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Review

Low-coordinate E_1 ligand complexes of Group 15 elements—A developing area

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Dedicated to Prof. Dr. H. Brunner on the occasion of his 70th birthday.

Contents

Abstract

A survey of transition–metal complexes with substituent-free Group 15 E_1 ligands of coordination numbers 1 and 2 is presented. Such ligands exhibit interesting bonding properties and diverse reactivity patterns including cycloadditions, redox, and single-atom transfer. The various modes of coordination and relevant aspects to each regarding synthesis, bonding, and reactivity are summarized.

Keywords: Group 15 elements; Pnicogenido ligands; Multiple bonds

1. Introduction

Complexes possessing heavier substituent-free pnicogenido ligands (E^{3-}) of Group 15 elements (E = P, As, Sb, Bi) have received considerable attention [1]. A specific challenge in this field lies in the synthesis of complexes with E_1 ligands in environments of coordination numbers 1 and 2. For phosphorus,

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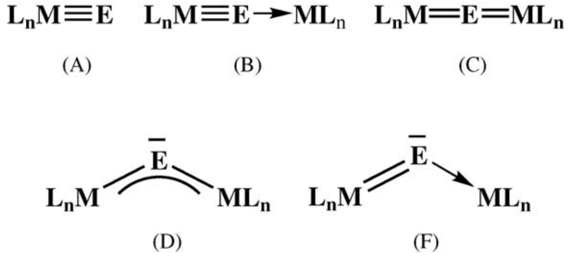
it has been established that low coordination within organic or metallic moieties generally leads to situations of interesting electronic structure and high reactivity [2]. Transition–metal complexes bearing E_1 ligands in low coordination are of particular interest for all heavier pnicogens due to their participation in M–E multiple bonding.

Complexes with multiple bonds between transition metals and main-group elements have been the subject of intense investigation [3]. For transition–metal complexes with terminal triply bonded pnicogen ligands, examples had for a long time been known exclusively for nitrogen [4,5], as represented by complexes of the type $[Cl_4MN]^-$ (M = Mo, W, Re, Ru, Os) [6] possessing very short metal–nitrogen bond distances. Such complexes exhibit a high nucleophilicity towards Lewis acids like BF_3 and a high propensity for intermolecular aggregation [4,7].

The existence of triply bonded ligands for phosphorus and the heavier congeners had been the subject of speculation for years [8,9]. In 1995, a breakthrough in the field occurred in which the first examples of phosphido complexes of type **B** were verified in our group [10] and the first examples of terminal phosphido complexes of type **A** were independently published by the groups of Cummins and co-workers [11] and Schrock and co-workers [12]. Since this time, ensuing studies in these and other research groups have led both to more highly reactive phosphido complexes and to complexes with heavier terminal pnictide ligands. The state of triply bonded terminal phosphido ligand complexes has been recently reviewed [13].

Bridging pnictinidene ligands of coordination number 2 have been known ever since the symmetrically bridging cationic heterocumulenes were first reported by Huttner and co-workers (type **C**) [14]. Since then, both neutral and anionic cumulenes have appeared in the literature, and the methods for obtaining such compounds have been widely diversified.

Currently, the classes of heavier E_1 ligands of coordination numbers 1 and 2 can be summarized by a total of five coordination modes (Scheme 1). Types **A** and **B**, respectively, represent triply bonded pnictido complexes with and without additional coordination to a Lewis acid. Type **C** represents the growing class of heterocumulenes, for which examples are known for all pnicogens. Types **D** and **F** constitute a rare class of substituent-free E_1 ligands in bent coordination, for which only few examples are known. In recent years, the number of representatives for each of the above classes has grown, and understanding of the bonding situations has increased, while further examples from the heavier Group 15 elements are continually being added to this still developing area. With the principal structural types **A**–**F** serving as a point of orientation, the low-coordinate E_1 ligand complexes are classified and discussed in the following review.



Scheme 1.

2. Complexes with terminal E_1 ligands (CN 1)

2.1. Early speculation

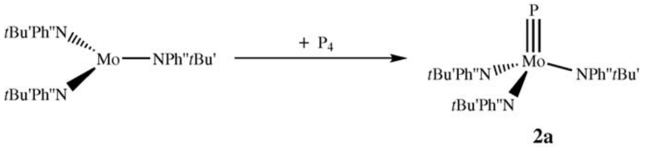
The first speculation about the existence of a terminal phosphido complex was derived from experiments of Becker et al. in 1985 [15]. Reaction of $[W_2(OtBu)_6]$ with the phosphaalkyne $tBuC\equiv P$ resulted in the identification of products involving central WPC_2 and WP_2C four-membered rings, leading to the hypothesis that the alkylidyne and phosphido intermediates $[(tBuO)_3W\equiv CtBu]$ and $[(tBuO)_3W\equiv P]$, respectively, were formed along the reaction pathway. The rapid reaction of these species with an additional equivalent of $tBuC\equiv P$ could not be hindered, and the cycloaddition product $[(tBuO)_2W(CtBu)_2P(OtBu)]$ could be detected by NMR spectroscopy [15,16]. Later on, by low temperature ^{31}P NMR studies of a reaction between $[W(OtBu)_6]$ and $MesC\equiv P$, the formation of a phosphido complex intermediate $[(tBuO)_3W\equiv P]$ (**1**) was shown in the Scheer group [17].

Similar speculation resulted in 1987 from work by Chisholm et al. [18] in which the reaction of $[W_2(ONp)_6L_2]$ (Np = neopentyl, L = $HNMe_2$, pyridine) with white phosphorus, P_4, led to the isolation of two tetrahedral complexes with P_1 and P_3 ligands [18]. The P_1 ligand product, $[W_3(ONp)_6(\mu_2\text{-}ONp)_3(\mu_3\text{-}P)]$ was accordingly attributed to the generation of the transient phosphido species $[(NpO)_3W\equiv P]$ and its rapid cycloaddition reaction with an equivalent of the starting material $[W_2(ONp)_6L_2]$. In this case, the proposed phosphido intermediate could not be observed spectroscopically, but its formation was justified on the basis of established transformations leading to analogous trinuclear alkoxy molybdenum and tungsten complexes with capped alkylidyne [19], oxo [20], and imido [21] ligands.

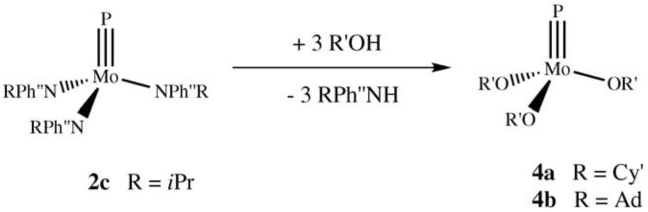
Speculation about complexes with terminal arsenido ligands has also arisen from the observed products of similar reactions carried out by Ziegler et al. The co-photolysis of the trinuclear complexes $[\{CpM(CO)_2\}_3(\mu_3\text{-}As)]$ (M = Mo, W) with $[CpM'(CO)_2]$ (M′ = Co, Rh) [22] or with $[Fe_2(CO)_9]$ and $[Fe(CO)_5]$ [22,23] resulted in the proposed formation of the metal–metal triply bonded complexes $[\{CpM(CO)_2\}_2]$ and the arsenido complex $[Cp(CO)_2M\equiv As]$ as reactive intermediates. Speculation about terminal stibido complexes has been limited to the experiments of Rheingold et al., in which anionic stibido complexes $[(CO)_nM\equiv Sb]^-$ ($n = 4$, M = Cr, Mo, W; $n = 3$, M = Fe) could be detected in an ion-cyclotron spectrometer (FT-ICR) by the reaction of metal carbonyl complexes with Sb_2^- species generated in the gas phase by laser evaporation of antimony metal [24].

2.2. Synthetic methods leading to isolable complexes

A characteristic of the above terminal pnictido complexes is the extremely high ‘side-on’ reactivity of the transition metal–pnicogen triple bond, as evidenced by the many



Scheme 2.



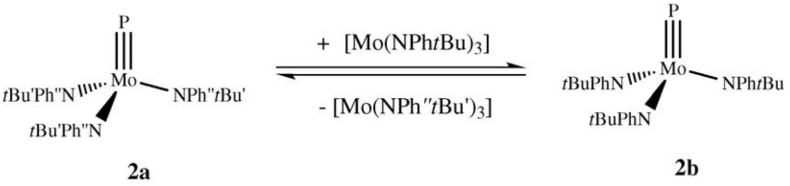
Scheme 5.

cycloaddition reactions where phosphido complexes were proposed as reactive intermediates [9]. In order to check the early speculation of Becker et al. [15], the reaction between $[(\text{tBuO})_3\text{W}{\equiv}\text{W}(\text{OtBu})_3]$ and MesC≡P was followed by variable-temperature ^{31}P NMR spectroscopy in the Scheer group [17]. In the temperature range between 213 and 283 K, the reaction intermediate $[(t\text{BuO})_3\text{W}{\equiv}\text{P}]$ (**1**) could be identified by its downfield ^{31}P NMR chemical shift of 845 ppm and a small ^1J(WP) of 176 Hz, both characteristic features of this class of compounds. Above 263 K, the subsequent reaction with MesC≡P occurred, leading to four-membered ring products. In order to counter the observed high reactivity, bulky auxiliary ligands on the transition metal had to be incorporated, and this strategy has since led to isolable pnictido complexes.

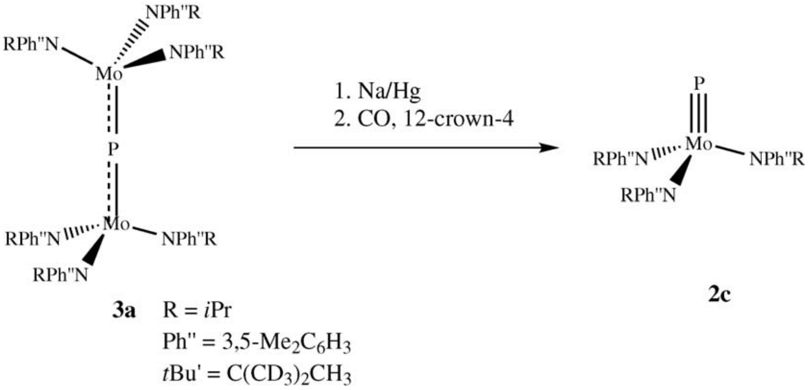
One of the first stable phosphido complexes, $[(t\text{Bu}'\text{Ph}''\text{N})_3\text{Mo}{\equiv}\text{P}]$ ($t\text{Bu}' = \text{C(CD}_3)\text{CH}_3$, $\text{Ph}'' = 3{,}5\text{-Me}_2\text{C}_6\text{H}_3$) (**2a**), was synthesized by Cummins and co-workers [11] in 79% yield by treating the tris(amido)molybdenum complex $[(t\text{Bu}'\text{Ph}''\text{N})_3\text{Mo}]$ [25] with an excess of white phosphorus in diethyl ether at room temperature. **2a** exists as a monomer with C_3 symmetry in the solid state as well as in solution. Its high stability is due to the steric protection of the Mo≡P triple bond by the bulky substituents at the amido ligands. Only the 'end-on' position of the P^{3-} ligand is accessible, and thus the phosphido ligand of **2a** can be transferred to $[(t\text{BuPhN})_3\text{Mo}]$ via a heterocumulene intermediate to give $[(t\text{BuPhN})_3\text{Mo}{\equiv}\text{P}]$ (**2b**) [26]. The related stable phosphide-bridged heterocumulene $[(i\text{PrPh}''\text{N})_3\text{Mo}{=}\text{P}{=}\text{Mo}(\text{NPh}''i\text{Pr})_3]$ (**3a**) could be isolated when $[(i\text{PrPh}''\text{N})_3\text{Mo}]$ was treated with white phosphorus. Reduction of **3a** with sodium amalgam in THF followed by oxidation with CO led to $[(i\text{PrPh}''\text{N})_3\text{Mo}{\equiv}\text{P}]$ (**2c**) [27]. Obviously, even the sterically less demanding $i\text{PrPh}''\text{N}$ tris(amido) set can efficiently stabilize the molybdenum-phosphorus triple bond (Schemes 2–4).

