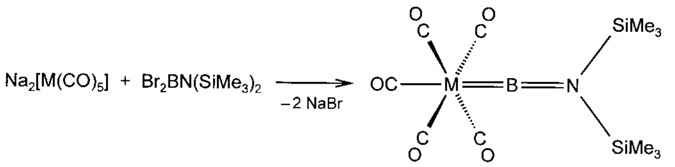
Synthesis and Structure of the First Terminal Borylene Complexes**

Holger Braunschweig,* Carsten Kollann, and
Ulli Englert

Over the last years a new class of transition metal complexes displaying two-center two-electron (2c–2e) bonds between the metal center and a threefold-coordinated boron atom has been established.[1] These compounds include a large number of structurally characterized boryl complexes, mostly derived from catecholborane[2a–g] and nitrogen-substituted boranes,[3a–c] but there are only very few examples of complexes with bridging borylene ligands such as $[(\mu\text{-BR})\{(C_5H_5)Mn(CO)_2\}_2]$ and $[\{\mu\text{-BN}(SiMe_3)_2\}(\mu\text{-CO})\{(C_5H_5)Fe(CO)\}_2]$.[4a–c, 3c] The coordination of the borylene BR ligand to a single metal center leads to formation of terminal borylene complexes with boron in coordination number two and a metal–boron double bond.[18]

An earlier report on such a compound describes the iron–borylene complex $[(CO)_4Fe(BNMe_2)]$, the structure of which was deduced from elemental analysis and IR and ^{11}B NMR spectroscopy.[5] The ^{11}B NMR shift at $\delta = -18$, however, strongly conflicts with the signals of the complexes described in the present paper, and also with the signal $\delta = 88.2$ for $[(CO)_4Fe\{BN(SiMe_3)_2\}]$.[6] Clearly, a structure needs to be ascribed to the reported iron complex which does not contain an iron–borylene unit.

The borylene complexes $[(CO)_5M\{BN(SiMe_3)_2\}]$ (M = Cr: **1a**; W: **1b**) were obtained according to Equation (1) in yields of about 30% as light brown crystalline solids. Both products exhibit considerable stability: They show no sign of decomposition in solution at ambient temperature after several days, and in the crystalline state they can be handled in air for about one hour.



$$\mathrm{Na_2[M(CO)_5] + Br_2BN(SiMe_3)_2 \xrightarrow[-2\,NaBr]{} (OC)_5M{=}B{=}N(SiMe_3)_2} \qquad (1)$$

1a, M = Cr
1b, M = W

The structure of **1a** and **1b** in solution was deduced from the NMR and IR data. The ^{1}H NMR spectra show sharp singlets for the protons of the SiMe$_3$ groups, while the ^{13}C NMR spectra contain a signal for the methyl groups of the $N(SiMe_3)_2$ substituents along with two signals in a 1:4 ratio for the axial and equatorial carbonyl ligands. In comparison with amino-substituted boryl complexes, the borylene complexes exhibit considerably low field shifted ^{11}B NMR signals at $\delta = 92.3$ (**1a**) and 86.6 (**1b**), which are close to the range observed for bridged aminoborylene complexes. As expected for these octahedral complexes, the IR spectra show three bands for the carbonyl groups which are considerably shifted to lower wavenumbers with respect to those for corresponding vinylidene complexes.[7]

The results of the X-ray structure analysis of **1b** (Figure 1) show that the molecule adopts C_1 symmetry in the crystal.[8] The W(CO)$_5$ moiety exhibits C-W-C angles of about 90° and very similar W–C and C–O distances, and thus displays approximately C_{4v} symmetry. The Si1-Si2-B plane is twisted by 37.2(2)° with respect to the C4-C2-C3 plane. The tungsten–boron bond together with the W-B-N angle are clearly the most interesting features of this structure: The bond length is 215.1(7) pm, and the three central atoms are arranged in an almost ideal linear way with an angle of 177.9(5)°. Compared to the metal–boron bond in $[(C_5H_5)(CO)_3W\{B(NMe_2)BCl(NMe_2)\}]$, which is the only structurally characterized amino-substituted boryl complex of tungsten,[3a] the W–B bond of **1b** is shorter by about 22 pm, but still longer by 8 pm than that of the alkyl-substituted boryl complex $[(tpb')(CO)_2W\{BEt(CH_2\text{-}p\text{-}MeC_6H_4)\}]$ (tpb′ = tris(3,5-dimethylpyrazol-1-yl)hydroborate), which is stabilized by an agostic C–H interaction.[9]

