



Halogenation of Lewis acid/base stabilised phosphanylboranes

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ARTICLE INFO

Article history:

Received 18 August 2008
Received in revised form 23 September 2008
Accepted 24 September 2008
Available online 30 September 2008

Dedicated to Professor Christoph Elschenbroich on the occasion of his 70th birthday.

Keywords:

Lewis-acid/base-stabilised phosphanylborane
Phosphorous
Boron
Halogenation
Iodine
Bromine

ABSTRACT

The reaction pattern of the Lewis-acid/base stabilised phosphanylborane $[(\text{CO})_5\text{W}(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ (**1**) with elemental halogens is comprehensively studied. The reaction with iodine and bromine leads to a selective halogenation at the tungstencarbonyl moiety under formation of $[\text{WX}_2(\text{CO})_4(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ ($\text{X} = \text{I}$ (**2**), Br (**3**)). Whereas **2** is a stable product the brominated compound **3** dimerises easily to $[\text{WBr}_2(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]_2$ (**4**) under loss of CO. The CO elimination reaction of **3** is extensively studied. If **3** is reacted with $[\text{Et}_4\text{N}][\text{Br}]$ the ionic compound $[\text{Et}_4\text{N}][\text{WBr}_3(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ (**5**) is formed. Otherwise, if **3** is combined with the donor ligand $[\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3]$, the complex $[\text{WBr}_2(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)_2]$ (**6**) is obtained. Compounds **2–6** are comprehensively characterised by X-ray diffraction analysis, NMR, and IR spectroscopy.

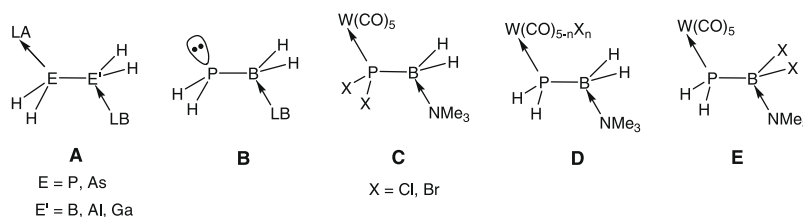
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1. Introduction

Group 13/15 element compounds play an important role in the design of semiconducting layers as well as for novel inorganic polymers [1]. We are particularly interested in controlled polymerisation processes of 13/15 element compounds, which are derived from the parent compounds of the formula $[\text{H}_2\text{EE}'\text{H}_2]$ ($\text{E} = \text{P}, \text{As}$; $\text{E}' = \text{B}, \text{Al}, \text{Ga}$). We were able to show the synthesis of the first Lewis-acid (LA) and Lewis-base (LB) stabilised parent compounds of the phosphanylalanes and gallanes [2] as well as the corresponding arsanil- and phosphanylboranes of type **A** [3]. One of the aspects of initial investigations concerning the reactivity of the LA/LB stabilised phosphanylborane $[\text{W}(\text{CO})_5(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ (**1**), was the elimination of the transition metal moiety to synthe-

size the parent compound of the phosphanylborane **B**, stabilised only by a Lewis base. Thus, the novel primary boranylphosphine $[\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3]$ has been synthesised [4].

Another interesting question regarding the reactivity of $[\text{W}(\text{CO})_5(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ (**1**) is the behaviour towards different halogenation reagents. Recently, we surprisingly discovered the selective double halogenation of **1** at the phosphorus atom using CX_4 ($\text{X} = \text{Cl}, \text{Br}$) as reactants to yield compounds of type **C** [5]. In addition to these findings we have been interested to investigate halogenation reactions with elemental dihalogens in a more general manner. Besides the halogenation at the tungsten atom (type **D**), in principle, the substitution of hydrogens at the pnictogen (type **C**) as well as at the boron atom (type **E**) is possible. In contrast to the halogenation with CX_4 to give the type **C** complexes,



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we now find that the reaction with Br₂ and I₂ leads to halogenation at the tungsten atom under the loss of CO to form type **D** complexes which show a great diversity in a subsequent reactivity pattern. The results of these investigations we report herein after.

2. Experimental

2.1. General remarks

All manipulations are performed under an atmosphere of dry nitrogen using standard glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. NMR Spectra were recorded on a Bruker Avance 400 (400.13 MHz for ¹H, 192.55 MHz for ¹¹B and 161.98 MHz for ³¹P) and the chemical shifts are referenced to external standards (¹H: SiMe₄, ¹¹B: BF₃·Et₂O, ³¹P: 85% H₃PO₄). IR spectra were recorded either on a Bruker IFS 280 or a Varian FTS 2000 spectrometer. ESI-MS spectra were measured on a Finnigan Thermoquest TSQ 7000 mass-spectrometer. Starting materials were synthesized using published procedures: **1** [3] and [H₂PBH₂·NMe₃] [4].

2.2. Preparations

2.2.1. [W(CO)₄(H₂PBH₂·NMe₃)] (**2**)

To a solution of [(CO)₅W(H₂PBH₂·NMe₃)] (**1**) (200 mg, 0.466 mmol) in CH₂Cl₂ (25 ml) an equimolar amount of iodine (118 mg, 0.466 mmol) is added at 0 °C. The colour of the solution changes from pale yellow to yellow. After stirring for 14 h the solvent is removed in vacuo until incipient crystallisation. Compound **2** is obtained at -20 °C as pale yellow plates (250 mg, 0.383 mmol, 82%). **2**: Anal. Calc. for BC₇H₁₃I₂NO₄PW (654.62): C, 12.84; H, 2.00. Found: C, 12.68; H, 1.86%. ¹H NMR (CD₂Cl₂, 300 K): δ = 2.81 (s, 9H, NMe₃), 4.24 ppm (dm, ¹J(H,P) = 333 Hz, 2H, PH₂), ³¹P NMR (CD₂Cl₂, 300 K): δ = -150.3 ppm (t, br, ¹J(P,H) = 333 Hz, PH₂), ³¹P{¹H} NMR (CD₂Cl₂, 300 K): δ = -150.3 ppm (s, br, PH₂), ¹¹B NMR (CD₂Cl₂, 300 K): δ = -150.3 ppm (s, br, BH₂); IR (KBr): ν̄ = 3000 (w), 2963 (w), 2925 (w), 2424 (m, BH), 2401 (w, BH), 2340 (w, PH), 2300 (w, PH), 2072 (vs, CO), 2021 (vs, CO), 1981 (vs, CO), 1948 (vs, CO), 1481 (m), 1466 (m), 1411 (w), 1241 (w), 1153 (w), 1127 (m), 1098 (m), 1057 (m), 976 (m), 866 (m), 800 (m), 762 (m), 710 (w), 535 (s), 500 (m), 479 (s) cm⁻¹.

