

Metal complexes of di-phosphorus imines. An exploration of multifunctional phosphorus–nitrogen ligand–metal chemistry

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The development of a hard-soft ligand system, $R_2PQPR_2=NR'$ (where Q represents a backbone moiety such as CH_2 , NR, *o*- C_6H_4 , etc.), by partial oxidation of *bis*(phosphines) with azides is described. These systems form a variety of complexes and compounds with transition metals depending on the nature of the metal. Bidentate chelation of the P and N centers is common with soft metals but hard centers such as Ti coordinate only through the N. Some examples show only coordination of the soft P center. When the imine is formed with a trimethylsilyl group, elimination of trimethylsilyl chloride from metal chlorides occurs to yield derivatives with a metal–N σ bond. In these systems, the soft metals further coordinate through P whereas the harder Ti leaves the P free for further coordination. The silyl group may also migrate to the terminal oxygen of metal-oxo precursors thus forming bound iminato ligands. Bimetallic systems can be accessed. The *bis*(phosphoranimines), $H_2C(R_2P=NR)_2$, formed by uncontrolled complete oxidation of a *bis*(phosphine), have been explored and show, with hard transition metals and main group metal alkyls, interesting new methanide and methandiide derivatives in which the methylene group is deprotonated and the metal center is bound to the carbon. A suite of complexes in which there is clearly a M=C double bond between Ti, Zr or Hf and the carbon has been discovered. Easy access to these systems is provided by the novel dilithium salt, $Li_2C(R_2P=NR)_2$. Bridging dimeric carbene complexes have also been characterized.

COMPLEXATION of metals with phosphorus-based ligands has an extensive and venerable history¹; phosphines are prototypical 'soft' ligands. Many of these resultant metal–phosphine complexes have diverse applications including use in homogeneous catalytic systems². In addition to the generally robust nature of the metal complexes, the extensive substitutional chemistry of phosphorus offers a wealth of opportunity for the modification of the nature of the ligand to control the reactivity of the system. Phosphines

are also readily oxidized by chalcogen reagents to phosphine oxides and phosphine sulfides, which themselves have an extensive 'hard' or 'soft' coordination chemistry according to the nature of the chalcogen.

Phosphorus–nitrogen chemistry covers a large and diverse field in which trivalent and pentavalent phosphorus species are well known and single and multiple bond chemistry is extensive. Commenting on this chemistry, Greenwood and Earnshaw³, in their comprehensive textbook, write that 'the phosphorus–nitrogen bond is one of the most intriguing in Chemistry'. One of the more intriguing and useful reactions of phosphines is the Staudinger reaction⁴ in which an azide is used to oxidize a P(III) phosphine to a P(V) iminophosphorane of the type $R_3P=N-R'$ and thus a phosphorus–nitrogen multiply bonded link is developed. In the context of ligand chemistry, another 'hard' ligating center, the imino nitrogen, is provided. The development of trimethylsilyl azide^{5,6} has provided an extremely useful (and stable) azide which smoothly oxidizes phosphines to the silyl iminophosphoranes ($R' = SiMe_3$). A further reaction pathway is opened with this reagent in this system because simple trimethyl silyl halide elimination from the silylated imine and a metal halide can be used to form a direct metal–nitrogen σ bond. In the case of metal oxide precursors, the silyl group may migrate from nitrogen to oxygen to form a siloxane along with the σ bound imide. Much work has been done with this class of compounds and a variety of bonding modes of the imides with metals have been identified^{7–15}. These versatile ligands may function as uninegative anions (i.e. $R_3P=N^-$), or as contributors of 1, 2 or 4 electrons to the metal center. Under the right circumstances there can be considerable multiple bond character in the M–N bond in $R_3P=N-M$ complexes^{11–14,16}. Subtle changes in the basicities of the iminato nitrogen can be effected by the appropriate choice of the substituents on the phosphorus (R) or the nitrogen (R') and, as we describe below, there are simple routes to certain substitutions on the nitrogen which avoid the azide route. In addition, the Kirsanov reaction of dihalogenophosphoranes with amines¹⁵ and

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the Mitsunobi^{15,17,18} condensation of phosphines with an amine promoted by diethyl azodicarboxylate (DAAD) yield phosphinimines with varied substituents on the nitrogen. These latter reactions are not however as useful as the Staudinger reaction for the selective oxidation process described below.

Our interest in the iminophosphorane systems evolved in the context of developing the chemistry of multifunctional phosphorus based ligand systems with an aim of formulating highly effective homogeneous catalysis systems. Our approach was to develop chelating ligands with multifunctional character in order to provide at least two *different* sites for complexation and binding so that, when the chelate complexes are formed, the inherent difference in binding action of the two sites would provide, in general, one metal linkage which is weaker than the other. Thus a point of preferential reactivity is provided. Severing the weaker link opens a reaction site (without completely dissociating the ligand) to form a system, briefly depicted in the scheme, which then can react in a cyclic process using the typical organometallic reaction types (oxidative addition, reductive elimination, base addition and dissociation, alkyl migrations, etc.) to carry out a reaction process. With the reactive site opened, the reagent (S) binds to the metal and is then transformed on the metal by means of attack of other reagents (e.g., CO, H₂) or adds more substrate (as in an oligomerization or polymerization reaction) to form the transformed, bound entity T. Dissociating the product from the carrier complex regenerates the reactive intermediate which may then repeat the reaction cycle or return to be stored in the stabilized form of the initial chelated precursor. For an effective and long-lived catalyst system the precursor should be stable to the degradation processes inherent in the solution and it should also be able to provide a good supply of the reactive species from which the catalytic activity derives. Satisfaction of both requirements is a challenging non-predictable requirement which has stimulated considerable empirical exploration. Keeping the stabilizing ligand attached to the metal as a mono-coordinated multidentate ligand enhances the potential stability of the system because the ligand, being tethered, is readily

available to the metal for the stabilization step. Entropy effects are minimized and large concentrations of stabilizing ligand are not required in the solution. On the premise that systems with bi- or multi-functional ligating character which included a phosphine and another binding site of different character could be useful for the assembly of catalytic systems, we undertook an exploration of iminophosphorano-phosphine chemistry.

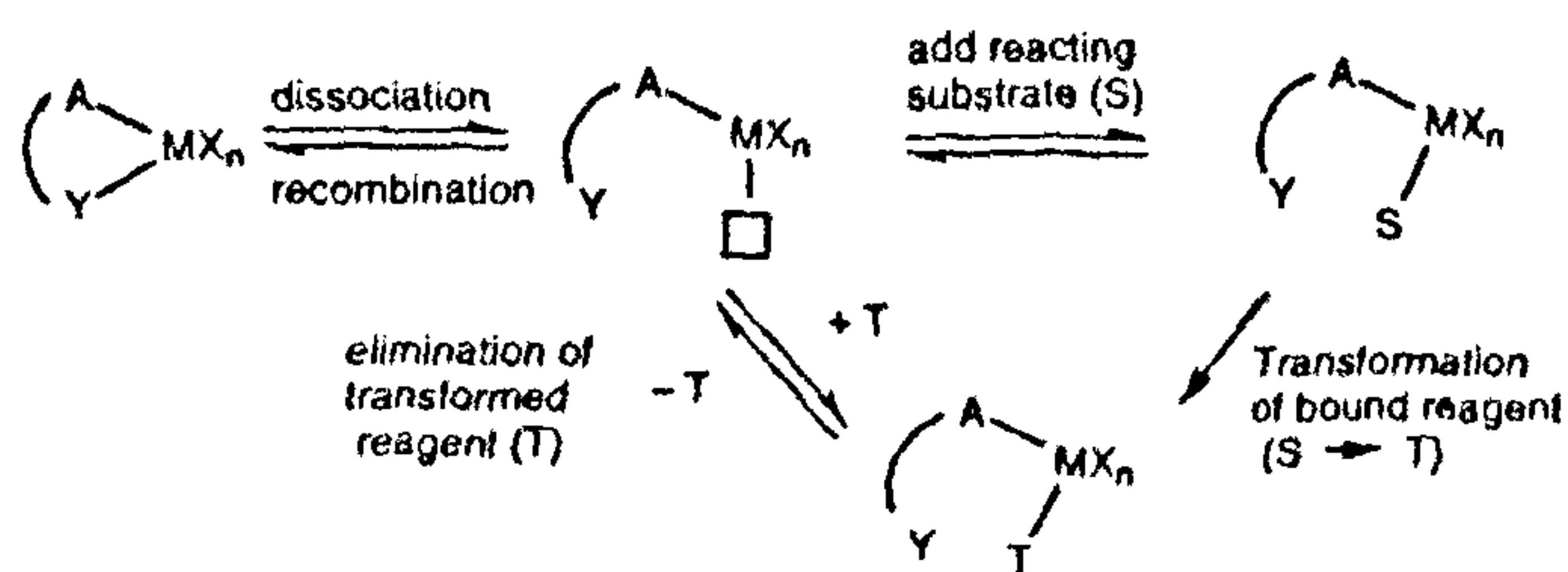
The development of iminophosphorano-phosphines

To prepare the ligands we developed the approach of selectively oxidizing one phosphorus center in a *bis*-phosphine with an azide to form iminophosphorano-phosphines. The oxidized phosphorus center in these systems then becomes part of the molecular backbone conferring framework stability and carrying substitutional influences for tuning the reactivity. Not unimportantly, the phosphorus NMR probe provides diagnostic chemical shift and coupling constant information. It also appears that the incorporation of the phosphorus backbone element as part of the structural framework offers some relaxation of the ring strain constraints imposed by carbon structural elements in the chelated rings.

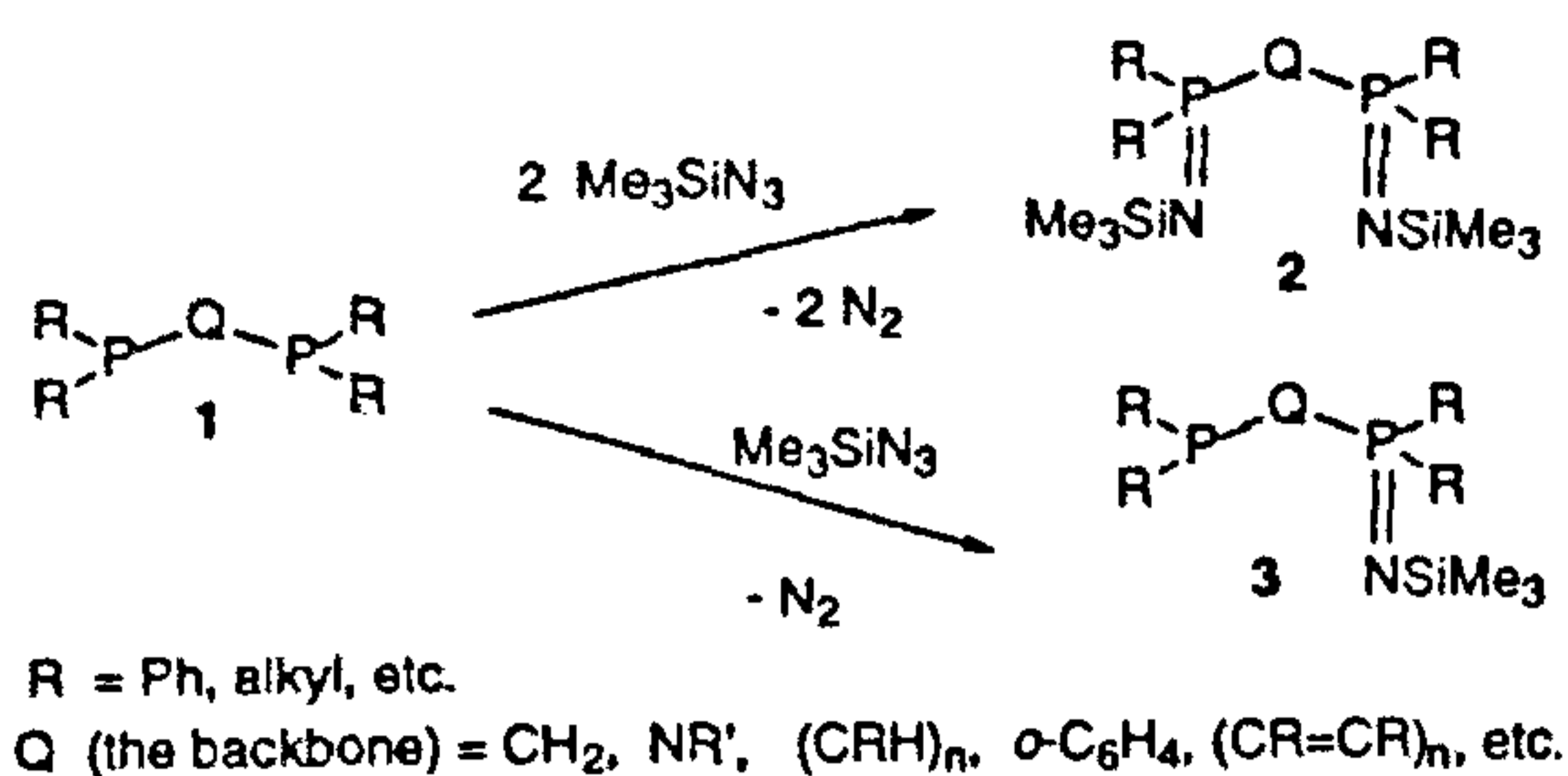
Selectively oxidizing one center of a *bis*-phosphine with an azide forms an imine on one phosphorus center and provides a hard donor center. The remaining phosphine acts as a typical soft coordination center. Even at this stage of the process we see how control of the system can be exerted through the use of differently substituted *bis*(phosphines). We have used a variety of azides in addition to trimethylsilyl azide; tetrafluorobenzyl azide¹⁹ is readily accessible, stable and reactive, the commercially available phosphinic azide (PhO)₂P(O)N₃ introduces a third phosphorus with all of the attendant coupling constant signatures as well as an additional possible hard coordination site in the form of the phosphoryl oxygen. The most versatile of the azides however is trimethylsilylazide because it opens additional possibilities through substitution and bond formation reactions at the nitrogen with organics or metals.

