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Metal element triple bonds of the heavier group 15 elements[1]

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Contents

Abstract

Complexes with terminal pnictinido ligands (except nitrogen) are a new class of compounds the first examples being phosphido[2] ligands which were isolated and structurally characterized in 1995 by Cummins and Schrock. As long as 10 years ago, however, speculation on the existence of possible reaction intermediates containing $M{\equiv}E$ species was given both with and without spectroscopic evidence. This article will summarize the past and current stages in this field and give the presently known properties and characteristics of such ligands. © 1997 Elsevier Science S.A.

Keywords: Pnicogenido complexes; Metal–group 15 element triple bonds; Phosphinidene complexes; PS/PO ligand complexes

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[1] Dedicated to Prof. Dr. G. Huttner on the occasion of his 60th birthday.

[2] The term phosphido ligand for the P^{3-} ligand corresponds to the IUPAC guidelines (compare also: arsenido, antimonido- and bismutido ligands). Hitherto this name has often been used incorrectly for the R_2P ligand.

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1. Introduction

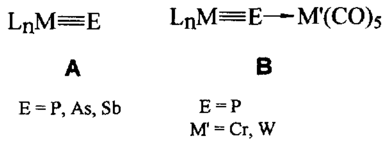
In recent years interest in complexes containing multiple bonds between transition metal and main group elements has risen dramatically [1]. This field is dominated by compounds with terminal ligands from elements of the first row of the periodic table with $M{=}E$ (e.g. $E{=}CR_2$, NR, O) or $M{\equiv}E$ units ($E{=}CR$, N). The synthesis of complexes containing the higher homologues of the main group elements was first achieved in the early 1990s when, for example, Parkin et al. succeeded in synthesizing the first complexes with terminal tellurido ligands [2].

For complexes containing ligands of group 15 elements the situation can be characterized as follows: Coordination compounds with terminal nitrido ligands have been known for a long time [3,4]. Examples include square-pyramidal complexes of the type $[MNCl_4]^-$ (M = Mo, W, Re, Ru, Os) [5], characterized by a very short metal–nitrogen bond. The Lewis base properties of the nitrido ligands are shown with the addition of Lewis acids such as BF_3, and their tendency towards intermolecular association [3]. Recently work on cyclotrimerisation reactions was also published [6]. For the heavier group 15 elements, there are a small number of linear coordinated phosphinidene complexes (cf. 3.2), but until recently, no examples of isolated and completely characterized compounds with a terminal E_1 ligand, containing a metal–pnictinido formal triple bond have been reported; although numerous examples of coordination polyhedra with E_1 ligands are known [7]. In 1995 a breakthrough occurred in this field with the first isolated and structurally characterized complexes containing metal–phosphorus triple bonds, independently obtained by the groups of Cummins [8] and Schrock [9].

2. Metal element triple bond species as intermediates

Generally two types (A and B) of pnicogenido complexes are described when discussing intermediates of reactions characterized by 15 VE L_nM fragments coordinated via a triple bond to the 3 VE E_1 ligand. Both types obey the noble gas rule.

Since the species are sterically unencumbered they stabilize themselves via cyclodimerisation or with other reactive compounds, via cyclization reactions. In the case of phosphido ligands coordinated additionally to metal pentacarbonyls (type B) this high reactivity can be partially hindered. The isolation of such cyclised reaction products as well as so-called "precursor molecules" led to speculation about the existence of $M{\equiv}E$ species.



$$L_nM{\equiv}E \qquad L_nM{\equiv}E{\rightarrow}M'(CO)_5$$

A E = P, As, Sb

B E = P, M' = Cr, W

Fig. 1. Types of pnicogenido complexes.

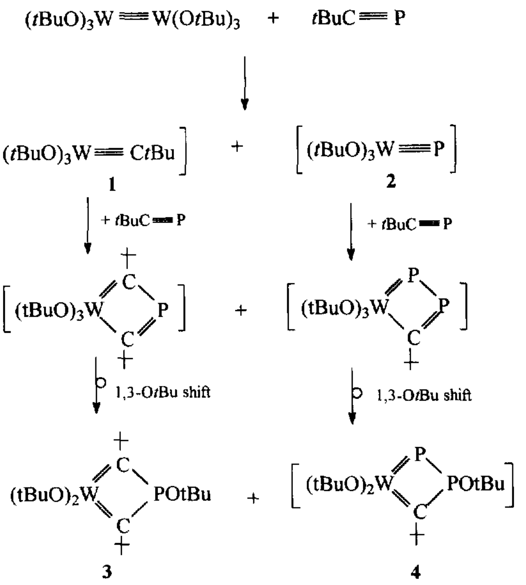
2.1. Phosphido complexes

The possibility of a phosphido complex intermediate was first suggested in 1985 by Becker et al. [10], from the reaction of $[W_2(OtBu)_6]$ with the phosphaalkyne $tBuC{\equiv}P$. Based on the identification of **3**, with a WC_2P four-membered ring, and on data from ^{31}P-NMR spectroscopy for a possible intermediate **4**, a reaction pathway as shown in Scheme 1 was proposed [10a, 11]. Accordingly, a metathesis reaction between the phosphaalkyne $tBuC{\equiv}P$ and the tungsten complex $[W_2(OtBu)_6]$ proceeds to afford the alkylidyne compound **1** and the phosphido complex **2**. Further rapid reaction with phosphaalkyne produces intermediates with four-membered rings which stabilize themselves by a 1,3-migration of an alkoxy group to give the final products **3** and **4**. Facts supporting the first step methathesis reaction are the known generation of alkylidyne complexes by the reaction of $[W_2(OtBu)_6]$ with alkynes Eq. (1) and of nitrido complexes using nitriles Eq. (2) [12].

