The Stabilisation of Monomeric Parent Compounds of Phosphanyl- and Arsanylboranes

Ulf Vogel,[a] Petra Hoemensch,[a] Karl-Christian Schwan,[a] Alexey Y. Timoshkin,[b] and Manfred Scheer*[a]

Dedicated to Professor Dieter Fenske in occasion of his 60th birthday

Abstract: The structures of the parent compounds of phosphanyl- and arsanylboranes, H_2BPH_2 and H_2BAsH_2, were calculated by DFT-B3LYP methods. Such compounds have not previously been obtained preparatively. By applying the concept of Lewis acid/base stabilisation, $[(CO)_5W(H_2EBH_2 \cdot NMe_3)]$ (E = P (**3**), As (**4**)) derivatives have been synthesised by the metathesis reactions between $Li[(CO)_5WEH_2]$ and ClH_2BNMe_3 (E = P, As). Comprehensive thermodynamic studies on these systems verify the high stability of the Lewis acid/base stabilised complexes. Unexpected based on the thermodynamic calculations, UV radiation of the phosphanylborane **3** leads to the dinuclear phosphanido-bridged complex $[(CO)_8W_2(\mu\text{-}PHBH_2 \cdot NMe_3)_2]$ (**5**) by H_2 and CO elimination.

Keywords: arsenic · boron · density functional calculations · phosphorus · tungsten

Introduction

The chemistry of phosphanylboranes $(R_2BPR'_2)_n$ has been explored for a number of years now and a large number of compounds is known today.[1] For the corresponding arsanylboranes $(R_2BAsR'_2)_n$ only a very small number of compounds has been synthesised.[2] Monomeric compounds of both types have up to now been stabilised exclusively by bulky substituents at the Group 13 and Group 15 elements. Without the bulky substituents an intermolecular oligomerisation occurs between the lone pair of the Group 15 element and the acceptor orbital of the boron atom. The parent compounds H_2BPH_2 and H_2BAsH_2 have never been experimentally detected, but ab initio calculations on the structure of the first compound have been performed.[3]

As we have shown, the yet unknown compounds phosphanylalane H_2AlPH_2 and phosphanylgallane H_2GaPH_2 can be stabilised by coordination of a Lewis acid *and* a Lewis base. The complexes $[(CO)_5W(H_2PE'H_2 \cdot NMe_3)]$ (**1**) (E' = Al (**a**), Ga (**b**)) could be obtained by H_2 elimination reactions between $[(CO)_5WPH_3]$ and $H_3E \cdot NMe_3$.[4] Preparative attempts to synthesise the corresponding boron compounds by a similar reaction between $[(CO)_5WEH_3]$ (E = P, As) and $H_3B \cdot NMe_3$ have however proven unsuccessful.

Herein we report the results of our theoretical studies on the parent compounds of the phosphanyl- and arsanylboranes and for the first time on the synthesis of both compounds as Lewis acid/base stabilised derivatives.

Results and Discussion

DFT calculations: The structures of H_2BPH_2 and H_2BAsH_2 among others were calculated at the DFT-B3LYP level of theory as a part of the thermodynamic studies.[5] The structures (Figure 1) reveal C_s-symmetric molecules with almost planar boron and pyramidal Group 15 element centres (Figure 1). The calculated B–E distances are 1.873 (E = P) and 1.990 Å (E = As).

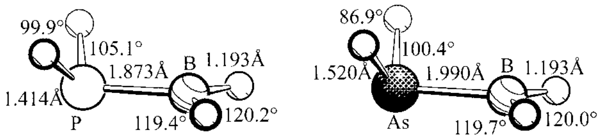

Figure 1. Comparison of the calculated structures of H_2PBH_2 (left) and H_2AsBH_2 (right).