Our prototypical system was developed through the use of carefully controlled oxidation of the readily available *bis*(diphenylphosphino)methane (dppm), **1**, with azidotrimethylsilane which formed the heterodifunctional iminophosphorano-phosphine **3** in good yields^{16,20-23}.

This route, applicable to a variety of bridged diphosphorus compounds, provides ready access to substituted iminophosphorano-phosphines. Available backbones that we have employed encompass a variety



Scheme 1.



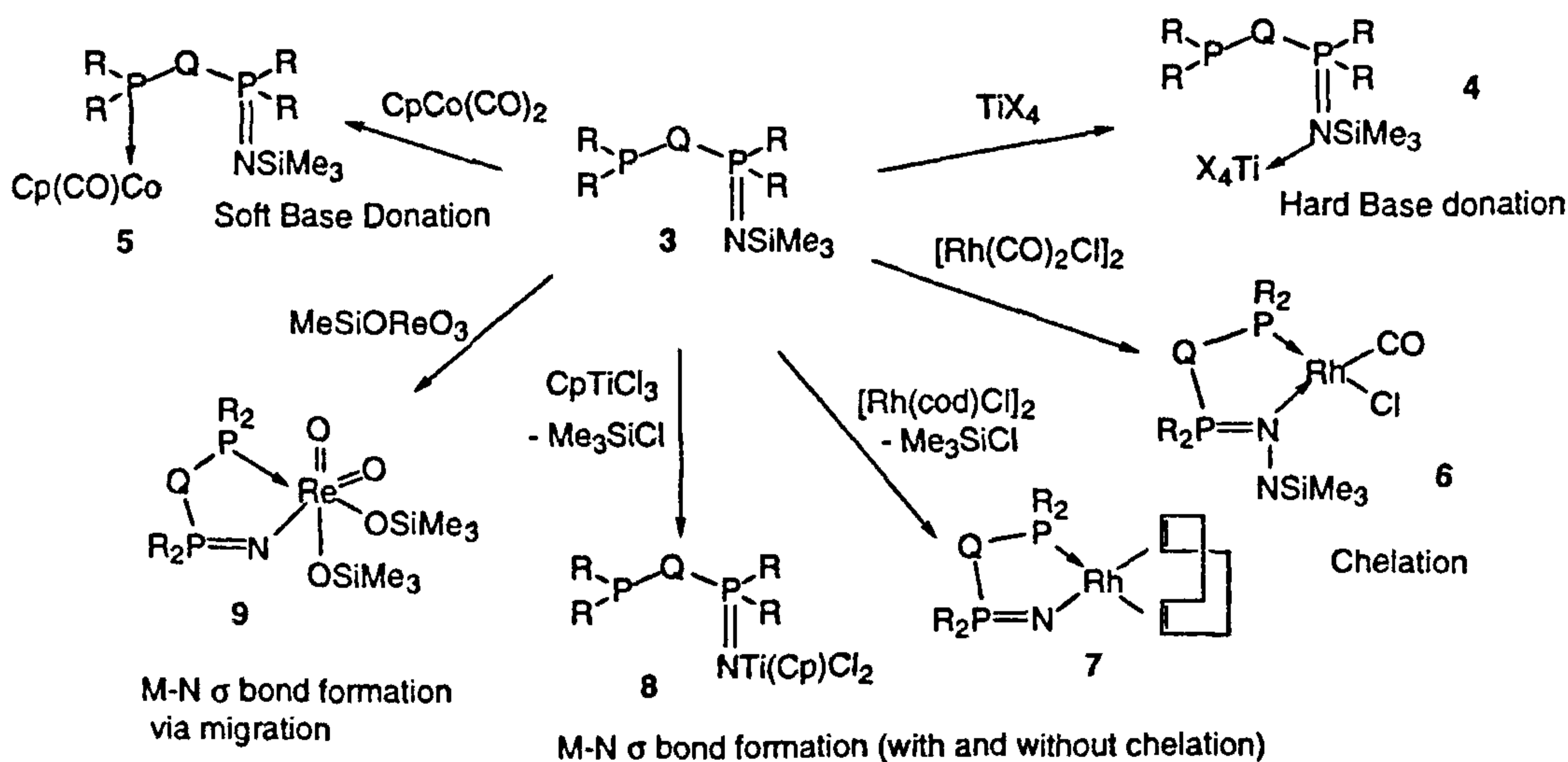
Scheme 2.

of bridging species (Q) such as CH_2 , $(\text{CH}_2)_n$, $\text{HC}=\text{CH}$, $o\text{-C}_6\text{H}_4$, NR , etc., which span a range of connecting components including linkages with saturated or unsaturated character which we shall discuss below. Although, in the case of the alkane backbones, ensuring limited oxidation requires subtle reaction control, we have found that some constrained backbone structures ($o\text{-C}_6\text{H}_4$ and *cis*-ethylene)²⁴ and some nitrogen bridge backbones²⁵ naturally limit the oxidation process to favour the production of the desired mono-oxidized systems, thus careful control of conditions is not always required. The loss of control or the use of excess reagent in cases where complete oxidation is facile leads to the bis(iminophosphoranes) **2**. We did not pursue this system in early studies however we have recently shown²⁶⁻²⁹ that these ligands provide new and exciting chemistry which will be described below.

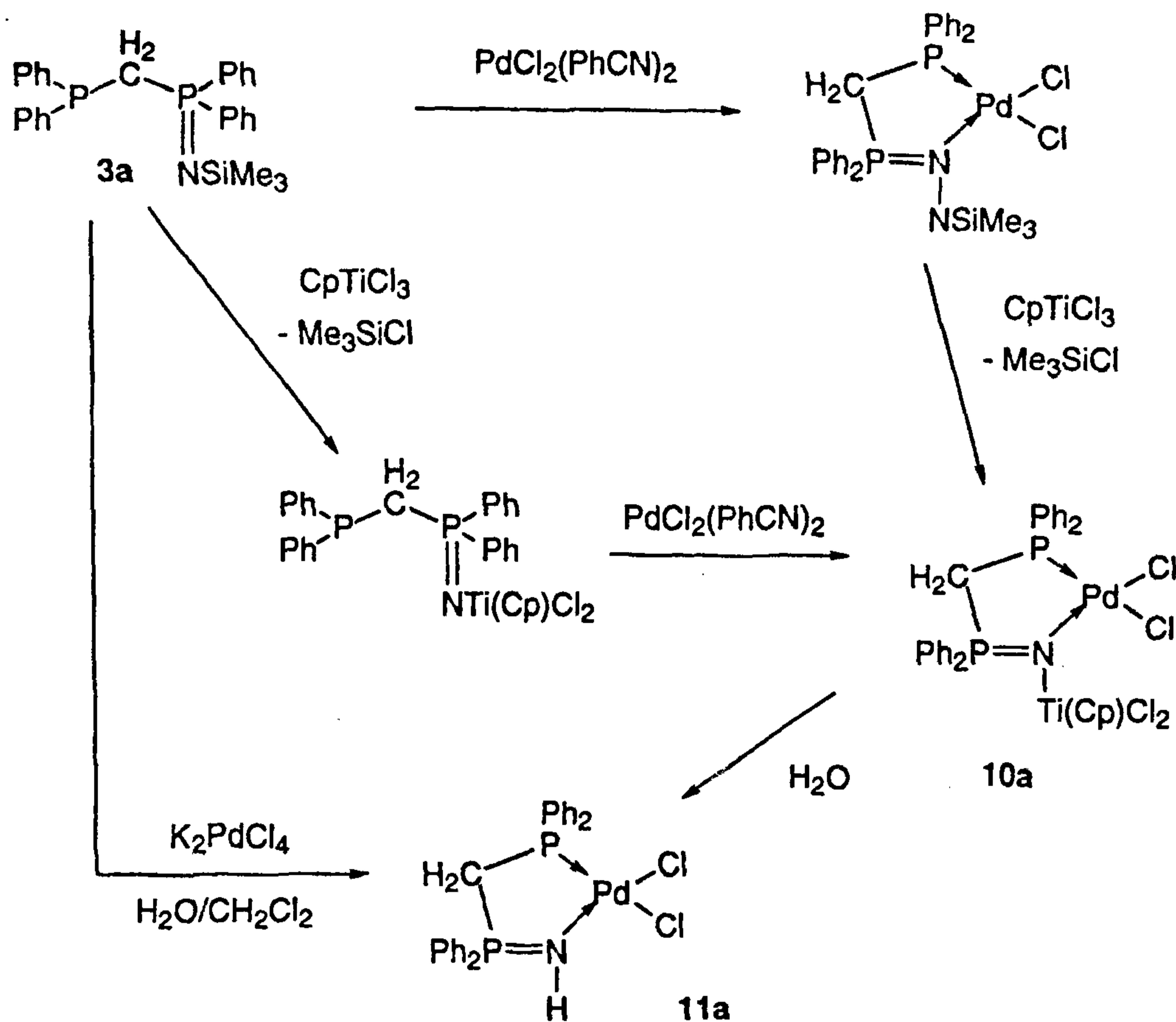
The mixed iminophosphorano-phosphine ligands of the type **3** readily form complexes and compounds with transition metals (Scheme 3). The nature of the product is a function of both the character of the ligand and the nature of the metal complex. We can certainly expect monodentate action, for example, hard metal centers may coordinate exclusively to the nitrogen (hard) end of the ligand to give complexes such as **4** thus leaving the phosphine end free for subsequent coordination to a soft metal. Alternatively, the soft phosphine end alone may coordinate to give species such as **5** and again subsequent chemistry could be developed. Our interest however was focused on the pursuit of bi-functional ligand behaviour.

Chelation of the metal is very typical and is exemplified by complexes such as **6**. A wide selection of such complexes has been made^{20,21,30}. In this context, the product is influenced by the metal precursor; for example **3** (**3a**, $\text{Q} = \text{CH}_2$, $\text{R} = \text{Ph}$) gave, with the $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ dimer, a simple chelated complex of the type **6** by elimination of one CO whereas the $[\text{Rh}(\text{cod})\text{Cl}]_2$ dimer eliminated Me_3SiCl to form **7** wherein the ligand is a bound anionic imide^{20,21}. The structure of a chelated Rh complex is illustrated in Figure 1 (ref. 30).

Other examples of the formation of complexes containing M-N σ bonds are prevalent; simple reaction of **3** (**3a**, $\text{Q} = \text{CH}_2$, $\text{R} = \text{Ph}$) with CpTiCl_3 gave **8** (Scheme 3) by elimination of Me_3SiCl . In this case the hard Ti center does not bind the soft phosphine so the latter center is free for further reaction³¹. With this strategy, bimetallic combinations can be constructed, for



Scheme 3.



Scheme 4.