The alcoholysis of **2c** leading to substitution of the amido ligands by alkoxy groups was also reported [28]. Thus, the reaction of **2c** with 1-methylcyclohexanol provided the stable phosphido complex $[(\text{Cy}'\text{O})_3\text{Mo}{\equiv}\text{P}]$ (**4a**) as a yellow crystalline solid in 57% yield after recrystallization from diethyl ether. Use of the slightly less bulky alcohols led to slow dimerization of the terminal Mo≡P unit after alcoholysis. In the case of 1-adamantanol, the phosphido complex $[(\text{AdO})_3\text{Mo}{\equiv}\text{P}]$ (**4b**) formed after alcoholysis of **2c** exhibits a half-life of ca. 6 h in toluene at 20 °C. Rapid dimerization occurs when **2c** is treated with three equivalents of 2,6-dimethylphenol, in which case the alcoholysis is incomplete and the green–brown $[\{\text{PMo}(\text{NPh}''i\text{Pr})(\text{OPh}')_2\}_2]$ was isolated in 51% yield (Scheme 5).

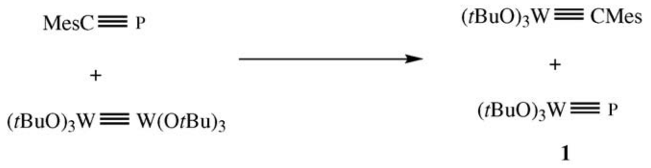
In this context, the high 'side-on' reactivity of $[(t\text{BuO})_3\text{W}{\equiv}\text{P}]$ (**1**) is comparable, and based on the employed synthesis by the metathesis of $[\text{W}_2(\text{O}t\text{Bu})_6]$ with phosphaalkyne, the local excess of phosphaalkyne leads to a cyclization reaction to form



Scheme 3.



Scheme 4.



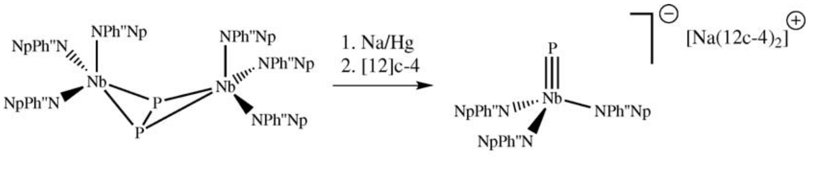
Scheme 6.

four-membered ring products, which proceeds faster than the metathesis reaction for the formation of the phosphido complex **1** [17]. **1** was characterized by ^{31}P NMR spectroscopy in the temperature range from 215 to 263 K and could only be isolated by trapping with [M(CO)$_5$(thf)] (M = Cr, W; thf = tetrahydrofuran) to give [(tBuO)$_3$W≡P → M(CO)$_5$] (M = Cr (**5a**), W (**5b**)) [17] (cf. 3.2) (Scheme 6).

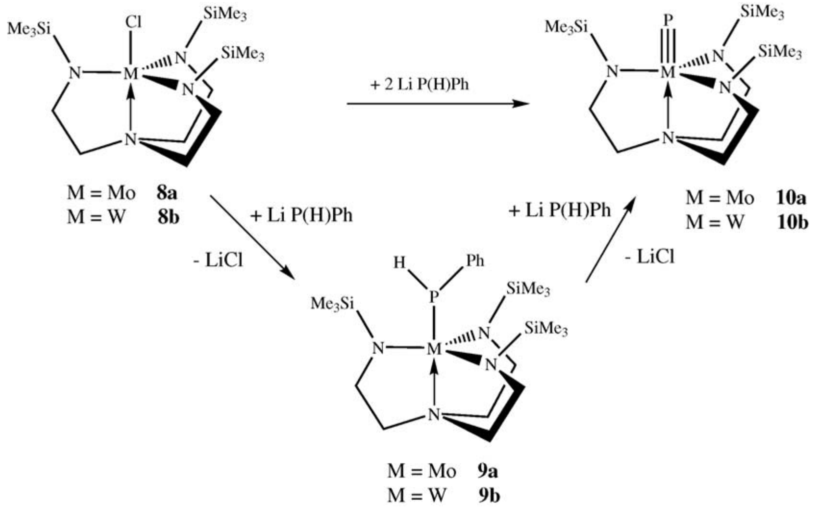
Recently, Cummins et al. have reported the reaction of the niobaziridine–hydride complex [Nb(H)(η^2-tBu(H)C=NPh″)(NPh″Np)$_2$] (Np = CH$_2$CMe$_3$) with white phosphorus leading quantitatively to the bridging diphosphide complex [(μ,η^2:η^2-P$_2$){Nb(NPh″Np)$_3$}$_2$] [29]. Reduction of the diphosphide complex with sodium amalgam afforded the sodium etherate dimer {[Na(Et$_2$O)][(NpPh″N)$_3$Nb≡P]}$_2$ (**6a**) in good yield [30]. Based on ^{31}P NMR spectroscopic data, it was proposed that **6a** forms monomeric [Na(thf)$_x$][(NpPh″N)$_3$Nb≡P] (**6b**) species in THF solution. A complete spatial separation of the sodium ion from the phosphorus nucleus to give the phosphido complex [Na([12]c-4)$_2$][(NpPh″N)$_3$Nb≡P] (**6c**) was achieved by treating a THF solution of **6a** with two equivalents of 12-crown-4 (Scheme 7). The anionic phosphido complexes **6** represent well-defined Nb analogues of the tantalum phosphido complex Li[(N$_3$N)Ta≡P] (**7**) (N$_3$N = TREN = (Me$_3$SiNCH$_2$CH$_2$)$_3$N), generated in situ by P–C bond cleavage of [(N$_3$N)Ta=PPh] with excess lithium [31]. Whereas the triple-bond character in **6a** and **6b** remains ambiguous, for **6c**, a Nb≡P triple bond was suggested. DFT calculations on the model complex [(H$_2$N)$_3$NbP]$^-$ led to the interpretation of a triple-bond character of the niobium–phosphorus bond [30]. The nucleophilic behavior of the terminal phosphido ligand in **6b** was explored in reactions with electrophiles. Thus, the nonlinear phosphinidene complexes [(NpPh″N)$_3$Nb=PEMe$_3$] (E = Si, Sn) [30] were prepared by reaction of **6b** with trimethylsilyl or trimethylstannyl chloride, while reactions with R$_2$PCl (R = tBu, Ph) afforded the phosphanylphosphinidene complexes [(NpPh″N)$_3$Nb(η^2-PPR$_2$)] [30]. **6b** reacts also with GeCl$_2$·dioxane, SnCl$_2$, or Pb(OTf)$_2$ to give the complexes [(*cyclo*-μ,η^3:η^3-EP$_2$){Nb(NPh″Np)$_3$}$_2$] (E = Ge, Sn and Pb) [32] which contain a μ,η^3:η^3-*cyclo*-EP$_2$ three-membered ring supported between the two niobium centers. It was also shown that **6b** reacts readily with pivaloyl and adamantoyl chloride to give the corresponding acylphosphinidenes which readily undergo retro [2 + 2]-fragmentation in solution, leading to the phosphaalkynes tBuC≡P and 1-AdC≡P along with the oxoniobium complex [(NpPh″N)$_3$NbO] [33].

Simultaneously with the synthesis of **2c**, Schrock and coworkers reported the synthesis of a phosphido complex which is stabilized by a tris(amido)amine ligand [12]. Thus, the reaction of [(N$_3$N)MCl] (N$_3$N = TREN = (Me$_3$SiNCH$_2$CH$_2$)$_3$N; M = Mo (**8a**), W (**8b**)) with two equivalents of LiP(H)Ph leads smoothly, via the intermediate formation of [(N$_3$N)M–P(H)Ph] (M = Mo (**9a**), W (**9b**)) to the stable phosphido complexes [(N$_3$N)M≡P] (M = Mo (**10a**), W (**10b**)) [12,34]. Using a 1:1 molar ratio of the reagents, **9a** could be isolated, whereas **9b** was observed only in traces. Thermal decomposition of **9a** did not lead to **10a**, but deprotonation with LiP(H)Ph or PhLi gave a supposed anionic intermediate of **9**, which decomposes to **10**. On the basis of the supposed anionic intermediates of **9**, it was expected that **8** should also react with Li$_2$PPh to give **10**. Indeed **8b** reacted with Li$_2$PPh to give **10b**; however, **8a** in reaction with Li$_2$PPh did not give **10a**. **10b** can also be prepared by treating **8b** with LiPH$_2$, but it is not known whether the decomposition mechanism of [(N$_3$N)W–PH$_2$] is via α,α-dehydrogenation or a base-catalysed deprotonation (Scheme 8).

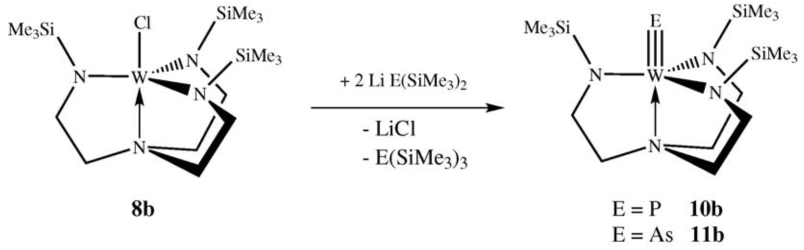
An alternative synthetic route for the phosphido complex **10b** was developed in the Scheer group by treating **8b** with LiP(SiMe$_3$)$_2$ in toluene at 80 °C [35] (Scheme 9). The expected intermediate [(N$_3$N)WP(SiMe$_3$)$_2$] was not observed by monitoring the reaction by ^{31}P NMR spectroscopy. However, an increase of the amount of **10b** was accompanied by an increase of the amount of P(SiMe$_3$)$_3$. Obviously the formation of [(N$_3$N)WP(SiMe$_3$)$_2$] is the rate-determining step, and the metallation of the phosphanido intermediate takes place rapidly as indicated by the formation of P(SiMe$_3$)$_3$. Since the [E(SiMe$_3$)$_2$]$^-$ anions are also known for the heavier homologues, this strategy would be expected to offer a general synthetic route to terminal pnictido complexes. Indeed the reaction of **8b** with LiAs(SiMe$_3$)$_2$ led to the first arsenido complex [(N$_3$N)W≡As] (**11b**). On the other hand, **8b** did not react with LiE(SiMe$_3$)$_2$ (E = Sb, Bi). Probably, the cone formed from the three SiMe$_3$ groups around the W–Cl fragment in **8b** is too narrow and sterically hinders the reaction of the bulky [E(SiMe$_3$)$_2$]$^-$ (E = Sb, Bi) anions with **8b**. An alternative synthesis of the arsenido complex **11b** was achieved in the Schrock group by treating [(N$_3$N)WPh] with a slight excess of H$_2$AsPh at room temperature in the dark over 2 days [34]. [(N$_3$N)Mo≡As] (**11a**) was obtained by treating **8a** with LiAs(H)Ph, a method which failed for the synthesis of the tungsten complex **11b**.



Scheme 7.



Scheme 8.



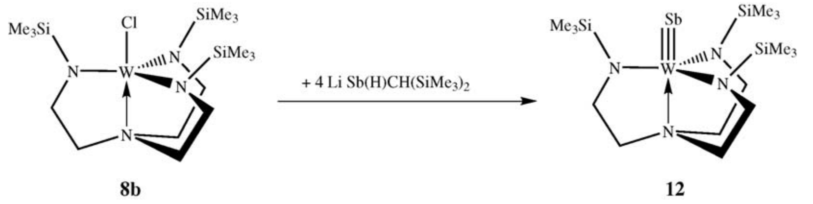
Scheme 9.