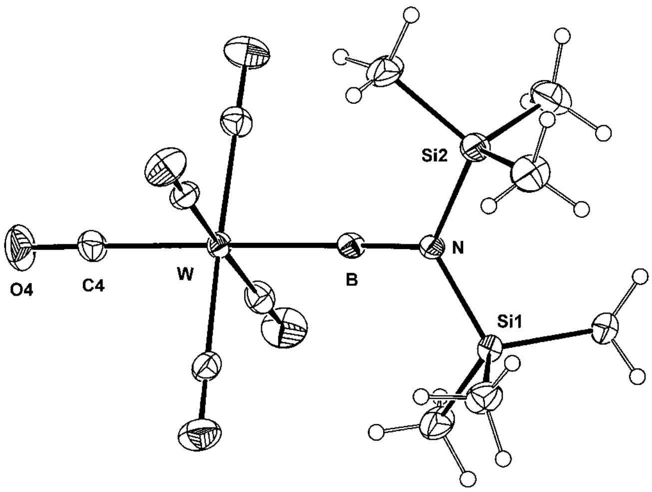


Figure 1. Structure of **1b** in the crystal (ellipsoids at the 30% probability level; the hydrogen atoms are shown with arbitrary radii).[17] Selected bond lengths [Å] and angles [°]: W–B 2.151(7), B–N 1.338(8); W-B-N 177.9(5).

The boron–nitrogen bond length of 133.8(8) pm is somewhat shorter than in the alkylidene(amino)borane $(Me_3Si)_2C{=}B{=}N\mathit{i}Pr_2$ (136.3(4) pm), which also shows a double bond between a twofold-coordinated boron atom and a threefold-coordinated nitrogen atom.[10] The geometry of the axial CO group resembles those of the equatorial CO groups, thus indicating that there is no *trans* effect of the borylene ligand. These observations together with the IR data correspond to a description of the metal–boron double bond in terms of strong boron-to-metal σ donation and weaker π backbonding from the metal to boron. For aminoborylene complexes of first row transition metals this conclusion was predicted on the basis of ab initio calculations.[11]

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[*] Dr. H. Braunschweig, C. Kollann, Dr. U. Englert Institut für Anorganische Chemie der Technischen Hochschule
Templergraben 55, D-52056 Aachen (Germany)
Fax: (+49) 241-888-8288
E-mail: holger.braunschweig@ac.rwth-aachen.de

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Experimental Section

1a: In analogy to the known synthesis of $Na_2[M(CO)_5]$ (M = Cr, W)[12] a solution of $[Me_3NCr(CO)_5]$ (1.21 g, 4.82 mmol) in THF (30 mL) was cooled to −78 °C, and a solution of $NaC_{10}H_8$ (57.8 mL, 0.20 M in THF were added dropwise over a period of 20 min. When the addition was complete all volatile materials were removed under high vacuum (0 °C/0.001 Torr). The remaining yellow solid was treated with Et_2O (50 mL) at 0 °C, filtered, and washed with Et_2O (2 × 10 mL). The light yellow product was dried briefly under high vacuum and subsequently suspended in toluene (30 mL) at 0 °C. $Br_2BN(SiMe_3)_2$[13] (1.36 g, 4.00 mmol) was added dropwise by a syringe, and the color of the suspension quickly turned from orange to dark brown. After the reation mixture was stirred for 30 min at 0 °C, it was warmed to ambient temperature and all volatile materials were removed under high vacuum. The dark brown residue was suspended in hexane (30 mL) and filtered, and the remaining solid was rinsed with hexane (10 mL). The filtrate was concentrated under vacuum to 20 mL and stored at −30 °C. After 72 h $[(Me_3Si)_2NBCr(CO)_5]$ (0.35 g, 36.7 %) was obtained as light brown crystals. All NMR spectra were recorded in in [D_6]benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.14$ (s, $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 92.3$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.6$ ($SiMe_3$), 217.6 (CO_{eq}), 218.0 (CO_{ax}); IR (toluene): $\tilde{\nu} = 2064$ (w), 1981 (m), 1942 (vs) cm^{-1} (CO); elemental analysis calcd for $C_{11}H_{18}CrNBO_5Si_2$: C 36.37, H 5.00, N 3.86; found: C 35.47, H 5.10, N 3.72.

