Reactivity of a Phosphanylalane Complex towards Lewis Bases

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Dedicated to Prof. R. Schmutzler on the occasion of his 70th birthday

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The reactivity of the Lewis acid/base stabilized complex of phosphanylalane $[(CO)_5W(H_2PAlH_2{\cdot}NMe_3)]$ (**1**) towards the Lewis bases THF and NMe_3 has been investigated. The reaction with THF leads to decomposition of the complex. One of the decomposition products was identified as containing the anion $[\{(CO)_5W\}_2PH_2]^-$ (**2**). This anion could be synthesized independently by reaction of $[(CO)_5WPH_3]$ with KH in the presence of $[(CO)_5W(THF)]$ and was isolated as the tetraphenylphosphonium salt $[Ph_4P][\{(CO)_5W\}_2PH_2]$ (**2a**). The treatment of **1** with NMe_3 leads to the formation of $[(CO)_5W(H_2PAlH_2{\cdot}2\,NMe_3)]$ (**3**) containing a five-coordinate aluminum atom. Compound **3** exhibits a fast exchange of the NMe_3 ligands in solution containing an excess of NMe_3. The products were characterized by spectroscopic methods and X-ray crystallography.

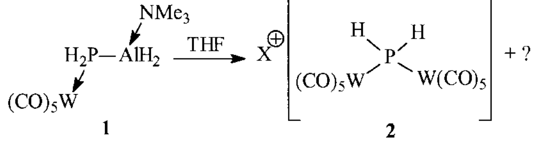
Introduction

Compounds containing bonds between group 13 and group 15 elements are especially interesting due to their potential use as molecular precursors for the generation of thin films of group 13/15 semiconductors. Compounds of the type $(R_2EE'R'_2)_n$ (R, R′: organic substituents, E′: group 13 element, E: group 15 element) have been intensively investigated[1] and usually form oligomeric structural frameworks. These compounds are monomeric if they possess bulky R and R′ groups to block the intermolecular aggregation. To obtain monomers, the steric influence of the substituents can be neglected if both a Lewis base is coordinated at the group 13 element and the group 15 element still possesses bulky substituents or if, besides the Lewis base at the group 13 element, the lone pair of the group 15 element is occupied by a Lewis acid. Examples of the former mode are the compounds $[Mes_2EAlH_2{\cdot}NMe_3]$,[2] obtained by the treatment of $ClAlH_2{\cdot}NMe_3$ with $LiEMes_2$ (E = P, As), and $[(Me_3Si)_2EAlMe_2{\cdot}dmap]$[3] synthesized by treating oligomers of the type $[Me_2AlE(Me_3Si)_2]_n$ (E = P, As; n = 2, 3) with the Lewis base *N*,*N*′-dimethylaminopyridine (dmap). We developed the latter concept of monomeric group 13/15 compounds by the stabilization of the hydrogen substituted parent compounds $[(CO)_5W(PH_2E'H_2{\cdot}NMe_3)]$ (**1**: E′ = Al, **2**: E′ = Ga, **3**: E′ = B). These phosphanylalane and -gallane complexes were synthesized by a hydrogen elimination reaction,[4] whereas the boron compound was accessible by a salt elimination route.[5] Herein we report on the reactivity of **1** towards the Lewis bases THF and NMe_3, respectively.

Results and Discussion

Decomposition of 1 in THF

Upon dissolving in THF, **1** reacted with vigorous H_2 evolution [Equation (1)]. The ^{31}P NMR spectrum of the reaction mixture gave some hints of the possible formation of an anionic complex with the formula of **2**. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows two main P containing products as single peaks having tungsten satellites which split into triplets when the proton coupled spectrum was recorded. Compound **2** shows a triplet at −267.7 ppm ($^1J_{P,H}$ = 268, $^1J_{W,P}$ = 146 Hz). The other product, whose structure could not be assigned yet, shows a triplet at −100.3 ppm ($^1J_{P,H}$ = 340, $^1J_{W,P}$ = 220 Hz). The ratio of the integrals of the tungsten satellites towards the central peak of **2** suggests that two tungsten atoms are bound to each phosphorus atom as in $[\{(CO)_5W\}_2PH_2]^-$. By adding Ph_4PBr to the mixture of reaction (1) some yellow crystals appeared which were identified crystallographically by their unit cell to be $[Ph_4P][\{(CO)_5W\}_2PH_2]$ (**2a**) (cf. discussion below).



