Reaction behaviour of a complex containing a tungsten phosphorus triple bond with σ-acceptor compounds of group 13

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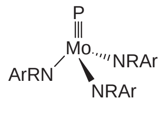
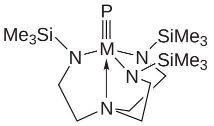
$[LW{\equiv}P{\rightarrow}GaCl_3]$ 5 [L = $N(CH_2CH_2NSiMe_3)_3$] is prepared by treatment of $[LW{\equiv}P]$ with $(GaCl_3)_2$; decomposition of 5 in CH_2Cl_2 affords dimerisation under Me_3SiCl elimination to give a cationic W_2P_2 tetrahedral complex 6; both complexes are structurally characterised.

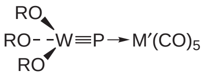
In 1995 Cummins[1] and Schrock[2] and their coworkers succeeded in the synthesis and the first structural characterisation of complexes **1** and **2**, respectively, containing a metal phosphorus triple bond. Our synthetic goal, however, has been directed towards the alkoxide substituted complexes **3** where the phosphido ligand coordinates additionally to a metal pentacarbonyl fragment.[3] The $^1J_{WP}$ coupling constant was observed to be 554 (**3a**) and 536 Hz (**3b**) for the triple bond and appeared to be in contradiction with the 138 Hz found for the W complex **2a**. To shed light onto this problem we decided to synthesise **2a** (M′ = W) *via* the reaction of [WCl(L)] [L = $N(CH_2CH_2NSiMe_3)_3$] with $Li[P(SiMe_3)_2]$. Subsequent reaction with $[M'(CO)_5(thf)]$ leads to the *trans*-substituted complexes **4**.[4] ^{31}P NMR data (**4a**: δ 679.8, $^1J_{WP}$ 426 Hz; **4b**: δ 728.1, $^1J_{WP}$ 413 Hz) combined with theoretical calculations reveal that the linear coordination of a complex fragment to the phosphido atom is responsible for a dramatic increase of the s character of the triple bond and consequently for the increase of the coupling constant. In further studies it was of interest how coupling constant and triple bond length behave by coordination of a simple σ-acceptor group. Herein we report our results of the reaction of **2a** with group 13 Lewis acids.



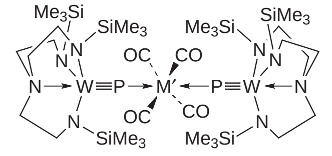
R = $C(CD_3)_2CH_3$
Ar = $C_6H_3Me_2$-3,5
1



M = W(**a**), Mo(**b**)
2



R = Bu^t
M′ = W(**a**), Cr(**b**)
3



M′ = W(**a**), Cr(**b**)
4

The reaction of **2a** with $BH_3{\cdot}SMe_2$ only led to an insoluble solid. Elemental analysis did not indicate the formation of the expected adduct $[LW{\equiv}P{\rightarrow}BH_3]$. Even following the reaction by ^{31}P NMR only showed that the starting material disappeared but no new signal could be detected. In the reaction of **2a** with $BF_3{\cdot}OEt_2$ in CH_2Cl_2, however, a ^{31}P NMR signal at δ 607 ($^1J_{WP}$ 478 Hz) could be observed for a short time. Then the reaction mixture became black and insoluble black material precipitated.

Reaction of **2a** with the dimer $[GaCl_3]_2$ in a 2 : 1 ratio in toluene led to the isolation of a yellow crystalline compound **5**, which is sparingly soluble in toluene, thf and CH_2Cl_2.‡ The $^{31}P\{^1H\}$ NMR spectrum of **5** reveals one signal at δ 366 bearing one pair of satellites with $^1J_{WP}$ = 712 Hz. The high field shift as well as the considerable increase of the coupling constant is consistent with those found in **4.** However, the observed coupling constant is one of the largest for these triple bond systems. Almost identical NMR data were detected in the structurally uncharacterised complex $[LW{=}PMe]^+$-$[OTf]^-$ (δ 339, $^1J_{WP}$ = 748 Hz) synthesised by Schrock and coworkers.[5]

The molecular structure of **5** was established by a single-crystal X-ray diffraction study.§ The main feature of the molecular structure of **5** is the entirely linear arrangement of the N_{ax}–W–P–Ga axis (Fig. 1). The Cl atoms of the $GaCl_3$ group are slightly disordered. The orientations of the Cl atoms are slightly eclipsed to the W–N(2) bonds, but staggered to the N(1)–C(1) bond. The W≡P bonding distance is 2.168(4) Å which is only slightly longer than the bond length found in **2a** (2.162 Å). This indicates the replacement of almost the same amount of phosphorus 3p σ-contribution to the W≡P bond in **2a** by 3s-orbital contribution of the former lone pair of the phosphorus, produced through the coordination to a σ-acceptor such as $GaCl_3$. This finds further support from the dramatic increase of $^1J_{WP}$. Owing to the remarkable backbonding ability of the W≡P moiety to the W^0 centre the triple bond length increases from 2.162(4) in **2a** to 2.202(2) Å in **4a**.[4] The most significant difference in bonding distances in comparison to **2a** occurs for the N_{ax}–W bond which is shortened by 0.10 Å. This is probably

