

Review

Phosphorus-substituted carbene complexes: Chelates, pincers and spirocycles

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Abstract

The syntheses, structural characterizations and reactivity patterns of main group and late transition metal carbene complexes of the bis(phosphoranimino)methandiide, $[\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]^{2-}$, and the carbodiphosphorane, $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$, are described and compared to previously reviewed early transition metal analogues. Bimetallic spirocyclic aluminum complexes of the former ligand are accessed by spontaneous double deprotonation of the central carbon atom of the parent, $\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$, by two equivalents of AlMe_3 , whereas the synthesis of platinum complexes requires the intermediacy of the tetralithium dimer, $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]_2$, and elimination of LiCl from a metal chloride precursor. In contrast to the early transition metal analogues, which are *N,C,N*-pincer, Schrock-type alkylidenes, the *C,N*-chelated platinum complexes are more akin to Fischer carbenes, and their chemistry is dominated by the nucleophilicity of free nitrogen atom and insertions into labile N–Si bonds. Chelated and pincer carbene complexes of rhodium result from single and double orthometallations, respectively, of the phenyl rings in $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$; the latter compounds represent a wholly new class of *C,C,C*-pincer complexes. Electronic structure calculations show that the metal–carbon interaction in these compounds may be described as a dative, two-electron, $\text{C} \rightarrow \text{M}$ σ -bond. The free bis(phosphoranimino)methandiide and carbodiphosphorane ligands, while not having formal six valence electron resonance forms, may be thought of as having “pull–pull” Fischer carbene character, but the metal to which they become coordinated ultimately dictates their chemistry.

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1. Introduction

Ligand systems incorporating phosphorus are widely used in coordination chemistry and have found extensive application in homogeneous catalysis. Most common are those wherein a phosphine unit is a ligating center, but phosphorus atoms in various valence and coordination states can also be incorporated as bound low-valent substituents, or as “scaffold” (non-coordinating framework) elements. Either as a ligation center or as a framework element, phosphorus offers a rich substitutional chemistry and a range of geometrical environments, properties that often make it more versatile than carbon in the design and synthesis of new ligand architectures. As a bonus, the NMR active ^{31}P nucleus is a source of informative spectroscopic data. Over the years, we have explored many variants of phosphorus-containing systems, and have assembled hard/soft donor combinations providing versatile coordination modes for a variety of transition metals [1,2]. Some of our complexes have proven to be useful homogeneous catalysts for hydrogenation [3] carbonylation [4] and polymerization [5] reactions. Recently, we have pursued the development of a remarkable set of phosphorus-based carbene complexes, which we discovered in 1998 [6] and which continue to yield exciting new chemistry.

Over the last two decades, the chemistry of stable, singlet carbenes has expanded dramatically [7]. Of primary interest to us are phosphorus-containing systems, which, since the isolation of $(^i\text{Pr}_2\text{N})_2\text{P}-\text{C}-\text{SiMe}_3$ in 1988 by Bertrand and co-workers [8], have become increasingly important. Representative recent examples of the incorporation of tricoordinate phosphorus into stable carbenes include a four-membered *N*-heterocyclic carbene (NHC) containing a phosphorus atom within the cycle that is not bonded to the carbene carbon atom [9] as well as systems where phosphorus is alpha to the carbene center as in the fluorinated aryl derivative of the first stable, singlet carbene, $(^i\text{Pr}_2\text{N})_2\text{P}-\text{C}-(\text{C}_6\text{H}_3(\text{CF}_3)_2)$ [10]. This ligand, unlike its silyl progenitor, has been shown to coordinate to Rh thus dispelling the notion that these systems were ineffective donors and also illustrating the dramatic effect of substitution on the character of the ligand [10]. Other remarkable examples are the bis(phosphanyl)carbenium ion isolated from protonation of 1,3-diphosphanycyclobutane-2,4-diyl [11] and the heterocyclic four membered P–N–C–P ring carbene reported in early 2005 also by Bertrand and co-workers [12]. Four-coordinate phosphonium centres have also recently been linked to the carbene, as

in $[^i\text{Bu}_2\text{MeP}-\text{C}-\text{N}^i\text{Pr}_2][\text{CF}_3\text{SO}_3]$ [13] and $[\text{R}_3\text{P}-\text{C}-\text{N}^i\text{Pr}_2][\text{CF}_3\text{SO}_3]$ ($\text{R} = \text{Cy}, \text{Ph}$), again by the Bertrand group [14].

Herein, we survey our recent advances in accessing complexes of the bis(phosphoranimino)methandiide and carbodiphosphorane ($\text{R}_3\text{P}=\text{C}=\text{PR}_3$) ligand systems in which a carbene type carbon may be formed and bound to metals. Although a formal carbene resonance form (six valence electrons on the central carbon atom) cannot be drawn for either of these systems, we feel that they have strong (and underappreciated) parallels with the heteroatom-substituted Bertrand (phosphanyl-aryl, or -silyl) and Arduengo (*N*-heterocyclic) carbenes in that all of these species have ylidic resonance forms that allocate eight valence electrons to the “carbene” carbon atom and form complexes in which they act as bent, two-electron σ -donors (Chart 1). Like the Bertrand (**A**) and Arduengo carbenes (**B**), the carbodiphosphoranes (**C**) are electrically neutral. The bis(phosphoranimino)methandiides (**D**), on the other hand, are dianionic, but the central P–C–P fragment, as in the other classes of heteroatom supported carbenes, is net neutral in this simple resonance description. However, in contrast to the Arduengo (“push–push”) and Bertrand (“push–pull”) carbenes, the non-coordinated carbodiphosphoranes and bis(phosphoranimino)methandiides can be thought of as “pull–pull” carbene systems because the electron-withdrawing phosphonium or phosphoranimine substituents deplete electron density on the central, formally C^{2-} atom to give it distinctly carbene character. In efforts parallel to ours, other filled-octet, phosphorus-containing compounds for which formal carbene resonance forms cannot be drawn, such as the bis(thiophosphinoyl)methandiides [16] and more elaborate variations of the bis(phosphoranimino)methandiides [17,18] have also begun to be thought of as having carbene character.

It is important to note that while the non-coordinated carbodiphosphoranes and bis(phosphoranimino)methandiides have distinct similarities to the carbenes mentioned above, the metals to which these ligands become coordinated ultimately dictate their electronic character. Thus,

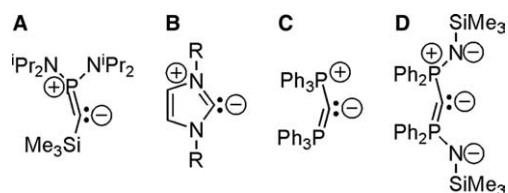


Chart 1. Ylidic resonance forms in heteroatom-substituted carbenes.

