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Diborane(4)yl Complexes of Molybdenum and Ruthenium

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Introduction

A large number of structurally authentic boryl complexes was reported over the last years,[1a,b] which were mostly obtained from 1,2-dioxobenzo- or catecholborane and its derivatives either by salt elimination[2a−d] or by oxidative addition of a suitable boron element bond to a metal center.[3a−g] In the latter case the use of dicatecholdiborane(4) generally leads to formation of transition metal diboryl complexes with cleavage of the boron boron bond. In addition, some bridging borylene complexes of manganese and cobalt also derive from diboranes(4), again with cleavage of the boron boron bond.[4a−d] The knowledge of diborane(4)yl complexes, however, being obtained with preservation of the boron boron bond by salt elimination reactions from $B_2(NMe)_2Cl_2$ and corresponding anionic transition metal complexes was so far restricted to only two examples of the type $[Cl(Me_2N)B{-}B(NMe_2)M(C_5H_5)(CO)_n]$ $[M(C_5H_5)(CO)_n = Fe(C_5H_5)(CO)_2, W(C_5H_5)(CO)_3]$ (**A**, **B**).[5] This paper describes the synthesis of novel diborane(4)yl complexes of ruthenium and molybdenum, which are not accessible from chlorine substituted diboranes(4), including the first characterization of a ruthenium boryl complex in the crystal.

Experimental Section

All manipulations were carried out in dry nitrogen atmosphere in Schlenk glassware. Solvents were dried by standard procedures, distilled and stored under nitrogen and molecular sieves. $B_2(NMe_2)_2Br_2$,[6] $Na[Ru(C_5H_5)(CO)_2]$,[7] and $K[Mo(C_5H_5)(CO)_3]$[8] were synthesized according to known procedures. NMR: Varian Unity 500 at 499.843 in C_6D_6 (^1H, standard TMS intern), 150.364 (^{11}B, standard $BF_3{\cdot}OEt_2$ in C_6D_6 extern), 125.639 MHz ($^{13}C\{^1H\}$, APT, standard TMS intern). Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, model 1106. IR: Perkin-Elmer FT-IR 1720 x in hexane.

Preparation of 2-Bromo-1-[(η^5-cyclopentadienyl)dicarbonylruthenium]-1,2-bis(dimethylamino)diborane(4) (1a). $B_2(NMe_2)_2Br_2$ (1.39 g, 5.20 mmol) was added to a suspension of $Na[(C_5H_5)Ru(CO)_2]$ (1.27 g, 5.20 mmol) in benzene (20 mL) at ambient temperature. The reaction mixture was stirred for 24 h. After removal of the solvent in high vacuum, the solid residue was extracted with 30 mL of hexane. After filtration and cooling to −30 °C, 0.50 g (24%) of pure **1a** were obtained as brown crystals, mp 58 °C. ^1H NMR: $\delta = 2.55, 2.79, 2.84$ and 2.85 (4s, 3H each, NMe_2), 4.84 (s, 5H, C_5H_5). ^{11}B NMR: $\delta = 39.7$ (BBr), 63.3 (BRu). ^{13}C NMR: $\delta = 39.47, 41.76, 45.35$ and 47.23 (NMe_2), 87.52 (C_5H_5), 203.21 and 203.76 (CO). IR: $\nu = 2005$ (m) and 1945 (m) cm^{-1} (C═O). $C_{11}H_{17}B_2BrN_2O_2Ru$ (411.86): calcd C 32.08, H 4.16, N 6.80; found C 32.44, H 4.36, N 6.80.

Preparation of 2-Bromo-1-[(η^5-cyclopentadienyl)tricarbonylmolybdenum]-1,2-bis(dimethylamino)diborane(4) (1b). $B_2(NMe_2)_2Br_2$ (1.00 g, 3.70 mmol) was added to a suspension of $K[(C_5H_5)Mo(CO)_3]$ (1.05 g, 3.70 mmol) in benzene (20 mL) at ambient temperature. The reaction mixture was stirred for 24 h. After removal of the solvent in high vacuum, the solid residue was extracted with 30 mL of hexane. After filtration and cooling to −30 °C 0.88 g (55%) of pure **1b** were obtained as red crystals, mp. 88 °C. ^1H NMR: $\delta = 2.44, 2.61, 2.65$ and 2.83 (4s, 3H each, NMe_2), 4.99 (s, 5H, C_5H_5). ^{11}B NMR: $\delta = 38.2$ (BBr), 65.6 (BMo). ^{13}C NMR: $\delta = 39.40, 41.93, 42.45$ and 47.67 (NMe_2), 93.67 (C_5H_5), 224.60, 227.78, and 233.53 (CO). IR: $\nu = 1985$(m), 1901(m) and 1887(m) cm^{-1} (C═O). $C_{12}H_{17}B_2BrMoN_2O_3$ (434.74): calcd C 33.15, N 6.44, H 3.94; found C 32.95, N 6.35, H 4.00.