$$(tBuO)_3W{\equiv}W(OtBu)_3 + R'C{\equiv}CR \longrightarrow (tBuO)_3W{\equiv}CR + (tBuO)_3W{\equiv}CR' \quad (1)$$

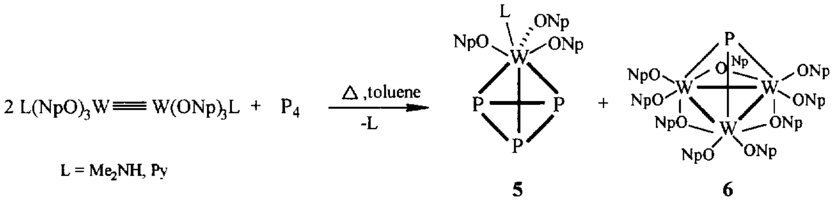
$$(tBuO)_3W{\equiv}W(OtBu)_3 + RC{\equiv}N \longrightarrow (tBuO)_3W{\equiv}CR + (tBuO)_3W{\equiv}N \quad (2)$$

In 1987 Chisholm and coworkers carried out the reaction of $[W_2(ONp)_6L_2]$ (Np = Neopentyl, L = $HNMe_2$, Py) with P_4 phosphorus. They observed the formation of



Scheme 1. Proposed reaction pathway for the formation of 3.

tetrahedral complexes with either P_1 or P_3 ligands, respectively, Eq. (3) [13]. It was speculated that a trinuclear cluster **6** was a product of a conproportionation of $[W_2(ONp)_6]$ and a reactive phosphido complex $[(NpO)_3W{\equiv}P]$, Eq. (4). This assumption is supported by the established formation of alkylidyne [14], oxo [15] and imido [16] capped trinuclear clusters of molybdenum and tungsten ligated by alkoxide groups in an analogous manner as the proposed reaction Eq. (4).



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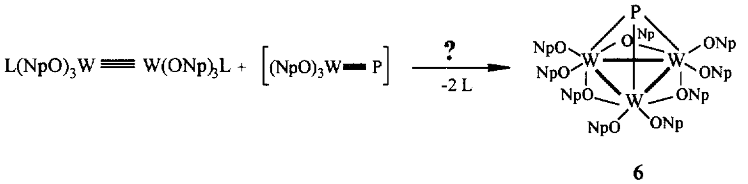

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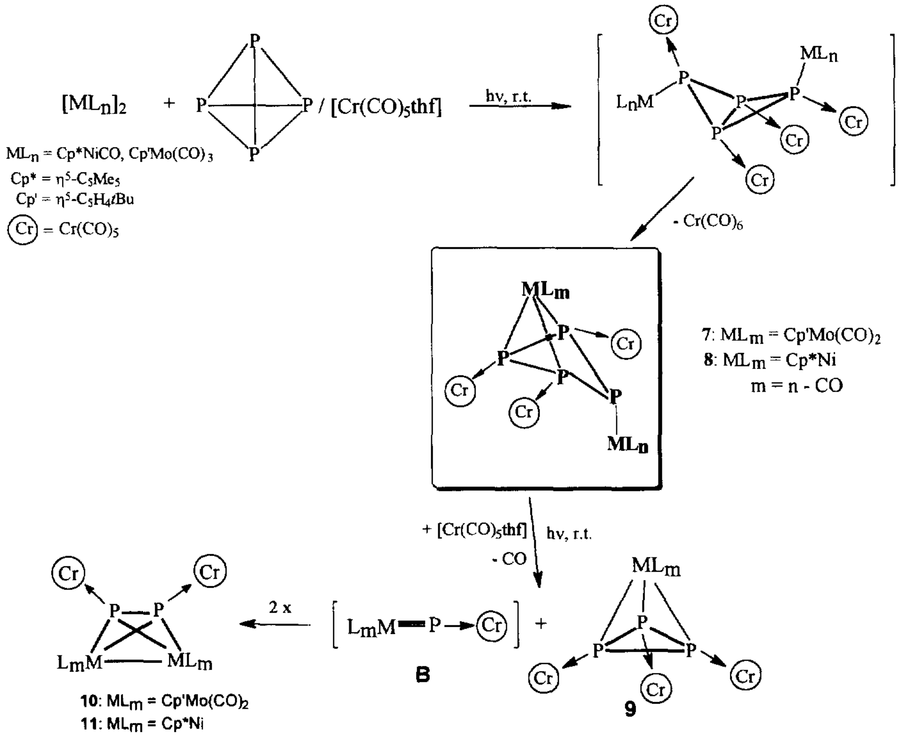
In recent years our group has developed a concept for studying the transformation pathway of the P_4 tetrahedron in the coordination sphere of transition metal complexes [17]. By the addition of simple carbonyl complexes such as $[Cr(CO)_5(thf)]$ to the reaction solutions of P_4 with the corresponding coordination compounds, it is possible to stabilize intermediates through the coordination of the lone pairs on the phosphorus atoms to the ML_5 carbonyl complexes (three-component-reaction) [17]. By studying the transformation pathway of tetrahedral P_4 in the coordination sphere of transition metals with an odd number of valence electrons, we observed a P_1/P_3 fragmentation of the P_4 molecule [18] with a possible phosphido complex intermediate of the type **B** ($M' = Cr$). In the case of the reaction of P_4 with complexes of the type $[Cp'Mo(CO)_3]_2$ and $[Cp^*NiCO]_2$ it has been possible to isolate and structurally characterize the precursor molecules **7** and **8** of this fragmentation, where the P_3/P_1 fragmentation is pre-formed (Scheme 2).