The scarcity and low thermal stability of the stibanido anions has thus far limited the outlook to synthesizing stable stibido complexes. However, the reaction of Li[Sb(H)CH$(SiMe_3)_2$], generated in situ from $(Me_3Si)_2CHSbH_2$ [36] and *n*BuLi, with **8b** leads to the formation of [$(N_3N)W{\equiv}Sb$] (**12**), the first stable complex containing an antimony–tungsten triple bond [37]. Due to the instability of the lithiated stibane, it was necessary to use an excess of $RSbH_2$ and *n*BuLi in order to achieve total consumption of **8b**. The degradation of the TREN ligand and decomposition of Li[Sb(H)CH$(SiMe_3)_2$] lead to a relatively low yield (9%) of **12** and give rise to side products such as [$(N_3N)W{\equiv}CCH_3$] and Sb_7^{3-}. The reaction of the sterically less encumbering [$Me_3SiCH_2(H)Sb$]$^-$ moiety with **8b** yields [$(N_3N)W{\equiv}CSiMe_3$] instead of the targeted **12**. In this case, the low thermal stability of Li[Sb(H)CH_2SiMe_3] results in transmetalation reactions with the formation of Li[CH_2SiMe_3], which reacts with **8b** to give [$(N_3N)W{\equiv}CSiMe_3$]. A complex with a transition metal–bismuth triple bond has not been synthesized so far (Scheme 10).

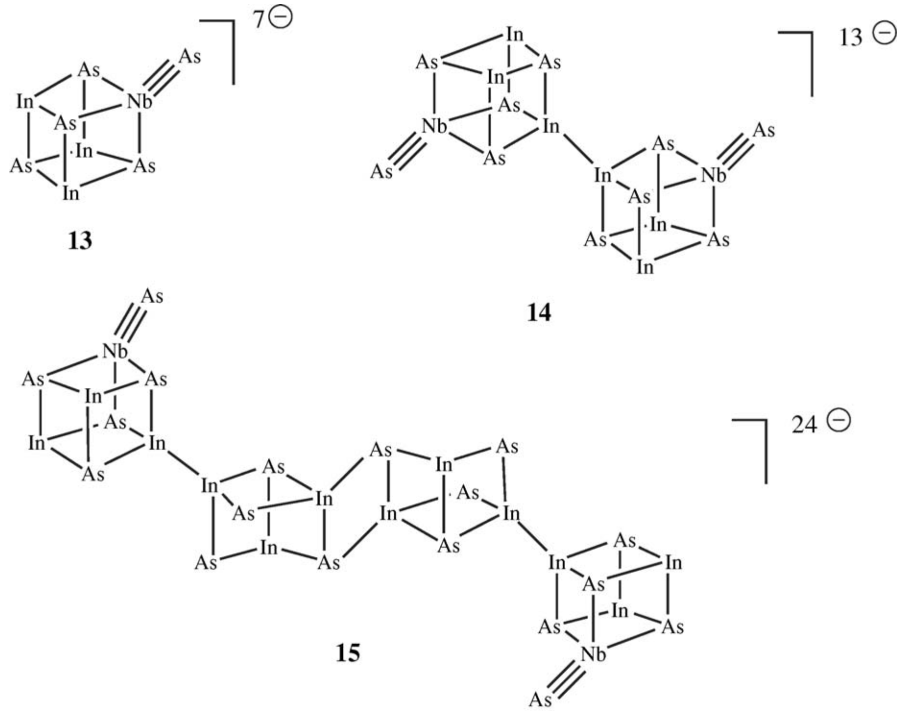
The phosphido complexes **10** were successfully synthesized for molybdenum and tungsten. Efforts to obtain analogous complexes of chromium failed [38] due probably to the low stability of the Cr^{6+} oxidation state, which renders the formation of such a triple-bond complex unfavorable.

A series of unusual Zintl-phase compounds $Cs_7NbIn_3As_5$ (**13**) [39], $Cs_{13}Nb_2In_6As_{10}$ (**14**), and $Cs_{24}Nb_2In_{12}As_{18}$ (**15**) [40], which each contain a triply bonded Nb≡As unit, was reported by Sevov et al. The structure of the anion in **13** comprises a distorted In_3As_4Nb cubane, whereby an arsenic atom is attached to Nb in a terminal fashion. Two such cubanes with "handles" are linked together through an In–In bond in **14**, whereas in **15** the two cubanes with "handles" are joined through two In_3As_4 pseudocubanes (one corner is missing). The two In_3As_4 pseudocubanes are bonded together along one edge by two In–As bonds (Scheme 11).

13 and **15** were synthesized by heating a stoichiometric mixture of the corresponding elements in a niobium container at 800/500 and 650 °C, respectively. The synthesis of **14** required



Scheme 10.



13

14

15

Scheme 11.

a Cs:Nb:In:As = 20:3:9:15 stoichiometry and 700 °C. **13** is a black, crystalline solid, and **14** and **15** are dark grey to black, crystalline solids. **13** and **15** are diamagnetic, whereas **14** is paramagnetic with one unpaired electron per formula unit as determined by magnetic measurements. The potassium salts of the transition–metal Zintl-phase anions $[NbInAs_6]^{9-}$ (**16a**) and $[Nb_2As_6]^{10-}$ (**16b**), each containing two bridging and four terminal arsenic atoms, were prepared from the corresponding elements in a typical solid-state synthesis [41]. Discussion about the bonding situation in the Zintl-type anions is given in Section 2.3.

2.3. Bonding situation

The nature of the transition metal–phosphorus bond in phosphido complexes, which were proposed as intermediates in some chemical transformations, i.e. the metathesis reaction of $[W_2(OtBu)_6]_2$ with phosphaalkynes and those mentioned in Section 2.1, had for many years remained unclear. However, it was postulated on the basis of the isolated reaction products that they contain a transition metal–phosphorus triple bond. Through the synthesis of stable complexes, it has become possible to map out the nature of the $M\equiv P$ bond more precisely (Table 1).

The way to stable pnictido complexes was opened up by use of bulky auxiliary ligands. In TREN complexes, the three $SiMe_3$ groups form a cavity in which the $M\equiv E$ triple bond can be stabilized and create a situation on the metal atom in which the d_{xz} and d_{yz} metal orbitals are mostly unoccupied and available for π-bonding with the pnicogen ligand. Additionally, the TREN complexes have a C_3 symmetry enforced by the backbone of the amido ligand [43], and the metal atom is additionally stabilized through donation of the axial amino group. In the complexes **10**–**12** (Fig. 1), the metal atom has a trigonal bipyramidal geometry in which the terminal pnictido ligand occupies an axial position, whereas in the complexes **2**, **4**, and **6**, the metal atom exhibits a tetrahedral geometry.

All structurally characterized pnictido complexes possess a very short $M\equiv E$ bond length (Table 1). A large number of covalent radii of triple bonds for main-group and transition metals have been reported [44]; such calculated values represent a valuable orientation point for estimating whether a bond distance would represent a triple bond. Furthermore, due to the advantage of ^{31}P NMR spectroscopy, the phosphido complexes allowed us a deeper insight into the constitution of the transition–metal phosphorus triple bond. A characteristic feature of the phosphido complexes is the extremely low-field chemical shift and in the case of tungsten complexes the unexpectedly small ^{1}J(WP) cou-

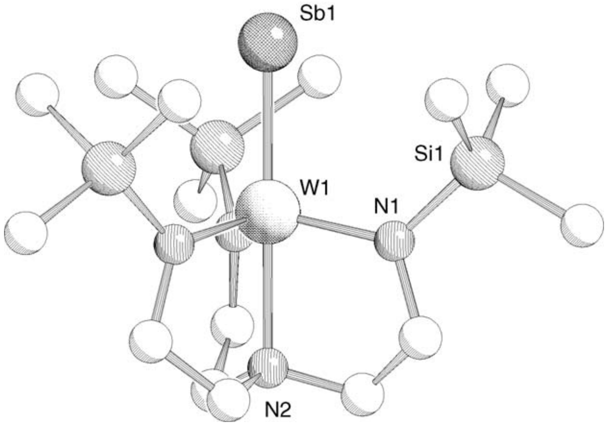


Fig. 1. Molecular structure of $[(N_3N)W\equiv Sb]$ (**12**). H atoms have been omitted for clarity.

Table 1
M–E bonding distances and ^{31}P NMR data for terminal transition–metal pnictido complexes (type **A**)

Complex	d (M–E) (Å)	δ ^{31}P (ppm)	Ref.
(tBuO)$_3$W≡P (**1**)		845 (^1J(WP) = 176 Hz)	[17]
(tBuPh″N)$_3$Mo≡P (**2a**)	2.119(4)	1216	[11]
(tBuPhN)$_3$Mo≡P (**2b**)		1226	[26]
(iPrPh″N)$_3$Mo≡P (**2c**)	2.116(3)	1256	[27]
((2-Ad)Ph″N)$_3$Mo≡P (**2d**)	2.107(3)	1215	[42]
(Cy′O)$_3$Mo≡P (**4a**)	2.114(2)	1130	[28]
(AdO)$_3$Mo≡P (**4b**)		1124	[28]
{[Na(Et$_2$O)]$^+$[(NpPh″N)$_3$Nb≡P]$^-$}$_2$ (**6a**)		949.2 ($\Delta\nu_{1/2}$ = 495 Hz)	[30]
[Na(thf)$_x$]$^+$[(NpPh″N)$_3$Nb≡P]$^-$ (**6b**)		1019.8 ($\Delta\nu_{1/2}$ = 166 Hz)	[30]
[Na([12]c-4)$_2$]$^+$[(NpPh″N)$_3$Nb≡P]$^-$ (**6c**)	2.186(2)	1110.2 ($\Delta\nu_{1/2}$ = 170 Hz)	[30]
Li$^+$[(N$_3$N)Ta≡P]$^-$ (**7**)		575 ($\Delta\nu_{1/2}$ = ca. 600 Hz)	[31]
(N$_3$N)Mo≡P (**10a**)		1346	[12]
(N$_3$N)W≡P (**10b**)	2.162(4)	1080 (^1J(WP) = 138 Hz)	[12]
(N$_3$N)Mo≡As (**11a**)	2.252(3)		[34]
(N$_3$N)W≡As (**11b**)	2.2903(11)		[35]
(N$_3$N)W≡Sb (**12**)	2.5255(17)		[37]

pling constants. Both properties became a distinguishing mark for the phosphido complexes. The alkylidyne complexes, which are closely related to the phosphido complexes, also exhibit a low-field ^{13}C NMR chemical shift, their resonance signals appearing in the range from 200 to 400 ppm [3]. The low-field chemical shift of the phosphido complexes is also correlated by the drastic low-field ^{13}C NMR shift in the isolobal carbide complex K(2,2,2-crypt)$^+$[(tBu′Ph″N)$_3$Mo≡^{13}C]$^-$ (δ ^{13}C = 501 ppm) [45,46] as well as by the low-field ^{15}N NMR shift in the terminal nitride complex [(tBu′Ph″N)$_3$Mo≡^{15}N] (δ ^{15}N = 480 ppm) [47]. However, the phosphorus nucleus in phosphaalkynes [48] and iminophosphenium cations [49] is much more shielded in comparison to the phosphido complexes. The ^{31}P chemical shift in the molybdenum complexes, by comparing **10a** and **10b**, is 260 ppm higher than in the tungsten complex, but only 100 ppm separates the signals of the Mo complex **2a** and the anionic niobium complex **6c**. It was shown that the ^{31}P chemical shift in complexes **6** is very sensitive to coordination to alkali metals [30]. Thus, the shifts of the resonance signals in ^{31}P NMR spectra for **6a**, **6b**, and **6c** at 949.2, 1019.8, and 1110.2 ppm, respectively, were explained by formation of sodium-bridged dimers (**6a**), ion-pair contacts (**6b**), and separated ions (**6c**), respectively, in solution.

