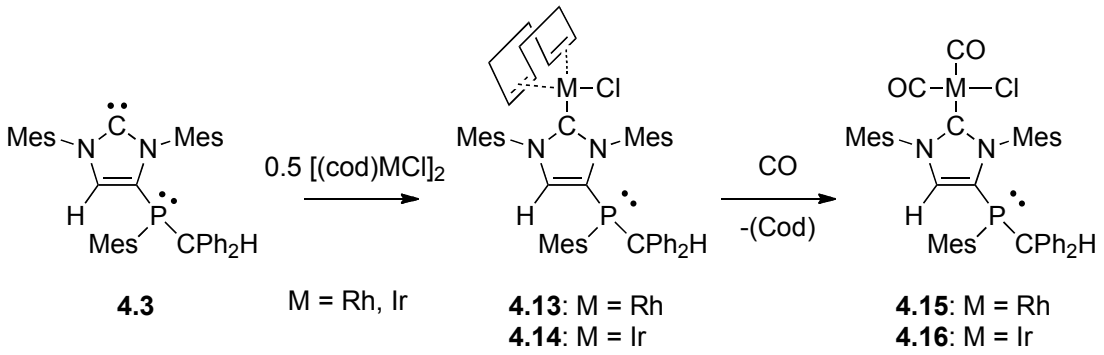
Ligand	$\%V_{bur}$[a,b]		Cone Angle (°)[a]
	C-Au d = 2.00 Å	P-Au d = 2.28 Å	P-M d = 2.28
IMe	26.3		
ICy	27.4		
IMes	36.5		
IAd	39.8		
CAAC	51.2		
IPr*	55.1		
4.3[c]	36.2	57.0	221[e] 275[f]
PMe_3		23.3	118
PPh_3		29.9	145
PCy_3		33.4	170
$PtBu_3$		38.1	182
Mes(Me)P-CPh_2H[d]		41.1	184[e] 199[f]
$PMes_3$		45.0	212

[a] Unless otherwise noted, tabulated values were obtained from reference[300]; [b] Parameters of SambVca calculations: (1) 3.50 Å was selected as the value for the sphere radius, (2) L-M bond lengths were set to 2.00 Å and 2.28 Å for NHCs and phosphines, respectively, (3) hydrogen atoms were omitted and (4) scaled Bondi radii were used as recommended by Cavallo[298]; [c] Structures used to calculate $\%V_{bur}$ extracted from X-ray crystal structure of complex **4.9**; [d] Structure used to calculate $\%V_{bur}$ extracted from X-ray crystal structure of Mes(Me)(AuCl)P-CPh_2H; [e] Tolman's cone angle was determined from X-ray crystallographic data where a van der Waals radius of 1.00 Å was used for hydrogen[302]; [f] Predicted Tolman's cone angle = $4.786(\%V_{bur}) + 2.037$ ($R^2 = 0.981$).

Comparing **4.3** with other carbene ligands, its steric demand ($\%V_{bur}$ = 36.2) falls about midway in the observed range for carbenes ($\%V_{bur}$: 26.3 – 55.1) and is very similar to that of the parent IMes ($\%V_{bur}$ = 36.5). This suggests that, at least when steric consideration of other ligands are minimized, the effect of the bulky phosphine moiety at the 4-position on the steric environment around the carbene functionality at C2 is minimal. In contrast, compared to other phosphine ligands (e.g. $PMes_3$: $\%V_{bur}$ = 45.0), it is clear that the phosphine functionality of **4.3** is very sterically demanding ($\%V_{bur}$ = 57.0). Remarkably, based on the buried volume, the predicted Tolman's cone angle based

on linear regression would be 275°,[300] which is substantially larger than the value calculated from the X-ray crystallographic structure of **4.9**.[302] This difference presumably reflects twisting of the bulky substituents into a propeller-like shape in order to minimize the steric interactions. Interestingly, a simple addition of the buried volumes of both the carbene and phosphine functionalities in **4.9** (%V_{bur} = 93.2) supports the possible formation of coordination polymers from mono-gold complex **4.12**; however, it is clear such a gold-mediated interaction between NHC **4.3** ligands would be highly strained, as indicated by the detection of only monomeric units in solution.

Having established that NHC **4.3** can act as a bifunctional ligand, it would be interesting to determine the effect the phosphino-functionality attached to the backbone might have on the donor properties of the carbene. It is well established that substituting halides for the protons at the C4 and C5 positions greatly reduces the σ-donating properties of IMesX (X = Cl, Br) as compared to IMes.[234] The most widely used method to ascertain the donor strength of carbene ligands involves the comparison of the CO stretching frequencies in their respective metal carbonyl complexes.[303] Although a number of different metal systems have been studied and, thus different donor-strength scales established, the most common are those based on rhodium and iridium complexes of the type $LM(CO)_2Cl$ (M = Rh, Ir). Therefore, to assess the donor properties of NHC **4.3**, complexes **4.13**-**4.16** were isolated in moderate to good yields (79% – 90%) following the procedure outlined in Scheme 4.9.



4.3 **4.13**: M = Rh, **4.14**: M = Ir **4.15**: M = Rh, **4.16**: M = Ir

Scheme 4.9 Formation of Rh and Ir cod- and carbonyl-complexes

The C-coordination, as opposed to P-coordination, of the metals in complexes **4.13**-**4.16** is supported by ^{31}P NMR spectroscopy, the phosphine resonances for the complexes are shifted only slightly relative to that of the free NHC **4.3**, and by $^{13}C\{^{1}H\}$ NMR spectroscopy, the carbene resonances for the complexes are shifted significantly upfield relative to that of the free NHC **4.3** and consistent with analogous IMes-complexes (Table 4.1). For complexes **4.14** and **4.16**, the proposed carbene binding to the iridium center was confirmed by X-ray crystallographic analysis and their molecular structures are depicted in Figures 4.17 and 4.18, respectively. Both cod complexes **4.13** and **4.14** appear as a mixture of rotational isomers (~2:1 ratio) in solution. This observation may indicate restricted rotation about both the C-M and C-P bonds where the P-lone pair can be effectively thought as either pointing towards or away from the chlorine atom. A similar observation has been made for IMesRh(cod)Cl, where restricted rotation about the C-Rh bond renders the *o*-methyl groups on the mesityl rings magnetically inequivalent since they can be near either the chlorine or cod ligands.[260]