Although the main pathway of the reaction starting with $[Cp^*Ni(CO)]$ is the formation of a Ni_2P_4 prismane complex under photochemical conditions, the NiP_3 complex **9** and the Ni_2P_2 tetrahedral product **11** are also obtained [18a]. For the corresponding reaction starting with $[Cp'Mo(CO)_3]_2$ the Mo_2P_2 tetrahedral complex **10** is the main product [18b]. The formation of **10** and **11** can be viewed as dimerisation of two phosphido complex intermediates of type **B**.

Another approach for phosphido ligand intermediates of type **B** is the reaction of chlorophosphinidene complexes with different metalates forming 15 electron fragments (Scheme 3) [19]. Via metal phosphorus bond formation and the elimination of a metal hexacarbonyl the highly reactive triple bond species B can be formed. Stabilization of these intermediates proceeds once again by dimerisation reactions



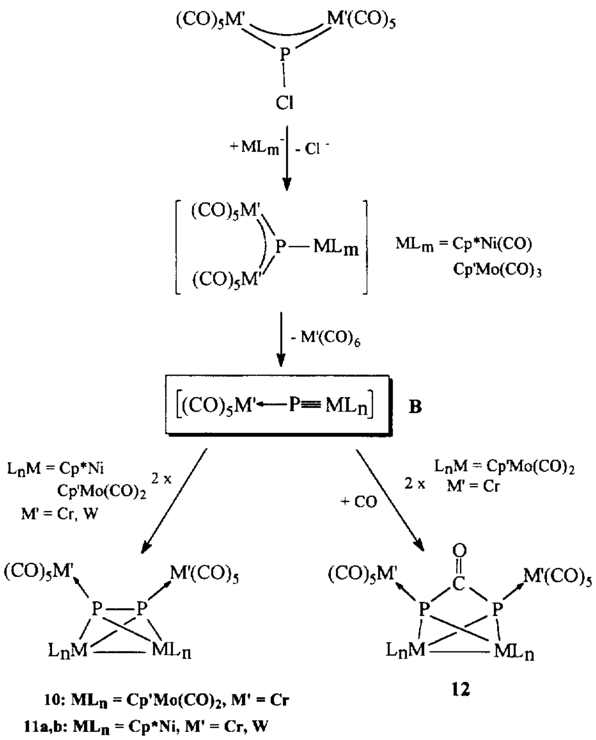
Scheme 2. Reaction pathway of the reaction between $[Cp^{*}NiCO]_2$ or $[Cp'Mo(CO)_3]$ and P_4 in the presence of $[Cr(CO)_5thf]$.

to give the M_2P_2 tetrahedral complexes **10** and **11**, which are isolated as the main products.

There is considerable supporting evidence for the proposed reaction pathway: (A) The reaction with $Cp'Mo(CO)_3$ metalate gives a CO inserted product **12** as well as the Mo_2P_2 tetrahedral complex **10** in about the same yield. It was shown that under the conditions used there is no way for the CO insertion to occur starting from the Mo_2P_2 complex **10**, concluding that this process occurs during the P–P bond formation. (B) The reaction shown in Scheme 4 of an equimolar mixture of the chlorophosphinidene complexes of chromium and tungsten with $[Cp^{*}NiCO]^{-}$ results, in addition to **11a,b**, in a mixed substituted product **13** in a statistical ratio of 1:1:2.

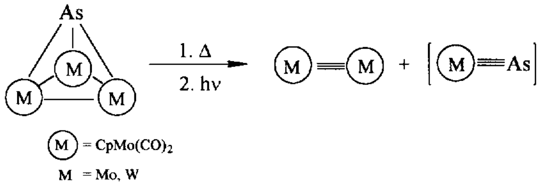
2.2. *Arsenido complexes*

Ziegler et al. postulated the existence of species $[Cp(CO)_2M{\equiv}As]$ (M = Mo, W) as intermediates during the thermolysis and co-photolysis, respectively, of $[\{CpM(CO)_2\}_3(\mu_3\text{-}As)]$ Eq. (5). The metal–metal triply bonded compounds $[\{CpM(CO)_2\}_2]$ (M = Mo, W) were isolated and the existence of the arsenido species



Scheme 3. Proposed reaction pathway of the reactions of chlorophosphinidene complexes with different metalates forming 15 VE fragments.