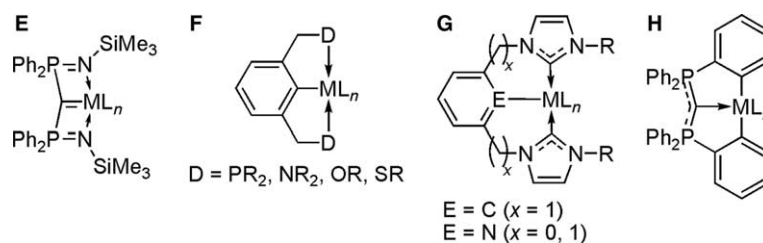


Chart 2. Structural types in pincer complexes.

group four metal complexes of the bis(phosphoranimino)methandiides are distinctly nucleophilic, Schrock-type alkylidenes while their platinum analogues retain Fischer character (vide infra).

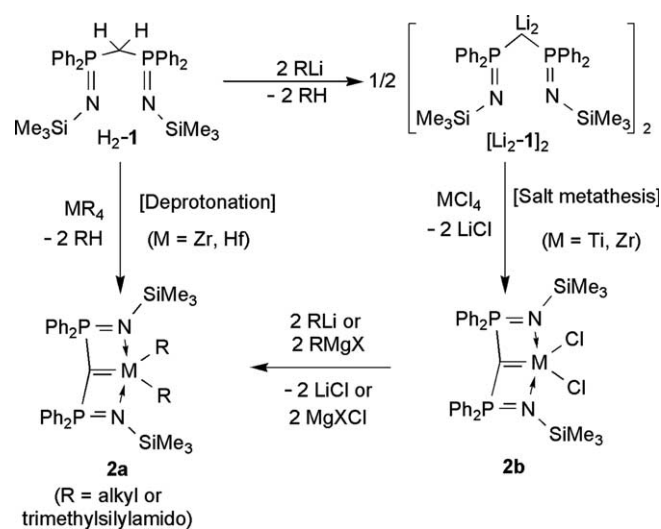
In our early chemistry, we commonly generated “pincer” structures (Chart 2, E [2]) and a few dimetallic saddle-shaped complexes, but in our more recent work, other structural motifs have arisen, including chelates, and spirocyclic bridging carbene architectures. The pincer complexes in our hands, E and very recently, H, relate to the large established body of this general geometrical class, F [20], which now also includes NHC variations, G [21].

2. Bis(iminophosphorane)-substituted carbene complexes

2.1. Early transition metal complexes – our initial investigations

Our 2001 review in this journal [2] summarized the syntheses, structural characterizations and reactivity patterns of early transition metal and lanthanide complexes of bis(phosphoranimino)-substituted carbenes, which were the results of our first efforts with this ligand system. Our earliest carbene systems were derived from bis(diphenylphosphino(trimethylsilylimino))methane ($\text{CH}_2(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2$; **H₂-1**) [15] which is obtained by a straightforward Staudinger oxidation of both of the phosphorus atoms of bis(diphenylphosphino)methane (dppm). Trimethylsilyl azide, which is safely handled, even at high temperatures, provides for the convenient installation of a bulky substituent on the imine nitrogen atoms. Other suitable azides (e.g., adamantyl azide), which do not result in the installation of labile N–Si bonds, can also be used. Our development of the metal chemistry has focussed on **H₂-1**, and its derivative, $[\text{Li}_2\text{-1}]_2$ (**6(a)**) (vide infra), but we have also investigated other derivatives bearing methyl and cyclohexyl groups on the phosphorus atoms, and we have used other bulky groups (e.g., adamantyl) on the nitrogen atoms [2].

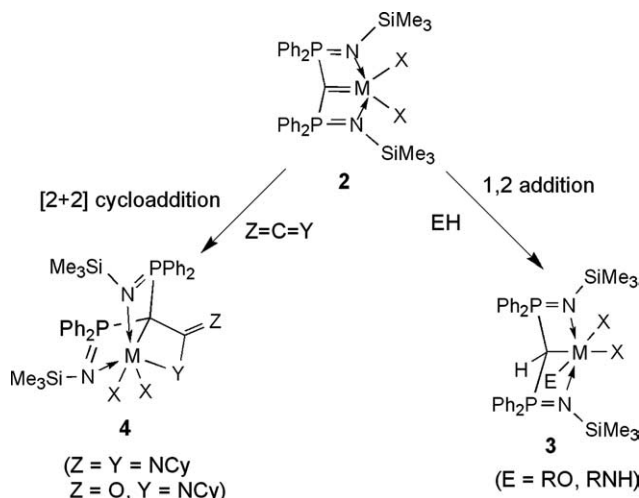
Initial access to early metal “pincer” carbene complexes was provided by the facile deprotonation of **H₂-1** by metal alkyls or bis(trimethylsilyl)amides with concomitant elimination of alkane or silylated amine (Scheme 1). This occurred readily because the strongly electron-withdrawing phosphoranimine groups significantly enhanced the acidity of the methylene protons in **H₂-1** with respect to those in dppm. The resultant *N,C,N*-pincer complexes contained



Scheme 1. Key early transition metal bis(phosphoranimino)methandiide “pincer” chemistry.

strong, short, metal–carbon interactions with double-bond character. Synthetic limitations on the system (i.e., unstable or inaccessible metal precursors) were almost totally removed by the discovery by ourselves [6a] and independently by others [22] in 1999 of the structurally unusual organolithium complex, $[\text{Li}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]_2$ ($[\text{Li}_2\text{-1}]_2$), easily obtained by double deprotonation of the methylene C-atom of **H₂-1** with alkyl- or aryllithium reagents. The dimer $[\text{Li}_2\text{-1}]_2$ is remarkably inert for an organolithium compound. Structurally, it contains a square planar array of Li cations capped by two orthogonal $[\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]^{2-}$ units in which the C-atoms lie above and below the centre of the square plane, and the N-atoms bridge its edges. The core appears as a small cluster and this seems to be a very stable arrangement that renders the compound stable to air for short periods in the solid state. It has provided entry to many different metal systems (Scheme 1).

Structural data and reactivity patterns of our early transition metal pincer carbene complexes containing **1** conclusively demonstrated that these compounds were best described as Schrock-type alkylidenes (Scheme 2) [6]. The $\text{M}=\text{C}$ bond parameters suggested higher bond order, and reactions of electrophiles such as HOR and heteroallenes gave, respectively, 1,2 additions across and $[2+2]$ cycloadditions to the metal–carbon bond which preserved the



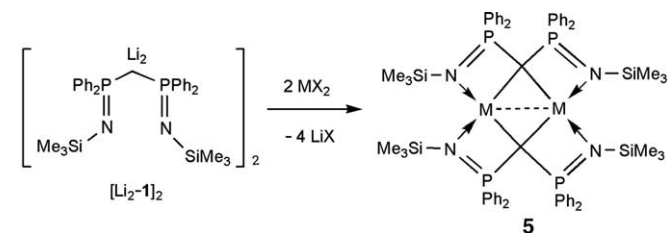
Scheme 2. Additions to early metal pincer complexes ($M = \text{Zr}, \text{Hf}; X = \text{Cl}$).

connection but as a slightly longer (and weaker, single) bond (Scheme 2).

