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Reviews

Triple Bonds between Transition Metals and the Heavier Elements of Groups 14 and 15[†]

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In the mid-1990s, the first examples of complexes containing triple bonds between transition metals and heavier analogues of the carbon as well as the nitrogen groups were reported, thus signaling the beginning of a new era in organometallic chemistry. Since then the progress in this field has been tremendous, with a large number of representative complexes being isolated and characterized. This review highlights the astonishing development of the chemistry of complexes containing triple bonds between transition metals and the heavier elements of groups 14 and 15 since its birth. The synthesis and the structural and spectroscopic features of these compounds are comprehensively discussed. Furthermore, the elucidation of their bonding modes by quantum-chemical methods as well as the relation between the reactivities of these complexes and their electronic structures are presented.

Introduction

Complexes containing triple bonds between transition metals and either group 14 or group 15 elements form two extremely fascinating compound classes encountered in organometallic chemistry research. These compounds are intriguing not only due to their undeniably exotic nature derived from their unusual bonding characteristics but also due to the interesting electronic and photophysical properties that they exhibit and the broad palette of chemical processes, both catalytic and stoichiometric, in which they participate.[1−4]

The first examples of compounds containing a transition metal triply bonded to a group 14 element were reported by Fischer and co-workers in 1973 as a series of transition metal−carbyne or −alkylidyne complexes of the general formula [RC≡M(CO)$_4$X] (R = methyl (CH$_3$ or Me), phenyl (C$_6$H$_5$ or Ph); M = Cr, Mo, W; X = Cl, Br, I) (**1**; Figure 1).[5] Two years later, Fischer and his co-workers also reported the synthesis and characterization of the first carbyne complex cation, [MeC≡Cr(CO)$_4$PMe$_3$]$^+$ (**2**),[6] and since then, the study of the chemistry of complexes containing M≡C triple bonds (M = transition metal) has matured into a thriving area of research.[1] One of the most recent highlights in the area, reported by Cummins and co-workers in 1997, was the isolation of the first carbide complex anion, [C≡Mo{N(R)R′}$_3$]$^-$ (R = 2-methylhexadeuteriopropyl (C(CD$_3$)$_2$Me); R′ = 3,5-dimethylphenyl (3,5-Me$_2$C$_6$H$_3$)) (**3**; Figure 1), which is the first compound featuring a one-coordinate carbon atom bonded to a metal center.[7,8] Even more recently, neutral carbide complexes demonstrating remarkable catalytic activity have been reported.[9]

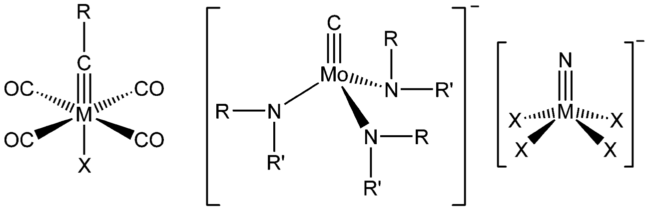

Figure 1. Representations of the structures of [RC≡M(CO)$_4$X] (R = Me, Ph; M = Cr, Mo, W; X = Cl, Br, I (**1**)), [C≡Mo{N(R)R′}$_3$]$^-$ (R = C(CD$_3$)$_2$Me; R′ = 3,5-Me$_2$C$_6$H$_3$ (**3**)), and [N≡MX$_4$]$^-$ (M = Mo, W, Re, Ru, Os; X = F, Cl, Br, I (**4**)).

A study of the history of compounds containing transition metals triply bonded to group 15 elements reveals that transition metal−nitride complexes, for example, of the type [N≡MX$_4$]$^-$ (M = Mo, W, Re, Ru, Os; X = F, Cl, Br, I) (**4**; Figure 1), are also an established class of compounds and have been known

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[†] Dedicated to Prof. John F. Nixon on the occasion of his 70th birthday.

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even longer than the carbyne complexes of Fischer and co-workers.[10,11]

Despite the breathtaking rate at which the chemistry of complexes containing M≡C and M≡N triple bonds (M = transition metal) has developed, and still continues to flourish, it was not until the mid-1990s that the existence of analogous compounds of the heavier group 14 and 15 elements could be unambiguously confirmed: the groups of Scheer,[12,13] Schrock,[14] and Cummins[15] reported independently the first examples of transition metal−phosphide complexes in 1995, while the first transition metal−germylyne complex was reported by Power in 1996.[16] These groundbreaking discoveries signaled that the "taming" of the heavier homologues of carbon and nitrogen was no longer a seemingly unattainable goal, and the astonishing progress that has been made in this field is reviewed herein.

Triple Bonds between Transition Metals and the Heavier Elements of Group 14

Compounds containing multiple bonds involving carbon, such as alkenes, alkynes, nitriles, and carbonyl compounds, are abundant and display remarkably diverse structures and reactivity patterns. In fact, the chemistry of carbon owes much of its richness to the propensity of the element to readily form homo- and heteronuclear multiple bonds. In contrast, the heavier group 14 elements show an impeded tendency to engage in multiple bonding.[17]

The reluctance of the heavier group 14 elements to form homonuclear multiple bonds is beautifully illustrated by the structural features of the alkyne analogues E_2R_2 (R = bis[bis(trimethylsilyl)methyl](2-propyl)silyl ($Si(CH(SiMe_3)_2)_2(CMe_2H)$), E = Si (**5a**);[18] R = 2,6-bis(2-propyl)phenyl ($2,6\text{-}(CMe_2H)_2C_6H_3$), E = Ge (**5b**),[19] Sn (**5c**);[20] R = 2,4,6-tris(2-propyl)phenyl ($2,4,6\text{-}(CMe_2H)_3C_6H_2$), E = Pb (**5d**))[21] (Figure 2). In the silicon, germanium, and tin derivatives **5a**−**c** the bulky substituents assume a trans geometry: the Si−Si−Si angle in **5a** is 137.44°, and the C−E−E angles in **5b**,**c** are 128.7 and 125.24°, respectively. Furthermore, the E−E bond lengths in **5a**−**c** are noticeably shorter than those in compounds containing E−E single bonds. These structural parameters, in conjunction with quantum-chemical calculations,[18,22] suggest that multiple bonding is present in **5a**−**c**. The lead derivative **5d** displays a trans-bent geometry as well, but the C−Pb−Pb angle is nearly a right angle (94.26°) and the Pb−Pb bond length is longer than that of the Pb−Pb single bond in hexaphenyldiplumbane.[23] Thus, compound **5d**, which is formally a diplumbyne, should rather be viewed as a diplumbylene with a Pb−Pb single bond and a lone pair of electrons at each lead atom.

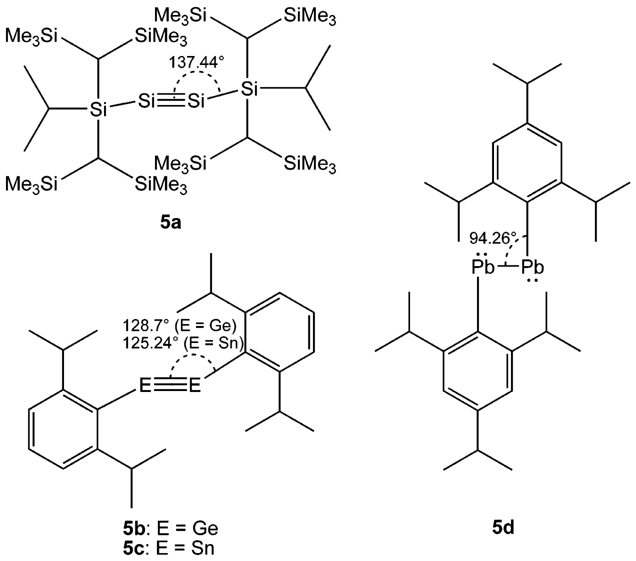

Figure 2. Representations of the structures of the alkyne analogues **5a**−**d**.

The brief discussion of the alkyne analogues **5a**−**d** underlines the difficulty of forcing the heavier group 14 elements into multiple bonding and thus serves to emphasize the challenges faced by synthetic chemists whose aim was the preparation of complexes containing M≡E triple bonds (M = transition metal; E = Si, Ge, Sn, Pb). The results of their commendable efforts in this direction are presented below in the order of increasing atomic number.

Silicon. To date, only one transition metal−silicon complex exhibiting appreciable silylyne character exists, which was reported by Tilley and Mork in 2003.[24] With the neutral silylene [Cp*(dmpe)(H)Mo = Si(Cl)Mes] (**6**: Cp* = pentamethylcyclopentadienyl (C_5Me_5); dmpe = 1,2-bis(dimethylphosphino)ethane ($1,2\text{-}(Me_2P)_2C_2H_4$); Mes = mesityl or 2,4,6-trimethylphenyl ($2,4,6\text{-}Me_3C_6H_2$)) as the starting material, the complex $[Cp^*(dmpe)(H)MoSiMes][B(C_6F_5)_4]$ (**7**$[B(C_6F_5)_4]$) could be generated by a simple anion exchange reaction (eq 1) and isolated as amber crystals.

$$\underset{\mathbf{6}}{[Cp^*(dmpe)(H)Mo{=}Si(Cl)Mes]} + LiB(C_6F_5)_4 \xrightarrow{C_6H_5F} \underset{\mathbf{7}[B(C_6F_5)_4]}{[Cp^*(dmpe)(H)MoSiMes][B(C_6F_5)_4]} + LiCl \quad (1)$$

$$Cp^* = C_5Me_5;\ dmpe = 1,2\text{-}(Me_2P)_2C_2H_4;\ Mes = 2,4,6\text{-}Me_3C_6H_2$$

In accordance with one's expectations of a complex with silylyne character (structure **7a**) (Figure 3), the $^{29}Si\{^1H\}$ NMR spectrum of the complex cation **7** displays a resonance at δ 289 ppm, which is shifted significantly downfield with respect to that of **6** (δ 182 ppm). Furthermore, the coupling constant between the Si atom and the hydride moiety is very small (J_{SiH}

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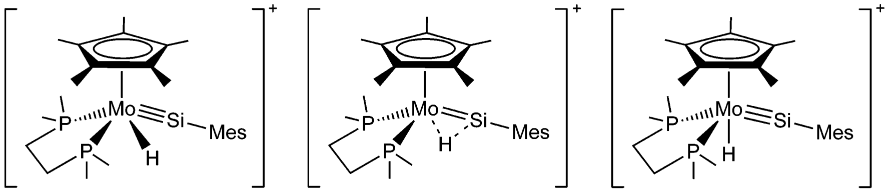


7a **7b** **7c**

Figure 3. Possible structures for the complex cation [Cp*(dmpe)(H)MoSiMes]$^+$ (**7**).

Table 1. Germylyne Complexes of the Formula [RGe≡MCp(CO)$_2$] Isolated by Power and Co-workers and Selected Structural Parameters Thereof

complex	M	R	M−Ge (Å)	M−Ge−C (deg)
12a	Mo	2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$	2.271(1)	172.2(2)
12b	W	2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$	2.277(1)	170.9(3)
12c	Cr	2,6-{2,4,6-$(CMe_2H)_3C_6H_2\}_2C_6H_3$	2.167(1)	175.99(6)
12d	Mo	2,6-{2,4,6-$(CMe_2H)_3C_6H_2\}_2C_6H_3$	2.272(8)	174.3(1)
12e	W	2,6-{2,4,6-$(CMe_2H)_3C_6H_2\}_2C_6H_3$		

= 15 Hz). X-ray crystallographic characterization of **7**[B(C_6F_5)$_4$] revealed a very short Mo−Si bond length (2.219(2) Å), which not only is appreciably shorter than that of **6** (2.288(2) Å) but also is the shortest bond of its kind to be reported. However, the X-ray structure of the complex cation **7** suggests that the hydride moiety assumes a bridging position between the molybdenum and silicon atoms (structure **7b**) (Figure 3) and thus presents a nonclassical Si−H interaction. The room-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra of **7**[B(C_6F_5)$_4$] in solution are indicative of a cation structure which possesses C_s symmetry (structure **7c**) (Figure 3), whereas at −30 °C an asymmetric species fitting to either **7a** or **7b** is observed. The NMR data thus suggest that a species with true silylyne character may exist, at least transiently, in solution. Density functional theory (DFT) calculations are in favor of structure **7b** and thus support the results of the X-ray diffraction study.

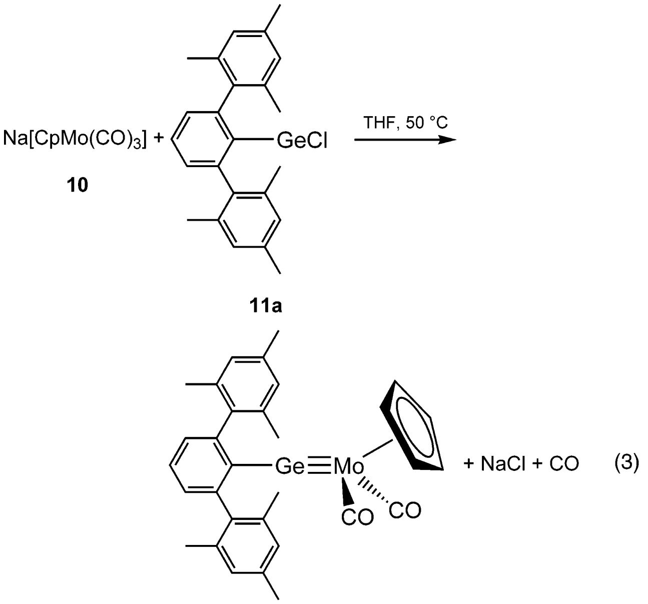
Preliminary reactivity studies have shown that **7**[B(C_6F_5)$_4$] reacts with $LiCH_2SiMe_3$ to yield the neutral silylene complex [Cp*(dmpe)(H)Mo=Si(CH_2SiMe_3Mes)] (**8**) (eq 2), hence demonstrating the electrophilic nature of the silicon atom in **7**.[24]

$$\underset{\mathbf{7}[B(C_6F_5)_4]}{[Cp^*(dmpe)(H)MoSiMes][B(C_6F_5)_4]} + LiCH_2SiMe_3 \xrightarrow{C_6H_5F} \underset{\mathbf{8}}{[Cp^*(dmpe)(H)Mo{=}Si\{CH_2SiMe_3\}Mes]} + LiB(C_6F_5)_4 \quad (2)$$

$$Cp^* = C_5Me_5;\ dmpe = 1,2\text{-}(Me_2P)_2C_2H_4;\ Mes = 2,4,6\text{-}Me_3C_6H_2$$

Even weaker nucleophiles, such as pyridine and 2,2′-bipyridine, coordinate to the silicon atom in **7** and most probably result in the formation of species similar to the previously reported complex cations [Cp*(Me_3P)$_2$RuSi(L)(STol-*p*)]$^{2+}$ (L = 2,2′-bipyridine, phenanthroline; Tol-*p* = *p*-tolyl (4-MeC_6H_4) (**9**)), which may be regarded formally as base-stabilized transition metal−silylyne complexes, although the Si atom in each complex is found in a distorted-tetrahedral environment.[25]