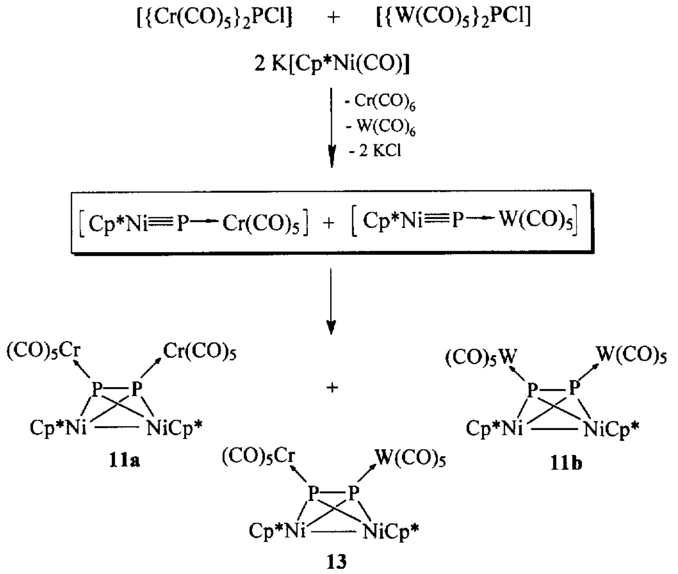
was indirectly deduced from the nature of the reaction products with $[CpM'(CO)_2]$ ($M'=Co$, Rh) [20a,b] (Scheme 5) and with $[Fe_2(CO)_9]$ and $[Fe(CO)_5]$ [21a,b].



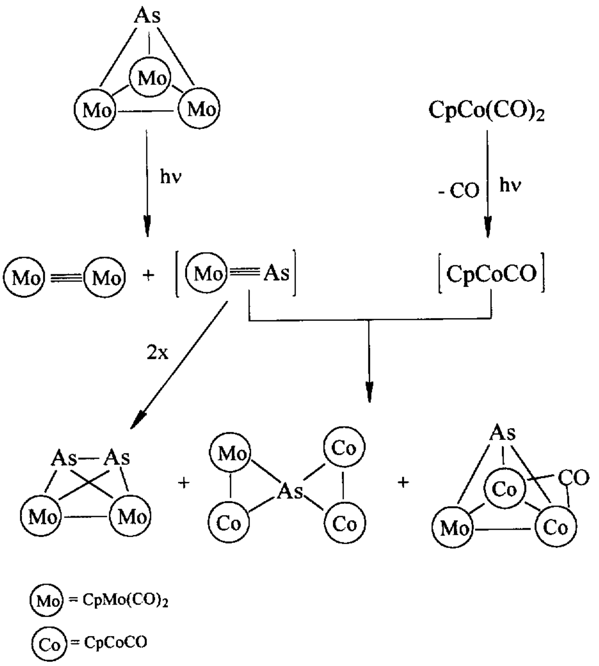
(5)

2.3. Stibido complexes

Rheingold et al. reported a gas-phase reaction of Sb_2^- species, generated by laser evaporation of antimony metal, with carbonyl complexes in an ion-cyclotron spectrometer (FT-ICR) [22]. Under these conditions the formation of the anionic complexes $[(CO)_nM{\equiv}Sb]^-$ ($n=4$, $M=Cr$, Mo, W; $n=3$, $M=Fe$) was detected. *Ab-initio*-MP2 calculations on the Mo complex indicated a square-pyramidal structure (C_{4v} symmetry) with a $Mo{\equiv}Sb$ bond length of 2.55 Å.



Scheme 4. Reaction of $[\{(CO)_5M'\}_2PCl]$ (M′ = Cr, W) with $K[Cp^*Ni(CO)]$.

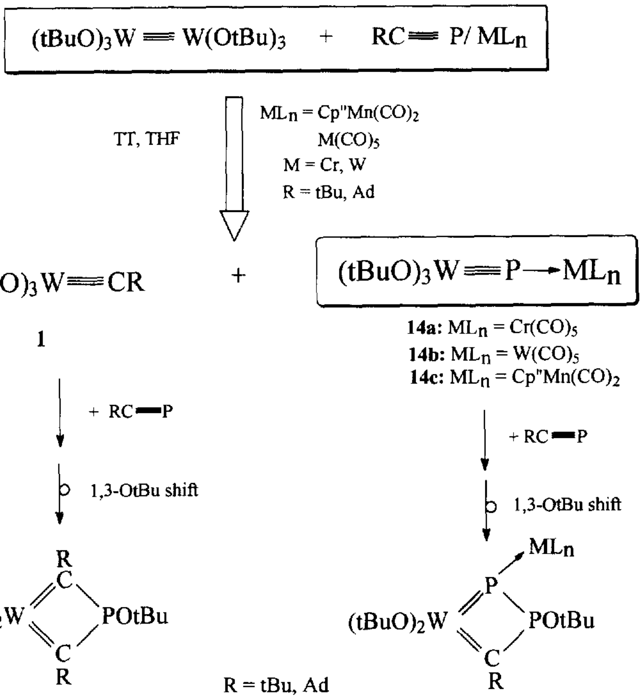


Scheme 5. Proposed reaction pathway of the photolysis of $[\{CpM(CO)_2\}_3(\mu_3\text{-As})]$ with $[CpCo(CO)_2$.]