1b: As described for **1a** $[Me_3NW(CO)_5]$[14] (0.85 g, 2.22 mmol) was treated with a solution of $NaC_{10}H_8$ (26.7 mL, 0.20 M) and then with $Br_2BN(SiMe_3)_2$ (0.68 g, 2.00 mmol). $[(Me_3Si)_2NBW(CO)_5]$ (0.24 g, 24.3 %) was obtained as light brown crystals. All NMR spectra were recorded in [D_6]benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.12$ (s, $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 86.6$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.9$ ($SiMe_3$), 196.5 (CO_{ax}), 197.2 (CO_{eq}); IR (toluene): $\tilde{\nu} = 2075$ (w), 1967 (m), 1941 (vs) cm^{-1} (CO); elemental analysis calcd for $C_{11}H_{18}NBO_5Si_2W$: C 26.68, H 3.66, N 2.83; found: C 26.29, H 3.59 N 2.72.

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[8] a) Crystal structure determination of **1b**: $C_{11}H_{18}BNO_5Si_2W$, Enraf-Nonius CAD4 diffractometer; MoK_α radiation ($\lambda = 0.7107$ Å, graphite monochromator); $T = 203$ K. Light brown rod, $0.16 \times 0.12 \times 0.08$ mm³, triclinic, space group $P\bar{1}$ (no. 2); $a = 9.250(1)$, $b = 9.302(1)$, $c = 12.109(2)$ Å, $\alpha = 109.53(1)$, $\beta = 98.54(1)$, $\gamma = 101.48(1)°$, $V = 935.8(3)$ Å³, $Z = 2$, $\rho_{calcd} = 1.74$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 63.81$ cm^{-1}, $F(000) = 476$, 5222 measured reflections ($3 < \theta < 26°$), $\omega - 2\theta$ scans. The empirical absorption correction on the basis of azimuthal scans provided transmission factors between 0.722 and 0.999.[15] The structure was solved by Patterson methods with use of the SDP program;[16] 3349 independent reflections with $I > \sigma(I)$, 190 variables. All non-hydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atoms were included as riding (C–H = 98 pm, $U_{iso}(H) = 1.3\,U_{iso}(C)$). $R = 0.032$, $R_w = 0.034$, $w^{-1} = \sigma^2(F_o)$, GOF = 0.950. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101812. 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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[18] Note added in proof (August 10, 1998): Recently the synthesis and structure of the borylene complex $[(\eta^5\text{-}Me_5C_5)BFe(CO)_4]$ was published. However, this compound shows a single bond between iron and a sixfold-coordinated boron atom. A. H. Cowley, V. Lomelí, A. Voigt, *J. Am. Chem. Soc.* **1998**, *120*, 6401–6402.

Remarkable Reaction of Hetero-S-Block-Metal Amides with Molecular Oxygen: Cationic $(NMNMg)_2$ Ring Products (M = Li or Na) with Anionic Oxo or Peroxo Cores

Alan R. Kennedy, Robert E. Mulvey,* and René B. Rowlings

Intensively studied since the early 1980s, the structural chemistry of lithium and sodium amides is based predominantly on $(NM)_n$ rings (M = Li or Na) which can remain discrete or self-associate by "ring-laddering".[1] Lithium 2,2,6,6-tetramethylpiperidide (LTMP) is representative of the former type as highlighted in a recent textbook:[2] two-coordinate Li centers bridge pairs of amide N centers in a tetrameric octagonal ring core. Considerably less work has been carried out on heterometallic amide systems where lithium or sodium is combined with a second metal. Recently

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[*] Prof. R. E. Mulvey, Dr. A. R. Kennedy, R. B. Rowlings
Department of Pure and Applied Chemistry
University of Strathclyde
Glasgow, G1 1XL (UK)
Fax: (+45) 141-552-0876
E-mail: R.E.Mulvey@strath.ac.uk

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