2.2.2. [WBr₂(CO)₄(H₂PBH₂·NMe₃)] (**3**)

[(CO)₅W(H₂PBH₂·NMe₃)] (**1**) (382 mg, 0.891 mmol) in Et₂O (15 ml) is allowed to react with 1.5 ml (0.891 mmol) of a 0.59 M Br₂ solution in pentane at -25 °C. After stirring over night the solution is concentrated by blowing a CO stream over the reaction mixture. The solution is kept at -25 °C under a CO atmosphere to give pale yellow crystals of **3** (429 mg, 0.765 mmol, 86%). Compound **3**: Anal. Calc. for BC₇H₁₃Br₂NO₄PW (560.62): C, 15.00; H, 2.34. Found: C, 14.76; H, 2.66%. ¹H NMR (toluene-*d*₈, 300 K): δ = 2.79 (d, ⁴J(H,P) = 1 Hz, 9H, NMe₃), 3.55 ppm (dm, ¹J(H,P) = 331 Hz, 2H, PH₂), ³¹P NMR (toluene-*d*₈, 300 K): δ = -133.1 ppm (t(br), ¹J(P,H) = 333 Hz, PH₂), ³¹P{¹H} NMR (toluene-*d*₈, 300 K): δ = -133.1 ppm (s(br), ¹J(P,H) = 333 Hz, PH₂), ¹¹B NMR (toluene-*d*₈, 300 K): δ = -10.1 ppm (s, br, BH₂); IR (KBr): ν̄ = 3000 (w), 2964 (w), 2926 (w), 2450 (m, BH), 2409 (w, BH), 2347 (w, PH), 2301 (w, PH), 2099 (vs, CO), 2027 (vs, CO), 1990 (vs, CO), 1946 (vs, CO), 1484 (m), 1465 (m), 1412 (w), 1262 (s), 1154 (w), 1128 (m), 1098 (vs), 1060 (s), 1022 (vs), 977 (w), 863 (m), 802 (vs), 760 (w), 706 (w), 536 (w), 500 (m) cm⁻¹.

2.2.3. [WBr₂(CO)₃(H₂PBH₂·NMe₃)]₂ (**4**)

To [(CO)₅W(H₂PBH₂·NMe₃)] (**1**) (125 mg, 0.292 mmol) dissolved in toluene (10 ml) 0.68 ml a 0.47 M Br₂ solution (0.32 mmol) in pentane is added dropwise at -25 °C. The mixture is vigorously

stirred for 12 h. The solid residue is separated by filtration and washed twice with toluene (about 10 ml). The combined filtrate and washings are heated to 50–60 °C for a short time to complete the CO elimination. When the resulting orange solution reaches room temperature **4** is obtained as yellow needles (131 mg, 0.123 mmol, 84%). Compound **4**: Anal. Calc. for B₂Br₄C₁₂H₂₆N₂O₆P₂W₂ (1065.21): C, 13.53; H, 2.46. Found: C, 13.79; H, 2.80%. ¹H NMR (CD₂Cl₂, 300 K): δ = 2.77 (s, 9H, NMe₃), 4.18 ppm (dm, ¹J(H,P) = 339 Hz, 2H, PH₂), ³¹P NMR (CD₂Cl₂, 193 K): δ = -116.3 ppm (t, br, ¹J(P,H) = 339 Hz, PH₂), ³¹P{¹H} NMR (CD₂Cl₂, 193 K): δ = -116.3 ppm (s, br, PH₂), ¹¹B NMR (CD₂Cl₂, 300 K): δ = -9.3 ppm (s, br, BH₂); IR (KBr): ν̄ = 3003 (w), 2949 (w), 2446 (m, BH), 2414 (m, BH), 2348 (m, PH), 2303 (m, PH), 2021 (vs, CO), 1935 (vs, CO), 1921 (vs, CO), 1482 (s), 1467 (s), 1261 (w), 1244 (w), 1156 (m), 1128 (s), 1094 (m), 1063 (m), 1017 (w), 975 (w), 866 (w), 784 (vs), 737 (w), 479 (w), 448 (w) cm⁻¹.

2.2.4. Synthesis of [Et₄N][WBr₂(CO)₃(H₂PBH₂·NMe₃)] (**5**)

Et₄NBr (53 mg, 0.253 mmol) is added at room temperature to [WBr₂(CO)₃(H₂PBH₂·NMe₃)]₂ (**4**) (135 mg, 0.127 mmol) dissolved in CH₂Cl₂ (20 ml) and vigorously stirred for 12 h. Afterwards the solvent is reduced to 2 ml in vacuo. After adding THF (2–3 ml) the mixture is layered with *n*-hexane (4 ml). After 24 h, **5** crystallises at room temperature as yellow plates (162 mg, 0.218 mmol, 86%). **5**: Anal. Calc. for B₁Br₃C₁₄H₃₃N₂O₃P₁W₁ (742.76): C, 22.64; H, 4.48. Found: C, 22.91; H, 4.78%. ¹H NMR (CD₂Cl₂, 300 K): δ = 1.35 (t, ³J(H,H) = 6 Hz, 12H, NEt₄), 2.79 (d, ⁴J(H,P) = 1 Hz, 9H, NMe₃), 3.31 (q, ³J(H,H) = 7 Hz, 8H, NEt₄), 4.11 ppm (dt, ¹J(H,P) = 338 Hz, ³J(H,H) = 6 Hz, 2H, PH₂), ³¹P NMR (CD₂Cl₂, 300 K): δ = -98.6 ppm (t, ¹J(P,H) = 338 Hz, PH₂), ³¹P{¹H} NMR (CD₂Cl₂, 300 K): δ = -98.6 ppm (s, br, PH₂), ¹¹B NMR (CD₂Cl₂, 300 K): δ = -9.0 ppm (s, br, BH₂); positive ion MS (ESI, THF/CH₃CN): *m/z* (%): 612 ([A]⁺, 4%), negative ion MS (ESI, THF/CH₃CN): *m/z* (%): 130 ([K]⁺, 100%); IR (KBr): ν̄ = 3006 (w), 2988 (w), 2948 (w), 2426 (m, BH), 2396 (w, BH), 2336 (w, PH), 2302 (w, PH), 2010 (vs, CO), 1940 (sh, CO), 1919 (vs, CO), 1863 (vs, CO), 1481 (m), 1460 (m), 1393 (w), 1247 (w), 1171 (w), 1129 (w), 1087 (w), 1052 (w), 1000 (w), 864 (w), 795 (s), 590 (m) cm⁻¹.