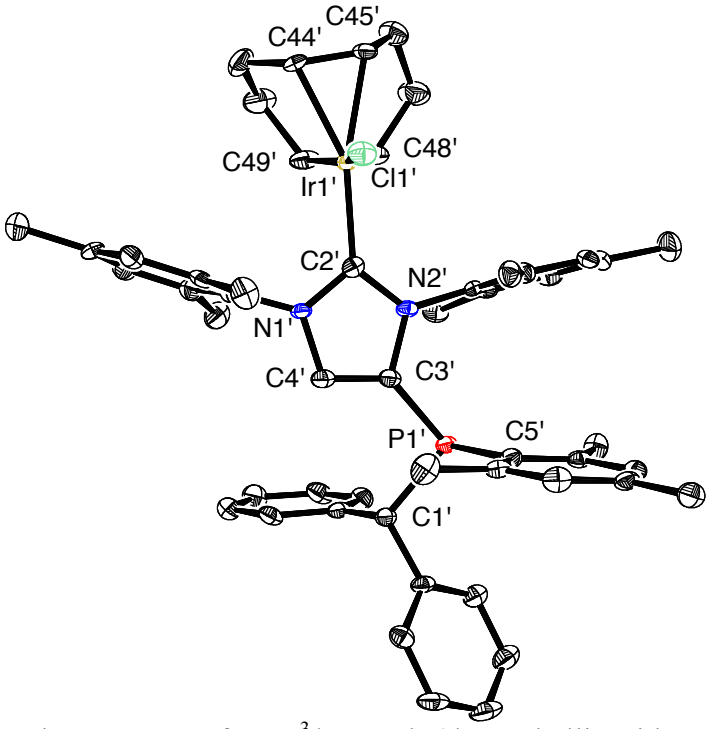


Figure 4.17 Molecular structure of **4.14**·$^{3}/_{2}CH_2Cl_2$ (thermal ellipsoids set at 30% probability). The other enantiomer is metrically equivalent and so not shown. The dichloromethane atoms and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.878(6), P1-C3 1.828(6), P1-C5 1.853(6), C2-N1 1.368(7), C2-N2 1.359(8), C4-N1 1.382(7), C3-N2 1.410(7), C3-C4 1.342(8), C2-Ir1 2.054(6), Ir1-Cl1 2.368(2), C44-C45 1.385(9), C48-C49 1.388(11), Ir1-C44 2.195(6), Ir1-C45 2.159(6) , Ir1-C48 2.102(7) , Ir1-C49 2.086(7); N1-C2-N2 103.7(5), C3-C4-N1 108.0(5), C4-C3-N2 105.4(5), C2-Ir1-Cl1 93.4(2), C2-Ir1-C44 164.0(2) , C2-Ir1-C45 158.8(2) , C2-Ir1-C48 92.4(3), C2-Ir1-C49 91.8(3), N1-C4-C3-P1 174.0(5).

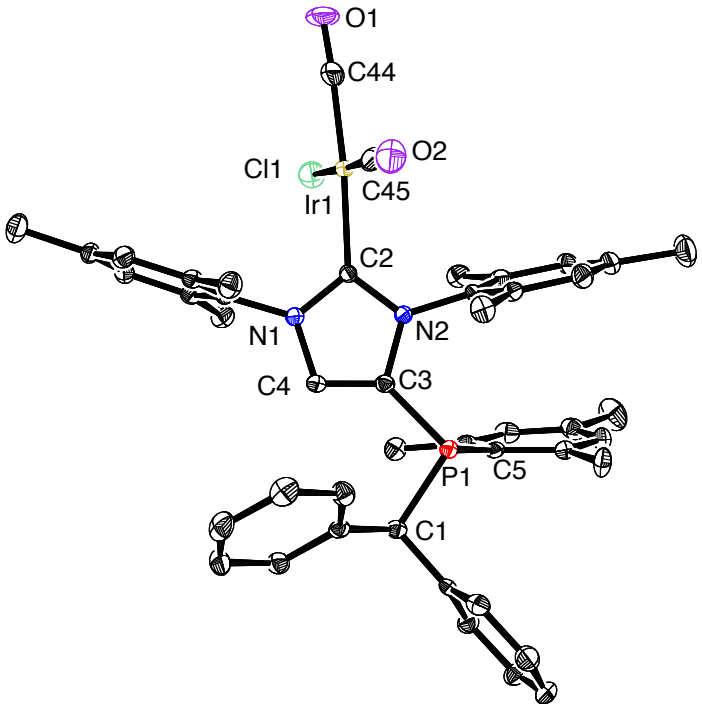


Figure 4.18 Molecular structure of **4.16**·C_7H_8 (thermal ellipsoids set at 30% probability). The toluene atoms and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.874(2), P1-C3 1.824(2), P1-C5 1.846(2), C2-N1 1.356(3), C2-N2 1.361(3), C4-N1 1.386(3), C3-N2 1.411(3), C3-C4 1.354(3), C2-Ir1 2.071(2), Ir1-Cl1 2.351(1), Ir1-Cl1b 2.329(7), C44-O1 1.147(3), Ir1-C44 1.880(3), C45-O2 1.144(6), Ir1-C45 1.823(5), C45b-O2b 1.155(12), Ir1-C45b 1.831(11); N1-C2-N2 104.3(2), C3-C4-N1 107.9(2), C4-C3-N2 104.9(2), C2-Ir1-Cl1 90.8(1), C2-Ir1-Cl1b 91.0(2), C2-Ir1-C44 175.5(1), C2-Ir1-C45 91.8(2), C2-Ir1-C45b 88.8(5), N1-C4-C3-P1 167.4(2).

For both complexes **4.14** and **4.16**, the coordination of Ir(cod)Cl and $Ir(CO)_2Cl$ by NHC **4.3** has no significant effect upon the heterocyclic bond lengths and the changes in the endocyclic angles at C(2), N(1), and N(2) are similar to, but smaller than, those observed for the related gold(I) complexes discussed previously (Table 4.7). These results parallel the coordination chemistry of the parent IMes, however, due to the wide range and large ESD's in the bond lengths reported for the structure of $IMesIr(CO)_2Cl$,[261] any comparison must be made cautiously. Likewise, the C-Ir bonds in both complexes **4.14** and **4.16** do not vary significantly from those in the related IMes complexes. As it was observed for complexes **4.9** and **4.10**, the asymmetrical nature of the NHC **4.3** is evident upon examining the N-C-Ir angles in **4.16** [N(1)-C(2)-Ir(1):

126.6(2)° and N(2)-C(2)-Ir(1): 129.0(2)°]. In order to accommodate the larger Ir(cod)Cl fragment, the distortion in complex **4.14** is larger [N(1)-C(2)-Ir(1): 125.3(4)° and N(1)'-C(2)'-Ir(1)': 125.0(4)°; N(2)-C(2)-Ir(1): 131.2(4)° and N(2)'-C(2)'-Ir(1)': 131.2(4)°]. Notably, due to the bulk of the Ir(cod)Cl fragment, even the symmetric IMes undergoes a similar, albeit smaller, asymmetrical distortion upon binding the metal [N(1)-C(2)-Ir(1): 126.9(6)°; N(2)-C(2)-Ir(1): 129.8(6)°].

Table 4.7 Selected bond distances (Å) and angles (°) for complexes **4.14**, **4.16** and related species.

	IMes	IMesIr(cod)Cl	IMesIr(CO)$_2$Cl	**4.3**	**4.14**	**4.16**
Bond distances (Å)						
N(1)-C(2)	1.365(4)	1.366(10)	1.39(3)	1.363(2)	1.363(11)	1.356(3)
C(2)-N(2)	1.371(4)	1.367(10)	1.33(3)	1.366(3)	1.364(11)	1.361(3)
N(2)-C(3)	1.378(4)	1.388(10)	1.37(3)	1.406(2)	1.410(10)	1.411(3)
C(3)-C(4)	1.331(5)	1.334(11)	1.30(3)	1.349(3)	1.347(11)	1.354(3)
C(4)-N(1)	1.381(4)	1.385(10)	1.36(3)	1.388(2)	1.388(10)	1.386(3)
C(2)-Ir(1)		2.052(7)	2.08(2)		2.055(8)	2.071(2)
Ir(1)-Cl(1)		2.359(1)	2.337(8)		2.371(3)	2.351(1)
Bond Angles (°)						
C(2)-N(1)-C(3)	112.8(3)	111.1(6)	109(2)	113.1(2)	111.2(7)	111.2(2)
N(1)-C(2)-N(2)	101.4(2)	103.3(6)	104(2)	101.2(2)	103.7(7)	104.3(2)
C(2)-N(2)-C(3)	112.8(3)	111.7(6)	111(2)	114.1(2)	112.0(7)	111.7(2)
N(2)-C(3)-C(4)	106.5(3)	106.5(7)	107(2)	104.4(2)	105.1(7)	104.9(2)
N(1)-C(4)-C(3)	106.5(3)	107.5(7)	109(3)	107.2(2)	108.1(7)	107.9(2)
N(1)-C(2)-Ir(1)		126.9(6)	125(2)		125.2(6)	126.6(2)
N(2)-C(2)-Ir(1)		129.8(6)	130(2)		131.1(6)	129.0(2)
C(2)-Ir(1)-Cl(1)		90.0(1)	90.2(7)		93.3(3)	90.9(2)
Reference	[262]	[261]	[261]	This work	This work	This work