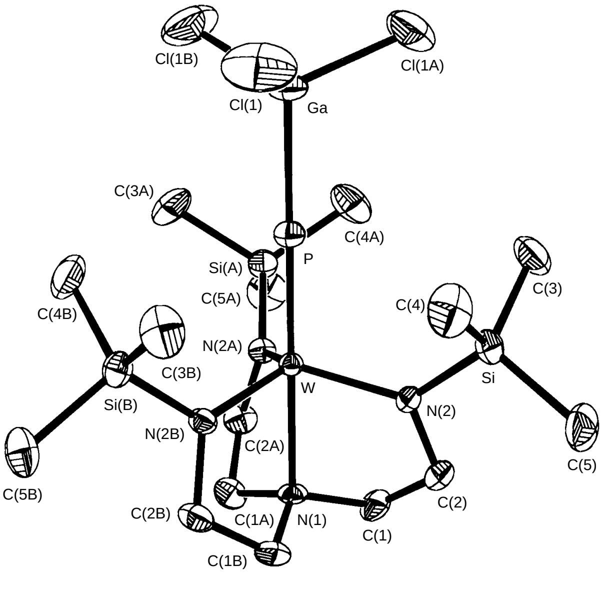


Fig. 1 Molecular structure of **5** (only one position of the Cl atoms is drawn for clarity). Selected bond lengths (Å) and angles (°): W–P 2.168(4), P–Ga 2.335(4), W–N(1) 2.248(10), W–N(2) 1.967(3), Ga–Cl(1) 2.159(11), Ga–Cl(2) 2.186(12), N(1)–W–P 180.0, W–P–Ga 180.0, N(1)–W–N(2) 77.52(8).

due to a reduced electron density at the metal core which results in a higher acceptor ability of the W atom. The Ga–P distance is 2.335(4) Å. This is consistent for Ga–P single bonds as found in *e.g.* $GaCl_3(PMe_3)$ (2.353 Å).[6]

The structural features of **5** were modelled using the B-P86/SVP density functional approximation.[7] The structural optimisation resulted in a molecular shape best described in terms of C_3 symmetry. There is good agreement between the calculated and experimentally observed structural parameters [calc.: d(W≡P) = 2.186 Å, $d(\mathrm{W{-}N_{eq}})$ = 2.007 Å; exptl.: d(P–Ga) = 2.335(4) Å, d(W≡P) = 2.168(4) Å, $d(\mathrm{W{-}N_{eq}})$ = 1.967(3) Å]. The only exceptions are the calculated distances for P–Ga and $\mathrm{W{-}N_{ax}}$, which are longer by 0.1 and 0.2 Å, respectively. For the latter bond, the same effect was found in the calculated and experimental structures of **2a** and **4a**.[4]

Electronic energies, calculated with the B-P86/SVP (B3-LYP/ SVP) approximation, show reaction of **2a** with 0.5 $(GaCl_3)_2$ to be exothermic at -68 (-61) kJ mol^{-1}. The same methods calculated the energies for the reaction of **2a** with $BH_3\cdot$thf to be -22 (-2) kJ mol^{-1}.[4] In accordance with the experimental observation the formation of a BH_3 adduct seems to be less favoured in comparison with the preferred formation of the $GaCl_3$ adduct **5**.¶

However, a solution of **5** in CH_2Cl_2 appears to be unstable. After a few days the yellow–brown colour of the solution disappears. Red, star shaped crystals of **6** and an amorphous solid precipitated. According to a $^{31}P\{^1H\}$ NMR study the CH_2Cl_2 solution contains no detectable amounts of phosphorus. The red crystalline compound was examined by X-ray diffraction,§ but only a weak data set was obtained. However, it was possible to solve the structure to a reasonable degree. The structure revealed a tetrahedral $[W_2P_2]^+$ moiety, where the W atoms are coordinated by two tren type ligands (Fig. 2). These are linked together by two $GaCl_2$ groups which are in the former position of the $SiMe_3$ moieties. Furthermore, all $SiMe_3$ groups are removed and $[GaCl_4]^-$ and Cl^- occur as counter ions. The W–P bonds are now 2.462(12) and 2.473(10) Å and the W–W bond is 2.585(2) Å. A related nitrido bridged tungsten dimer is $[W_2(\eta^5\text{-}C_5H_4Pr^i)Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$ with an analogous W–W distance of 2.5923(5) Å.[8] Obviously, in the first step of the conversion of **5** the Si–N bond is cleaved to form the thermodynamically stable $SiClMe_3$. The replacement by $GaCl_2$ moieties leads to a rearrangement resulting in the formation of the W_2P_2 complex **6**.