Solid-state ^{31}P MAS-NMR spectra and ^{31}P chemical shielding tensors were reported for complexes **2a**,**b** and **10**, showing an extreme ^{31}P deshielding and large chemical shift anisotropy (CSA) (2393 ppm for **10a**) [50]. These effects were explained in terms of considerable paramagnetic shielding at directions perpendicular to the M≡P triple bond. This paramagnetic shielding was attributed to the field induced mixing between σ(M–P) and π*(M–P) MO's and the small energy gap between these orbitals. This explanation is based on DFT calculations at the B3LYP level on the model complex [(H$_2$N)$_3$Mo≡P] as well as on P$_2$, PN, and PCH. For the tungsten phosphido complexes the characteristically small ^1J(WP) coupling constants have been interpreted as a low degree of s-character in the σ-portion of the M≡P triple bond. A similarly small ^1J(MoC) coupling constant was also found for [(tBu′Ph″N)$_3$Mo≡^{13}C]$^-$ based on ^{13}C CP/MAS-NMR measurements [46]. This view has been supported for the phosphido complex **10b** by calculations using the PESHO method [51], which show small contributions of the tungsten 6s and phosphorus 3s orbitals to the W–P σ-bond [35].

The complexes **10b**, **11**, **12**, and the hypothetical complex [(N$_3$N)W≡Bi] were analysed computationally [37], and it was found that the W≡E bond is a true triple bond showing only weak polarization, in agreement with calculations on the model complexes [N(CH$_2$CH$_2$NH)$_3$M≡P] (M = Mo, W) [52]. A similar situation was also found by the bonding analysis of the hypothetical alkoxy complexes [(MeO)$_3$M≡E] (E = N–Bi); however, for E = N, it was found that the M–E σ and π-bonding orbital are always polarized towards the nitrogen atom [53]. A natural bond orbital (NBO) scheme and Wiberg bond-indices analysis for **10b**, **11**, **12**, and [(N$_3$N)W≡Bi] showed an almost completely sd-hybridized W atom with a slight increase in s-character for heavier pnicogen atoms. This situation reveals more s-character than the earlier published results using the PESHO method [35], which indicate a largely d-character of the tungsten contribution.

The metal–pnicogen triple bonds have also been analysed according to their stretching frequencies and force constants derived from Raman spectroscopic data [54]. In the series [(N$_3$N)W≡E] (E = P, As, Sb), the increase in the size of the pnicogen atom, and consequently of the W≡E bond length, is accompanied by a decrease in the stretching frequencies. Complexes **10** and **11** exhibit isolated M≡E stretching frequencies, whereas in **12**, a relatively strong coupling with other framework vibration modes was found [37]. Generally, the force constant for the tungsten complexes is greater than for the molybdenum complexes, a trend which is also found in the literature data for transition–metal nitride and oxo complexes [3].

The very short Nb–As(exo) distance (2.390(2) Å) found in the Zintl complex **13** provides evidence for a niobium–arsenic multiple bond, which is, however, strongly polarized. It was postulated that the multiple bonding is based on the π interactions between the empty d_{xz} and d_{yz} orbitals on Nb and the filled p_π orbitals on arsenic [39].

3. E_1 ligand complexes in an asymmetric coordination mode (CN 2)

In this chapter, the synthesis and the reactivity pattern of type **B** complexes, asymmetrically coordinated E_1 ligands of CN 2, are described.

3.1. Early speculation

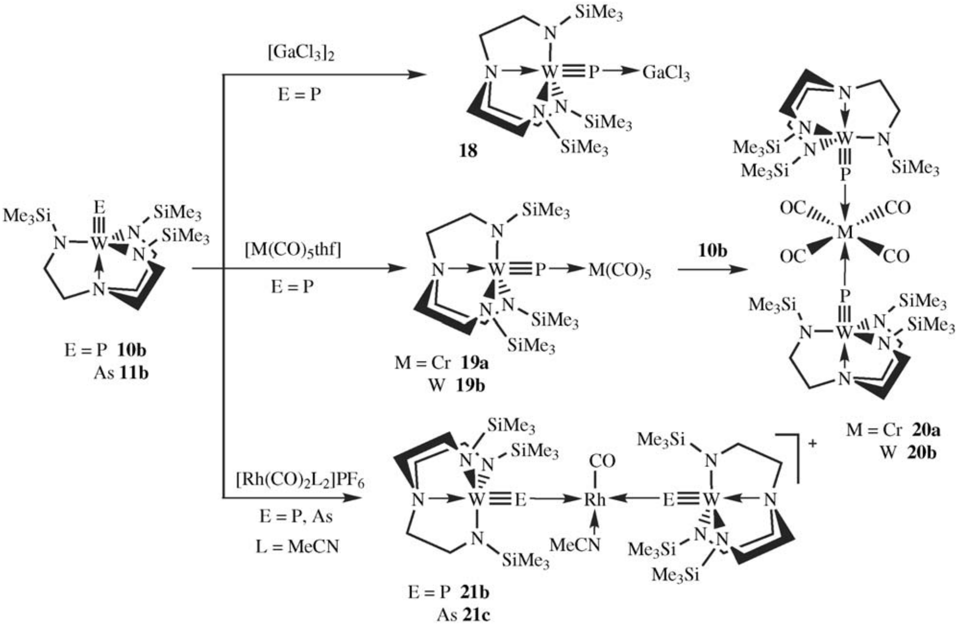
The Scheer group has long been interested in studying the transformation pathway of P_4 tetrahedron in the coordination sphere of transition–metal complexes [55]. Carrying out P_4 degradation reactions in the presence of the Lewis-acidic complexes such as [Cr(CO)$_5$(thf)] has enabled isolation of intermediates along their respective reaction pathways. In cases of reactant complexes with the transition metal possessing an odd number of valence electrons, as in $[L_nM]_2$ (ML_n = Cp*Ni(CO), Cp′Mo(CO)$_3$), a P_1/P_3 fragmentation of the P_4 tetrahedron was observed, leading to the postulation of Lewis-acid coordinated phosphido intermediates of the type [L_nM≡P → Cr(CO)$_5$] (ML_n = Cp*Ni(CO) (**17a**), Cp′Mo(CO)$_3$ (**17b**)) [56]. An alternative approach to such intermediates was developed [57], whereby chlorophosphinidene complexes of the type [{(CO)$_5$M}$_2$PCl] (M = Cr, W) were treated with transition metalates [Cp*Ni(CO)]$^-$ or [Cp′Mo(CO)$_3$]$^-$, serving as a source of 15-electron fragments capable of triple-bond formation with phosphorus. Lewis-acid coordinated phosphido intermediates [L_nM≡P → M′(CO)$_5$] were proposed based on isolation of phosphatetrahedrane products of the type [{L_nM}$_2$(μ,η^2-P_2){M′(CO)$_5$}$_2$] (L_nM = Cp*Ni, Cp′Mo(CO)$_2$; M′ = Cr, W).

3.2. Synthetic methods leading to isolable complexes

The neutral phosphido and arsenido complexes described in Section 2 display a distinct 'end-on' reactivity, which has allowed for the synthesis of a series of Lewis-acid coordinated pnictido complexes. In cases where the Lewis acid is a 16-electron transition–metal fragment or a Group 13 trihalide, the triple bond is held intact while the second bond is essentially dative. However, for cases where the capping moiety is a transition–metal fragment of fewer than 16 electrons, the bonding situation changes substantially (see Section 4.2).

Scheer et al. have investigated the reactivity pattern of a terminal-coordinated phosphido complex possessing the TREN ligand system. Coordination of [(N_3N)W≡P] with the σ-acceptor $GaCl_3$ results in the Lewis acid–base adduct [(N_3N)W≡P→$GaCl_3$] (**18**) with an entirely linear geometry throughout the N_{ax}–W–P–Ga axis [58]. Complex **18** is stable in halogen-free solvents, but decomposes slowly in CH_2Cl_2 under apparent loss of Me_3SiCl. Thereby the steric protection of the triple bond is reduced, and the 'side-on' reactivity and formation of a W_2P_2 tetrahedral complex were achieved. Accordingly, attempts to synthesize the borane adduct [(N_3N)W≡P→BH_3] by reaction of **10b** with $BH_3·SEt_2$ led to elimination of Me_3SiH and apparent polymerization products. However, in reactions of phosphido complex **10b** with $BF_3·OEt_2$ a short-lived borane adduct could be detected in the ^{31}P NMR spectra (δ 607 ppm, ^1J(WP) = 478 Hz) [58], for which the chemical shift and ^1J(WP) coupling constant are comparable with those of other Lewis-acid coordinated phosphido complexes.

Reaction of [(N_3N)W≡P] with transition–metal carbonyl complexes [M(CO)$_5$(thf)] (M = Cr, W) resulted in the initial formation of the one-to-one phosphido-metal carbonyl adducts [(N_3N)W≡P→M(CO)$_5$] (M = Cr (**19a**), W (**19b**)), which were observed in the ^{31}P NMR spectra. However, fast substitution of a second phosphido complex **10b** on the metal carbonyl at the *trans*-position led to isolation of the trinuclear bis(phosphido) complexes **20** (Scheme 12) [35]. The driving force of the bis-substitution reaction was experimentally shown to be the formation of [M(CO)$_6$] as well as according to calculation



Scheme 12.

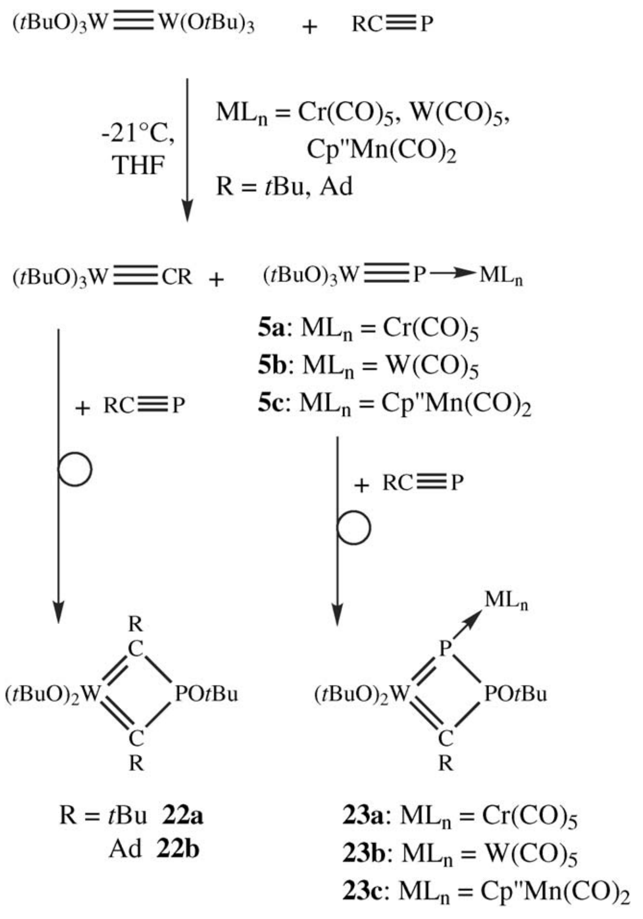
Table 2
M–E bonding distances and ^{31}P NMR data for Lewis-acid coordinated pnictido complexes (type **B**)