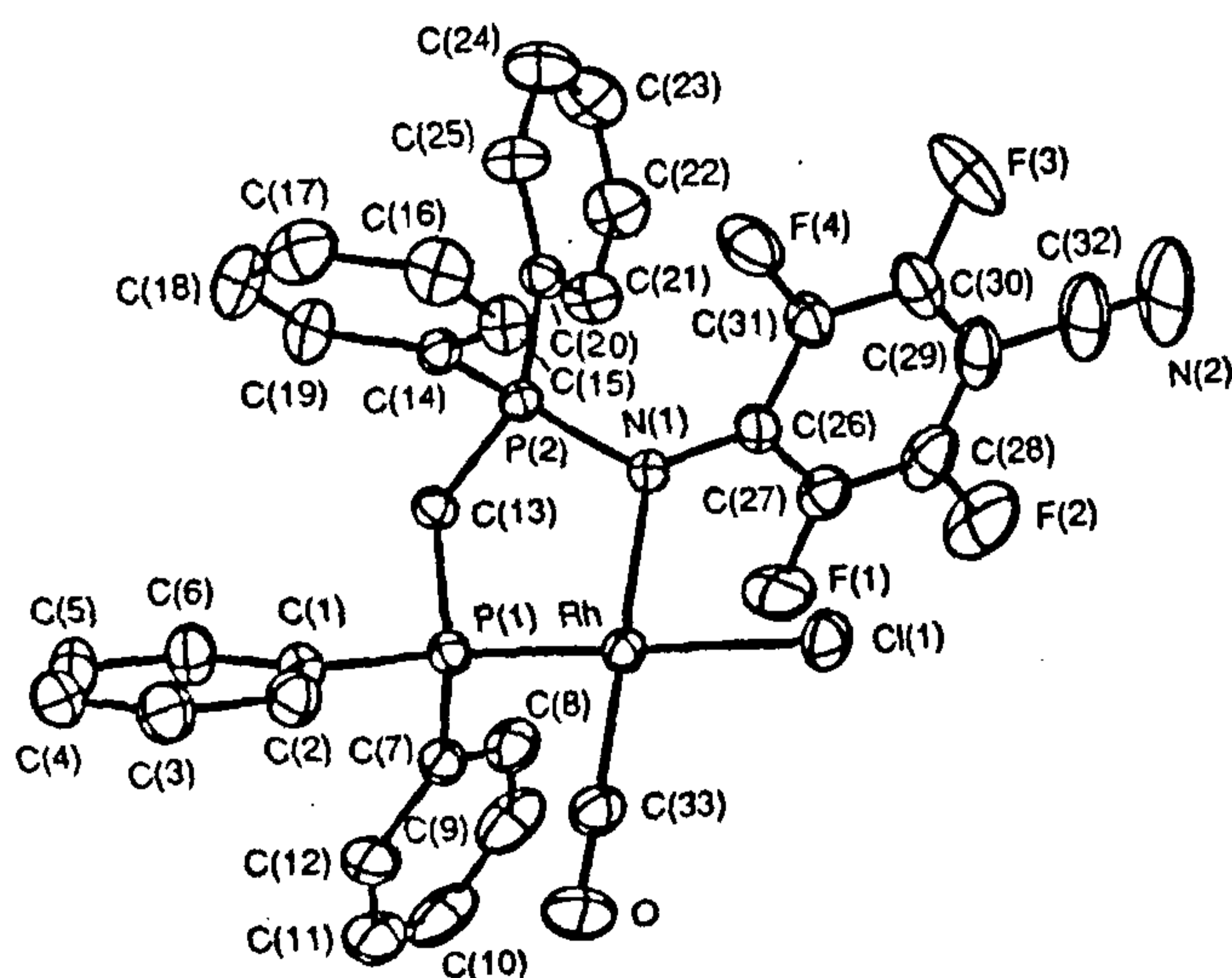


Figure 1. The molecular structure³⁰ of 4-CN-C₆F₄-N=PPh₂CH₂PPh₂Rh(CO)Cl. (Reproduced with permission).

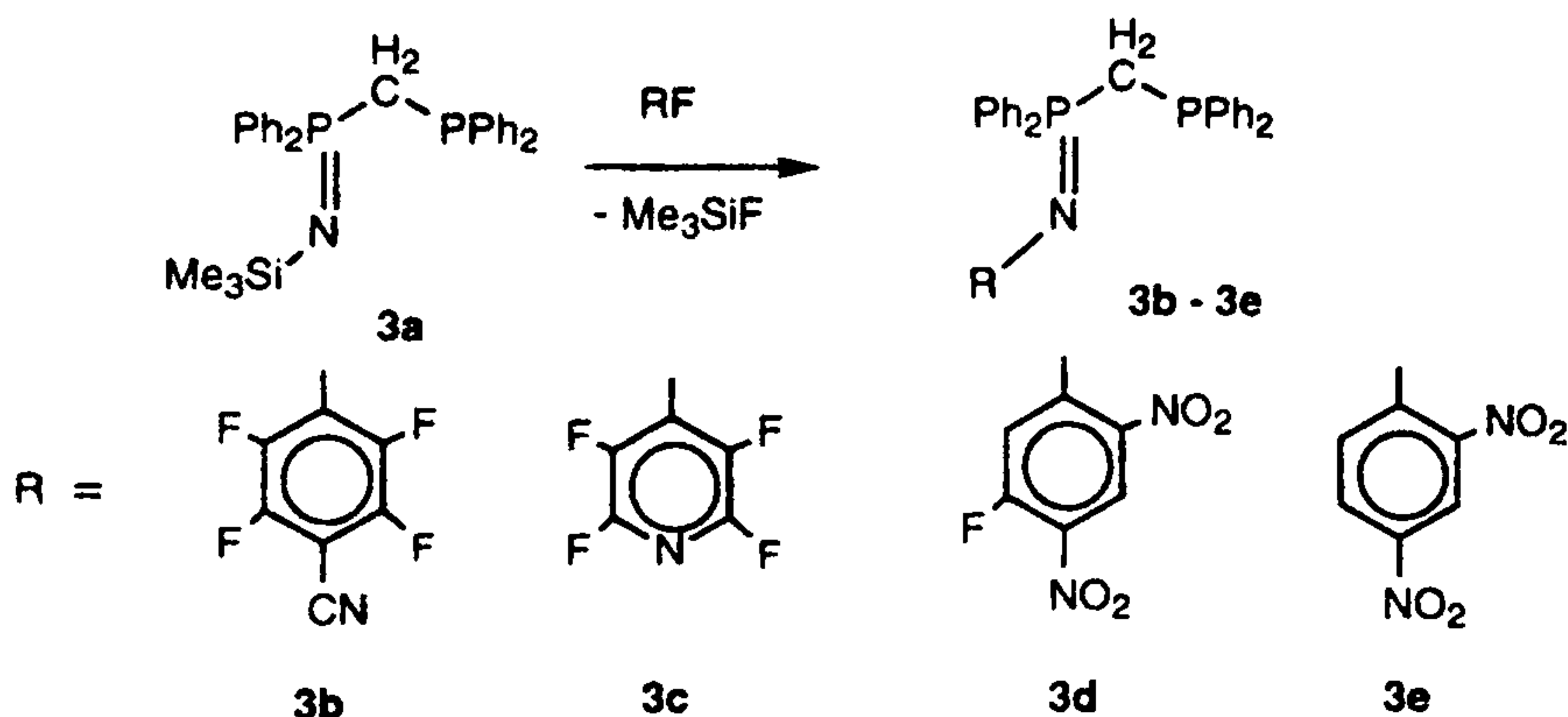
example we developed a sequence of reactions for Ti/Pd heterobimetallics (e.g. **10**, Scheme 4) (ref. 32). Systems such as this however have not yet been exploited. The metal nitrogen or Si–N bonds are sensitive to hydrolysis and ultimately a complex of the imine was formed. The

imines are typically not stable but the reaction of a type 3 system, specifically **3a** with, for example, a Pd or Pt salt, can be carried out in mixed water/solvent medium and the imine form trapped as a stable complex (**11a**)²². Careful hydrolysis with methanol in organic solvents also yields the imine in solution but we have not isolated these free imines. In solution, the imine converts over time to the phosphine oxide.

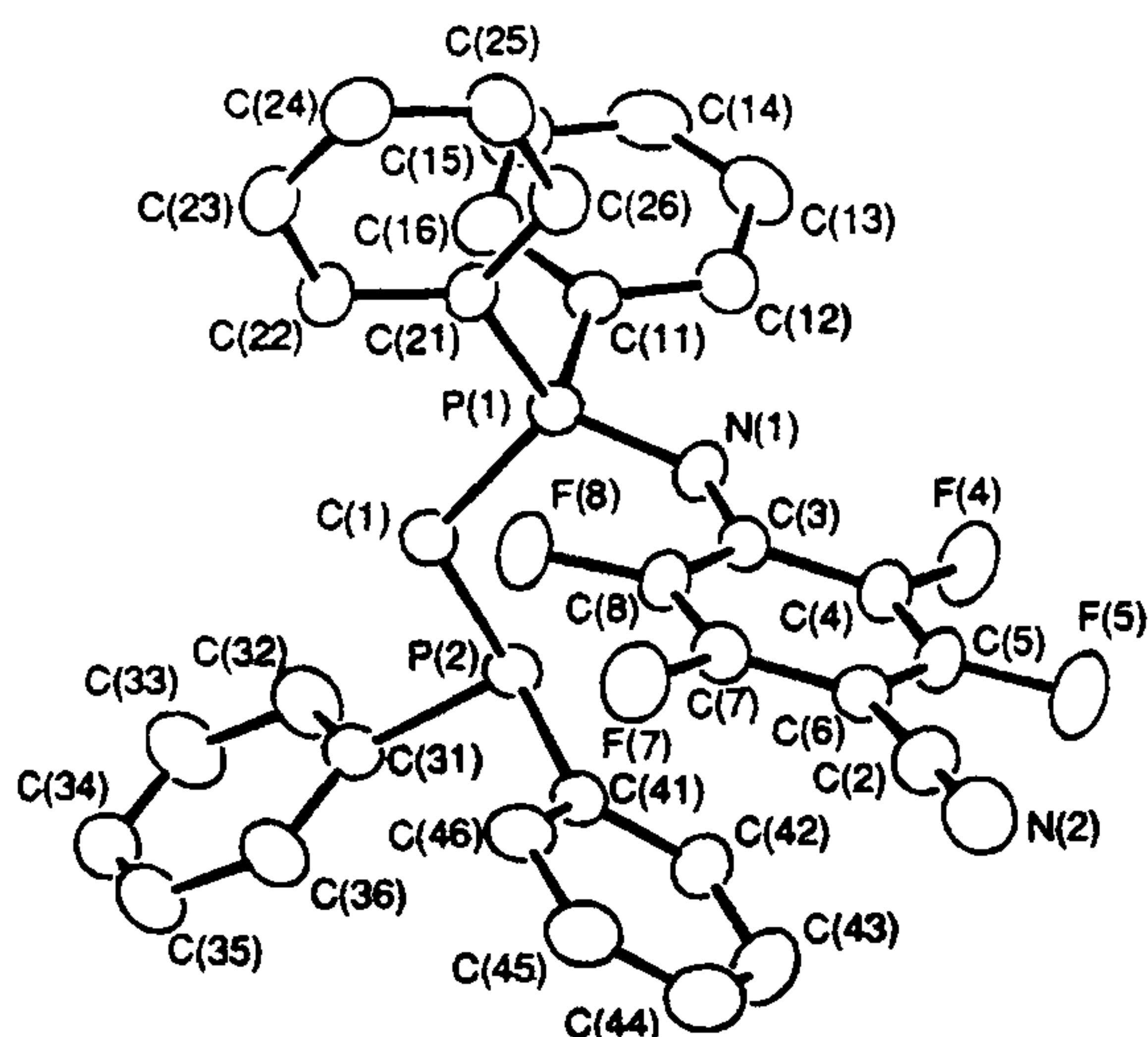
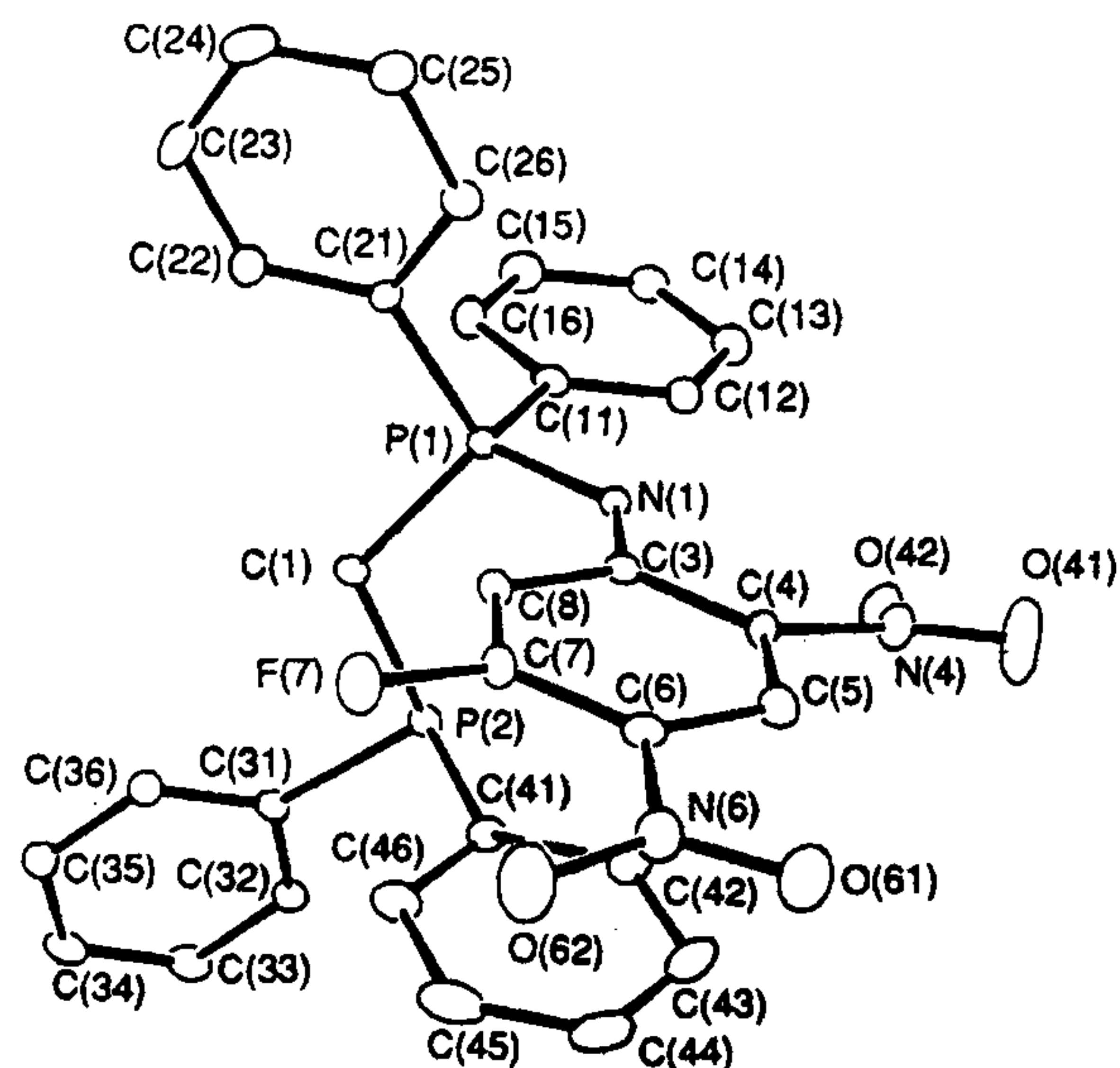
When **3a** was reacted with Re(VII) oxo species, the greater affinity of Si for O vs N led to migration of the Me₃Si group from N to O to form **9** (Scheme 3) and a M–N bond¹⁶.

