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Mini Review

Early transition metal and lanthanide bis(iminophosphorano)methandiide complexes; 'pincer' and bridging bis(phosphorus) metal carbenes

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Abstract

The spontaneous double deprotonation of bis(iminophosphorano)methane ligands with alkyl or bis(trimethylsilyl)amido metal precursors yields 'pincer' carbenes of Group 4 and lanthanide metals. The generality of the system is extended with the dilithiumbis(iminophosphorano)methandiide salt which is obtained by lithiating bis(trimethylsilylimino(diphenylphosphorano))methane with two moles of lithium alkyl. This dilithium salt reacts with metal halides with metathetical elimination of LiCl to access the same types of pincer complexes. Herein the synthesis of a complete triad of Group 4 'pincer' complexes is reviewed and their reaction chemistry demonstrating (a) nucleophilic alkylation, (b) the Lewis Acidity of the metal, (c) 1,2 addition across the M=C carbene bond and (d) [2 + 2] cycloaddition across this M=C bond is surveyed. The structural data for the 'pincer' complexes suggests strongly that there is a M=C carbene double bond. The addition reactions also support this interpretation because a M–C bond persists after the addition. The reactivity pattern also strongly suggests that the chemistry of this carbene center is similar to the metal alkylidene complexes, and not the Fischer heteroatom carbene complexes. The chemistry extends to many other elements. The extension to Sm as a representative lanthanide is described. This species adopts a structure very similar to the Group 4 'pincers'. Chromium(II) gave a novel bridging carbene dimer instead of the monomeric pincer. This bridging structure is developing as another structural motif in this system. © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords: Transition metals; Lanthanide bis(iminophosphorano)methandiide; Bridging bis(phosphorus) metal carbenes

1. Introduction

1.1. Carbene complexes

The substantial growth of carbene chemistry [1] over the last decade has secured the place of these important species in chemistry. Carbenes have long been recognized as reaction intermediates and are widely implicated in catalytic processes (e.g. olefin metathesis reactions [2–5], Fischer–Tropsch processes [6] and metal-catalyzed carbene transfers with diazo compounds [7].) and organic transformation reactions [1f,8–12]. In early days these entities were proposed as intermediates in reaction systems and sometimes trapped as derivatives. Recently, however, a wealth of stable carbenes has been isolated and fully characterized and this has led, in turn, to an extensive derivative chemistry. Both the stable carbene and the related, extensive, metal–carbene chemistry derived therefrom has recently been thoroughly reviewed [13].

Our interest in this area was triggered by the discovery [14] that a unique 'pincer' carbene complex could be obtained from bis(iminophosphorano)methane ligands by deprotonation of the methylene backbone either by suitable metal precursors [14] or by the initial lithium deprotonation of the ligand followed by metathetical reactions with metal halides [15]. Our focus has been on the development of the metal carbene complexes, and in

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particular at present, those of the early transition metals [14,16–20] and lanthanides [21]. We have also studied the aluminum system which is not reviewed here [22,23].

Extensive systems of Group 5, 6 and 7 carbene complexes exist [1]. Fewer examples of Group 4 metal carbenes are known being limited to a few titanium [24], and zirconium alkylidene complexes [25] and the zirconium Fischer carbene complexes [26]. Hafnium alkylidene species are particularly rare. Attempts at isolation gave orthometallated [27] or dimeric products [28]. It was therefore of some interest to see if a complete set of carbenes could be prepared for this group.

Heteroatom substituted carbene metal complexes in general and of the Group 4 metals in particular have not received much attention [29]. In addition, those of phosphorus are also rare. Recent advances in the Bertrand laboratory has however provided a wealth of phosphino carbenes, many of which have been verified by structural studies [13]. Almost all of these species have only one phosphorus substituent on the carbon, the other generally being a silyl substituent [13]. Two phosphinophosphoniocarbenes, verified by structural characterization, were also prepared by this group [13,30–32]. Our system provided a bis-phosphorus carbene center and so becomes an example of the relatively rare group of bisphosphorus complexes.

Several phosphino carbenes with one phosphorus substituent have been structurally characterized. Almost invariably, the structures show that the complexes are metallacycles in which the phosphorus is also bound to the metal as well as the carbon. In these cases the ligand is acting as a 4-electron donor [13]. One M=C phosphorus substituted system which shows the M=C center clearly is the uranium phosphoylide system, $Cp_3UC(H)PR_3$ [33,34]. Fischer also reported a low yield synthesis of a complex of the formula $(OC)_5W{=}C(NEt_2)PMePh$ [35] but no structure was reported.

There is no reason in principle why there cannot be two phosphorus substituents attached to the carbene center. If the two phosphorus centers are pentavalent then such complexes would be formal derivatives of a carbodi(phosphorane). These parent carbo(diphosphorane) species have been summarized in a recent book [36]. In this context there are four known structurally characterized carbodi(phosphorane) complexes $[O_3Re{=}C(PPh_3)_2]^+[ReO_4]^-$ [37], $[Tp'(OC)_2W{=}C(PMe_3)_2]^+[PF_6]^-$ [38], $(CO)_3Ni{=}C(PPh_3)_2$ and $(CO)_2Ni{=}C(PPh_3)_2$ [39] and in each case structural detail suggests that there is a substantial M=C bond character established between the metal and carbon. Other carbodi(phosphorane) adducts with tungsten and platinum have been reported [40] but without supporting structural verification. These carbodi(phosphorane) complexes have a loose relationship to our present system.