Germanium. The first example of a transition metal−germylyne complex, which was also the first compound containing a triple bond between a transition metal and a heavier homologue of carbon, was reported by the group of Power.[16] A remarkably simple salt elimination reaction between Na[CpMo(CO)$_3$] (Cp = cyclopentadienyl (C_5H_5) (**10**)) and RGeCl (R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) (**11a**)), performed under relatively mild conditions in tetrahydrofuran (THF), led to the isolation of the germylyne complex [RGe≡MoCp(CO)$_2$] (**12a**) as thermally stable red crystals (eq 3). The stability of this complex was attributed to the sterically demanding organic substituent on the germanium atom. X-ray crystallographic characterization of **12a** revealed that the coordination mode at the germanium atom is essentially linear (Mo−Ge−C = 172.2(2)°) and that the Mo−Ge bond length is particularly short (2.271(1) Å) compared to complexes containing Mo−Ge single bonds (~2.6 Å).[26] The presence of a Mo≡Ge triple bond in **12a** is thus implied by these structural features and is also supported by DFT calculations performed on the model compound [CH_3Ge≡MoCp(CO)$_2$] (**12′**) by Frenking and co-workers, which predict a bond order of 3 for the Mo−Ge bond.[27] Power and co-workers have, in the meantime, been able to isolate several germylyne complexes of the general formula [RGe≡MCp(CO)$_2$] (R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$), 2,6-bis[2,4,6-tris(2-propyl)phenyl]phenyl (2,6-{2,4,6-$(CMe_2H)_3C_6H_2\}_2C_6H_3$); M = Cr, Mo, W (**12b**−**e**) (Table 1).[28]



10 **11a** **12a**

The group of Filippou chose an entirely different approach to the synthesis of transition metal−germylyne compounds. The

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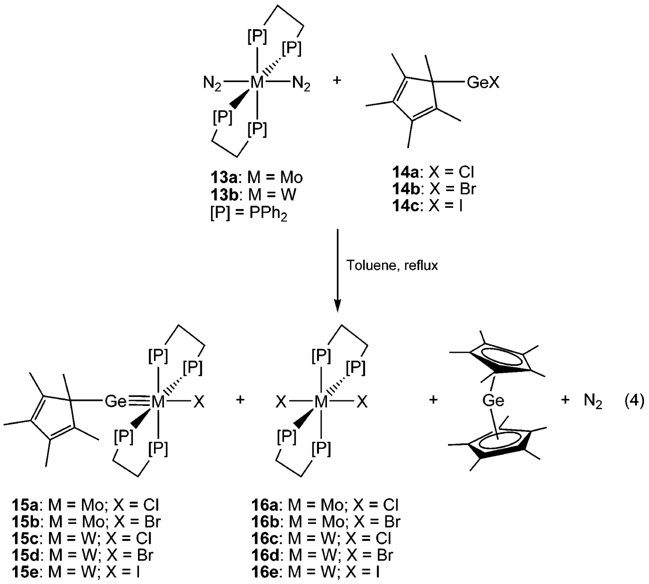
complexes $[M(dppe)_2(N_2)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane $(1,2\text{-}(Ph_2P)_2C_2H_4)$; M = Mo (**13a**), W (**13b**)) reacted with the germylenes [Cp*GeX] (X = Cl (**14a**), Br (**14b**), I (**14c**)) to yield the germylyne complexes $[Cp^*Ge{\equiv}M(dppe)_2X]$ (**15a**−**e**) as orange-brown to red-brown solids (eq 4), the reactions being driven by the thermal elimination of N_2 from **13a**,**b**.[29,30] The compounds **15a**−**e** are very air-sensitive yet display astonishing thermal stability, with decomposition temperatures in excess of 200 °C. The structures of the compounds were determined by X-ray diffraction and possess structural features indicative of the presence of M−Ge triple bonding: the M−Ge bonds are very short, the Cp* substituent is bound in an η^1 fashion to the germanium atom, and the M−Ge−C sequence is essentially linear (Table 2). Interestingly, although the formation of **15a**−**e** is accompanied by the formation of $GeCp^*_2$ and the dihalo complexes $[M(dppe)_2X_2]$ (M = Mo, W; X = Cl, Br, I (**16a**−**e**)), the reactions yielding the W derivatives **15c**−**e** proceed much more selectively than those yielding the molybdenum derivatives **15a**,**b**.



Solution NMR spectroscopic measurements on the complexes **15a**−**e** suggest that the Cp* group in each of these complexes undergoes a haptotropic shift which is fast on the NMR time scale.[29,30] DFT calculations conducted on the model compounds $[CpGe{\equiv}W(L)_4Cl]$ (L = CO, PH_3 (**15′**)) demonstrated that the structure of lowest energy for these complexes is one in which the Cp group is bound as an η^1 ligand.[30] The structures containing the Cp group as an η^2 ligand represent transition states for the haptotropic shift of this group, and the activation barrier thereof is low. In addition, the increase in the hapticity of the Cp ligand results in significant bending of the germylyne ligand at the germanium atom.

Filippou and co-workers have also investigated the reactivity of the W derivatives **15c**,**e** (X = Cl, I) (Scheme 1) and have found that the iodide complex is generally much more reactive than the chloride complex.[31] Thus, the hydrido−germylyne complex $[Cp^*Ge{\equiv}W(dppe)_2H]$ (**17**) as well as the series of pseudohalo−germylyne complexes $[Cp^*Ge{\equiv}W(dppe)_2Y]$ (Y = NCO (**18a**), NCS (**18b**), N_3 (**18c**), CN (**18d**)) could be isolated and characterized. The synthesis of the first cationic germylyne complex, $[Cp^*Ge{\equiv}W(dppe)_2(NCMe_3)][B(C_6F_5)_4]$ (**19**$[B(C_6F_5)_4]$), was also accomplished.

Table 2. Germylyne Complexes Isolated by Filippou and Co-workers and Selected Structural Parameters Thereof

complex[a]	M−Ge (Å)[b]	M−Ge−E (deg)[b,c]
$[Cp^*Ge{\equiv}Mo(dppe)_2Cl]$ (**15a**)	2.319(1)	172.0(1)
$[Cp^*Ge{\equiv}Mo(dppe)_2Br]$ (**15b**)	2.310(1)	171.6(2)
$[Cp^*Ge{\equiv}W(dppe)_2Cl]$ (**15c**)	2.302(1)	172.2(2)
$[Cp^*Ge{\equiv}W(dppe)_2Br]$ (**15d**)	2.293(1)	172.4(2)
$[Cp^*Ge{\equiv}W(dppe)_2I]$ (**15e**)	2.306(1)	172.6(2)
$[Cp^*Ge{\equiv}W(dppe)_2H]$ (**17**)	2.310(1)	176.8(1)
$[Cp^*Ge{\equiv}W(dppe)_2NCO]$ (**18a**)	2.299(1)	172.0(1)
$[Cp^*Ge{\equiv}W(dppe)_2NCS]$ (**18b**)		
$[Cp^*Ge{\equiv}W(dppe)_2N_3]$ (**18c**)		
$[Cp^*Ge{\equiv}W(dppe)_2CN]$ (**18d**)	2.318(1)	172.2(1)
$[Cp^*Ge{\equiv}W(dppe)_2(NCMe)][B(C_6F_5)_4]$ (**19**$[B(C_6F_5)_4]$)	2.303(1)	174.31(7)
$[RGe{\equiv}Mo(PMe_3)_4Cl]$ (**22a**)		
$[RGe{\equiv}W(PMe_3)_4Cl]$ (**22b**)	2.338(1)	177.9(3)
$[RGe{\equiv}W(PMe_3)_4I]$ (**22c**)	2.321(1)	175.79(7)
$[RGe{\equiv}W(PMe_3)_4NCS]$ (**24**)		
$[RGe{\equiv}W(PMe_3)_4H]$ (**25**)	2.324(1)	178.9(2)
$[Cp^*Ge{\equiv}Mo(depe)_2Cl]$ (**27a**)		
$[Cp^*Ge{\equiv}Mo(depe)_2Br]$ (**27b**)	2.280(1)	177.46(8)
$[Cp^*Ge{\equiv}W(depe)_2Cl]$ (**27c**)		
$[Cp^*Ge{\equiv}W(depe)_2Br]$ (**27d**)		
$[Cl(depe)_2Mo{\equiv}GeGe{\equiv}Mo(depe)_2Cl]$ (**28a**)		
$[Cl(depe)_2W{\equiv}GeGe{\equiv}W(depe)_2Cl]$ (**28b**)	2.309(1)	175.13(3)

[a] Legend: Cp* = pentamethylcyclopentadienyl (C_5Me_5); dppe = 1,2-bis(diphenylphosphino)ethane $(1,2\text{-}(Ph_2P)_2C_2H_4)$; R = 2,6-bis[2,4,6-tris(2-propyl)phenyl]phenyl $(2,6\text{-}\{2,4,6\text{-}(CMe_2H)_3C_6H_2\}_2C_6H_3)$; depe = 1,2-bis(diethylphosphino)ethane $(1,2\text{-}\{(C_2H_5)_2P\}_2C_2H_4)$. [b] M = Mo, W. [c] E = C, Ge.

Still another approach to the preparation of germylyne complexes has been reported very recently by Filippou and co-workers.[32] In this synthesis, the electron-rich complexes $[Mo(PMe_3)_6]$ (**20**) and $[W(CH_2PMe_2)H(PMe_3)_5]$ (**21**), respectively, were employed in the activation of RGeCl (R = 2,6-bis[2,4,6-tris(2-propyl)phenyl]phenyl $(2,6\text{-}\{2,4,6\text{-}(CMe_2H)_3C_6H_2\}_2C_6H_3)$ (**11b**)), thereby yielding the germylyne complexes $[RGe{\equiv}M(PMe_3)_4Cl]$ (M = Mo (**22a**), W (**22b**)) (Scheme 2). Depending on the reaction conditions, the tungsten derivative **22b** may be either formed directly or formed via the thermolabile hydrido−germylene $[R(Me_2PCH_2)Ge{=}W(H)(PMe_3)_3Cl]$ (**23**). The complexes **22b** and **23** could be characterized by X-ray crystallography, and as expected, the W−Ge bond in **22b** (2.324(1) Å) is markedly shorter than that of **23** (2.454(1) Å). Moreover, the W−Ge−C sequence in **22b** is essentially linear (178.9(2)°).

Preliminary reactivity studies have shown that **22b** can be used to access other germylyne complexes (Scheme 3).[32] Thus, the iodo−germylyne complex $[RGe{\equiv}W(PMe_3)_4I]$ (**22c**) may be obtained by the reaction of **22b** with LiI, while reaction with KNCS yielded the isothiocyanato−germylyne complex $[RGe{\equiv}W(PMe_3)_4NCS]$ (**24**). The reaction of **22b** with $LiNMe_2$, however, led to the unexpected formation of the hydrido−germylyne complex $[RGe{\equiv}W(PMe_3)_4H]$ (**25**). The intermediate species in this reaction most probably is a dimethylamido−germylyne complex, which is readily prone to β-hydride elimination.

Perhaps the most exciting development in the area of germylyne complexes since their discovery is the isolation of binuclear complexes containing M≡GeGe≡M chains (M = Mo,

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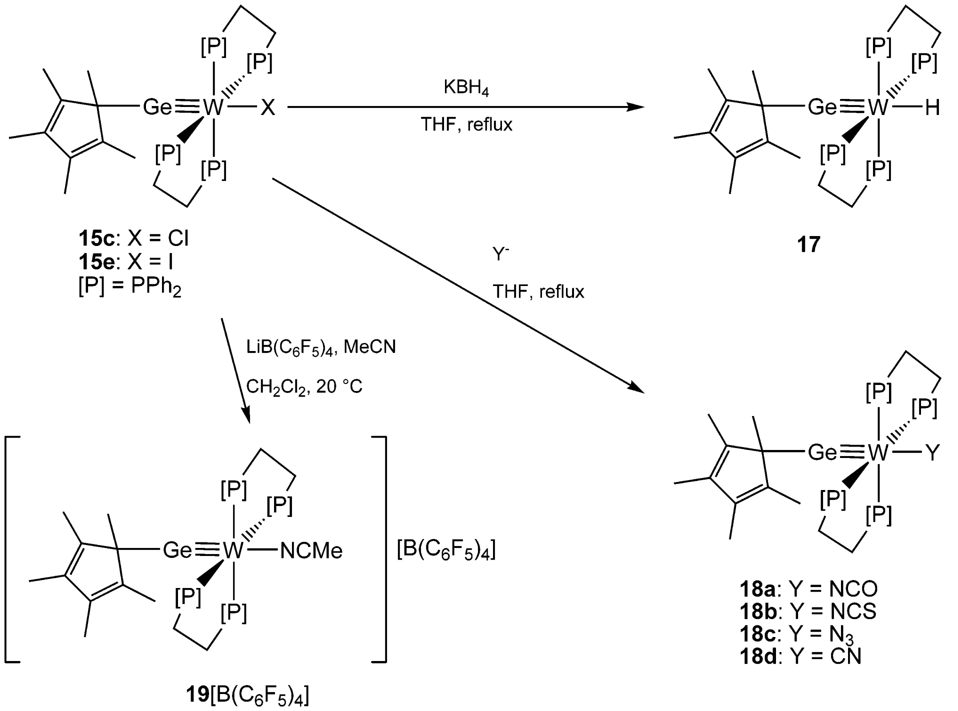
(29) Filippou, A. C.; Portius, P.; Philippopoulos, A. I. *Organometallics* **2002**, *21*, 653−661.

(30) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Neumann, D. U. *Angew. Chem.* **2000**, *112*, 2881−2884; *Angew. Chem., Int. Ed.* **2000**, *39*, 2778−2781.

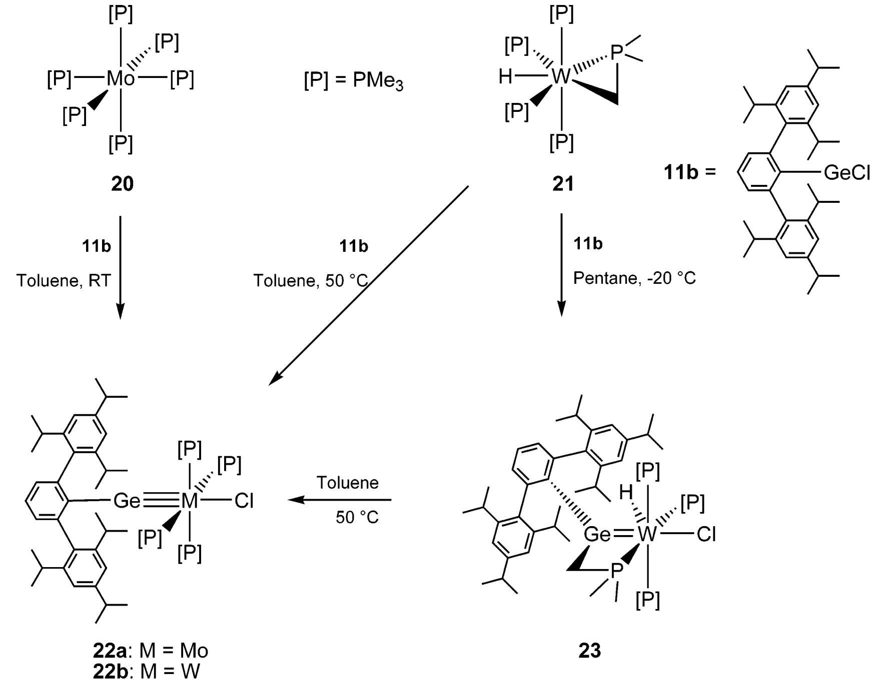
(31) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Schnakenburg, G. *Organometallics* **2004**, *23*, 4503−4512.

(32) Filippou, A. C.; Weidemann, N.; Philippopoulos, A. I.; Schnakenburg, G. *Angew. Chem.* **2006**, *118*, 6133−6137; *Angew. Chem., Int. Ed.* **2006**, *45*, 5987−5991.