Some low valent metal halides reacted with $[\text{Li}_2\text{-1}]_2$ to form bridged carbene species such as the complexes of Cr [6d] (and also Mn and Fe) (Scheme 3). The structures show a planar M_2C_2 ring with a “saddle” arrangement adopted by the supporting ligand structure. The nitrogen coordination appears to be an essential component of the system. Although the metal atoms are close to each other and the magnetic moments are lower than the spin configuration would suggest, low temperature magnetic studies did not reveal any unusual magnetic coupling. These complexes provided the first examples of bridging carbenes in this system.

2.2. Main group metal complexes

Aluminum [23] and zinc [24] methyls react at room temperature with $\text{H}_2\text{-1}$ to give *N,N*-chelated methanides via single deprotonation events. Thus, reaction of $\text{H}_2\text{-1}$ with 1 equiv. of AlMe_3 in toluene solution at room temperature gave the monomeric aluminum bis(phosphoramino)methanide, $[\text{AlMe}_2\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa^2\text{N}\}]$ (**6a**) (Scheme 4, Fig. 1) which has a tetrahedral Al center and an $\text{R}_2\text{M}(\text{acac})$ like structure [6e]. This aluminum product was unstable



Scheme 3. Synthesis of “saddle shaped” bridging carbene complexes ($M = \text{Mn}, \text{Cr}, \text{Fe}$).

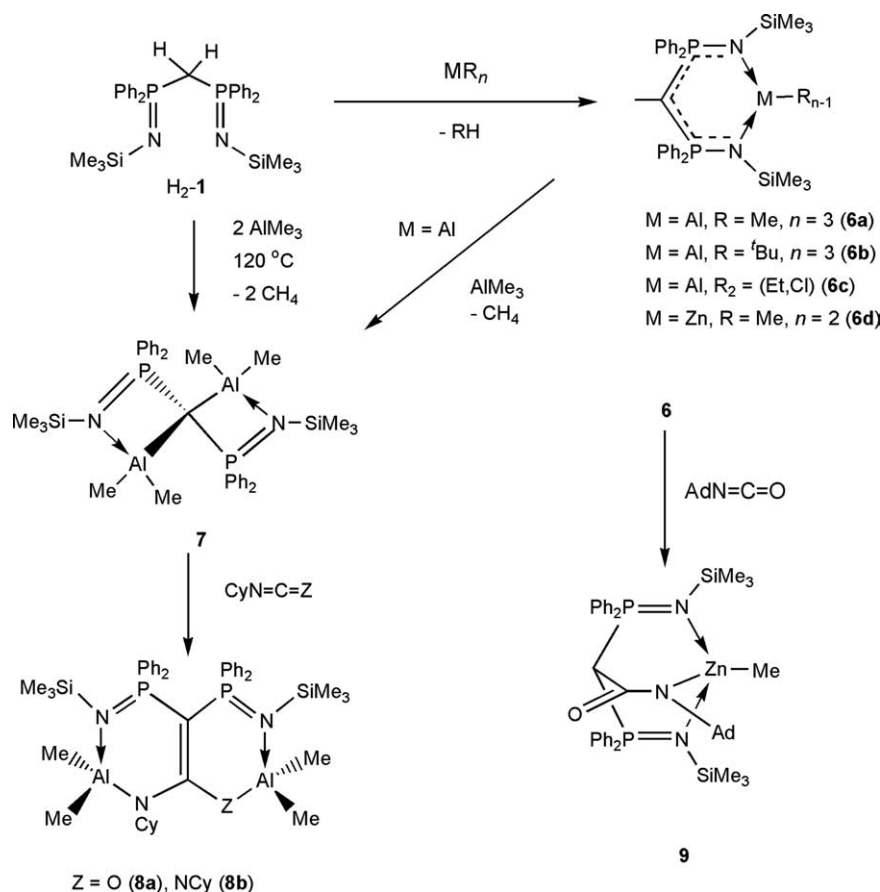
and decomposed to the dialuminum spirocycle, $[\text{Al}_2\text{Me}_4\{\mu\text{-C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C}, \kappa\text{N}; \kappa\text{C}, \kappa\text{N}'\}]$ (**7**, Fig. 2) which could be directly accessed with 2 molar equivalents of AlMe_3 at higher temperatures [6e]. Other aluminum alkyl precursors gave differently substituted versions of the methanide system **6** (**6b** and **6c**, Scheme 4, and *vide infra*).

The reaction of ZnMe_2 with $\text{H}_2\text{-1}$ gave the analogous tricoordinate Zn complex $[\text{ZnMe}\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa^2\text{N}\}]$ (**6d**, Fig. 3) but in this case there is a close interaction between the Zn atom and the methine CH group that gives a boat conformation [24].

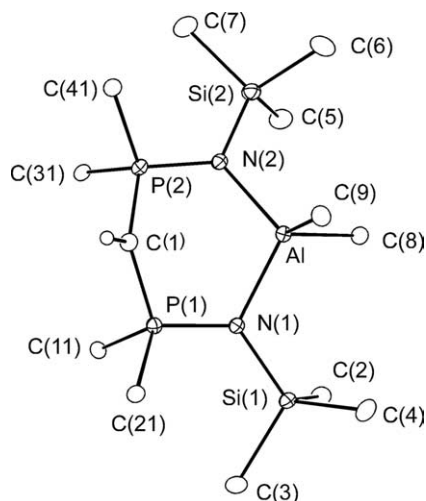
Earlier workers had observed double deprotonation of the related ligands $\text{CH}_2(\text{Ph}_2\text{P}=\text{E})_2$ ($\text{E} = \text{O}, \text{S}$) by AlMe_3 , but the products were bridged tri- and tetrametallic complexes, $[\text{Al}(\text{R})\{\text{C}(\text{Ph}_2\text{P}=\text{O})_2\}]_2[\text{Al}(\text{R})_2]_2$ ($\text{R} = \text{Me}$ [23a], Et [23b]) and $[\text{Al}(\text{R})_2\{\text{C}(\text{Ph}_2\text{P}=\text{S})_2\}]_2[\text{Al}(\text{R})_2]_2$ ($\text{R} = \text{Bu}$ [23c]). Our system was therefore unique in allowing the stepwise synthesis and isolation of both mono- and bimetallic methanide and methandiide complexes with monomeric structures. The former can be readily converted to the latter. We suspect that the steric bulk of the trimethylsilyl substituents on the phosphoramino nitrogen atoms conferred a greater degree of steric control.