2.2.5. Synthesis of [WBr₂(CO)₃(H₂PBH₂·NMe₃)]₂ (**6**)

A mixture of [WBr₂(CO)₃(H₂PBH₂·NMe₃)]₂ (**4**) (107 mg, 0.101 mmol) in THF (10 ml) and H₂PBH₂·NMe₃ (0.025 ml, 21 mg, 0.201 mmol) is stirred at room temperature for 5 h. The solution is filtered over Celite and the solvent removed in vacuo. Compound **6** is obtained as a pale yellow solid (84 mg, 0.132 mmol, 66%). Compound **6**: Anal. Calc. for B₂Br₂C₉H₂₆N₂O₃P₂W (637.53): C, 16.96; H, 4.11. Found: C, 17.27; H, 4.43%. ¹H NMR (benzene-*d*₆, 300 K): δ = 2.80 (s, 9H, NMe₃), 3.95 ppm (dt, ¹J(H,P) = 331 Hz, ³J(H,H) = 7 Hz, 2H, PH₂), ³¹P NMR (benzene-*d*₆, 300 K, 85% H₃PO₄ ext.): δ = -116.5 ppm (s, br, PH₂), ¹¹B NMR (benzene-*d*₆, 300 K): δ = -9.0 ppm (s, br, BH₂); IR (THF): ν̄ = 2432 (m, BH), 2395 (m, BH), 2342 (w, PH), 2016 (vs, CO), 1932 (vs, CO), 1901 (vs, CO), 1779 (w), 1261 (s), 1082 (vs), 807 (m), 704 (w), 542 (w), 503 (w) cm⁻¹.

2.3. X-ray structure determination

The crystal structure analyses of the products were performed on a STOE IPDS diffractometer with Mo-Kα radiation (λ = 0.71073 Å) for **4** and **6** and Ag-Kα radiation (λ = 0.56087 Å) for **2** and **5a**. The crystal structure analysis of **3** and **5** was performed on an Oxford Diffraction Gemini Ultra diffractometer with Cu-Kα radiation (λ = 1.54180 Å). The structures are solved by direct methods with the program SHELXS-97 [6], and full matrix least squares refinement on *F*² in SHELXL-97 [6] is performed with aniso-

tropic displacements for non-H atoms. Hydrogen atoms at the carbon atoms are located in idealised positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus and boron atoms are localised by residual electron density and freely refined.

3. Results and discussion

3.1. Synthesis and X-ray crystallographic characterisation

The reaction of **1** in CH_2Cl_2 with elemental iodine, yields the halogenated compound $[\text{Wl}_2(\text{CO})_4(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ (**2**) (Scheme 1) [7]. The oxidative addition with the halogens leads to a compound with a heptacoordinated tungsten atom under simultaneous CO elimination. The product is remarkably stable in solution under inert gas conditions, however, the solid product decomposes under the influence of light after a few days.

Whereas the iodine compound **2** represents a stable monomer, the analogous reaction of **1** with bromine results in the dimeric compound $[\text{WBr}_2(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]_2$ (**4**) (Scheme 2), due to further loss of CO from the first formed bromination product **3** (Scheme 1). The reaction (1) was, thus, repeated in Et_2O at -25°C under an atmosphere of CO to prevent the loss of a second CO molecule (Scheme 1). To obtain the pure monomeric compound **3** as a crystalline product, it is necessary to reduce the solvent by using a stream of CO. Compound **3** crystallises at -25°C as pale yellow prisms, which are extremely sensitive regarding the loss of CO. Similar observations were made by Vahrenkamp et al. for the bromination of complexes of the formulae $[(\text{CO})_5\text{WPR}_3]$ ($\text{R} = \text{Me}, \text{Bu}$) [8].

The dimeric product **4** can be prepared in high yields in toluene by adding a bromine/pentane solution at -25°C to **1** in a molar ratio of 1:1. To complete the CO elimination, the reaction mixture is heated for a short period of time to $50\text{--}60^\circ\text{C}$ (Scheme 2). In **4**, the two tungsten moieties are bridged by two bromine atoms which also results in two sevenfold coordinated tungsten atoms. In gen-

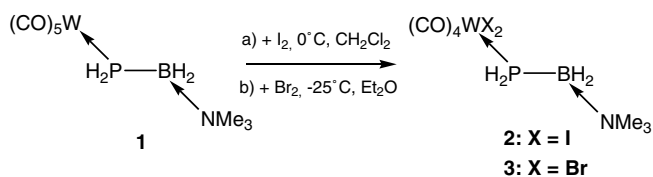
eral, the W halogenated carbonyl compounds, which contain sevenfold coordinated tungsten atoms in the formal oxidation state of +2, are useful synthetic building blocks in many subsequent reactions [9].

The X-ray crystallographic determination (see Table 1) of the structure of the monomeric compounds **2** and **3** reveal an antiperiplanar [10] arrangement of the LA and LB around the B–P axis (Fig. 1). Both compounds crystallise in the monoclinic space group $P2_1/c$ but are not isomorphous. The structural feature of both is a $\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3$ moiety, which coordinates to a tungsten atom containing already four carbonyl ligands and two halogens. Consequently, a heptacoordinated tungsten atom is formed. The increased number of ligands and the higher oxidation state at the tungsten atom has a small influence on the length of the W–P bond in comparison with the starting material **1**. In both cases the bond is slightly elongated, but the effect is marginal for the bromine compound **3**. In contrast, in **2** the halogenation leads to a noticeable increase of the W–P bond distance (**2**: $2.575(3)\text{Å}$, **1**: $2.542(2)\text{Å}$).