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[a] Prof. Dr. M. Scheer, Dr. U. Vogel, P. Hoemensch,
Dipl. Chem. K.-C. Schwan
Institut für Anorganische Chemie der Universität Karlsruhe,
76128 Karlsruhe (Germany)
Fax: (+49) 721/608-7021
E-mail: mascheer@chemie.uni-karlsruhe.de

[b] Dr. A. Y. Timoshkin
Institut für Anorganische Chemie
Philipps-Universität Marburg, 35032 Marburg (Germany)
E-mail: alextim@chemie.uni-marburg.de

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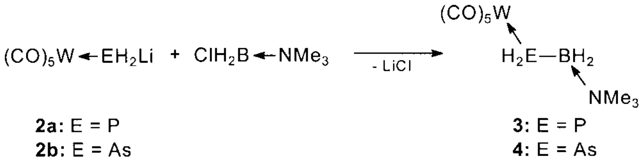
The Lewis acid/base stabilised phosphanlyalanes and -gallanes **1a**,**b** could be obtained by H_2 elimination reactions between $[(CO)_5WPH_3]$ and $H_3E \cdot NMe_3$, whereas the corresponding phosphanylborane could not be obtained by an analogous route. In agreement with this our DFT calculations[5] (Table 1) have shown that the latter reaction is for the P case indeed only slightly exothermic by 21 kJ mol^{-1} (Table 1, entry 1). Since the standard entropy is negative for this reaction ($\Delta S^0_{298} = -63.4\ J\,mol^{-1}\,K^{-1}$), it is only slightly thermodynamically favourable at 298 K ($\Delta G^0_{298} = -2.4\ kJ\,mol^{-1}$), but unfavourable at, for example, 373 K ($\Delta G^0_{373} = 3.9\ kJ\,mol^{-1}$). For the As compound the process of H_2 elimination is slightly more exothermic (−34.3 kJ mol^{-1}) and the Gibbs energies are negative both at 298 K (−19.3 kJ mol^{-1}), and 373 K (−15.5 kJ mol^{-1}). Note that P- and As-containing compounds exhibit similar thermodynamic properties (Table 1). The H_2 elimination reaction starting from unprotected H_3B and EH_3 is slightly favourable thermodynamically. Protecting groups bring 100–110 kJ mol^{-1} for the coordination of NMe_3 and 120 kJ mol^{-1} for $W(CO)_5$; thus the total stabilisation energy both with donor and acceptor (263 and 271 kJ mol^{-1} for P and As, respectively, Table 1, entry 6) is sufficient to prevent the dimerisation of monomers H_2BEH_2 (133 and 113 kJ mol^{-1}, respectively, Table 1, entry 3).

From the thermodynamic point of view, H_2 elimination reactions are more favourable for the As compound than for the P complex, reflecting the lower stability of the As−H bond compared to the P−H bond. The fact that reaction (1; see Table 1, entry 1) does not occur experimentally also for the reaction starting from $[H_3AsW(CO)_5]$, reflects the importance of the kinetic factors of these reactions as well as the lower stability of the formed product (c.f. discussion below).

Synthesis of the Lewis acid/base stabilised phosphanyl- and arsanylboranes: Based on the theoretical and preparative results, we have chosen a salt elimination route for the synthesis of the phosphanyl- as well as arsanylborane complexes. $[(CO)_5WPH_3]$ can be metallated in toluene with *n*BuLi.[6, 7] The resulting complex $Li[(CO)_5WPH_2]$ (**2a**) is then treated with $ClH_2B \cdot NMe_3$ in toluene to give $[(CO)_5W(H_2PBH_2 \cdot NMe_3)]$ (**3**) in good yield (Scheme 1). The corresponding arsenic-containing compound $[(CO)_5W(H_2AsBH_2 \cdot NMe_3)]$ (**4**) has been synthesised in a similar reaction sequence starting from $Li[(CO)_5WAsH_2]$ (**2b**). To our knowledge **4** is the first structurally characterised monomeric transition metal complex of an arsanylborane.[8] Compounds **3** and **4** are obtained as light yellow crystals from toluene. They are slightly soluble in hexane but readily soluble in toluene and CH_2Cl_2. In contrast to the aluminium-containing compound **1a** complexes **3** and **4** are remarkably stable towards decomposition. Compound **1a** evolves H_2 when it is dissolved in toluene or CH_2Cl_2. In contrast, the boron-containing complex **3** does not eliminate H_2 in these solvents even in refluxing toluene. The arsenic complex **4** is stable in toluene at room temperature, but decomposes when heated to 60 °C.[9]



Scheme 1. Reactions of **2** with $ClBH_2 \cdot NMe_3$.