Although the average bond lengths and angles related to the cod ligands do not vary significantly, the Ir(1)-Cl(1) bond length is slightly longer and C(2)-Ir(1)-Cl(1) bond angle is significantly larger in complex **4.14** (Ir(1)-Cl(1): 2.371(3) Å; C(2)-Ir(1)-Cl(1): 93.3(3)°) than in IMes·Ir(cod)Cl (Ir(1)-Cl(1): 2.359(1) Å; C(2)-Ir(1)-Cl(1): 90.0(1)°). Overall, this suggests that, despite the very similar metrical parameters, the coordination environment around the Ir(I) centers differs when coordinated by NHC **4.3** as opposed to

IMes. Unfortunately, buried volume calculations for complexes **4.14** and **4.16** failed to reveal any notable differences between NHC **4.3** and IMes as ligands for Ir(I) (Table 4.8). An explanation may lie in the relative flexibility of the ligands. For IMes, depending on the crowding around the metal, $\%V_{bur}$ values range from 30.7 to 38.2%,[300] indicating the ligand has the capacity to rearrange itself to modify its steric demand, presumably involving rotation about the N-C_{Mes} bonds. While both ligands might be essentially the same "size," presumably NHC **4.3** is less flexible due to restricted rotation. If this is correct, it could explain the distortion of the C-Ir-Cl angle in complex **4.14** and the diastereoselectivity in the formation of the biscarbene salt **4.10**. To test this hypothesis, additional complexes of NHC **4.3** would have to be prepared and compared to see if the range of buried volumes differs from that of IMes.

Table 4.8 $\%V_{bur}$ for NHC **4.3** and related species based on their complexes with Ir(cod)Cl and $Ir(CO)_2Cl$.

Ligand	$\%V_{bur}$[a,b]	
	C-Ir(cod)Cl d = 2.00 Å	C-Ir$(CO)_2$Cl d = 2.00 Å
ICy	27.3	27.6
IMes	33.0	33.8
4.3	33.0[c]	34.3[d]
I*t*Bu	35.7	37.6
IPr	34.9	34.5

[a] Unless otherwise noted, tabulated values were obtained from reference[300]; [b] Parameters of SambVca calculations: (1) 3.50 Å was selected as the value for the sphere radius, (2) L-M bond lengths were set to 2.00 Å and 2.28 Å for NHCs and phosphines, respectively, (3) hydrogen atoms were omitted and (4) scaled Bondi radii were used as recommended by Cavallo[298]; [c] Structures used to calculate $\%V_{bur}$ extracted from X-ray crystal structure of complex **4.14**; [d] Structures used to calculate $\%V_{bur}$ extracted from X-ray crystal structure of complex **4.16**.

The ATR-IR (Attenuated Total Reflectance) spectra of complexes **4.15** and **4.16** were collected and their CO stretching frequencies are presented in Table 4.9. It is noteworthy, however, that IR stretching frequencies for a compound can vary depending on the technology used, and so care must be taken when comparing data collected by

different techniques. Therefore, the ATR-IR spectra for $IMesRh(CO)_2Cl$ and $IMesIr(CO)_2Cl$ were also measured for comparison.

Table 4.9 ATR-IR CO stretching frequencies for complexes **4.15** and **4.16** and comparative examples.

		CO Stretching Frequencies (cm^{-1})			
	Method	*trans*	*Cis*	Average	Reference
4.15	ATR	1983	2071	2027	This work
$IMesRh(CO)_2Cl$	ATR	1984	2066	2025	This work
$IMesRh(CO)_2Cl$	CH_2Cl_2	1996	2081	2039	[260]
4.16	ATR	1967	2056	2011	This work
$IMesIr(CO)_2Cl$	ATR	1971	2055	2013	This work
$IMesIr(CO)_2Cl$	CH_2Cl_2	1980	2066	2023	[261]
$(IPrCl)Ir(CO)_2Cl$	CH_2Cl_2	1985	2071	2028	[261]
$IPrIr(CO)_2Cl$	CH_2Cl_2	1981	2067	2024	[261]
ItBuIr$(CO)_2Cl$	CH_2Cl_2	1980	2065	2022	[261]
$PPh_3Ir(CO)_2Cl$	$CHCl_3$	2002	2085	2044	[304]
$PCy_3Ir(CO)_2Cl$	$CHCl_3$	1984	2072	2028	[304]

There are two predominant approaches for analyzing the IR data of these square-planar metal carbonyl complexes.[305] The first is to compare only the *trans*-CO stretching frequencies and the second is to compare the average value of both the *cis*- and *trans*-stretching frequencies. As the *trans*-CO stretching frequency is less affected by the steric bulk of the carbene donor, it tends to provide clearer insight into the σ-donor properties of the ligand. Furthermore, the averaged scale is narrower. This is a disadvantage since, in contrast to the analogous phosphine complexes in which different donor strengths results in significantly different stretching frequencies [$\nu_{CO}^{avg}(PPh_3) = 2044\ cm^{-1}$; $\nu_{CO}^{avg}(PCy_3) = 2028.0\ cm^{-1}$], [261] different NHC complexes tend to exhibit very little difference in stretching frequencies [$\nu_{CO}^{avg}(IMes) = 2023\ cm^{-1}$; $\nu_{CO}^{avg}(It\text{Bu}) = 2022\ cm^{-1}$]. [261] While it would appear preferable to consider only the first method, the second method can provide insights into stereoelectronic properties in cases where steric effects are severe.

For the Ir system, the *trans*-CO stretching frequencies (**4.16**: 1967 cm^{-1} versus $IMesIr(CO)_2Cl$: 1971 cm^{-1}) are consistent with NHC **4.3** being a stronger donor than IMes. Interestingly, comparing the *trans*-CO stretching frequencies for $(IPr)Ir(CO)_2Cl$ with $(IPrCl)Ir(CO)_2Cl$, the carbene with electron-withdrawing chlorides at the 4,5-positions is a weaker donor by ~4 cm^{-1}. This small difference, equal in magnitude but opposite in sign to that observed between NHC **4.3** and IMes, correlates to a profound difference in the reactivity, where the chlorinated derivative is air and moisture stable.[234] For the Rh systems, the data suggests NHC **4.3** might be a slightly stronger donor, but the small difference in frequencies ($\Delta\nu$ = 1 cm^{-1}) make meaningful comparison difficult. The averaged data is less conclusive. While the averaged Ir data is consistent with NHC **4.3** being a stronger donor (**4.16**: 2011 cm^{-1} versus $IMesIr(CO)_2Cl$: 2013 cm^{-1}), the averaged Rh data suggests the opposite may be true (**4.15**: 2027 cm^{-1} versus $IMesRh(CO)_2Cl$: 2025 cm^{-1}). The reason for why there is an apparent reversal of ligand donor strengths and for why NHC **4.3** would appear to be a poorer donor for Rh(I) than for Ir(I) is not certain, but may reflect the relative flexibility of the ligands in relation to the smaller Rh(I) center. However, pending further crystallographic data, such a rationale remains speculative.

