Molybdenum-Boron Bonds in the Crystal – Structural Characterization of $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ and $[(\eta^5\text{-}C_5H_5)(OC)_3Mo\text{-}\{B(NMe_2)\text{-}B(NMe_2)Br\}]$

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Structural characterization of the solvent-free ionic complex $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ and the molybdenum boryl complex $[(\eta^5\text{-}C_5H_5)(OC)_3Mo\text{-}\{B(NMe_2)\text{-}B(NMe_2)Br\}]$ is reported.

Key words: Half-sandwich Molybdenum Complexes, Boranes, Diboranes(4), Boryl Complexes, X-Ray Diffraction

Introduction

Alkali metal salts $M'[(\eta^5\text{-}C_5H_5)M(CO)_n]$ (M' = alkali metal, $M(CO)_n$ = *e. g.* $Fe(CO)_2$, $Ru(CO)_2$, $Mo(CO)_3$, $W(CO)_3$) [1 – 7] are important starting materials for a wide range of half-sandwich complexes with covalent metal-metal and metal-element bonds. However, since these highly reactive anionic species are commonly prepared and reacted *in situ*, little is known about their solid-state structures, and only a few of them have been crystallographically characterized so far, such as $[Li(TMEDA)_2][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ [4] and $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ [1]. In the case of the former, the coordination of the alkali metal cation by suitable ligands (in this case: TMEDA) commonly imposes the formation of ion pairs in the solid state. In contrast, $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ [1] represents a very particular case as it forms a two-dimensional network in the crystal, due to the absence of coordinating ligands at the potassium cation.

We and others have frequently employed the molybdenum species $[Li(TMEDA)_2][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ for the preparation of corresponding half-sandwich complexes with Mo–B bonds [8 – 14]. While the bonding patterns such as boryl [4], diboran(4)yl [9, 15] as well as base-stabilized boryl complexes [16], have been unequivocally established in solution by IR and multinuclear NMR spectroscopy, very few crystallographic data have been published on molybdenum boryl complexes of the general formula $[L_xM\text{-}BR_2]$. In fact, the rather complex diboran(4)yl compound $[(\eta^5\text{-}C_5H_5)(OC)_3Mo\text{-}B(NMe_2)\text{-}B(NMe_2)\text{-}OC{\equiv}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ [17] appears to represent the only structurally characterized $Mo\text{-}BR_2$ species with three-coordinate boron. However, it should be noted that in the case of the aforementioned base-stabilized molybdenum boryl complexes of the type $[L_xMo\text{-}BR_2(base)]$, which comprise four-coordinate boron, a few structurally characterized examples have been reported, *e. g.* $[(\eta^5\text{-}C_5Me_5)(OC)_3Mo\text{-}BH_2\text{-}(PMe_3)]$ [18].

The absence of structural data on molybdenum boryl bonds is somewhat surprising, considering the excessive knowledge on boryl complexes in general [19, 20] and the well-established class of diboran(4)yl complexes in particular, which without exception were derived from the aforementioned alkali metal salts $M'[(\eta^5\text{-}C_5H_5)M(CO)_n]$ [9, 15].

In this paper we report on the structural characterization of both $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ (**1**) and the molybdenum diboran(4)yl complex $[(\eta^5\text{-}C_5H_5)(OC)_3\text{-}Mo\text{-}\{B(NMe_2)\text{-}B(NMe_2)Br\}]$ derived therefrom.

Results and Discussion

*Synthesis and Structure of **1***

The synthesis of $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ (**1**) was achieved according to Eq. 1 in analogy to previously described procedures [3, 9].

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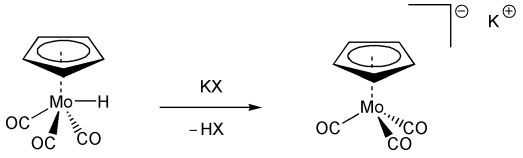

(1)

Solvent-free single crystals of **1** suitable for X-ray analysis were obtained from thf solution, which was layered with hexane and stored for one week at ambient temperature. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and forms a two-dimensional network due to the presence of oxygen-potassium interactions. To the best of our knowledge, to date, only the solvent-free compound $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ displays a similar extended solid-state structure as determined by X-ray diffraction [1].