A measure of control over coordinative reactivity of the complexes can be introduced through variation of the substituents on the nitrogen (Scheme 5). The reaction of an activated fluorinated aromatic allows facile replacement of the Me₃Si substituent on the nitrogen thus providing access to a variety of aromatic imines³⁰.

The fluorine which is displaced is that located *para* to an electron withdrawing activating group. Thus fluorine *para* to CN in C₆F₅(CN) or *para* to the heterocyclic nitrogen in C₅F₅N is eliminated as Me₃SiF to bind the fluoroaromatic to the imine^{20,30}. Iminophosphorano-phosphines substituted with these electron withdrawing



Scheme 5.

Figure 2. The molecular structure of $\text{PPh}_2\text{CH}_2\text{PPh}_2=\text{N}(4\text{-(CN)C}_6\text{F}_4)$ ³⁰. (Reproduced with permission).Figure 3. The molecular structure of $\text{PPh}_2\text{CH}_2\text{PPh}_2=\text{N}(2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3)$ ³⁰. (Reproduced with permission).

aromatic substituents (3b, 3d) are illustrated in Figures 2 and 3 (ref. 30). The aromatic compound need contain only the one activated fluorine as demonstrated by the reaction of 1-(F)-2,4-(NO₂)₂C₆H₃; in this case the product carries no fluorine substituents on the aromatic ring³⁰. This reaction provides a safe route to nitro-aromatic phosphoranimines which are, in principle, accessible through mono-oxidation of the appropriate bisphosphines with the appropriate azide (the Staudinger reaction) although this reaction is potentially dangerous. With this fluorine elimination route, dangerous azide preparation is not necessary.

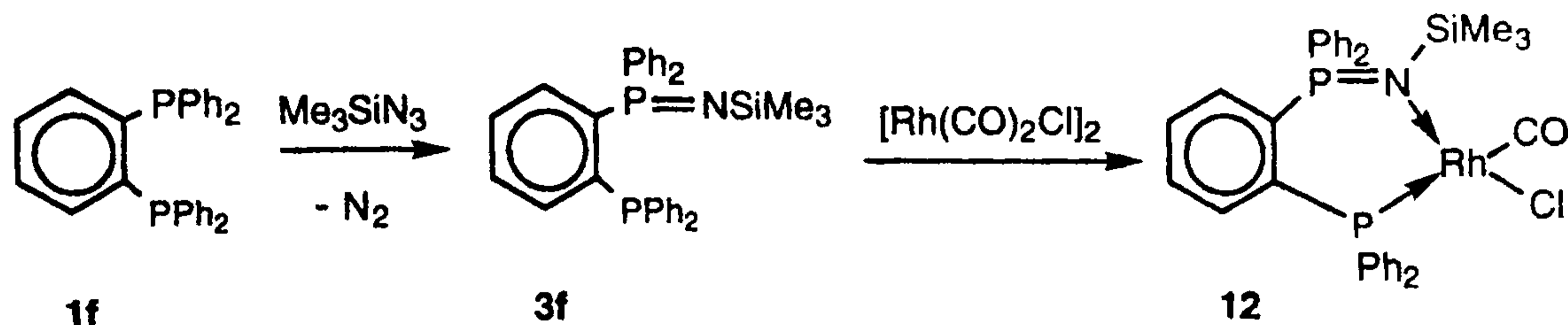
Some other useful ligand chemistry can be developed from the silylated iminophosphorano-phosphine. Control of chalcogen oxidation is usually difficult because the typical reagents are not sterically constrained (*vide infra*) and are quite reactive, so it is difficult to make the

mono-oxidized phosphine-phosphine oxide or phosphine-phosphine sulfide of the *bis*(phosphines)³³. These species are easily made from a Wittig type reaction of species such as 3 (Scheme 6) and an aldehyde, carbon disulfide, etc.³⁴.



Scheme 6.

The transition metal chemistry of these ligand systems is extensive and very rich and we have explored only a small segment of it. Several variants of the system have



Scheme 7.

provided very effective catalytic systems for processes such as carbonylation of methanol, hydrogenation³⁵, oligomerization and polymerization of olefins. Some of this work is being exploited in more depth.

Other connecting backbones

Exploring the chemistry of other backbone systems in the early days led us to the *o*-C₆H₄ system wherein we discovered that, even in the presence of excess azide and under strenuous conditions, the second phosphine center could not be transformed to a phosphinimine and only **3f** (Q = *o*-C₆H₄, R = Ph) could be prepared. In contrast, this *bis*(phosphine) (**1f**, Q = *o*-C₆H₄, R = Ph) was readily converted to the di-sulfide or the di-oxide by normal chalcogen reagents.

In order to ascertain the reason for the reluctance for the azide oxidation at the second phosphine centre, we compared the reactions of *cis*-1,2-*bis*(diphenylphosphino)ethylene and *trans*-1,2-*bis*(diphenylphosphino)ethylene³⁶, using 4-cyanotetrafluorophenyl azide¹⁹ which is easily made and relatively reactive, more so than Me₃SiN₃. We found that the *cis* ethylene bisphosphine behaves similarly to that of *bis*(diphenylphosphino)benzene and stops at the first oxidation step but the *trans*-compound, wherein there is no steric interference, is fully converted to the *bis*-oxidized derivative. It is generally accepted that the Staudinger oxidation proceeds through the formation of a cyclic phosphazide intermediate^{4,7,15,37,38} but in this case, steric crowding in the ligand inhibits the second oxidation step. The crystal structure of **3f** (Figure 4) (ref. 24) shows, quite clearly, if we assume that the N and P lone pairs are appropriately disposed relative to the other substituents, that they are directed towards each other. The rigid backbone, P(1)-C(1)-C(2)-P(2), is essentially planar and the phosphorus–nitrogen double bond forms a dihedral angle of 60° with respect to this plane and this rigid backbone and the P=N double bond prevents the separation of the unreacted P and the imine N structural units. Thus the formation of a second phosphazide intermediate, which must fit into this space, is strongly inhibited even under strenuous conditions. The lone pair of electrons on the phosphorus and nitrogen atoms in the ligand extend in an overlapping fashion towards each

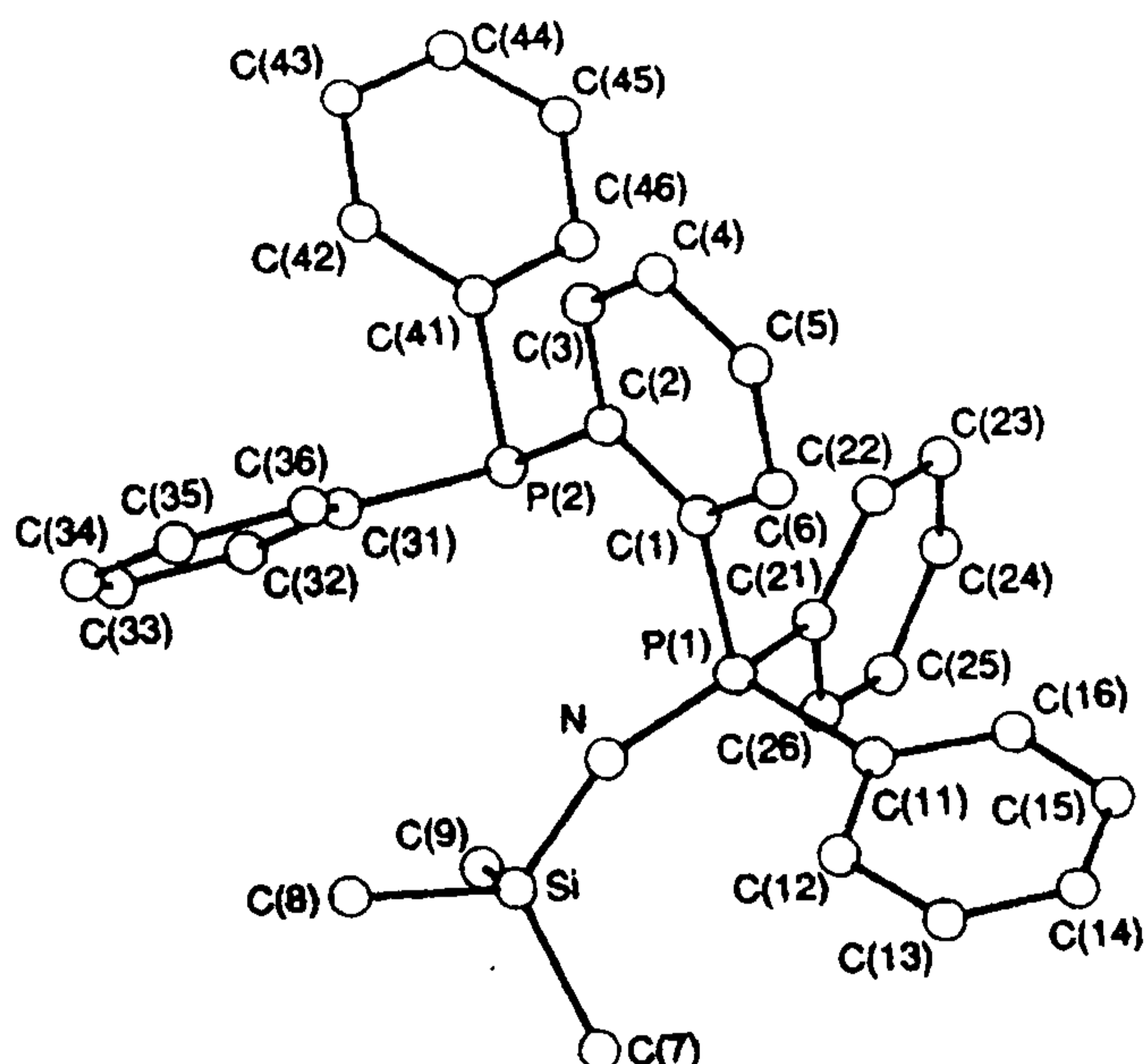
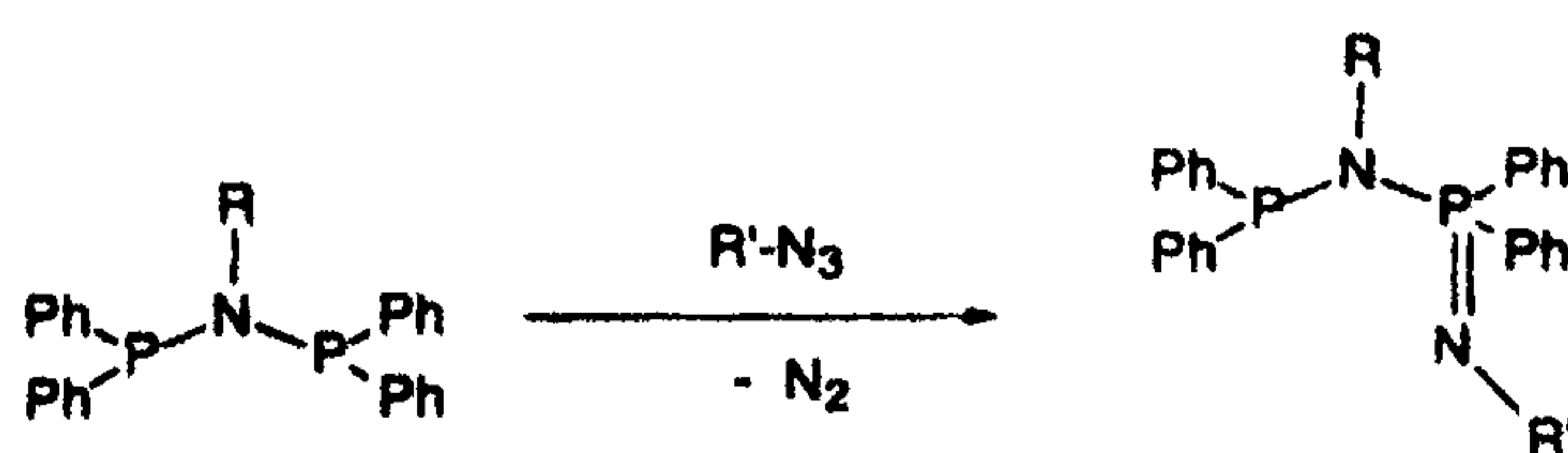