Scheme 1. Reactions of the Germylyne Complexes 15c,e



Scheme 2. Synthesis of the Germylyne Complexes 22a,b



W).[33] Treatment of the dinitrogen complexes $[M(depe)_2(N_2)_2]$ (depe = 1,2-bis(diethylphosphino)ethane (1,2-$\{(C_2H_5)_2P\}_2C_2H_4$); M = Mo (**26a**), W (**26b**)) with [Cp*GeX] (X = Cl (**14a**), Br (**14b**)) in toluene gave the halo−germylyne complexes [Cp*Ge≡M(depe)$_2$X] (**27a**−**d**) (Scheme 4). Thermolysis of the chlorogermylyne complexes **27a**,**c** in the solid state yielded the binuclear germylyne complexes [Cl(depe)$_2$M≡GeGe≡M(depe)$_2$Cl] (**28a**,**b**) (Scheme 4). The other products observed (Cp*H, 1,2,3,4-tetramethylfulvalene, GeCp*$_2$) during the thermolysis of the molybdenum derivative **27a** are indicative of a radical reaction pathway which most likely involves homolytic Ge−Cp* bond cleavage. The [•Ge≡M(depe)$_2$Cl] radicals thus formed dimerize to the complexes **28a**,**b**. Complex **28b** could be characterized by X-ray crystallography and features an almost linear W−Ge−Ge−W chain (W−Ge−Ge = 175.13(3)°) and the shortest Ge−Ge single bond (2.362(1) Å) known, which is indicative of π-conjugation in the W≡GeGe≡W sequence.

DFT calculations performed on the model compound [Cl(H$_3$P)$_4$WGe$_2$W(PH$_3$)$_4$Cl] (**28′**) yielded six minimum structures, which can be divided into three structural types (**28′A**−**C**; Figure 4) that are distinguished by the coordination mode of the Ge$_2$ ligand.[33] In **28′A**, the Ge$_2$ unit is coordinated end-on to the tungsten centers ($\mu,\eta^1{:}\eta^1$ coordination mode), while in **28′B**,**C**

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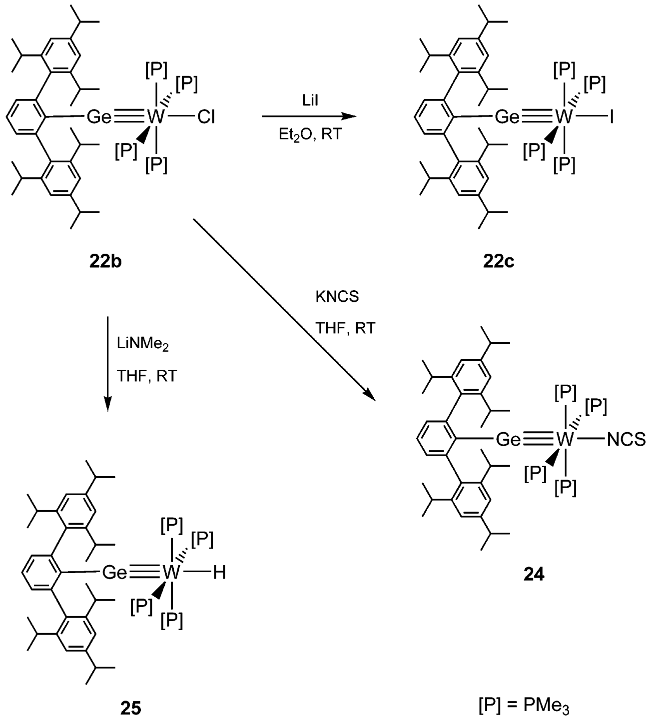
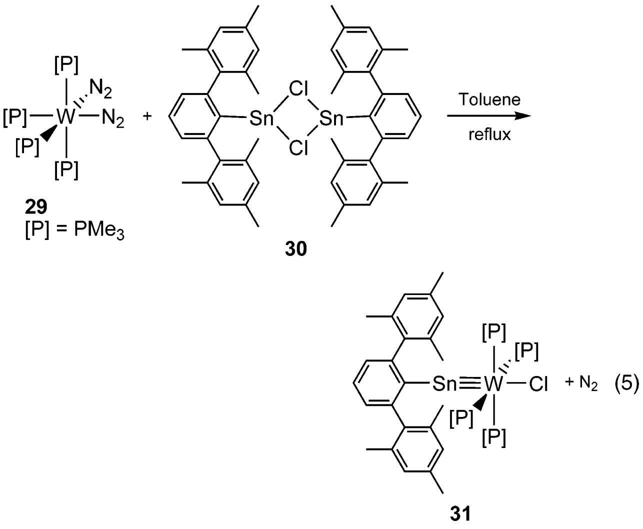
(33) Filippou, A. C.; Schnakenburg, G.; Philippopoulos, A. I.; Weidemann, N. *Angew. Chem.* **2005**, *117*, 6133−6139; *Angew. Chem., Int. Ed.* **2005**, *44*, 5979−5985.

Scheme 3. Reactions of the Germylyne Complex 22b



side-on coordination of this unit is exhibited ($\mu,\eta^2{:}\eta^2$ coordination mode). The difference between **28′B** and **28′C** is that, in the former structural type, the W$_2$Ge$_2$ moiety is planar, whereas in the latter type, this moiety is folded along the Ge−Ge axis (butterfly structure). Furthermore, two conformational isomers are possible for each of the three structural types **28′A**−**C**: that is, one conformer in which the [W(PH$_3$)$_4$Cl] fragments are eclipsed and one in which they are staggered with respect to each other. The **28′A**-type conformers (end-on coordinated Ge$_2$ ligand) are the most stable compounds, the eclipsed conformer being marginally more stable than the staggered conformer, and are at least 9 kJ mol^{-1} more stable than the **28′B**-type conformers (side-on coordinated Ge$_2$ ligand, planar W$_2$Ge$_2$ moiety) and at least 64 kJ mol^{-1} more stable than the **28′C**-type conformers (side-on coordinated Ge$_2$ ligand, folded W$_2$-Ge$_2$ moiety). The results of the calculations on the **28′A**-type eclipsed conformer also suggest π-conjugation in the W≡GeGe≡W sequence, which is consistent with the noticeably short Ge−Ge single bond in **28b**.

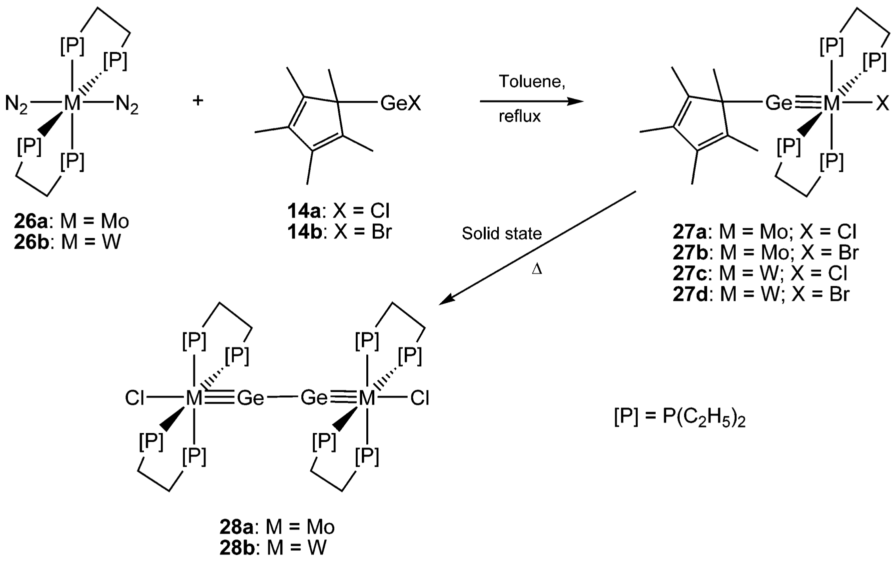
Tin. Filippou's "dinitrogen elimination method"[30] was successful not only in the preparation of several germylyne complexes but also in the synthesis of the first stannylyne complex.[34] The compound [W(PMe$_3$)$_4$(N$_2$)$_2$] (**29**) reacted with [RSnCl]$_2$ (R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) (**30**)) to yield the extremely air-sensitive stannylyne complex [RSn≡W(PMe$_3$)$_4$Cl] (**31**) (eq 5). Crystals

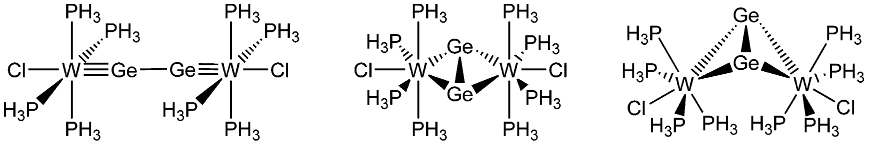


of **31** were characterized by X-ray crystallography, and it was found that the unit cell of the compound contains two independent molecules of **31**. Furthermore, the coordination mode of the tin atom is essentially linear (W−Sn−C = 178.2(1)° (average of both independent molecules)) and the W−Sn bond (2.490(1) Å (average of both independent molecules)) is at least 0.2 Å shorter than those found in complexes containing W=Sn double bonds. As expected, the solution ^{119}Sn{^{1}H} NMR spectrum of **31** displays a quintet (δ 340.1 ppm, $^2J_{\mathrm{SnP}}$ = 134 Hz), which is shifted upfield with respect to the signal of the starting material **30** and other stannylenes.

Filippou and co-workers were also able to prepare the stannylyne complex [RSn≡W(dppe)$_2$Cl] (R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) (**32**)), which they then used to generate the cationic stannylyne complex

Scheme 4. Synthesis of the Germylyne Complexes 28a,b

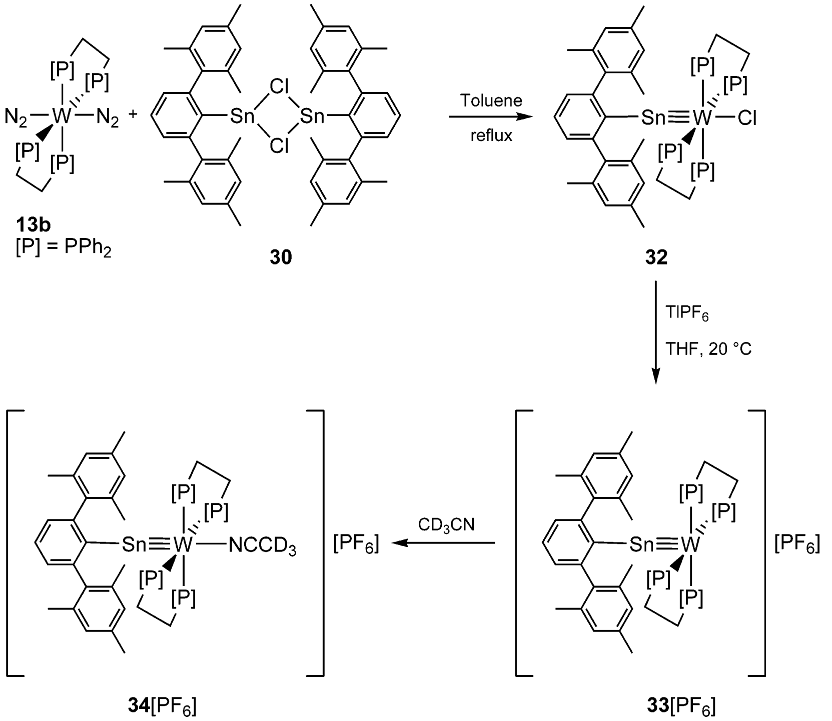




28'A **28'B** **28'C**

Figure 4. Representations of the three structural types (**28′A−C**) to which the six minimum structures calculated by DFT methods for the model compound $[Cl(H_3P)_4WGe_2W(PH_3)_4Cl]$ (**28′**) belong.

Scheme 5. Synthesis of the Stannylyne Complexes 32, 33[PF$_6$], and 34[PF$_6$]



$[RSn{\equiv}W(dppe)_2][PF_6]$ (**33**[PF$_6$]) (Scheme 5).[35] The preparation of **32** was accompanied by the formation of elemental tin, RH, and $[W(dppe)_2Cl_2]$ (**16c**), and the reaction is thus not as selective as that leading to the formation of **31**.[34] X-ray crystallographic characterization of **32** revealed an almost linearly coordinated tin atom (W−Sn−C = 175.88(8)°) and a short W−Sn bond (2.504(1) Å). DFT calculations on the model complex $[MeSn{\equiv}W(PH_3)_4Cl]$ (**32′**) predict a C_s-symmetric structure as the structure of minimum energy, in which the tin atom exhibits a linear coordination geometry.[35] The W−Sn bond comprises one σ bond, polarized toward the tin atom, and two virtually degenerate π bonds, polarized toward the tungsten atom.

The 16-electron square-pyramidal cationic stannylyne complex **33**[PF$_6$] could be readily prepared as an air-sensitive green solid via chloride abstraction from **32** using $TlPF_6$ (Scheme 5). Dissolution of **33**[PF$_6$] in CD_3CN yielded the 18-electron cationic trideuterioacetonitrilato−stannylyne complex $[RSn{\equiv}W(dppe)_2(NCCD_3)][PF_6]$ (**34**[PF$_6$]). The structure of **33**[PF$_6$], determined by X-ray crystallography, demonstrates that the cations in the compound are well separated from the anions and that the tungsten atom is in a square-pyramidal coordination environment. The tin atom displays nearly linear coordination (W−Sn−C = 178.77(9)°), and the W−Sn bond length (2.464(1) Å) is the shortest reported so far.

Lead. The facile preparation of germylyne and stannylyne complexes via the "dinitrogen elimination method"[30] encouraged Filippou and co-workers to apply the same strategy in the synthesis of the first plumbylyne complexes.[36,37] The dinitrogen complexes $[M(PMe_3)_4(N_2)_2]$ (M = Mo (**35**), W (**29**)) reacted with $[RPbX]_2$ (R = 2,6-bis[2,4,6-tris(2-propyl)phenyl]phenyl (2,6-$\{2,4,6\text{-}(CMe_2H)_3C_6H_2\}_2C_6H_3$); X = Br (**36a**), I (**36b**)) to yield the plumbylyne complexes $[RPb{\equiv}M(PMe_3)_4X]$ (**37a−c**) (Scheme 6). The crystal structures of **37a−c** are indicative of the presence of a Mo≡Pb triple bond in each complex, since the coordination geometry at the lead atoms is practically linear and the Mo−Pb bonds are particularly short (Table 3). The bromide ligand in **37b** can be easily abstracted using $LiB(C_6F_5)_4$ or $NaB\{C_6H_3(CF_3)_2\}_4$, and thus the cationic plumbylyne complexes $[RPb{\equiv}W(PMe_3)_5][B(C_6F_5)_4]$ (**38**[B(C$_6$F$_5$)$_4$]) and $[RPb{\equiv}W(PMe_3)_4(NCPh)][B\{C_6H_3(CF_3)_2\}_4]$ (**39**[B{C$_6$H$_3$(CF$_3$)$_2$}$_4$]) could be readily prepared (Scheme 6). The crystal structures of the compounds demonstrate that the coordination geometry at the lead atoms in the cations **38** and **39** is essentially linear and that the W−Pb bonds are short (Table 3). These structural parameters are therefore consistent with the presence of W≡Pb triple bonds in **38** and **39**.