Overall, these results suggest that the good σ-donating properties of IMes are retained, and possibly improved, upon functionalization by phosphorus and, coupled with the potential for cooperative behaviour between metals bound to both P and C, this may lead to exciting new catalytic reactivity.

4.3 Conclusions

In summary, we have demonstrated that phosphaalkenes will react with NHCs to give unprecedented 4-phosphino-2-carbenes. Bifunctional NHC **4.3** is an effective ligand for Au(I), Rh(I) and Ir(I) metal centers and exhibits stereoelectronic properties similar to that of IMes. This is a highly unusual reaction for free NHCs and DFT calculations suggest this may occur via an *a*NHC intermediate. This work opens the door to abnormal reactions of NHCs with other unstaturated molecules and to the development of novel bifunctional ligands for use in catalysis.

4.4 Experimental

4.4.1 General Considerations

Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen. Hexanes, dichloromethane and toluene were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. Tetrahydrofuran was distilled from Na/benzophenone. C_6D_6 was stored over molecular sieves (4Å) before use and ampules of CD_2Cl_2 were used as received from CIL. IMes,[262] phosphaalkenes **4.2**, **4.4**, and **4.6**[51] and (tht)AuCl[306] were prepared following literature procedures. The $(M(cod)Cl)_2$ (M = Rh, Ir) were used as obtained from Strem. The CO was used as received from Praxair. ^{31}P, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers with chemical shifts (δ) in parts per million (ppm). Chemical shifts are referenced and reported relative to 85% H_3PO_4 as an external standard (δ = 0.0 for ^{31}P) or referenced to TMS and measured

relative to residual solvent peak (C_6HD_5 or $CHDCl_2$: δ = 7.16 or 5.32 for ^1H, respectively; C_6D_6 or CD_2Cl_2: δ = 128 or 53.8 for ^{13}C, respectively). Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV). IR spectra were recorded on a Thermo IR spectrometer with attenuated total reflection (ATR) attachment.

4.4.2 Synthesis of 4.3

To a solution of **4.1** (500 mg, 1.64 mmol) in THF (2 mL) was added a solution of **4.2** (520 mg, 1.64 mmol) in THF (2 mL). The mixture was sealed in a bomb and heated at 70 °C overnight. Upon cooling, an aliquot was removed and ^{31}P NMR spectroscopy indicated quantitative conversion of the phosphaalkene (δ = 233) to a new compound (δ = -37.3). Volatiles were removed in vacuo and the product was recrystallized from benzene. Yield: 800 mg (78%).

^{31}P NMR (162 MHz, C_6D_6): δ = -37.9. ^1H NMR (400 MHz, C_6D_6): δ = 7.56-6.39 (m, 16H, aromatic), 6.64 (d, J_{HP} = 2.0 Hz, 1H, vinyl), 5.23 (d, J_{HP} = 4.4 Hz, 1H, CPh_2H), 2.64 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.14 (s, 6H), 1.92 (s, 3H), 1.86 (d, J_{HP} = 2.4 Hz, 3H), 1.78 (s, 3H), 1.52 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 220.3 (d, J_{CP} = 5 Hz), 147.8, 147.4, 144.6 (d, J_{CP} = 5 Hz), 142.6, 142.4, 141.9, 141.8, 139.7 (d, J_{CP} = 2 Hz), 139.2, 137.9, 137.4, 137.2 (2C), 136.7, 135.4, 130.4, 129.2, 129.1, 128.8, 128.7 (d, J_{CP} = 2 Hz), 128.3, 128.2, 128.1, 128.0, 127.9, 126.8 (d, J_{CP} = 2 Hz), 126.6 (d, J_{CP} = 2 Hz), 125.8, 125.6, 48.2 (d, J_{CP} = 10 Hz), 23.6 (d, J_{CP} = 36 Hz), 21.6, 21.0 (2C), 20.9, 18.8 (d, J_{CP} = 8 Hz), 18.4, 17.6, 17.0. MS (EI, 70 eV): 621, 620 [2, 5; M^+]; 455, 454, 453 [10, 50, 100; M^+-$CHPh_2$]; 168, 167 [18, 85; $CHPh_2^+$]. Anal. Calcd for $C_{43}H_{45}N_2P$: C, 83.19; H, 7.31; N, 4.51; Found: C, 83.10; H 7.44; N 4.61.

4.4.3 Synthesis of 4.5

To a solution of **4.1** (304 mg, 1 mmol) in THF (2 mL) was added a solution of **4.4** (352 mg, 1 mmol) in THF (2 mL). The mixture was stirred overnight. An aliquot was removed and ^{31}P NMR spectroscopy indicated quantitative conversion of the phosphaalkene (δ = 234) to a new compound (δ = -36.7). Slow evaporation of the solvent afforded crystals suitable for X-ray crystallography. Yield (**4.5**·½THF): 560 mg (81%).

^{31}P NMR (162 MHz, C_6D_6): δ = -37.4. ^{19}F NMR (282 MHz, C_6D_6): δ = -116.0, -116.1. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.28-6.40 (m, 15H, 14 aromatic + 1 vinyl), 5.05 (d, J_{HP} = 3.3 Hz, 1H, CPh_2H), 2.57 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.15 (s, 6H), 1.93 (s, 3H), 1.78 (d, J_{HP} = 2.8 Hz, 3H), 1.77 (s, 3H), 1.49 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 220.4 (br s), 161.9 (dd, $^{5}J_{CP}$ = 3 Hz, $^{1}J_{CF}$ = 246 Hz), 160.8 (dd, $^{5}J_{CP}$ = 3 Hz, $^{1}J_{CF}$ = 245 Hz), 147.7, 147.4, 144.3, 140.1, 139.0, 138.1 (d, J_{CP} = 3 Hz), 137.9 (d, J_{CP} = 3 Hz), 137.7, 137.6, 137.4, 137.3 (J_{CP} = 3 Hz), 137.1, 136.5, 135.2, 130.6 (d, J = 8 Hz), 130.5, 130.4 (d, J = 7 Hz), 129.6 (d, J = 7 Hz), 129.5 (d, J = 8 Hz), 129.4 (d, J = 8 Hz), 129.3, 129.2, 129.1, 127.9, 125.2 (d, $^{1}J_{CP}$ = 20 Hz), 115.7 (d, $^{2}J_{CF}$ = 21 Hz), 115.1 (d, $^{2}J_{CF}$ = 21 Hz), 46.3 (d, $^{1}J_{CP}$ = 10 Hz), 23.5 (d, J_{CP} = 35 Hz), 21.5, 21.0 (2C), 20.9, 18.8 (d, J_{CP} = 7 Hz), 18.4, 17.3, 17.0. MS (EI, 70 eV): 657, 656 [3, 6; M^+]; 454, 543 [36, 100; M^+-$CH(C_6H_4F)_2$]; 204, 203 [5, 13; $CH(C_6H_4F)_2^+$].

4.4.4 Synthesis of 4.7

To a solution of **4.1** (104 mg, 0.34 mmol) in C_6D_6 (2 mL) was added a solution of phosphaalkene **4.6** (106 mg, 0.33 mmol) in C_6D_6 (2 mL). The mixture was sealed in a bomb and heated at 100 °C overnight. Upon cooling, an aliquot was removed and ^{31}P NMR spectroscopy indicated quantitative conversion of the phosphaalkenes (δ = 261,

242) to new compounds (δ = -33.7, -35.3). Slow evaporation of the solvent afforded crystals suitable for X-ray crystallography. Yield (**4.7**·½C_6D_6): 160 mg (73%).