Figure 4. The molecular structure of *o*-PPh₂C₆H₄PPh₂=NSiMe₃ (ref. 24). (Reproduced with permission).

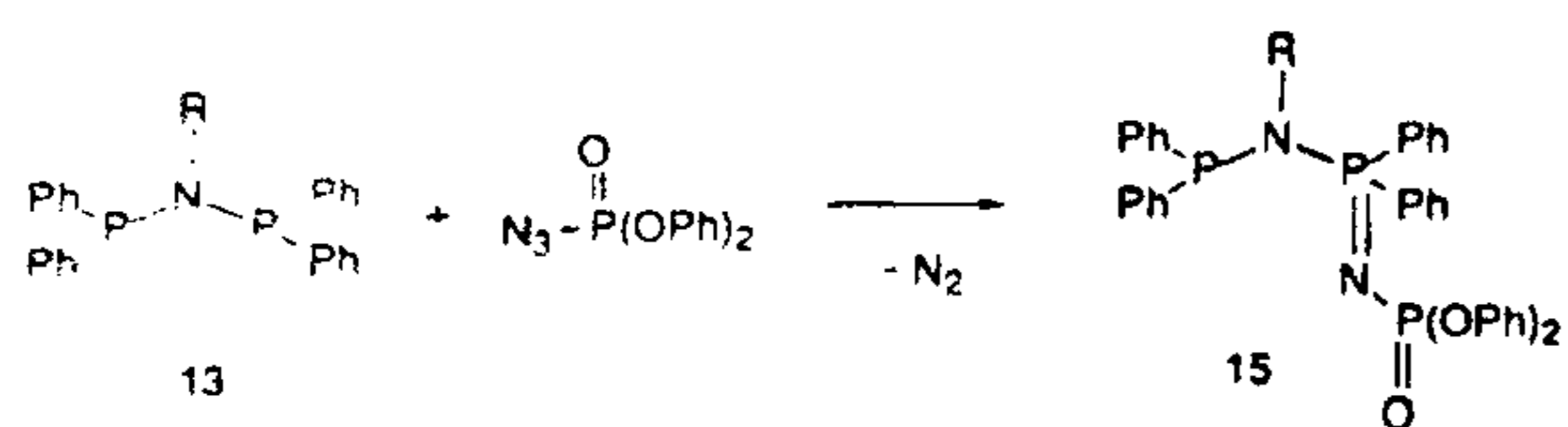
other thus facilitating chelating ability; in accord we see that chelation such as formation of **12** occurs readily (Figure 5) (ref. 24).

Iminophosphoranoaminophosphines of the general type Ph₂P-N(R)-PR₂(E) (R = Ph, Me, Et, etc., E = N-C₆H₄-*p*-CH₃ and N-C₆F₄-*p*-CN, NP(O)(OPh)₂) can be prepared by analogous azide oxidation routes. Thus the *bis*(phosphino)amines, Ph₂PN(R)PPh₂ (R = CH₃, C₂H₅, etc.) react with one mole of azide to form the nitrogen bridged iminophosphoranoaminophosphines (Scheme 8).

With phosphinic azide (Scheme 9) one obtains a ligand which contains also a phosphine oxide substituent, making it a triphosphorus, trifunctional ligand.



Scheme 8.



Scheme 9.

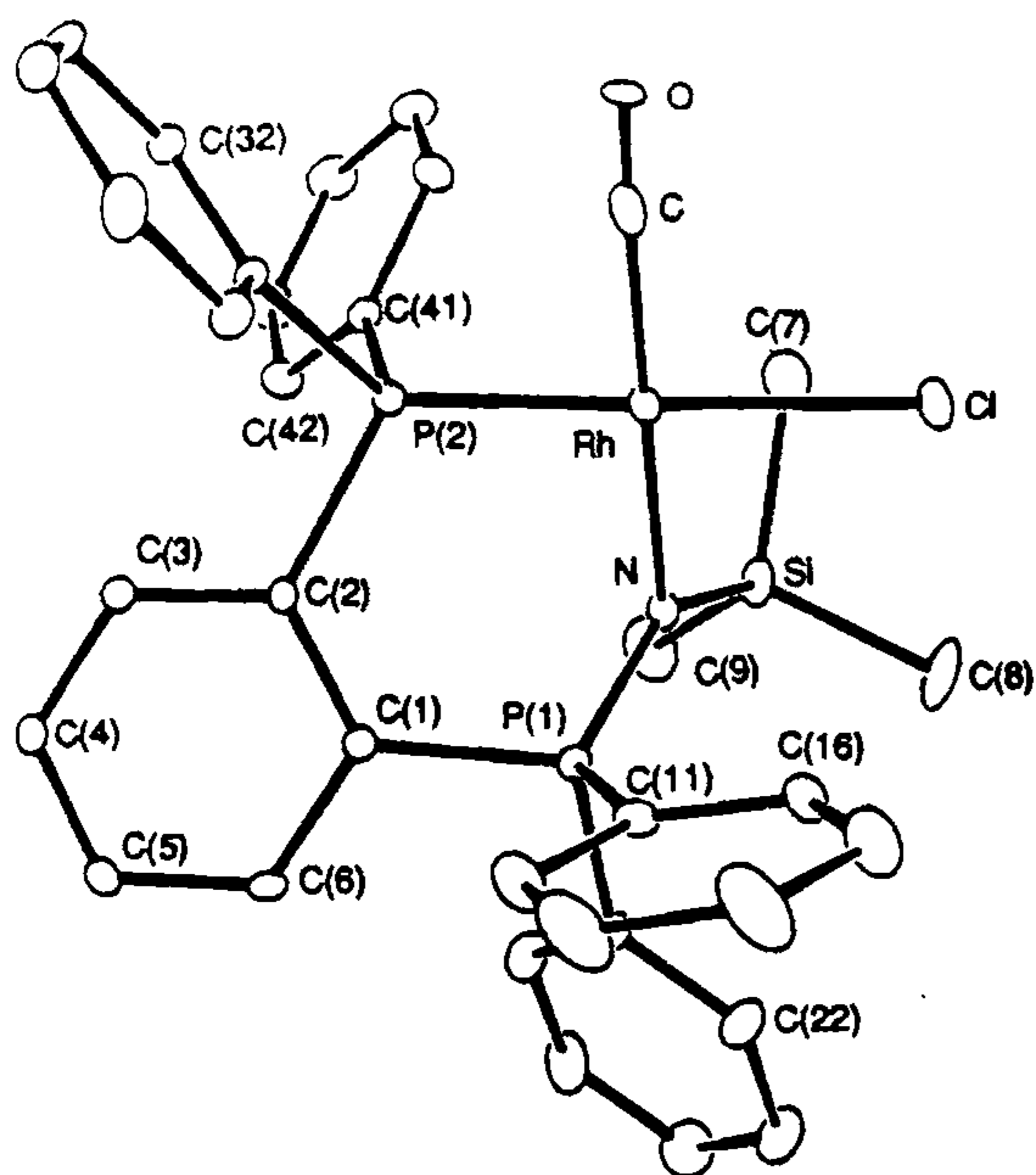


Figure 5. The molecular structure of the complex²⁴ $\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2\text{PPh}_2\text{Rh}(\text{CO})\text{Cl}$. (Reproduced with permission).

Surprisingly, the phenyl amino analog suffered significant P–N backbone cleavage which we suspect occurs because the slower reaction rate in this case allowed hydrolysis to compete (Scheme 10).

The ^{31}P NMR spectra of 15 show three well separated phosphorus signals with equal relative intensities with the attendant coupling constants which shows that the central phosphorus is coupled to both of the peripheral

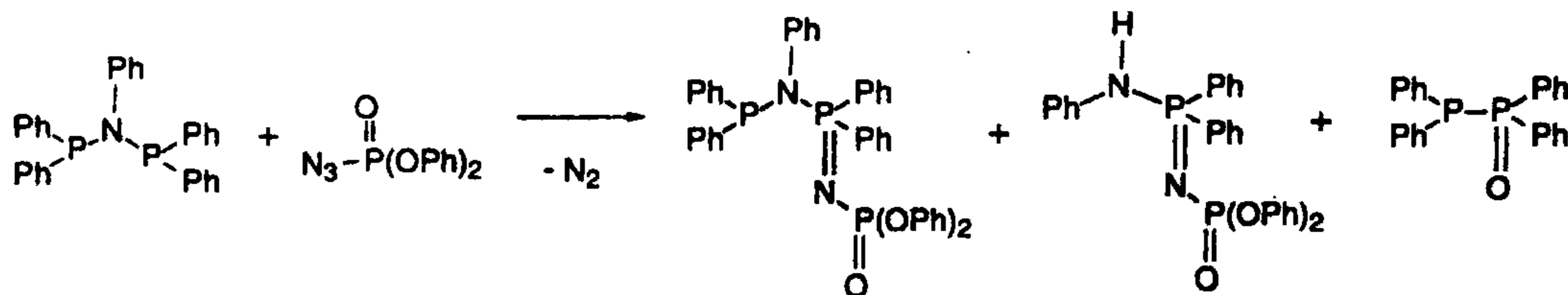
phosphorus centers but these phosphorus centers are not coupled to each other. Each phosphorus signal is well separated from the others.

Many chelated complexes of metals with the aminophosphoranimido-phosphines can be formed. Those formed by the triphosphorus molecules (e.g. 15, Scheme 11) are of greater interest because of the possibility of alternate complexation modes or more than bidentate behaviour^{25,39,40}. Thus complexes such as 16–18 amongst others are readily formed. The core framework of the structures of 17 and 18 is shown in Figure 6 (ref. 25).