In each crystal layer the $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ anions are assembled in a way that the cyclopentadienyl groups are facing outwards. These anions are cross-linked *via* potassium cations. Fig. 1 shows a section of the crystal lattice, as viewed along the crystallographic *a* and *c* axis, respectively. The two-dimensional nets are oriented orthogonally with respect to the *b* axis, and they are alternately positioned at the origin and at 1/2 of the lattice vector *b* (the second position is generated *via* a glide plane at 1/2 at 1/4 of the *b* vector).

Despite the interactions with potassium cations, the geometry of the $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ anion is that of an almost undistorted three-legged piano stool; all distances between the molybdenum atom and the carbonyl groups are in a similar range (1.921(2)–1.949(2) Å) and likewise, the Cp_{cent}–Mo–C angles are very similar (126.2 – 129.0 °). The potassium cations are surrounded by oxygen atoms originating from six different anions (Fig. 2). Five short K–O distances of 2.699(2) – 2.778(2) Å and a longer one of 3.422(2) Å (sum of covalent radii: 2.76 Å) are in agree-

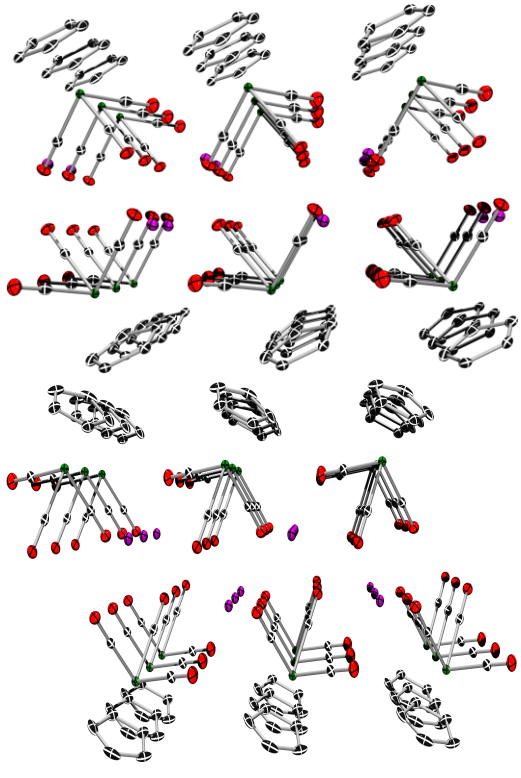

Fig. 1 (color online). Crystal structure of **1**. View along the crystallographic *a* (top) and *c* axis (bottom). Displacement ellipsoids are at the 50 % probability level. Hydrogen atoms are omitted for clarity.

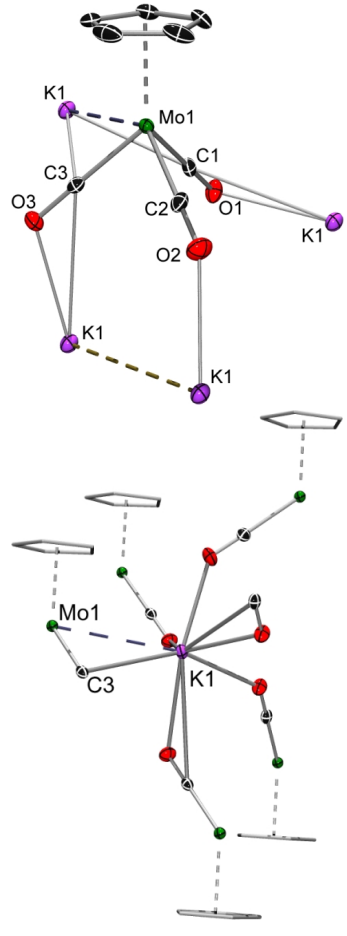

Fig. 2 (color online). Surrounding of the $[(\eta^5\text{-}C_5H_5)\text{-}Mo(CO)_3]^-$ anion (top) and of the potassium cation (bottom) in crystalline **1**. Displacement ellipsoids are at the 50 % probability level. Hydrogen atoms are omitted for clarity.