The reactions of **6a** and **6d** with heteroallenes resulted in the formation of new carbon–carbon bonds, most remarkably C=C double bonds between the formerly bridging methylene carbon atom in **7** and the central carbon atom in the heteroallene. Thus, reaction of **7** with cyclohexylisocyanate, $\text{CyN}=\text{C}=\text{O}$ or bis(cyclohexyl)carbodiimide (Scheme 4) gave, respectively, $[(\text{AlMe}_2)_2\mu\text{-}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{C}=\text{C}(\text{CyN})(\text{O}))\text{-}\kappa\text{N}, \kappa\text{N}'; \kappa\text{C}, \kappa\text{O}]$ (**8a**) or $[(\text{AlMe}_2)_2\{\mu\text{-}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{C}=\text{C}(\text{CyN})_2\text{-}\kappa\text{N}, \kappa\text{N}'; \kappa\text{N}'', \kappa\text{N}'''\}]$ (**8b**, Fig. 4) [25]. In both cases, an excess of the heteroallene gave neither further homologation nor insertion into the available Al–Me bonds of **8a** and **8b**. The Zn complex **6d** added the isocyanate to form **9**, which has a new C–C bond to the methine carbon atom (Fig. 5) [24].

The dialuminum spirocyclic carbene **7** proved to be a very effective transition metal-free ethylene polymerization precatalyst when activated by a molar equivalent of trityl tetrafluoroborate [5]. By contrast, the monometallic precatalysts, $[\text{AlR}_2\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa^2\text{N}\}]$ ($\text{R} = \text{Me}$ (**6a**), Bu (**6b**)) or $[\text{AlClEt}\{\text{CH}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa^2\text{N}\}]$ (**6c**), which contain monoanionic *N,N*-chelating ligands and whose structures are similar to **6a** (reminiscent of AlR_2 (acac) complexes), were only modestly active under similar conditions [5]. This suggests that dialuminum species may prove to be generally more effective polymerization catalysts than monometallic complexes. The main group chemistry of the bis(phosphoramino) ligands is potentially large and varied and deserves further investigation. Others have recently reported interesting related complexes of Sn and Pb [26]. We also found that the alkali metals formed monomeric or dimeric complexes with this ligand system [27] instead of the frequently encountered polymeric materials. These complexes could become useful reagents similar to the dilithiated species, $[\text{Li}_2\text{-1}]_2$.



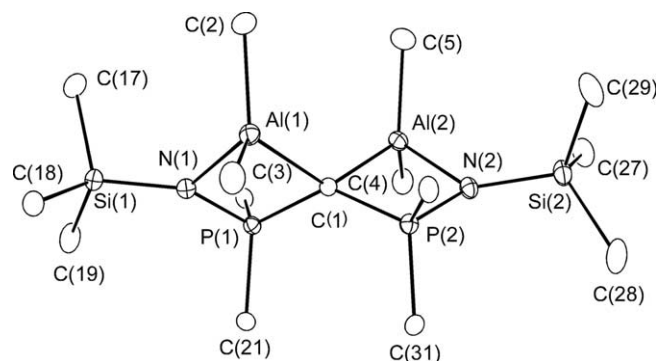
Scheme 4. Syntheses and reactions of aluminum and zinc bis(phosphoranimino)-methanide and -methandiide complexes.

Fig. 1. ORTEP representation (20% ellipsoids) of the molecular structure of **6a**. Only the *ipso* carbon atoms of the phenyl rings are shown and all but the methine hydrogen atoms have been omitted for clarity (reproduced with permission).

2.3. Platinum bis(phosphoranimino)methandiide complexes

2.3.1. Platinum carbenes

Following the successful development of the chemistry of a considerable fraction of the early and middle portion of the transition metal block, and having found a few interesting

Fig. 2. ORTEP representation (20% ellipsoids) of the molecular structure of **7**. Only the *ipso* carbon atoms of the phenyl rings are shown and hydrogen atoms have been omitted for clarity (reproduced with permission).

main group complexes, we wanted to explore the synthesis and reactivity of carbene complexes of the late transition elements. The dilithiated salt reagent provided an efficient route to these compounds. Thus, reaction of $[\text{Li}_2\text{-1}]_2$ with 2 equiv. of $[\text{PtCl}_2(\eta^4\text{-cod})]$ in Et_2O gave $[(\eta^4\text{-cod})\text{Pt}\{\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2\text{-}\kappa\text{C}, \kappa\text{N}\}]$ (**10**, Scheme 5, Fig. 6) as a red-orange crystalline powder in good yield [28].

The coordination environment around the Pt-atom is a slightly distorted square plane. Here for the first time in our hands, ligand **1** adopted a $\kappa\text{C}, \kappa\text{N}$ chelate coordination

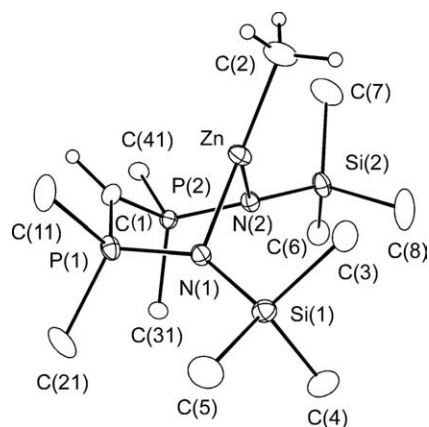


Fig. 3. ORTEP representation (20% ellipsoids) of the molecular structure of **6d**. Only the *ipso* carbon atoms of the phenyl rings are shown and the trimethylsilyl hydrogen atoms have been omitted for clarity (reproduced with permission).

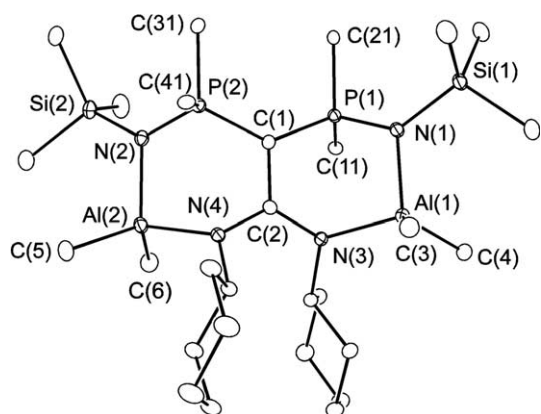


Fig. 4. ORTEP representation (20% ellipsoids) of the molecular structure of **8b**. Only the *ipso* carbon atoms of the phenyl rings are shown and hydrogen atoms have been omitted for clarity (reproduced with permission).

