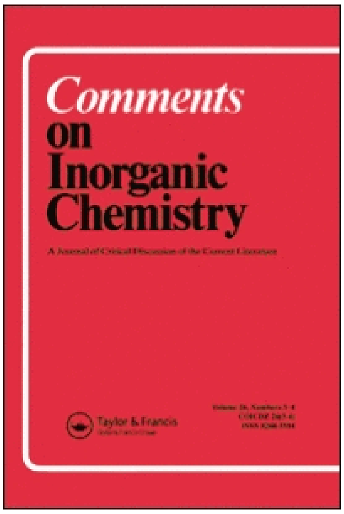

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Transition Metal Chemistry of a Novel and Versatile Heterodifunctional Phosphorus-Nitrogen Ligand System

K. V. Katti[a]; R. G. Cavell[a]
[a] Department of Chemistry, University of Alberta, Alberta, Canada

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Transition Metal Chemistry of a Novel and Versatile Heterodifunctional Phosphorus–Nitrogen Ligand System

K. V. KATTI and R. G. CAVELL
Department of Chemistry,
University of Alberta,
Edmonton, Alberta,
Canada T6G 2G2

Key Words: *ligands, heterobifunctional, phosphorus nitrogen, imine, phosphine, transition metal, chelate, bimetallic*

I. INTRODUCTION

There is considerable current interest in the chemistry of transition metal complexes containing ligands with distinctly different heteroatomic donor atoms because of the key role that such systems are likely to play in the development of useful catalysts for specific chemical transformations.[1] Use of heterodifunctional ligands: $R_2P-C_6H_4-CO_2^-$,[2] $R_2P-C_6H_4-SO_3^-$,[3] $R_2P-CH{=}C(R)OH$[4] and $R_2P-CH_2)_n-P(O)R_2$[1o] or functionalized substituents such as $O-CH_2PR_2$[1h] are but a few examples of a large class of heterodifunctional phosphines, the metal complexes of which have found important industrial applications as useful homogeneous catalysts and catalyst precursors. Despite the importance of heterofunctional phosphine

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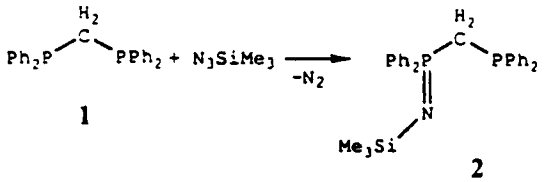
ligands in general, efforts to develop the chemistry of this class of main group systems and also to develop directed synthetic strategies which can be applied to the synthesis of a series of ligands in which the structure and substituents may be varied to "tune" the reactivity of one or more of the heteroatoms has been spotty. A unified and systematic approach to the synthesis of carefully designed heterodifunctional ligands would therefore present considerable opportunities for the formation of a variety of metal complexes with useful chemical and stereochemical catalytic properties. Herein we describe our development of a novel and unified approach to the synthesis of heterodifunctional phosphines (and arsines) and the new transition metal organometallic and coordination chemistry that has emerged from the use of this ligand system.

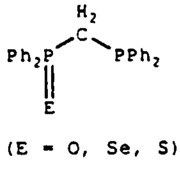
II. A SYNTHETIC APPROACH TO HETERODIFUNCTIONAL LIGANDS

Our approach to the synthesis of new heterodifunctional ligands involved the partial oxidation of alkane diphosphines with azidotrimethylsilane via the well-known Staudinger reaction (Eq. (1)).[5]



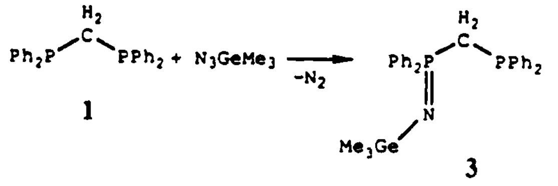
1 2 (1)

Although the partially oxidized products of 1, the monoxide,[6] monoselenide[7] and the monosulfide[8] are known, the formation of 2 represents the first example of a partial oxidation of 1 with a nitrogen base.



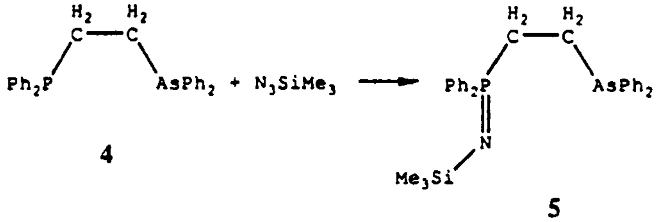
(E = O, Se, S)

This approach is general and has been applied to diphosphines of alkane chain lengths of up to 6. Use of azidotrimethyl germane produced a germyl functionalized phosphoraniminophosphine 3 (Eq. (2)).[9]



(2)

The closely related phosphoranimino arsine, $Me_3SiN{=}PPh_2(CH_2)_2AsPh_2$, can also be obtained from a Staudinger reaction with ARPHOS (Eq. (3)).



(3)

Under the conditions used the oxidation of ARPHOS was selective at phosphorus even when the reaction was carried out in the presence of excess amounts of Me_3SiN_3.[10] Unlike the preparations of $(E)PPh_2CH_2PPh_2$ (E = O, S or Se) which are tedious and produce low yields,[6-8] our new heterodifunctional ligands 2, 3 and 5 can be produced by straightforward one-step syntheses in almost quantitative yields.

