**Keywords:** dihydroxylations · dioxygenases · enzyme mimetics · iron · oxidations

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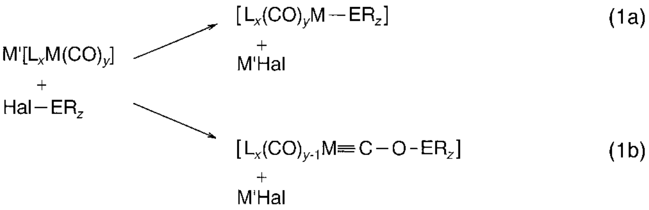
# Unique Rearrangement of an Oxycarbyne Complex: Synthesis and Structure of Novel Diborane(4)yl Complexes**

Holger Braunschweig,* Margot Koster, and Karl W. Klinkhammer

The salt elimination reaction between mononuclear anionic transition metal carbonyl complexes $M'[L_xM(CO)_y]$ and main group element halides $HalER_z$ is a fundamental reaction in transition metal chemistry, and has had a pivotal role in establishing complexes $[L_x(CO)_yM{-}ER_z]$ with bonds between main group elements and transition metals [Eq. (1a)].[1a,b] The general formation of M–E bonds suggests that the transition metal acts as the nucleophilic center in these reactions.[1b] There is, however, spectroscopic and experimental evidence that the carbonyl oxygen atom also displays some nucleophilic character in anionic complexes $M'[L_xM(CO)_y]$, especially towards hard and bulky Lewis acids.[2a–d] The addition of the carbonyl oxygen atom to the element E with salt elimination [Eq. (1b)] is expected to lead to the formation of transiton metal oxycarbyne complexes of the type $[L_x(CO)_{y-1}M{\equiv}C{-}O{-}ER_z]$; this alternative pathway to the common formation of $[L_x(CO)_yM{-}ER_z]$ [Eq. (1a)], however, has only been observed in one example.[3]



Over the last six years, salt elimination reactions have been very successfully employed in the synthesis of transition metal complexes of boron, especially for boryl and borylene complexes.[4a,b] Recently, we described the synthesis and characterization of the first diborane(4)yl complexes $[(\eta^5\text{-}C_5H_5)(CO)_nM\{B(NMe_2)B(NMe_2)Hal\}]$ (M = Fe, Ru, $n = 2$; M = Mo, W, $n = 3$; Hal = Cl, Br), which were obtained by this method from reactions of the corresponding anionic transition metal complexes and $B_2(NMe_2)_2Hal_2$.[5a,b]

In contrast to the known reactivity of $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) towards 1,2-dibromo- and 1,2-dichlorodiboranes(4), the corresponding reactions with $B_2(NMe_2)_2I_2$ give the dinuclear oxycarbyne complexes **1a**, **b** (Scheme 1). These products were formed by a nucleophilic attack of a CO oxygen atom on each boron center with elimination of two equivalents of KI. Both products, which were isolated as

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[*] Dr. H. Braunschweig, M. Koster
Institut für Anorganische Chemie der Technischen Hochschule
D-52056 Aachen (Germany)
Fax: (+49) 241-8888288
E-mail: holger.braunschweig@ac.rwth-aachen.de

Dr. K. W. Klinkhammer
Institut für Anorganische Chemie der Universität Stuttgart
Pfaffenwaldring 55, D-70569 Stuttgart (Germany)

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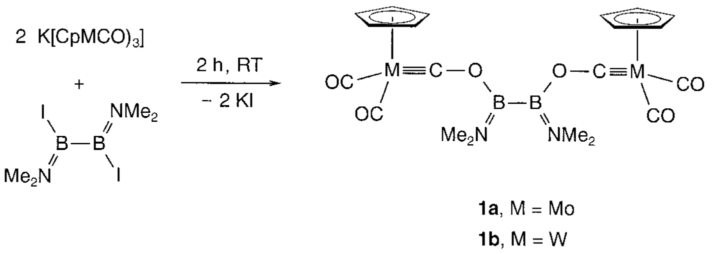
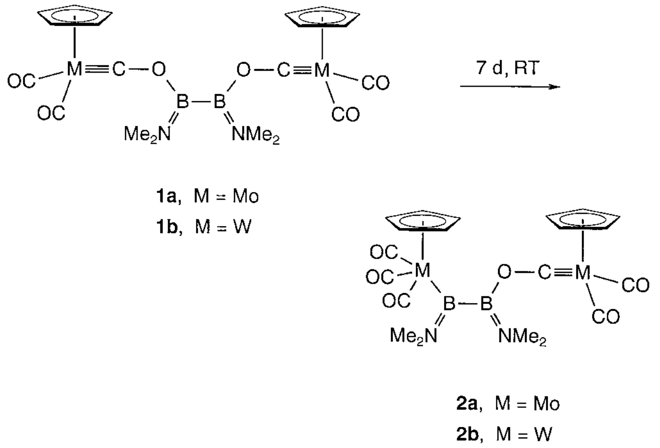