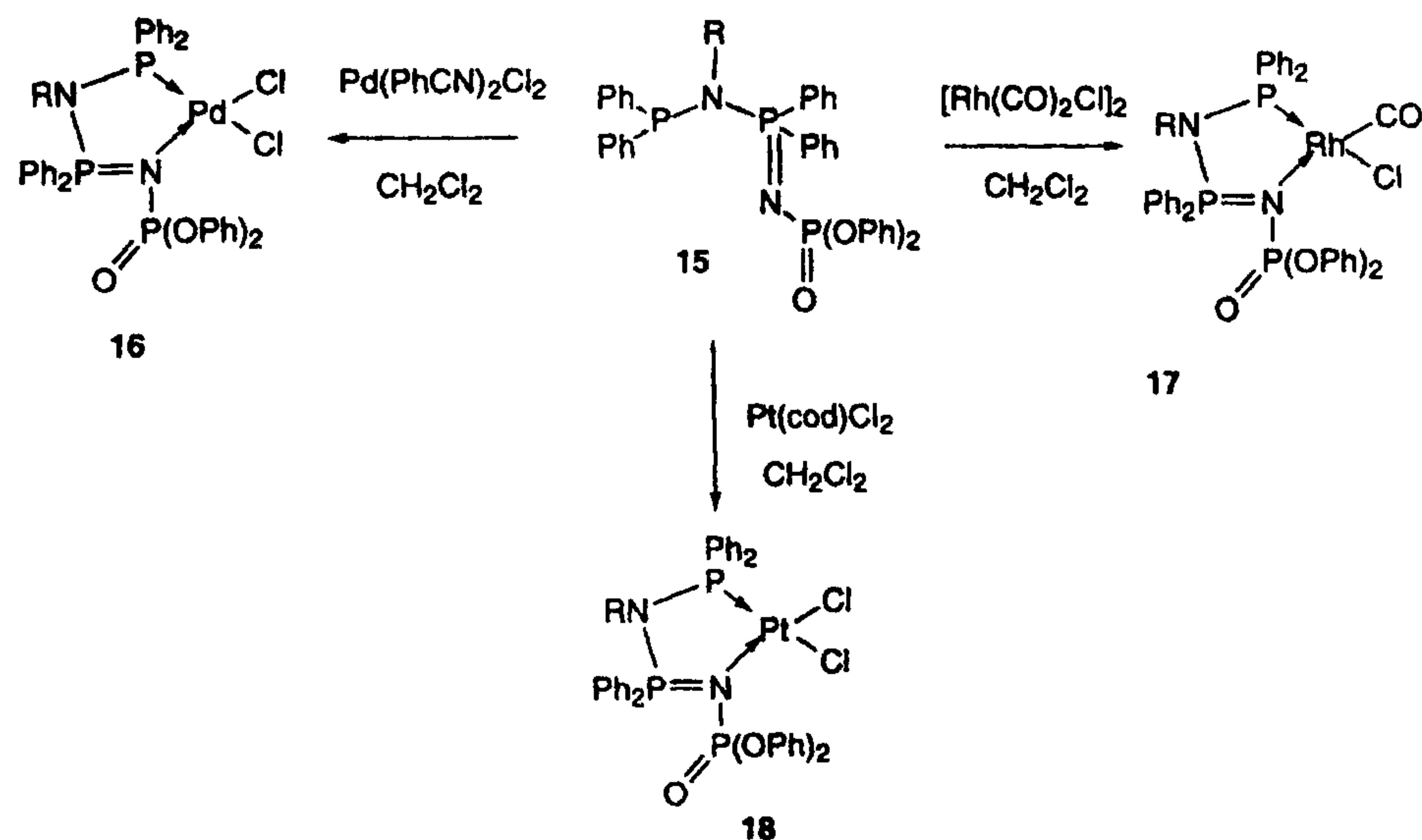
The question as to which of the remaining base atoms of the ligand completes the chelate, the imine nitrogen or the phosphoryl oxygen, was addressed by the X-ray structures of 17 and 18 (Figure 6) but could also be addressed by the ^{31}P NMR spectra. Complexes 16–18 exhibit three distinct phosphorus signals for the P^{III} , $\text{P}^{\text{V}}_{[\text{N}]}$ and $\text{P}^{\text{V}}_{[\text{O}]}$ centres upon complexation. The chemical shifts of the P^{III} centres are also shifted to lower field by approximately 50 ppm relative to the free ligands. The chemical shift of the $\text{P}^{\text{V}}_{[\text{N}]}$ centres is also shifted by 30 ppm to low field relative to the free ligands, whereas the chemical shifts due to the $\text{P}^{\text{V}}_{[\text{O}]}$ centres are shifted by only approximately 6 ppm to lower field strongly suggesting that the $\text{P}^{\text{V}}_{[\text{O}]}$ centre is not involved in the coordination to the metal, verified by single-crystal X-ray analysis (Figure 6).

P–N bonding in the ligands and the complexes

Some P=N and N–R and N–Si bond lengths and the angles at the nitrogen are collected in Table 1. In the phosphinimine reference systems and systems in which normal organic substituents are attached to the N, the P=N bond displays lengths typical for a double bond and angles at the N of close to 120° (e.g. $\text{Ph}_2\text{FP}=\text{NMe}$, $\angle\text{P}=\text{N}-\text{C} = 119^\circ$)⁴¹. The silylated derivatives show even shorter P=N lengths and wider angles at the nitrogen, typically the length of the P=N linkage is short and the angle larger than the expected 120° , as the angle increases the P=N bond length decreases. The effect is



Scheme 10.



Scheme 11.

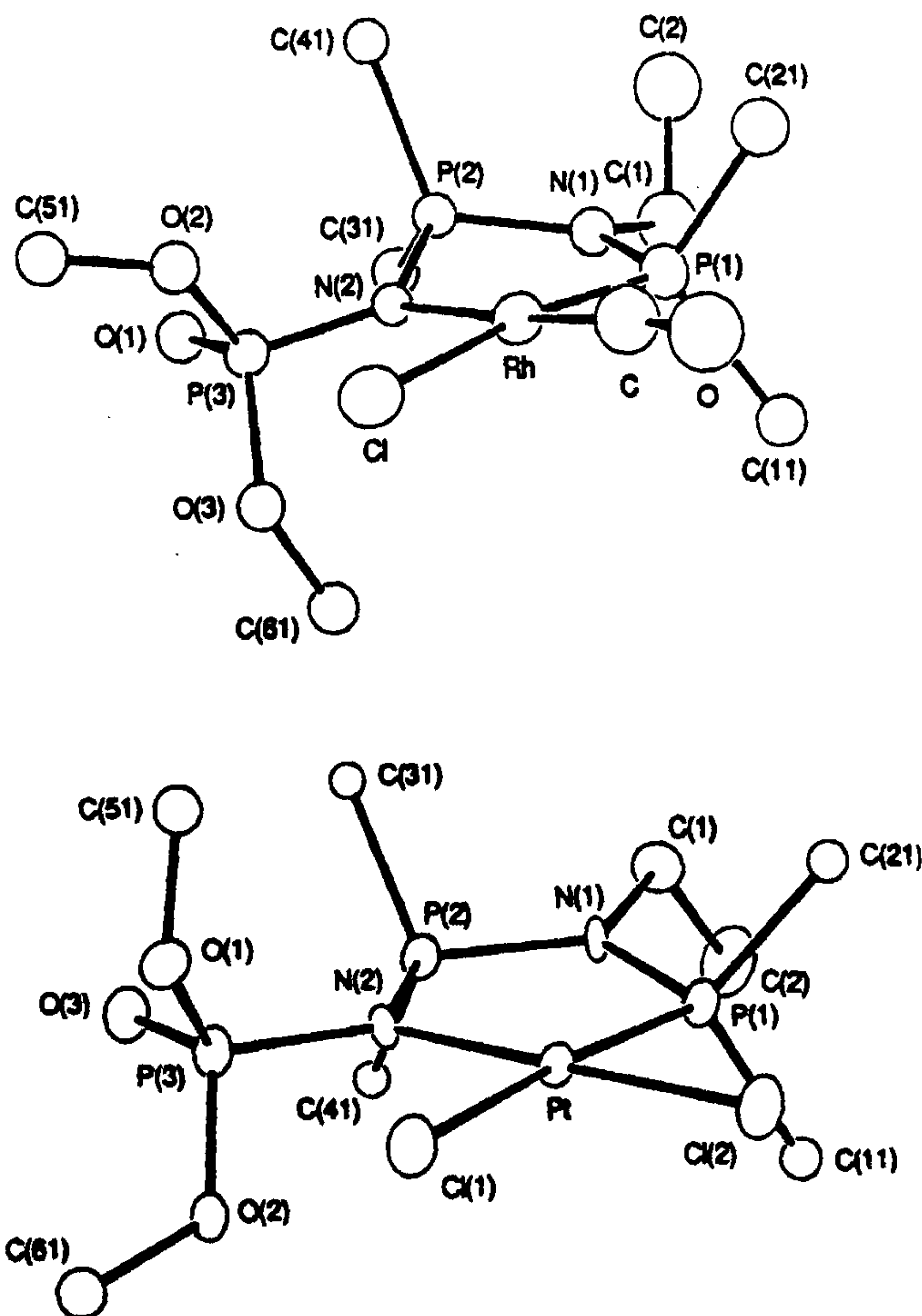


Figure 6. The central ligand core structures²⁵ of the (top) Rh(CO)Cl and (bottom) PtCl₂ complexes of Ph₂PN(C₂H₅)Ph₂P=NP(O)(OPh)₂. (Reproduced with permission).

probably due to electron withdrawal into the substituent which is large for Si. Related molecules prepared by us wherein the nitrogen is substituted by electron

 Table 1. Structural data for some *N*-substituted iminophosphanes

Compound	d(P=N) Å	Angle P=N-R (deg)	Ref.
Ph ₃ P=NPh	1.602	130.4	50
Ph ₃ P=NC ₆ H ₄ - <i>p</i> -Br	1.567	124.2	51
Ph ₃ P=NCN	1.595	123.0	52
Ph ₃ P=NP(CF ₃) ₂	1.576	131.0	53
Me ₃ P=NSiMe ₃ ^a	1.542	144.6	54
Ph ₂ FP=NMe	1.641	119.1	41
Ph ₂ PCH ₂ PPh ₂ (=NR)			
R = 5-F-2,4-(NO ₂) ₂ C ₆ H ₂	1.589	128.8	30
R = 4-(CN)C ₆ F ₄	1.567	132.9	30
R = SiMe ₃	1.529	150.2	55
1-(Ph ₂ P)-2-(Ph ₂ P(=NSiMe ₃))C ₆ H ₄	1.529	152.7	24

^aGas phase electron diffraction structure.

Table 2. Some selected coordinated ligand bond lengths in complexes 17 and 18

Parameter	Complex 17	Complex 18
Lengths (Å)		
P(1)-N(1)	1.78	1.70
P(2)-N(1)	1.64	1.67
P(2)-N(2)	1.58	1.67
P(3)-N(2)	1.57	1.63
Angles (deg)		
P(2)-N(2)-P(3)	113.5	113.9
P(1)-N(1)-P(2)	119.4	120.2

withdrawing fluorinated and nitrated aromatics show a larger angle and shorter bond, something between the

typical aromatic and the silylated species (e.g. $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{NAr}$ [$\text{Ar} = 5\text{-F}, 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_2$, ($\text{P}=\text{N}$ 1.589(5) Å, $\text{P}-\text{N}-\text{Ar}$ 128.8°(4)) and $\text{Ar} = 4\text{-(CN)C}_6\text{F}_4$ ($\text{P}=\text{N}$ 1.567(4) Å $\text{P}-\text{N}-\text{Ar}$ 132.9°(3))] ³⁰. Metallated (Ti) analogs and related systems show, in the case of early transition metals, profound shortening and opening of the angle and some of our silylated molecules are more closely reminiscent of the near linear *N*-trimethylsilylimido-metal systems (e.g., $\text{Cl}_3\text{V}=\text{N}-\text{SiMe}_3$, $\angle\text{V}=\text{N}-\text{Si}=177.5(1)^\circ$) ⁴².