1.2. The 'Pincer' complexes

In addition to the recent advances in carbene chemistry there have been parallel advances in the chemistry of 'pincer' bis-chelate metal complexes. Relevant to the present case, in which we are also developing the 'pincer' structure, are the extensive systems described by van Koten [41–43] and by Milstein [44] in which an (ortho) disubstituted phenyl ring carrying a pair of flexible arms, which in turn carries a Lewis Base donor (typically an amine or a phosphine), is itself bound directly to a metal with the subsequent chelation of the bases to form the tridentate 'pincer' complex. Four, five or six coordinate 'pincer' complexes are obtained. Also related are the bis(ortho imine) substituted pyridine ligands described by Gibson et al. which likewise form 'pincer' type bis(chelate) complexes [45,46]. The interest in these latter systems has derived from their usefulness for various homogeneously catalyzed processes, especially homogeneous polymerization of olefins. In this context the α-diimine complexes used by Brookhart and others for olefin polymerization [47–49] provide numerous members of the constrained, non-metallocene metal complex systems used for this purpose. The geometrical constraints imposed on the metal reaction center by the ligand structure and connectivity places these systems into the class of 'constrained geometry' species. The 'pincer' type complexes have the additional contributing factor of stabilization introduced by the chelate structure. These 'pincer' complexes have properties which are similar to the cyclopentadienyl and tethered cyclopentadienyl metal derivatives but without the cyclopentadienyl substituent. Much metal–ligand complex chemistry has been developed on this structural framework to explore their catalytic potential.

Here we survey our encapsulated metal carbene 'pincer' system derived from bis(iminophosphorano)methane. We have considered this system to be a carbene because these complexes clearly contain a metal–carbon bond of order greater than one. In addition, derived as they are from bis(phosphines), these complexes provide rare examples of a 'carbene' center substituted by two phosphorus atoms. The nature of this 'carbene' center is addressed below; are these phosphorus substituted species heteroatom carbenes similar to the 'Fischer' type or do they have an alkylidene character?

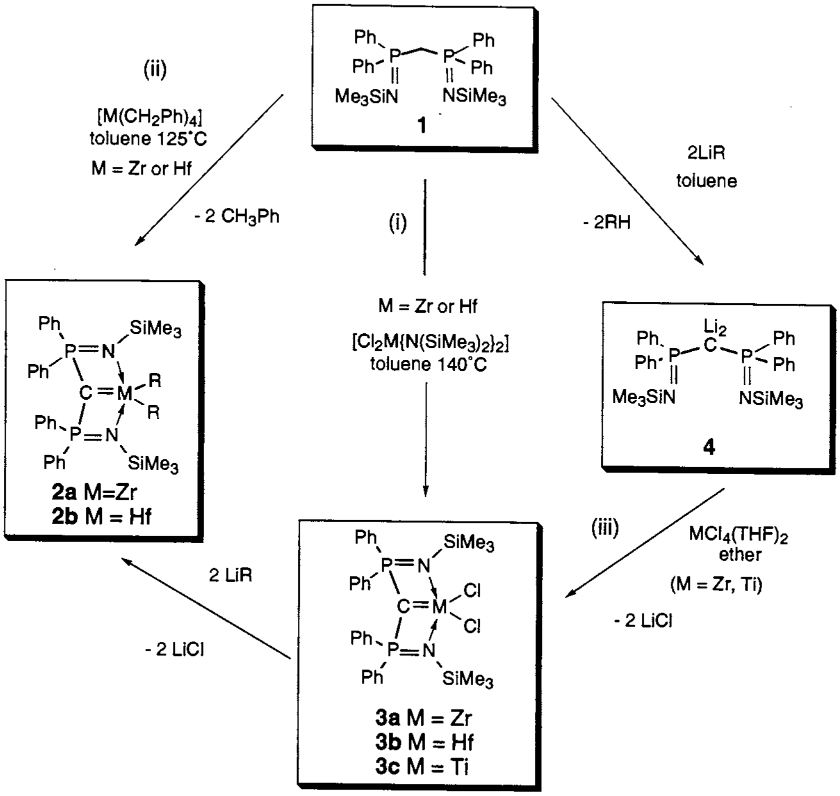
2. The Group 4 'pincer' carbenes of bis(iminophosphorano)methane

Our system [14] was formed from bis(iminophosphorano)methane ligands in several ways (Scheme 1). We initially found that (i) elimination of hexamethyldisilazane from a metal di(bis(trimethylsilyl)amido) metal complex (Scheme 1, path (i)) [17] or (ii) alkane elimination from a metal alkyl complex (Scheme 1, path (ii)) [18] could be carried out with the heavier Group 4 (Zr, Hf) metal amides or alkyls. The reactions were carried out at relatively high temperatures in a solvent, therefore the products are stable at these temperatures but, more importantly, the metal precursors must also be stable under the reaction conditions. This is not the case for these same precursors of Ti hence paths (i) and (ii) could be used to access only the Zr and Hf species. In each case, this elimination route has precedence although we were somewhat surprised to observe hexamethyldisilazane (HMDS) elimination from the metal chloro(bis(dimethylsilylamides) rather than a preferential trimethyl silyl chloride elimination as is typical for reactions of silylated imines with metal halides. This synthetic pathway does emphasize the high acidity of the backbone protons and the low proton acidity of HMDS.

Deprotonation of the backbone methylene unit of bis(iminophosphorano)methane ligands is precedented. The moderate acidity of these methylene protons has been previously exploited for the synthesis of singly deprotonated derivatives through a mono-lithiation procedure [50]. Although double deprotonation in bis(phosphino)methanes has not been systematically exploited, it has been encountered in a few cases, often as the result of further decomposition of the singly deprotonated derivatives [51,52]. In these cases a dimetallated carbon spirocycle results. Several group 10 and group 13 metal complexes obtained in this way have been described structurally [52–56]. In addition, the presence of a few doubly deprotonated methanide ligands have been suggested [57,58] but without crystal structure evidence.

The initially discovered routes to our M=C 'pincers', summarized in Scheme 1 as path (i) and path (ii), although efficient and straightforward, required the preparation of special metal precursors which imposed limitations on the metals which could be explored. In many cases the requisite alkyl or amido complexes are not available because of their inherent instability. Even moderate stability may not be sufficient to withstand the typical conditions which were used for the deprotonation conditions employed in paths (i) and (ii) of Scheme 1. For example, in the Group IV case, we could readily access the M=Zr and M=Hf species but the titanium complex was not accessible because neither type of the necessary titanium precursor was sufficiently stable under the deprotonation reaction conditions to survive.