Compounds 2 and 3 present an interesting conformational problem. NMR spectra of fresh CH_2Cl_2 or $CHCl_3$ solutions of the product at normal probe temperatures (^1H, ^{31}P (Fig. 1) and ^{29}Si) show a pattern of complexity (three AX doublets of doublets) consistent with the presence of at least three different conformers. The distribution of conformers is determined by the maximum temperature experienced during synthesis of the material which in these cases is best done in the absence of solvent.[5] The silyl derivative 2 shows only one isomer in solution after a recrystallization

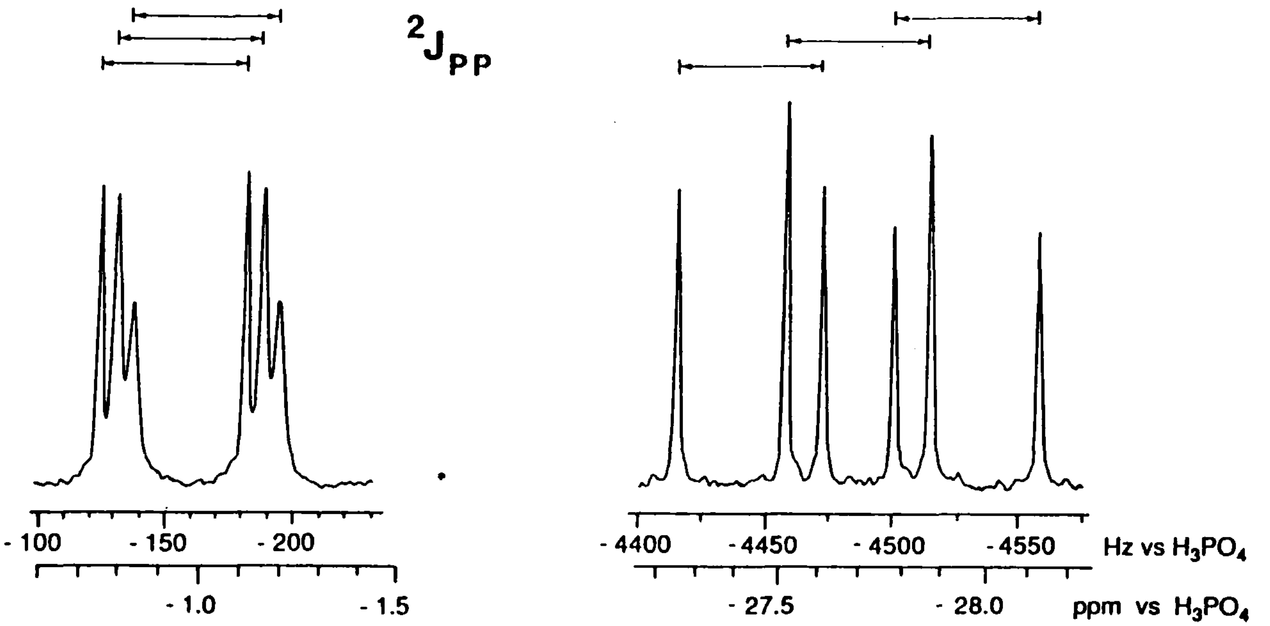
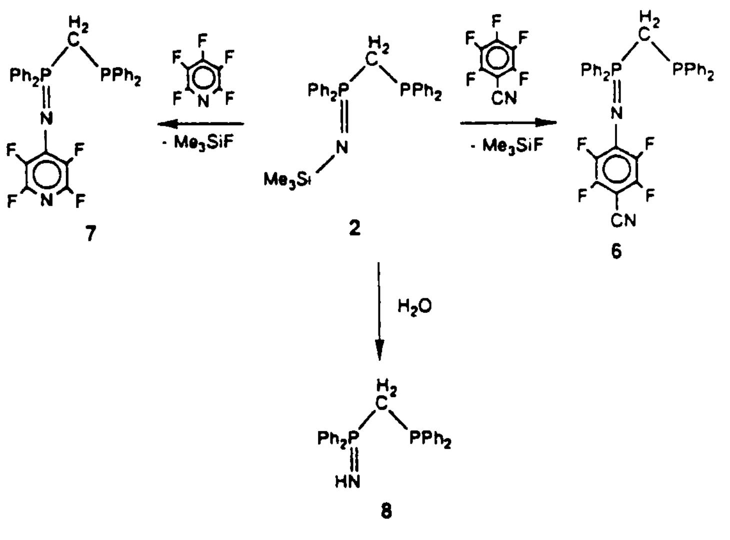


FIGURE 1 $^{31}P\{^1H\}$ NMR (161.98 MHz) spectrum of 2 in CD_2Cl_2 showing three distinct doublet signals in both the high field (P^V) and lower field P^{III} regions. Shifts and ^2J values for the P^V region (left to right) are (−0.94 ppm, 57.20 Hz; −0.98 ppm, 57.15 Hz; −1.02 ppm, 56.99 Hz) and for the P^{III} region (−27.43 ppm, 57.18 Hz; −27.69 ppm, 57.02 Hz; −27.96 ppm, 57.02 Hz). The distributions differ from those shown in Ref. 5 because the sample was a freshly prepared material with different thermal history. The coupling constants and shifts agree within experimental error.