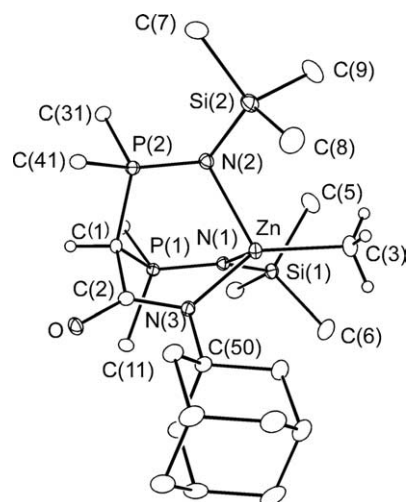
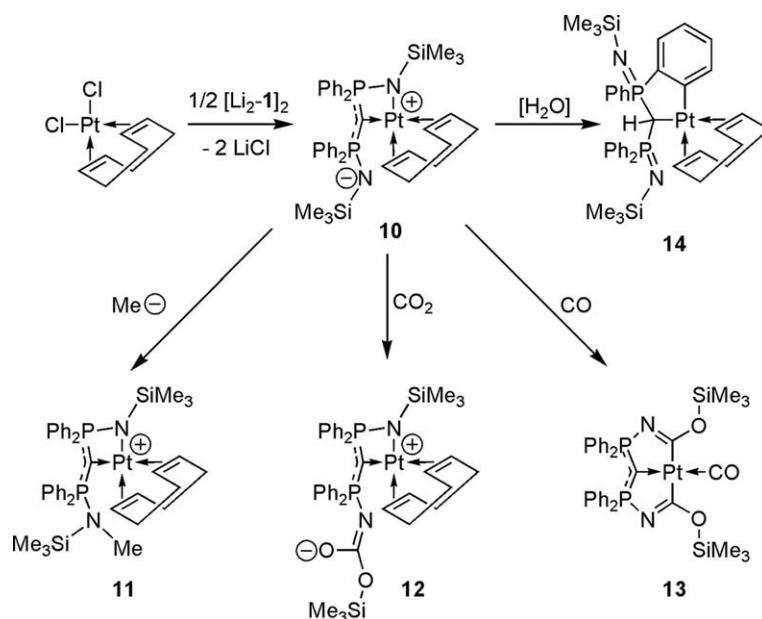


Fig. 5. ORTEP representation (20% ellipsoids) of the molecular structure of **9**. Only the *ipso* carbon atoms of the phenyl rings are shown and the trimethylsilyl and adamantyl hydrogen atoms have been omitted for clarity (reproduced with permission).

mode in which only one of the two N-atoms of the ligand coordinates to form a four-membered chelate ring with Pt; the other is “dangling.” The question had arisen in the context of all earlier work as to whether coordination of both N-centres was necessary to stabilize the complexes. However, **10** showed that only one coordinated N-atom was sufficient to stabilize a complex bearing an $M = C$ (higher order) bond. Clearly the nature of the metal exerts a strong influence. It is still not clear whether $M = C$ complexes of **1** in which neither nitrogen is coordinated can also be made.

The carbene C-atom in **10** is planar and C(1), P(1), P(2) and Pt also form a perfect plane. The Pt–C(carbene) distance in **10** is appreciably longer (2.021(5) Å) than those typically found for both NHC complexes of 2- and 4-coor-



Scheme 5. Synthesis and reactions of the platinum carbene, **10**.

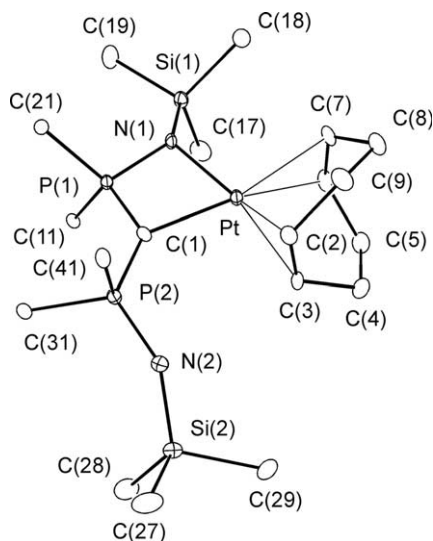


Fig. 6. ORTEP representation (20% ellipsoids) of the molecular structure of **10**. Only the *ipso* carbon atoms of the phenyl rings are shown and the hydrogen atoms have been omitted for clarity (reproduced with permission).

dinate Pt (1.93–1.97 Å) [29–31] and Fischer carbene complexes of 4-coordinate Pt (1.87–1.96 Å) [32–37]. Indeed, the Pt–C(carbene) distance in **10** is unusual in that it is more like those found for Fischer carbene complexes of 5- [38] and 6-coordinate [39] Pt (1.99–2.01 Å). Nevertheless, the Pt–C(carbene) bond in **10** is notably shorter than typical Pt–C(alkyl) single bonds (2.07–2.15 Å) [40] and subsequent chemistry (Section 2.3.3) developed at this center shows that the bond order is >1. Table 1 collects other metrical data for **10**.

Both of the P–C(carbene) lengths in **10**, particularly that of the endocyclic bond, are considerably shorter than that found for P–C(methylene) in H_2 -**1** (1.697(5) (endo) and 1.721(5) (exo) vs. 1.827(1) Å), while the P–N distances, again particularly that of the endocyclic bond, are appreciably longer (1.631(4) (endo) and 1.550(4) (exo) vs. 1.539(2) Å) [15b]. These observations are consistent with electronic delocalisation within the framework of coordi-

nated **1**. Generally speaking, there is an inverse relationship between the C–P and the P–N distances complexes of the bis(phosphoranimino)methandiides. Both of these lengths are intermediate between single and double bonds: C–P=N and C=P–N are the limiting resonance forms.

In contrast to the early transition element pincer chemistry, we found that the reactivity of **10** was dominated by the presence of the uncoordinated N-atom; reactions with electrophiles demonstrated that this centre was more nucleophilic than the carbene C-atom. Thus, reacting **10** with an excess of $MeOSO_2CF_3$ (MeOTf) cleanly gave the *N*-methylated complex, $[Pt(\eta^4-cod)\{C(Ph_2P=NSiMe_3)(Ph_2P=N(Me)SiMe_3)-\kappa C, \kappa N\}][OTf]$ (**11**)[OTf], with no evidence of C(carbene)–CH₃ bond formation, while reaction with CO₂ gave $[Pt(\eta^4-cod)\{C(Ph_2P=NSiMe_3)(Ph_2P=NC(O)OSiMe_3)-\kappa C, \kappa N\}]$ (**12**) as an insertion into the N–Si bond (Scheme 5). The Fischer carbene nature of **10** was confirmed by the fact that all of our attempts to add an electrophile to the carbene carbon atom were unsuccessful. Another notable feature of the reactivity of **10** was that substitution of the cod ligand proved not to be possible using a wide variety of ligands.

2.3.2. A triple carbene pincer complex

The nucleophilicity of the N-donors and C-to-O migration of the trimethylsilyl group was also evident in the reaction between **10** and 1 atm of CO gas at room temperature, which resulted in the rapid and quantitative formation of the remarkable triple carbene pincer complex, $[(CO)Pt\{\eta^3-C(Ph_2P=NCOSiMe_3)_2\}]$ (**13**, Scheme 5, Fig. 7) [41]. This transformation presumably occurred via initial displacement of the cod and 2-fold attack by free iminophosphorane nitrogen atoms on coordinated CO, followed by trimethylsilyl group migration. This ultimately resulted in the insertion of CO into both N–Si bonds and the concomitant formation of two new Fischer carbene donors.