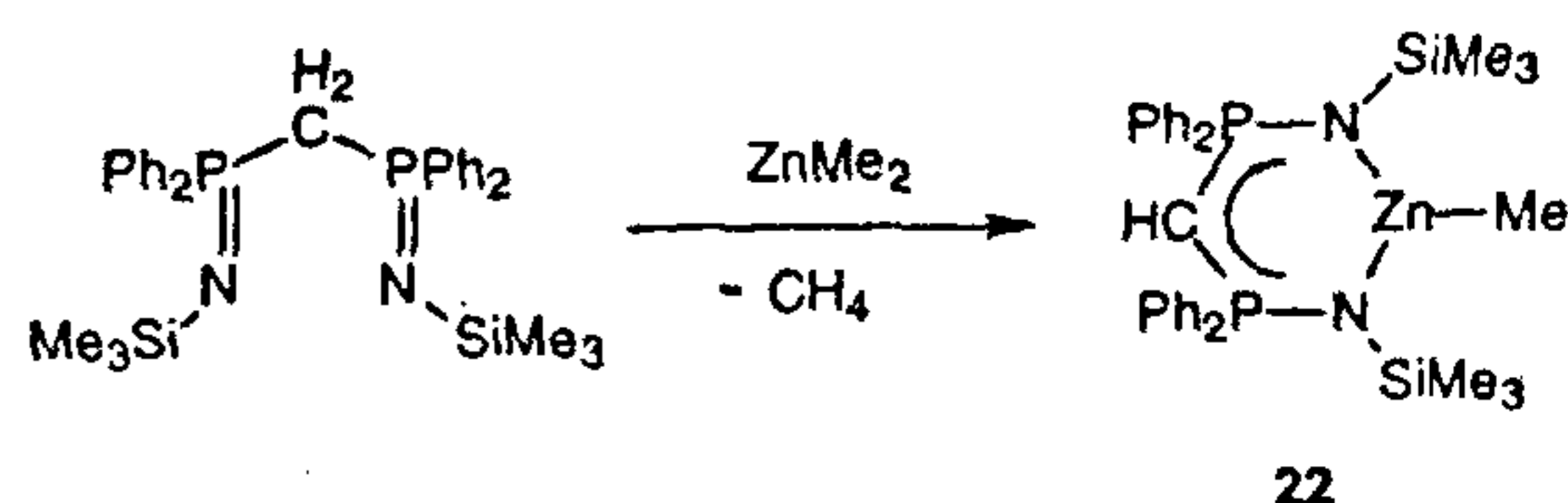
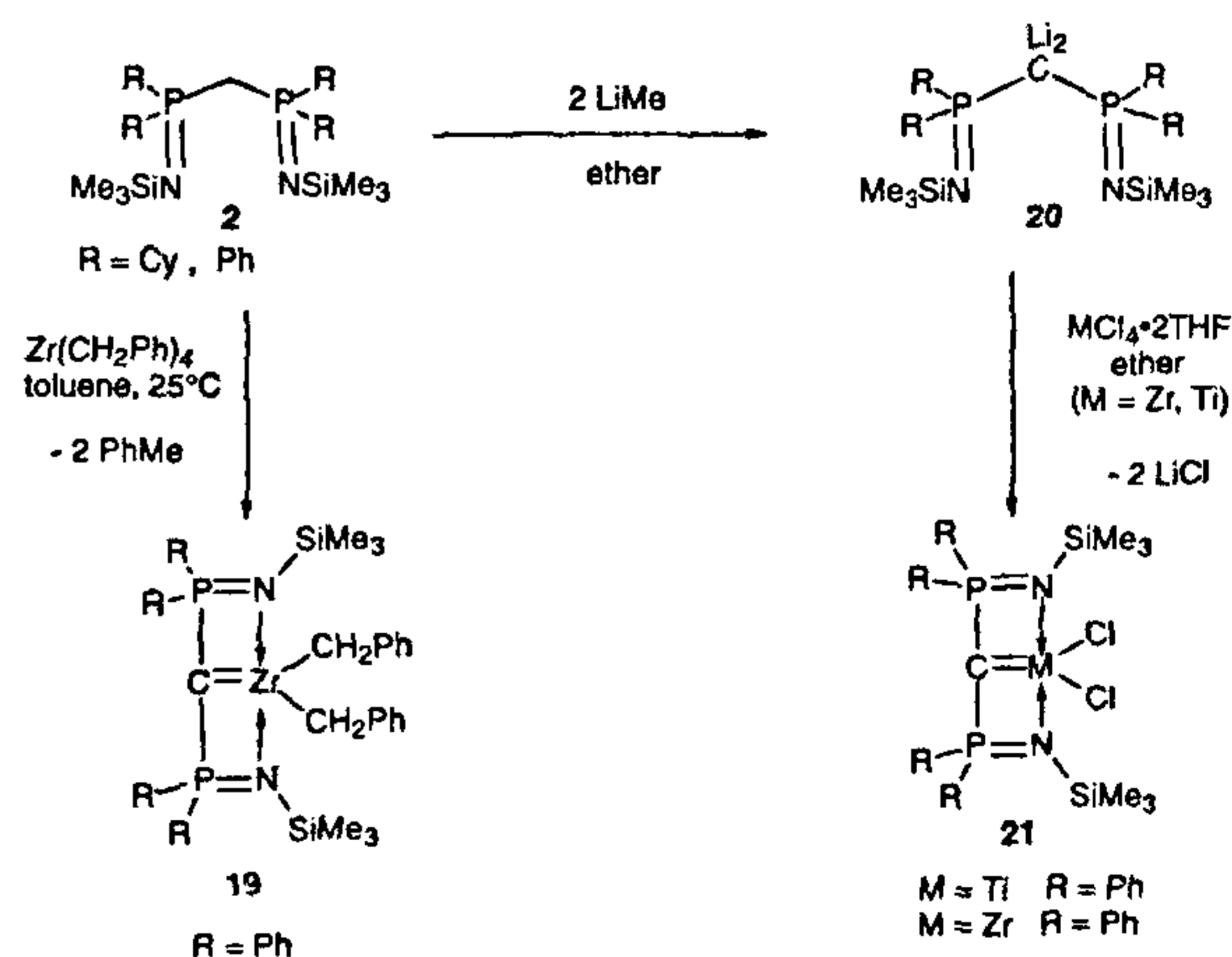
Upon chelation of the phosphinimine-phosphines, there is a decrease in the $\text{P}=\text{N}-\text{Si}$ angle and a lengthening of the $\text{P}=\text{N}$ bond ^{24,25,30}. Monodentate phosphinimines show similar lengthening of the $\text{P}=\text{N}$ bond and a sharpening of the $\text{P}-\text{N}-\text{R}$ angle upon coordination (e.g. $\text{Ph}_3\text{P}=\text{N}(\text{SiMe}_3)\text{CuCl}_2$ ¹⁴), in keeping with the return of electron density to the nitrogen center under the influence of interactions with the metal.

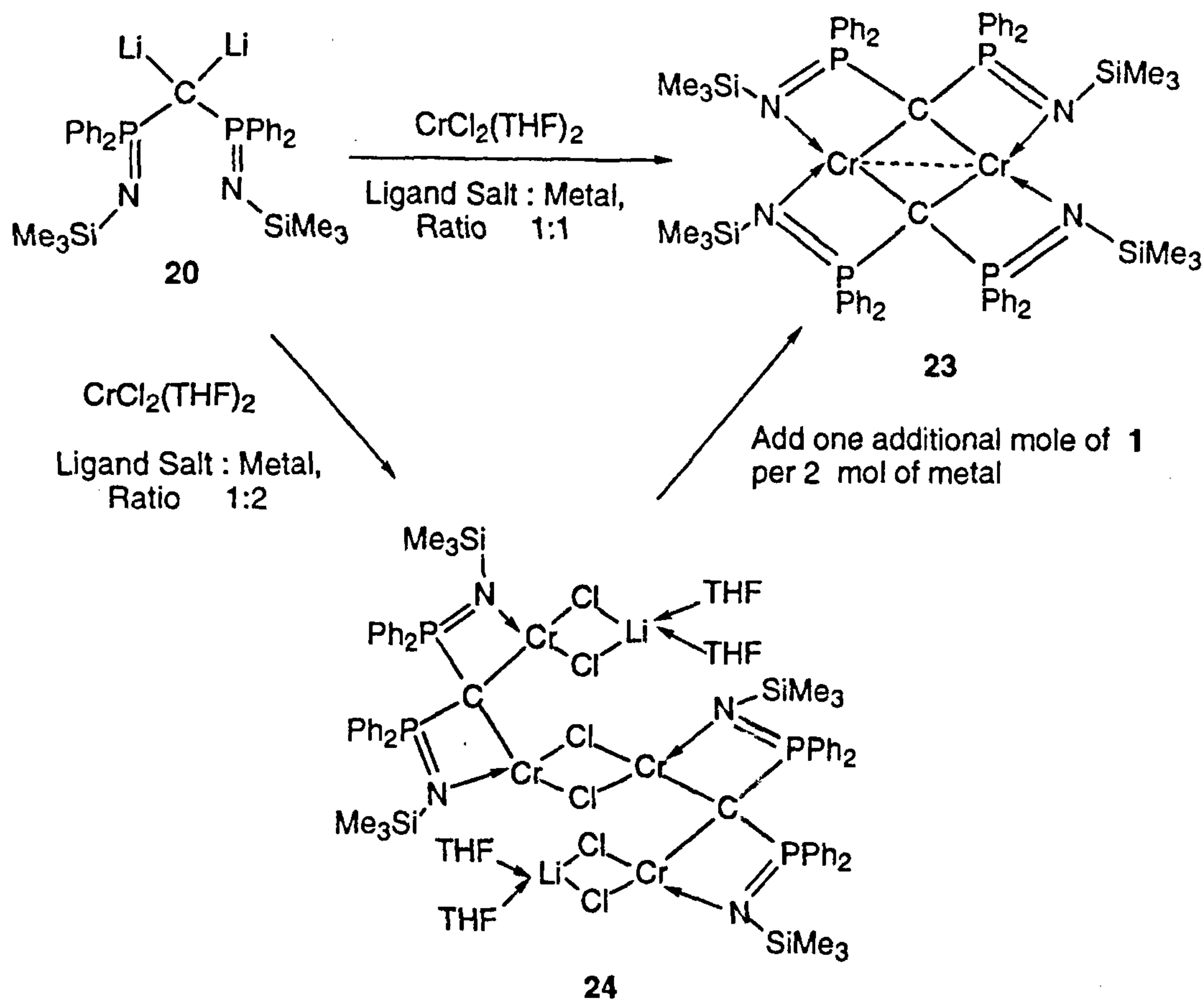
The phosphine imine complexes **17** and **18** display some interesting features of delocalization throughout the ligand backbone and the interplay between $\text{P}=\text{N}$ and $\text{P}-\text{N}$ bonding. The structures (see Figure 6) show a *cis* chelated ligand forming a square planar environment around the metal atom. The notable features of the structures are (i) the near planarity of the backbone amine nitrogen and (ii) the relatively short $\text{P}^{\text{V}}(2)-\text{N}(1)_{\text{amine}}$ distances of 1.64–1.67 Å which are closer to the value typically associated with $\text{P}=\text{N}$ bond lengths in cyclic phosphazenes indicating that the $\text{P}^{\text{V}}(2)-\text{N}(1)_{\text{amine}}$ nitrogen links have more multiple bond character than the $\text{P}^{\text{III}}(1)-\text{N}(1)_{\text{amine}}$ nitrogen bonds (both of which are a relatively long (1.78 or 1.70 Å respectively) which in the first case is typical of a single bond value. The $\text{P}^{\text{V}}(2)-\text{N}(2)_{\text{imine}}$ bond distances are short (1.58, 1.67 Å) at the short end of the range for typical $\text{P}-\text{N}$ double bond lengths. This shortening is notable in both complexes and may be due, in part, to the substantial electron withdrawing character of the phosphine oxide substituent on the imine nitrogen. Rather surprisingly, the $\text{P}(3)-\text{N}(2)$ bonds are also notably short in both **17** (1.63 Å) and especially in **18** (1.57 Å) whereas this is formally a $\text{P}-\text{N}$ single bond. This might be due to substantial electron withdrawing effects by the phosphine oxide substituent. The backbone of **18** in particular shows essentially equivalent bond lengths between the bridging $\text{P}^{\text{V}}(2)$ and both the amine and imine nitrogen atoms (1.67(1) Å in both cases). The bond lengths do not indicate a different bond order between this phosphorus and the two nitrogen atoms. The shortening of the $\text{P}^{\text{V}}(3)-\text{N}(2)$ bond length in **18** is not as marked as in **17**, the value in **18** is however also indicative of substantial double bond rather than single bond character. Thus there is extensive delocalization throughout the chelated backbone in these ligands which extends into the linkage to the phosphine imide. The $\text{M}-\text{N}$ bond lengths in these complexes reflect the

difference in hard/soft character of the metal center induced by the halide or CO substituents. The R complex obviously has a more electron rich center springing from the character of CO as opposed to Cl, the second ligand on the Pt center and this difference rationalizes the difference in $\text{M}-\text{N}$ bond lengths and has some effect on the ligand delocalization pattern. Thus the $\text{P}-\text{N}$ interactions are indeed 'intriguing' ³.