^{31}P NMR (121 MHz, C_6D_6): δ = -33.7, -35.3. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.34-6.18 (m, 32H, 30 aromatic + 2 vinyl), 5.67 (d, $^{2}J_{HP}$ = 5 Hz, 1H, CPh_2H), 5.52 (d, $^{2}J_{HP}$ = 5 Hz, 1H, CPh_2H), 2.74 (s, 3H), 2.65 (s, 3H), 2.37 (s, 3H), 2.35 (br s, 3H), 2.29 (br s, 3H), 2.26 (s, 3H), 2.16 (s, 6H), 2.15 (s, 6H), 2.12 (d, J_{HP} = 4 Hz, 3H), 1.93 (d, J_{HP} = 3 Hz, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.81 (br s, 6H), 1.51 (s, 3H), 1.50 (s, 3H). MS (EI, 70 eV): 622, 621 [3, 7; M^+]; 454, 453 [36, 100; M^+-CHPh(C_5H_4N)]; 169, 168 [12, 60; CHPh(C_5H_4N)$^+$].

4.4.5 Synthesis of 4.9

To a solution of (tht)AuCl (210 mg, 0.66 mmol) in THF (2 mL) was added a solution of **4.3** (200 mg, 0.32 mmol) in THF (2 mL). The mixture was stirred for an hour and then the volatiles were removed in vacuo. The crude product was recrystallized from dichloromethane/ethanol. Yield: 190 mg (55%).

^{31}P NMR (162 MHz, CD_2Cl_2): δ = -0.14 (d, J_{HP} = 16 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.06-6.13 (m, 16H, aromatic), 6.70 (1H, vinyl), 5.57 (d, J_{HP} = 16 Hz, 1H, CPh_2H), 2.62 (br s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 2.10 (s, 3H), 2.09 (bs, 3H), 1.78 (3H), 1.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 177.6, 144.6 (d, J_{CP} = 3 Hz), 141.6, 141.1, 137.2, 137.1 (d, J_{CP} = 4 Hz), 136.7, 135.9, 135.1, 134.9, 134.4, 132.9, 131.5, 131.4 (2C), 130.4, 130.3 (d, J_{CP} = 7 Hz), 130.1, 130.0, 129.9, 129.8, 129.7, 129.3, 129.2 (d, J_{CP} = 3 Hz), 128.8 (d, J_{CP} = 5 Hz), 125.0 (d, J_{CP} = 58 Hz), 117.8 (d, J_{CP} = 63 Hz), 50.7 (d, J_{CP} = 36 Hz), 21.6, 21.5 (2C), 21.3, 18.5, 17.9, 16.7. MS (EI, 70 eV): 853, 852 [2, 1; M^+-AuCl], 688, 687, 686, 685, 684 [1, 3, 6, 7, 14; M^+-

AuCl-$CHPh_2$]; 168, 167 [39, 100; $CHPh_2^+$]. Anal. Calcd for $C_{43}H_{45}N_2PAu_2Cl_2 \cdot CH_2Cl_2$: C, 45.15; H 4.05; N 2.39; Found: C, 45.85; H 4.32; N 2.54.

4.4.6 Synthesis of 4.10

To a solution of 3 (200 mg, 0.32 mmol) in THF (2 mL) was added a solution of (tht)AuCl (50 mg, 0.16 mmol) in THF (5 mL). The mixture was stirred for an hour, during which time a white precipitated formed. The volatiles were removed in vacuo. Crystals suitable for X-ray crystallography were obtained by recrystallization from dichloromethane/pentane in air. Yield: 170 mg (72%).

^{31}P NMR (162 MHz, CD_2Cl_2): δ = -37.8. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.56-6.43 (m, 32H, aromatic), 6.59 (d, J_{HP} = 2 Hz, 1H, vinyl), 5.20 (d, J_{HP} = 5 Hz, 1H, CPh_2H), 2.46 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H), 1.67 (d, J_{PH} = 3 Hz, 3H), 1.60 (s, 3H), 1.46 (d, J_{HP} = 3 Hz, 3H), 1.16 (d, J_{HP} = 1 Hz, 3H), 0.71 (d, J_{HP} = 3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 186.5, 148.3, 147.9, 144.6, 141.6 (d, J_{CP} = 14 Hz), 141.5, 140.7 (d, J_{CP} = 15 Hz), 140.0, 139.8, 136.5, 135.7, 135.0, 134.9, 134.4, 133.1, 132.7 (d, J_{CP} = 24 Hz), 130.8, 129.5 (2C), 129.4, 129.3, 129.2, 128.9 (2C), 128.7, 128.2 (2C), 128.1, 127.8, 127.3, 123.1 (d, J_{CP} = 17 Hz), 47.5 (d, J_{CP} = 8 Hz), 23.2 (d, J_{CP} = 35 Hz), 21.7, 21.5, 21.4, 21.2, 17.9 (d, J_{CP} = 6 Hz), 17.5, 16.7, 16.2. Anal. Calcd for $C_{86}H_{90}N_4P_2AuCl \cdot H_2O$: C, 69.23; H, 6.21; N, 3.76; Found: C, 69.28; H, 6.20; N, 3.74.

4.4.7 Synthesis of 4.13

To a solution of $[(cod)RhCl]_2$ (100 mg, 0.20 mmol) in THF (2 mL) was added a solution of **4.3** (266 mg, 0.41 mmol) in THF (2 mL). The mixture was stirred for an hour and then the volatiles were removed in vacuo. The crude product was recrystallized from THF/pentane. Yield: 310 mg (88%).

^{31}P NMR (162 MHz, CD_2Cl_2): δ = -38.4 (64%), -39.1 (36%). ^{1}H NMR (400 MHz, CD_2Cl_2) (major): δ = 7.66-6.49 (m, 17H, 16 aromatic + 1 vinyl), 5.26 (d, J_{HP} = 4 Hz, 1H, CPh_2H), 4.33 (m, 2H, CH^{cod}), 3.24 (m, 2H, CH^{cod}), 2.60 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.74 (m, 4H, CH_2^{cod}), 1.58 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.50 (s, 4H, CH_2^{cod}), 1.41 (s, 3H, CH_3). ^{1}H NMR (400 MHz, CD_2Cl_2) (minor): δ = 7.64-6.52 (m, 17H, 16 aromatic + 1 vinyl), 5.24 (d, J_{HP} = 4 Hz, 1H, CPh_2H), 4.33 (m, 2H, CH^{cod}), 3.33 (m, 2H, CH^{cod}), 2.62 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.74 (m, 4H, CH_2^{cod}), 1.59 (s, 3H, CH_3), 1.50 (s, 4H, CH_2^{cod}), 1.13 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 186.2 (d, J_{CRh} = 51 Hz, major N-C-N), 185.5 (d, J_{CRh} = 50 Hz, minor N-C-N). MS (EI, 70 eV): 869, 868, 867, 866 [10, 24, 28, 50; M^+]; 831, 830 [4, 6; M^+-HCl]; 723, 722 [5, 12; M^+-HCl-C_8H_{12}]; 623, 622, 621 [12, 50, 100; $PIMesH^+$]; 455, 454 [22, 44; $PIMesH^+$-$CHPh_2$]; 306, 305 [5, 22; $IMesH^+$]; 304, 303 [14, 53; $IMes^+$-H]; 168, 167 [12, 52; $CHPh_2^+$]. Anal. Calcd for $C_{51}H_{57}ClN_2PRh$: C, 70.62; H 6.62; N 3.23; Found: C, 70.33; H 6.57; N 3.30.