step and does not show fluxional behavior. The initial mixture of conformational isomers must therefore be a metastable state. Remarkably, dissolving **2**, as prepared, in acetonitrile with stirring eventually gives only one isomer. We explain this behavior as a slow recrystallization effect because **2** is poorly soluble in CH_3CN. Specific recrystallization of **3** is required to form one isomer. Notably, however, all reactions of **2** and **3** in whatever initial stereochemical form give only one product. An exception to this uniformity of the product stereochemistry was achieved in the case of a controlled hydrolysis of **2** in CH_2Cl_2 (Scheme 1) which gave **8** in solution showing the same conformational distribution as existed before hydrolysis. All three pairs of P(V) and P(III) doublets therefore react in the same way toward hydrolytic cleavage of the silyl group. In this case the reaction conditions were carefully controlled in order to preserve the conformational distribution if possible. We think that the conformational behavior of these derivatives as initially prepared arises because free rotation about the ligand backbone is hindered in the glassy viscous product which is first obtained. However, the rearrangement is also slow in solution,



SCHEME 1

suggesting that the process of interconversion must have a relatively high barrier. Some control over the isomeric distribution of the product may be introduced by the synthesis route and may be a facet of the mechanism of formation. Some possible conformations of **2** are depicted in Fig. 2.

We have further prepared[5,9,11,12] a series of closely related phosphoranimine phosphines, either by reaction of **2** or **3** with activated fluoroaromatics (**6**, **7**) (Scheme 1), reaction of the diphosphine with fluoroaromatic or adamantyl azides or by hydrolysis of **2** (**8**, R=H). The fluoroaromatic and adamantyl products are crystalline solids and do not show isomeric distribution in the products and this is probably the result of the crystallization of the product. We emphasize again that the conformationally mixed materials **2** and **3** give only *one* product (in the reactions with fluoroaromatics

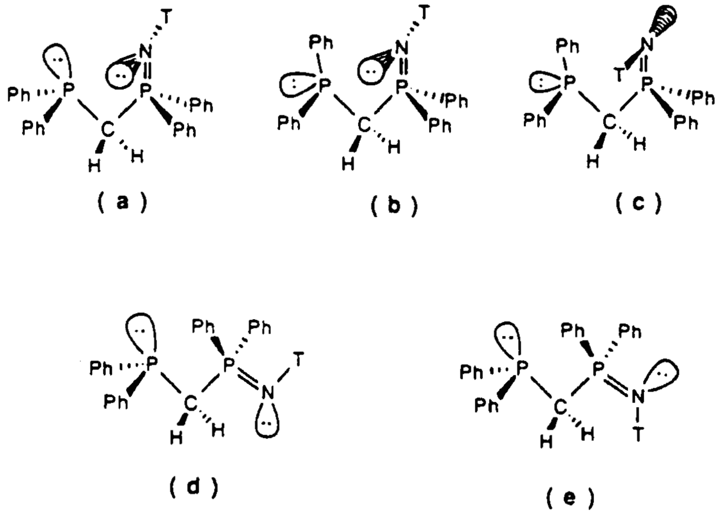
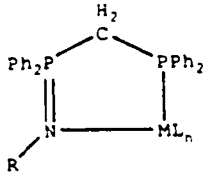


FIGURE 2 A representation of five likely possible conformational isomers of 2 (T = $SiMe_3$). The structures a–c have lone pairs and $SiMe_3$ groups more or less perpendicular to the plane of the paper. Conformations in which (according to models) phenyl and/or $SiMe_3$ groups are in apparent conflict and the conformation containing proximal lone pairs on N and P^{III} (i.e., rotate (a) 90° about the P=N bond toward P^{III}) have been rejected. Similar analysis suggests that (c) is probably also an unlikely conformation. If rotation about the P=N bond is unrestricted, b ≡ c and d ≡ e.

described in Scheme 1 and in all the reactions described below) so the conformational distribution of initial product does not strongly influence the course of the reaction.

III. ELECTRONIC CHARACTERISTICS AND BASICITY CONTROL OF PHOSPHORANIMINE PHOSPHINES

The phosphoranimine phosphine system, $RN{=}PPh_2CH_2PPh_2$, is distinguished from the conventional alkane diphosphines by its structural diversity and chemical flexibility. The phosphoranimine functionality in ligands (**2**–**8**) is isoelectronic to phosphine oxide ($R_3P{=}O$) and these types of systems can function as a 1,[13] a 2[13] or a 4[13,14] electron donor to transition metals. The "hard" nitrogen base center is predisposed to combination with early transition metals and metals in high oxidation states. In addition, the pendant phosphine (R_2P) functionality also incorporated in the ligand structure conveys an affinity for combination with the soft metals (i.e., the "late" transition metals or "early" transition metals in a low-oxidation state). Several reaction modes may be envisaged; the ligand may behave as a single hard or soft Lewis base or the diverse functionalities may act in concert utilizing cooperative interactions to achieve heteratomic chelation as in A.