Theoretical studies on the model compound $[PhPb{\equiv}Mo(PMe_3)_4Br]$ (**37′**), conducted by DFT methods, predicted a minimum structure of C_{2v} symmetry in which the lead atom exhibits linear coordination and the Mo−Pb bond is short.[36] Furthermore, the Mo−Pb bond in **37′** consists of one σ bond

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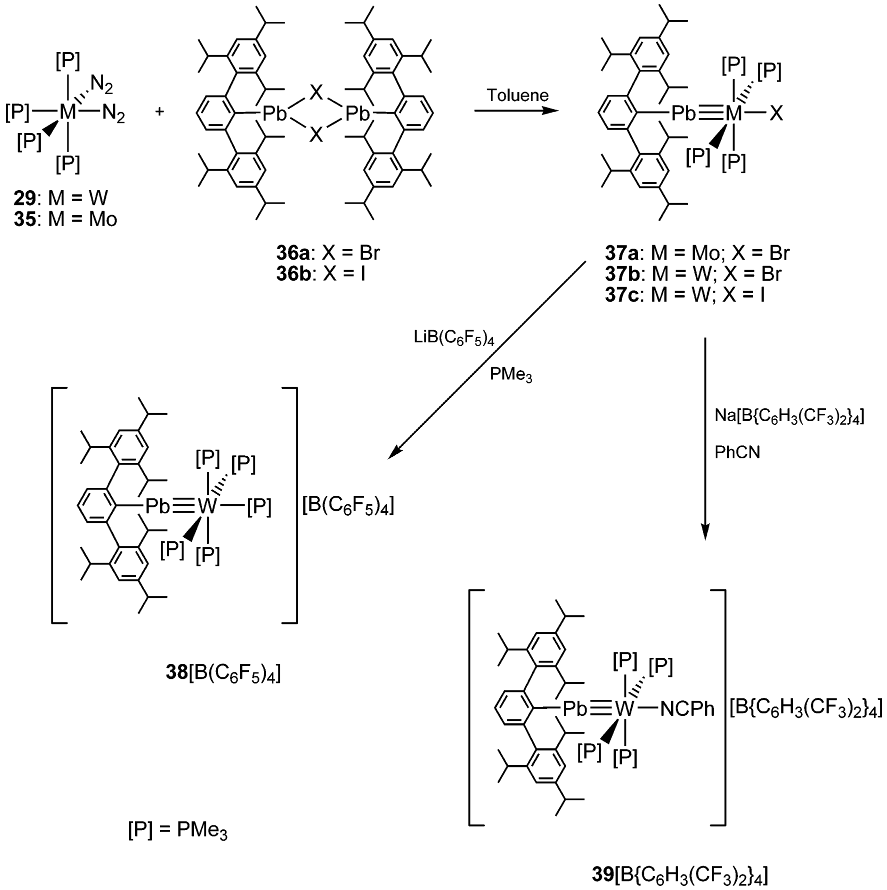
[34] Filippou, A. C.; Portius, P.; Philippopoulos, A. I.; Rohde, H. *Angew. Chem.* **2003**, *115*, 461−464; *Angew. Chem., Int. Ed.* **2003**, *42*, 445−447.

[35] Filippou, A. C.; Philippopoulos, A. I.; Schnakenburg, G. *Organometallics* **2003**, *22*, 3339−3341.

[36] Filippou, A. C.; Rohde, H.; Schnakenburg, G. *Angew. Chem.* **2004**, *116*, 2293−2297; *Angew. Chem., Int. Ed.* **2004**, *43*, 2243−2247.

[37] Filippou, A. C.; Weidemann, N.; Schnakenburg, G.; Rohde, H.; Philippopoulos, A. I. *Angew. Chem.* **2004**, *116*, 6674−6678; *Angew. Chem., Int. Ed.* **2004**, *43*, 6512−6516.

Scheme 6. Synthesis of the Plumbylyne Complexes 37a−c and Reactivity of 37b



29: M = W
35: M = Mo

36a: X = Br
36b: X = I

37a: M = Mo; X = Br
37b: M = W; X = Br
37c: M = W; X = I

38$[B(C_6F_5)_4]$

39$[B\{C_6H_3(CF_3)_2\}_4]$

[P] = PMe_3

and two π bonds, the σ bond being polarized toward the lead atom and the π bonds being polarized toward the molybdenum atom.

The structure of the cation **38** was optimized using quantum-chemical methods and the calculated W−Pb bond length (2.609 Å) and W−Pb−C angle (174.9°) are in good agreement with the experimentally determined values (Table 3).[37] The calculations also support the presence of a W≡Pb triple bond in **38** and predict that the Gibbs free energy of dissociation of **38** to the fragments $[W(PMe_3)_5]^-$ and $[PbR]^+$ is only 149.7 kJ mol^{-1}. Thus, **38** may be a potential $[PbR]^+$ transfer agent.

Triple Bonds between Transition Metals and the Heavier Elements of Group 15

Complexes containing transition metals triply bonded to nitrogen have been known for a long time. Representative examples of such nitrido complexes are compounds of the type $[NMCl_4]^-$ (M = Mo, W, Re, Ru, Os),[4,10] in which a very short metal−nitrogen distance occurs together with a high nucleophilicity toward Lewis acids. The breakthrough in the realization of corresponding stable complexes of the heavier homologues occurred only in 1995. The reason for this late development lies in the high reactivity of the M≡E (E = P, As, Sb, Bi) triple bonds, which present a high "side-on" as well as "end-on" reactivity. Thus, before 1995, highly reactive intermediates containing a metal−element triple bond were the subject of much speculation.[38]

Table 3. Stannylyne and Plumbylyne Complexes Isolated by Filippou and Co-workers and Selected Structural Parameters Thereof

complex[a]	M−Pb (Å)[b]	M−Pb−C (deg)[b]
$[RSn{\equiv}W(PMe_3)_4Cl]$ (**31**)	2.490(1)[c]	178.2(1)[c]
$[RSn{\equiv}W(dppe)_2Cl]$ (**32**)	2.504(1)	175.88(8)
$[RSn{\equiv}W(dppe)_2][PF_6]$ (**33**$[PF_6]$)	2.464(1)	178.77(9)
$[RSn{\equiv}W(dppe)_2(NCCD_3)][PF_6]$ (**34**$[PF_6]$)		
$[RPb{\equiv}Mo(PMe_3)_4Br]$ (**37a**)	2.550(1)	177.8(2)
$[RPb{\equiv}W(PMe_3)_4Br]$ (**37b**)	2.546(1)	177.5(2)
$[RPb{\equiv}W(PMe_3)_4I]$ (**37c**)	2.548(1)	175.79(8)
$[RPb{\equiv}W(PMe_3)_5][B(C_6F_5)_4]$ (**38**$[B(C_6F_5)_4]$)	2.574(1)	177.5(1)
$[RPb{\equiv}W(PMe_3)_4(NCPh)][B\{C_6H_3(CF_3)_2\}_4]$ (**39**$[B\{C_6H_3(CF_3)_2\}_4]$)	2.552(1)	171.7(1)

[a] In the tin complexes, R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-$(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$), while in the lead complexes, R = 2,6-bis[2,4,6-tris(2-propyl)phenyl]phenyl (2,6-$\{2,4,6\text{-}(CMe_2H)_3C_6H_2\}_2C_6H_3$); dppe = 1,2-bis(diphenylphosphino)ethane (1,2-$(Ph_2P)_2C_2H_4$). [b] M = Mo, W. [c] Average value of both independent molecules present in the crystal.

In order to synthesize stable transition metal complexes of the heavier group 15 elements containing triple bonds, two different strategies have been applied: (a) blocking the lone pair at the pnicogen atom through coordination to a Lewis acidic transition metal moiety, as shown in complexes of type **A** (Figure 5), and (b) introducing bulky organic substituents into the ligands on the transition metal, as shown in type **B** compounds (Figure 5). The kinetic stabilization of the metal−element triple bond is a common feature of these two approaches, but the reactivity patterns of the resulting compounds differ. In type **A** complexes, the side-on reactivity is enhanced by blocking the end-on reactivity, whereas in type **B** complexes the end-on reactivity is maintained exclusively. In complexes of type **B** the protection of the triple bond is realized through bulky organic substituents attached to the amido nitrogen atoms of the ligand bound to the transition metal. In contrast, the

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(38) Scheer, M. *Coord. Chem. Rev.* **1997**, *163*, 271−286.

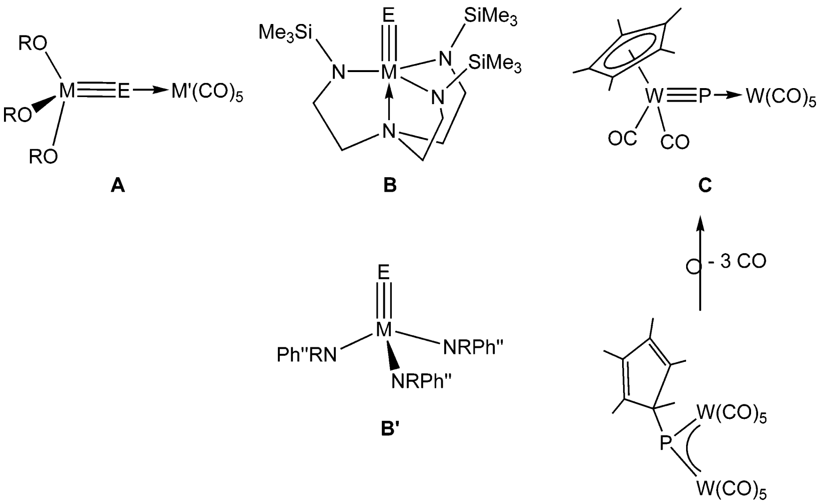


Figure 5. Representations of the structural types of complexes containing multiple bonds between transition metals and group 15 elements (E = P, As, Sb; R = organic group; Ph″ = 3,5-$Me_2C_6H_3$).

alkoxy ligands in type **A** complexes protect the triple bond in the solid state but are flexible in solution, thus promoting a side-on reactivity.

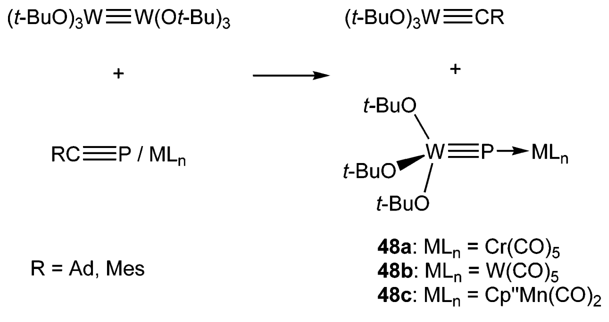
The high reactivity of such systems was a significant problem that the Scheer group was faced with while attempting to synthesize the type **A** complexes $[(t\text{-BuO})_3W{\equiv}P{\rightarrow}M(CO)_5]$ (*t*-Bu = CMe_3; M = Cr, Mo), which were first reported in 1995.[12] The presence of the triple-bond compounds in solution was confirmed by spectroscopic methods and could later on be corroborated by X-ray crystallographic characterization.[39] The groups of Schrock and Cummins chose the approach leading to type **B** complexes and, a few months after the report of the Scheer group, reported the synthesis of the terminal phosphido complexes $[(N_3N)W{\equiv}P]$ ($N_3N = N(CH_2CH_2NSiMe_3)_3$)[14] and $[(t\text{-Bu}'Ph'')_3Mo{\equiv}P]$ ($t\text{-Bu}' = C(CD_3)_2CH_3$, Ph″ = 3,5-$Me_2C_6H_3$)[15] of types **B** and **B′** (Figure 5), respectively. These structurally characterized complexes reveal exclusively end-on reactivity.

In order to expand the palette of complexes with a highly side-on reactive metal−element triple bond, the Scheer group developed a synthetic approach to intermediates of type **C** (Figure 5).[40] By inducing the migration of the σ-bound Cp* substituent at the phosphinidene phosphorus atom in $[Cp^*P\text{-}\{W(CO)_5\}_2]$, thermally[40] or photochemically,[41] the intermediate $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ (**40**), containing an η^5-coordinated Cp* ligand, was formed with loss of CO. In the absence of a trapping reagent, **40** dimerized to the tetrahedrane complex $[Cp^*_2(CO)_4W_2(\mu,\eta^2{:}\eta^1\text{-}P_2)\{W(CO)_5\}]$ (**41**) (Scheme 7), while in the presence of trapping reagents formal [2 + 2] cycloadditions were observed. Thus, reaction of *t*-BuC≡P with **40** in the presence of CO gave the diphosphacyclobutenonyl ligand complex **42**,[40] whereas reactions of alkynes with **40** yielded novel cage compounds (**43**, **44**) containing stabilized four-membered rings (Scheme 7).[42]

The focus of this section of the overview is on the synthesis, bonding, and reactivity patterns of stable pnicogenido complexes. The only previously speculated triple-bond-containing intermediates[38] included are those whose existence is supported by spectroscopic evidence. Furthermore, linearly coordinating phosphinidene and arsinidene complexes of type **D** (Figure 6), which formally contain triple bonds, have recently been reviewed[3,43] and will not be considered here. The double-bond species of type **E** (Figure 6) do not belong to the class of compounds reviewed herein and will also be excluded.

Phosphorus. The spectroscopic evidence for the side-on as well as end-on reactive triple-bond compound $[(t\text{-BuO})_3W{\equiv}P]$ (**45**), which is stable at low temperatures, was obtained by Scheer and co-workers in 1999.[39] On the basis of the earlier speculations of Becker and co-workers,[44] MesC≡P, instead of *t*-BuC≡P, was used in the metathesis reaction with $[W_2(O\text{-}t\text{-}Bu)_6]$ and monitored at low temperatures by ^{31}P NMR spectroscopy. The formation of $[(t\text{-BuO})_3W{\equiv}P]$, which is evidenced by the strongly downfield shifted ^{31}P NMR resonance at 845 ppm, combined with a small $^1J_{WP}$ coupling constant of 176 Hz, is apparent even at −60 °C. At −20 °C, the four-membered-ring products **46** and **47** could be detected. These are formed by a cyclization reaction of the triply bound metathesis products with MesC≡P and subsequent 1,3-OR migration from the tungsten atom to the phosphorus atom. The latter complexes are the only isolable products at ambient temperature (Scheme 8).