Complex	*d* (M–E) (Å)	^{31}P NMR (ppm)	^{1}J(WP) (Hz)	Ref.
$(N_3N)W{\equiv}P \rightarrow GaCl_3$ (**18**)	2.168(4)	366	712	[58]
$(t\mathrm{BuO})_3W{\equiv}P \rightarrow Cr(CO)_5$ (**5a**)		595.4	536	[10,17]
$(t\mathrm{BuO})_3W{\equiv}P \rightarrow W(CO)_5$ (**5b**)	2.132(4), 2.476(4)	546.0	554, 163	[10,17]
$(t\mathrm{BuO})_3W{\equiv}P \rightarrow MnCp''(CO)_2$ (**5c**)		614.0	566	[59]
$thf(Ph'O)_3W{\equiv}P \rightarrow Cr(CO)_5$ (**24c**)		773.4	549	[60]
$thf(Ph'O)_3W{\equiv}P \rightarrow W(CO)_5$ (**24d**)	2.1261(12), 2.4315(13)	718.5	562, 170	[60]
$(N_3N)W{\equiv}P \rightarrow Cr(CO)_5$ (**19a**)		708.1	442	[35]
$(N_3N)W{\equiv}P \rightarrow W(CO)_5$ (**19b**)		662.6	450, 135	[35]
$(N_3N)W{\equiv}P \rightarrow Cr(CO)_4 \leftarrow P{\equiv}W(N_3N)$ (**20a**)		728.1	413	[35]
$(N_3N)W{\equiv}P \rightarrow W(CO)_4 \leftarrow P{\equiv}W(N_3N)$ (**20b**)	2.202(2)	679.8	426, 151	[35]
trans-$[Rh\{(N_3N)Mo{\equiv}P\}_2(CO)(CH_3CN)]PF_6$ (**21a**)		791.1 (*d*, $J_{PRh} = 67$ Hz)		[34]
trans-$[Rh\{(N_3N)W{\equiv}P\}_2(CO)(CH_3CN)]PF_6$ (**21b**)	2.177(5), 2.173(5)	642.6 (*d*, $J_{PRh} = 79$ Hz)		[34]
$[Cp(CO)_2Mo{\equiv}P \rightarrow MoCp(1,3,5\text{-}t\mathrm{Bu}_3C_6H_3)]BAr'_4$ (**28**)	2.1685(9), 2.3573(9)	908.5		[62]

of the corresponding isodesmic reaction. Related trinuclear Lewis-acid coordinated pnictido complexes were synthesized in the Schrock group by reaction of $[(N_3N)M{\equiv}E]$ (M = Mo, W; E = P, As) with $[Rh(CO)_2(MeCN)_2]PF_6$, which produced *trans*-$[Rh\{E{\equiv}M(N_3N)\}_2(CO)(CH_3CN)]PF_6$ (M = Mo: E = P (**21a**); M = W: E = P (**21b**), As (**21c**)) [34]. The crystal structure of **21b** reveals an overall bowed arrangement of the W–P–Rh–P–W axis and a distorted square planar geometry about Rh. Furthermore, the As analogue **21c** was isolated, though no structural data are available. Based on physical and spectroscopic properties, the As compound **21c** was expected to have a geometry similar to **21b**. The ^{31}P NMR spectra of **21a** and **21b** showed similarities to those of the related metal–carbonyl-bridged complexes **20** (Table 2).

The metathesis of $[W_2(Ot\mathrm{Bu})_6]$ with phosphaalkyne $t\mathrm{BuC{\equiv}P}$ resulted in the observation of the intermediate phosphido complex $[(t\mathrm{BuO})_3W{\equiv}P]$ (**1**). To stabilize this intermediate, the Scheer group developed the strategy of generating it in the presence of the Lewis-acidic complexes $[M(CO)_5(thf)]$ or $[Cp''Mn(CO)_2(thf)]$, whereby the lone pair of the phosphido ligand is blocked. By this method, a different kind of kinetic stabilization was achieved for the overall complex in contrast to the steric shielding of bulky substituents around the metal–pnictido triple bond, which is usually employed for such stabilization.

While the Lewis-acid coordinated phosphido complexes $[(t\mathrm{BuO})_3W{\equiv}P \rightarrow M(CO)_5]$ (M = Cr, W) [10,17] and $[(t\mathrm{BuO})_3W{\equiv}P \rightarrow MnCp''(CO)_2]$ [59] were initially observed only in the reaction mixtures, further reactions with $t\mathrm{BuC{\equiv}P}$ could not be completely hindered, and cycloaddition reactions occurred to form the products **22** and **23** (Scheme 13). From these reaction mixtures, only the cycloaddition product **22** could be isolated. Tweaking of the steric parameters of the phosphalkyne reactant as well as the tungsten alkoxy dimer and the reaction conditions led to the first successfully isolated Lewis-acid coordinated phosphido complexes **5** by Scheer et al. Thus, besides the sterics of the reactants used, the reaction conditions were optimized such that at low temperatures (<−40 °C) the metathesis reaction was allowed to be completed over a longer time period, and only afterwards the reaction mixture was allowed to come to room temperature. Since the cycloaddition reaction occurs only at temperatures above −20 °C in the described procedure, all phosphaalkyne was used for the completed metathesis reaction. Reaction of $[W_2(Ot\mathrm{Bu})_6]$ with $\mathrm{MesC{\equiv}P}$ in the presence of $[M(CO)_5(thf)]$ (M = Cr, W) resulted in the isolation and characterization of $[(t\mathrm{BuO})_3W{\equiv}P \rightarrow M(CO)_5]$ (M = Cr, W) (Fig. 2; Scheme 14). It was also found that the phosphaalkyne $t\mathrm{BuC{\equiv}P}$ could be successfully employed when using slightly more sterically encumbered alkoxide ligands in the tungsten triple-bond dimer [60]. Thus, reaction of $[W_2(OPh')_6]$ (Ph′ = 2,6-dimethylphenyl)



Scheme 13.

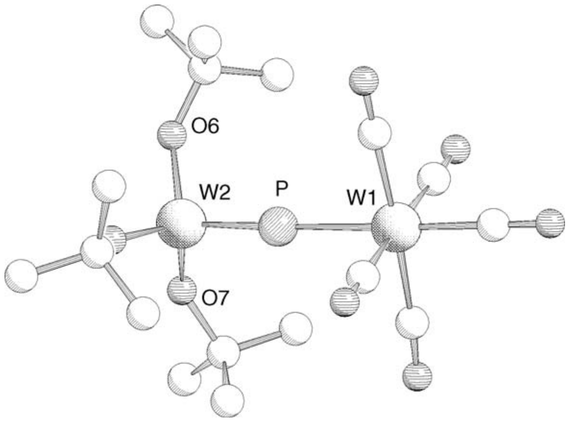


Fig. 2. Molecular structure of $[(t\mathrm{BuO})_3\mathrm{W{\equiv}P} \rightarrow \mathrm{W(CO)_5}]$ (**5b**). H atoms have been omitted for clarity.

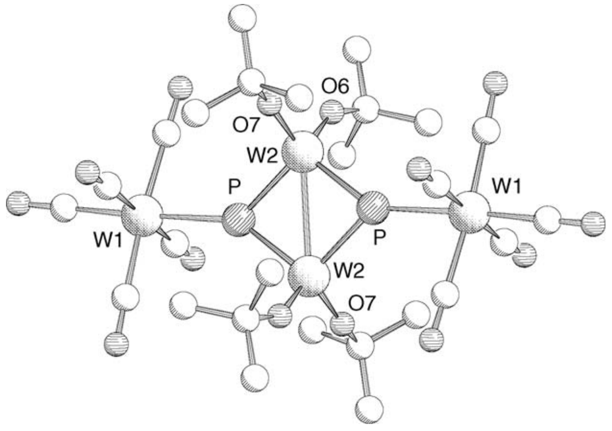


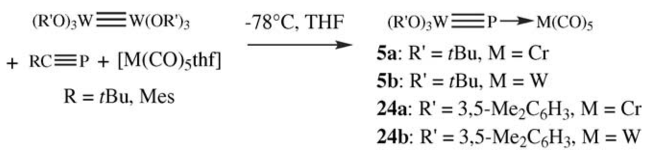
Fig. 3. Molecular structure of $[\{(t\mathrm{BuO})_2\mathrm{W}(\mu,\eta^2{:}\eta^1\text{-P} \rightarrow \mathrm{W(CO)_5}\}_2]$ (**25**). H atoms have been omitted for clarity.

with *t*BuC≡P in the presence of $[\mathrm{M(CO)_5(thf)}]$ led to the formation of complexes $[(\mathrm{Ph'O})_3\mathrm{W{\equiv}P} \rightarrow \mathrm{M(CO)_5}]$ (M = Cr (**24a**), W (**24b**)), which were isolated as their THF adducts $[\mathrm{thf(Ph'O)_3W{\equiv}P} \rightarrow \mathrm{M(CO)_5}]$ (M = Cr (**24c**), W (**24d**)). For this latter reaction, MesC≡P was also successfully used.

Unlike the predominant ‘end-on’ reactivity generally exhibited by the complexes with terminal $\mathrm{E_1}$ ligands, the alkoxide-supported, Lewis-acid coordinated phosphido complexes display distinctive ‘side-on’ reactivity, a property stemming both from the relative lack of steric crowding and from the flexibility of the alkoxide ligands. Furthermore, DFT calculations show the π-character of the HOMO orbital, reflecting the dominant ‘side-on’ reactivity of complexes **5** and **24** [60]. Though complexes **5**, **24** are stable in the solid state and in *n*-pentane at room temperature, allowing either to stand in toluene solution at room temperature results over a longer period of time in formal reductive dimerization via cycloaddition and loss of two RO ligands to complex **25** with a planar $\mathrm{P_2W_2}$ core (Fig. 3).

A related cycloaddition and reductive W–W bond formation occur in the reaction of **24d** with $[(\mathrm{Ph'O})_4\mathrm{W{=}O}]$, from which complex **26** was isolated possessing a nearly planar $\mathrm{W_2PO}$ core. The reaction of **24d** with $[(\mathrm{Ph_3P})_2\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})]$ results in side-on coordination of the tungsten–phosphorus triple bond to the Pt center, and subsequent rearrangement of a phenyl group to form complex **27** with a $\mathrm{WP_2Pt}$ four-membered ring system. The latter reaction involves cleavage of one P–C bond, and this occurs at much lower temperatures (ca. −10 °C) than the high temperatures normally required for related processes observed in homogeneous catalysis [61] (Scheme 15).

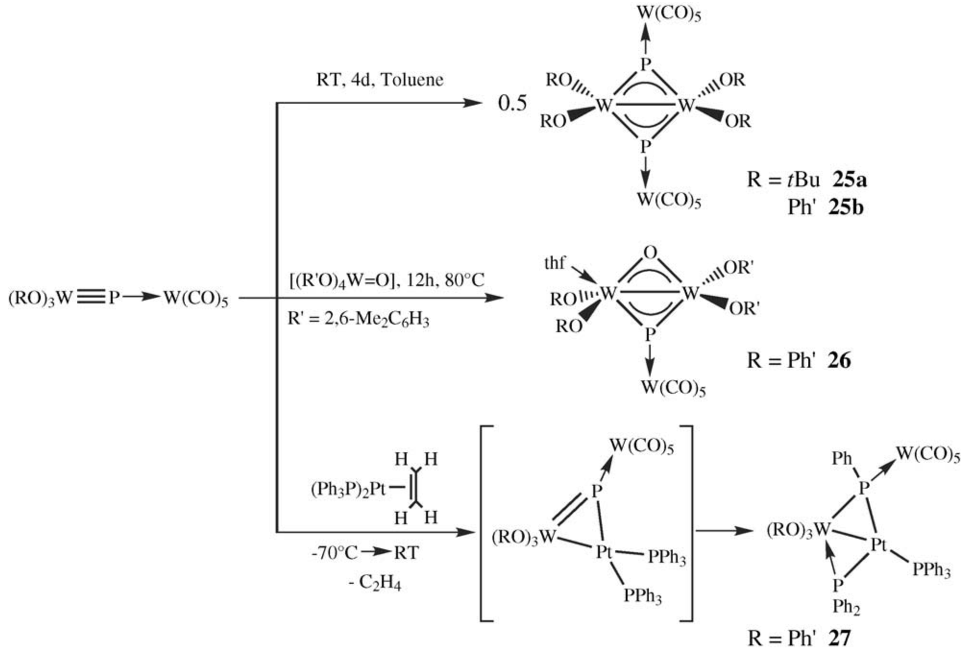
A further type of asymmetrically bridging molybdenum(IV) phosphido complex was recently reported by Ruiz and coworkers [62], representing a rare example of a lower-valent Group 6 metal with a triply bonded pnictido ligand. Photolysis of the dimolybdenum complex $[\mathrm{Mo_2Cp_2}(\mu\text{-PMes*})(\mathrm{CO})_4]$ (Mes* = 2,4,6-*t*$\mathrm{Bu_3}$-$\mathrm{C_6H_2}$), followed by protonation, proton migration, and P-aryl bond cleavage, produced the cationic complex $[\mathrm{Cp(CO)_2Mo{\equiv}P{-}Mo(Mes^*)Cp}]^+$ (**28**) in high yield. In this complex, the phosphido ligand is slightly bent (169.3°), and formal Mo–P bond orders of three and one were proposed (Scheme 16).