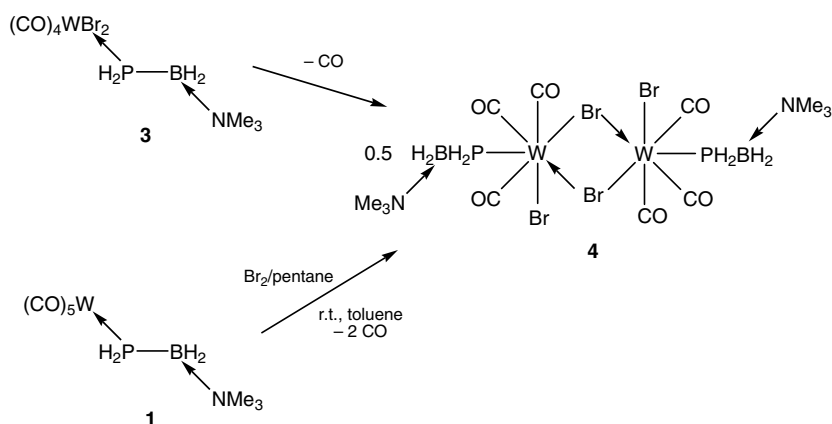
The tungsten atom in both compounds possesses the coordination number of seven. The geometry can be described as a monocapped octahedron with the C(2) acting as a capping atom. The sum of the angles in the nearby square plane defined by the atoms C(1), C(3), X(2), and P is about 355.5° (**2**) and 359.5° (**3**). The distorted axial positions are occupied by the halogen X(1) and the atom C(4). The arrangement of the different ligands is a consequence of the different σ -donor and π -acceptor abilities of the single ligands. The carbonyl group, as the strongest π -acceptor, prefers the capping position and in *trans* position to it a weak π -acceptor ligand like a halogen or the phosphanylborane ligand. Hence, no CO group has another one in *trans* position.

The binuclear compound **4** crystallises in the space group $P2_1/c$, with one molecule of toluene in the unit cell. The molecular structure of **4** reveals two tungsten atoms, each surrounded by seven ligands (Fig. 2).

The two polyhedral units around the tungsten atoms are bridged by the bromine atoms Br(1) and Br(2). This results in a square plane between the bromine atoms Br(1) and Br(2) and both tungsten atoms (angle: 359.53°). The structure of the complex reminds of the core of the compound $[\text{W}_2\text{Br}_4(\text{CO})_8]$, reported by Cotton et al. [11]. The W–Br distance of the bridging bromine atoms in **4** are longer than those of the terminal halogens, which are about $0.056(1)\text{Å}$ shorter. The two phosphanylborane moieties are in an antiperiplanar arrangement with a $\text{P}(1)\text{--W}(1)\text{--W}(2)\text{--P}(2)$ angle of $174.87(1)^\circ$. The tungsten atoms represent monocapped octahedral geometries, with the C(2) and the C(8) along each acting as the capping atom.



Scheme 1. Reaction of **1** with elemental halogens.



Scheme 2. Formation of the Br bridged complex **4**.

Table 1
Crystallographic data for compounds **2–6**.

	2	3	4 × C ₇ H ₈	5	5a × OC ₄ H ₈	6
Empirical formula	BC ₇ H ₁₃ I ₂ NO ₄ PW	BBr ₂ C ₇ H ₁₃ NO ₄ PW	B ₂ Br ₄ C ₁₉ H ₃₄ N ₂ O ₆ P ₂ W ₂	B ₁ Br ₃ C ₁₄ H ₃₃ N ₂ O ₃ P ₁ W ₁	B ₁ Br ₃ C ₁₃ H ₃₁ N ₂ O ₄ P ₁ W ₁	B ₂ Br ₂ C ₉ H ₂₆ N ₂ O ₃ P ₂ W
Formula mass (g mol ⁻¹)	654.60	560.60	1157.32	742.78	744.77	637.52
Collection <i>T</i> (K)	203(2)	150(1)	173(1)	123(2)	203(2)	100(1)
λ (Å)	0.56087	1.54184	0.71073	1.54184	0.56087	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	7.073(2)	10.128(1)	15.359(2)	9.5299(2)	10.527(2)	17.442(4)
<i>b</i> (Å)	19.496(4)	12.263(1)	16.241(2)	16.4596(2)	10.635(2)	12.378(3)
<i>c</i> (Å)	12.120(2)	13.471(1)	14.202(2)	15.6760(2)	12.071(2)	19.730(4)
α (°)	90	90	90	90	103.20(3)	90
β (°)	98.50(3)	113.86(1)	98.74(2)	96.818(2)	97.66(3)	90
γ (°)	90	90	90	90	103.70(3)	90
<i>V</i> (Å ³)	1652.9(6)	1530.1(1)	3501.7(5)	2441.52(7)	1252.9(4)	4259.7(17)
<i>Z</i>	4	4	4	4	2	8
<i>D</i> _{calc} (g cm ⁻³)	2.631	2.434	2.195	2.021	1.974	1.988
μ (mm ⁻¹)	5.792	21.135	11.252	15.263	5.088	9.332
<i>F</i> (000)	1176	1032	2152	1416	708	2416
Crystal dimensions (mm)	0.30 × 0.20 × 0.04	0.20 × 0.04 × 0.02	0.22 × 0.05 × 0.05	0.10 × 0.03 × 0.02	0.30 × 0.20 × 0.06	0.20 × 0.06 × 0.02
2θ Range	3.2–42.0	9.6–102.4	3.84–51.6	7.82–124.16	2.8–44.82	4.2–50.0
Index ranges	−9 ≤ <i>h</i> ≤ 8 −24 ≤ <i>k</i> ≤ 24 −15 ≤ <i>l</i> ≤ 15	−10 ≤ <i>h</i> ≤ 10 −12 ≤ <i>k</i> ≤ 12 −12 ≤ <i>l</i> ≤ 13	−18 ≤ <i>h</i> ≤ 18 −19 ≤ <i>k</i> ≤ 18 −17 ≤ <i>l</i> ≤ 17	−6 ≤ <i>h</i> ≤ 10 −17 ≤ <i>k</i> ≤ 18 −18 ≤ <i>l</i> ≤ 15	−14 ≤ <i>h</i> ≤ 12 −12 ≤ <i>k</i> ≤ 14 −16 ≤ <i>l</i> ≤ 16	−20 ≤ <i>h</i> ≤ 20 −14 ≤ <i>k</i> ≤ 12 −23 ≤ <i>l</i> ≤ 23
Reflections collected	10857	7564	26309	8139	9467	19007
Independent reflections	3509	1644	6742	3741	5987	3753
Goodness-of-fit on <i>F</i> ²	1.150	0.965	0.804	0.983	1.074	1.029
<i>R</i> _{int}	0.1267	0.0277	0.0555	0.0220	0.0344	0.1221
Parameters	173	169	358	242	252	228
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0461	0.0252	0.0575	0.0249	0.0363	0.0589
w <i>R</i> ₂ ^b (all data)	0.1166	0.0477	0.0617	0.0615	0.0990	0.1045
Max/min Δρ (e Å ⁻³)	2.130/−2.667	0.654/−0.505	1.765/−0.692	1.597/−0.708	2.291/−2.742	1.859/−1.329