These spectroscopic observations paved the way to the side-product-free synthesis and isolation of the triply bonded complexes $[(t\text{-BuO})_3W{\equiv}P{\rightarrow}ML_n]$ ($ML_n = M(CO)_5$ (M = Cr (**48a**), W (**48b**)) and $Cp''Mn(CO)_2$ ($Cp'' = t\text{-}Bu_2C_5H_3$ (**48c**))[39] by the metathesis reaction of $[(t\text{-BuO})_3W{\equiv}W(Ot\text{-Bu})_3]$ with MesC≡P in the presence of $[M(CO)_5(THF)]$ (M = Cr, Mo) or $[Cp''Mn(CO)_2(THF)]$ (eq 6). The key step was the long reaction time at low temperatures (between −40 to −20 °C), which ensured that all MesC≡P was used for the metathesis and that no subsequent reaction could occur to form the four-membered-



(6)

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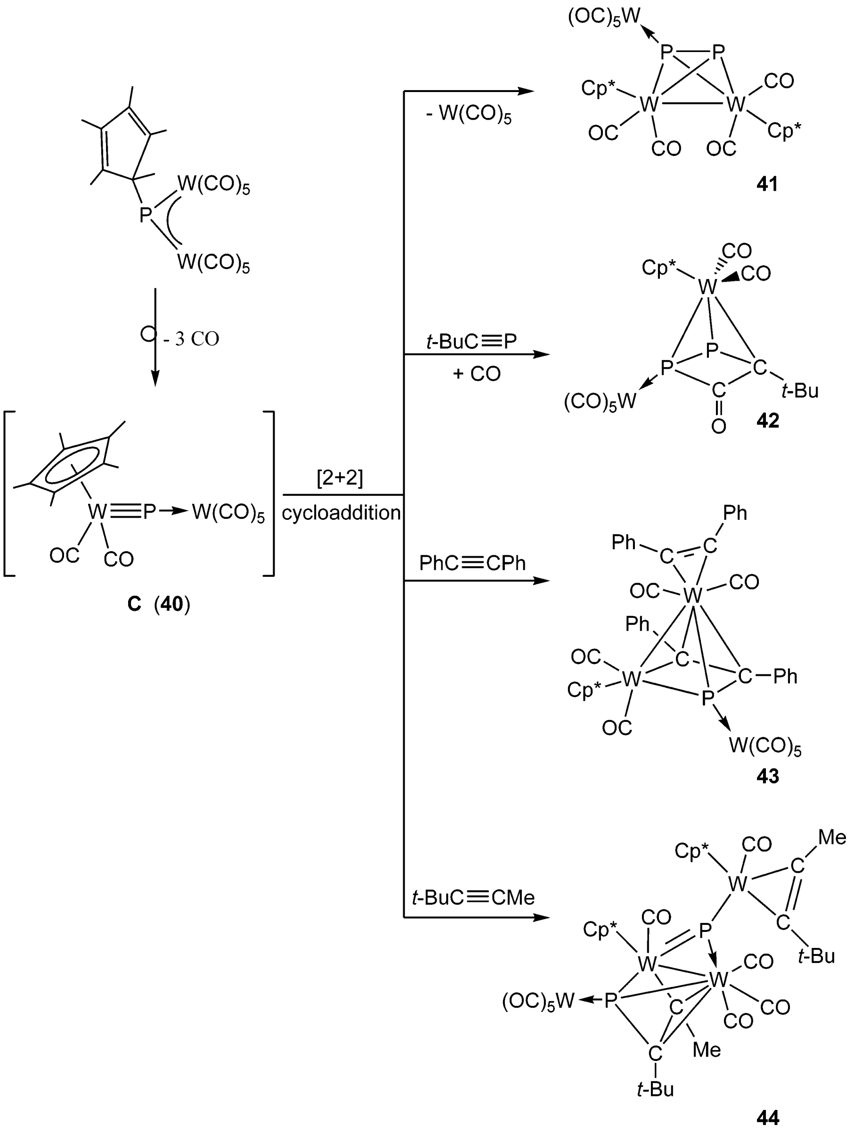
(39) Scheer, M.; Kramkowski, P.; Schuster, K. *Organometallics* **1999**, *18*, 2874−2883.

(40) Scheer, M.; Leiner, E.; Kramkowski, P.; Schiffer, M.; Baum, G. *Chem. Eur. J.* **1998**, *4*, 1917−1923.

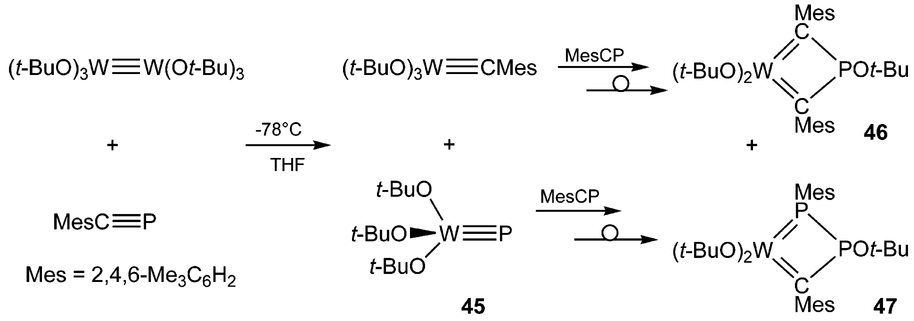
(41) Schiffer, M.; Leiner, E.; Scheer, M. *Eur. J. Inorg. Chem.* **2001**, 1661−1663.

(42) Schiffer, M.; Scheer, M. *Chem. Eur. J.* **2001**, *7*, 1855−1861.

Scheme 7. Subsequent Reactions of Complexes of Type C



Scheme 8. Generation of 45 and Its Subsequent Reactions



ring derivatives **46** and **47**. The use of the bulkier phosphaalkyne MesC≡P was necessary, since the use of *t*-BuC≡P or AdC≡P (Ad = 1-adamantyl) in this metathesis reaction led predominantly to the formation of the four-membered-ring derivatives. Thus, in addition to the correct temperature regime, the steric demand of the starting materials must be taken into account. For instance, if *t*-BuC≡P is the phosphaalkyne of choice in these three-component reactions, the bulkiness of the triply bonded

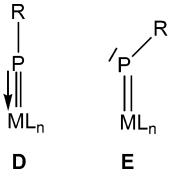


Figure 6. Representations of the structural types of phosphinidene complexes.

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(44) (a) Binger, P., *Multiple Bonds and Low Coordination in Phosphorus Chemistry*. G. Thieme Verlag: Stuttgart, Germany, 1990. (b) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildenbrand, U.; Westerhausen, M. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 349. (c) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weber, U.; Westerhausen, M. *Nova Acta Leopold.* **1985**, *59*, 55.

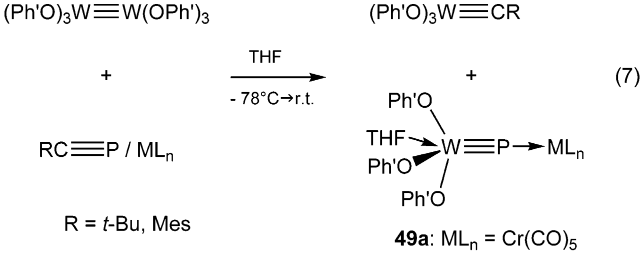
Table 4. Selected Structural and Spectroscopic Parameters of Complexes of Type A

complex[a]	d(M−P) (Å)	$\delta(^{31}P)$ (ppm)	$^1J_{WP}$ (Hz)	ref
$[(t\text{-BuO})_3W{\equiv}P]$ (**45**)		845.0	176	39
$[(t\text{-BuO})_3W{\equiv}P{\rightarrow}Cr(CO)_5]$ (**48a**)		595.4	536	39
$[(t\text{-BuO})_3W{\equiv}P{\rightarrow}W(CO)_5]$ (**48b**)	2.132(4), 2.476(4)	546.0	554, 163	39
$[(t\text{-BuO})_3W{\equiv}P{\rightarrow}MnCp''(CO)_2]$ (**48c**)		614.0	566	47
$[(THF)(Ph'O)_3W{\equiv}P{\rightarrow}Cr(CO)_5]$ (**49a**)		773.4	549	45
$[(THF)(Ph'O)_3W{\equiv}P{\rightarrow}W(CO)_5]$ (**49b**)	2.126(1), 2.432(1)	718.5	562, 170	45
$[(Cy'O)_3Mo{\equiv}P]$ (**56a**)	2.114(2)	1130		48
$[(AdO)_3Mo{\equiv}P]$ (**56b**)		1124		48

[a] Legend: Ph′ = 2,6-$Me_2C_6H_3$; Cy′ = 1-methylcyclohexyl; Ad = 1-adamantyl.

tungsten alkoxide dimer must be increased by using the methyl-substituted aryloxy derivative $[(Ph'O)_3W{\equiv}W(OPh')_3]$ (Ph′ = 2,6-$Me_2C_6H_3$).

The metathesis reaction of $[(Ph'O)_3W{\equiv}W(OPh')_3]$ (Ph′ = 2,6-$Me_2C_6H_3$) with t-BuC≡P in the presence of $[M(CO)_5(THF)]$ (M = Cr, W) led to $[(THF)(Ph'O)_3W{\equiv}P{\rightarrow}M(CO)_5]$ (M = Cr (**49a**), W (**49b**)) in 66% and 53% isolated yields, respectively (eq 7).[45] The electron-donating properties of the Ph′O ligands are not sufficient to compensate the electron deficiency on the tungsten atom, and therefore, a THF molecule also coordinates to the tungsten atom. In the solid state, complexes **48b** and **49b** contain two different W−P distances; one is shorter and corresponds to the W≡P triple bond (2.132(4) Å (**48b**); 2.126(1) Å (**49b**)), and one is longer and corresponds to the coordinative W→P bond (2.476(4) Å (**48b**), 2.432(5) Å (**49b**)).

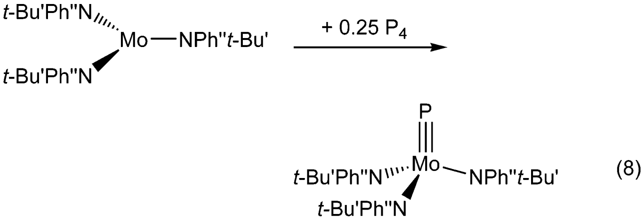


49a: $ML_n = Cr(CO)_5$
49b: $ML_n = W(CO)_5$

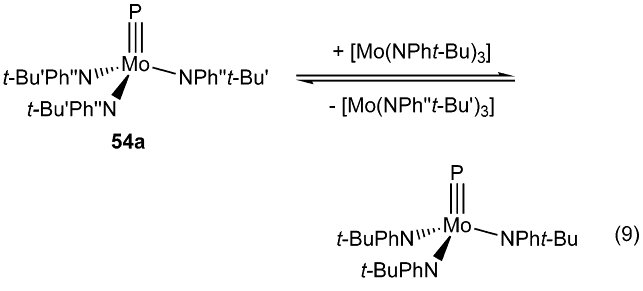
Theoretical calculations at the BP86 and B3LYP levels of theory on the model complexes $[(RO)_3M{\equiv}E]$ (R = H, CH_3; M = Mo, W; E = N, P, As, Sb, Bi) and $[(t\text{-BuO})_3Mo{\equiv}P]$ have shown that the metal−pnicogen bond is a genuine triple bond containing one σ bond and two degenerate π bonds.[46] The σ bonds are polarized toward the pnicogen atom, whereas the π bonds are only slightly polarized toward the metal atom. The coordination of the phosphorus lone pair in $[(HO)_3W{\equiv}P]$ to a $W(CO)_5$ fragment leads to a shortening of the W−P distance due to rehybridization of the phosphorus lone pair. In contrast, the coordination of the THF molecule to the tungsten center in $[(THF)(HO)_3W{\equiv}P{\rightarrow}W(CO)_5]$ leads to the elongation of the W≡P triple bond, since the donation of the oxygen lone pair occurs in the W−P σ^* molecular orbital of $[(HO)_3W{\equiv}P{\rightarrow}W(CO)_5]$.[45] These bonding features are reflected in the NMR data (Table 4). In the ^{31}P NMR spectrum of $[(t\text{-BuO})_3W{\equiv}P]$ (**45**), the phosphorus atom resonates at low field and reveals a small $^1J_{WP}$ coupling constant, while the compounds **48** and **49** show signals at a much higher field together with a large $^1J_{WP}$ coupling constant, which reflects the s character of the bond. The increased s character of the bond is a result of rehybridization of the lone pair of electrons at the phosphorus atom, which possess significant s character, induced by coordination of a Lewis acid.

Complexes of type **A** are highly side-on reactive, since the alkoxy groups are flexible in solution and only in the solid state do they efficiently protect the W≡P triple bond. Thus, in toluene, **48b** and **49b** undergo reductive dimerization reactions with formal elimination of alkoxy groups to form the phosphametallacycles **50** and **51**, respectively, containing a planar W_2P_2 core (Scheme 9).[39,45] Further, **48b** reacted with $[(Ph'O)_4W{=}O]$ (Ph′ = 2,6-$Me_2C_6H_3$) via reductive cycloaddition and formal Ph′O elimination to give **52** (Scheme 9), which contains a nearly planar W_2PO core. In the reaction of **49b** with $[(Ph_3P)_2Pt(C_2H_4)]$ an intermediate was postulated in which **49b** is side-on coordinated to the Pt complex moiety. This intermediate underwent further rearrangement reactions (1,3-Ph shift) to form **53** (Scheme 9).[45]

The use of bulky amido substituents as protecting groups around the transition metals allowed the synthesis of stable phosphido complexes of type **B** and **B′**. By reacting the tris(amido)molybdenum(III) complex $[(t\text{-Bu}'Ph''N)_3Mo]$ (t-Bu′ = $C(CD_3)_2CH_3$, Ph″ = 3,5-$Me_2C_6H_3$) with white phosphorus, Cummins and co-workers were able to isolate one of the first stable and structurally characterized phosphido complexes ($[(t\text{-Bu}'Ph''N)_3Mo{\equiv}P]$ (**54a**)) in good yield (eq 8).[14] The starting complex is a high-spin complex with three unpaired electrons localized on molybdenum, which provides an ideal environment for reaction with phosphorus. In the complex **54a**, the bulky amido substituents stabilize the Mo≡P triple bond kinetically and hinder side-on reactivity. In contrast, the lone pair of electrons at the phosphorus atom is still accessible and the phosphido ligand in **54a** can be transferred via a heterocumulene



54a



54b

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[45] Kramkowski, P.; Baum, G.; Radius, U.; Kaupp, M.; Scheer, M. *Chem. Eur. J.* **1999**, *5*, 2890−2898.