Scheme 14.

3.3. Generation of reactive intermediates from phosphinidenes

A method of generating highly reactive Lewis-acid coordinated phosphido ligands supported by lower-valent tungsten complexes were devised in the Scheer group [63]. Thus, thermolysis of the phosphinidene precursor $[\mathrm{Cp^*P\{W(CO)_5\}_2}]$ (**29**) in refluxing toluene results in migration of the Cp* ring from phosphorus in a η^1-bonding mode to tungsten in η^5-coordination and generation of the intermediate $[\mathrm{Cp^*(CO)_2W{\equiv}P} \rightarrow \mathrm{W(CO)_5}]$ (**30**). Complex **30** is not stable under the thermal reaction conditions and undergoes cyclization reactions to produce the isolable phosphatetrahedrane $[\mathrm{Cp^*_2(CO)_4W_2}(\mu,\eta^2{:}\eta^1\text{-}\mathrm{P_2})\{\mathrm{W(CO)_5}\}]$ (**31**) as the main product (Scheme 17). The identity of the phosphido intermediate was further evidenced in studies including photolysis [64] of the phosphinidene complex **29** and in subsequent trapping reactions with phosphaalkynes [63] and alkynes [65]. Thermolysis of **29** in the presence of *t*BuC≡P resulted in isolation of the diphosphacylcobutenone complex **32**, representing formal cycloaddition of the phosphaalkyne with $[\mathrm{Cp^*(CO)_2W{\equiv}P} \rightarrow \mathrm{W(CO)_5}]$ and insertion of one equivalent of CO. Furthermore, reaction of **30** with, e.g. PhC≡CPh leads to the formation of **33**, which indicated that after the [2 + 2] cyclization reaction the formed $\mathrm{WPC_2}$ four-membered ring is stabilized by the tungsten carbonyl fragment. Experiments directed at the extension of this synthetic concept to the congeners As [66] and, preliminarily, Sb [67] for generation of reactive species $[\mathrm{L}_n\mathrm{M{\equiv}E} \rightarrow \mathrm{M'(CO)_5}]$ of the heavier Group 15 elements have been reported.

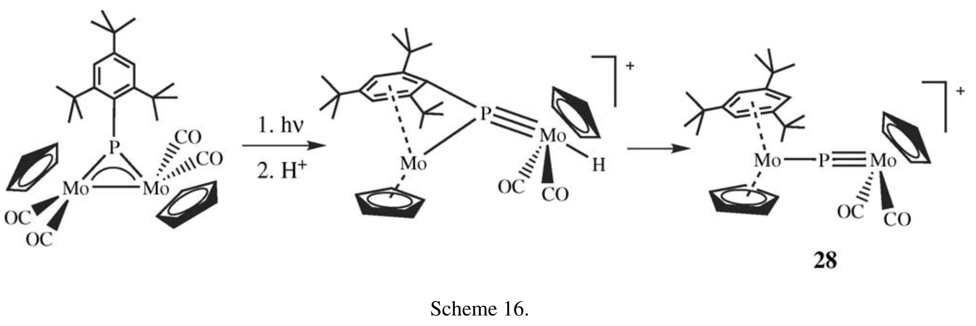


Scheme 15.

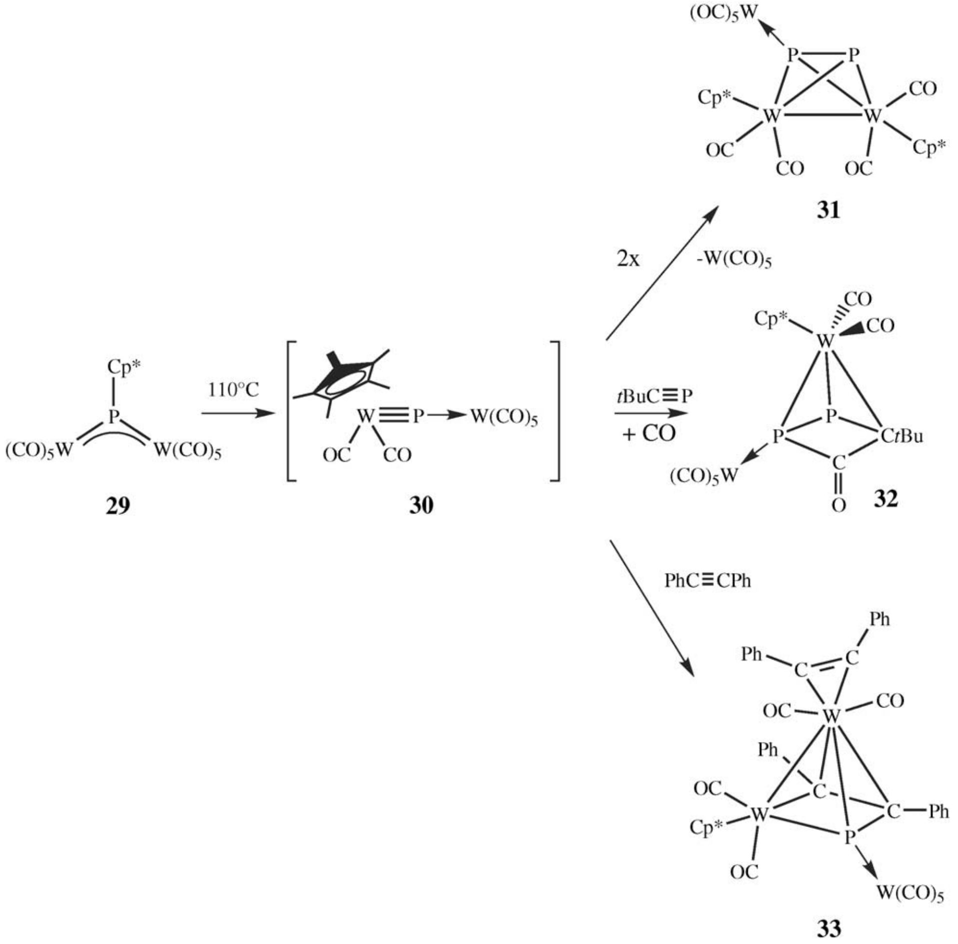
3.4. Bonding situation

For all Lewis-acid coordinated phosphido complexes in Table 2, in comparison with the terminal-coordinated phosphido complexes, an upfield shift of the ^{31}P NMR signal is observed for all examples for which ^{31}P NMR data is available for the uncoordinated parent phosphido complex, with the most sizeable shift exhibited by coordination to GaCl$_3$ in $[(N_3N)W{\equiv}P \rightarrow GaCl_3]$. Coordination to GaCl$_3$ also results in a slight lengthening of the W≡P bond, from 2.162 Å in **10b** to 2.168(4) Å in **18**, indicating a redistribution of σ-contribution from the P lone pair in **10b** back into the W≡P bond in **18** upon coordination to the pure σ-acceptor. This view is supported by the pronounced increase in the coupling constant ^{1}J(WP), from 138 Hz in **10b** to 712 Hz in **18**. In contrast, upon coordination of $[(N_3N)W{\equiv}P]$ to the σ-acceptor/π-donor fragments $[M(CO)_n]$ and $[Rh(CO)(MeCN)]^+$ the W≡P bond lengths are more appreciably lengthened (**20b**: 2.202(2) Å; **21b**: 2.177(5), 2.173(5) Å), as attributable to donation of electron density from π back bonding into the antibonding orbitals on P. The ^{1}J(WP) coupling constants are increased for **19** and **20**, though not as dramatically as for $[(N_3N)W{\equiv}P \rightarrow GaCl_3]$, suggesting the low s-character of the triple bond is not as strongly augmented by coordination to the transition–metal fragments.

Coordination of $[(tBuO)_3W{\equiv}P]$ to transition–metal moieties in **5** induces a similar upfield shift of the ^{31}P NMR signal and increase in the ^{1}J(WP) coupling constants. As with the Lewis-acid coordinated phosphido complexes above, increase in ^{1}J(WP) indicates an increase in the s character in the W≡P bond. This interpretation of the larger coupling constant was supported by calculations using BP86 density functional theory on the model complexes $[(HO)_3W{\equiv}P]$, $[(HO)_3W{\equiv}P \rightarrow W(CO)_5]$, and $[thf(HO)_3W{\equiv}P \rightarrow W(CO)_5]$, which showed that coordination of $[(HO)_3W{\equiv}P]$ to the $[W(CO)_5]$ fragment resulted in rehybridization of the lone pair on P from sp$^{0.14}$ to sp$^{0.98}$ in $[(HO)_3W{\equiv}P \rightarrow W(CO)_5]$ [60]. Additionally, the coordination to $[W(CO)_5]$ resulted in a slight shortening of the W≡P bond length, also in accordance with an increase in s character. The observed W≡P bond length of 2.1261(12) Å in $[thf(ArO)_3W{\equiv}P \rightarrow W(CO)_5]$ remains the shortest W–P bond distance known, while no structural data for the parent phosphido complexes $[(RO)_3W{\equiv}P]$ are available for comparison. Calculations of $[(HO)_3W{\equiv}P]$ and $[(HO)_3W{\equiv}P \rightarrow W(CO)_5]$ using BP86/SVP density



Scheme 16.



Scheme 17.

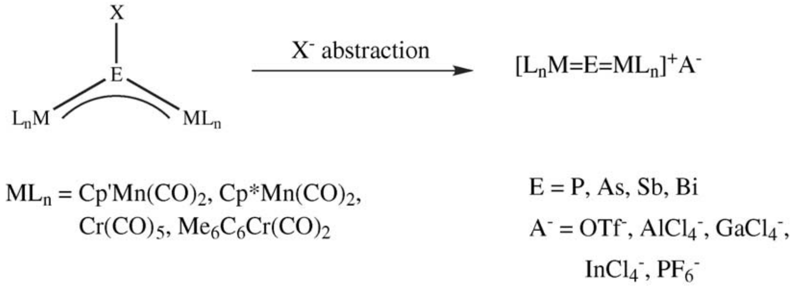
functional theory with RI–J approximations [68] revealed π-type HOMO orbitals. The results of this analysis imply an expected “side-on” reactivity pattern, which was borne out in the reactivity studies of $[(RO)_3W{\equiv}P \rightarrow W(CO)_5]$ shown above.

4. Linear E_1 heterocumulene complexes (CN 2)

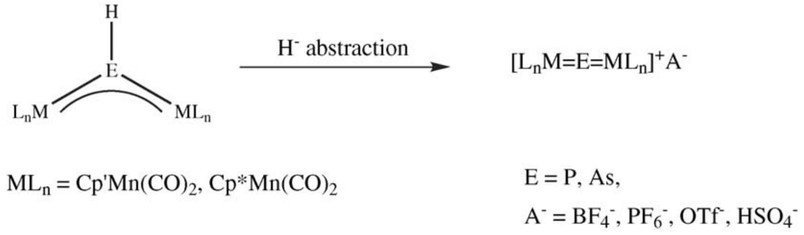
4.1. Cationic heterocumulene complexes

Complexes incorporating a symmetrically bridging pnicogen E_1 ligand of coordination number 2, hereafter referred to as Group 15 heterocumulenes, were first synthesized in the group of Huttner. Employing the readily available pnicogen(III) halides EX_3 as starting materials, halopnictinidene complexes of the type $[\{L_nM\}_2EX]$ have long been accessible [69]. Though cleavage of the remaining E-halide bond at first proved troublesome with a variety of halide abstractors, the silyl triflate Me_3SiOTf was shown to be effective in abstracting chloride from the chloroarsinidene complex $[\{Cp'(CO)_2Mn\}_2AsCl]$ ($Cp' = CH_3C_5H_4$), generating the cationic heterocumulene complex $[Cp'(CO)_2Mn{=}As{=}Mn(CO)_2Cp']^+OTf^-$ (**34a**) in good yield [14]. This synthetic strategy was subsequently generalized for a variety of halide abstractors and for the entire series of heavier pnicogen heterocumulenes (E = As [70], Sb [70,71], Bi [72]) (Scheme 18). The Bi complex $[Cp'(CO)_2Mn{=}Bi{=}Mn(CO)_2Cp']^+OTf^-$ could not be isolated in crystalline form and was trapped as its 2,2′-bipyridine adduct and compared to the formally isoelectronic Groups 14 and 13 chelate adducts $[\{Cp'(CO)_2Mn\}_2Pb(bpy)]$ [73] and $[\{(CO)_4Fe\}_2Tl(bpy)]^-$ [74], respectively. An alternative approach to such complexes for P [75] and As [76] was concurrently developed, in which phosphinidene and arsinidene complexes are treated with hydride abstracting agents (Scheme 19). This alternative route not only circumvents the relative inertness of some pnictinidene–halide bonds, but also increases the number of potential counterions in the final complex. This proved advantageous in the isolation of $[Cp^*(CO)_2Mn{=}As{=}Mn(CO)_2Cp^*]^+BF_4^-$ (**34b**), which was shown to offer higher-quality crystals than the corresponding triflate compound, whose structure determination was unsatisfactory due to disorder of the triflate anion.