4.4.8 Synthesis of 4.14

To a solution of $[(cod)IrCl]_2$ (50 mg, 0.07 mmol) in THF (2 mL) was added a solution of **4.3** (94 mg, 0.15 mmol) in THF (2 mL). The mixture was stirred for an hour and then the volatiles were removed in vacuo. The crude product was recrystallized from dichloromethane/pentane. Yield: 113 mg (79%).

^{31}P NMR (162 MHz, CD_2Cl_2): δ = -38.5 (62%), -39.3 (38%). ^{1}H NMR (400 MHz, CD_2Cl_2) (major): δ = 7.67-6.49 (m, 17H, 16 aromatic + 1 vinyl), 5.27 (d, J_{HP} = 4 Hz, 1H, CPh_2H), 3.94 (m, 2H, CH^{cod}), 2.96 (br m, 2H, CH^{cod}), 2.63 (s, 3H, CH_3), 2.37 (s, 3H,

CH_3), 2.35 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.56 (br m, 4H, CH_2^{cod}), 1.55 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.24 (s, 3H, CH_2^{cod}). ^{1}H NMR (400 MHz, CD_2Cl_2) (minor): δ = 7.65-6.52 (m, 17H, 16 aromatic + 1 vinyl), 5.25 (d, J_{HP} = 4 Hz, 1H, CPh_2H), 3.91 (m, 2H, CH^{cod}), 2.96 (br m, 2H, CH^{cod}), 2.63 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.17 (s, 6H, 2 x CH_3), 1.83 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.56 (br m, 4H, CH_2^{cod}), 1.24 (s, 3H, CH_2^{cod}), 1.18 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 183.7 (s, major N-C-N), 182.8 (s, minor N-C-N). MS (EI, 70 eV): 960, 959, 958, 957, 956, 955, 954 [5, 18, 42, 55, 100, 29, 50; M^+]; 920, 919, 918 [2, 3, 6; M^+-HCl]; 792, 791, 790, 789, 788, 787 [2, 5, 6, 14, 4, 6; M^+-$CHPh_2$]; 455, 454, 453 [12, 23, 30; $PIMes^+$-$CHPh_2$]; 168, 167 [25, 99; $CHPh_2^+$]. Anal. Calcd for $C_{51}H_{57}ClN_2PIr$: C, 64.03; H 6.01; N 2.39; Found: C, 64.04; H 6.00; N 3.00.

4.4.9 Synthesis of 4.15

A stream of CO gas was bubbled through a stirred solution of **4.13** (100 mg, 0.12 mmol) in dichloromethane (5 mL) for 15 minutes. The solvent was removed in vacuo and the product washed with hexanes. Yield: 85 mg (90%).

^{31}P NMR (162 MHz, CD_2Cl_2): δ = -38.6. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.67-6.51 (m, 17H, 16 aromatic + 1 vinyl), 5.29 (d, J_{HP} = 4 Hz, 1H, CPh_2H), 2.63 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.56 (d, J_{HP} = 3 Hz, 3H, CH_3), 1.23 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 185.7 (d, J_{CRh} = 54 Hz, CO), 183.4 (d, J_{CRh} = 74 Hz, N-C-N), 178.6 (d, J_{CRh} = 47 Hz, CO). IR ν_{CO} (cm^{-1}): 2070.5, 1983.2. Anal. Calcd for $C_{45}H_{45}ClO_2N_2PRh$: C, 66.30; H 5.56; N 3.44; Found: C, 66.34; H 5.82; N 3.17.

4.4.10 Synthesis of 4.16

A stream of CO gas was bubbled through a stirred solution of **4.14** (50 mg, 0.05 mmol) in dichloromethane (5 mL) for 15 minutes. The solvent was removed in vacuo. Yield (**4.16**·cod): 43 mg (81%).

^{31}P NMR (162 MHz, CD_2Cl_2): δ = -38.8. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.66-6.51 (m, 17H, 16 aromatic + 1 vinyl), 5.29 (d, J_{HP} = 5 Hz, 1H, CPh_2H), 2.63 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.55 (d, J_{HP} = 3 Hz, 3H, CH_3), 1.22 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 180.8 (CO), 177.1 (N-C-N), 169.1 (CO), 148.3, 148.0, 145.0 (d, J_{CP} = 5 Hz), 141.8 (d, J_{CP} = 13 Hz), 141.4 (d, J_{CP} = 19 Hz), 141.3, 141.1, 140.2, 140.0, 137.3, 136.7, 136.0, 135.6, 135.3, 133.9, 133.3, 133.0, 130.9, 130.4, 129.6, 129.5, 129.4, 129.0, 128.8, 128.4, 128.3, 127.8, 127.2, 123.6 (d, J_{CP} = 21 Hz), 47.8 (d, J_{CP} = 8 Hz), 23.3 (d, J_{CP} = 35 Hz), 21.8, 21.5, 21.4, 21.3, 19.5 (d, J_{CP} = 17 Hz), 18.9, 18.2, 17.5. MS (EI, 70 eV): 907, 906, 905, 904, 903, 902 [1, 2, 2, 4, 1, 2; M^+]; 879, 878, 877, 876, 875, 874 [3, 6, 8, 16, 4, 8; M^+-CO]; 792, 791, 790, 789, 788, 787 [2, 5, 6, 14, 4, 6; M^+-$CHPh_2$]; 684, 683, 682, 681, 680, 679 [1, 3, 4, 9, 3, 8; $PIMesIrCl^+$-$CHPh_2$]; 168, 167 [28, 100; $CHPh_2^+$]. IR νCO (cm^{-1}): 2056.2, 1966.6. Anal. Calcd for $C_{45}H_{45}ClN_2O_2PIr·C_8H_{12}$: C, 62.67; H 5.36; N 2.81; Found: C, 63.04; H 5.42; N 2.81.

4.4.11 X-Ray Crystallography

All single crystals were immersed in oil and mounted on a glass fiber. Data were collected at 173±0.1K on a Bruker X8 APEX 2 diffractomer with graphite-monochromated Mo Kα radiation. Data was collected and integrated using the Bruker SAINT[152] software package and corrected for absorption effect TWINABS[154] (for

4.14) and SADABS[153] (for all others). All data sets were corrected for Lorentz and polarization effects. All structures were solved by direct methods[155] and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXTL[156] crystallographic software package from Bruker-AXS. All data sets were corrected for Lorentz and polarization effects. Additional crystal data and details of the data collection and structure refinement are given in Table 4.10.

The crystals of **4.3**, **4.7** and **4.9** presented no crystallographic complications. The structure of **4.5**, **4.10**, and **4.16** each exhibited some disorder. For **4.5**, it appears the oxygen atom is disordered to every position of the ring; however, since the solvate simply seems to be filling a void space in the crystal, the same site is occupied by a partial benzene molecule in **4.3** and **4.7**, the partial THF molecule was modeled as a single species. In **4.10**, the oxygen of the water solvate could be refined anisotropically, but it was not possible to assign protons to specific Q-peaks. In **4.16**, the Cl and CO ligands cis to the carbene ligand are disordered over both positions, with the major isomer (83%) being shown in Figure 4.16. The crystal of **4.14** was a two component twin, present in a 3:2 ratio, where the minor component is related to the major component by a 180° rotation about the (1 0 0) reciprocal axis.