A

Further, the reactive N–Si or N–Ge bonds in **2** and **3** provide an additional site of reactivity toward metal halides and oxides which can be used to form M–N σ bonds[11] and this may occur in concert with soft base coordination. Finally, the reactive N–Si or N–Ge bonds in **2** or **3** can also be used as a means of "tuning" the basicity of the iminato nitrogen through simple substitution reactions as

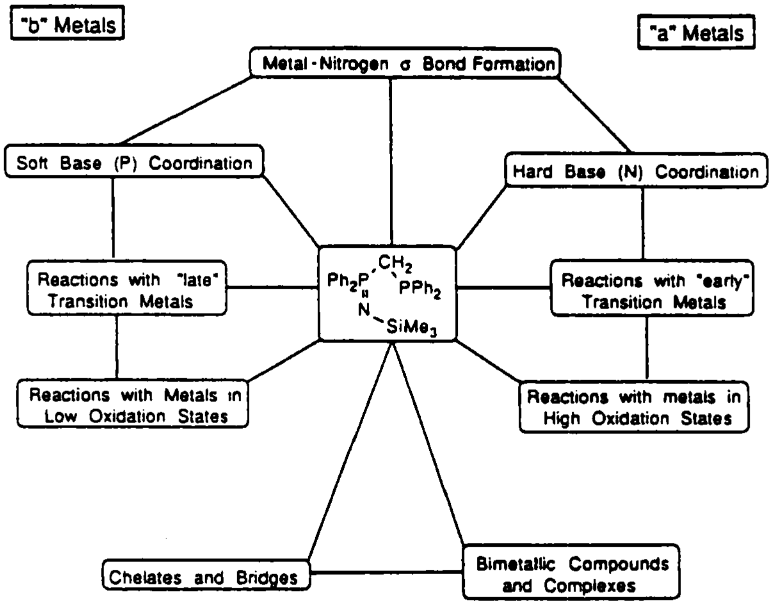


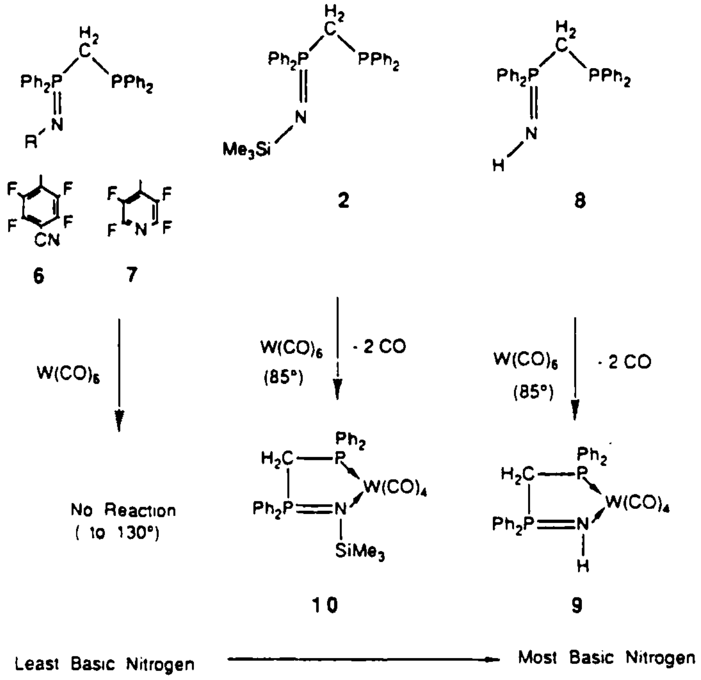
FIGURE 3 An illustration of the relationships of the phosphorus–nitrogen heterobifunctional ligand system with "a" and "b", "early" and "late" and high and low oxidation states of transition metals. Combinations of behavior are to be expected.

illustrated in Scheme 1. The high/low, "early/late" relationships are schematically interconnected in Fig. 3 in order to illustrate the versatility of the system. We have demonstrated all these facets of the reactivity of these molecules[5,9–12,15] and the details are discussed in the following sections. The extensive chemical flexibility provided by our ligand system ultimately allows systematic alteration of the electronic characteristics of a ligand series to an extent which is rare for coordinating ligands. The parent phosphoranimine phosphine ligands **2** and **3** would appear therefore to provide access to a variety of ligands of carefully modified basicity and so create a versatile ligand system which may greatly surpass even the considerable chemical capabilities of conventional mono and ditertiary phosphines.

IV. TRANSITION METAL CHEMISTRY OF PHOSPHORANIMINE PHOSPHINES AND A PHOSPHORANIMINE ARSINE

(A) Reactions with "Early" Transition Metals

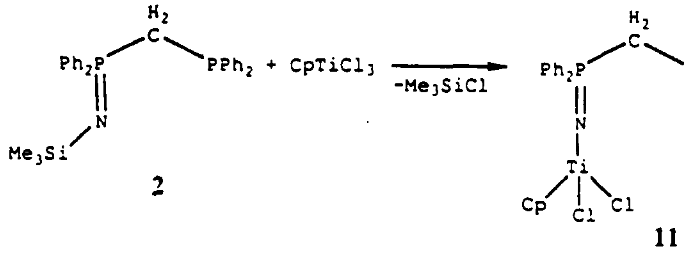
Tungsten and molybdenum carbonyls reacted cleanly with **2** to give the first examples of a potentially large class of cyclometallaphosphoraniminato phosphines (Scheme 2).[10] The contrasting reactivities of $W(CO)_6$ with a selected set of phosphoranimine phosphine ligands which differ in the basicity of the interacting nitrogen center (Scheme 2) shows that such basicity alterations can introduce reactivity control. The sequence also suggests that cooperative interactions between the soft P(III) and the hard nitrogen



SCHEME 2

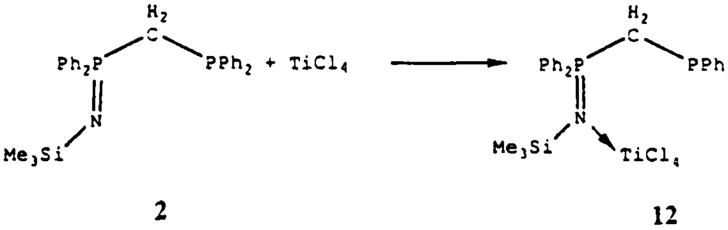
functionalities may be important in directing the chemistry of the system.