ment with those observed in the structure of K[(η^5-C_5H_5)Fe(CO)$_2$]. The Mo–K distance of 3.652(1) Å is slightly elongated compared to the non-linear bridging linkage Mo···H···K in [K(18-crown-6)][MoCp$_2$H] (3.614 Å), thus suggesting a rather weak electrostatic interaction [23]. Despite the observation that the K–K contacts of 4.063(1) and 4.413(1) Å are relatively short, they are presumably not involved in the bonding, as both of them are bridged by two oxygen atoms each.

Structure of ***2***

Although the synthesis of [(η^5-C_5H_5)(OC)$_3$Mo-{B(NMe$_2$)-B(NMe$_2$)Br}] has already been published in 1999, its solid-state structure remained unknown. Compound **2** was now prepared according to Eq. 2 and isolated after work-up in 55 % yield as an orange-red, highly air- and moisture-sensitive solid material [9].

Slow evaporation of a saturated toluene solution of **2** at −30 °C provided single crystals suitable for X-ray diffraction (Fig. 3). Compound **2** crystallizes as orange blocks in the non-centrosymmetric space group *Pna*2$_1$ with Z = 4. Similar to its precursor **1**, complex **2** displays a four-legged piano stool geometry with three similar Mo–C distances of 1.955(2)–1.978(2) Å and one Mo–B separation of 2.367(2) Å. The latter is comparable to the Mo–B distance of 2.348(4) Å found in the only known molybdenum boryl complex [(η^5-C_5H_5)(OC)$_3$MoB(NMe$_2$)-B(NMe$_2$)OC≡Mo(CO)$_2$(η5-C_5H_5)] [17]. The terminal molybdenum borylene complex [(OC)$_5$Mo=BN(SiMe$_3$)$_2$] [24] (2.151(7) Å), as well as the boryl-bridged heterodinuclear borylene [(OC)$_4$Mo(μ-CO){μ-BN(SiMe$_3$)$_2$}Pd(PCy$_3$)] (2.235(4) Å) exhibit both considerably shorter Mo–B distances. The planes of both boryl groups in **2** are, as expected for a non-conjugated system, almost perpendicular to each other. The deviation of the atoms from the least-squares plane in each boryl moiety amounts to 0.004 – 0.018 Å, and the angle between the planes was found to be 96.2°. These observations indicate the lack of pronounced π interaction between the metal and the boron atoms.

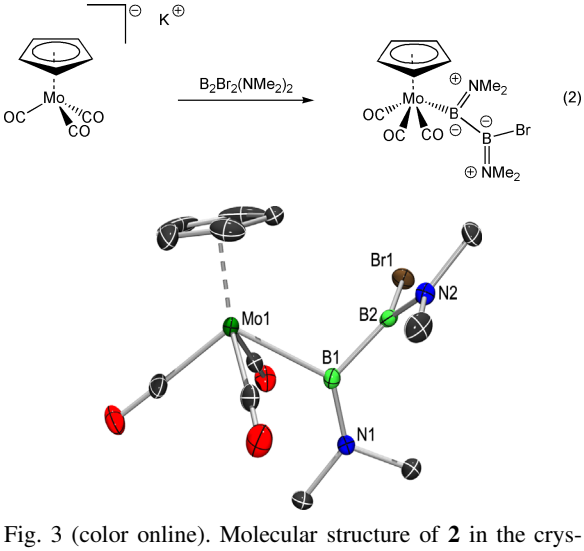

Fig. 3 (color online). Molecular structure of **2** in the crystal. Displacement ellipsoids are at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk or glove box techniques. Solvents were dried according to standard procedures or by using the MBraun solvent purification system (SPS) and stored under argon over molecular sieves. B$_2$(NMe$_2$)$_2$Br$_2$ was prepared according to literature procedures [21]. The NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS *via* the residual proton of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to external BF$_3$·OEt$_2$.