The generality of our system was enormously enhanced by the discovery of the dilithium salt of the bis(phosphoranimide) ligand (**4**) which is accessed by simply reacting the ligand with two moles of Li methyl or phenyl (Scheme 1) [15]. This opened the general



Scheme 1.

route (Scheme 1, path (iii)) of a simple metathetical LiCl salt elimination from a metal halide to the 'pincer complex' (Scheme 1, path (iii)) [14]. This latter route provides unsurpassed access to a variety of systems because special metal precursors such as the metal amides and alkyls can be avoided if necessary. Complexes of many different metals can be accessed [14,17–21].

Overall these systems of complexes are potentially very versatile because there is a wealth of established phosphorus and nitrogen ligand substitutional chemistry which can be applied to the assembly of the ligand framework. Scheme 1 summarizes the more complete picture which presently exists for the system derived from the bis(di(phenylphosphino))methane. Many of the steps have been demonstrated [20] for ligands based on the analogous methyl and cyclohexyl phosphorus ligands but a complete set of reactions has not been established for these systems. Chemical modifications can be easily introduced to both the ligand and the metal centers to control or 'tune' the stability of the system and the reactivity of the carbon–metal combination.

This development has therefore provided a completely new and truly unique group of non-metallocene, non-carbonyl, organometallic carbene complexes of metals. These compounds possess a structural character which is related to the 'constrained geometry' organometallic catalyst systems derived from the metallocenes [59]. Ours, like the other 'pincer' systems [41–46], however do not carry any cyclopentadienyl substituents. In addition, and in contrast to the complexes described by others [41–46], our 'pincer' complexes contain a M=C bond and therefore present a potentially more extensive reactivity, some of which will be described below. Our system can be easily 'tuned' for reactivity control at the backbone and at the metal with a variety of substituents on that backbone or on the metal.

The hafnium bis(iminophosphorano)methandiide complexes [17] which display the same metal–carbon bond features as the Ti and Zr [14,18] complexes in a 'pincer' structure, were readily isolated which contrasts with the general scarcity of Hf organometallic carbenes (vide supra). A particular feature provided by the present system is that the complete triad of metal complexes of Ti, Zr and Hf in which all metal centers have the same ligand and the resultant complexes are isostructural can be readily assembled [17,18,20]. This allows comparisons of the chemistry down the entire metal series without the usual attendant qualifications for ligand variances, which arise from the different sources of each carbene complex. All too often, organometallics of the reactive metal groups such as the early transition metals can be prepared for only limited combinations of ligand and metal and thus, direct analogs are absent.

The reaction of $[ZrCl_2\{N(SiMe_3)_2\}_2]$ [60] with $CH_2(Ph_2P{=}NSiMe_3)_2$ (**1**) in refluxing toluene gave $[ZrCl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3 C,N,N'\}]$ (**3b**) [17]. A similar reaction under these same conditions with $HfCl_2\{N(SiMe_3)_2\}_2$ [60] gave the hafnium methandiide analog, $[HfCl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3 C,N,N'\}]$, (**3a**) [17]. To access the Ti complex, **3c**, however, the $CH_2(Ph_2P{=}NSiMe_3)_2$, ligand **1** was first treated with either methyl or phenyl lithium and the resultant $Li_2C(Ph_2P{=}NSiMe_3)_2$ salt, (**4**), was then reacted with $TiCl_4$ [14]. The lithium salt route can also be used to prepare **3a** and **3b** from the MCl_4 precursors however we have found the amide reaction to be somewhat cleaner and therefore more efficient. The entire system readily forms good quality crystals and so we have been able to obtain extensive structural characterization of these species. Selected structural metrical data and NMR parameters are given for the 'pincer' carbene complexes and their derivatives in Table 1. This derivation of the connectivity and the metrical structural data has been essential to the proof of structure and to the deduction of the nature of the bonding interactions between the metal and the carbon center. The complexes are highly soluble in both relatively polar and in aromatic solvents such as diethyl ether, benzene and toluene and they also have relatively high thermal stability which can be attributed to the steric protection of the carbene center by the formation of the tridentate chelate 'pincer' structure.

3. The 'carbene' nature of the 'pincer' complexes

The nature and reactivity of prototypical carbene complexes, $M{=}CR_2$ depends greatly on the electronic and steric nature of the substituent, R. Those containing one or two highly electronegative heteroatom substituents, such as O, N and perhaps also S, and therefore provide an electrophilic center at the carbon, are designated as Fischer carbenes. Alkylidene (or Schrock) carbene complexes, in contrast, have only hydrogen or carbon substituents on the carbon (which is generally bound to a transition metal in a high oxidation state), and provide a nucleophilic carbon [1,8–10,61].

Typically the ^{31}P-NMR spectra of the complexes of type **3** consist only of one sharp singlet due to two equivalent phosphorus centers in all the carbene complexes. Values are given in Table 1. The $^{13}C\{^1H\}$ APT spectrum gave a positive triplet signal ($^1J_{PC} \sim 145$ Hz) for the carbene which collapsed to a positive singlet upon phosphorus decoupling. The shift values are also summarized in Table 1. In general, these shift values differ from those of organo-carbene complexes however the attachment of phosphorus will profoundly alter the electronic environment of the carbon center in a way, which we cannot predict at this time.