Photolysis of the Lewis acid/base stabilised phosphanylarsanylborane: As mentioned above, **3** does not lose H_2 even in refluxing toluene. Thus, we tried to induce H_2 elimination by UV irradiation. Photolysis of **3** in toluene results in a loss of H_2 and CO to yield the dimeric product $[(CO)_8W_2(\mu\text{-}PHBH_2 \cdot NMe_3)_2]$ (**5**), in which two tungsten atoms are bridged by two $[HPBH_2 \cdot NMe_3]$ ligands (Scheme 2). This experimental result was theoretically unexpected, since the calculated gas-phase reaction (see Table 1, entry 8) is endothermic by 165 kJ mol^{-1}. While this reaction is entropically favourable ($\Delta S^0_{298} = 190.4\ J\,mol^{-1}\,K^{-1}$), apparently the long irradiation time together with the solution conditions promoted the generation

Table 1. Calculated standard enthalpies ΔH^0_{298} [kJ mol^{-1}], Gibbs energies ΔG^0_{298} [kJ mol^{-1}] and entropies ΔS^0_{298} [J K^{-1} mol^{-1}] of gas-phase reactions. Calculations done at the B3LYP/6–31G*(ECP on W) level of theory.

Entry	Process	E	ΔH^0_{298}	ΔS^0_{298}	ΔG^0_{298}
1	$[Me_3N \cdot BH_3] + [H_3E\{W(CO)_5\}] \rightarrow [Me_3N \cdot H_2BPH_2\{W(CO)_5\}] + H_2$	P	−21.3	−63.4	−2.4
		As	−34.4	−50.5	−19.3
2	$BH_3 + EH_3 \rightarrow H_2BPH_2 + H_2$	P	−17.0	−13.7	−12.9
		As	−9.4	−12.9	−5.5
3	$2\,H_2BEH_2 \rightarrow [H_2BEH_2]_2$	P	−132.8	−185.0	−77.7
		As	−113.2	−186.4	−57.7
4	$H_2BEH_2 + NMe_3 \rightarrow [Me_3N \cdot H_2BEH_2]$	P	−98.1	−170.9	−47.2
		As	−111.8	−169.2	−61.3
5	$H_2BEH_2 + W(CO)_5 \rightarrow [H_2BEH_2\{W(CO)_5\}]$	P	−121.2	−138.8	−79.8
		As	−120.4	−168.9	−70.1
6	$H_2BEH_2 + NMe_3 + W(CO)_5 \rightarrow [Me_3N \cdot H_2BEH_2\{W(CO)_5\}]$	P	−262.5	−346.0	−159.3
		As	−271.0	−339.8	−81.5
7	$[Me_3N \cdot H_2EPH_2\{W(CO)_5\}] \rightarrow H_2EPH_2 + [Me_3N \cdot W(CO)_5]$	P	178.4	151.0	97.9
		As	172.2	159.6	108.3
8	$2\,[Me_3N \cdot H_2BPH_2\{W(CO)_5\}] \rightarrow [W(CO)_4 \cdot HEBH_2 \cdot NMe_3]_2 + H_2 + 2\,CO$	P	164.8	190.4	108.0
		As	127.2	181.3	73.2

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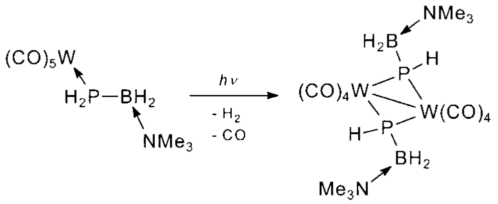

3 5

Scheme 2. Photolysis of **3** in toluene.

of **5**. Complex **5** can be obtained as an orange microcrystalline powder from toluene. It is slightly soluble in hexane and readily soluble in toluene and CH_2Cl_2.

