Phosphine-Substituted Diborane(4)yl Complexes of Tungsten

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The reaction of the 1,2-dihalodiborane(4) $B_2(NMe_2)_2Cl_2$ with the lithium tungsten salts Li[(η^5-C_5H_5)(R_3P)$(OC)_2$W] [R = Me (**3a**), Ph (**3b**)] yields *via* alkali salt elimination the phosphine-substituted diborane(4)yl tungsten complexes [(η^5-C_5H_5)(R_3P)$(OC)_2$W-{B(NMe_2)-B(NMe_2)Cl}] [R = Me (**4a**), Ph (**4b**)]. Both compounds have been fully characterized in solution by NMR and IR spectroscopy and **4a** additionally by X-ray diffraction analysis.

Key words: Half-Sandwich Tungsten Complexes, Boranes, Diboranes(4), Boryl Complexes

Introduction

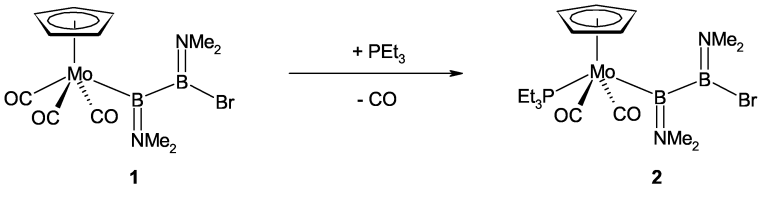
During the past decade transition metal complexes of boron in addition to metallaboranes and metal borides have become established as another class of compounds made up by direct metal-boron interactions [1 – 3]. Reaction of 1,2-diaminodihalodiboranes(4) with anionic transition metal complexes has led to the first diborane(4)yl complexes [(η^5-C_5H_5)$(OC)_n$M-{B(NMe_2)-B(NMe_2)Cl}] [M$(CO)_n$ = Fe$(CO)_2$; M$(CO)_n$ = W$(CO)_3$ [4, 5]], and [(η^5-C_5H_5)$(OC)_n$M-{B(NMe_2)-B(NMe_2)Br}] [M$(CO)_n$ = Ru$(CO)_2$; M$(CO)_n$ = Mo$(CO)_3$ (**1**) [4, 6]] which were obtained *via* salt elimination reactions. The latter complex (**1**) was modified by PEt_3/CO exchange to give the only phosphine-substituted diborane(4)yl complex [(η^5-C_5H_5)(Et_3P)$(OC)_2$Mo-{B(NMe_2)-B(NMe_2)Br}] (**2**) [4, 6] (eq. (1)).

In the present paper we report on the synthesis, spectroscopic and structural characterisation of the first phosphine-substituted diborane(4)yl complexes of tungsten. The phosphine modification was realized in order to investigate its influence on the W–B bond.

Results and Discussion

The complexes [(η^5-C_5H_5)(R_3P)$(OC)_2$W-{B(NMe_2)-B(NMe_2)Cl}] [R = Me (**4a**), Ph (**4b**)] are obtained from the corresponding dihalodiborane(4) and the phosphine-substituted anionic tungsten complexes Li[Cp(R_3P)$(OC)_2$W] [R = Me (**3a**), Ph (**3b**)] after 20 h at ambient temperature in benzene, according to eq. (2). **3a, b** are isolated as pale brown powders in 64% (**4a**) and 36% (**4b**) yield, respectively, and show low solubility in pentane and an improved one in diethylether and aromatic solvents. **4a, b** can be stored under argon atmosphere at −30 °C for several months but show signs of decomposition after 2 d in benzene solution at ambient temperature.