Table 1
Selected spectroscopic and structural parameters for ‘pincer’ carbenes and some of their derivatives

Compound [a]	^{13}C (ppm)	^{31}P (ppm)	$^{1}J_{PC}$ (ppm)	M=C length (Å)	P–C–P angle (°)	Sum C angles (°)	CPN angle (avg.)	NMN angle (°)	Dihedral angle (°)	Reference
Pincer Carbenes										
MX_2 derivatives										
$\mathrm{TiCl_2\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$	191.0	12.6	145	2.008(4)	157.3(3)	344.5	97.4(2)	148.9(1)	11.1	[14]
$\mathrm{ZrCl_2\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$	101.7	15.7	146	2.190(8)	148.3(5)	334.3	100.0(4)	137.8(3)	22.2	[14]
$\mathrm{ZrCl_2\{\mathit{C}(Cy_2P{=}\mathit{N}T)_2\}}$ [b]	86.9	35.5	156	2.171(5)	169.2(4)	356.9	100.3(2)	142.5(2)	5.6	[20]
$\mathrm{HfCl_2\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$	84.6	12.2	145							
$\mathrm{HfCl_2\{\mathit{C}(Cy_2P{=}\mathit{N}T)_2\}}$	66.6	32.6	158	2.162(6)	169.9(4)	357.0	100.4(3)	143.3(2)	5.4	[17]
$\mathrm{Sm(NCy_2)(THF)}$- $\mathrm{\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$		43.3		2.467(4)	138.0(3)	321.1	108.0(2)	120.6(1)	37.7	[21]
Metal alkyl derivatives										
$\mathrm{ZrBz_2\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$	84.7	12.4	164	2.240(6)	144.3(4)	328.2	101.8(3)	136.6(2)	24.7	[18]
$\mathrm{ZrBz_2\{\mathit{C}(Ph_2P{=}\mathit{N}Ad)_2\}}$	82.8	12.6	171	2.208(3)	168.0(2)	360.0	98.3(2)	138.2(1)	0	[18]
$\mathrm{HfNp_2\{\mathit{C}(Ph_2P{=}\mathit{N}Ad)_2\}}$	71.6	10.3	160							[16]
$\mathrm{ZrBz\{\mathit{N}(Ad)C(Bz)\mathit{O}\}}$- $\mathrm{\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$ [b]	89.9	13.0	171	2.209(6)	164.0(4)	353.4	101.6(3)	138.7(2)	10.3	[20]
Derivatives	(M–C bond)									
Base Adducts, 1,2 and 2+2 additions										
$\mathrm{HfCl_2(THF)\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$ [b]				2.214(2)	166.7(2)	352.2	101.7(1)	141.0(1)	10.8	[20]
$\mathrm{HfCl_2(AdCN)\{\mathit{C}(Ph_2P{=}\mathit{N}T)_2\}}$	83.4	11.4	153	2.211(6)	170.6(4)	355.2	102.4(3)	142.1(2)	4.3	[16]
$\mathrm{ZrCl_2(OAd)}$- $\mathrm{\{\mathit{C}(H)(Ph_2P{=}\mathit{N}T)_2\}}$				2.478(3)						[16]
$\mathrm{HfCl_2(N(H)tol)}$- $\mathrm{\{\mathit{C}(H)(Ph_2P{=}\mathit{N}T)_2\}}$		22.2		2.437(6)						[16]
$\mathrm{ZrCl_3\{\mathit{C}(H)(Me_2P{=}\mathit{N}T)_2\}}$ [b]				2.439(5)						[20]
$\mathrm{ZrCl_3\{\mathit{C}(H)(Ph_2P{=}\mathit{N}T)_2\}}$ [b]				2.465(3)						[20]
$\mathrm{HfCl_2X\{\mathit{C}(Me)(Ph_2P{=}\mathit{N}T)_2\}}$ [b]				2.386(6)						[20]
$\mathrm{ZrCl_2\{\mathit{C}(NCy)\mathit{N}(Cy))}$- $\mathrm{(Ph_2P{=}\mathit{N}T)_2)\}}$	15.5	21.0	96.0	2.467(4)						[16]
$\mathrm{HfCl_2\{\mathit{C}(C(O)\mathit{N}(Ad))}$- $\mathrm{(Ph_2P{=}\mathit{N}T)_2)\}}$		22.2		2.431(6)						[16]

[a] $T = SiMe_3$, $Me = CH_3$, Ad = adamantyl, Bz = benzyl, Np = neopentyl. The italic atoms in complex ligand(s) are those bonded to the metal.

[b] Unpublished data from our Laboratory.

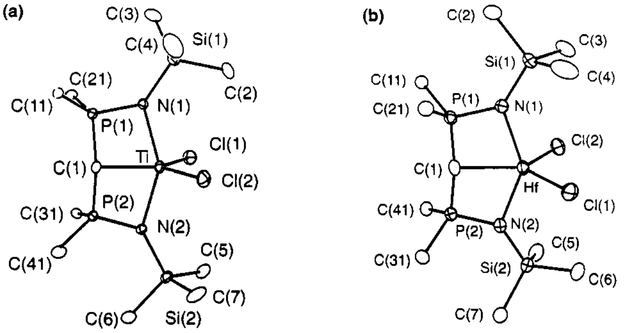


Fig. 1. Views of the central portions of (a) $[TiCl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ (**3c**) [14] and (b) $[HfCl_2\{C(Cy_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ (**3b**) [17]. All hydrogen atoms have been removed from (a) and all hydrogen and carbon atoms (except the *ipso* carbon atoms of the cyclohexyl groups) have been removed for clarity. Reproduced with permission.

The molecular structures provide the strongest evidence of the 'carbene' character. The structures are similar throughout (see Fig. 1) being based on a frame comprised of two nearly planar, fused, four-membered rings {formed by M, N, P and the carbene C} sharing an edge defined by the M=C carbene bond. The carbene atom is displaced by varying amounts from the plane defined by the M, both P and both N atoms. The P–C–P angles range from 144 to 176° (see Table 1). The two four membered rings are not coplanar. They form a distorted 'open book' conformation, which is defined by a dihedral angle (listed in Table 1). No systematic relationship between the substituents and the dihedral angle is apparent, probably because this angle is dependent on a complex interplay of steric and electronic effects between the substituents on the phosphorus, the nitrogen and the metal. The M=C(1) bond distances, (listed in Table 1) are relatively short but not remarkably or extraordinarily so. The values are however suggestive of a carbene adduct with the metal. Even though the bonds are not extraordinarily short, it is clear that from both (i) the values of these bond lengths themselves and (ii) the changes which accompany additions across this M=C bond which indicate that a bond remains after such additions (vide infra), that the bond order in the parent carbene complex is greater than one so the appellation of a carbene character to this center is appropriate.