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{1/2}$.

Both polyhedral units are very similar and, therefore, only one is discussed in the following (Fig. 3). The W–P distances (2.511(2) and 2.503(2) Å) are shorter compared to the starting material **1** (2.542(2) Å). This is consistent with the different *trans* oriented ligands in **4** and **1** and the metal-phosphorous π-back-donation behaviour of them. In **4**, a bridging bromide ligand as a non π-acceptor ligand is in the *trans* position, whereas in **1** a

strong π-accepting CO ligand is *trans* located. The square plane base of the octahedron, defined by the atoms P(1), Br(1), Br(2) and C(3), is almost planar (sum of angles: 356.38°). The distorted angle of the axial atoms Br(3) and C(1) is 153.6(2)°, due to the influence of the additional capping C(2) atom. The conformation of the ligands also depends on the different σ-donor and π-acceptor properties.

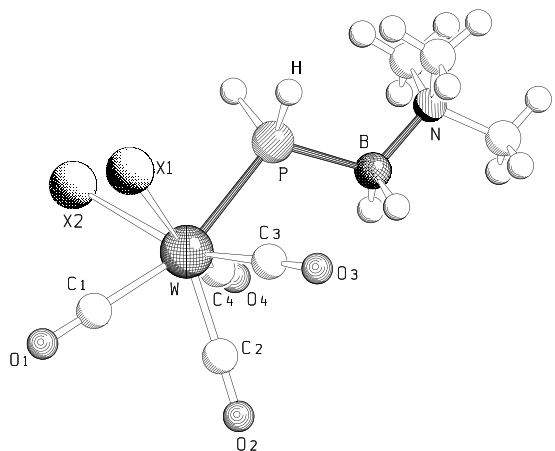


Fig. 1. Molecular structure of [WX₂(CO)₄(H₂PBH₂ · NMe₃)] (X = I (**2**), Br (**3**)) in the crystal. Selected bond lengths (Å) and angles (°): **2**: W–P 2.575(3), P–B 1.968(9), N–B 1.593(11), W–C(1) 2.050(8), W–C(2) 1.988(8), W–C(3) 2.027(7), W–C(4) 2.039(8), W–I(1) 2.845(1), W–I(2) 2.866(1), I(1)–W–C(4) 156.7(2), C(1)–W–C(3) 113.0(3), P–W–C(3) 75.3(3), I(2)–W–P 90.4(1), I(2)–W–C(1) 76.8(2), P–B–N 116.5(6), I(2)–W–C(3) 159.6(2), I(1)–W–C(4) 156.7(2); **3**: W–P 2.545(2), P–B 1.951(8), N–B 1.601(10), W–C(1) 2.088(6), W–C(2) 1.988(7), W–C(3) 2.024(6), W–C(4) 2.025(6), W–Br(1) 2.630(2), W–Br(2) 2.663(1), Br(1)–W–C(4) 153.0(2), C(1)–W–C(3) 109.4(3), P–W–C(4) 74.7(2), Br(2)–W–P 91.6(1), Br(2)–W–C(1) 78.8(2), P–B–N 116.3(5), Br(2)–W–C(3) 161.7(3), Br(1)–W–C(4) 153.0(2).