The reaction of **2** with $CpTiCl_3$ in diethyl ether afforded the Ti(IV) functionalized phosphoraniminato phosphine in 90% yield by metathetical elimination of Me_3SiCl (Eq. (4)).[5]



(4)

Compound **11**, which contains a Ti(IV)–N σ bond represents the first example of a potentially large class of transition metal functionalized phosphoraniminato phosphines. Although the ligand backbone of **2** is related to the symmetrically substituted phosphoraniminato ligands, $^{-}N{=}PR_3$, which have been extensively used to stabilize high-oxidation-state transition metals[16–18] and actinides,[19] the presence of the free P(III) center in both **2** and **11** allows further reaction of the bound ligand with a variety of additional transition metal derivatives (discussed in the following sections) and permits the exploitation of the heterodifunctionality of the ligands in the quest for bimetallic derivatives. A stable Ti(IV) Lewis Acid-Base phosphoraniminato phosphine complex **12** was obtained in quantitative yields from the reaction (Eq. (5)) of $TiCl_4$ with **2**. Interestingly, Me_3SiCl was not eliminated in this case and the P(III) center also remained unaffected.[15]



(5)

A new mode of reactivity of the bifunctional phosphine **2** and the arsine **5** ligands resulting in formation of M–N σ bonds was observed in their reactions with trimethylsilyloxyperrhenate, $Me_3SiOReO_3$. The metallacycles

$\overline{\text{N=PPh}_2\text{CH}_2\text{PPh}_2\text{Re}}\text{O}_2(\text{OSiMe}_3)_2$ **13**

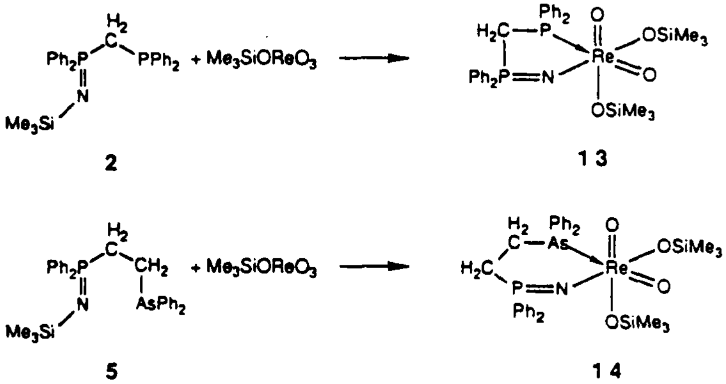
and

$\overline{\text{N=PPh}_2(\text{CH}_2)_2\text{AsPh}_2\text{Re}}\text{O}_2(\text{OSiMe}_3)_2$ **14**

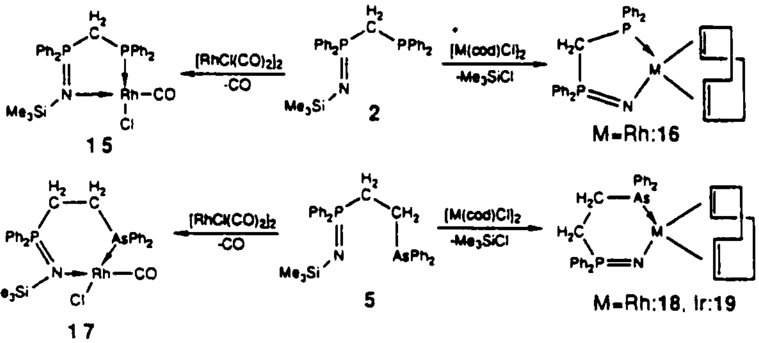
were obtained in almost quantitative yields (Scheme 3) *via* migration of the $SiMe_3$ group to one of the terminal oxygens on Re.[12] The phosphorus NMR data of **13** and **14** suggested significant delocalization of electron density in the Re–N=P framework. Si-29 (INEPT) NMR spectroscopic data supports lower symmetry-structural arrangements for $OSiMe_3$ groups in **13** and **14** and are consistent with the cis-cioxo structure shown.