An alternate formulation of the ligand as a dianionic carbodi(phosphorane) species, $\{R'N\text{–}PR_2{=}C{=}PR_2\text{–}NR'\}^{-2}$ [36] seems unlikely because there is then a reduced electron density on the carbon and we would expect the ligand to attach to the metal only through the anionic nitrogen centers to form an acetylacetonate-like structure. Preliminary theoretical analysis of our complexes with a 'single point energy calculation' carried out at the density functional level [18] gives a charge distribution which indicates a substantial dianionic character at the central carbon and not on the terminal nitrogen centers thus implying that this carbon has 'carbene' donor character toward the metal center.

All structural data therefore indicate a definite and strong connectivity of the carbon to the metal. Our complexes, although not structurally similar to the carbodi(phosphorane) complexes, do, in some cases, have similar NMR parameters, for example our shift values are similar to those of the carbodi(phosphorane) cationic complexes $[O_3Re{=}C(PPh_3)_2]^+$ $[ReO_4]^-$ [37] and $[Tp'(OC)_2W{=}C(PMe_3)_2]^+$ $[PF_6]^-$ [38] (Tp' = $[HB(N_2C_3Me_2H)_3]^-$) but more carbene like than those of the late metal carbodi(phosphorane) complexes $(CO)_3Ni{=}C(PPh_3)_2$ and $(CO)_2Ni{=}C(PPh_3)_2$ [39]. The chemical shift argument for defining 'carbene' character may be useful for organometallics but is not likely to be definitive especially when phosphorus atoms are bound to the carbon in question.

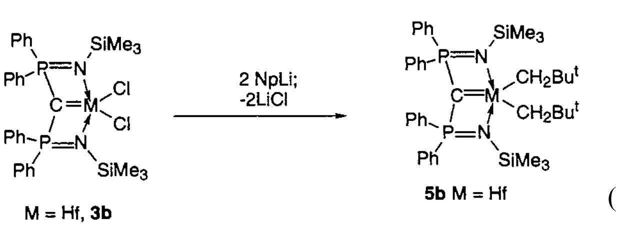
The M=C bond distances in our complexes are similar to those in these characterized carbodi(phosphorane) complexes [37–39]. In all these cases the phenyl or methyl substituents on the phosphorus cannot interact with the metal so the PR_3 units are bent away to make very shallow ((Re) 123.1(4)° [37], (W) 114.5(8)° [38] and (Ni) 124.6(2) and 132.1(2)° [39], respectively) angles at the carbene carbon. In the 'pincer' chelate complexes the imine nitrogen is coordinated to the metal and this in turn pulls the phosphorus closer to the metal to enlarge the P–C–P angle. Notably the carbon attachment to the metal does not seem to be significantly diminished by this chelation. Clearly the formation of the chelate has a profound effect on the structure (and, we think, the stability) of the complexes but the electronic character of the M=C bond is not extraordinarily different between the two cases. The carbodi(phosphorane) complexes are not conceptually different from the metal–(stable) carbene complex adducts derived from the cyclic and acyclic diamino carbenes, such as Arduengo's carbene [13,62,63].

That there is some delocalization within the ring structures which supports the assignment of some ylidic character to the structure which is supported by the fact that the bond distances within the bicyclic framework are altered in comparison with related values in parent bis(iminophosphorano)methanes [20, 50h]. Specifically, the P=N bond distances are slightly elongated and the endocyclic P–C bond distances are significantly shorter. The exocyclic P–C bond distances are not affected and so provide the contrast for comparison of bond lengths between the ligated form and the free ligand molecule. This strong delocalization of π electron density appears to arise within each of the two four-membered rings and is due to an effective conjugation of the M=C bond with the P=N bonds (Scheme 2). This delocalization and resultant stabilization does not negate the description of the species as a carbene complex.

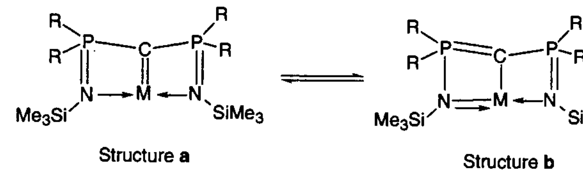
4. Reactivity of the Group 4 ‘pincer’ complexes

4.1. Nucleophilic alkylation

The halide substituents of **3** are readily replaced by alkyl groups using simple lithium reagents. Thus, reaction of **3b** with NpLi (Np = neopentyl) gave [HfNp$_2${C(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*,*N*′}], (**5b**) (Eq. (1)) [16]. It is notable that the carbon center in the complex was not attacked under these reaction conditions as is also the case for alkylidene complexes [64]. The carbene center in Fischer type carbene complexes is attacked by alkyl lithium to form an anionic carbon species [1j,65]. As described above, similar dialkylbis(iminophosphorano)methandiide complexes **2** were also obtained by direct reaction of metal–tetraalkyl precursors and the bis(iminophosphorano)methane ligand [18]. Grignard reagents react with the halide complexes of type **3** to yield similar alkyl derivatives [20].



(1)



Scheme 2.

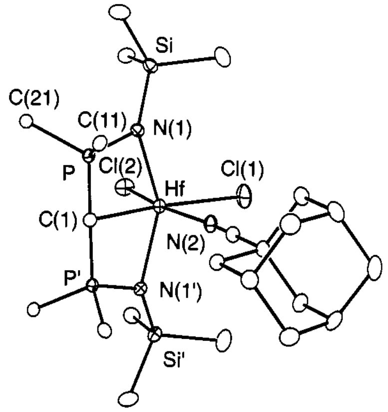
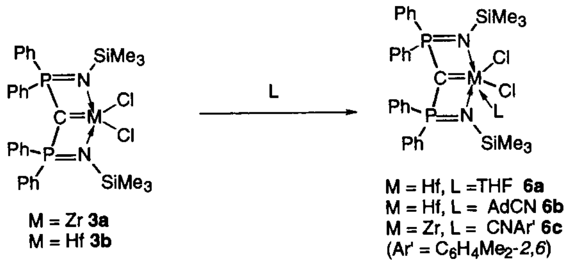


Fig. 2. A view of the central portion of [Hf(AdCN)Cl$_2${C(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*,*N*′}] (**6b**) [16] without the hydrogen atoms. All of the carbon atoms except the *ipso* carbon atoms of the phenyl groups on phosphorus have also been removed. The adamantyl group is shown in full except for its hydrogen atoms. Reproduced with permission.