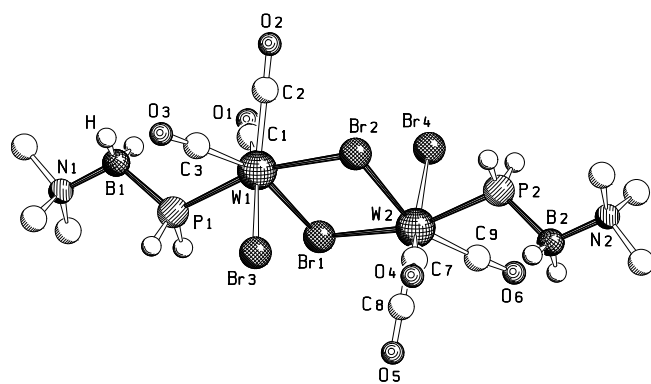


Fig. 2. Molecular structure of [WBr₂(CO)₃(H₂PBH₂ · NMe₃)]₂ (**4**) in the crystal. The solvent and the hydrogen atoms at the methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)–P(1) 2.511(2), W(2)–P(2) 2.503(2), W(1)–Br(1) 2.701(1), W(1)–Br(2) 2.710(2), W(1)–Br(3) 2.647(2), W(2)–Br(1) 2.713(2), W(2)–Br(2) 2.706(2), W(2)–Br(4) 2.654(2), W(1)–C(1) 1.992(8), W(1)–C(2) 1.998(8), W(1)–C(3) 1.988(8), W(2)–C(7) 1.998(9), W(2)–C(8) 1.984(8), W(2)–C(9) 1.977(8), P(1)–B(1) 1.975(10), P(2)–B(2) 1.971(10), N(1)–B(1) 1.590(11), N(2)–B(2) 1.596(13); Br(1)–W(1)–Br(2) 79.6(1), W(1)–Br(2)–W(2) 100.2(1), Br(1)–W(2)–Br(2) 79.4(1), W(1)–Br(1)–W(2) 100.2(1), Br(1)–W(1)–P(1) 90.1(1), Br(1)–W(1)–Br(3) 84.1(1), Br(2)–W(2)–Br(4) 84.3(1), Br(1)–W(1)–C(3) 159.6(2), Br(3)–W(1)–C(1) 153.6(2), Br(3)–W(1)–C(2) 135.0(2), Br(2)–W(2)–C(8) 126.5(2), Br(2)–W(2)–P(2) 89.0(1), W(2)–P(2)–B(2) 118.1(3), W(1)–P(1)–B(1) 117.5(3); Br(3)–W(1)–W(2)–Br(4) 179.7(1), P(1)–W(1)–W(2)–P(2) 174.8(1).

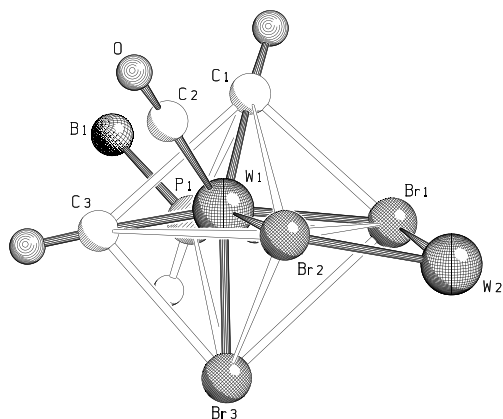


Fig. 3. Polyhedral diagram of the ligand sphere of **4** around the tungsten atom W(1).

3.2. Reactivity pattern of $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)]_2$ (**4**) and the X-ray structural characterisation of the products

The brominated monomer **3** is extremely sensitive to the loss of CO. If no donor ligand is present in solution, the monomer **3** dimerises to **4**, which is also sensitive to donors, due to the weak Br → W bond of the bridging bromide ligands. Hence, both compounds react readily with Lewis-bases like the bromide anion or a primary phosphine like the phosphanylborane $[H_2PBH_2 \cdot NMe_3]$. By this way, the ionic compound $[Et_4N][WBr_3(CO)_3(H_2PBH_2 \cdot NMe_3)]$ (**5**) is formed when $[Et_4N][Br]$ is used as a reagent (Scheme 3). The reaction with the phosphanylborane yields $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)_2]$ (**6**), which contains two $H_2PBH_2 \cdot NMe_3$ ligands in a *trans* arrangement.

For the preparation of **5** and **6** the dimer **4** is dissolved in THF and CH_2Cl_2 , respectively, and treated with $H_2PBH_2 \cdot NMe_3$ or Et_4NBr . After work-up the products **5** and **6** are obtained as yellow crystals. Whereas **5** crystallises in the orthorhombic space group *Pbca* (Fig. 4) [12], **6** crystallises in the monoclinic space group *P2₁/c* (Fig. 5). The common feature of both products **5** and **6** is a tungsten atom which is surrounded by seven ligands in a distorted capped octahedral geometry. In both compounds the C(2)O(2) ligand occu-

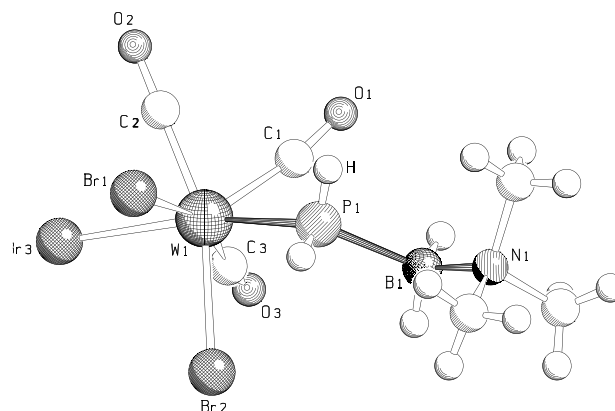


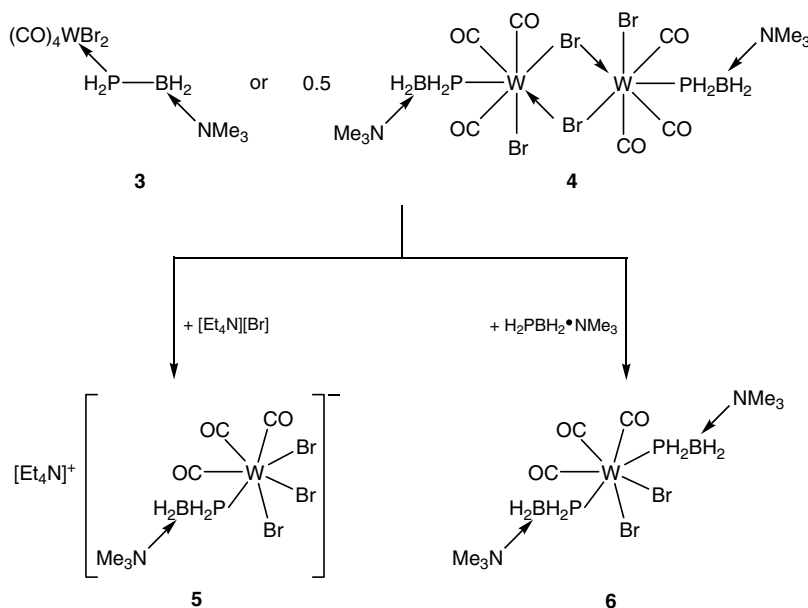
Fig. 4. Molecular structure of the anion in $[Et_4N][WBr_3(CO)_3(H_2PBH_2 \cdot NMe_3)]$ (**5**) in the crystal. Selected bond lengths (Å) and angles (°): W(1)–C(1) 1.947(5), W(1)–C(2) 1.996(6), W(1)–C(3) 1.986(5), O(2)–C(2) 1.144(6), W(1)–Br(1) 2.652(1), W(1)–Br(2) 2.655(1), W(1)–Br(3) 2.698(1), W(1)–P(1) 2.498(1), P(1)–B(1) 1.963(6), N(1)–B(1) 1.598(7); Br(3)–W(1)–P(1) 161.12(3), Br(1)–W(1)–C(1) 125.52(13), P(1)–W(1)–C(3) 113.09(15), Br(1)–W(1)–Br(2) 88.28(2), Br(1)–W(1)–Br(3) 89.56(2), Br(2)–W(1)–Br(3) 88.74(2), Br(3)–W(1)–C(3) 77.04(15), Br(2)–W(1)–P(1) 77.52(3).

pies the capping position. Whereas in the ionic compound **5** the original phosphanylborane moiety possesses a bromide ion *trans* to it (Br(3)–W(1)–P(1) 161.1(2)°), in **6**, a further phosphanylborane ligand is located in the *trans* position (P(1)–W(1)–P(2): 156.9(1)°).