(B) Reactions with Late-Transition Metals

The heterodifunctional ligand system showed contrasting reactivities toward $[Rh(CO)_2Cl]_2$ and [Rh or $Ir(cod)Cl]_2$ giving rise to



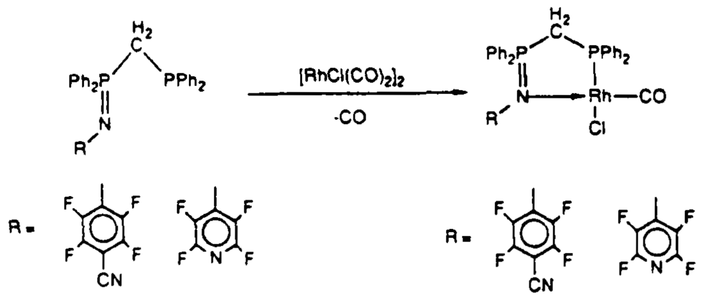
SCHEME 3



SCHEME 4

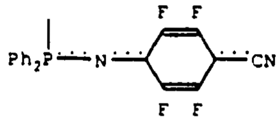
ities toward $[Rh(CO)_2Cl]_2$ and [Rh or $Ir(cod)Cl]_2$ giving rise to new metallacycles with Rh–N coordinate, **15**, and Rh– or Ir–N covalent, **16**, σ bonds, respectively (Scheme 4).[10,11] Parallel reactions with the arsine ligand **5** also (Scheme 4) yielded similar results. These products demonstrate that the iminato nitrogen may act as either a two electron Lewis base or a univalent anion bound to Rh(I) or Ir(I) to give 16-electron M(I) species.[10,11] The difference in reactivity between the cod and carbonyl complexes (Scheme 4) with **2** and **5** is significant and we rationalize this difference by proposing that **2** (or **5**) first react with Rh(I) or Ir(I) complexes to first form the monodentate coordination complex (presumably through the arsane (or phosphine)) end. In the case of the Rh carbonyl complexes, displacement of the relatively labile CO by the nitrogen base yields a stable 16-electron complex which then cannot eliminate Me_3SiCl to form an imide unless another ligand can be provided to stabilize the formally 14-electron product which has been formed by this elimination process. In contrast the M(cod) complexes might provide a route for subsequent Me_3SiCl elimination in a second step using a sequence in which the nitrogen donor site first coordinates to the Rh(I) or Ir(I) center to force the cod substituent to act as a two-electron donor. This intermediate may then eliminate Me_3SiCl to form the imide **16** (or **18**) which is immediately stabilized as a 16-electron species by reestablishment of the cod ligand as a four electron donor.

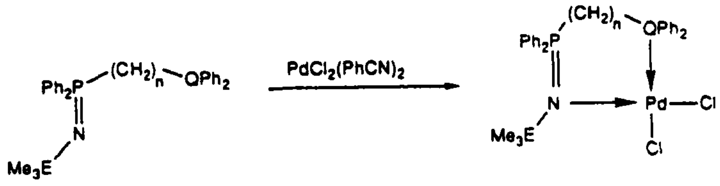
The dramatic electronic effects exerted by the highly electro-



SCHEME 5

negative fluoroaromatic substituents on ligands as in **6** and **7** (Scheme 5) in their complexes with metals is apparent from the ^{31}P NMR spectroscopic data. The large difference of 43 ppm between the chemical shifts of the P(III) and P(V) centers in the parent ligand **6** has been reduced to only 3.9 ppm in **21** (and 3.32 ppm in **20**). Such small differences in NMR chemical shifts between centers with a large formal-valence state difference (P(III) versus P(V)) appears to be unprecedented. It seems that the highly electronegative fluoroaromatic substituent decreases the basicity of the $-N{=}PPh_2$ nitrogen which in turn reduces the strength of the coordination interaction of this nitrogen with the Rh(I) center. However, the electron density from the electron rich Rh(I) center can be delocalized via the imine nitrogen toward the fluoroaromatic substituent. This electronic effect possibly leads to reduced back bonding of Rh(I) with the P(III) phosphine center and this is manifested by the unusual proximity of the shifts for the two kinds of phosphorus in **20** and **21**. A similar electronic interaction between the phosphoranimine phosphorus and the fluoroaromatic substituent through an extended conjugated path such as:





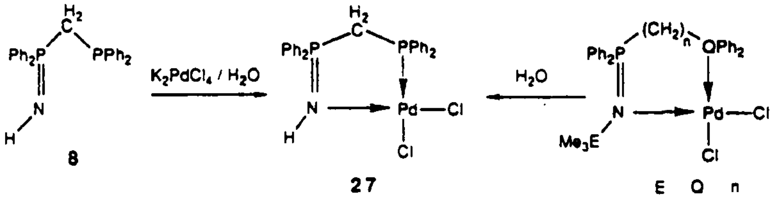
	E	Q	n
2	Si	P	1
3	Ge	P	1
22	Si	P	2
5	Si	As	2

	E	Q	n
23	Si	P	1
24	Ge	P	1
25	Si	P	2
26	Si	As	2

SCHEME 6

may account for the slight deshielding of the phosphoranimine phosphorus (two bonds away from Rh(I)) compared to the directly bound Rh(I)-P(III) center in **20** and **21**. These electronic changes induced by fluoroaromatic substituents illustrate the chemical flexibility offered by the ligands of the type **2**.

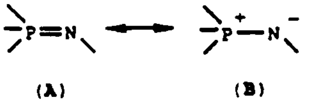
A series of reactions that gave new heteroatomic chelated Pd(II) metallacyclic compounds is illustrated in Scheme 6.[9] Reaction of **2** or **3** in a mixed aqueous/organic solvent system with Pd(II) salts proceeds with the initial hydrolytic cleavage of the silyl or germyl substituent to form the free imine **8** which then complexed *in situ* with Pd(II) to form **27**.[9] For an alternative route the silyl and germyl complexes of Pd(II), **23** and **24**, can be smoothly converted to **27** by means of aqueous hydrolysis (Scheme 7).