4.2. The acidity of the metal center

The bis(iminophosphorano)methandiide complexes **3** react readily with coordinating solvents, (e.g. THF, a nitrile or an isonitrile) to form the Lewis-base adducts [M(L)Cl$_2${C(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*,*N*′}] {M = Hf, L = THF **6a**; M = Hf, L = AdCN **6b** (Ad = adamantyl); M=Zr, L=CN(C$_6$H$_4$Me$_2$-2,6) **6c**} (eq (2)). Because M=C complexes generally yield insertion products with isonitriles or nitriles [1j,64,66], the formation of adducts in the present case is unique, and may be due to the strong electrophilic character and coordinative unsaturation of the metal center.



(2)

The crystal structures of **6a** [20] and **6b** [16] show that the tridentate pincer-type chelate frame, present in the starting complexes, is preserved in these base adducts. A view of [Hf(AdCN)Cl$_2${C(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*, *N*′}] (**6b**) [16] is shown in Fig. 2. The structure contains a mirror plane of symmetry containing the atoms Hf, C(1), Cl(1), Cl(2) and N(2). The P–C–P angle (170.6(4)°) approaches linearity and the C(1) atom deviates by 0.12 Å from the least-square plane containing P, N(1), Hf, N(1′) and P′ atoms. The Hf–C bond distance (2.211(6) Å) is slightly longer than that observed for an analogous cyclohexyl substituted complex, [HfCl$_2$-{C(Cy$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*,*N*′}] (2.162(6) Å) (Table 1) [17] which contains no additional donor ligand group so, presuming that the M=C bond lengths are not greatly perturbed by the replacement of the Ph on phosphorus by a Cy group, the donor action of the Lewis Base increases the M=C bond length by only about 3%.

4.3. 1,2-Addition across the M=C bond

The methandiide complexes **3** react smoothly with compounds (EX) containing acidic protons such as aromatic amines, phenols or aliphatic alcohols to yield the C$_\alpha$-protonated product, [MCl$_2$(X){EC(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*,*N*′}] as a result of 1,2-addition of the substrate across the M=C$_\alpha$ bond, (Eq. (3)) [14,16,20]. Representative products **7a** (M=Zr) [14,20] and **7b** (M=Hf) [16], isolated from the reactions of adamantanol and *p*-toluidine, respectively, are shown in Scheme 2. Likewise methyl iodide [16], gave low yields of [HfCl$_2$(I){MeC(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C*,*N*,*N*′}] (**7c**) in a

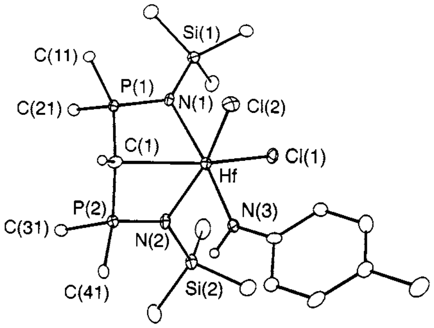


Fig. 3. A view of [$HfCl_2(HN(p\text{-tolyl}))\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}$] (**7b**) [16] without hydrogen atoms and all carbon atoms of the phenyl rings (except the *ipso* carbon atom) on phosphorus. The carbon structure of the *p*-tolyl group is shown. Reproduced with permission.

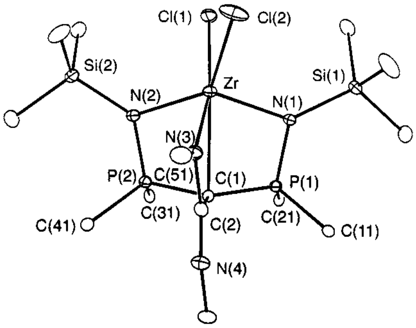
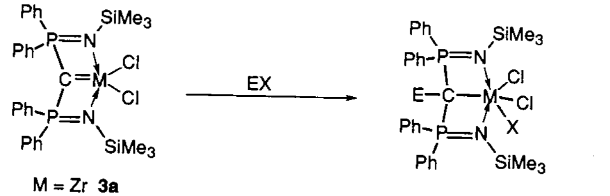


Fig. 4. A view of the central portion of [$ZrCl_2\{(C(NCy)\text{-}NCy)C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,N,N',N''\}$] (**9a**) [16]. The hydrogen atoms and all phenyl and cyclohexyl carbon (except the *ipso*) atoms have been removed for clarity.

mixture of reaction products. This reaction is also complicated by scrambling of the halide. It is however clear that the electrophilic (E) moiety adds specifically to the carbene center as is observed with Schrock carbenes [64] in further support of our classification of the carbon center in these Group IV complexes as alkylidene-like.

The complex [$HfCl_2(HN(p\text{-tolyl}))\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}$] (**7b**) [16] is illustrated in Fig. 3. The geometry about the hafnium center is that of a highly distorted octahedron, which presumably arises because of the constrained *fac*-coordination geometry of the tri-coordinated ligand. The structure contains the two nearly planar four-membered {M, C, P, N} rings which are seen in the parent carbene complex and which share a common M–C edge in an open-book conformation. The 'book' however is much more 'closed' because of the formation of the *fac*-octahedral geometry at the metal. The connectivity and metrical parameters (Table 1) both clearly indicate that a metal–carbon bond is maintained. The bond order is clearly reduced in the products again substantiating the attribution of a multiply bonded character to the link in the parent complexes. The increase of the M–C bond distances is consistent with the reduction of formal bond order from two in the parent compound to one upon addition across the initial M=C bond.