Spectroscopic properties: The EI mass spectra of **3** and **4** show the appropriate molecular ion as well as characteristic fragment ion peaks. The IR spectra of **3** and **4** reveal absorptions for the C–O valence stretching frequencies of the $W(CO)_5$ moiety as well as the B–H and the E–H stretching frequencies. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a broad signal that displays a doublet structure ($\delta = -184.2$ ppm, $J = 63$ Hz). This signal is split into a triplet ($^1J(P,H) = 297$ Hz) when it is recorded without proton decoupling. If the spectrum is recorded with additional ^{11}B decoupling, the signal also displays tungsten satellites ($^1J(P,W) = 177$ Hz). In comparison with $[(CO)_5WPH_3]$ ($^1J(P,W) = 215.8$ Hz) the $^1J(P,W)$ coupling of **3** clearly reveals that the BH_2NMe_3 unit is less electronegative than the H substituent.[10] The $^{11}B\{^1H\}$ NMR spectrum of **3** shows a broad signal with a doublet structure at $\delta = -7.6$ ppm ($^1J(B,P) = 36$ Hz), which only broadens when the proton-coupled ^{11}B spectrum is recorded. In the $^{11}B\{^{31}P\}$ experiment a triplet structure is revealed due to the coupling with the two protons ($^1J(B,H) \approx 105$ Hz). The ^1H NMR spectrum of **4** shows a multiplet at $\delta = 1.27$ ppm for the AsH_2 protons. For the BH_2 protons a characteristically broad quartet signal at $\delta = 2.3$ ppm is detected with a $^1J(H,B)$ coupling of 117 Hz. The NMe_3 protons give rise to a singlet at $\delta = 1.46$ ppm. In the $^{11}B\{^1H\}$ spectrum of **4** a singlet is detected at $\delta = -7.0$ ppm, which splits into a triplet in the ^{11}B NMR spectrum due to the coupling with the two protons attached to the boron atom.

The mass spectrum of **5** shows the molecular ion as well as characteristic fragmentation peaks. In its $^{11}B\{^1H\}$ NMR spectrum **5** shows a broad singlet at $\delta = -1.4$ ppm. When the spectrum is recorded without proton decoupling, the signal gets even broader, but the supposed triplet structure of the signal can not be resolved. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows a broad peak at $\delta = 53.7$ ppm. This signal reveals a doublet ($^1J(P,H) = 293$ Hz) with tungsten satellites ($^1J(P,W) = 119$ Hz) in the $^{31}P\{^{11}B\}$ NMR experiment. The ^1H NMR spectrum of **5** shows a singlet for the NMe_3 protons at $\delta = 2.08$ ppm as well as a triplet of doublets at $\delta = 5.84$ ppm for the PH protons ($^1J(H,P) = 293$ Hz, $^3J(H,H) = 7$ Hz).

Crystal structural analysis: X-ray structure analyses have been performed for the isostructural compounds **3** and **4** (Figure 2). The central motif of both structures is a H_2EBH_2 unit (E = P (**3**), E = As (**4**)) which is coordinated to a $[W(CO)_5]$ fragment through the Group 15 element lone pair. Additionally, the boron atom achieves a coordination number of four by the coordination of the Lewis base NMe_3. The substituents around the E–B bond adopt a staggered geometry (N-B-E-W **3**: 177.7°; **4**: 177.1°). The B–P bond length in **3** (1.955(4) Å) is longer than in the calculated structure for H_2PBH_2 (1.90 Å[3b] or 1.905 Å[3c]). This finding is not surprising since π-bonding interactions are discussed for the latter compound, which are not possible in **3**. In comparison to other compounds with four-coordinate boron and phosphorus atoms, the B–P bond length in **3** shows no remarkable difference (c.f. 1.948(2) Å in $(Ph_2PBH_2)_3$[11]). Similar observations can be made for the structure of the arsenic-containing complex **4**. The B–As bond length (2.067(9) Å) is longer than the calculated distance of 1.990 Å for H_2AsBH_2.[5]

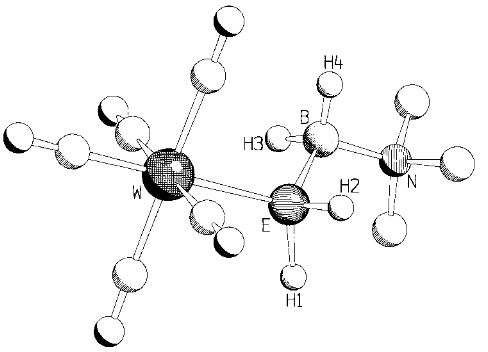

Figure 2. Molecular structure of $[\{(CO)_5W\}H_2EBH_2 \cdot NMe_3]$ **3** (E = P) and **4** (E = As) in the crystal (hydrogen atoms at the amine are omitted for clarity). Selected bond lengths [Å] and angles [°]: **3**: W–P 2.542(2), B–P 1.955(4), B–N 1.603(5); B-P-W 116.4(1), N-B-P 116.0(3); **4**: W–As 2.635(1), B–As 2.067(9), B–N 1.61(1); B-As-W 117.2(3), N-B-E 116.0(6).