	E	Q	n
23	Si	P	1
24	Ge	P	1

SCHEME 7

In general free phosphoraninimines are unstable and the compound **27** represents the first example of a complex containing a free phosphoraninimine phosphine framework. The electronic effects of the highly basic iminato nitrogen in the free ligand **8** and its metal complex **27** are also reflected in the chemical shifts of the phosphiniminato phosphorus center in these compounds. Very marked deshielding of the iminato phosphorus ($N{=}PPh_2$) in these two compounds (**8** and **27**) compared to the analogous free ligand **2** and its metal complex **23** (and also in **24** and **25**) is an apparent consequence of electron density withdrawal by the highly basic iminato nitrogen in **8** and subsequent delocalization of electronic charge across the Pd(II) center in **27**. A similar effect is expected in **2** and **3** (and also in their metal complexes **23** and **24**, respectively); however the ability of Si or Ge substituents to participate in π bonding may modify the delocalization across the Pd center. An X-ray crystallographic investigation of **27** further illuminates the nature of the P–N bond (Fig. 4). The structure of the phosphoraninimines, in general, can be represented as a resonance hybrid of the double bond form (A) and the dipolar form (B).



The P–N bond length in **27** (1.599(6) Å) is within the range of values for covalent radii (1.64 Å)[20] for a double bond and is not significantly different from those of $[N(PPh_3)_2]^+$ (1.60 Å),[21] $Ph_2FP{=}NMe$ (1.641 Å)[22] and $Ph_3P{=}NC_6H_4Br(p)$ (1.56 Å).[23] This means that the P–N bond length observed in **27** is indicative of a large contribution from the double bond form (A) with little or no contribution from the dipolar form (B). The *cis* geometry of the $HNPPh_2CH_2PPh_2$ framework around the square planar Pd(II) center in **27** is similar to the structure reported for the Rh(I) complex of the phosphine–phosphine oxide ligand,[1(b)] $Ph_2PCH_2P(O)Ph_2$ which is isoelectronic with **8**.[9]

(C) Phosphoranimine Phosphines and Phosphoranimine Arsines as Frameworks for "Early–Late" Transition Metal Heterobimetallic Compounds

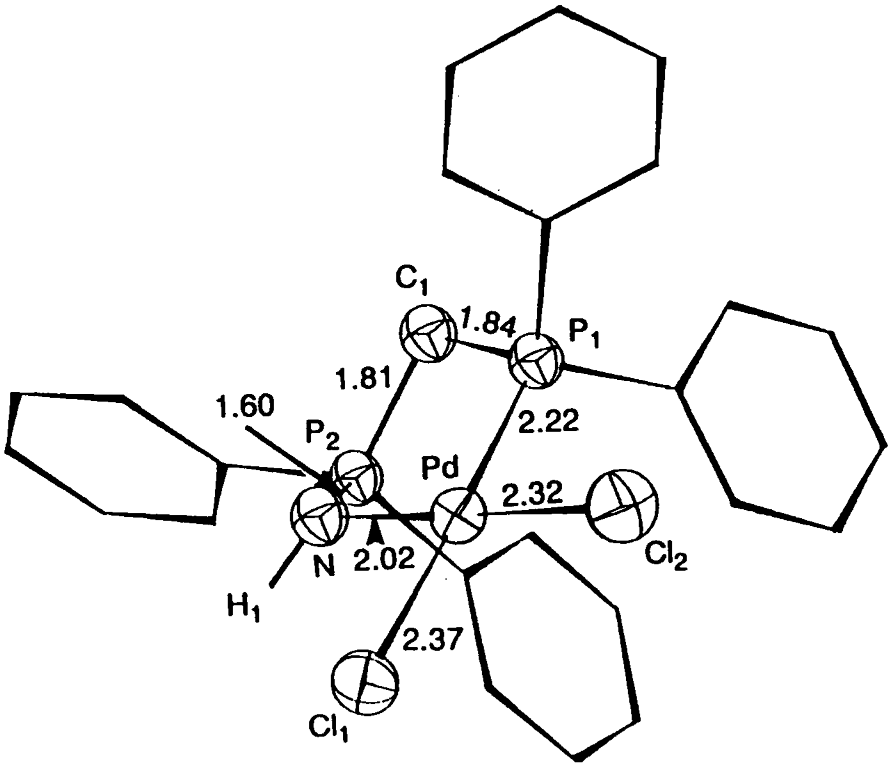
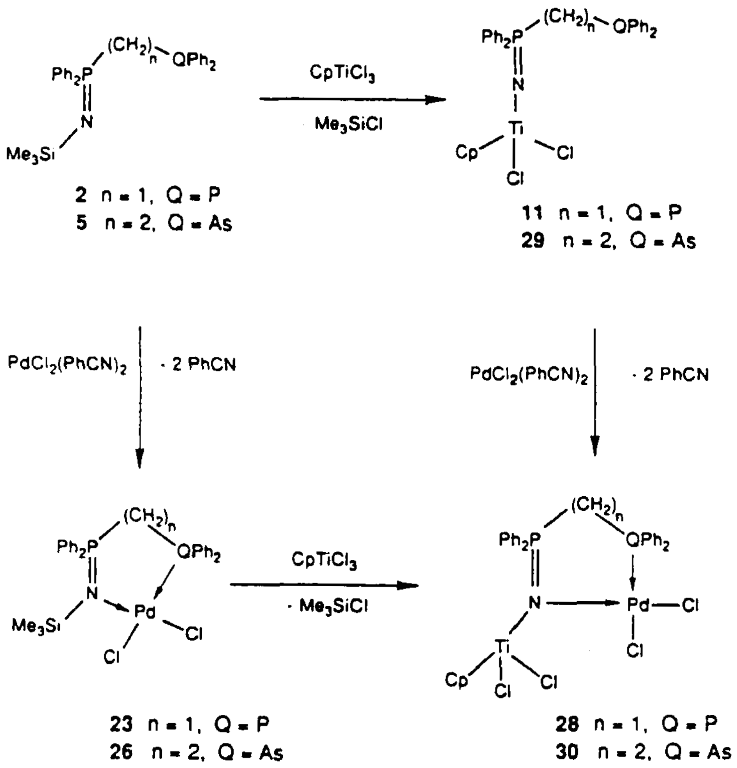