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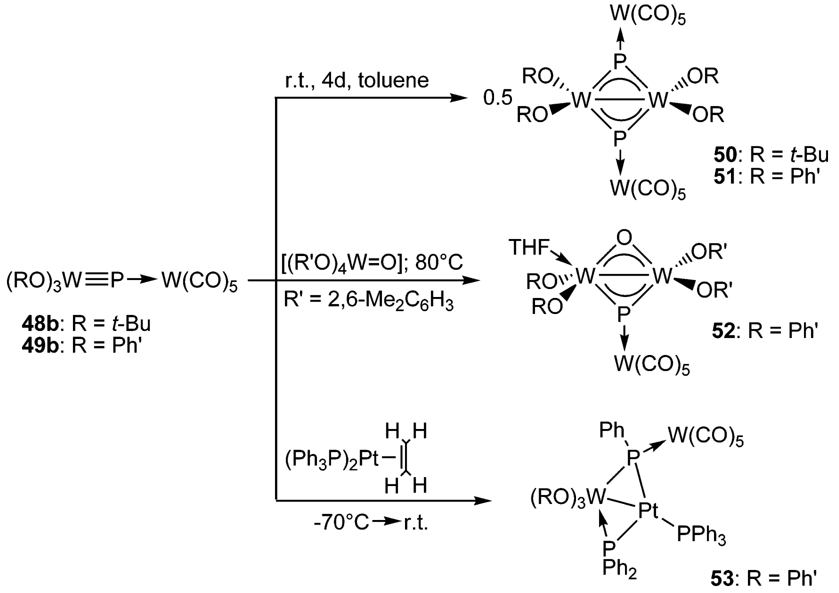
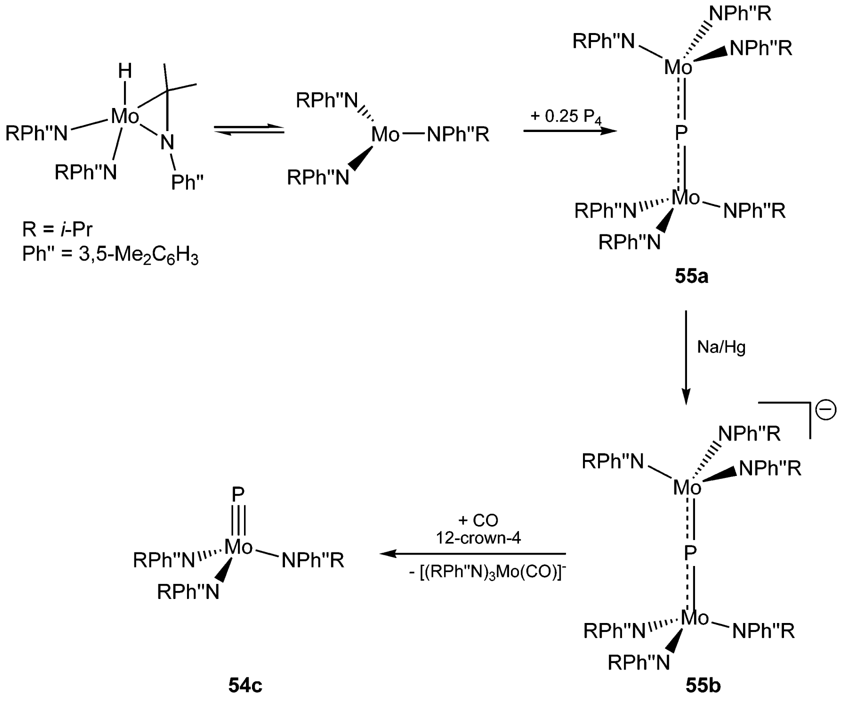
Scheme 9. Reactivity of Complexes of Type A

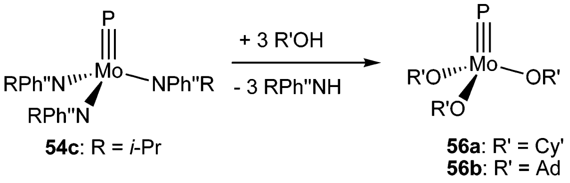


Scheme 10. Synthesis of the Heterocumulene Complexes 55 and Subsequent Formation of the Phosphido Complex 54c



intermediate to a second tris(amido)molybdenum complex, $[(t\text{-BuPhN})_3\text{Mo}]$, to give the phosphido complex $[(t\text{-BuPhN})_3\text{Mo}{\equiv}\text{P}]$ (**54b**) (eq 9).[49] Reducing the steric bulk of the amido groups by substituting the *t*-Bu by *i*-Pr groups (*i*-Pr = CMe_2H) led to the isolation of the heterocumulene intermediate $[(i\text{-PrPh}''\text{N})_3\text{Mo}{=}\text{P}{=}\text{Mo}(\text{NPh}''i\text{-Pr})_3]$ (**55a**). Reduction of **55a** with Na/Hg alloy followed by cleavage of the phosphorus bridge in **55b** gave the phosphido complex $[(i\text{-PrPh}''\text{N})_3\text{Mo}{\equiv}\text{P}]$ (**54c**) in good yield (Scheme 10).[50] It was further shown that **54c** forms the heterodinuclear bridging complex $[(\text{RPh}''\text{N})_3\text{Nb}(\mu\text{-P})\text{Mo}(\text{NPh}''i\text{-Pr})_3]$ (R = $(\text{CH}_3)_3\text{CCH}_2$).[51] When $[(2\text{-AdPh}''\text{N})_3\text{Mo}]$ (2-Ad = 2-adamantyl, Ph″ = $3,5\text{-Me}_2\text{C}_6\text{H}_3$) was reacted with white phosphorus, the corresponding phosphido complex $[(2\text{-Ad-Ph}''\text{N})_3\text{Mo}{\equiv}\text{P}]$ (**54d**) was also synthesized.[52]

Substitution of the amido ligands in **54c** with alkoxy groups proceeded smoothly if bulky alcohols were used (eq 10). The reaction of **54c** with 1-methylcyclohexanol (Cy′OH) provided the stable terminal phosphido complex $[(\text{Cy}'\text{O})_3\text{Mo}{\equiv}\text{P}]$ (**56a**)



(10)

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[49] Johnson, M. J. A.; Lee, P. M.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *Angew. Chem.* **1997**, *109*, 110−113; *Angew. Chem., Int. Ed.* **1997**, *36*, 87−91.

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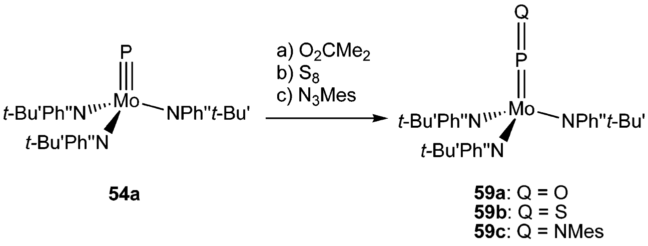
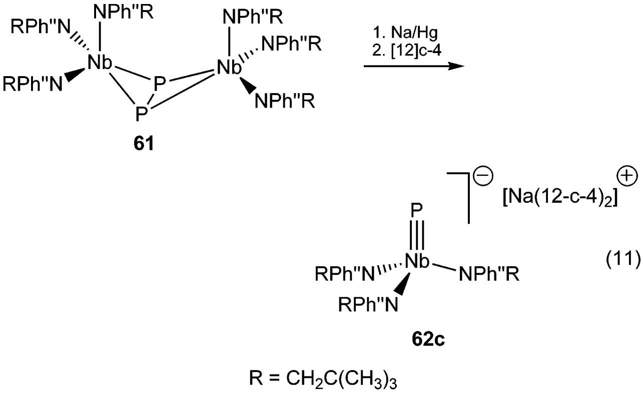
Scheme 11. Synthesis of PQ-Ligand-Containing Complexes



in 57% isolated yield. The use of slightly less bulky alcohols led to the dimerization of the $\mathrm{Mo{\equiv}P}$ units. Alcoholysis of **54c** with 1-adamantanol (AdOH) gave $[(\mathrm{AdO})_3\mathrm{Mo{\equiv}P}]$ (**56b**), which has a half-life ($t_{1/2}$) of ca. 6 h in toluene at 20 °C. Dimerization of **56b** to $[\{\mathrm{PMo(OAd)_3}\}_2]$ (**57**) proceeded smoothly and was complete in approximately 1 day. An incomplete alcoholysis of **54c** and a rapid dimerization of the $\mathrm{Mo{\equiv}P}$ unit with the formation of $[\{\mathrm{PMo(N\text{-}}i\text{-}\mathrm{PrPh'')(OPh')_2}\}_2]$ ($\mathrm{Ph'} = 2{,}6\text{-}\mathrm{Me_2C_6H_2}$) (**58**) occurred if 2,6-dimethylphenol was used in the alcoholysis reaction.[48] These facts show that, by reducing the steric demand of the substituents via alcoholysis of the type **B′** complexes, a side-on reactivity pattern of these complexes is encouraged.

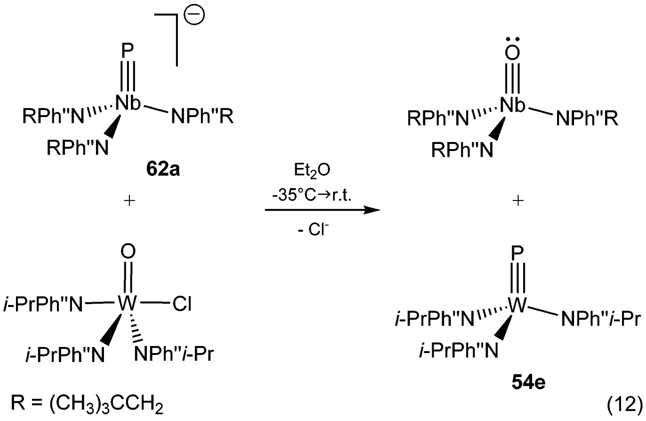
The end-on reactivity of type **B′** complexes can be further exploited in the formation of novel phosphachalcogenido ligands. Thus, **54a** could be oxidized with dimethyldioxirane, elemental sulfur, cyclohexene sulfide, ethylene sulfide, or mesityl azide to the corresponding PQ-ligand-containing complexes $[(t\text{-}\mathrm{Bu'Ph''N})_3\mathrm{Mo(PQ)}]$ ($t\text{-}\mathrm{Bu'} = \mathrm{C(CD_3)_2CH_3}$, $\mathrm{Ph''} = 3{,}5\text{-}\mathrm{Me_2C_6H_3}$, Q = O (**59a**),[53] S (**59b**),[8,15] NMes (**59c**);[15] Scheme 11). Characteristic of the complexes **59** is the linear Mo−P−Q unit with a Mo−P distance slightly shorter than that in the starting phosphido complex **54a**. The rehybridization of the phosphorus atom is responsible for the shortening of the Mo−P bond length upon oxidation. Furthermore, it has been shown that the phosphorus atom in **59a** is accessible to nucleophilic attack. Accordingly, **59a** reacted with $[\mathrm{Cp_2ZrMe_2}]$ by the addition of a Zr−Me bond to the P=O double bond to form $[(t\text{-}\mathrm{Bu'Ph''N})_3\mathrm{MoP(Me)OZr(Me)Cp_2}]$ (**60**). The phosphorus atom in **60** is essentially planar, thereby indicating Mo−P π bonding.[53]

Phosphorus is able to form triple bonds not only with group 6 metals (Mo and W) but also with group 5 metals (Nb and Ta). Cummins and co-workers reported the reaction of the niobaziridine−hydride complex $[\mathrm{Nb(H)}(\eta^2\text{-}t\text{-}\mathrm{Bu(H)C{=}NPh''})(\mathrm{NPh''R})_2]$ ($\mathrm{R} = \mathrm{(CH_3)_3CCH_2}$) with white phosphorus, which led quantitatively to the symmetrically bridged diphosphorus complex $[(\mu,\eta^2{:}\eta^2\text{-}\mathrm{P_2})\{\mathrm{Nb(NPh''R)_3}\}_2]$ (**61**).[51] Na/Hg alloy cleaved the $\mathrm{P_2}$ bridge in **61** to give the dimeric complex $\{[\mathrm{Na(Et_2O)}][(\mathrm{RPh''N})_3\mathrm{Nb(P)}]\}_2$ (**62a**) in good yield.[54] On the basis of ^{31}P NMR investigations, it was thought that in THF **62a** forms the monomeric species $[\mathrm{Na(THF)}_x][(\mathrm{RPh''N})\mathrm{Nb(P)}]$ (**62b**). The complete separation of the ion pair to form $[\mathrm{Na(12\text{-}crown\text{-}4)_2}][(\mathrm{RPh''N})\mathrm{Nb{\equiv}P}]$ (**62c**) was achieved by adding 12-crown-4 to a THF solution of **62a** (eq 11). The triple-bond nature of the $\mathrm{Nb{\equiv}P}$ bond is reflected by the ^{31}P NMR chemical shift (δ 1019.8 (**62b**); δ 1110.2 (**62c**) ppm) as well as by DFT calculations on the model compound $[(\mathrm{H_2N})_3\mathrm{Nb{\equiv}P}]^-$.



(11)

Reactivity studies on **62b** show that the phosphido phosphorus atom possesses nucleophilic character and reacts with electrophiles such as $\mathrm{Me_3ECl}$ (E = Si, Sn) and $\mathrm{R'_2PCl}$ (R′ = *t*-Bu, Ph) to yield the nonlinear phosphinidene complexes $[(\mathrm{RPh''N})\mathrm{Nb{=}PEMe_3}]$ (E = Si, Sn) and the η^2-bonded phosphinophosphinidene complexes $[(\mathrm{RPh''N})\mathrm{Nb}(\eta^2\text{-}\mathrm{PPR'_2})]$, respectively.[54] It has been shown that **62b** reacts further with $\mathrm{GeCl_2{\cdot}(dioxane)}$, $\mathrm{SnCl_2}$, and $\mathrm{Pb(OTf)_2}$ to yield the complexes $[\{(\mathrm{RPh''N})_3\mathrm{Nb}\}_2(\mu,\eta^3{:}\eta^3\text{-}cyclo\text{-}\mathrm{EP_2})]$ (E = Ge, Sn, Pb), which contain a $\mu,\eta^3{:}\eta^3$-cyclo-$\mathrm{EP_2}$ three-membered ring coordinated between two niobium centers.[55] The reaction of **62b** with pivaloyl chloride (*t*-BuC(O)Cl) or 1-adamantyl chloride (1-AdC(O)Cl) afforded the metallacyclic compounds $[(\mathrm{RPh''N})_3\overline{\mathrm{NbPC(R')O}}]$ (R′ = *t*-Bu, Ad), which in solution undergo retro [2 + 2] fragmentation with elimination of the corresponding phosphaalkyne and formation of the oxo complex $[(\mathrm{RPh''N})_3\mathrm{NbO}]$.[56] In an analogous manner, **62a** reacted with the tungsten oxochloride $[(i\text{-}\mathrm{PrPh''N})_3\mathrm{W(O)Cl}]$, generated from $[(i\text{-}\mathrm{PrPh''N})_3\mathrm{W{\equiv}N}]$ and *t*-BuC(O)Cl, and gave the phosphido complex $[(i\text{-}\mathrm{PrPh''N})_3\mathrm{W{\equiv}P}]$ (**54e**) (eq 12).[57]



(12)

The expected heterobimetallic intermediate $[(\mathrm{RPh''N})_3\mathrm{Nb}(\mu\text{-P})(\mu\text{-O})\mathrm{W(NPh''\text{-}}i\text{-}\mathrm{Pr})_3]$ could not be observed by ^{31}P NMR spectroscopy, even at low temperatures. Although the complex **54e** is of relatively low nucleophilic character, it reacted with an electrophilic phosphenium species, generated from $\mathrm{Ph_2PCl}$ and $\mathrm{Me_3SiOTf}$ ($\mathrm{TfO} = \mathrm{CF_3SO_3}$), and gave the (diphenylphosphanyl)phosphinidene complex $[(i\text{-}\mathrm{PrPh''N})_3\mathrm{W}(\eta^2\text{-}\mathrm{PPPh_2})][\mathrm{OTf}]$.[57]

The activation of white phosphorus and dinitrogen with the aziridine hydride niobium system was reviewed.[58] Recently, Cummins and co-workers reported the synthesis of $[(\mathrm{RPh''N})_3\mathrm{Nb}$-

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(52) Cherry, J. P. F.; Johnson, A. R.; Baraldo, L. M.; Tsai, Y. C.; Cummins, C. C.; Kryatov, S. V.; Rybak-Akimova, E. V.; Capps, K. B.; Hoff, C. D.; Haar, C. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2001**, *123*, 7271−7286.

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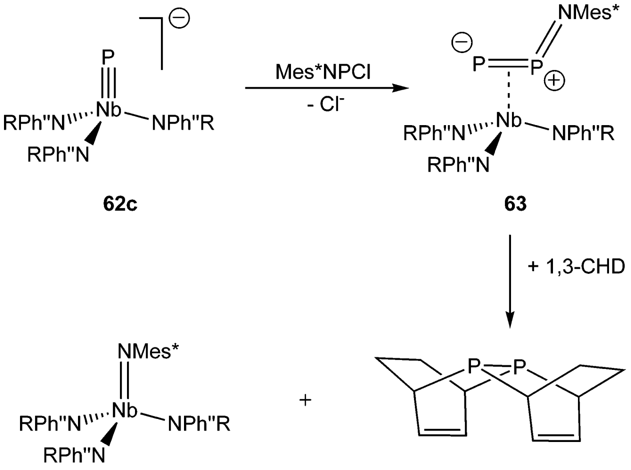
(54) Figueroa, J. S.; Cummins, C. C. *Angew. Chem.* **2004**, *116*, 1002−1006; *Angew. Chem., Int. Ed.* **2004**, *43*, 984−988.