Scheme 1. Synthesis of **1a**, **b**.

yellow crystalline materials in about 32 % yield, proved to be extremely sensitive towards air and moisture. The structure of the molecules in solution was derived from NMR spectroscopic investigations. In the $^{11}B$ NMR spectra only one signal is detected for the two equivalent boron atoms; characteristic for the formation of boron–oxygen bonds instead of boron–metal bonds is the highfield shift of these $^{11}B$ NMR signals to $\delta = 31.1$ (**1a**) and 30.8 (**1b**), which is in sharp contrast to the deshielded signals of the metal-coordinated boron atoms of the corresponding diborane(4)yl complexes $[(\eta^5\text{-}C_5H_5)M(CO)_3\{B(NMe_2)B(NMe_2)Hal\}]$ (M = Mo, W; Hal = Cl, Br) at $\delta \approx 63$.[5a,b] The two equivalent $Me_2N$ groups display double sets of signals in the $^1H$ and $^{13}C$ NMR spectra, which is due to a hindered rotation with respect to the boron–nitrogen double bond. The carbyne carbon atoms show signals in the $^{13}C$ NMR spectra at $\delta = 245.18$ (**1a**) and 242.72 (**1b**), which are in the expected range for oxycarbyne complexes.[3]

Interestingly, the complexes **1a**, **b** could be obtained only after short reaction times of about 2 h, since they proved to undergo a quantitative rearrangement at ambient temperature in solution yielding the thermodynamically more stable diborane(4)yl complexes **2a**, **b** (Scheme 2). This rearrangement occurs with a 1,3-shift of one boryl group from the carbyne oxygen atom to the metal center with restoration of the former carbonyl ligand. An analogous rearrangement of the second M≡C–O–B moiety does not occur, evidently for steric reasons.[5a,b] Although 1,3-silatropic shifts from transition metal centers to acyl oxygen atoms are well known,[6] the opposite intramolecular migration of a main group element from oxygen to a transition metal has not been observed before.



Scheme 2. Formation of **2a**, **b** by quantitative rearrangement of **1a**, **b**.

Complexes **2a**, **b** were isolated quantitatively after stirring solutions of **1a**, **b** in benzene for 7 d at ambient temperature as yellow crystalline solids, which proved to be moderately sensitive towards air and water. In solution they display two $^{11}B$ NMR signals: one almost unchanged at higher field for the oxygen-bound boron atom ($\delta = 31.5$ (**2a**), 32.6 (**2b**)), and a second deshielded one for the metal-coordinated boron atom ($\delta = 65.2$ (**2a**), 62.7 (**2b**)). Due to the $C_1$ symmetry of the molecule in solution two Cp and two $NMe_2$ resonances are found, the latter again doubled because of the hindered rotation with respect to the boron–nitrogen double bond. The presence of the carbyne carbon atom is confirmed by signals at $\delta = 241.20$ (**2a**) and 239.02 (**2b**) in the $^{13}C$ NMR spectra.

The results of the X-ray structure analysis of **2a** (Figure 1) show that the molecule also adopts $C_1$ symmetry in the crystal.[7] The geometry of the central $B_2(NMe_2)_2$ unit resembles that of corresponding diborane(4)yl complexes,[5a,b] thus showing a boron–boron distance of 170.4(6) pm and boron–nitrogen distances of 137.4(5) pm (B1–N5), and 139.8(5) pm (B2–N6) ; the latter are in the expected range for boron–nitrogen double bonds. The boron–metal distance of 234.8(4) pm corresponds to the value of 237.0(8) pm for the boron–tungsten distance in $[(\eta^5\text{-}C_5H_5)W(CO)_3\{B(NMe_2)B(NMe_2)Cl\}]$.[5a] Complex **2a** is the first structurally characterized boryl complex with a molybdenum–boron linkage. The Mo≡C–O moiety displays the expected linear arrangement with an Mo1-C1-O1 angle of 174.9(3)° and an molybdenum–carbon distance of 182.5(4) pm, which is characteristic for a corresponding triple bond.[8] The B1–O1 distance of 146.0(5) pm, and the C1-O1-B1 angle of 127.4(3)° together with the corresponding data of the B–N linkage mentioned above reveal that the bonding at the boron atom is best described as comprising a B–O single bond and a B–N double bond.[9]