The molecular structure of **5** is depicted in Figure 3 and reveals a $W_2(CO)_8$ fragment bridged by two $HPBH_2 \cdot NMe_3$ ligands, which adopt a *trans* arrangement. All bond lengths are in the expected ranges. The W–W′ distance (3.041(1) Å) is only slightly longer than in other tungsten complexes with bridging phosphanido ligands (c.f. $[W_2(CO)_8(\mu\text{-PH}t\text{Bu})_2]$ 3.017(2) Å,[12] $[W_2(CO)_8(\mu\text{-PPh}_2)_2]$ 3.026(1) Å[13]). The B–P bond length in **5** (1.963(2) Å) does not differ significantly from that in **3** (1.955(4) Å).

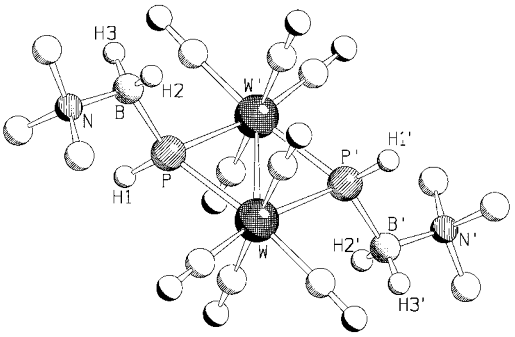

Figure 3. Molecular structure of $[(CO)_8W_2(\mu\text{-PHBH}_2 \cdot NMe_3)_2]$ **5** in the crystal (hydrogen atoms at the amine are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.501(3), W–P′ 2.515(3), W–W′ 3.040(1), P–B 1.96(2), B–N 1.61(2); P-W-P′ 105.37(9), P-W-W′ 52.90(7), P′-W-W′ 52.47(7), B-P-W 129.8(6), B-P-W′ 114.0(5), W-P-W′ 74.63(9), N-B-P 117(1).

Conclusion

By using our concept of Lewis acid/base stabilisation the parent compounds H_2EBH_2 ($E = P$, As) were stabilised for the first time. The metathesis reaction employed between $Li[(CO)_5WEH_2]$ (**2**) and $ClH_2B \cdot NMe_3$ to give $[(CO)_5W(H_2EBH_2 \cdot NMe_3)]$ (**3** and **4**) in good yields, together with the H_2 elimination reaction applied for the recently reported approach to the corresponding phosphanylalans and -gallanes $[(CO)_5W(H_2PE'H_2 \cdot NMe_3)]$ ($E' = Al$, Ga), opens broad possibilities for the synthesis of further mixed main group element containing derivatives. In contrast to the phosphanylalanes and -gallanes the novel boron complexes show much more stability towards H_2 elimination. Nevertheless, by applying some means of activation, such as photolytic or ultrasonic conditions, these starting materials open up broad potential for the synthesis of novel Group 13/15 oligomers coordinated to transition metals as well as for their own coordination chemistry. Furthermore, these volatile molecules could be valuable precursors for CVD processes.

Experimental Section

All reactions were performed under an atmosphere of dry argon with standard vacuum, Schlenk, and glove-box techniques. Solvents were purified and degassed by standard procedures. NMR spectra were recorded at 25 °C on a Bruker AC 250 (^1H: 250.133 MHz, ^{31}P: 101.256 MHz; standard Me_4Si (^1H), 85 % H_3PO_4 (^{31}P)), AMX 300 (^{11}B: 96.296 MHz; standard $F_3B \cdot OEt_2$). IR spectra were recorded in THF solutions on a Bruker IFS28 FT-IR spectrometer. The Raman spectra were recorded on a Bruker FRA-106. Mass spectra were recorded on a Finnigan MAT 711 spectrometer at 70 eV. Correct elemental analysis was performed by the analytical laboratory at the Institut für Anorganische Chemie Karlsruhe.

Reagents: Unless otherwise stated, commercial grade chemicals were used without further purification. $[(CO)_5WPH_3]$ and $[(CO)_5WAsH_3]$ were prepared by literature methods.[14]

Crystal structure analysis: Crystal structure analyses of **3**–**5** were performed on a STOE IPDS diffractometer with $Ag_{K\alpha}$ radiation ($\lambda = 0.56087$ Å). The structures were solved by direct methods with the program SHELXS-97,[15a] and full-matrix least-squares refinement on F^2 in SHELXL-97[15b] was performed with anisotropic displacements for non-H atoms. In **5** two solvent molecules of toluene were found. Hydrogen atoms at the carbon atoms were located in idealised positions and refined isotropically according to a riding model. The hydrogen atoms at the phosphorus, arsenic and boron atoms were freely refined. Further details of the structural refinement are given in Table 2.