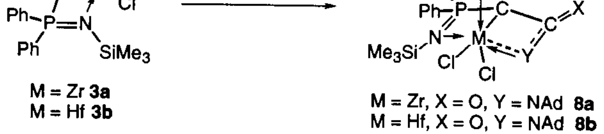
M = Zr **3a**
M = Hf **3b**

M = Zr, E = H, X = OAd **7a**
M = Hf, E = H, X = HN(*p*-tolyl) **7b**
M = Hf, E = Me, X = I **7c**

(3)

4.4. 2 + 2 cycloaddition reactions

Heteroallenes such as RNCO and RN=C=NR react readily with methandiide complexes **3** (and **2**) [20] to form [2 + 2]-cycloaddition products **8** and **9** as illustrated in (Eq. (4)) [14,16,20]. A representative structure, that of [$ZrCl_2\{(C(NCy)NCy)C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,N,N',N''\}$], (**9a**), is shown in Fig. 4. The addition of the heteroallene to the 'pincer' chelate creates a tetradentate propeller shaped, dianionic ligand bonded to the metal by the central carbon, the two originally bound nitrogen atoms of the ligand and the remaining appropriate NR fragment of the heteroallene. Two chloride ligands complete the coordination at the metal. Notably the oxygen of the isocyanate group does NOT become bound to these oxophilic metal centers nor does the oxophilic metal extract oxygen from the isocyanate. The three nitrogen substituents of the new tetradentate ligand adopt a tripodal arrangement and lie at the corners of an almost regular triangle. Notably the ligand remains bound also through the carbon to the metal. Again, the M–C distance increases relative to the parent carbon as expected because the bond order is reduced from two to one by the cycloaddition, but because the carbon is still attached to the metal as indicated by the short M–C distance, it is clear that the original interaction was one of a multiple bond. Hence the formation of this structure again supports the designation of the original carbon bonded complexes as M=C 'carbenes'. Were this metal–carbon interaction to be removed completely, then the complex would adopt a typical tripod, tridentate, ligation structure similar to species such as the tris(pyrazolyl)borate complexes.



(4)

M = Zr **3a**
M = Hf **3b**

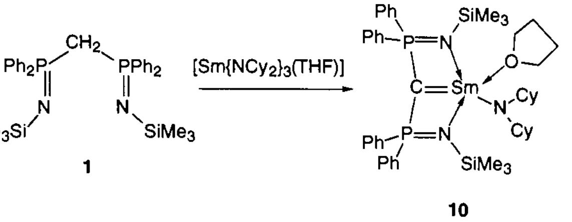
M = Zr, X = O, Y = NAd **8a**
M = Hf, X = O, Y = NAd **8b**
M = Zr, X = Y = NCy **9a**
M = Hf, X = Y = N(*p*-tolyl) **9b**

In all reactions shown here, the bis(iminophosphorano)methandiide complexes therefore behave in a manner consistent with the presence of a nucleophilic central carbon and so they resemble organometallic alkylidene complexes. Also, the preservation of an M–C bond after 1,2-addition and [2 + 2]-cycloaddition reactions confirms the property of multiple metal–carbon bond character which was assigned to the primary complexes. The facility of C–C bond formation processes and the preservation of isolated oxo centers in these complexes of these highly oxophilic metals, even in the presence of oxygen centers on the ligands, suggests useful applications to synthesis.

5. Other metal chemistry of the bis(iminophosphorano)methanides

5.1. Lanthanide complex

The monomeric complex of Sm, **10**, which shows the same M=C bond feature as the Group 4 complexes described above, was readily formed by the same route as in represented in Scheme 1 (path (i); namely double deprotonation of the bis(iminophosphorano)methane ligand by samarium tris(dicyclohexylamine) (Eq. (5)) [21]. Two of the amides were eliminated as HMDS and, because the reaction was done in THF, a solvent molecule was added to the coordination sphere to produce the same type of pincer structure as was seen in the Group 4 complexes.



(5)

The only previously known carbene complexes of lanthanide metals are the adducts of the neutral carbene ligands [62,63,67].

The structure of the Sm complex [Sm-{C(Ph$_2$P=NSiMe$_3$)$_2$-κ^3C,N,N'}(NCy$_2$)(THF)], (**10**), a yellow air-sensitive crystalline solid, was similar to that of the Group 4 complexes with the same core of two nearly planar, fused four membered rings with a Sm–C(1) shared edge. Parameters are given in Table 1. The samarium to carbon bond distance {Sm–C(1) = 2.467(4) Å} is considerably shorter (10%) than average Sm–alkyl single bond distances [68] {average 2.743 Å, median 2.738 Å} and is also shorter than the related distances in neutral carbene ligand complexes [63,64,68] of samarium as well as other lanthanides which again supports the formulation of the linkage as one possessing multiple bond character. The same open book structure as is found in the Group 4 complexes is present but here the dihedral angle (at 37.7(1))° is a little larger. The P–C–P bond angle is 138.0(3)°. The Sm–N bond distances to the phosphinimine nitrogen atoms are longer than the Sm–N bond distances to the nitrogen atom of the dicyclohexylamido group indicating that the imine groups are best described as neutral donor substituents.

The bond distances within the ligand framework in **10** show the same pattern as that of the Group 4 complexes with the P=N bond distances which are elongated and endocyclic P–C bond distances which are significantly shortened relative to the free ligands [20,50h,69]. The exocyclic P–C distances are unaffected. The electron delocalization in **10** is similar to that observed in the Group 4 complexes (Scheme 2) and the complex has some ylidic character but the Sm complex clearly shows an identifiable metal–carbene interaction.

The complex is paramagnetic so the NMR resonances are broad as expected. The ^{31}P-NMR signal appeared at a lower field than for the Group 4 complexes.