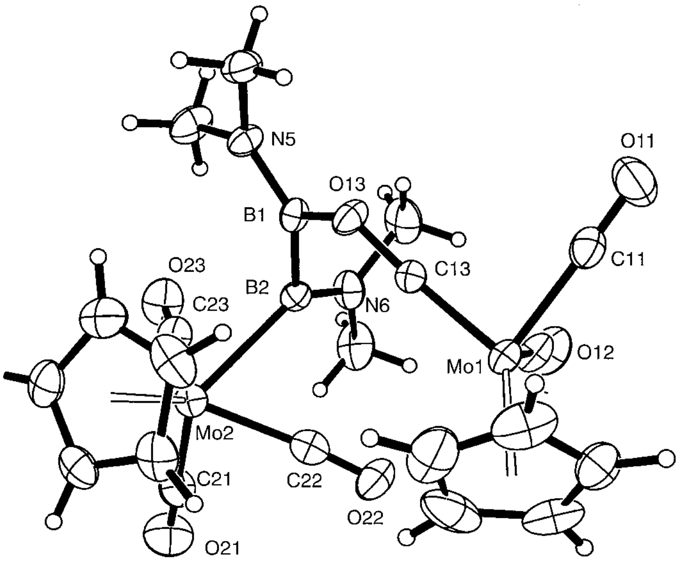


Figure 1. Structure of **2a** in the crystal. Selected distances [pm] and angle [°]: Mo2–B2 234.8(4), B2–N6 139.8(5), B1–N5 137.4(5), B1–B2 170.4(6), Mo1–C13 182.5(4); O13-C13-Mo1 174.9(3).

## *Experimental Section*

**1a**: A solution of $B_2(NMe_2)_2I_2$ [10] (0.98 g, 2.70 mmol) in benzene (10 mL) was added dropwise to a suspension of $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$[11] (1.53 g, 5.30 mmol) in benzene (10 mL). After stirring the mixture for 1 h at ambient temperature, all volatile materials were removed under high vacuum (0.001 Torr). The residue was suspended in hexane (30 mL), filtered, and the remaining solid was rinsed with hexane (10 mL). The filtrate was concentrated under vacuum to 20 mL and stored at $-30\,^\circ C$. After 48 h **1a** (0.53 g, 32.7%) was obtained as a yellow, very air- and moisture-sensitive crystalline material. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. $^1H$ NMR (500 MHz, TMS): $\delta = 2.31$, 2.37 (s, 6H, $N(CH_3)_2$), 5.22 (s, 10H, $C_5H_5$); $^{11}B$ NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 31.1$ (BO); $^{13}C$ NMR (126 MHz, TMS): $\delta = 35.28$, 39.33 ($N(CH_3)_2$), 91.31 ($C_5H_5$), 229.49 (CO), 245.18 (carbyne-C); elemental analysis (%) calcd for $C_{20}H_{22}B_2Mo_2N_2O_6$ (599.90): C 40.04, H 3.70, N 4.67; found: C 39.52, H 3.83, N 4.66.

**1b**: As described for **1a** a suspension of $K[(\eta^5\text{-}C_5H_5)W(CO)_3]$[11] (1.19 g, 3.20 mmol) in benzene was treated with a solution of $B_2(NMe_2)_2I_2$ (0.58 g, 1.60 mmol) in benzene. Complex **1b** (0.40 g, 32.2%) was obtained as yellow, very air- and moisture-sensitive crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. $^1H$ NMR (500 MHz, TMS): $\delta = 2.39$, 2.41 (s, 6H, $N(CH_3)_2$), 5.15 (s, 10H, $C_5H_5$); $^{11}B$ NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 30.8$ (BO); $^{13}C$ NMR (126 MHz, TMS): $\delta = 35.31$, 39.44 ($N(CH_3)_2$), 89.80 ($C_5H_5$), 220.11 (CO), 242.72 (carbyne-C); elemental analysis (%) calcd for $C_{20}H_{22}B_2N_2O_6W_2$ (775.72): C 30.97, H 2.86, N 3.61; found: C 30.17, H 2.84, N 3.37.