Potassium-[(η^5-cyclopentadienyl)molybdenumtricarbonyl] ***(1)***

0.16 g (4.1 mmol) KH was added to a solution of 1.00 g (4.1 mmol) of [(η^5-C_5H_5)(CO)$_3$MoH] in 30 mL of thf at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. After warming to r. t. the mixture was kept stirring for further 2 h. The formation of hydrogen was observed during the reaction. The resulting solution was concentrated *in vacuo* to a volume of 5 mL and treated with 200 mL of hexanes. The colorless precipitate of **1** was filtered off and dried *in vacuo* (0.99 g, 3.5 mmol, 85 %.)

2-Bromo-1-[(η^5cyclopentadienyl)molybdenumtricarbonyl]-1,2-bis(dimethylamino)-diborane(4) ***(2)***

0.76 g (2.8 mmol) B$_2$(NMe$_2$)$_2$Br$_2$ was added to a suspension of 0.80 g (2.8 mmol) K[(η^5-C_5H_5)Mo(CO)$_3$] in 20 mL of benzene at ambient temperature, and the mixture was stirred for 24 h. After removal of the solvent the residue was extracted with 30 mL of hexanes yielding **2** as an orange-red powder (0.99 g, 1.6 mmol, 55 %). – ^{1}H NMR (400 MHz; C$_6$D$_6$; 25 °C): δ = 2.44, 2.61, 2.65, 2.83 (s, 3H, NMe$_2$), 4.99 (s, 5H, CH$_{Cp}$). – ^{11}B NMR (64.2 MHz; C$_6$D$_6$; 25 °C): δ =

38.2 (BBr), δ = 65.6 (BMo). – ^{13}C NMR (100 MHz; C_6D_6; 25 °C): δ = 39.40, 41.39, 42.54, 47.67 (CH_{NMe}), 93.67, (CH_{CP}), 224.60, 227.78, 233.53 (CO).

Crystal structure determinations

The crystal data of **1** and **2** were collected on a Bruker X8APEX diffractometer equipped with a CCD area detector and multi-layer mirror-monochromatized MoK_α radiation (λ = 0.71073 Å). The structures were solved using Direct Methods, expanded using Fourier techniques, and refined with the SHELX software package [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included as fixed-atom contributions in the structure factor calculations.

*Crystal data for **1**:* $C_8H_5KMoO_3$, M_r = 284.16, colorless plate, 0.05 × 0.16 × 0.39 mm^3, monoclinic, space group $P2_1/n$, a = 5.6156(8), b = 26.117(4), c = 6.4372(9) Å, β = 98.106(3)°, V = 934.7(2) Å^3, Z = 4, D_{calcd} = 2.02 g cm^{-3}, μ = 1.8 mm^{-1}, F(000) = 552 e, T = 100(2) K, R_1 = 0.0230, wR_2 = 0.0488 for 2295 independent reflections ($2\theta \leq 56.56°$) and 118 refined parameters, $\Delta\rho_{fin}$ (max / min) = 0.43 / −0.53 e Å^{-3}.

*Crystal data for **2**:* $C_{12}H_{17}B_2BrMoN_2O_3$, M_r = 434.75, orange block, 0.19 × 0.18 × 0.15 mm^3, orthorhombic, space group $Pna2_1$, a = 21.6173(12), b = 10.3012(6), c = 7.5422(4) Å, V = 1679.53(16) Å^3, Z = 4, D_{calcd} = 1.72 g cm^{-3}, μ = 3.2 mm^{-1}, F(000) = 856, T = 100(2) K, R_1 = 0.0190, wR_2 = 0.0382 for 4097 independent reflections ($2\theta \leq 56.6°$) and 194 refined parameters, x(Flack) = 0.048(4), $\Delta\rho_{fin}$ (max / min) = 0.32 / −0.24 e Å^{-3}.

CCDC 773458 (**1**) and 773459 (**2**) 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.

Acknowledgement

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