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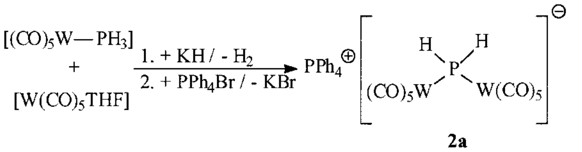
In order to develop a more efficient approach to **2a** it was synthesized by the reaction of $[(CO)_5WPH_3]$ with KH in the presence of $[(CO)_5W(THF)]$ [Equation (2)]. Cation exchange using PPh_4Br and crystallization from CH_2Cl_2/*n*-hexane afforded pure $[PPh_4][\{(CO)_5W\}_2PH_2]$ (**2a**) which showed identical NMR spectra to the decomposition product **2**. The IR spectrum of **2a** revealed a PH stretching absorption at 2306 cm^{-1} as well as three CO valence stretching modes at 2048, 1930 and 1872 cm^{-1} for the two $W(CO)_5$ moieties showing a local C_{4v} symmetry.



2a (2)

The X-ray Crystal Structure Analysis of 2a

The molecular structure of **2a** shows a $[PPh_4]^+$ cation and a $[\{(CO)_5W\}_2PH_2]^-$ anion. An ORTEP plot of the anion is depicted in Figure 1, while selected bond lengths and angles are listed in Table 1.

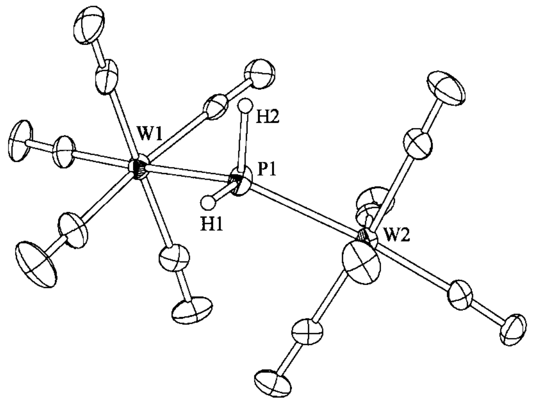


Figure 1. Molecular structure of the anion of **2a** in the crystal (ORTEP plot, 50% probability displacement ellipsoids)

Table 1. Selected bond lengths [Å] and angles [°] for **2a**

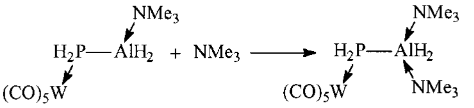
W1−P	2.579(2)	W2−P	2.580(2)
W−C$_{trans}$ [a]	1.978(8)	W−C$_{cis}$ [a]	2.029(9)
W1−P−W2	126.79(7)		

[a] Averaged bond lengths.

The anion of **2a** (Figure 1) shows a PH_2 group which is coordinated to two $W(CO)_5$ moieties. The W−P bond lengths are 2.579(2) and 2.580(2) Å, respectively, and the W1−P−W2 angle is 126.79(7)°. Comparison of these values with the compounds $[Cp(CO)_3W(\mu\text{-}PPh_2)W(CO)_5]$ [W−P−W 118.4(1)°; W−P 2.626(3) Å],[6] $[Cp(CO)_2Fe(\mu\text{-}PPh_2)W(CO)_5]$ (W−P−Fe 118.42(6)°; W−P 2.581(1) Å)[7] and $[Et_4N][Cp'(CO)_2Mn(\mu\text{-}PPh_2)W(CO)_5]$ (Cp′ = η^5-C_5H_4Me) [W−P−Mn 119.8(1)°; W−P 2.622(3) Å][8] show that, in particular, the W−P−W angle is significantly larger in **2a**. This can be explained by the low steric shielding of the H substituents at the P atom. Complex **2a** represents the first parent compound (R = H) of the class $[(L_nM)_2PR_2]^-$, which exists amongst only a few organic substituted examples.[8]