Complexes **34** exhibit nearly linear geometry about the bridging pnicogenido ligand. The antimony complex $[Me_6C_6(CO)_2Cr{=}Sb{=}Cr(CO)_2C_6Me_6]^+GaCl_4^-$ (**35**) displays the largest deviation from linearity with an angle of 161.6°. In general, the cationic heterocumulenes react as electrophiles toward a variety of common monodentate anions, i.e. halides



Scheme 18.



Scheme 19.

and pseudohalides, to regenerate pnictinidene complexes of the type [{L$_n$M}$_2$EX] (X = Cl, Br, I, SCN).

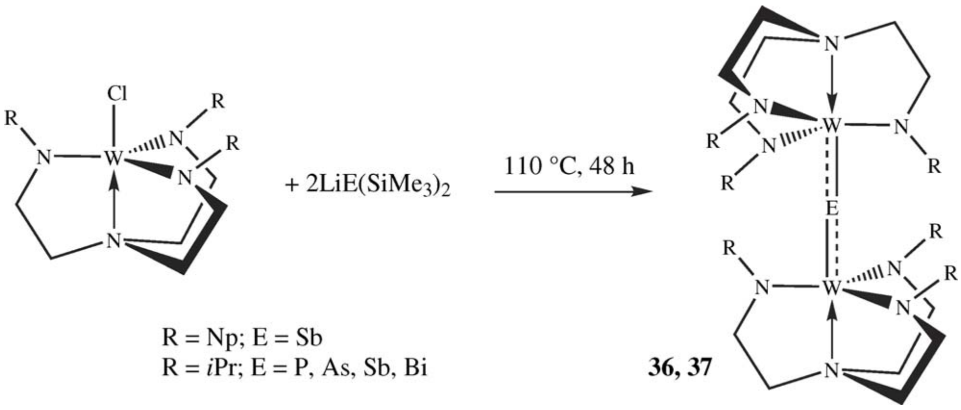
4.2. Neutral heterocumulene complexes

In the cationic heterocumulene work of Huttner et al. attempts to reduce the cationic complex [Cp′(CO)$_2$Mn=As=Mn(CO)$_2$Cp′]$^+$OTf$^-$ to a neutral moiety were carried out. These experiments, instead of generating the corresponding neutral heterocumulene, resulted in dimerization to the complex [{Cp′(CO)$_2$Mn}$_2$AsAs{MnCp′(CO)$_2$}$_2$]. This pathway predominates presumably due to the relatively unencumbering Cp′Mn(CO)$_2$ fragments coupled with the propensity of arsenic to form element–element bonds upon reduction of an As(III) precursor.

In contrast, use of bulky ligands at the transition metal has enabled the synthesis of neutral heterocumulenes. In the work of Scheer et al. experiments were carried out with tungsten complexes bearing TREN-type ligands (RNCH$_2$CH$_2$)$_3$N (R = *i*Pr [77], Np [78]) with the goal of synthesizing complexes possessing terminal W–E triple bonds of the heavier Group 15 elements. For reactions of [{(RNCH$_2$CH$_2$)$_3$N}WCl] with LiE(SiMe$_3$)$_2$ (E = P, As, Sb, Bi) in refluxing toluene for 2 days, the lower degree of steric protection from the *i*Pr and Np groups, as compared to that of SiMe$_3$, resulted in direct formation of tungsten-element neutral heterocumulenes [{[(RNCH$_2$CH$_2$)$_3$N]W}$_2$E] (R = *i*Pr: E = P (**36a**), As (**36b**), Sb (**36c**), Bi (**36d**); R = Np: E = Sb (**37**)). Since synthetic procedures for LiE(SiMe$_3$)$_2$ are known for all Group 15 elements, this route allowed access to the complete series of heavier heterocumulenes (E = P–Bi), each member of which was crystallographically characterized with the exception of E = Bi, which was spectroscopically characterized. Attempts to synthesize the related cationic heterocumulene [{[(RNCH$_2$CH$_2$)$_3$N]W}$_2$P]$^+$ (R = *i*Pr) by reaction of [{[(RNCH$_2$CH$_2$)$_3$N]W}$_2$P] with [Cp$_2$Fe]$^+$[BF$_4$]$^-$ failed, thus illustrating the kinetic stability of this class of complex (Scheme 20).

Neutral heterocumulenes of phosphorus have also been isolated by Cummins et al. by reaction of the terminal phosphido complex [(*i*PrPhN)$_3$Mo≡P] with the trivalent three-coordinate tris(amido) molybdenum complex [(*i*PrPhN)$_3$Mo] [26]. This type of reaction was originally shown as a method of single-atom phosphido transfer from one (RArN)$_3$Mo fragment to another. Through investigations of this transfer process, the intermediate heterocummulene complexes [(*t*BuPhN)$_3$Mo=P=Mo(NPh*t*Bu)$_3$] (**3b**) could be isolated and structurally characterized. While reaction of the associated tris(*N-tert*-butylanilide) molybdenum complex [(*t*BuPh″N)$_3$Mo] with P$_4$ yields exclusively the terminal phosphido complex, treating the sterically less hindered *i*Pr-substituted analogue [(*i*PrPh″N)$_3$Mo] with P$_4$ yields the phosphido-bridged complex [(*i*PrPh″N)$_3$Mo=P=Mo(NPh″*i*Pr)$_3$] (**3a**) [27]. This route offers an alternative synthesis of the neutral heterocummulene by direct transformation of P$_4$. The mechanism of this transformation and of the formation of [(*i*PrPhN)$_3$Mo≡P] was recently elucidated by quantum chemical calculations and kinetic and thermodynamic studies, which showed a complex multi-step mechanism and ruled out direct abstraction of a P atom from P$_4$ [79].

Due to the facile phosphido-transfer capabilities displayed by the tris(amido) molybdenum complexes, the field of heterodinuclear phosphido-bridged complexes has been opened up. Reaction of the phosphido complex [(*i*PrPh″N)$_3$Mo≡P] with the unsaturated niobaziridine–hydride complex [Nb(H)(η^2-*t*Bu(H)C=NPh″)(NPh″Np)$_2$] results in the quantitative formation of the asymmetrically bridged complex [(NpPh″N)$_3$Nb=P-Mo(NPh″*i*Pr)$_3$] (**38**) [80]. In contrast to the associated paramagnetic dimolybdenum phosphides (**3**), replacement of the tris(amido) molybdenum fragment with a tris(amido)niobium fragment results in a diagmagnetic complex, thus allowing ^{31}P NMR measurements for this new type of heteronuclear



Scheme 20.

phosphido-bridged complex. The ^{31}P NMR spectrum of **38** displays a singlet at 666.6 ppm.

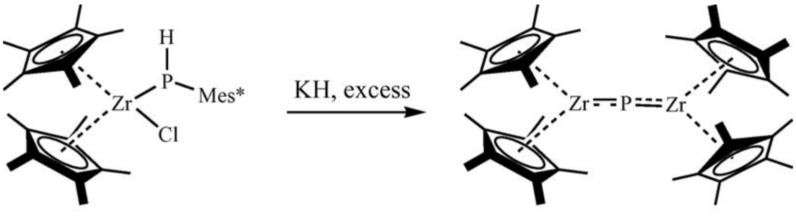
An interesting possibility for forming bridging phosphido complexes via pnicogen–carbon cleavage reactions has been shown by Stephan and co-workers [81]. The precursor zirconium complex [$Cp^*_2Zr(P(H)Mes^*)Cl$] ($Mes^* = 2,4,6$-$t$$Bu_3$-$C_6H_2$) with a bulky primary phosphanide ligand was generated in solution and treated with excess KH, resulting in the neutral linear phosphido-bridged complex [$Cp^*_2Zr{=}P{=}ZrCp^*_2$] (**39**) in low yield. This complex represents the only example of a low-coordinate E_1 ligand supported by a Group 4 transition metal (Scheme 21).

4.3. Anionic heterocumulene complexes

To date only one example of an anionic heavier Group 15 transition–metal heterocumulene has been described. Starting from the neutral phosphorus cumulene complex **3a**, the Cummins group showed that it is possible to reduce the bridged phosphorus species by one electron to the anionic cumulene [27]. Thus, reaction of [(iPrPh$''$N)$_3$Mo=P=Mo(NPh$''$$i$Pr)$_3$] with an excess (20 equivalents) of sodium amalgam in THF produced the corresponding purple anionic complex [Na(thf)][(iPrPh$''$N)$_3$Mo=P=Mo(NPh$''$$i$Pr)$_3$] (**40**) in 68% yield. The structure of this complex shows a contact between the sodium cation and the phosphido ligand (3.228(4) Å) as well as π-interaction of the sodium cation with one of the aryl groups of the anilide ligands, resulting in an asymmetric geometry in the solid state. However, ^{1}H and ^{13}C NMR spectra revealed equivalent anilide ligands in C_6D_6 solution at room temperature, indicating a fluxional process. In contrast to the neutral, symmetrically bridged cumulene species **3a**, **40** is diamagnetic, displaying a ^{31}P NMR shift at $\delta = 794$ ppm.

4.4. Bonding situation

For the series of cationic to neutral to anionic, symmetrically bridged cumulene complexes $[L_nM{=}E{=}ML_n]^m$ ($m = +1$, 0, -1), the question arises to what extent the addition of an electron influences bonding to the bridging pnicogenido ligand E. Though no complete series representing the three different charges is known for a given metal fragment ML_n, some direct individual comparisons and conclusions can be made. For the cationic cumulene complexes, a significant shortening of the M–E bond length was observed in comparison to the corresponding parent pnictinidine complexes $[\{L_nM\}_2EY]$ (Y = Cl, H), suggesting a strengthening of the M–E bond. Accordingly, the carbonyl absorptions in the IR spectra are shifted to higher frequencies, and the UV–vis spectra reveal a shift to shorter wavelengths for absorptions ascribed to the ππ*-transition. Except for [$Me_6C_6(CO)_2Cr{=}Sb{=}Cr(CO)_2C_6Me_6$]$GaCl_4$ (**35**) each cationic complex displays a torsion angle of approximately 90° along the M–E–M axis (Table 3), in accordance with the description of such complexes as cationic allene analogues. Based on these observations, a M–E bond order of 2 was assigned. For complex **35**, a relative lack of rotation along the Cr–Sb–Cr axis (Z–Cr–Cr–Z torsion angle = 3.9°) was observed, which stands in contrast to the expected 90° for allene-type complexes. However, the description as an allene analogue was upheld based on the argument that, in contrast to organic allenes, the two transition–metal fragments possess d-type orbitals perpendicular to each other that participate in π-bonding to



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Scheme 21.