The methandiide chemistry of the bis(phosphoranimines)

As mentioned at the beginning of this survey uncontrolled oxidation of the bis(phosphino)methane our prototypical precursor gives a doubly oxidized species, $\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$ (Scheme 2, **2a**, $\text{R} = \text{Ph}$ $\text{Q} = \text{CH}_2$). Although the acidity of the methylene proton in the backbone of this ligand system has long been recognized, systematic and complete deprotonation has not been exploited. Furthermore, it was not recognized that this carbon could be multiply bound to a metal. A few cases of accidental deprotonation of this site have been recorded by us and others. We have now found that we can purposely induce the elimination of alkane (to form compounds of type **19** in Scheme 12) or **22** in Scheme 13 from suitable metal alkyls ^{26–28,43,44} respectively. There are two basic types of complexes those in which the carbon is bound to the metal center





Scheme 14.

with a double bond (**19**, **21** in Scheme 12) and those in which the ligand has suffered only single deprotonation and acts as an analog of acac (e.g. the Zn complex **22** in Scheme 13) (ref. 44). In addition, some metals give M₂C₂ dimer structures (see Scheme 14) in which the carbene acts as a bridge between two metals: In this system, the tetrametallic intermediate illustrated (**24**, Scheme 14) has also been isolated and structurally characterized²⁹.

In the new multiply bonded 'carbene' complexes of the type **19** or **21**, the central carbon is bound to the metal with a M=C (carbene) bond, an interpretation which is supported by the short M=C bond length.

So far, the optimum system for facile deprotonation has been R=Ph (**2a**, in Scheme 2) presumably because the backbone protons in **2a** are the most acidic of the system. The chelation of the imine arms of the ligand to the metal creates tridentate 'pincer' complexes which have structures similar to systems developed by others but within a different chemical system^{45,46}. We further showed that the CH₂ backbone center of **2a** could easily be fully deprotonated to form the dilithium salt (Scheme 12) (ref. 27) (independently discovered by Ong and Stephan⁴⁷) by the simple expedient of reaction of the phenyl *bis*(phosphine) with two moles of RLi. This

dilithium salt is a seminal reagent because it provides a direct and simple route to these M=C complexes²⁹.

Thus a straightforward metathetical reaction of the dilithiated salt²⁷ with metal tetrahalides gives [MCl₂{C(Ph₂P=NSiMe₃)₂-κ³C,N,N'}] complexes (Scheme 12) via clean elimination of LiCl (ref. 26). The structure of the Ti complex, which is illustrative of all complexes of this type, is shown in Figure 7 (ref. 26). These complexes are pale yellow or colourless crystalline solids which are highly soluble in relatively polar and aromatic solvents such as diethyl ether, benzene and toluene and thermally very stable (typically, toluene solutions of the complexes can be heated under an argon atmosphere in a closed container to 140°C for days without appreciable decomposition).

There are several points worthy of note in the structure of complexes such as **19** and **21** (Figure 7). The basic frame consists of two nearly planar, fused, four-membered rings {M, N(1), P(1), C(1) and M, N(2), P(2), C(1)} subtended from the shared edge defined by the M=C(1) bond. The P(1)-C(1)-P(2) angle approaches linearity, deviating by about 10–20°. The C(1) center is sometimes lifted out of the plane slightly but in all cases the two four-membered rings form a distorted 'open book' conformation. The four-membered

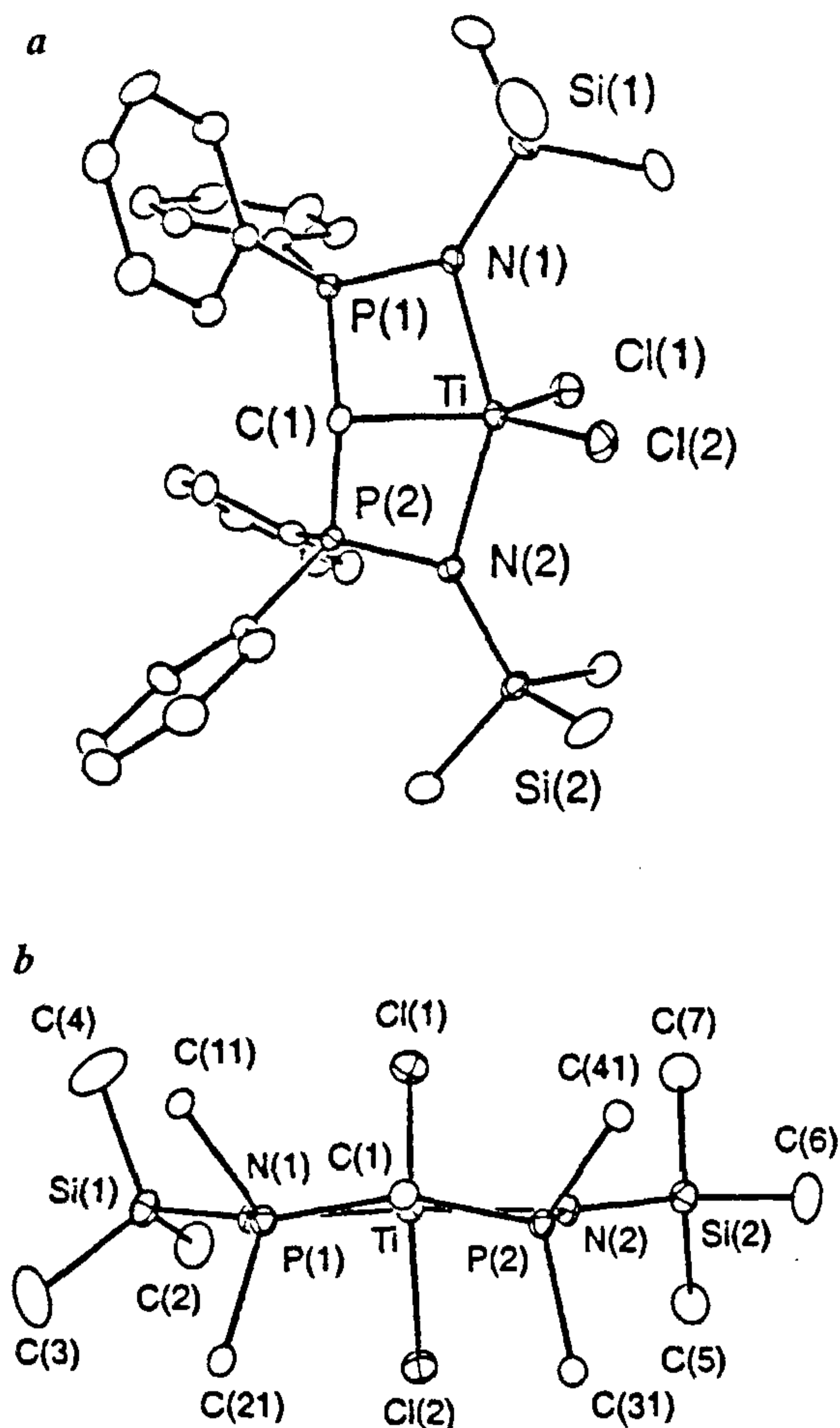
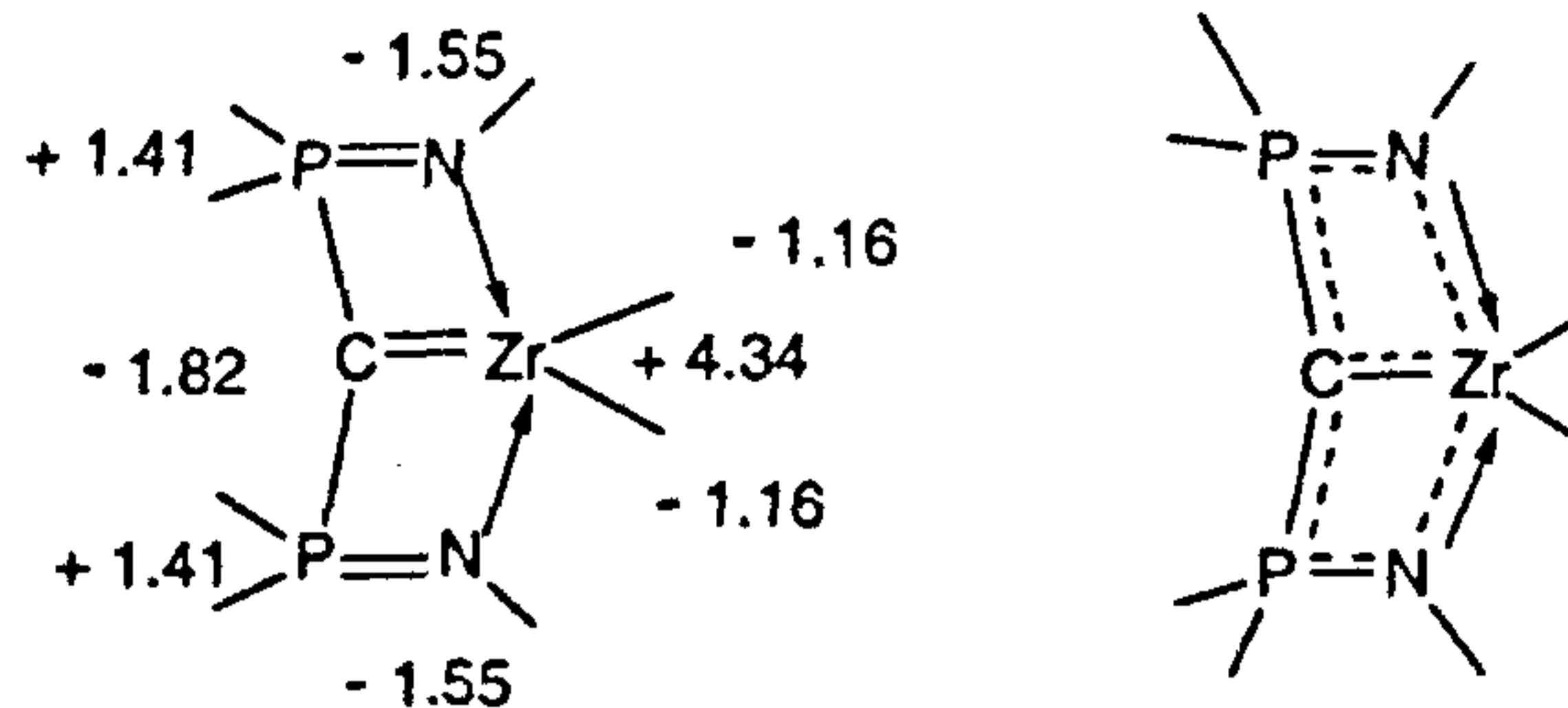


Figure 7. Molecular structure views²⁶ of $[\text{TiCl}_2\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2-\kappa^3\text{C}, \text{N}, \text{N}'\}]$ showing *a*, the view of the molecule (with non-essential peripheral atoms removed) and; *b*, a projection of the side view of the central plane. (Reproduced with permission).

rings do not appear to be appreciably strained. The $\text{M}=\text{C}(1)$ bond distances are short compared to related alkyl complexes and consistent with multiple bond character which would be appropriate for description of a 'carbene'.

These complexes such as **19** and **21** show interesting reactivity at the carbon center which is consistent with a 'carbene' description. There is a question as to whether these are Fischer (heteroatom) 'carbenes' or more alkylidene (Schrock) type centers. The complexes **19** and **21** however react in a fashion⁴³ more suggestive of alkylidene 'carbenes' which might be expected if we classify phosphorus not as a typical 'heteroatom' but more as a 'copy' of carbon⁴⁸.

A preliminary theoretical analysis of these complexes in the form of a 'single point energy calculation' carried



Scheme 15.

out at the density functional level⁴⁹ gives a charge distribution for **19** (Scheme 15) (ref. 28) which indicates a substantial dianionic character at the central carbon and implies that this carbon may act as a 'carbene' donor to the metal center.

Summary

The system of phosphorus–nitrogen has revealed substantial chemistry of both an unexpected character and versatility. There have also been some surprising results and there is much opportunity for further developments. The P–N bond does indeed display a remarkable range of chemistry.

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