3. Metal element triple bonds in stable compounds

3.1. Phosphido and arsenido complexes

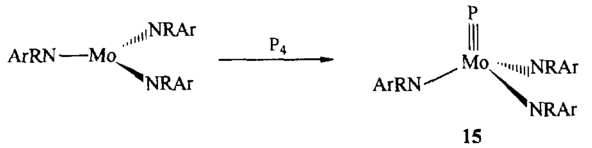
Using the concept of the three-component-reaction to stabilize reactive intermediates, in our laboratories the reaction shown in Scheme 1 was carried out in the presence of Lewis acidic carbonyl complexes; resulting in the formation of the alkylidyne complex **1** and the phosphido complexes **14** [23]. However, a subsequent reaction with additional *t*BuC≡P followed by 1,3-migration of the alkoxy ligand to form compounds with four-membered rings, cannot be completely prevented (Scheme 6). Due to the decomposition of the products the reaction mixture could not be separated by column chromatography: The enrichment of **14** in solution was achieved by fractional crystallization. The best results (25% yields) are obtained for complex **14c** using the Cp"Mn(CO)$_2$ substituted derivative, reflecting the need for a larger steric influence to hinder further reactions of the triply bonded compound. The ^{31}P NMR chemical shifts at $\delta = 595.4$ (**14a**), 544.6 (**14b**) and 614.0 (**14c**), the large $^1J(^{183}W,^{31}P)$ coupling constants of 536 Hz (**14a**), 554 Hz (**14b**) and 566 Hz (**14c**), and the appearance of a second coupling in the case of the [W(CO)$_5$]-substituted product **14b** of $J = 163$ Hz together with the ratio of the signal integrals proves the existence of **14**.



Scheme 6. Reaction of [W$_2$(O*t*Bu)$_6$] with RC≡P in the presence of a Lewis acid carbonyl compound.

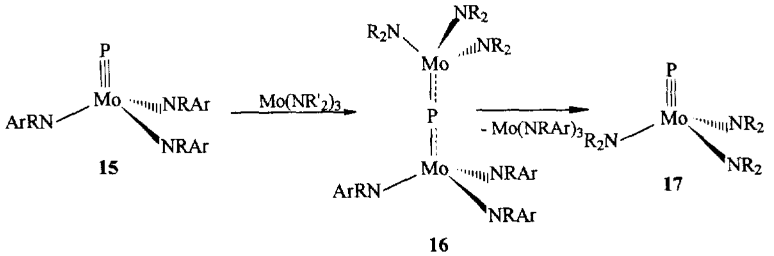
The first isolated and structurally characterized phosphido complex **15** was obtained from the reaction of a molybdenum(III) complex with P_4 in good yields (79%) Eq. (6) [8]. The molybdenum starting material $[Mo(NRAr)_3]$ is planar, the three unpaired electrons localized on the Mo atom [24]. This complex is extremely reactive and can cleave N–N bonds in N_2O [24] and even in N_2 [25] under very mild conditions to form nitrido complexes and nitrosyl complexes. Interesting is the comparison of **15** with the nearly isostructural nitrido complex $[(Ph_2N)_3Mo{\equiv}N]$ [46]. Due to the larger phosphorus atom, the angle E≡Mo–N in **15** is, with a value of 104.8(2)°, larger than that (100.9° average) in the nitrido complex.

Furthermore it was also shown that the phosphido ligand in **15** can be transferred to a second molybdenum fragment Eq. (7). The intermediate **16** was isolated and characterized by X-ray analysis [26]. The Mo–P bond is lengthened from 2.119(4) Å in **15** to 2.2429(6) Å.



(6)

R = $C(CD_3)_2CH_3$; Ar = 3,5-$C_6H_3Me_2$

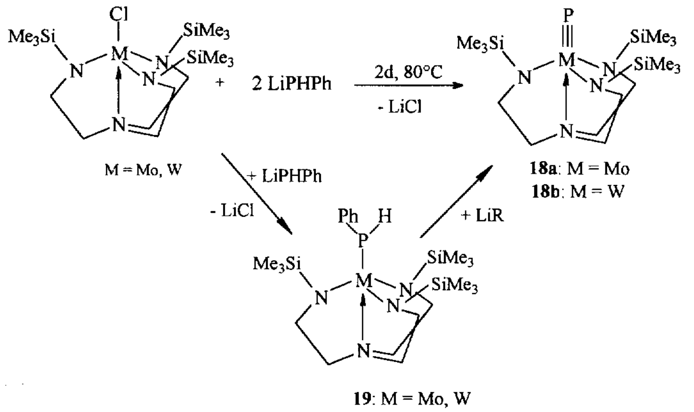


(7)