Both new complexes were characterised in solution by IR and multinuclear NMR spectroscopy. **4a, b** show ^{11}B NMR resonances at 66.02 (**4a**) and 64.76 ppm (**4b**) for the tungsten-bound boron atoms, the nuclei being deshielded with respect to those of the starting material, while the resonances for the halogen-substituted boron atoms appear at 41.78 (**4a**) and 37.60 ppm (**4b**), thus matching those of the non-coordinated dibor-



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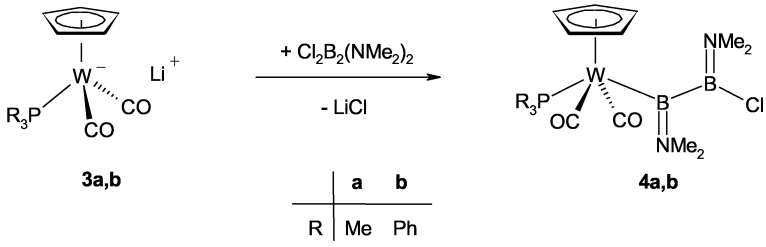

(2)

anes(4). The complexes **4a, b** show each four singulets for the dimethylamino groups in the ^{1}H and ^{13}C NMR spectra, thus proving a restricted rotation with respect to both boron–nitrogen double bonds [4 – 6]. Surprisingly, two resonances were detected for the C atoms of the carbonyl ligands in the ^{13}C NMR spectra of **4a, b**. This finding could indicate either a *cis*-disposition of the respective CO groups, which is, however, not realized in the related tungsten borylcomplex [(η^5-C_5Me_5)(Me_3P)$(OC)_2$W-($BcatMe_2$)] [($BcatMe_2$) = B-1,2-$O_2C_6H_2$-3,5-Me_2] [7], or a *trans*-arrangement of the CO groups coinciding with a hindered rotation about the boron–boron bond (the latter orientation of the CO groups was confirmed for **4a** in the crystalline state – *vide infra*). Attempts to establish the stereochemistry in solution by a VT NMR spectroscopic study, though, failed due to the thermal lability of **4a, b**. In the ^{31}P NMR spectra appears in each case one resonance at −9.22 (**4a**) and 42.56 ppm (**4b**), respectively, accompanied by ^{183}W satellites [$^{1}J_{WP}$ = 326.9 Hz (**4a**), 335.3 Hz (**4b**)]. The ^{31}P NMR shift for **4a** (−9.22 ppm) is very close to that of [(η^5-C_5Me_5)(Me_3P)$(OC)_2$W-($BcatMe_2$)] [($BcatMe_2$) = B-1,2-$O_2C_6H_2$-3,5-Me_2] (−10.61 ppm, $^{1}J_{WP}$ = 273.4 Hz ppm) [7]. **4a, b** show each two CO-stretching frequencies in the IR spectra at 1927 and 1803 (**4a**) and 1929 and 1805 cm^{-1} (**4b**) which are comparable to those found for the molybdenum phosphine complex **2**.

X-ray diffraction analysis. The molecular structure of *trans*-[(η^5-C_5H_5)(Me_3P)$(OC)_2$W-{B(NMe_2)-B(NMe_2)Cl}] (**4a**) has been confirmed by an X-ray diffraction study (Fig. 1). Yellow crystals of **4a**, suitable for X-ray analysis, are obtained upon slow evaporation of a saturated benzene solution at room temperature.

The molecule **4a** adopts C_1 symmetry in the crystal and reveals a tetragonal monopyramidal arrangement of cyclopentadienyl-, diborane(4)yl-, trimethylphosphine- and carbonyl ligands at the tungsten atom. The most crucial feature of **4a** exhibited by the X-ray structure study is the *trans* position of the phosphine ligand with respect to the diborane(4)yl substitutent. The determined W–P distance amounts to 2.405(6) Å which is close to the corresponding value in the parent PMe_3-substituted hydrido complex *cis*-[(η^5-C_5H_5)(Me_3P)$(OC)_2$WH [2.398(17) Å] [8]. As expected, the boron and nitrogen atoms are trigonal-planar coordinated and both boryl units are almost perpendicular to each other showing a torsion angle of −93.77(2)° (N1-B1-B2-N2). Both B–N distances are about 2 pm longer than those of the tricarbonyl derivative [(η^5-C_5H_5)$(OC)_3$W-{B(NMe_2)-B(NMe_2)Cl}] [1.376(3) and 1.38(1) Å] [4, 5]. The bond distance of 2.327(3) Å, found for W1-B1, supports the notion that an increased electron density at a central transition metal atom – evoked by the introduction of a phosphine ligand – strengthens the transition metal–boron bond. In fact, the tungsten–boron bond distance in the tricarbonyl counterpart [(η^5-C_5H_5)$(OC)_3$W-{B(NMe_2)-B(NMe_2)Cl}] [4, 5] is about 5 pm longer than that in **4a**. The boron–boron bond of **4a** [B1-B2 1.694(4) Å] is not affected by the phosphine ligand and is almost as long as that in [(η^5-C_5H_5)$(OC)_3$W-{B(NMe_2)-B(NMe_2)Cl}] [B1-B2 1.690(1) Å]. Due to the increased sterical requirements of the PMe_3 ligand in relation to CO, the angles B1-W1-P1 [128.2(6)°] and W1-B1-N1 [131.4(17)°] are enlarged with respect to the corresponding ones in [(η^5-C_5H_5)$(OC)_3$W-{B(NMe_2)-B(NMe_2)Cl}] [117.4(3)° and 128.4(5)°, respectively]. In addition, we found that both tungsten–C-carbonyl bonds are slightly different in length [W1-C1 1.943(2) *vs*. W1-C2 1.932(2)].