(55) Figueroa, J. S.; Cummins, C. C. *Angew. Chem.* **2005**, *117*, 4668−4672; *Angew. Chem., Int. Ed.* **2005**, *44*, 4592−4596.

(56) Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916−13917.

Scheme 12. Synthesis and Reactivity of the Diphosphorus Azide Complex 63



(η^2-PPNMes*)] (Mes* = 2,4,6-*t*-$Bu_3C_6H_2$) (**63**), which contains a P_2N moiety, by reacting **62a** with Mes*N=PCl. Complex **63** acts as a P_2 transfer agent. Successful P_2 trapping reactions by suitable organic acceptors were carried out.[59] When **63** was heated in neat 1,3-cyclohexadiene, the double Diels–Alder adduct of P_2 with 2 equiv of 1,3-cyclohexadiene was obtained (Scheme 12).

Schrock and co-workers have used the tris(amido)amine ligand N_3N ($N_3N = N(CH_2CH_2NSiMe_3)_3$) to stabilize complexes containing transition metal–phosphorus triple bonds,[14] and the publication of their results was concomitant with the report of the synthesis and characterization of **54a**. When $[(N_3N)MCl]$ (M = Mo (**64a**), W (**64b**)) was reacted with 2 equiv of LiP(H)Ph (Scheme 13), the phosphido complexes $[(N_3N)M{\equiv}P]$ ($N_3N = N(CH_2CH_2NSiMe_3)_3$; M = Mo (**65a**), W (**65b**)) of type **B** were formed.[14,60] The reaction proceeds via the intermediately formed phenylphosphanido complex $[(N_3N)MP(H)Ph]$ (M = Mo (**66a**), W (**66b**)). Using a 1:1 ratio of the reactants, **66a** was isolated and structurally characterized while **66b** was observed only in trace amounts. Thermal decomposition of **66a** did not produce **65a**, while the reaction of **66a** with LiP(H)Ph or PhLi afforded **65a**.

Attempts to synthesize $[(N_3N)Ta{\equiv}P]^-$ by reacting $[(N_3N)Ta{=}PPh]$ with excess lithium in THF led to the formation of $[(N_3N)Ta{=}PLi]$. On the basis of the phosphorus ^{31}P NMR chemical shift (δ 575 ppm) it was proposed that in solution the lithium atom is bound to the phosphorus atom.[61] Quenching $[(N_3N)Ta{=}PLi]$ with alkyl and silyl halides gave the corresponding phosphinidene complexes $[(N_3N)Ta{=}PR]$ (R = Me, *n*-Bu, $SiMe_3$, $SiMe_2Ph$).

An alternative route to the synthesis of the phosphido complex **65b** was developed by Scheer and co-workers.[62] Thus, **64b** was reacted with 2 equiv of $LiP(SiMe_3)_2$ at 80 °C to give the phosphido complex **65b**. The reaction was monitored by ^{31}P NMR spectroscopy, but the expected intermediate $[(N_3N)WP(SiMe_3)_2]$ was not observed. However, as the amount of $LiP(SiMe_3)_2$ decreased, due to reaction with **64b**, and the amount of $P(SiMe_3)_3$ increased, the reaction of **64b** with $LiP(SiMe_3)_2$ was the rate-determining step of the reaction. This reaction principle was introduced in the synthesis of the heavier homologues of $[(N_3N)M{\equiv}E]$ (E = P, As, Sb, Bi) using the known $LiE(SiMe_3)_2$ compounds. As described below, this method has so far been successful in the synthesis of the corresponding arsenido derivative of **65**.

In complexes of type **B**, the bulky Me_3Si groups form a cone in which the M≡P triple bond can be accommodated, thereby hindering its side-on reactivity. However, the lone pair of electrons on the phosphorus atom is still open to attack. Accordingly, the phosphido complex **65b** reacts with Lewis acids to give the expected Lewis acid adducts. The reaction of **65b** with $[M(CO)_5(THF)]$ (M = Cr, W) led to the formation of $[(N_3N)W{\equiv}P{\rightarrow}M(CO)_5]$ (M = Cr (**67a**), W (**67b**)), which reacted further with 1 equiv of **65b** with CO elimination to give *trans*-$[\{(N_3N)W{\equiv}P\}_2M(CO)_4]$ (M = Cr (**68a**), W (**68b**)) (Scheme 14).[62] As verified by experiment and by theoretical calculations, the high formation enthalpy of $W(CO)_6$ is responsible for the CO elimination and formation of **68**. Complexes similar to **68**, i.e., *trans*-$[\{(N_3N)M{\equiv}P\}_2Rh(MeCN)(CO)][PF_6]$ (M = Mo (**69a**), W (**69b**)), were synthesized by reacting **65** with $[Rh(CO)_2(MeCN)_2][PF_6]$ generated in situ from $[Rh(CO)_2Cl_2]$ and $TlPF_6$.[60] In contrast to **68**, the W–P–Rh–W–P core in **69b** is slightly bent, revealing a banana-like geometry. No structural data were reported for **69a**, but since the spectroscopic data are very similar to those of **69b**, a comparable structure was predicted. Coordination of a phosphido complex to a Lewis acidic main group compound was realized in $[(N_3N)W{\equiv}P{\rightarrow}GaCl_3]$ (**70**) by reacting **65b** with $GaCl_3$. **70** is stable in halogen-free solvents but decomposes in CH_2Cl_2 via formal Me_3SiCl elimination to a complex containing a W_2P_2 tetrahedral core.[63] This example shows that if the bulkiness of the protecting substituents is reduced, a side-on reactivity of type **B** complexes can be achieved. A BF_3 analogue of **70**, $[(N_3N)W{\equiv}P{\rightarrow}BF_3]$, was generated by reacting **65b** with $BF_3{\cdot}OEt_2$, but it is unstable and decomposes with the formation of polymeric products. However, ^{31}P NMR spectra of the compound could be recorded.[63]

Schrock and co-workers have shown that **65b** reacts with electrophiles such as MeOTf to give the linear phosphinidene complex $[(N_3N)W(PMe)][OTf]$ (**71**). The synthesis of the phosphinidene complexes $[(t\text{-}Bu_3SiO)_3Nb{=}PR]$ (R = H, Me) also was reported.[64] Similarly to **54a**, the phosphido complex **65b** is readily oxidized by cyclohexene sulfide to give the terminal PS complex $[(N_3N)W(PS)]$ (**72**) (Scheme 14).[65] Characteristic of **72** is the linear N_{ax}–W–P–S unit and the short W–P and P–S distances. The bonding situation in **72** was analyzed by DFT calculations and can be best described as containing W=P and P=S double bonds.[65]

Type **B** complexes owe their high stability on one hand to the kinetic stabilization of the M≡P triple bond imparted by the bulky Me_3Si groups and on the other hand to the ability of the N_3N ligand to place the metal in an electronic situation (the metal d_{xz} and d_{yz} orbitals are mostly empty and available for π bonding) that is ideal for the realization of triple bonds with pnicogens.[66] The coordination of the axial nitrogen to the metal

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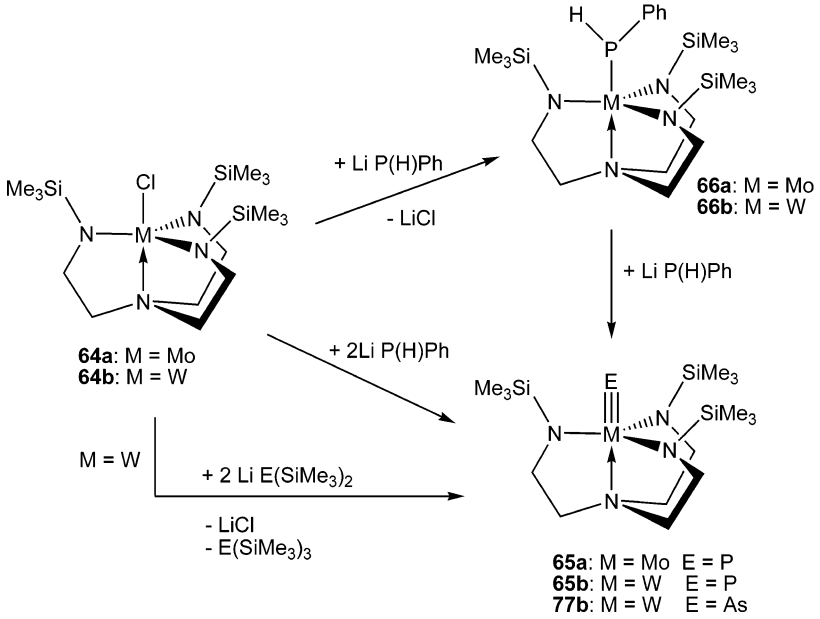
Scheme 13. Synthesis of the Phosphido Complexes 65



center provides additional stabilization and facilitates complexes of type **B** to obey the 18-electron rule, while the phosphido complexes of type **B′** are formally 16-electron species, due to the absence of an axial nitrogen donor. It should be noted that the three equatorial amido nitrogen atoms can formally donate a total of 7 electrons, because the a_2 combination of the lone pairs of the nitrogen ligands has no match on the metal atom.

All structurally characterized phosphido complexes are distinguished by very short metal−phosphorus distances. However, the bond order of a M≡P bond cannot be determined by inspection of the M−P distance alone. This is substantiated by the fact that upon oxidation of the phosphorus atom in complexes of types **B** (**54a**) and **B′** (**65b**), the M−P bond length in the products (**59** and **72**, respectively) is shortened, although the bond order determined independently by DFT calculations decreases.[65,67] This shortening of the M−P distance was attributed to the rehybridization of the phosphorus atom. By employing theoretical calculations, a similar condition was predicted for the complexes of type **A**.[45] In contrast, coordination of the phosphido ligand in complexes of type **B** to Lewis acidic transition-metal fragments slightly elongates the M−P distance in comparison to the starting phosphido complex. Nevertheless, the triple bond and the donor−acceptor bond are clearly different (Table 5). The calculated triple-bond covalent radii of a large number of elements were reported and provide guidelines for triple-bond distances.[68]

In addition to the short M−P distances, a second feature of phosphido complexes is their ^{31}P NMR chemical shifts, which are a spectroscopic window to the electronic structure of the M≡P triple bond (Tables 4 and 5). All known phosphido complexes are characterized by extremely downfield shifted ^{31}P NMR resonances (δ varies between 1019.8 ppm ([Na(THF)$_x$]-[(RPh″N)$_3$Nb≡P] (R = $(CH_3)_3CCH_2$) (**62b**) and 1346 ppm ([(N$_3$N)Mo≡P] (**65a**)) and small $^1J_{WP}$ coupling constants (for example, 138 and 193 Hz for **65b** and **54e**, respectively). The ^{31}P NMR chemical shift is a very sensitive parameter, which can be used to distinguish between the formation of dimers, ion pairs, or monomers in solution, as was observed for **62** (δ 949.2 (**62a**), 1019.8 (**62b**), 1110.2 (**62c**) ppm). The chemical shifts of the molybdenum-containing complexes **65a** and **54c**, respectively, appear 260 and 235 ppm higher than those of their tungsten analogues **65b** and **54e**, while that of the niobium complex **62c** is only 100 ppm lower than that of **65b** (Table 5). The ^{13}C NMR chemical shift of the carbide complex [K(2,2,2-crypt)][(RPh″N)Nb≡C] (δ 501 ppm;[7,69] 2,2,2-crypt = N(CH$_2$-CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$)$_3$N, R = $(CH_3)_3CCH_2$) and the ^{15}N NMR chemical shift of the terminal nitrido complex [(RPh″N)-Nb≡^{15}N] (δ 480 ppm;[70] R = $(CH_3)_3CCH_2$) are shifted strongly downfield, suggesting that the low-field chemical shift is a characteristic feature of nuclei possessing triple bonds to transition metals. The unusual chemical shift and a large anisotropy was also observed in the solid-state ^{31}P MAS NMR spectra of complexes **65** and **54**.[71] This unexpected behavior was explained in terms of large paramagnetic shielding in directions perpendicular to the triple bond. Theoretical calculations (DFT) on the model compounds [(H$_2$N)$_3$M≡P], P$_2$, PN, and PCH show that the large paramagnetic shielding is caused by the field-induced mixing between the σ(M−P) and π^*(M−P) molecular orbitals. The small metal−phosphorus coupling constant $^1J_{MP}$ was attributed to the low s character of the metal−phosphorus σ bond, as also predicted by theoretical calculations on **65b** using the PESHO method.[62] In contrast, the NBO method showed a higher s character for this bond.[67,72]

The M≡P stretching frequencies and force constants of the phosphido complexes **65** and the M≡N and M≡As stretching frequencies of their nitrido and arsenido (**77**) analogues (see below) also were reported.[73] These show that the force constants

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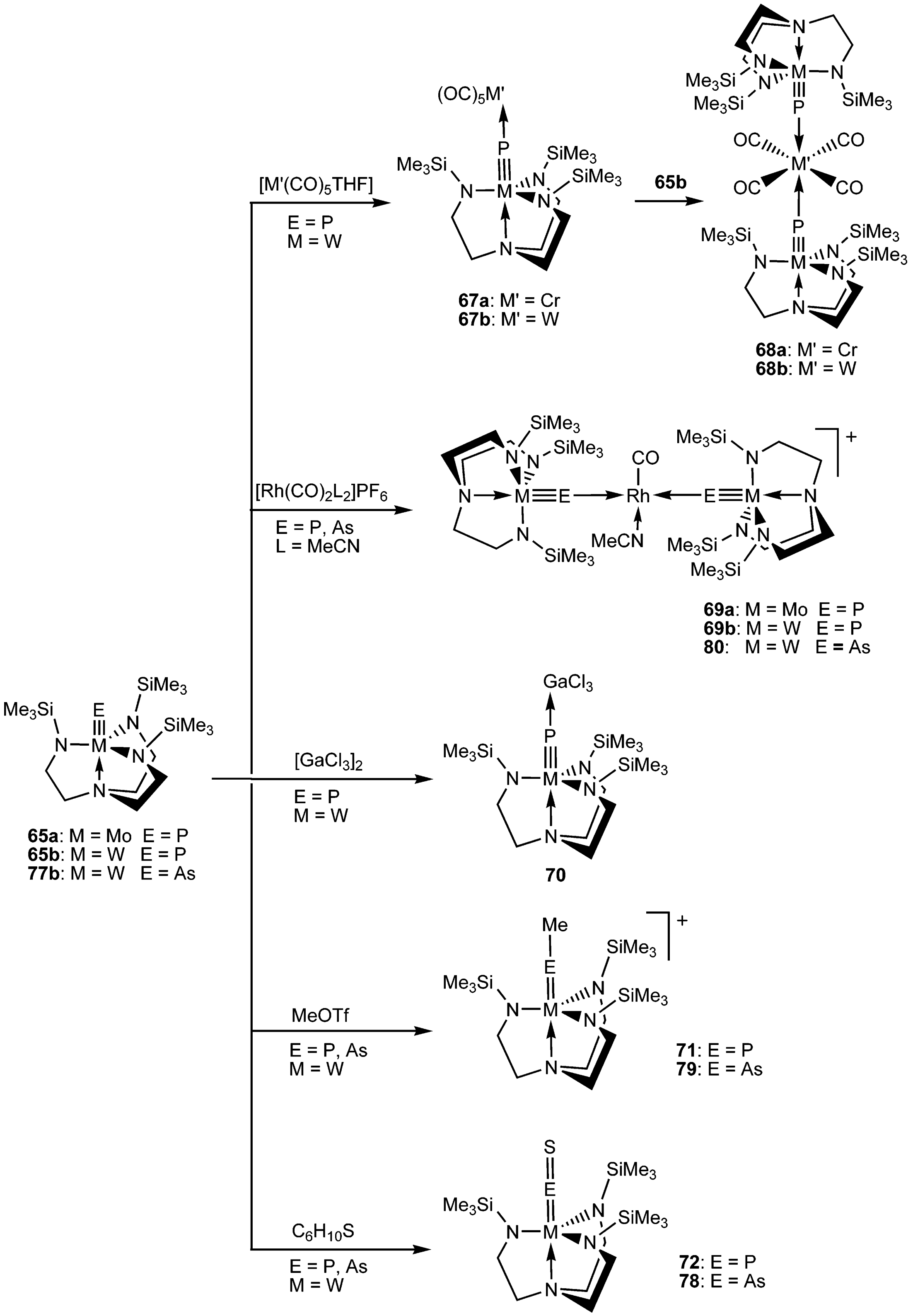
Scheme 14. Reactivity of the Pnictido Complexes 65 and 77



of the tungsten complexes are larger than those of the molybdenum complexes, while for both metals the force constant decreases upon increasing the M−E distance (M = Mo, W).