The degree of deviation of the W–P bond lengths from that of the starting material (**1**: 2.542(2) Å) is dependent on the nature of the *trans* oriented ligands in **5** and **6**. The bromide ligand in **5** reduces the W–P-bond to 2.498(1) Å. In the molecular structure of **6** one W–P bond is slightly elongated (W(1)–P(1) 2.546(2) Å) while the other is slightly shorter (W(1)–P(2) 2.528(2) Å) in comparison to **1**.

3.3. Spectroscopic properties of the products

The ^{11}B and $^{11}B\{^1H\}$ NMR of the monomeric complexes **2** and **3** reveal only broad singlets at $\delta = -9.4$ ppm (**2**) and $\delta = -10.1$ ppm (**3**), respectively. Yet, in the phosphorus NMR spectra broad triplets at $\delta = -150.3$ ppm ($^1J(P,H) = 333$ Hz) (**2**) and $\delta = -133.1$ ppm ($^1J(P,H) = 333$ Hz) (**3**) are detected, due to coupling of the P atom



Scheme 3. Reaction of the brominated compounds **3** and **4** with donors.

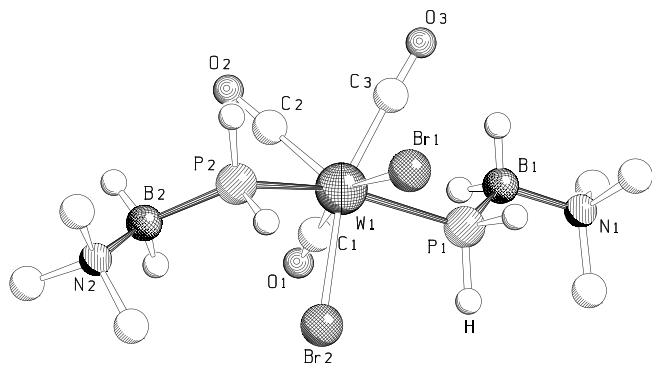


Fig. 5. Molecular structure of $[\text{WBr}_2(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)_2]$ (**6**) in the crystal. The hydrogen atoms of the methyl groups are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): W(1)–Br(1) 2.676(2), W(1)–Br(2) 2.655(2), W(1)–P(1) 2.546(2), W(1)–P(2) 2.528(2), W(1)–C(1) 2.002(9), W(1)–C(2) 1.949(8), W(1)–C(3) 1.994(11), P(1)–B(1) 1.950(11), P(2)–B(2) 1.975(11), O(1)–C(1) 1.137(12), O(2)–C(2) 1.171(11), O(3)–C(3) 1.139(13), N(1)–B(1) 1.613(12), N(2)–B(2) 1.604(12); Br(1)–W(1)–Br(2) 87.0(1), Br(1)–W(1)–C(1) 158.2(3), Br(1)–W(1)–C(2) 129.5(3), Br(1)–W(1)–C(3) 80.9(3), P(1)–W(1)–P(2) 156.9(1), W(1)–P(1)–B(1) 119.6(3), W(1)–P(2)–B(2) 115.7(3), P(1)–W(1)–C(3) 76.3(3), P(2)–W(1)–C(3) 116.4(3), Br(2)–W(1)–P(2) 76.0(2), Br(2)–W(1)–P(1) 87.1(1), C(1)–W(1)–C(3) 108.0(4).

with two hydrogen atoms. Unfortunately, the proton decoupled ^{31}P NMR spectra show only very broad singlets. The expected fine splitting into a 1:1:1:1 quartet due to the coupling with the ^{11}B nucleus could not be resolved. The same is observed for the dimeric compound **4**, for which broad singlets are revealed in the ^{31}P NMR ($\delta = -116.3$ ppm) and in the ^{11}B NMR ($\delta = -9.3$ ppm) spectra only. Vahrenkamp et al. proposed fluxional behaviour of the ligand sphere around the tungsten atoms in compounds of the formula $[\text{WX}_2(\text{CO})_4(\text{PR}_3)]$ ($\text{X} = \text{Br}, \text{I}$) and $[\text{WBr}_2(\text{CO})_3(\text{PR}_3)]_2$ ($\text{R} = \text{Me}, \text{Bu}$) [8]. Hence, the poorly resolved fine splitting in **4** as well as the strong line broadening could be indicative of a fast molecular dynamic around the central metal atom. However, lowering the temperature for the NMR measurement to 193 K shows no influence on the signal splitting. The NMR spectroscopic investigation of **6** reveals only broad signals in the ^{31}P NMR as well as in the ^{11}B NMR spectra at $\delta = -116.5$ ppm and $\delta = -9.0$ ppm, respectively. However, the proton coupled ^{31}P NMR of **5** shows a broad signal with a triplet structure at $\delta = -98.6$ ppm and a coupling constant of $^1J(\text{P},\text{H}) = 338$ Hz. The solid state IR spectra of the three compounds **2**, **3**, and **4** are in accordance with their X-ray structures. All spectra show typical B–H and P–H stretching frequencies. The four CO valence stretching frequencies of the monomer complexes **2** and **3** are in good agreement with those found for $[\text{WX}_2(\text{CO})_4(\text{PMe}_3)]$ ($\text{X} = \text{Br}, \text{I}$) [8]. The distorted C_s symmetry of **4** gives rise to three bands which are also in a good agreement with $[\text{WBr}_2(\text{CO})_3(\text{PMe}_3)]_2$ [8]. The IR spectra of **5** and **6** show also three CO stretching frequencies at 2010, 1919, 1863 cm^{-1} (**5**) and 2016, 1932, 1901 cm^{-1} (**6**), respectively, thus demonstrating a local C_s symmetry around the tungsten atom. These data are in good agreement with those found e.g. in $[\text{WBr}_2(\text{CO})_3(\text{PMe}_3)_2]$ (2029, 1941, 1904 cm^{-1}) [8a]. In both compounds (**5** and **6**) the P–H and B–H stretching frequencies could be detected. All attempts to obtain analysable mass spectra of the products failed due to the easy decomposition of the products. Thus, in the mass spectra of the compounds **2–4** and **6** neither a molecular ion nor characteristic fragmentation peaks could be detected. Only the ESI MS spectra of the ionic compound **5** reveal the corresponding molecular ion peaks of the anion and the cation.