Experimental Section

All manipulations were conducted either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Solvents (benzene and pentane) were purified by distillation from appropriate drying agents (sodium and sodium wire) under dry argon, immediately prior to use. C_6D_6 was degassed by three

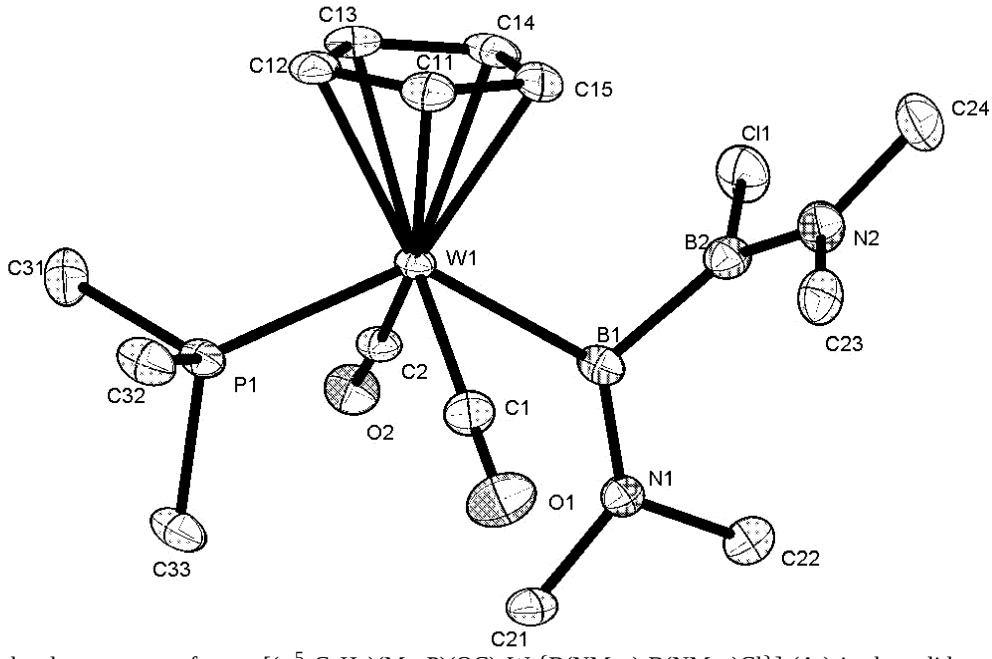

Fig. 1. Molecular structure of *trans*-[(η^5-C_5H_5)(Me_3P)$(OC)_2$W-{B(NMe_2)-B(NMe_2)Cl}] (**4a**) in the solid state with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms have been omitted for clarity. – Selected bond lengths [Å], bond and torsion angles [°]: W1-B1 2.327(3), B1-B2 1.694(4), W1-P1 2.405(6), W1-C1 1.943(2), W1-C2 1.932(2), C1-O1 1.169(3), C2-O2 1.178(3), B1-N1 1.409(3), B2-N2 1.390(4), B2-Cl1 1.823(3), W1-B1-B2 1.117(16), W1-B1-N1 131.4(17), B1-W1-P1 128.2(6), N1-B1-B2-N2 −93.77(2).