All three metal-bound carbon atoms of the iminophosphorane ligand are planar and the bond lengths are short. The central carbene center provides the shortest bond: the Pt–C(1) bond length is 2.002(5) Å, but the others are

Table 1

Selected bond distances and angles for a range of chelated, spirocyclic and pincer carbene complexes (standard deviations in parentheses)

| Compound | M–C (Å) | C–P (Å) | P–N (Å) | P–C–P (°) | Σ angles at C (°) |
|-----------|----------|----------|----------|------------|--------------------------|
| 7 | 2.121(3) | 1.751(3) | 1.612(3) | 133.1(2) | – ^a |
| | 2.117(3) | 1.746(3) | 1.615(3) | | |
| 10 | 2.021(5) | 1.697(5) | 1.631(4) | 134.0(3) | 360.0 |
| | | 1.721(5) | 1.550(4) | | |
| 13 | 2.002(5) | 1.701(6) | 1.653(5) | 133.3(3) | 356.8 |
| | 2.059(6) | 1.702(6) | 1.658(5) | | |
| | 2.048(6) | | | | |
| 18 | 2.165(2) | 1.692(2) | – | 124.50(13) | 360.0 |
| | | 1.693(2) | | | |
| 19 | 2.202(3) | 1.672(3) | – | 138.32(18) | 359.8 |
| | | 1.675(3) | | | |

^a Spiro carbon center.

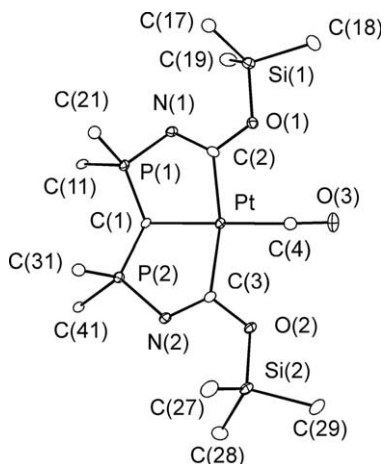


Fig. 7. ORTEP representation (20% ellipsoids) of the molecular structure of **13**. Only the *ipso* carbon atoms of the phenyl rings are shown and the hydrogen atoms have been omitted for clarity (reproduced with permission).

comparable (Pt–C(2) 2.059(6) Å and Pt–C(3) 2.048(6) Å). All are slightly shorter than the corresponding bond length found in the parent **10**. Once again there is structural evidence for electronic delocalisation within the ligand framework. See Table 1 for other structural parameters.

2.3.3. Orthometallation

The carbene complex **10** undergoes an orthometallation reaction which appears to be catalyzed by small amounts of water. Heating **10** in an organic solvent containing controlled amounts of added water gave the orthometallated complex, $[(\eta^4\text{-cod})\text{Pt}\{\eta^2\text{-CH}(\text{PhP}(\text{C}_6\text{H}_4)\text{NSiMe}_3)(\text{Ph}_2\text{PN-SiMe}_3)\}]$ (**14**, Scheme 5, Fig. 8) [28]. There was no reaction in dry solvent under the same conditions. The orthometallated complex **14** does not display the kind of charge delocalisation found in **10**, but rather is typical of orthometallated aryl Pt complexes. The C–P and P=N distances in **14** are, on average, longer (1.814(6) vs. 1.709(5) Å) and shorter (1.552(5) vs. 1.591(4) Å), respectively, than the corresponding lengths in **10** and fall within the accepted ranges of single C–P and double P=N bonds.

2.3.4. Rearrangement to a platinacycphosphazene

The *N*-methylated complex **11** reacted (Scheme 6) with stoichiometric quantities of H₂O diluted in solvent (uncontrolled addition of water gave intractable products) to give

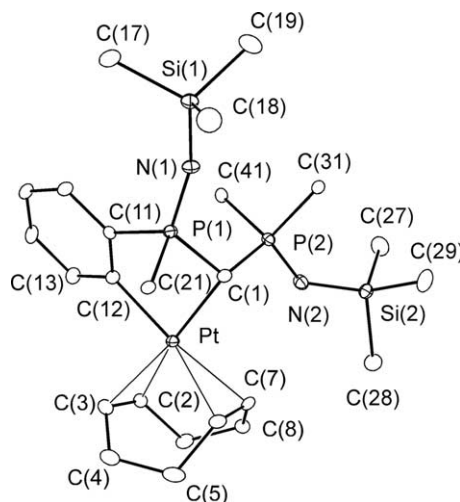
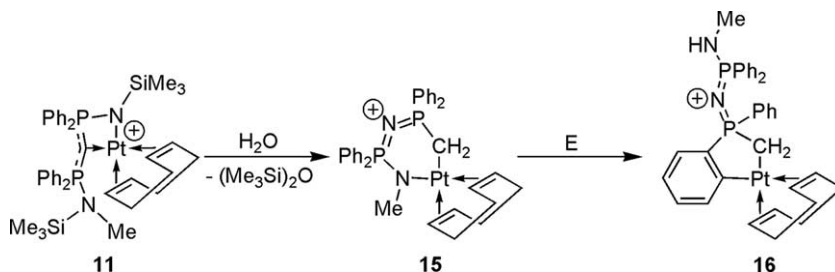


Fig. 8. ORTEP representation (20% ellipsoids) of the molecular structure of **14**. Only the *ipso* carbon atoms of all but the orthometallated phenyl rings are shown and hydrogen atoms have been omitted for clarity (reproduced with permission).

an unusual platinacycphosphazene, $[(\eta^4\text{-cod})\text{Pt}\{\text{CH}_2\text{P}(\text{Ph}_2)\text{N}(\text{Ph}_2)\text{N}(\text{Me})\text{-}\kappa\text{C},\kappa\text{N}}][\text{OTf}]$ (**15**) [OTf] wherein both N–Si bonds have been hydrolyzed and a remarkable N–P–C–P–N to C–P–N–P–N rearrangement has taken place [42]. The reaction was complete within 24 h. The rearranged platinacyclic carbaphosphazene **15** (Fig. 9) was insensitive to and insoluble in H₂O; heating a THF solution containing it and H₂O to 65 °C for several days had no effect. In the solid state, it was likewise insensitive to several days' exposure to air.

We believe that the rearrangement of **11** to **15** is initiated by the hydrolysis of a N–Si bond, which is itself promoted by the presence of the iminium group (a resonance form of **11** as shown in Scheme 6) which enhances the electrophilicity of the silicon atom and renders it susceptible to attack by H₂O. This is borne out by the fact that **10**, which bears no iminium groups, does not undergo N–P–C–P–N to C–P–N–P–N rearrangement in the presence of H₂O; instead, it is orthometallated to give **14**. The key rearrangement step is the nucleophilic attack by a generated P=NH group on the other P^V centre, ultimately leading to P–C bond cleavage.

In the presence of sub-stoichiometric quantities of Lewis acids (E), **15** converted into the orthometallated isomer,



Scheme 6. Reaction of the platinum carbene, **11**, with H₂O, and onward reaction with electrophiles. The species are all cations and the OTf[−] anion is common to all.