Reaction of 1 with NMe$_3$

In contrast to the reaction with THF, **1** did not show decomposition when allowed to react with the nitrogen-centered Lewis base NMe_3. The product of this reaction is complex **3** which contains a pentacoordinated Al atom in a trigonal bipyramidal arrangement containing two NMe_3 molecules [Equation (3)]. A similar reaction is also known from $H_3Al{\cdot}NMe_3$ with NMe_3 which forms the adduct $H_3Al{\cdot}2\,NMe_3$,[9] exhibiting a trigonal bipyramidal coordinated aluminum atom.[10] The solid-state Raman spectrum of **3** showed bands in the region of the terminal CO stretching frequencies as well as for the PH valence at 2331 and 2315 cm^{-1} and one AlH stretch at 1744 cm^{-1}. The EI-mass spectrum did not show a molecular ion peak. However, $[(CO)_5WPH_2AlH_2{\cdot}NMe_3]^+$ was detected as the ion with the highest mass. Moreover, signals for its degradation, resulting from CO and NMe_3 loss were also found. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet at δ = −251 ppm which exhibits tungsten satellites ($^1J_{W,P}$ = 149 Hz). The ^1H NMR spectrum reveals a doublet for the PH_2 protons at δ = 1.58 ppm ($^1J_{P,H}$ = 268 Hz), a singlet for the NMe_3 groups at δ = 1.71 ppm and a broad signal for the AlH_2 protons at δ = 3.15 ppm.



1 **3** (3)

In the presence of an excess of trimethylamine, **3** shows dynamic behavior in solution which can be attributed to fast exchange of the coordinated trimethylamine molecules. The variable temperature ^1H NMR spectra are shown in Figure 2. At low temperatures two signals can be detected for the NMe_3 groups: one can be assigned to coordinated (A) and one to free trimethylamine (B). With rising temperature, the two signals are shifted towards each other, and at the coalescence temperature of ca. −45 °C only one broad signal is observed. At higher temperatures only one signal is detected for coordinated and free trimethylamine (C). For this process the free activation enthalpy at the coalescence temperature was calculated to be 45.3 kJ·mol^{-1}.

The Solid-State Structure of 3

The solid-state structure of **3** was determined by a single-crystal X-ray diffraction study. Selected bond lengths and angles are reported in Table 2. An ORTEP plot of the molecular structure of **3** is depicted in Figure 3. The central motif of the crystal structure of **3** is a H_2AlPH_2 moiety which is connected to a $W(CO)_5$ fragment by the P atom. Two NMe_3 molecules are coordinated to the Al atom,

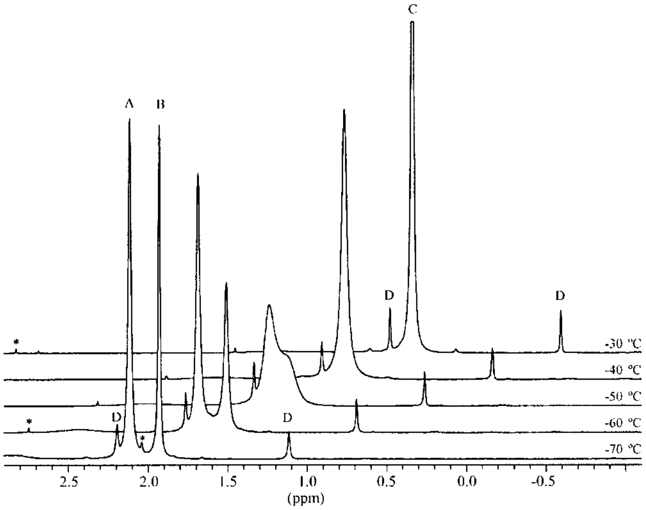


Figure 2. Variable temperature ^1H NMR spectra of a mixture of **3** and an excess of NMe_3 in CD_2Cl_2; at −70 °C the spectrum shows signals for coordinated NMe_3 (A), free NMe_3 (B) and the PH_2 protons (D); at −30 °C only the PH_2 protons and one signal for NMe_3 (C) are detected; impurities are marked with *

Table 2. Selected bond lengths [Å] and angles [°] for **3**

W−P	2.566(1)	P−Al	2.432(2)
Al−N1	2.160(4)	Al−N2	2.155(4)
$W-C_{trans}$ [a]	1.988(5)	$W-C_{cis}$ [a]	2.034(5)
Al−P−W	128.58(6)	N1−Al−P	94.7(1)
N2−Al−P	94.2(1)	N1−Al−N2	171.1(2)

[a] Averaged bond lengths.