5.2. Bridging carbene dimer complex

Chromium dichloride ultimately gave, with the Li salt, Li$_2${C(Ph$_2$P=NSiMe$_3$)$_2$}, (**4**) [15], after complete elimination of two moles of LiCl, the complex [Cr{μ_2-C(Ph$_2$P=NSiMe$_3$)$_2$-κ^4C,C',N,N'}]$_2$ (**11**) [19] as a paramagnetic, red, air-sensitive crystalline solid (Scheme 3). The intermediate [Cr$_2$(μ-Cl)$_2${μ_2-C(Ph$_2$P=NSiMe$_3$)$_2$-κ^4C,C',N,N'}(LiCl)(THF)$_2$]$_2$ (**12**) was quantitatively isolated when a 1:1 reaction ratio was used and this intermediate was structurally characterized. Interestingly we see in the intermediate the formation of a singly bridged carbene unit. In this intermediate each carbon is bridged by two Cr atoms and the Cr atoms are either capped by Li{Cl}$_2$ bridges or remain as part of the original μ^2-Cr$_2$Cl$_2$ bridge of the parent complex. More ligand readily converted **12** to **11**.

Complex **11**, [Cr{μ_2-C(Ph$_2$P=NSiMe$_3$)$_2$-κ^4C,C',N,N'}]$_2$, has a central square plane of two chromium atoms bridged by two carbene centers to form a planar Cr$_2$C$_2$ four membered ring. The ligand backbone forms four fused, four-membered, rings, which are assembled from the bridging carbene carbon, the metal, the phosphorus and the imine nitrogen atoms. These four Cr, N, P, C rings arrange themselves above and below the central Cr$_2$C$_2$ plane to create a saddle-like structure in which the geometry around each Cr is approximately tetrahedral. Each of the iminophosphorane nitrogen units coordinates to the metal to confer a μ_2-κ^4 coordination. The two planar four membered metallocyclic rings which are subtended around a specific carbene center {Cr(1), N(1), P(1), C(1) and Cr(2), N(2), P(2), C(1)} and {Cr(1), N(3), P(3), C(2) and N(4), P(4), C(2), Cr(2)} make respective dihedral angles of 46.8(1) and 44.8(2)°. The P–C–P bond angles (average 131.7(3)° in **11** and 131.4(2)° (**12**) although much tighter than the values typical for the Group 4 complexes, are similar to those in the Sm complex **10**. The P=N and P=C bond distances within the bicyclic frameworks of both **11** and **12** are a pattern consistent with the delocalization illustrated in Scheme 2 [50h,69] [and Avis, 1996 # 53] which describes the Group 4 and Sm complexes.

6. Summary

The double deprotonation of bis(iminophosphorano)methane ligands by means of the action of either alkyl or bis(trimethylsilyl)anido metal precursors yields 'pincer' carbenes of Group 4 and lanthanide metals. The dilithiumbis(iminophosphorano)methandiide salt obtained simply by lithiating bis(trimethylsilylimino(diphenylphosphorano))methane with two moles of lithium alkyl extends the generality of the system. The structural data for the 'pincer' complexes strongly suggests that there is a M=C carbene double bond which the reaction chemistry also supports. Four reaction types are surveyed; (a) the complexes undergo alkylation of the halides with lithium and grignard reagents to form metal alkyl 'pincer' complexes in which the carbene center is not affected. (b) The Lewis acidity of the metal was demonstrated by the addition of simple donors again without significant effect on the carbene structure. In addition, two types of addition reactions to the carbenes were demonstrated, namely (c) 1,2 addition across the M=C carbene bond which produces a complex in which a M–C bond of lower order is preserved. The electrophilic moiety (H, Me) adds to the C_α center as is typical of Schrock (alkylidene) carbenes, and (d) a [2 + 2] cycloaddition of heteroallenes across this M=C bond which creates new tetradentate ligands in which again a M–C bond is maintained. Both of these addition reactions reduce the M=C bond order to one but the fact that a M–C bond remains after these additions supports the original interpretation, based on structural results, that the 'pincer' carbenes have a double bond to the metal. This reactivity pattern is also consistent with alkylidene character of the carbene center in these pincer carbene complexes. The synthesis chemistry extends to many other elements and the extension to Sm as a representative lanthanide is surveyed. This Sm species adopts a structure very similar to the Group 4 'pincers'. Chromium(II) gave a novel bridging carbene dimer which is also developing as another structural motif in this system.

Acknowledgements

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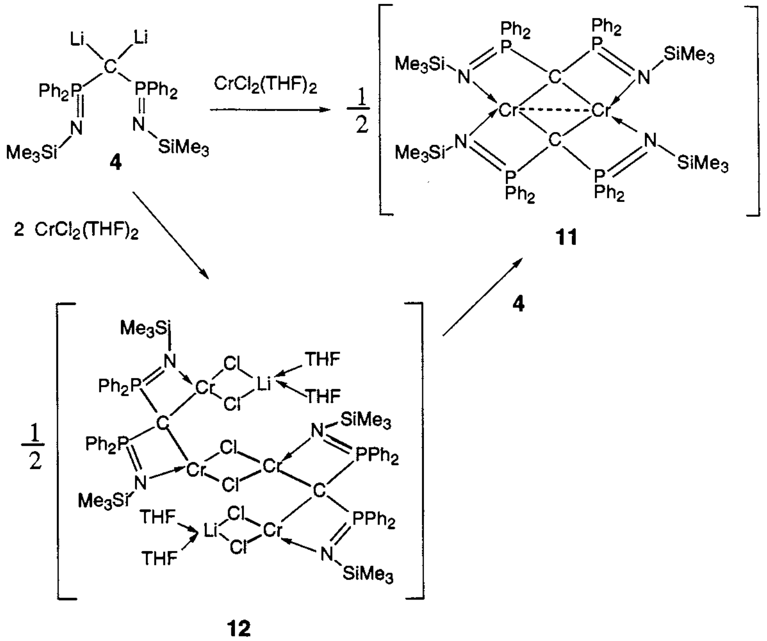

Scheme 3.

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