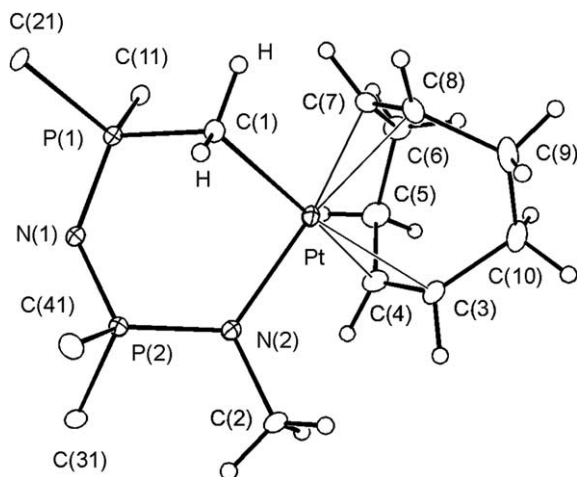


Fig. 9. ORTEP representation (20% ellipsoids) of the molecular structure of **15**. For clarity's sake, only the *ipso* carbon atoms of the phenyl rings are shown (reproduced with permission).

$[(\eta^4\text{-cod})\text{Pt}\{\text{CH}_2\text{P}(\text{C}_6\text{H}_4)\text{PhNPPH}_2\text{NH}(\text{Me})\text{-}\kappa\text{C},\kappa\text{C}'\}][\text{OTf}]$ (**16**)[OTf], Scheme 6, Fig. 10) in which N–Pt bonding was converted to C–Pt bonding; there was no incorporation of the electrophile into this product [42].

3. Carbodiphosphorane complexes

Thoughts about the independence of the “carbene” center in **1** and whether a stabilizing N-coordination was necessary made us interested in the coordination chemistry of the carbodiphosphoranes, $\text{R}_3\text{P}=\text{C}=\text{PR}_3$, or double ylides, $\text{R}_3\text{P}^+-\text{C}^{2-}=\text{PR}_3$, of which the bis(phosphoranimo)methandiides are formal derivatives. These investigations have

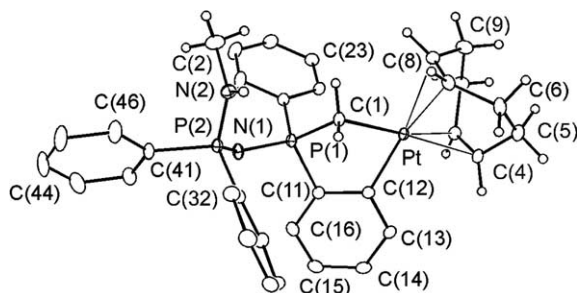


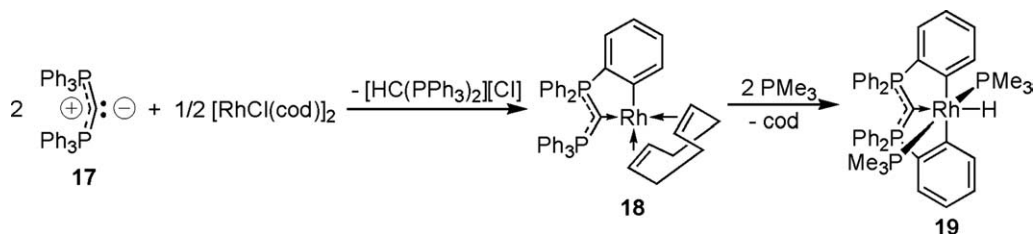
Fig. 10. ORTEP representation (20% ellipsoids) of the molecular structure of **16**. The phenyl hydrogen atoms have been omitted for clarity (reproduced with permission).

led to the discovery of an entirely new and intriguing class of pincer complexes (Chart 2, H).

Our approach to generating metal derivatives of the carbodiphosphoranes was to react them with precursors to coordinatively unsaturated metal complexes. The common halide- and sulphide-bridged bimetallic complexes of the late metals proved useful in this regard. We were led to this approach by the lack of reactivity of $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$ (**17**) in simple substitution reactions with common metal precursors bearing labile ligands. We thus concluded that **17**, although strongly basic, is only weakly nucleophilic. A corroboration of this is the fact that typical Wittig reactivity is almost completely unknown for the carbodiphosphoranes.

As discussed above, the carbodiphosphoranes may be conceptually related to Arduengo-type NHCs and Bertrand-type phosphanyl-silyl carbenes, even though, as discussed above, a formal carbene resonance form (six valence electrons on the central C-atom) cannot be drawn. As demonstrated by the following chemistry, **17** forms pincer complexes in which the C–M interaction may be thought of as a dative, two-electron $\text{C} \rightarrow \text{M}$ σ -bond. The complexes appear to be stabilized by orthometallation of one of the phenyl rings on each phosphorus atom to form the pincer. These new complexes (Chart 2, H) thus add to the developing set of cyclometallated pincers. Early investigations by Kaska et al. [43–45] into the coordination chemistry of **17** with platinum showed that complexes could be made, but structural characterization was not achieved. Recently, Petz and coworkers [46] have shown a simple monodentate coordination of **17** to $\text{Ni}(\text{CO})_3$.

Thus, $[\text{Rh}(\mu\text{-Cl})(\eta^4\text{-cod})_2]$ reacted with **17** first to form the *C,C*-chelated carbene complex, $[(\eta^4\text{-cod})\text{Rh}\{\eta^2\text{-C}(\text{P}(\text{C}_6\text{H}_4)\text{Ph}_2)(\text{PPh}_3)\}]$ (**18**, Scheme 7, Fig. 11) probably through a Rh(III) hydride intermediate [19]. Subsequent treatment of **18** with 2 equiv. of PMe_3 gave the Rh(III) *C,C*-pincer carbene complex, $[\text{HRh}(\text{PMe}_3)_2\{\eta^3\text{-C}(\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)_2)\}]$ (**19**, Fig. 12) in high yield through replacement of the cod ligand and a second phenyl orthometallation event on the free PPh_3 end of the ligand. *C,C*-pincer carbene structures are quite rare; to date we know of only two other such systems: the platinum carbene **13** and three substitutional variants of a group of Pd NHC pincer complexes of type **G** (Chart 2, E = C) reported by Crabtree and co-workers [21a] and Danopoulos et al. [21i]. See Table 1 for selected structural data for **18** and **19**.



Scheme 7. Rhodium hexaphenylcarbodiphosphorane complexes.