CCDC-189025 (**3**), CCDC-189026 (**4**) and CCDC-189027 ($\mathbf{5} \cdot 2\,C_7H_8$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Synthesis of $Li[(CO)_5WAsH_2]$ (2b): To a vigorously stirred solution of $[(CO)_5WAsH_3]$ (854 mg, 2.125 mmol) in toluene (20 mL) an equimolar amount of a solution of *n*BuLi in hexane diluted with toluene (10 mL) was added over a period of 1 h. The light brown powder of **2b** which is formed during the reaction was separated by filtration, washed with toluene (5 mL) and hexane (15 mL) and dried in vacuo (686 mg, 79 %). ^1H NMR (300 MHz, $[D_8]$THF, TMS ext.): $\delta = 0{,}89$ (s, 2 H).

Synthesis of $[(CO)_5W(H_2PBH_2 \cdot NMe_3)]$ (3): $Li[(CO)_5WPH_2]$ (884 mg, 2.32 mmol) was allowed to react with $ClBH_2 \cdot NMe_3$ (226 mg, 2.11 mmol) in toluene (25 mL) for 14 h. After separation from the insoluble residue by filtration over celite and reduction of the solvent volume to 3 mL, **3** was obtained at −20 °C as light yellow crystals (523 mg, 58 %). **3**: ^1H NMR (300 MHz, $[D_6]$benzene, TMS ext.): $\delta = 1.44$ (d, $^4J(H,P) = 2$ Hz, 9 H; NMe_3), 2.48 ppm (dm, $^1J(H,P) = 297$ Hz, 2 H; PH_2); $^{11}B\{^1H\}$ NMR (96 MHz, $[D_6]$benzene, $F_3B \cdot OEt_2$ ext.): $\delta = -7.6$ ppm (d, br, $^1J(P,B) =$

Table 2. Crystallographic data for compounds **3**–**5**.

	3	**4**	$\mathbf{5} \cdot 2\,C_7H_8$
formula	$C_8H_{13}BNO_5PW$	$C_8H_{13}AsBNO_5W$	$C_{21}H_{32}B_2N_2O_8P_2W_2$
M_r	428.82	472.77	891.75
crystal size [mm]	0.40 × 0.40 × 0.30	0.20 × 0.16 × 0.03	0.30 × 0.20 × 0.04
T [K]	203(2)	203(2)	203(2)
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
crystal system	monoclinic	monoclinic	monoclinic
a [Å]	10.650(2)	10.785(2)	21.142(4)
b [Å]	14.964(3)	14.909(3)	12.273(3)
c [Å]	9.806(2)	9.860(2)	12.720(3)
α [°]	90.00	90.00	90.00
β [°]	107.39(3)	107.24(3)	108.12(3)
γ [°]	90.00	90.00	90.00
V [Å^3]	1491.4(5)	1514.2(5)	3136.6(11)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.910	2.074	1.888
μ [mm^{-1}]	4.233	5.258	4.026
radiation [λ, Å]	0.56087	0.56087	0.56087
diffractometer	STOE IPDS	STOE IPDS	STOE IPDS
2Θ range [°]	$3.16 \le 2\Theta \le 44.70$	$3.12 \le 2\Theta \le 44.78$	$3.06 \le 2\Theta \le 44.42$
index range	$-13 \le h \le 14$	$-14 \le h \le 14$	$-28 \le h \le 28$
	$-20 \le k \le 20$	$-19 \le k \le 16$	$-16 \le k \le 16$
	$-13 \le l \le 13$	$-12 \le l \le 12$	$-16 \le l \le 16$
data/restrains/parameters	3854/0/173	3775/0/173	3840/0/185
independent reflections with $I > 2\sigma(I)$	3235 ($R_{int} = 0.0564$)	2558 ($R_{int} = 0.0612$)	3074 ($R_{int} = 0.0891$)
goodness-of-fit on F^2	1.065	1.026	1.226
R_1,[a] ωR_2[b] ($I > 2\sigma(I)$)	0.0277, 0.0608	0.0482, 0.1020	0.0707, 0.1554
R_1,[a] ωR_2[b] (all data)	0.0371, 0.0641	0.0816, 0.1146	0.0894, 0.1637
largest diff peak and hole [e$^-$/Å^{-3}]	1.160, −0.639	1.607, −1.060	2.728, −2.962

[a] $R = \Sigma|F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma\omega(F_o^2 - F_c^2)^2]/[\Sigma(F_o^2)^2]^{1/2}$.