R = $C(CD_3)_2CH_3$; Ar = 3,5-$C_6H_3Me_2$

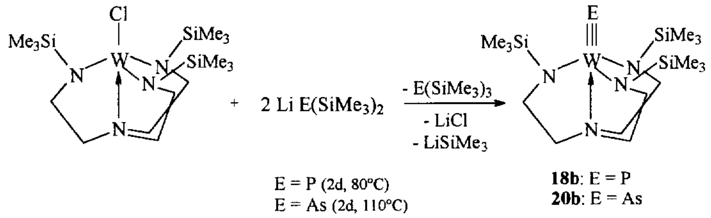
A report by Schrock et al. detailing the N_3N ligand ($N_3N = (Me_3SiNCH_2CH_2)_3N)$) for the synthesis of the phosphido complexes **18a,b** [9] appeared at the same time as that describing the above mentioned complex **15** [8]. This ligand promotes the formation of a multiple bond between the transition metal and the ligand *trans* to the intramolecular N donor. Thus $[(N_3N)MCl]$ (M = Mo, W) reacts with MeLi to give the corresponding $M{-}CH_3$ derivative. Under mild thermal conditions (80 °C), $[(N_3N)WCH_3]$ loses H_2 to form the alkylidyne complex $[(N_3N)WCH]$ [27]. The nitrido complex $[(N_3N)_3Mo{\equiv}N]$ [28] is also known. Using the same synthetic principle, the phosphido complexes **18a,b** are accessible in yields of about 60% and 50% Eq. (8). Obviously the phenylphosphanido complexes **19a,b** are precursors of **18a,b**, which need another equivalent of a base (either LiPHPh or LiR) [29] to give the triply bonded products Eq. (8). With LiAsHPh, the arsenido complex $[(N_3N)Mo{\equiv}As]$ **20a** was also obtained and the analogous W complex **20b** was recently described as a product of the reaction of $[(N_3N)WPh]$ with $PhAsH_2$

[29]. The ^{31}P-NMR shifts of the phosphido complexes display chemical shifts (1080–1346 ppm) at very low field. ^{31}P-MAS-NMR data were published for **15** and **18a,b** reporting the components of the chemical shielding tensors. For **15**, using the B3LYP density functional method, a relatively small energy gap between σ(Mo–P) and π*(Mo–P) MOs was shown to be responsible for the remarkable paramagnetic shielding at directions perpendicular to the M≡P bond [30].



(8)

Independent studies in our laboratories[3] probed the use of lithium-bis(trimethylsilyl)pnictides $[E(SiMe_3)_2]^-$ (E = P, As) in reaction Eq. (9) to afford the phosphido complex **18b** (65%) and the arsenido complex **20b** (48%) [31]. No Me_3Si substituted phosphanido derivative could be detected by following reaction Eq. (9) by ^{31}P NMR spectroscopy. Instead, with growing amounts of **18b**, an increase in the amount of $P(SiMe_3)_3$ is detected indicating the limiting step of reaction Eq. (9) to be the formation of the phosphanido complex $[(N_3N)W{-}P(SiMe_3)_2]$. In a fast reaction this is subsequently metalated by a second equivalent of $LiP(SiMe_3)_2$ with the elimination of $P(SiMe_3)_3$, forming the phosphido complex **18b** by, presumably, the metal-catalyzed elimination of $LiSiMe_3$. These conclusions are in accordance with the results on the reaction pathway of multiple P–P bond formation [32] as well as with the above mentioned findings by Schrock Eq. (8).



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[3] The ^{183}W,^{31}P coupling constant of **18b** (138 Hz) was in contradiction to the coupling constants observed for the carbonyl stabilized phosphido complexes **14a–c** (**14a**: 536 Hz, **14b**: 554 Hz) [23]. Therefore we decided to synthesize **18b**, starting with lithium-bis(trimethylsilyl)phosphanide and subsequent complexation with $[W(CO)_5(thf)]$. Furthermore, it opens the possibility to use bis(trimethylsilyl)pnictides $[E(SiMe_3)_2]^-$ (E = As, Sb, Bi) to synthesize complexes containing the heavier homologues of phosphorus.

Raman spectroscopic studies of the triply bonded metal ligand complexes of the type [$(N_3N)M{\equiv}E$] have provided the frequencies and force constants for the $M{\equiv}E$ oscillators (Table 1) [29]. The reduction in the $W{\equiv}E$ force constant [$k(W{\equiv}N) \gg k(W{\equiv}P) > k(W{\equiv}As)$] with increasing $W{\equiv}E$ bond length [$d(W{\equiv}N) = 1.70\text{-}1.75$ Å [33,34] $\ll d(W{\equiv}P) = 2.162(4)$ Å $< d(W{\equiv}As) = 2.2903(11)$ Å] is expected from the force constant/bond distance relationship. For a given E, it is found that $k(W{\equiv}E) > k(Mo{\equiv}E)$, a general trend which is also consistent with data from transition-metal oxo complexes, for which force constants involving 4d metals are typically smaller than those of 5d elements series [35,36].