FIGURE 4 The molecular structure of 27 showing the central molecular plane of the molecule. Bond lengths are given in Å. Phenyl substituents are shown as stylized hexagons. [Crystal structure by F. W. B. Einstein and R. J. Batchelor, Simon Fraser University, Burnaby, British Columbia (adapted from Ref. 9).]

The formation of heterobimetallic compounds involving an "early" and a "late" transition metal has been a target of synthetic investigations for quite some time because of the perception that such combinations may have useful applications for organic synthesis and catalyst precursors.[1g,1n,1o,24] However, one of the major difficulties encountered in the synthesis of such compounds has been the construction of suitable non-metal frameworks which can simultaneously bind with both the "early" and "late" transition metals which necessarily present widely differing chemical reactivities. Our ligand system opens a new and versatile approach to the construction of such "early–late" heterobimetallic compounds (Scheme 8).[25] The generality of this synthetic strategy has been



SCHEME 8

demonstrated by approaching the final Ti(IV)-Pd(II) heterobimetallic compounds **28** and **30** by two routes: (i) from the reaction of the metalated ligand containing the "early" transition metal **11** or **29** with $PdCl_2(PhCN)_2$ and (ii) from the reaction of the "late" transition metal complex **23** or **26** with the "early" transition metal compound (Scheme 8). Full ^{31}P NMR spectroscopic analysis of **28**, the resultant heterobimetallic species, and the comparison of the data with those of the precursors **11** and **23** confirms the formulation and reveals some unusual features deriving from the bimetallic constitution. Most notably there is a significant decrease of the $^2J_{PP}$ value in the series **11** (59.73 Hz), **23** (26.20 Hz) and **28** (8.00 Hz) which is indicative of substantial electronic effects on the bonding in the P-C-P unit as a result of the formation of the bimetallic Ti-N-Pd skeleton in **28**. The metallation of the phosphane (PPh_2) unit induces a considerable deshielding of the P(III) center as shown by the change of the ^{31}P NMR shift from -28.95 ppm in **11** to 16.16 ppm in **28** with the result that the chemical shift of the P(III) unit in both **28** and **23** (16.64 ppm) are very similar in keeping with the fact that both are bound to Pd(II). The differences in the chemical shifts of the phosphoraniniminato phosphorus ($-N{=}PPh_2$) unit in the series **11** (38.64 ppm), **23** (34.81 ppm) and **28** (33.40 ppm) are not significant although it is clear that this functionality in **28** is slightly shielded compared to **23**, presumably a result of the donation of electron density into the phosphazene framework by the electron rich Pd(II) center.

V. OUTLOOK

It is clear from the above that the ligand system which we have constructed is most versatile and can provide an almost limitless variety of combinations with transition metals of all kinds with a wide range of metal valence. The ligand is useful for organometallic systems as well as yielding a more traditional coordination chemistry. Furthermore the prospects of easily altering the basicity of one ligating site (N) or the utilization of this site for the formation of M-N σ bonds adds dimensions of variability which are unusual if not unprecedented for a ligand system. We have already demonstrated the most obvious applications of this ligand system to a variety of transition metal chemistry; coordination of the hard and/or soft base centers, chelate formation, M–N σ bonding with and without chelate stabilization, heterobimetallic complex formation with, most significantly, widely disparate (the "early–late" transition metals; high–low oxidation state) combinations. The practical applications of this ligand system are manifold and the most obvious application of the resultant complexes for the construction of catalytic systems is under investigation. Although we have used selective reactivity at nitrogen to modify the basicity of that center we could clearly also use this reaction point to bind the ligand framework to other systems including polymers. Furthermore additional control of the ligating and reaction chemistry may be introduced by changing the nature of the connecting backbone (we have already shown that diphosphines with C_2 to C_6 saturated alkane backbones can be used for phosphoranimine phosphine formation and that the analogous arsine is well behaved) and by changing the substituents on phosphorus. This latter prospect provides opportunities for almost infinite diversity. To date the chemistry has proven to be without undue complications and the reactions may be scaled up without difficulty. We hope that in the near future we shall be able to fully exploit this system to further our understanding of metal–ligand chemistry and most exciting of all, afford new developments in the area of heterobimetallic complexes of disparate metals.

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