4.4.12 Computational Details

Geometry optimization for all compounds presented in Figures 4.8-4.11 were performed using the Vosko-Wilk-Nusair local density approximation with exchange and correlation corrections from Becke[307] and Perdew,[308, 309] respectively (BP86). Slater-type orbitals[279] (STOs) were used for the triple zeta basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied

with no molecular symmetry. The general numerical integration was 6.0. Initial coordinates of compounds used for DFT calculations were obtained directly from the X-ray crystal structures when available. The DFT calculations were performed using the Amsterdam Density Functional (ADF) Package Software ADF2007.01 and ADF2010.01.[278-282] The run files corresponding to the geometry optimization will be provided in the Supporting Information of the paper in which these results are published.

Table 4.10. Crystallographic Data for Compounds **4.3**, **4.5**, **4.7**, **4.9**, **4.10**, **4.14** and **4.16**.

	4.3·0.5C_6H_6	**4.5**·0.5C_6H_6	**4.7**·0.5C_4H_8O	
Formula	$C_{46}H_{48}N_2P$	$C_{45}H_{47}N_3P$	$C_{45}H_{47}F_2ON_2P$	
FW	659.83	660.83	692.82	
cryst syst	monoclinic	Monoclinic	monoclinic	
space group	C2/c	C2/c	C2/c	
a (Å)	30.592(2)	30.427(4)	28.942(2)	
b (Å)	15.388(1)	14.980(2)	15.805(1)	
c (Å)	18.693(1)	18.825(2)	19.737(1)	
α (deg)	90	90	90	
β (deg)	117.843(2)	117.373(5)	118.977(2)	
γ (deg)	90	90	90	
V (Å^3)	7781.0(7)	7619.3(16)	7898.3(9)	
T (K)	173	173	173	
μ(Mo Kα) (cm^{-1})	1.04	1.07	1.13	
cryst size (mm^3)	0.5 × 0.35 × 0.2	0.7 × 0.4 × 0.1	0.5 × 0.4 × 0.1	
Calcd density (Mg m^{-3})	1.127	1.152	1.165	
2θ(max) (deg)	55.8	56	55.8	
no. of reflns	43060	34727	44723	
no. of unique data	9259	9162	9340	
R(int)	0.0492	0.1151	0.1	
refln/param ratio	20.12	19.91	19.75	
R1[a] ($I > 2\sigma(I)$)	0.0506	0.0673	0.644	
wR2 (all data)[b]	0.1401	0.1673	0.1561	
GOF	1.016	0.972	0.972	
	4.9·CH_2Cl_2	**4.10**·2CH_2Cl_2·H_2O	**4.14**·1.5CH_2Cl_2	**4.16**·C_7H_8
Formula	$C_{44}H_{47}Au_2Cl_4N_2P$	$C_{88}H_{96}AuCl_3N_4OP_2$	$C_{105}H_{120}Cl_8Ir_2N_4P_2$	$C_{52}H_{53}ClIrN_2O_2P$
Fw	1170.54	1661.84	2167.99	996.58
cryst syst	monoclinic	monoclinic	triclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/n$	P-1	Pbcn
a (Å)	15.736(1)	17.381(1)	15.941(1)	29.159(1)
b (Å)	17.923(1)	26.341(2)	16.121(1)	18.337(1)
c (Å)	16.645(1)	18.497(1)	20.855(2)	17.068(1)
α (deg)	90	90	89.941(4)	90
β (deg)	113.592(1)	108.149(2)	68.341(5)	90
γ (deg)	90	90	76.550(4)	90
V (Å^3)	4302.1(3)	8047.2(11)	4823.0(6)	9126.2(5)
T (K)	173	100	100	100
μ(Mo Kα) (cm^{-1})	71.31	20.82	30.61	30.61
cryst size (mm^3)	0.8 × 0.4 × 0.1	0.25 × 0.1 × 0.1	0.25 × 0.2 × 0.1	0.25 × 0.15 × 0.1
Calcd density (Mg m^{-3})	1.807	1.372	1.493	1.451
2θ(max) (deg)	55.8	49.4	56.4	55.8
no. of reflns	30967	59370	116130	67757
no. of unique data	10277	13713	36890	10883
R(int)	0.0449	0.0372	0.0482	0.029
refln/param ratio	20.93	14.78	33.26	19.72
R1[a] ($I > 2\sigma(I)$)	0.0344	0.0363	0.0468	0.0234
wR2 (all data)[b]	0.0891	0.0964	0.1329	0.0511
GOF	1.016	1.104	1.076	1.011

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2(F^2\ [\text{all data}]) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

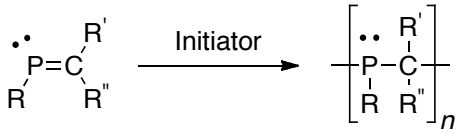
Chapter 5: Conclusion

The most exciting phrase to hear in science, the one that heralds the most discoveries, is not "Eureka!" (I found it!) but “That's funny...”

– Isaac Asimov

5.1 Summary of Thesis Work

As outlined in Chapter 1, the initial idea behind my project was to extend the P=C/C=C analogy[11, 12] to the synthesis of new poly(methylenephosphine) polymers (**5.1**) bearing bulky alkyl-P-substituents (Scheme 5.1).[85, 108] It is anticipated that phosphines centers in poly(methylenephosphine) **5.1** and related copolymers would be more electron rich than those present in polymers derived from phosphaalkene MesP=CPh_2 (**5.2**). As such, their use as macromolecular ligands may lead to more active polymer supported catalysts for reactions such as palladium-mediated Suzuki-Miyaura cross-couplings.[109, 110]

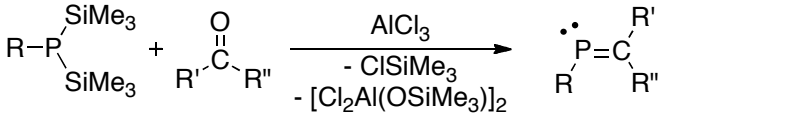


5.1: R = *t*Bu or Ad

Scheme 5.1 General polymerization of alkyl-P-substituted phosphaalkenes

Before such polymerization studies could begin, however, suitable phosphaalkene monomers would have to be synthesized. Whereas methods like the phospha-Peterson[32, 50, 122-129] reaction work well for preparing Mes-P-substituted phosphaalkenes,[51, 130] due to difficulties in generating the requisite alkylsilylphosphide intermediates, such methods are generally less well suited to the preparation of P-alkyl-substituted phosphaalkenes.[51]

The $AlCl_3$-mediated strategy presented Chapter 2 represents a significant improvement for the preparation of *t*BuP=CH*t*Bu (**5.3**), reducing the time required for its synthesis from 11 weeks to under one hour.[97] Preliminary investigations into the scope of this new methodology reveal it to be tolerant to a variety of substituents, including alkyl, aryl and even silyl substituents, and I used it to prepare AdP=CH*t*Bu (**5.4**), which is only the second known isolable Ad-P substituted phosphaalkene,[134] MesP=CPh_2 (**5.2**) and MesP=CH*t*Bu (**5.5**) on prepative scales (Scheme 5.2). Last, but not least, I synthesized $AlCl_3$ and $GaCl_3$ adducts of phosphaalkenes **5.3** and **5.4**. Whereas the free phosphaalkenes are liquids, I was able to obtain crystals of the Lewis-adducts suitable for characterization by X-ray crystallography, which revealed typical[144] P=C bonds lengths (avg. 1.64 Å) and that, as might be expected, the bulky alkyl substituents are configured in a *trans* arrangement.