36 Hz; BH_2); $^{11}B\{^{31}P\}$ NMR: $\delta = -7.6$ ppm (t, br, $^1J(H,B) = 105$ Hz; BH_2); $^{31}P\{^1H\}$ NMR (101 MHz, [D_6]benzene, H_3PO_4 ext.): $\delta = -184.2$ ppm (d, br, $J = 63$ Hz; PH_2); $^{31}P\{^{11}B\}$ NMR: $\delta = -184.2$ ppm (t, $^1J(P,H) = 297$ Hz, $^1J(P,W) = 177$ Hz; PH_2); MS (EI, 90 °C): *m*/*z* (%): 429 (52) [M^+], 401 (22) [$M^+ - CO$], 373 (27) [$M^+ - 2\,CO$], 369 (100) [$M^+ - 2\,CO - 4\,H$], 341 (67) [$M^+ - 3\,CO - 4\,H$], 313 (35) [$M^+ - 4\,CO - 4\,H$], 285 (24) [$M^+ - 5\,CO - 4\,H$]; IR (THF): $\tilde{\nu} = 2423$(w) (ν_{BH}), 2319(w) (ν_{PH}), 2066(m), 1971(sh), 1926(br), 1910(s) (ν_{CO}) cm^{-1}; Raman (solid-state): $\tilde{\nu} = 3007$ (w), 2951 (s), 2393 (w), 2323 (m), 2065 (m), 1959 (vs), 1935 (m), 1872 (s), 1469 (w), 1100 (w), 462 (m), 434 (s), 103 cm^{-1} (s).

Synthesis of [$(CO)_5W(H_2AsBH_2 \cdot NMe_3)$] (4): [$(CO)_5WAsH_2Li$] (686 mg, 1.682 mmol) was allowed to react with $ClBH_2 \cdot NMe_3$ (181 mg, 1.682 mmol) in toluene (10 mL) at 0 °C under ice cooling in the dark for 12 h. After separation from the insoluble residue by filtration over celite and reduction of the solution to dryness the residue was extracted with hexane/toluene (4:1; 30 mL). At −25 °C light yellow crystals of **4** were obtained (350 mg, 44%). **4**: ^1H NMR (300 MHz, [D_6]benzene, TMS ext.): $\delta = 1.27$ (m, 2H; AsH_2), 1.46 (s, 9H; NMe_3), 2.3 ppm (q, $^1J(H,B) = 117$ Hz, 2H, BH_2); $^{11}B\{^1H\}$ NMR (96 MHz, [D_6]benzene, $F_3B \cdot OEt_2$ ext.): $\delta = -7.0$ (s, br, BH_2); ^{11}B NMR: $\delta = -7.0$ ppm (t, br, $^1J(H,B) = 117$ Hz, BH_2); MS (EI, 90 °C): *m*/*z* (%): 473 (24) [M^+], 443 (5) [$M^+ - H$], 415 (19) [$M^+ - 2\,H - 2\,CO$], 387 (30) [$M^+ - 2\,H - 3\,CO$], 359 (19) [$M^+ - 2\,H - 4\,CO$], 72 (100) [$M^+ - (CO)_5WAsH_2$]; IR (THF): $\tilde{\nu} = 2125$(w) (ν_{BH}), 2065(m) (ν_{AsH}), 1970(sh), 1926(br), 1910(m) (ν_{CO}).