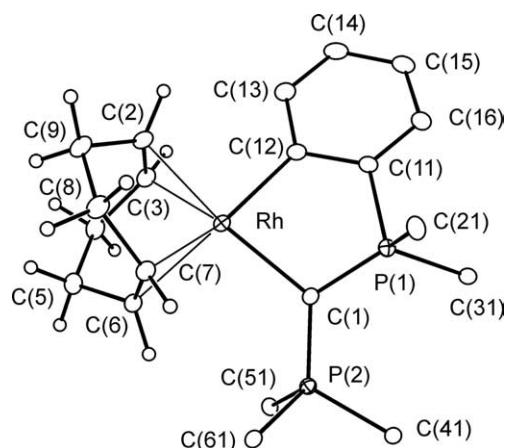


Fig. 11. ORTEP representation (20% ellipsoids) of the molecular structure of **18**. For clarity's sake, only the *ipso* carbon atoms of all but the orthometallated phenyl rings are shown (reproduced with permission).

The Rh atom in **18** has a distorted square-planar coordination geometry which is characteristic of Rh(I). The C(1) center is trigonal planar (sum of angles = 360.0°) indicative of sp^2 hybridisation. The Rh–C(1) bond in **18** (2.165(2) Å) is longer than those reported for related rhodium carbenes (2.00–2.10 Å) [10] and can be properly thought of as a single bond. The C(1)–P(1) and C(1)–P(2) bond lengths are almost identical in spite of the asymmetry of the ligand. Complex **18** can be formulated as a 16-electron Rh(I) complex in which the central C atom acts as a neutral, 2-electron, σ -donor. The bidentate carbene ligand in **18** is reminiscent of the *C,N*-bidentate platinum carbene complex **10**.

The Rh center in **19** has a distorted octahedral geometry. The Rh–C(1) bond (2.202(3) Å) is slightly longer than

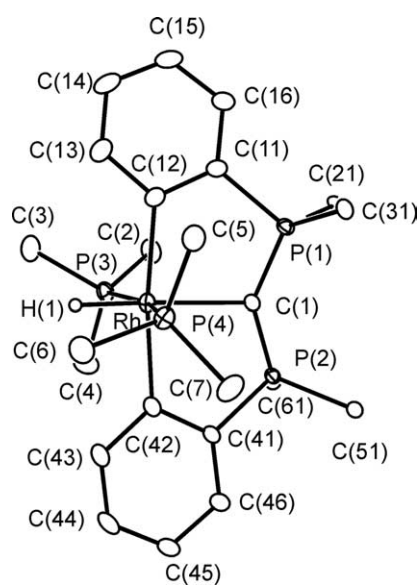


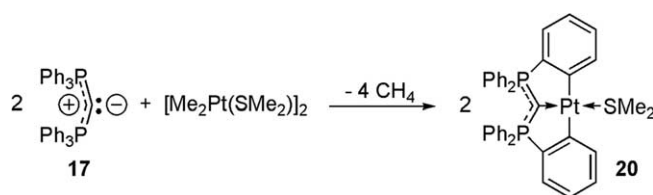
Fig. 12. ORTEP representation (20% ellipsoids) of the molecular structure of **19**. Only the *ipso* carbon atoms of all but the orthometallated phenyl rings are shown and all except the hydride hydrogen atoms have been omitted for clarity (reproduced with permission).

that in **18**. The sum of the angles around C(1) is 359.83°, indicative once again of sp^2 hybridisation. We formulate **19** as an 18-electron Rh(III) species in which the central carbon atom again acts as a neutral, 2-electron, σ -donor.

Although the C(1)–P bonds in **18** and **19** are in the range previously reported for $L_nM-C(PPh_3)_2$ complexes ($M = Re, Ni, Cu, Au$; 1.66–1.78 Å) [47], those in **18** (av. 1.693(2) Å) are slightly longer than those in **19** (av. 1.674(3) Å), indicating lower C(1)–P bond orders in **18**. The stronger Rh–C(1) bond in **18** may act to reduce the negative charge on C(1), and consequently the π -donation from C(1) to P.

Reaction of **17** with $[Me_2Pt(\mu-SMe_2)]_2$ gave an analogous Pt(II) *C,C,C*-pincer carbene complex, $[(Me_2S)Pt\{\eta^3-C(Ph_2P(C_6H_4)_2)\}]$ (**20**, Scheme 8) directly via double orthometallation with elimination of 2 equiv. of CH_4 . No intermediate species were observed in this reaction [19].

Preliminary electronic structure calculations at the density functional level for the model compound HRh(PH_3) $_2[\eta^3-C\{H_2P(C_6H_4)\}_2]$ **19'** revealed one π and two relatively deep molecular orbitals which are themselves bonding with respect to the Rh– $C_{carbene}$ axis. One of these σ - and the π -bonding MOs are paired with occupied antibonding orbitals and so the overall result appears to be no net Rh– $C_{carbene}$ bonding from these orbitals. One Rh– $C_{carbene}$ bonding orbital remains (HOMO-14, Fig. 13). The HOMO is largely a C-based p_z -orbital with small contributions from Rh and H. The Rh–C interaction can therefore be described as a single σ -bond between a Rh-based d-orbital and an sp^2 -like orbital on $C_{carbene}$ plus (as the HOMO) an occupied p_z -orbital on the $C_{carbene}$. The Mulliken charges are: Rh + 0.26, $C_{carbene}$ – 0.87, P + 0.40 (including H atoms), C_{phenyl} + 0.17. More detailed calculations are in progress.



Scheme 8. A platinum *C,C,C*-pincer carbene complex.

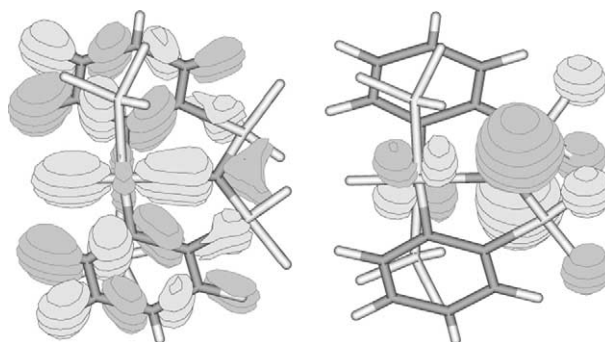


Fig. 13. Representations of the calculated Rh–C-bonding molecular orbital (HOMO-14, left) and the HOMO of **19'**.

4. Summary

We have successfully extended the organometallic chemistry of the bis(phosphoranimino)methandiides to include not only the early transition elements and the lanthanides, as previously reviewed, but also main group elements and platinum. The aluminum spirocycles are useful polymerization catalysts, and we are pursuing catalytic applications of the other complexes. Our unpublished studies deal with analogous homo- and heterobimetallic spirocyclic complexes of the late metals; these reports will appear in due course. In pursuing the chemistry of the carbodiphosphoranes, we have also succeeded in accessing a wholly new class of *C,C,C* pincer carbene complexes, which, unlike **G** (Chart 2), incorporates only a single carbene donor and two, as opposed to one cyclometallated phenyl rings. Carbodiphosphorane and bis(phosphoranimino)methandiide ligands may be thought of as “pull–pull” carbenes because the electron-withdrawing P^V substituents significantly deplete the charge at the central, formally C²⁻, carbon atom giving it distinct carbene character.

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