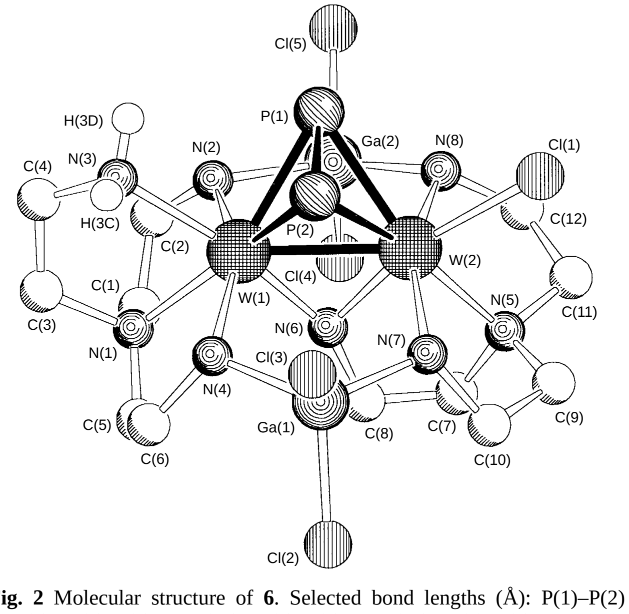


Fig. 2 Molecular structure of **6**. Selected bond lengths (Å): P(1)–P(2) 2.07(2), W(1)–P(1) 2.461(12), W(1)–P(2) 2.473(10), W(2)–P(1) 2.483(11), W(2)–P(2) 2.498(9); Cl(1)–W(2) 2.464(12), W(1)–W(2) 2.585(2), W(1)–N(6) 1.97(3), W(2)–N(6) 2.00(3).

The transformation of **5** into **6** could explain the instability of complexes of the type $[LW{\equiv}P{\rightarrow}EX_3]$ (E = B, Ga; X = H, F, Cl). Loss of $SiClMe_3$ or $SiHMe_3$ decreases the steric protection of the W≡P triple bond which results in arbitrary formation of higher aggregates of unknown composition. Deliberate attempts to remove $SiMe_3$ groups may activate the [LW≡P] complex with their preferred end-on reactivity to undergo side-on reactions. This is a goal for further investigations.

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Notes and References

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‡ *Spectroscopic data* for **5** ($[^2H_8]$thf): $^{31}P\{^1H\}$ NMR, δ 366, J_{WP} 712; ^1H NMR, δ 3.91 (t, 6 H, CH_2), 2.46 (t, 6 H, CH_2), 0.45 (s, 27 H, CH_3); $^{13}C\{^1H\}$ NMR, δ 55.16 (s, CH_2), 52.36 (s, CH_2), 5.38 (s, CH_3); correct elemental analysis.

§ *Crystal structure analysis*: **5**: $C_{15}H_{39}Cl_3GaN_4PSi_3W$, M = 750.66, trigonal, space group $P31c$, $a = b$ = 11.867(2), c = 12.207(2) Å, Z = 2, U = 1488.7(4) $Å^3$, D_c = 1.675 Mg m^{-3}, μ(Mo-Kα) = 52.9 cm^{-1}, F(000) = 740, T = 200(2) K. A total of 4631 reflections with $7.76 \leqslant 2\theta \leqslant 51.42°$ were collected on a STOE IPDS (image plate detector system) with Mo-Kα radiation (0.710 69 Å), of which 1811 were independent (R_{int} = 0.0364). The 1749 reflections with $I \geqslant 2\sigma(I)$ were used in the full least squares refinement. The structure was solved by direct methods (SHELXS-86) and standard Fourier techniques (SHELXL-93). Full matrix least squares refinement of the thermal parameters (anisotropic for all atoms except hydrogen) led to convergence with final residuals of R_1 = 0.0189 and wR_2 = 0.0461 and GOF = 1.078 for 110 variables. Residual electron density was found to be between 0.925 and -0.441 e $Å^{-3}$. **6**: $4[C_{45}H_{95}Cl_5Ga_2N_8P_2W_2][GaCl_4]Cl_3\cdot 3CH_2Cl_2$, M = 4681.56, tetragonal, space group $I\bar{4}$, $a = b$ = 22.059(3), c = 13.185(3) Å, U = 6416(2) $Å^3$, Z = 2 (for four molecules of the W_2P_2 complex), D_c = 2.421 Mg m^{-3}, F(000) = 4364, μ(Mo-Kα) = 98.24 cm^{-1}, 225 parameters, crystal size $0.08 \times 0.04 \times 0.02$ mm, T = 200(2) K. A total of 6756 reflections with $3.7 < \theta < 45°$ were collected on a STOE IPDS with Mo-Kα radiation (0.710 69 Å), 3757 of them were independent (R_{int} = 0.1825). 2867 reflections with $I \geqslant 2\sigma(I)$ were used in the full least squares refinement. The structure was solved as above. Full matrix least squares refinement of the thermal parameters (anisotropic for all W, Ga, P and Cl atoms except those of the solvent CH_2Cl_2) led to convergence with final residuals of wR_2 = 0.2245 for all reflections, corresponding to a conventional R_1 = 0.0952 for the observed F_o data. Residual electron density was found to be between 2.839 and -1.718 e $Å^{-3}$. CCDC 182/813.

¶ The reaction between **2a** and $BH_3\cdot$thf presumably leads to elimination of $HSiMe_3$.

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Received in Cambridge, UK, 9th February 1998; 8/01136B