Synthesis of [$(CO)_8W_2(\mu\text{-}PHBH_2 \cdot NMe_3)_2$] (5): A solution of [$W(CO)_5(H_2PBH_2 \cdot NMe_3)$] (**3**) (352 mg, 0.82 mmol) in toluene (40 mL) was irradiated with a UV lamp for 12 h in a Schlenk tube made of quartz glass. After removal of the solvent and recrystallisation from toluene, **5** was obtained as a microcrystalline orange powder (240 mg, 73%). ^1H NMR (300 MHz, [D_6]benzene, TMS ext.): $\delta = 2.08$ (s, 18H; NMe_3), 5.84 ppm (dt, $^1J(H,P) = 293$ Hz, $^3J(H,H) = 7$ Hz, 2H; PH); $^{11}B\{^1H\}$ NMR (96 MHz, [D_6]benzene, $F_3B \cdot OEt_2$ ext.): $\delta = -1.4$ ppm (s, br, BH_2); $^{31}P\{^1H\}$ NMR (101 MHz, [D_6]benzene, H_3PO_4 ext.): $\delta = 53.7$ ppm (s, br, PH); $^{31}P\{^{11}B\}$ NMR: $\delta = 53.7$ ppm (d, $^1J(P,H) = 293$ Hz, $^1J(P,W) = 119$ Hz, PH); MS (EI, 170 °C): *m*/*z*: 800 (2) [M^+], 772 (1) [$M^+ - CO$], 744 (2) [$M^+ - 2\,CO$], 716 (1) [$M^+ - 3\,CO$], 688 (1) [$M^+ - 4\,CO$], 681 (1) [$M^+ - 2\,NMe_3$].

Acknowledgement

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. A.Y.T. is grateful to the Alexander von Humboldt foundation for a research fellowship.

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[1] For a review see: R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343–379.

[2] a) M. S. Lube, R. L. Wells, P. S. White, *Main Group Met. Chem.* **1996**, *13*, 733–741; b) M. A. Mardones, A. H. Cowley, L. Contreras, R. A. Jones, C. J. Carrano, *J. Organomet. Chem.* **1993**, *455*, C1-C2; c) M. A. Petrie, M. M. Olmstead, H. Hope, R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 3221–3226; d) R. Goetze, H. Nöth, *Z. Naturforsch. B* **1975**, *30*, 875–882.

[3] a) T. L. Allen, W. H. Fink, *Inorg. Chem.* **1992**, *31*, 1703–1705; b) T. L. Allen, A. C. Scheiner, H. F. Schaefer III, *Inorg. Chem.* **1990**, *29*, 1930–1936; c) M. B. Coolidge, W. T. Borden, *J. Am. Chem. Soc.* **1990**, *112*, 1704–1706.

[4] U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2001**, *113*, 4541–4544; *Angew. Chem. Int. Ed.* **2001**, *40*, 4409–4412.

[5] a) DFT calculations have been performed using the standard Gaussian 98 program suite (Gaussian 98 (Revision A.1): M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Milliam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomberts, R. L. Martin, D. J. Fox, T. A. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian Inc., Pittsburgh, PA 1998). B3LYP functional (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785—793) has been used together with standard 6–31G* basis set for H, C, N, Al, P. Effective core potential basis set of Hay and Wadt (P. J. Hay, W. R. Wadt, *J. Chem. Phys.,* **1985**, *82*, 299—310) was used for W. All structures were fully optimised with subsequent vibrational analysis and correspond to the minimum on the potential energy surface.

[6] H. Schäfer, W. Leske, *Z. Anorg. Allg. Chem.* **1987**, *552*, 50–68.

[7] F. Nief, F. Mercier, F. Mathey, *J. Organomet. Chem.* **1987**, *328*, 349–355.

[8] Some transition metal complexes containing a B–As bond have been previously described, but these are BH_3 adducts of transition-metal-substituted arsanes: cf. R. Janta, R. Maisch, W. Malisch, E. Schmid, *Chem. Ber.* **1983**, *116*, 3951–3955; E. A. V. Ebsworth, R. O. Gould, R. A. Mayo, M. Walkinshaw, *J. Chem. Soc. Dalton Trans.* **1987**, 2831–2838.

[9] From these solutions a black insoluble precipitate is formed.

[10] F. Mercier, F. Mathey, C. Afiong-Akpan, J. F. Nixon, *J. Organomet. Chem.* **1988**, *348*, 361–367.

[11] G. J. Bullen, P. R. Mallinson, *J. Chem. Soc. Dalton Trans.* **1973**, 1295–1300.

[12] G. Huttner, J. Borm, L. Zsolnai, *J. Organomet. Chem.* **1986**, *304*, 309–321.

[13] S.-G. Shyu, M. Calligaris, G. Nardin, A. Wojcicki, *J. Am. Chem. Soc.* **1987**, *109*, 3617–3625.

[14] U. Vogel, M. Scheer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1593–1598.

[15] a) G. M. Sheldrick, SHELXS-97, University of Göttingen, **1998**; b) G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**.

Received: September 12, 2002 [F4420]