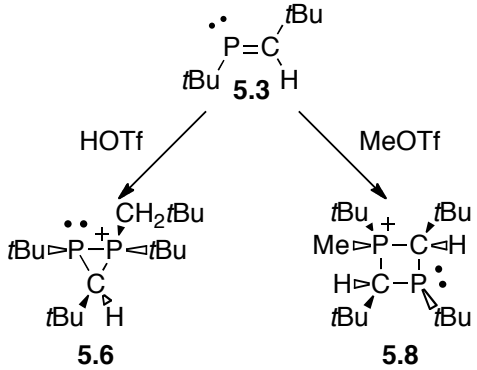


5.2: R = Mes; R' = R" = Ph
5.3: R = *t*Bu; R' = *t*Bu; R" = H
5.4: R = Ad; R' = *t*Bu; R" = H
5.5: R = Mes; R' = *t*Bu; R" = H

Scheme 5.2 Phosphaalkenes prepared on prepative scale using the Lewis acid-mediated synthesis

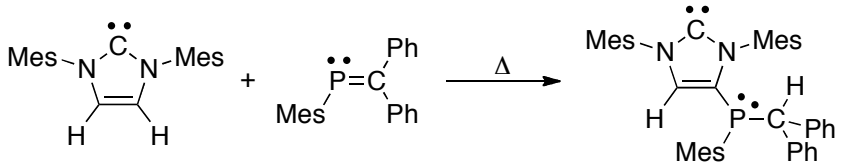
With a convenient synthesis of alkyl-P-substituted phosphaalkenes in hand, I began to explore the possible cationic polymerization these electron-rich phosphaalkenes with cationic initiators. As expected for "normal" phosphaalkenes ($^{\delta+}P=C^{\delta-}$),[74] treatment of phosphaalkene **5.3** results in addition of H^+ to the P=*C* atom to afford the phosphenium triflate intermediate [*t*BuP^+-CH_2*t*Bu] (**5.7**),[170] which can then react with a second equivalent of monomer to afford a rare diphosphiranium **5.6** (Scheme 5.3).[87, 101] The phosphenium triflate can also be trapped using 2-butyne to afford an aromatic

phosphirenium cation with a triflate counter-ion.[176] Unexpectedly, treating **5.3** with MeOTf affords the diphosphetanium **5.8** via a methylenephosphonium intermediate [*t*Bu(Me)P^{+}=CH*t*Bu] (**5.9**). Notably, the direct formation of methylenephosphonium from phosphaalkenes had been previously discounted.[310] Intriguingly, diphosphetanium **5.8** will react with two additional equivalents of MeOTf to afford an unprecedented dicationic diphosphetanium.



Scheme 5.3 Electrophile-dependent cyclodimerzation product from reactions of phosphaalkene **5.3** with EOTf (E = H or Me)

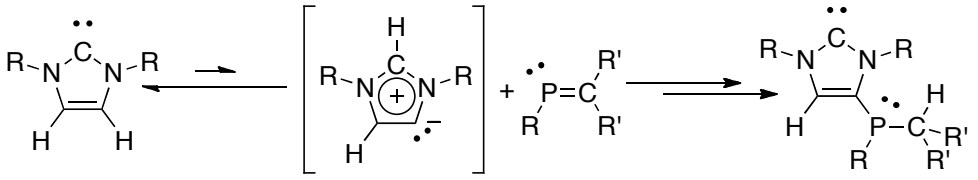
Finally, in Chapter 4, I describe the unexpected abnormal reaction of IMes, a N-heterocyclic carbene (NHC), with phosphaalkenes.[224-226, 228, 311] Although no reaction between IMes and phosphaalkene **5.2** was observed at ambient temperatures, heating the reaction mixture at 70 °C overnight afforded complete conversion of the phosphaalkene to a new P-containing product. X-ray crystallographic analysis confirmed unambiguously the formation of an unprecedented 4-phosphino-2-carbene **5.10** (Scheme 5.4). Remarkably, the reaction of IMes with MesP=C(4-$C_6H_4F)_2$ proceeded without needing to be heated.



5.2 **5.10**

Scheme 5.4 Formation of NHC **5.10** from IMes and phosphaalkenes **5.2**

Interestingly, computational studies into plausible mechanisms for this unanticipated transformation suggest the nucleophile that adds to the P=C bond is an abnormal NHC (*a*NHC) rather than a normal NHC (Scheme 5.5). Although the *a*NHC isomer is calculated to be ~50 kJ mol^{-1} less stable than its normal isomer, its involvement has been invoked previously in cases where access to the electrophilic center is inhibited by significant steric bulk.[236]



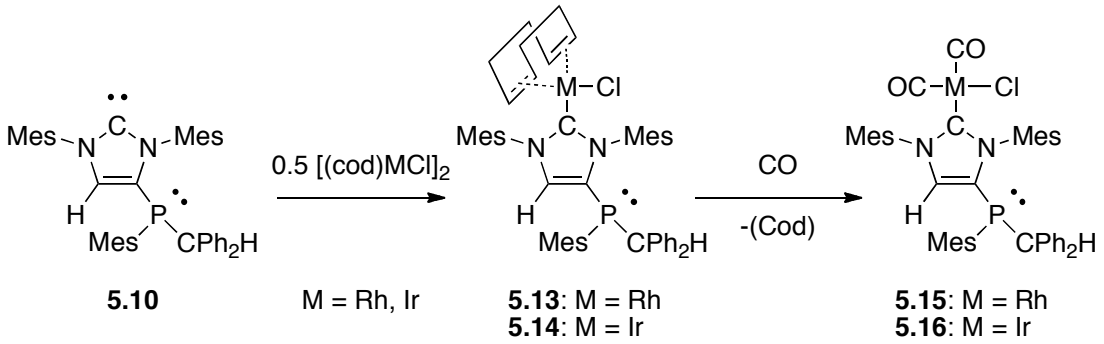
NHC *a*NHC

Scheme 5.5 Postulated mechanism for formation of 4-phosphino-2-carbenes

The coordination properties of this novel class of bifunctional ligands were also investigated. Treating carbene **5.10** with substoichiometric (tht)AuCl (0.5 equiv) afforded the biscarbene complex **5.11**, indicating that AuCl is preferentially coordinated by the carbene functionality. However, P-coordination of gold(I) will occur when carbene **5.10** is treated with two equivalents of AuCl to give the digold complex **5.12**.

A standard method for assessing the relative donor strength of NHC is done by comparing the carbonyl stretching frequencies of the respective metal carbonyl complexes $(NHC)M(CO)_2Cl$ (M = Rh, Ir). Therefore, I prepared complexes **5.13** and **5.14** from the reaction of the metal dimer $[M(cod)Cl]_2$ (M = Rh, Ir) with free carbene **5.10** (Scheme 5.6). Subsequently, I replaced the cod ligands by bubbling the respective

solutions of the metal complexes with CO to afford **5.15** and **5.16**. Notably, the IR data suggests that carbene **5.10** is as good, or possibly better, donor than unsubstituted IMes.



Scheme 5.6 Formation of Rh and Ir cod- and carbonyl-complexes

5.2 Closing Remarks

Essential to life, and yet a deadly poison, phosphorus is an intriguing element whose chemistry bridges both organic and inorganic chemistry. At the union of these two domains of synthetic chemistry lies the study of low-valent phosphorus species, such as phosphaalkenes. The reactivity of these remarkable compounds is often said to mimic that of low-valent carbon, yet, due to the presence of the phosphorus atom(s), the products of these reactions frequently possess properties and functionality unattainable from their so-called carbon counterparts (i.e. heterocycles). More over, the lessons learned in studying such exotic species can bring new insights to established fields of study (i.e. *a*NHCs). If this thesis has a take home message it is this: whether you consider yourself an organic, an inorganic, or, perhaps most appropriately, a synthetic chemists, the world of chemistry is a fascinating place to explore.

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