freeze-pump-thaw cycles and stored over molecular sieves. IR spectra were recorded as CH_2Cl_2 solutions between KBr plates on a Bruker Vector 22 FT-IR-spectrometer. ^{1}H, ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra were acquired on a Bruker Avance 200 NMR spectrometer at 200.1, 64.2 and 121.5 MHz, respectively and referenced to external TMS *via* the residual protio solvent (^{1}H), $BF_3{\cdot}OEt_2$ and 85% H_3PO_4. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer at 125.8 MHz and referenced to the solvent. Microanalyses for C, H and N were performed by Mr. C. P. Kneis (University of Würzburg) on a Leco CHNS-932 instrument. – Starting materials were prepared according to literature procedures: $B_2(NMe_2)_2Cl_2$ [9], Li[(η^5-C_5H_5)W$(CO)_2$(PMe_3)] (**3a**) [10] and Li[(η^5-C_5H_5)W$(CO)_2$(PPh_3)] (**3b**) [10].

*[(η^5-C_5H_5)(Me_3P)$(OC)_2$W-{B(NMe_2)-B(NMe_2)Cl}] (**4a**)*

300 mg (0.77 mmol) of Li[(η^5-C_5H_5)W$(CO)_2$(PMe_3)] (**3a**) suspended in 10 ml of benzene was treated with 139 mg (0.77 mmol) of $B_2(NMe_2)_2Cl_2$ and the reaction mixture stirred for 20 h at ambient temperature. All insoluble material was filtered off and the filtrate was evaporated to dryness. The residue was washed with 3 ml of pentane and then finally dried *in vacuo*. Yield: 260 mg (0.49 mmol; 64%). Pale brown powder. M. p. 82 °C. – **IR** (CH_2Cl_2): $\tilde{\nu}$(C=O) = 1927 (m), 1803 (m) cm^{-1}. – **^{1}H NMR** (200.1 MHz, C_6D_6): $\delta = 5.00$ (d, $^3J_{HCWP} = 1.4$ Hz, 5 H, Cp), 3.15 (s, 3 H, NMe_2), 3.02 (s, 3 H, NMe_2), 2.74 (s, 3 H, NMe_2), 2.65 (s, 3 H, NMe_2), 1.14 (d, $^2J_{HCP} = 9.1$ Hz, 9 H, PMe_3) ppm. – **^{11}B{^{1}H} NMR** (64.2 MHz, C_6D_6): $\delta = 66.02$ (s, BW), 41.78 (s, BCl) ppm. – **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6): $\delta = 224.36$ (d, $^2J_{CWP} = 15.3$ Hz, CO), 222.99 (d, $^2J_{CWP} = 15.4$ Hz, CO), 91.17 (s, $^1J_{CW} = 6.7$ Hz, Cp), 49.33 (s, NMe_2), 43.62 (s, NMe_2), 41.74 (s, NMe_2), 37.16 (s, NMe_2) ppm. – **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): $\delta = -9.22$ (s, $^1J_{PW} = 326.9$ Hz) ppm. – $C_{14}H_{26}B_2ClN_2O_2PW$ (526.26 g/mol): calcd. C 31.95, H 4.98, N 5.32; found C 31.03, H 4.66, N 5.26.