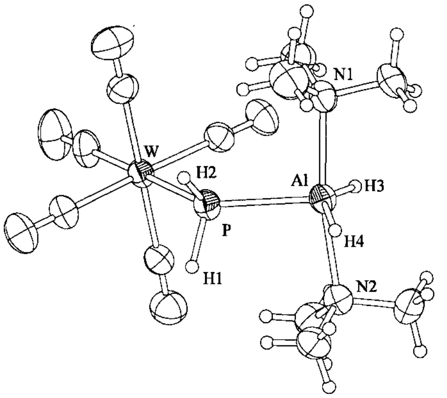


Figure 3. Molecular structure of **3** in the crystal (ORTEP drawing, 50% probability displacement ellipsoids)

which thus exhibits a coordination number of five in a distorted trigonal bipyramidal arrangement. Both trimethylamine ligands occupy the apical positions of the trigonal bipyramid with similar Al−N bond lengths of 2.160(4) and 2.155(4) Å, respectively. The N1−Al−N2 angle is 171.1(2)°. At 2.432(2) Å the Al−P bond length in **3** is significantly longer than in **1** [2.377(1) Å],[4] although in both compounds the aluminum atom is pentacoordinate (**1** reveals an intermolecular dimerization via H bridges). The longer Al−P bond in **3** can be attributed to the steric shielding at the aluminum atom by the second NMe_3 group. The slightly longer P−W bond (**3**: 2.566(1) Å, **1**: 2.549(1) Å] and the larger W−P−Al angle (**3**: 128.58(6)°, **1**: 118.44(4)°] in **3** further support this explanation.

Conclusion

The results have shown that the Lewis-acid/base stabilized phosphanylalane is very sensitive towards reactions with different Lewis bases. The ability of the Al atom to achieve pentacoordination enables firstly an addition of the Lewis base which leads, depending upon its nature, to stable adducts (as in the case of NMe_3) or to decomposition as in the case of THF via cleavage of the Al−P bond and removal of the Al moiety.

Experimental Section

General Remarks: All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. All solvents were dried via standard procedures and distilled freshly before use. NMe_3 was dried by condensing it over Na/benzophenone at −78 °C and stirring the mixture until the solution showed a dark blue color. PPh_4Br was heated to 100 °C in vacuo for one hour to remove traces of moisture. $[(CO)_5W(H_2PAlH_2{\cdot}NMe_3)]$ (**1**) was prepared according to our published method.[4] All NMR spectra were recorded on a Bruker AC 250 spectrometer with δ referenced to external $SiMe_4$ (^1H) or H_3PO_4 (^{31}P), respectively. IR spectra were measured on a Bruker IFS 28 instrument and Raman spectra on a Bruker FRA 106 spectrometer. All mass spectra were recorded on a Varian MAT 711 instrument at 70 eV.

$[Ph_4P][\{(CO)_5W\}_2PH_2]$ (2a): To a solution of $[(CO)_5W(THF)]$, which was produced by irradiating $[W(CO)_6]$ (352 mg, 1.00 mmol) in THF (50 mL), $[(CO)_5WPH_3]$ (358 mg, 1.00 mmol) and KH (40 mg, 1.00 mmol) were added subsequently. After the gas evolution had ceased the mixture was stirred for three hours to ensure complete reaction. To the clear yellow solution solid PPh_4Br (419 mg, 1.00 mmol) was added resulting in the formation of a white solid which was separated by filtration. The filtrate was reduced to dryness in vacuo and the remaining residue dissolved in CH_2Cl_2 (10 mL). After removal of the insoluble material by filtration the solution was layered with *n*-hexane (20 mL) affording yellow crystals of **2a** after two days. Yield 643 mg (63%). IR (CH_2Cl_2): $\tilde{\nu}$ = 3055 (m), 2987 (w), 2306 (w), 2048 (m), 1930 (vs), 1872 (s), 1440 (m), 1422 (m), 1271 (vs), 1259 (vs), 1109 (w), 896 (w) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ = 1.91 (d, $^1J_{P,H}$ = 268 Hz, 2 H, PH_2), 7.52−7.92 (m, 20 H, PPh_4) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = −267.7 (s, $^1J_{P,W}$ = 146 Hz, PH_2), 23.0 (s, PPh_4) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = −267.7 (t, $^1J_{P,H}$ = 268, $^1J_{P,W}$ = 146 Hz, PH_2), 23.0 (s, PPh_4) ppm.