By applying the B-P86/SVP density functional approximation equilibrium structures of the triple bond containing compounds **18b**, **20b**, **24** and **25** were calculated [31]. There is a good agreement between the calculated and experimentally observed structures with the exception of a longer intramolecular distance between N_{ax} and W. By PESHO analysis [31] we searched for the triple bonding characteristics of **18b** consisting of one d_σ–p_σ bond and two d_π–p_π bonds. Only a small contribution of the 6s W and the 3s orbital of P for the d_σ–p_σ bond is found. Coordination of **18b** to a simple σ acceptor (e.g. BH_3, calculated) leads to a small shortening of the $W{\equiv}P$ bond due to the increase of the 3s orbital participation of the phosphido ligand. With an approximately constant π-bonding contribution, the phosphorus-3s orbital contribution to a W–P bond increases whilst at the same time the phosphorus-3p σ-contribution decreases. Therefore the corresponding Fermi contact term results in an increase of the $^{183}W,^{31}P$ coupling constant upon linear coordination of a phosphido ligand complex to a σ acceptor and is both expected and experimentally observed. Moreover the phosphido complex **18b** is expected to have both σ-donor and π-acceptor abilities and can be characterized by similar, but less pronounced, ligating properties as CO.

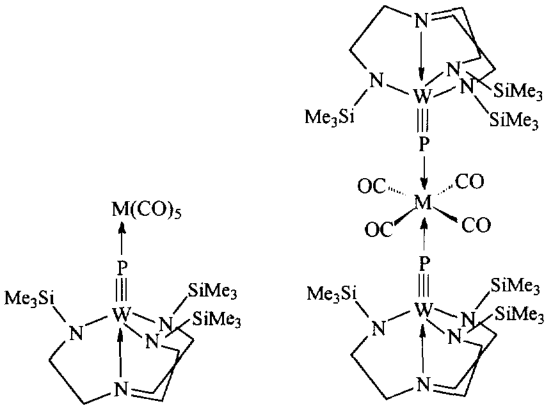
The bonding situation in the heavier pnicogenido complexes is comparable to that in the nitrido derivatives, however a stronger ionic character of the triple bond in the latter can be expected. Theoretical studies of mononuclear complexes of the type $L_4M{\equiv}N$ explain the favored (12–13 kJ mol^{-1}) tetragonal pyramidal structure with an apical N atom versus the trigonal bipyramidal alternative [47]. Bridging dinuclear nitrido complexes are comparable with organic polyenes [3, b] [48].

The formation of linear complexes with σ acceptors like Me^+ [29] and $GaCl_3$

Table 1
$M{\equiv}E$ streching frequencies and force constants for [$(N_3N)M{\equiv}E$] complexes [29]

Oscillator	ν ($M{\equiv}E$)(cm^{-1})	$k(M{\equiv}E)$(mdyn Å^{-1})[a]
$W{\equiv}^{14}N$	1015	7.90
$W{\equiv}^{15}N$	987	7.96
$W{\equiv}P$	516	4.16
$W{\equiv}As$	343	3.69
$Mo{\equiv}P$	521	3.74
$Mo{\equiv}As$	374	3.47

[a] Diatomic-oscillator approximation.



24a: M = Cr
24b: M = W

25a: M = Cr
25b: M = W

Fig. 2.

[37] is in fact possible, forming complexes **21–23** (Table 2). Furthermore **18b** reacts with $[M(CO)_5(thf)]$ (M = Cr, W) to form, at first, complexes **24** although a second substitution in the *trans*-position is preferred leading to the $M(CO)_4$ complexes **25** [31], (Fig. 2). The driving force of the *trans* substitution was found to be the formation of $M(CO)_6$ [31].

From experimental data the coordination of a σ acceptor as Me^+ and $GaCl_3$ or a σ-acceptor/π-donor as $M(CO)_n$ (M = Cr, W; $n = 4$, 5) results in a high field shift

Table 2
M$\equiv$E bond lengths and ^{31}P-NMR data of some pnicogenido complexes

	d(M$\equiv$E), (Å)	δ(^{31}P) (ppm)	J(^{183}W^{31}P) (Hz)	Ref.
$[(t\mathrm{BuO})_3W\equiv P\rightarrow Cr(CO)_5]$ **14a**		595.4	536	[23]
$[(t\mathrm{BuO})_3W\equiv P\rightarrow W(CO)_5]$ **14b**		544.6	554, 163	[23]
$[(t\mathrm{BuO})_3W\equiv P\rightarrow MnCp(CO)_2]$ **14c**		614.0	566	[49]
$[(ArRN)_3Mo\equiv P]$ **15**	2.119(4)	1216		[8]
$[(ArRN)_3MoPMo(NR_2)_3]$ **16**	2.2430(6)			[26]
$[(N_3N)Mo\equiv P]$ **18a**		1346		[9]
$[(N_3N)W\equiv P]$ **18b**	2.162(4)	1080	138	[9]
$[(N_3N)Mo\equiv As]$ **20a**	2.252(3)			[29]
$[(N_3N)W\equiv As]$ **20b**	2.2903(11)			[31]
$[(N_3N)W\equiv PMe]^+$ OTf^- **21a**			748	[29]
$[(N_3N)W\equiv AsMe]^+$ OTf^- **22a**	2.25			[29]
$[(N_3N)W\equiv P\rightarrow GaCl_3]$ **23**	2.168(4)	365	713	[37]
$[(N_3N)W\equiv P\rightarrow Cr(CO)_5]$ **24a**		708.1	442	[31]
$[(N_3N)W\equiv P\rightarrow W(CO)_5]$ **24b**		662.6	450, 135	[31]
$[(N_3N)W\equiv P\rightarrow Cr(CO)_4\leftarrow P\equiv W(N_3N)]$ **25a**		728.1	413	[31]
$[(N_3N)W\equiv P\rightarrow W(CO)_4\leftarrow P\equiv W(N_3N)]$ **25b**	2.202(2)	679.8	426, 151	[31]
$[(ArRN)_3MoPS]$ **26**		383		[8]