*[(η^5-C_5H_5)(Ph_3P)$(OC)_2$W-{B(NMe_2)-B(NMe_2)Cl}] (**4b**)*

Analogous to **4a** from 1.12 g (1.95 mmol) of Li[(η^5-C_5H_5)W$(CO)_2$(PPh_3)] (**3b**) and 350 mg (1.95 mmol) $B_2(NMe_2)_2Cl_2$ in 20 ml of benzene. Yield: 500 mg (0.70 mmol; 36%). Pale brown powder. M. p. 72 °C. – **IR** (CH_2Cl_2): $\tilde{\nu}$(C=O) = 1929 (m), 1805 (m) cm^{-1}. – **^{1}H NMR** (200.1 MHz, C_6D_6): $\delta = 7.77 - 7.61$ (m, 6 H, Ph), 7.11 – 6.95 (m, 9 H, Ph), 5.05 (d, $^3J_{HCWP} = 1.3$ Hz, 5 H, Cp), 2.93 (s, 3 H, NMe_2), 2.73 (s, 3 H, NMe_2), 2.68 (s, 3 H, NMe_2), 2.43 (s, 3 H, NMe_2) ppm. – **^{11}B{^{1}H} NMR** (64.2 MHz, C_6D_6): $\delta = 64.76$ (s, BW),

Table 1. Data for the crystal structure analysis.

Data	**4a**
Empirical formula	$C_{14}H_{26}B_2ClN_2O_2PW$
Formula weight [g·mol^{-1}]	526.26
Temperature [K]	138(2)
Radiation, λ [Å]	Mo-K$_\alpha$ 0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a [Å]	7.5401(2)
b [Å]	10.2611(2)
c [Å]	13.6221(3)
α [°]	71.8660(10)
β [°]	82.6320(10)
γ [°]	72.4350(10)
Volume (Å^3)	954.21(4)
Z	2
Calculated density [g·cm^{-3}]	1.832
Absorbtion coefficient [mm^{-1}]	6.284
$F(000)$	512
Theta range for collection [°]	1.57 to 26.37
Reflections collected	19230
Independent reflections	3875
Minimum/maximum transmision	0.443/0.885
Refinement method	Full-matrix last-squares on F^2
Data / parameters	3875 / 208
Goodness-of-fit on F^2	1.042
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0170$, $wR^2 = 0.0443$
R Indices (all data)	$R_1 = 0.0172$, $wR^2 = 0.0445$
Maximum/minimum residual electron density [e·Å^{-3}]	2.068/−0.679

37.60 (s, BCl) ppm. – **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6): $\delta = 225.38$ (d, $^2J_{CWP} = 15.5$ Hz, CO), 223.09 (d, $^2J_{CWP} = 15.5$ Hz, CO), 141.25 (d, $^1J_{CP} = 45.1$ Hz, *ipso*-C of C_6H_5), 137.55 (d, $^2J_{CCP} = 47.9$ Hz, *ortho*-C of C_6H_5), 133.84 (d, $^3J_{CCCP} = 11.8$ Hz, *meta*-C of C_6H_5), 129.80 (d, $^4J_{CCCCP} = 2.0$ Hz, *para*-C of C_6H_5), 92.34 (s, Cp), 48.68 (s, NMe_2), 43.45 (s, NMe_2), 41.55 (s, NMe_2), 36.76 (s, NMe_2) ppm. – **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): $\delta = 42.56$ (s, $^1J_{PW} = 335.3$ Hz) ppm. – $C_{29}H_{32}B_2ClN_2O_2PW$ (712.47 g/mol): calcd. C 48.89, H 4.53, N 3.91; found C 49.09, H 4.51, N 3.29.

Crystal structure determination

The crystal data of **4a** were collected with a Bruker APEX2 diffractometer with CCD area detector and multilayer mirror monochromated Mo-K$_\alpha$ radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized position and were included in structure factor calculations.

Crystal data for **4a**: $C_{14}H_{26}B_2ClN_2O_2PW$, $M_r = 526.26$, translucent plate, $0.155 \times 0.095 \times 0.02$, Triclinic space group $P\bar{1}$, $a = 7.5401(2)$, $b = 10.2611(2)$, $c = 13.6221(3)$, $\alpha = 71.8660(10)$, $\beta = 82.6320(10)$, $\gamma = 72.4350(10)$, $V = 954.21(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.832$ g·cm^{-3}, $\mu = 6.284$ cm^{-2}, $F(000) = 512$, $T = 138(2)$ K, $R_1 = 0.0172$, $wR^2 = 0.0445$, 3875 independent reflections [$2\theta \leq 52.74°$] and 208 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-291535. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223–336–033, e-mail: deposit@ccdc.cam.ac.uk).

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