By studying the reactivity of the phosphinidene complex [Mo$_2$Cp$_2$(μ-PR)(CO)$_4$] (R = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) (**73**), Ruiz and co-workers were able to isolate and characterize a new variety of asymmetrically bridged phosphido complexes containing a formal Mo≡P triple bond.[74,75] The photolysis of **73** led to the phosphido complex **74** and small amounts of its isomer **75** (Scheme 15).[74] Interconversion of **74** and **75** was brought about by traces of water or in dry CH$_2$Cl$_2$ in the presence of benzoic acid. Compound **74** reacts slowly with CO or *t*-BuNC to give the complexes [Mo$_2$Cp$_2$(μ-κ^1:κ^1,η^4-PR)(CO)$_2$L] (L = CO (**76a**), *t*-BuNC (**76b**)), in which the benzene ring is η^4 coordinated. It

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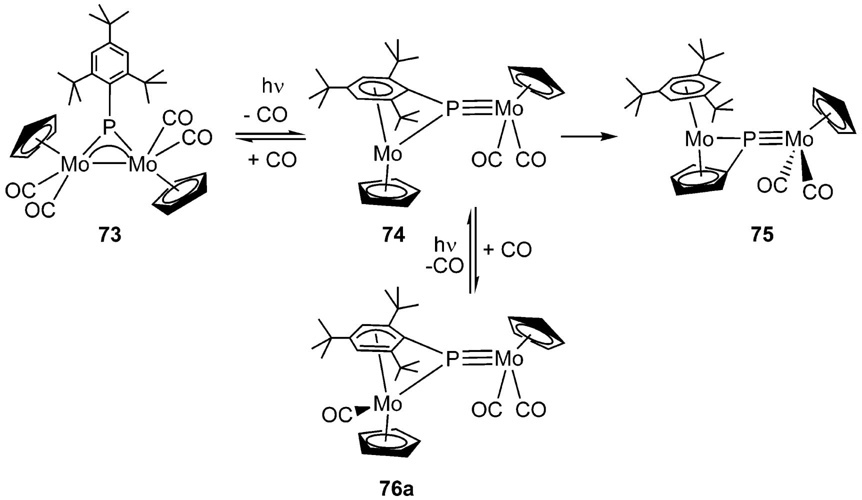
Table 5. Selected Structural and Spectroscopic Parameters of Type B and B′ Complexes

complex[a]	*d*(M−P) (Å)	δ(^{31}P) (ppm)	$^1J_{WP}$ (Hz)	ref
[(*t*-Bu′Ph″N)$_3$Mo≡P] (**54a**)	2.119(4)	1216		15
[(*t*-BuPhN)$_3$Mo≡P] (**54b**)		1226		49
[(*i*-PrPh″N)$_3$Mo≡P] (**54c**)	2.116(3)	1256		50
[((2-Ad)Ph″N)$_3$Mo≡P] (**54d**)	2.107(3)	1215		52
[(*i*-PrPh″N)$_3$W≡P] (**54e**)	2.119(3), 2.122(3)	1021	193	57
[Na(Et$_2$O)][(RPh″N)$_3$Nb≡P] (**62a**)		949.2		54
[Na(THF)$_x$][(RPh″N)$_3$Nb≡P] (**62b**)		1019.8		54
[Na(12-c-4)$_2$)][(RPh″N)$_3$Nb≡P] (**62c**)	2.186(2)	1110.2		54
[(N$_3$N)Ta=PLi]		575		61
[(N$_3$N)Mo≡P] (**65a**)		1346		14
[(N$_3$N)W≡P] (**65b**)	2.162(4)	1080	138	14
[(N$_3$N)W≡P→GaCl$_3$] (**70**)	2.168(4)	366	712	63
[(N$_3$N)W≡P→Cr(CO)$_5$] (**67a**)		708.1	442	62
[(N$_3$N)W≡P→W(CO)$_5$] (**67b**)		662.6	450, 135	62
trans-[{(N$_3$N)W≡P}$_2$Cr(CO)$_4$ (**68a**)		728.1	413	62
trans-[{(N$_3$N)W≡P}$_2$W(CO)$_4$] (**68b**)	2.202(2), 2.460(2)	679.8	426, 151	62
trans-[Rh{(N$_3$N)Mo≡P}$_2$(CO)(MeCN)][PF$_6$] (**69a**)		791.1	67	60
trans-[Rh{(N$_3$N)W≡P}$_2$(CO)(MeCN)][PF$_6$] (**69b**)	2.177(5), 2.173(5)	642.6	79	60

[a] Legend: *t*-Bu′ = C(CD$_3$)$_2$CH$_3$; Ph″ = 3,5-Me$_2$C$_6$H$_3$; in **62** R = (CH$_3$)$_3$CCH$_2$; N$_3$N = N(CH$_2$CH$_2$NSiMe$_3$)$_3$.

Scheme 15. Synthesis of the Phosphido-Type Complexes 74 and 75

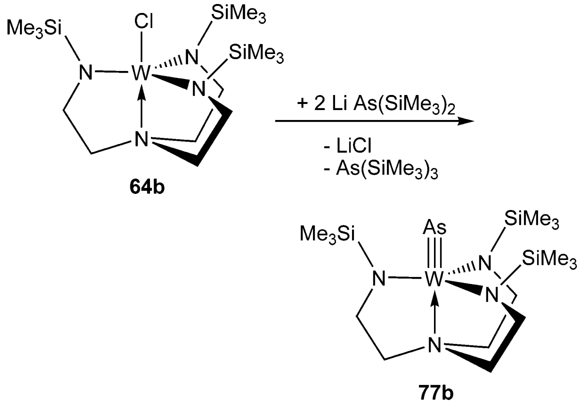


has been shown that **76a** is a genuine intermediate in the conversion of **73** to **74**.

In the solid state, complexes **74** and **76a** possess two different Mo−P distances, one being shorter (2.248(1) Å (**74**); 2.256(1) Å (**76a**)) and one being longer (2.363(1) Å (**74**); 2.355(2) Å (**76a**)). These complexes were described as containing a Mo≡P triple bond as well as a Mo−P single bond. However, DFT calculations revealed a π-bonding interaction delocalized over the Mo−P−Mo core and therefore a heterocumulene-like bonding situation is perhaps more likely.[75] The molybdenum−phosphinidene bonding can be described with a variety of canonical forms, but the deduction of their relative contribution is difficult.

Arsenic. The chemistry of the arsenido complexes is much less developed compared to that of the phosphido complexes. The only isolated complexes containing an M≡As triple bond are of type **B**. By reacting [(N$_3$N)WCl] (**64b**) with LiAs(SiMe$_3$)$_2$, Scheer and co-workers were able to synthesize and structurally characterize the first arsenido complex, [(N$_3$N)W≡As] (**77b**) (eq 13).[62] Schrock and co-workers were also successful in obtaining **77b** by the reaction of [(N$_3$N)WPh] with PhAsH$_2$, which proceeds via benzene elimination.[60] Interestingly, the reaction of [(N$_3$N)WCl] (**64b**) with 2 equiv of LiAs(H)Ph yields traces of [(N$_3$N)W≡As] (**77b**) along with [(N$_3$N)WPh] as the main product. In contrast, [(N$_3$N)Mo≡As] (**77a**) was obtained readily from [(N$_3$N)MoCl] (**64a**) and LiAs(H)Ph, while the reaction of [(N$_3$N)MoPh] with PhAsH$_2$ yielded H$_3$[N$_3$N] as the only isolable product. In the reactions mentioned above, there was no indication of the existence of an intermediate complex similar to [(N$_3$N)MP(H)Ph] (M = (**66a**), W (**66b**)), as observed for the phosphido homologues. The arsenido complexes **77** possess a linear N−M−As core and a short M−As distance (2.252(3) Å (**77a**); 2.2903(11) Å (**77b**)).

Complex **77b** can be readily oxidized by cyclohexene sulfide to give [(N$_3$N)W(AsS)] (**78**) (Scheme 14; E = As), in which



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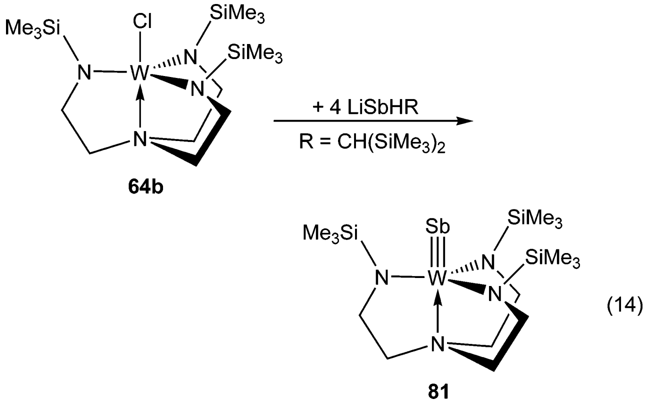
the AsS ligand is terminally coordinated.[65] Interestingly, the slightly shorter W−As distance in **78**, compared to the distance in **77b**, is attributable to the different hybridizations of the arsenic atoms in the two complexes (higher s character of the σ W−As bond in **78**). The reaction of **77b** with MeOTf gave the arsinidene complex $[(N_3N)W(AsMe)][OTf]$ (**79**).[60] The linear coordination of the arsinidene MeAs ligand in **79** was judged to be the result of electronic effects rather than steric factors. The Lewis adduct complex $[\{(N_3N)W{\equiv}As\}_2Rh(MeCN)(CO)][PF_6]$ (**80**) was synthesized by reacting **77b** with $[Rh(MeCN)_2(CO)_2][PF_6]$, generated in situ. Although no X-ray data were obtained for **80**, the compound is probably isostructural with its phosphorus analogue **69**, since the spectroscopic properties (IR, NMR) are comparable.[60]

A series of transition-metal Zintl phases (for example, $Cs_7NbIn_3As_5$) containing arsenic atoms in a coordination number of 1 were reported.[76] The Nb−As distances are short, and it was suggested that the Nb−As bond is a strongly polarized triple bond, on the basis of the interaction between the empty d_{xz} and d_{yz} orbitals of niobium and the filled π orbitals of arsenic. However, the presence of a true Nb−As triple bond in such highly charged species is questionable.

Antimony. Short-lived complexes of the type $[(CO)_nM{\equiv}Sb]^-$ ($n = 4$, M = Cr, Mo, W; $n = 3$, M = Fe) were generated in the gas phase in a Fourier transform ion cyclotron resonance spectrometer (FT-ICR) by reacting Sb_2^- with the corresponding metal carbonyl.[77] Theoretical calculations on $[SbMo(CO)_4]^-$ at the ab initio MP2 level of theory predict a Mo≡Sb triple bond with a bond order of 2.54.

Scheer and co-workers developed a general method for the synthesis of the phosphido and arsenido complexes **65b** and **77b** by reacting $[(N_3N)WCl]$ (**64b**) with $LiE(SiMe_3)_2$ (E = P, As). For E = Sb this method failed, due to the highly sterically hindered cavity of the N_3N ligand. Reducing the steric bulk of the amido ligands by substituting the Me_3Si groups with the sterically less demanding isopropyl or neopentyl groups gave the heterocumulene complexes $L_nM{=}E{=}ML_n$ ($L_n = N(CH_2CH_2NR)_3$, R = *i*-Pr, $(CH_3)_3CCH_2$, E = P, As, Sb, Bi).[78] The unavailability of isolable stibides of the type LiSbHR rendered the synthesis of stibido complexes of type **B** difficult.

The synthesis of the stable hydride $RSbH_2$ (R = $CH(SiMe_3)_2$)[79] allowed the in situ generation of the desired starting material LiSbHR, and so the synthesis and characterization of the first stable complex containing a transition metal−antimony triple bond have recently been accomplished.[72] The complex $[(N_3N)W{\equiv}Sb]$ (**81**) was afforded by the reaction of $[(N_3N)WCl]$ (**64a**) with LiSbHR (R = $CH(SiMe_3)_2$) generated in situ from $RSbH_2$ and *n*-BuLi (eq 14). The stibido complex **81** possesses a very short W−Sb distance (2.526(2) Å) and thus represents a triple bond. Theoretical calculations suggest that the W−Sb bond is a true triple bond with strong covalent character and only slight polarization toward the antimony atom.



Bismuth. Complexes containing a transition metal−bismuth triple bond have yet to be reported. This is probably due to the unavailability of suitable stable starting materials such as LiBiHR as well as the relative weakness of M−Bi bonds. Theoretical calculations on the model bismuthido complex $[(N_3N)W{\equiv}Bi]$ show that, once formed, the compound should be stable enough to be isolated. DFT calculations predict a true W≡Bi triple bond for the hypothetical complex $[(N_3N)W{\equiv}Bi]$ with a bond order of 2.27, which is essentially identical with that of the stibido complex **81** (bond order 2.28).[72]

Summary and Outlook

Triple bonding between transition metals and group 14 or group 15 elements was confined to carbon and nitrogen for many years. In the mid-1990s, however, this "monopoly" was lifted as the first examples of complexes containing triple bonds between transition metals and the heavier analogues of carbon and nitrogen were reported. Thus, a new chapter in organometallic chemistry was established, which has expanded at a tremendous rate over the past decade. Several remarkable complexes have been prepared using just a handful of generally applicable synthetic routes and the reactivity and properties of many of these complexes have been investigated. Theoretical studies have been crucial in the elucidation of the bonding situation in these complexes and are essential for the progress of this field.

The past decade has certainly been highly rewarding for the field, and it is expected that its future will be equally, if not more, rewarding, with many more complexes being isolated, new preparative methods being developed, and novel reactivity patterns being discovered. Obviously, two further targets for the future are the isolation of a transition metal−silicon complex with true silylyne character and the preparation of the first complex featuring a triple bond between a transition metal and a bismuth atom. Hopefully, the synthetic expertise that has been applied in "taming" the other heavier homologues of carbon and nitrogen will succeed in the cases of silicon and bismuth as well.

Acknowledgment. We wish to thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their comprehensive financial support.

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