**2a**: A solution of **1a** (0.20 g, 0.33 mmol) in benzene (10 mL) was stirred for 7 d at ambient temperature, then all volatile materials were removed under high vacuum (0.001 Torr). The residue was dissolved in hexane (20 mL). The resulting yellow solution was concentrated under vacuum to 10 mL and stored at $-30\,^\circ C$. After 48 h **2a** was obtained quantitatively as yellow crystals, which could be handled in air for a short period. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. $^1H$ NMR (500 MHz, TMS): $\delta =$ 2.16, 2.24, 2.79, 2.84 (s, 3H, $N(CH_3)$), 5.03, 5.20 (s, 5H, $C_5H_5$); $^{11}B$ NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 31.5$ (BO), 65.2 (BMo); $^{13}C$ NMR (126 MHz, TMS): $\delta = 34.78$, 38.32, 42.84, 48.95 ($N(CH_3)$), 91.50, 93.68 ($C_5H_5$), 224.11, 226.58, 229.75, 229.97, 233.78, (CO), 241.20 (carbyne-C); elemental analysis (%) calcd for $C_{20}H_{22}B_2Mo_2N_2O_6$ (599.90): C 40.04, H 3.70, N 4.67; found: C 39.59, H 3.65, N 4.66.

**2b**: As described for **2a** a solution of **1b** (0.20 g, 0.26 mmol) in benzene (10 mL) was stirred for 7 d. Complex **2b** was obtained quantitatively as yellow crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. $^1H$ NMR (500 MHz, TMS): $\delta = 2.21$, 2.26, 2.80, 2.87 (s, 3H, $N(CH_3)$), 5.04, 5.12 (s, 5H, $C_5H_5$); $^{11}B$ NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 32.6$ (BO), 62.7 (BW); $^{13}C$ NMR (126 MHz, TMS): $\delta = 34.74$, 38.46, 43.46, 49.29 ($N(CH_3)$), 89.92, 92.51 ($C_5H_5$), 215.47, 218.04, 220.38, 220.68, 223.42 (CO), 239.02 (carbyne-C); elemental analysis (%) calcd for $C_{20}H_{22}B_2N_2O_6W_2$ (775.72): C 30.97, H 2.86, N 3.61; found: C 30.39, H 3.07, N 3.50.

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[7] Crystal structure determination **2a**: X-ray-quality crystals were removed from a Schlenk tube and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber, and instantly placed in a low-temperature $N_2$ stream of a P4 four-circle diffractometer (Siemens). $M_r = 599.90$, monoclinic, space group $P2_1/c$, $a = 1760.7(4)$, $b = 845.6(2)$, $c = 1824.2(4)$ pm, $\beta = 117.55(3)^\circ$, $V = 2.4080(9)$ mm$^3$, $Z = 4$, $\rho_{calcd} = 1.655$ Mg m$^{-3}$, $F(000) = 1192$, $\lambda = 71.073$ pm, $T = 173$ K, $\mu(Mo_{K\alpha}) = 1.078$ mm$^{-1}$, crystal size: $0.4 \times 0.5 \times 0.2$ mm$^3$, $4.48^\circ < 2\theta < 58^\circ$; 7899 reflections were collected; empirical absorption correction using empirical $\psi$ scans; 6412 of 6415 unique reflections were used for refinement of 293 parameters; max./min. difference of electron density: $-786/715$ e nm$^{-3}$. $R1 = 0.045$ ($F > 4\sigma(F)$) and $wR2 = 0.101$ (all data) with $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = \{Sw(F_o^2 - F_o^2)^2/\Sigma w(F_o^2)^2\}^{0.5}$. Calculations were carried out with the SHELXTL PC 5.03[12] and SHELXL-97 [13] program systems. The phase problem was solved by direct methods and the structure was refined on $F_o^2$ by full-matrix least-squares techniques. Anisotropic thermal parameters were included for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined by using a riding model, including free rotation of methyl groups. Their isotropic thermal parameters were constrained to 1.2 (cyclopentadienyl H) or 1.5 $U_{eq}$ (methyl groups) times that of the bonded carbon. 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-116236. 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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