of the ^{31}P-NMR resonances and an increase of the ^{183}W,^{31}P coupling constants to about 400–750 Hz (Table 2). This increase in coupling constants is much stronger for σ acceptors (>700 Hz). For the latter complexes the $M{\equiv}E$ bond length stays more or less the same as predicted by theoretical studies [31], however a σ-acceptor/π-donor group like $M(CO)_n$ lengthens the triple bond distance due to the electron filling of antibonding orbitals at the pnictinido atom. It is interesting to note that the calculated $W{\equiv}Sb$ distance in the compound $[(N_3N)W{\equiv}Sb]$ is 2.514 Å [31].

The phosphido complex **15** reacts with sulfur to form the first example of a terminally bonded PS ligand complex **26** [8]. No X-ray crystal structure has yet been reported. In contrast, there has recently been a large number of PS [38] and PO [39] containing complexes reported where structural data show a capping phosphorus atom of the PY ligand on trinuclear and tetranuclear complexes.

3.2. *Linear coordinated phosphinidene complexes*

Two types of phosphinidene complexes L_nMPR exist: the bent complexes of type C and linear ones of type D. Table 3 summarizes the known examples of both types.

Metal phosphorus triple bonds are present in phosphinidene complexes with an almost linear MPR arrangement of type D. The filled p orbital of phosphorus can form an additional π bond to an empty d orbital on the metal. A comparison of the metal–phosphorus bond lengths between complexes of type C and D justifies this view and are demonstrated with the W complexes **28b** and **30** (Fig. 3, Table 3). The almost identical $W{\equiv}P$-distances observed in the linear phosphinidene complex **30** (2.169(1) Å) [44] and the phosphido complex **18b** (2.162(4) Å) (Table 2) also confirm this description. Once again, the observed coupling constants $^{1}J(^{183}W, ^{31}P)$ of **18b** (138 Hz) and **30** (649 Hz) appear to be, at first glance, in contradiction with this view. They are however in agreement with the above discussed increase of the coupling constants in the case of a linear "coordination" of a substituent at the terminal P_1 ligand. In the bent phosphinidene complex **28b** [42] in which there is only a formal double bond present (type C) the value of

Table 3
^{31}P-NMR data and MP bond lengths of phosphinidene complexes

	$\delta(^{31}P)$(ppm)	$J(^{183}W^{31}P)$(Hz)	d(ME)(Å)	L–M–P(°)	Ref.
$[Cp_2PMe_3Zr{=}PAr']$ **27**	729.4		2.505(4)	116.1(4)	[40]
$[Cp_2Mo{=}PAr']$ **28a**	799.5		2.370(2)	115.8(2)	[41]
$[Cp_2W{=}PAr']$ **28b**	661.1	153.5	2.349(5)	114.8(5)	[42]
$[(tBu_3SiO)_3Ta{=}PPh]$ **29a**	334.6				[43]
$[(tBu_3SiO)_3Ta{=}AsPh]$ **29b**			2.428(2)	107.2(4)	[43]
$[(Ph_2MeP)Cl_2(CO)W{\equiv}PAr']$ **30**	193.0	649	2.169(1)	168.2	[44]
$[(ArRN)_3Mo{\equiv}PNMes]$ **31**	159		2.085(5)	178.1(9)	[8]
$[(N_3N)Ta{\equiv}PR]$ R = Cy **32a**	209.8		2.145(7)	170.0	[45]
R = Ph **32b**	175.1				
R = *t*Bu **32c**	227.3				

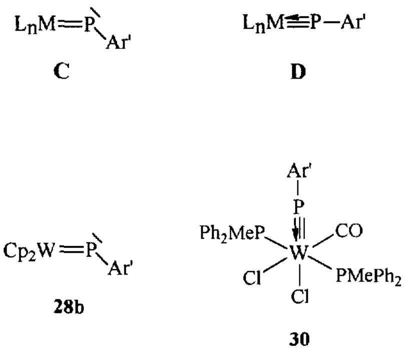


Fig. 3. Types of phosphinidene complexes.

$^1J(^{183}W, ^{31}P)$ is only 153.5 Hz. The NMR chemical shifts behave inversely: **15**: 1216 ppm; **18b**: 1080 ppm; **32a**: 209.8 ppm; **30**: 193 ppm; **28a**: 799.4 ppm; **28b**: 661.1 ppm.

4. Outlook

The synthesis of stable complexes with terminal phosphido and arsenido ligands is of fundamental importance and opens the field of coordination chemistry and reactivity of these ligand systems as well. The synthesis of analogous complexes with ligands of the heavier homologues, antimony and bismuth, has now moved within reach. Moreover, the experimental and theoretical evidence is now answering many fundamental questions on the properties of E_1 ligands.

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