Table 3
M–E bonding distances and M–E–M bonding angles for heterocumulene-type complexes (type **C**)

Complex	*d* (M–E) (Å)	Angle M–E–M (°)	Ref.
[Cp′(CO)$_2$Mn=As=Mn(CO)$_2$Cp′]O$_3$SCF$_3$ (**34a**)	2.142(3), 2.143(3)	174.8(1)	[76]
[Cp*(CO)$_2$Mn=As=Mn(CO)$_2$Cp*]BF$_4$ (**34b**)	2.142(2), 2.151(2)	176.3(1)	[14]
[Cp′(CO)$_2$Mn=As=Mn(CO)$_2$Cp′]GaCl$_4$ (**34c**)	2.118(2), 2.131(2) 2.153(2), 2.156(2)[a]	175.3(1) 170.9(1)[a]	[70]
[Me$_6$C$_6$(CO)$_2$Cr=Sb=Cr(CO)$_2$C$_6$Me$_6$]GaCl$_4$ (**35**)	2.378(2), 2.396(2)	161.6(1)	[71]
{[(*i*PrNCH$_2$CH$_2$)$_3$N]W}$_2$P (**36a**)	2.2331(4)	180.0	[77]
{[(*i*PrNCH$_2$CH$_2$)$_3$N]W}$_2$As (**36b**)	2.3331(5)	180.0	[77]
{[(*i*PrNCH$_2$CH$_2$)$_3$N]W}$_2$Sb (**36c**)	2.5275(5)	180.0	[77]
{[(NpNCH$_2$CH$_2$)$_3$N]W}$_2$Sb (**37**)	2.5738(8)	180.0	[78]
(*i*PrPh″N)$_3$Mo=P=Mo(NPh″*i*Pr)$_3$ (**3a**)	2.2164(4)	180.0	[27]
(*t*BuPhN)$_3$Mo=P=Mo(NPh*t*Bu)$_3$ (**3b**)	2.2430(6)	180.0	[26]
(NpPh″N)$_3$Nb=P-Mo(NPh″*i*Pr)$_3$ (**38**)	Nb-P: 2.294(13) Mo-P: 2.262(23)	170.55(4)	[80]
Cp*$_2$Zr=P=ZrCp*$_2$ (**39**)	2.545(3)	166.6(4)	[81]
[Na(thf)][(*i*PrPh″N)$_3$Mo=P=Mo(NPh″*i*Pr)$_3$] (**40**)	2.183(2), 2.197(2)	173.87(10)	[27]

[a] In the solid-state structure of **34c**, two crystallographically independent molecules are found, giving rise to two sets of structural data.

the bridging Sb ligand. The upfield shift of the ^{31}P NMR signal in [Cp′(CO)$_2$Mn=P=Mn(CO)$_2$Cp′]PF$_6$ ($\delta = 172$ ppm) in comparison to the parent complex [{Cp′(CO)$_2$Mn}$_2$PH] ($\delta = 816$ ppm) indicates a larger degree of participation of π-bonding in the cumulene complex.

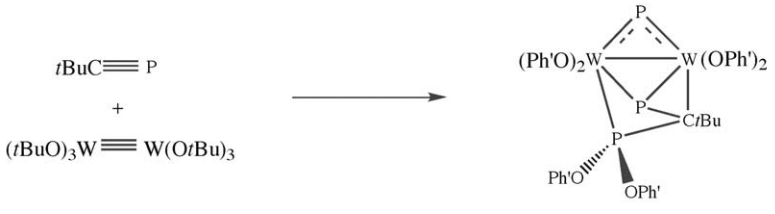
For the neutral cumulene-type complexes, short M–E bond distances are also observed, though these are longer than the associated triply bonded terminal pnictido species. No ^{31}P NMR data in the P congeners are available for the neutral, bridged paramagnetic compounds. The electronic configuration for the M–E–M system is likely $(1\pi_u)^4(1\pi_g)^3$, which suggests a mixed-valent M(IV)/M(V) species and a M–E bond order of either 1.5 or 2. The bonding situation in [(NpPh″N)$_3$Nb=P-Mo(NPh″*i*Pr)$_3$] (**38**) has not yet been investigated by theoretical calculations or reactivity studies, though it has been initially represented as having a Nb–P double bond and a Mo–P single bond [80].

The ^{31}P NMR shift of the anionic complex [Na(thf)][(*i*PrPh″N)$_3$Mo=P=Mo(N(*i*PrPh″)$_3$] (**40**) ($\delta = 794$) is found in the far downfield region, but significantly upfield from the parent terminal phosphide [(*i*PrPh″N)$_3$Mo≡P] ($\delta = 1256$). The Mo–P bond distances of **40** (2.183(2), 2.197(2) Å) are minimally shortened in comparison to those of the neutral phosphide-bridged species **3a** (2.2164(4) Å), indicating no significant increase in the Mo–P bond order. Calculations using the Amsterdam density functional package [see supporting information in reference 27] showed that the additional electron occupies a primarily nonbonding orbital, and therefore was not expected to heavily influence the Mo–P bonding.

5. Complexes with E$_1$ ligands in bent coordination mode (CN 2)

Very little has been reported on complexes with pnicogen ligands in a bridging, nonlinear coordination mode. This area of chemistry is established in large part only for nitrogen [4]. However, two phosphorus representatives as well as one antimony representative were reported. The reason for the scarcity of the bent coordination mode (types **D** and **F**) is due to the predominant tendency of the pnicogen atom to incorporate its lone pair into the bonding to form a coordination number three or linear heterocumulene-type complexes.

The first complex of type **D** was synthesized in the Scheer group by the metathesis reaction of [W$_2$(OPh′)$_6$] with *t*BuC≡P [82] (Scheme 22). A reaction mechanism for the formation of **41** was proposed as the dimerization of the intermediate phosphido complex [(Ph′O)$_3$W≡P], incorporation of a further equivalent phosphaalkyne, followed by a 1,3-Ph′O shift from tungsten to phosphorus with simultaneous W–W bond formation. Evidence for such a mechanism is provided by the isolable complex [(Ph′O)$_2$W{μ,η^2-PW(CO)$_5$}]$_2$ (**25b**) [60] which is clearly obtained by reductive dimerization of [thf(Ph′O)$_3$W≡P → W(CO)$_5$] (**24d**).



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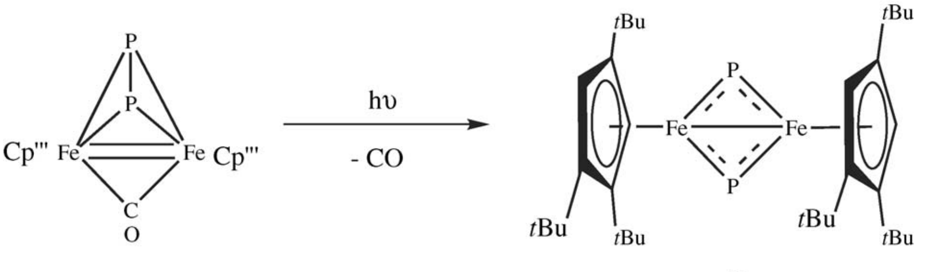
Scheme 22.



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Scheme 23.

The naked phosphorus atom in **41** bridges the two tungsten atoms in a slightly asymmetric fashion (Fig. 4), as revealed by the P–W bond lengths (2.301(2) and 2.284(2) Å). It was speculated that the reason for asymmetry of the phosphido bridge is the electronically different tungsten atoms. The ^{31}P NMR resonance for the substituent-free phosphorus ligand in **41** at $\delta = 831.8$ ppm with a relatively small ^{1}J(WP) coupling constant (216 Hz) attests to its phosphido character.

An extremely low-field ^{31}P chemical shift ($\delta = 1406.9$ ppm) was reported for the complex [(Cp‴Fe)$_2$(μ-P)$_2$] (**42**) [83] synthesized by Scherer and co-workers (Scheme 23). The structure of **42** consists of a rhombic, nearly planar Fe$_2$P$_2$ four-membered ring with short Fe–P (2.10 Å (av.)) and Fe–Fe (2.5004(4) Å) distances as determined by single-crystal X-ray diffraction (Fig. 5). The phosphorus ligands in **42** are three-electron donors, and a Fe=Fe double bond was proposed in order to achieve 18 valence electrons at each iron. **42** was synthesized by the photochemical activation of the diphosphadiferratetrahedrane [(Cp‴Fe)$_2$(μ-CO)(μ,η^2-P$_2$)].

The only complex containing a bent bridging di-coordinated antimony, as mentioned in a conference abstract, is [N{CH$_2$CH$_2$(Me$_3$Si)N}$_3$Ta(μ-Sb)(μ-N)Ta{N(SiMe$_3$)CH$_2$CH$_2$}$_2$N(CH$_2$CH$_2$-)] (**43**), with Sb(SiMe$_3$)$_3$ as the antimony source [84], though experimental details were not given. To the best of our knowledge, other complexes containing low-coordinate bent bridged heavier Group 15 elements have not been reported in the literature so far.

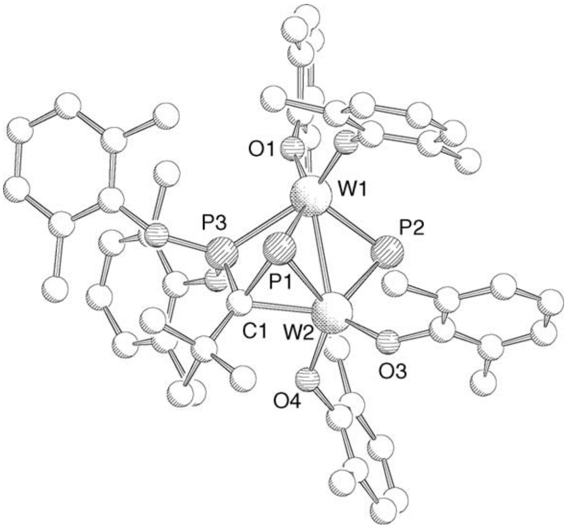

Fig. 4. Molecular structure of **41**. H atoms have been omitted for clarity.

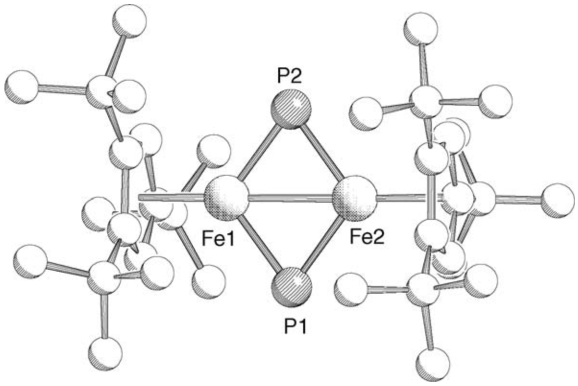

Fig. 5. Molecular structure of [(Cp‴Fe)$_2$(μ-P)$_2$] (**42**). H atoms have been omitted for clarity.

6. Conclusion

The overview has shown that the field of low-coordinate E$_1$ complexes of Group 15 elements is still a rapidly developing area of chemistry. The special challenges in this field include the following:

i. The high reaction potential of terminally as well as asymmetrically bridged pnictido ligand complexes of types **A** and **B**. Here, especially the high ‘side-on’ reactivity of the alkoxy substituted complexes **5** and **24** is of further interest. Furthermore, by partial alcoholysis the previously kinetically stabilized amido-substituted Mo-complexes **2** obtain ‘side-on’ reactivity, representing a way to increase the reaction potential of this class of compounds.
ii. In all classes of compounds, except in the neutral and cationic heterocumulene cases, the heavier congeners are missing. Thus, the synthesis, structural characterization, and study of the bonding situation of Sb and Bi complexes remain still a challenging field.
iii. The bent bridging coordination mode of E$_1$ complexes exists only in few, mainly P-containing examples. Considering the high interest in the reactivity study of complexes of the types **A** and **B**, it is to be expected that this field will also benefit

through these pursuits, and thus an increase in the number of complexes of type **F** can be expected.

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