4. Conclusion

The treatment of **1** with bromine and iodine results in a halogenation at the tungsten carbonyl moiety to give the products

$[\text{WX}_2(\text{CO})_4(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ ($\text{X} = \text{I}$ (**2**), Br (**3**)) in high yields. Here an oxidative addition reaction at the tungsten centre proceeds, whereas by using carbontetrahalides, a selective halogenation at the P atom occurs via a possible radical or ionic mechanism [5]. Compound **3** is very sensitive regarding the loss of CO. Consequently, it reacts with different donor molecules like $[\text{Et}_4\text{N}][\text{Br}]$ or $\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3$ to form $[\text{Et}_4\text{N}][\text{WBr}_3(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]$ (**5**) or $[\text{WBr}_2(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)_2]$ (**6**), respectively. Without the presence of a donor ligand, **3** dimerises under CO evolution to give $[\text{WBr}_2(\text{CO})_3(\text{H}_2\text{PBH}_2 \cdot \text{NMe}_3)]_2$ (**4**) which also shows the same subsequent reactions with a donor ligand like **3**. The arrangement of the ligands around the sevenfold coordinated tungsten atoms of the products is indicative of the tendency for the strong π -acceptor ligand CO to have a weaker acceptor in *trans* position.

Acknowledgments

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Appendix A. Supplementary material

CCDC 697822 (**2**), 697823 (**3**), 697824 (**4**), 697825 (**5**), 697826 (**5a**), and 697827 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.09.041](https://doi.org/10.1016/j.jorganchem.2008.09.041).

References

- (a) R.A. Fischer, J. Weiß, *Angew. Chem.* 111 (1999) 3002–3022;
(b) R.L. Wells, W.L. Gladfelter, *J. Cluster Sci.* 8 (1997) 217–238;
(c) D. Masuda, A.J. Hoshkin, T.W. Graham, C. Beddic, M.C. Fermin, N. Etkin, D.W. Stephan, *Chem. Eur. J.* 12 (2006) 8696–8707;
(d) T.J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* 12 (2006) 8634–8648;
(e) J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec, A.-C. Gaumont, *Chem. Commun.* (2003) 54–55.
- U. Vogel, A.Y. Timoshkin, M. Scheer, *Angew. Chem.* 113 (2001) 4541–4544. *Angew. Chem. Int. Ed.* 40 (2001) 4409–4412.
- (a) U. Vogel, P. Hoemensch, K.-Ch. Schwan, A.Y. Timoshkin, M. Scheer, *Chem. Eur. J.* 9 (2003) 515–519;
(b) U. Vogel, A.Y. Timoshkin, K.-Ch. Schwan, M. Bodensteiner, M. Scheer, *J. Organomet. Chem.* 691 (2006) 4556–4564;
(c) A. Adolf, M. Zabel, M. Scheer, *Eur. J. Inorg. Chem.* (2007) 2136–2143;
(d) A. Adolf, U. Vogel, M. Zabel, A.Y. Timoshkin, M. Scheer, *Eur. J. Inorg. Chem.* (2008) 3349–3482.
- K.-Ch. Schwan, A.Y. Timoshkin, M. Zabel, M. Scheer, *Chem. Eur. J.* 12 (2006) 4900–4908.
- K.-Ch. Schwan, A. Adolf, Ch. Thoms, M. Zabel, A.Y. Timoshkin, M. Scheer, *Dalton Trans.* (2008) 5054–5058.
- (a) G.M. Sheldrick, *SHELXS-97*, University of Göttingen, 1996;
(b) G.M. Sheldrick, *SHELXL-97*, University of Göttingen, 1997.
- An excess of the halogen leads to the decomposition of the complexes under the probable formation of tungsten halide species. No halogenation at the P atom is observed.
- (a) P. Umland, H. Vahrenkamp, *Chem. Ber.* 115 (1982) 3555–3564. and references therein;
(b) P. Umland, H. Vahrenkamp, *Chem. Ber.* 115 (1982) 3565–3579.
- (a) For a Survey G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 3, Pergamon Press, Oxford, 1982, pp. 1088–1095;
(b) J.L. Davidson, G. Vasapoll, *J. Organomet. Chem.* 241 (1983) C24–C26;
(c) R. Colton, *Coord. Chem. Rev.* 6 (1971) 269–284.
- In the following the Klyne–Prelog nomenclature is used. In the A–X–Y–B fragments the position of the two groups A and B are defined by the torsion angle AX₁YB, e.g. synperiplanar: $0 \pm 30^\circ$, (+)synclinal: $60 \pm 30^\circ$, (+)anticlinal: $120 \pm 30^\circ$ and antiperiplanar: $180 \pm 30^\circ$. W. Klyne, V. Prelog, *Experientia* 16 (1960) 521–523.
- F.A. Cotton, L.R. Falvello, J.H. Meadows, *Inorg. Chem.* 24 (1985) 514–517.
- As a product of the decomposition of **3** the complex $[\text{Me}_3\text{NH}][\text{W}(\text{CO})_3\text{Br}_3(\text{PH}_3\text{BH}_2 \cdot \text{NMe}_3)]$ (**5a**) could be obtained in small amounts and structural characterised by X-ray crystallography, showing the same structural parameters of the anion as in **5**.