$[(CO)_5W(H_2PAlH_2{\cdot}2\,NMe_3)]$ (3): NMe_3 (0.36 mmol) was condensed into a solution of $[(CO)_5W(H_2PAlH_2{\cdot}NMe_3)]$ (53 mg, 0.12 mmol) in *n*-hexane (20 mL) at −196 °C. The reaction mixture was allowed to warm to ambient temperature over 20 minutes. Any insoluble material formed was removed by filtration, and the solution was kept at −20 °C. Light yellowish colored crystals of **3** were formed over two days. Yield 32 mg (53%). Raman (solid state): $\tilde{\nu}$ = 3004 (w), 2977 (m), 2929 (m), 2905 (m), 2855 (m), 2788 (w), 2331 (m), 2315 (m), 2063 (s), 1956 (vs), 1936 (w), 1904 (s), 1880 (w), 1744 (w, br), 821 (w), 435 (m), 434 (m), 116 (m) cm^{-1}. ^1H NMR

Table 3. Crystallographic data for **2a** and **3**

	2	**3**
Empirical formula	$C_{34}H_{22}O_{10}P_2W_2$	$C_{11}H_{22}AlN_2O_5PW$
M_r	1020.16	504.11
T [K]	200(1)	200(1)
Crystal size	0.20 × 0.15 × 0.02	0.30 × 0.20 × 0.10
Space group	$P2_1/n$	$P2_1/n$
Crystal system	monoclinic	monoclinic
a (Å)	14.231(3)	11.559(2)
b (Å)	14.377(3)	10.957(2)
c (Å)	17.742(4)	15.371(3)
α [°]	90	90
β [°]	92.10(3)	102.11(3)
γ [°]	90	90
V [Å^{-3}]	3627.7(12)	1903.4(7)
Z	4	4
d_c [g cm^{-3}]	1.868	1.759
μ_c [mm^{-1}]	6.478	6.216
2θ range [°]	$3.64 \le 2\theta \le 52.00$	$5.18 \le 2\theta \le 52.00$
hkl range	$-17 \le h \le 17,-16 \le k \le 15,-21 \le l \le 21$	$-13 \le h \le 14,-13 \le k \le 13,-17 \le l \le 18$
Data/restraints/parameters	6631/0/441	3519/0/200
No. of unique data	6631 (R_{int} = 0.0594)	3519 (R_{int} = 0.1318)
Independent reflections [$I > 2\sigma(I)$]	4879	3256
Goodness-of fit on F^2	0.903	1.056
R_1 [a], wR_2 [b] [$I > 2\sigma(I)$]	0.0340, 0.0732	0.0325, 0.0856
R_1 [a], wR_2 [b] [all data]	0.0522, 0.0774	0.0346, 0.0867
Largest diff. peak/hole [e·Å^{-3}]	1.041, −1.364	1.665, −2.111

[a] $R = |F_o| - |F_c||/|F_o|$. [b] $wR_2 = [w(F_o^2 - F_c^2)^2]/[(F_o^2)^2]^{1/2}$

(250 MHz, [D$_8$]toluene, −50 °C): δ = 1.58 (d, $^1J_{P,H}$ = 268 Hz, 2 H, PH_2), 1.71 (s, 18 H, NMe_3), 3.15 (br. s, 2 H, AlH_2) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, [D$_8$]toluene, −70 °C): δ = −251 (s, $^1J_{P,W}$ = 149 Hz, PH_2) ppm. ^{31}P NMR (101 MHz, [D$_8$]toluene, −70 °C): δ = −251 (t, $^1J_{P,W}$ = 268, $^1J_{P,W}$ = 149 Hz, PH_2) ppm. EI-MS (70 °C): m/z = 445 ($M^+ - NMe_3$, 1%), 417 ($M^+ - NMe_3$ − CO, 1%), 386 (M^+ −2 NMe_3, 2%), 358 (M^+ −2 NMe_3 − CO, 13%), 330 (M^+ −2 NMe_3 − 2 CO, 5%), 302 (M^+ −2 NMe_3 − 3 CO, 16%), 302 (M^+ −2 NMe_3 − 3 CO, 16%), 272 (M^+ −2 NMe_3 − 4 CO − 2 H, 16%), 244 (M^+ −2 NMe_3 − 5 CO −2 H, 11%).

Variable Temperature NMR of 3: In a typical experiment [$(CO)_5W(H_2PAlH_2\cdot 2\,NMe_3)$] (30 mg, 0.06 mmol) was weighed into an NMR tube, and NMe_3 (0.18 mmol) was condensed into the tube at −196 °C. CD_2Cl_2 was then condensed into the tube, and it was sealed in vacuo. After variable temperature NMR measurements, starting from −70 °C, the samples decompose slowly at room temperature.

X-ray Crystallographic Studies: Crystal structure analyses of **2a** and **3** were performed on a STOE IPDS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with the program SHELXS-97,[11a] and full-matrix least-squares refinements on F^2 using SHELXL-97[11b] were performed with anisotropic displacements for non-H atoms. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus and aluminum atoms were freely refined. Further details of the structural refinements are given in Table 3.

CCDC-218817 and -218818 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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