Crystal Structure Determination of 1a. Geometry and intensity data were collected on an ENRAF-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Crystal data, collection parameters and convergence results are compiled in Table 1. After Lorentz and polarization corrections, an empirical absorption correction based on azimuthal scans[9] was applied before averaging symmetry related intensity data. The structure was solved by direct methods,[10] refined with the SDP program system.[11] In the final refinement cycles hydrogen atoms were included in riding geometry with fixed isotropic displacement parameters ($d_{C-H} = 0.98$ Å, $U_{iso}(H) = 130U_{eq}(C)$). Further details of the crystal structure determination are available on request from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-104612.

Results and Discussion

The use of the moderately reactive $B_2(NMe_2)_2Cl_2$ for the synthesis of diboran(4)yl complexes is restricted to the iron and tungsten compounds $[Cl(Me_2N)B{-}B(NMe_2)M(C_5H_5)(CO)_n]$ $[M(C_5H_5)(CO)_n = Fe(C_5H_5)(CO)_2, W(C_5H_5)(CO)_3]$ (**A**, **B**).[5] To expand this salt elimination reaction on diborane(4)yl complexes of various transition metals, we applied the more reactive corresponding bromo diborane(4) derivative $B_2(NMe_2)_2Br_2$.

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Table 1. Crystallographic Data, Data Collection Parameters, and Convergence Results for **1a**

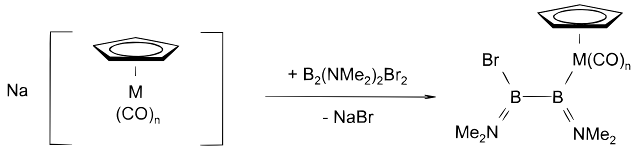
formula	$RuBrO_2N_2C_{11}B_2H_{17}$	wavelength (Å)	0.710 73
fw	411.87	T, °C	−70
crystal size (mm^3)	0.36 × 0.40 × 0.48	scan range (deg)	2.1−28.0
space group (no.)	$P\bar{1}$ (2)	scan mode	ω
a (Å)	9.696(1)	absorption correction	empirical
b (Å)	10.053(1)	(min/max)	(0.665/0.999)
c (Å)	9.156(2)	reflcns measd	4912
a (deg)	99.16(1)	indep reflcns	3828
β (deg)	115.306(9)	obsd reflcns	3489 [$I > 1.0\sigma(I)$]
γ (deg)	87.05(1)	variables refined	172
V ($Å^3$)	796.4(4)	R^a	0.033
Z	2	$R_w{}^b$	0.039
μ (cm^{-1})	34.48	GOF	1.16
D_{calc} (g cm^{-3})	1.72	max. residual electron density (e $Å^{-3}$)	0.739

[a] $R = \Sigma (||F_o| - |F_c||)/\Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$. $GOF = [\Sigma w(|F_o| - |F_c|)^2/n_{obs} - n_{var}]^{1/2}$, n_{obs}, no. of observations; n_{var}, no. of variables refined.

Table 2. Selected Bond Distances (pm) and Angles (deg) for **1a**

B1−Ru	217.3(3)	Ru−B1−B2	113.0(2)
B1−B2	167.4(4)	Ru−B1−N1	124.5(2)
B1−N1	139.3(4)	N1−B1−B2	122.4(2)
B2−N2	138.0(4)	Br−B2−N2	117.3(2)
B2−Br	199.6(3)	Br−B2−B1	114.6(2)
Ru−C1	185.9(3)	N2−B2−B1	127.9(3)
Ru−C2	186.2(3)	Ru−N1−B2−B1// N2−Br−B1−B2	92.52(7)
C1−O1	114.0(4)		
C2−O2	114.4(4)	Ru−N1−B2−B1// $Cp_{(center)}$−B1−Ru	103.37(7)

According to eq 1 the ruthenium and molybdenum diboran(4)-yl complexes **1a** and **1b** were obtained as brown and red crystals, respectively. Solutions of both compounds in hexane or benzene show no signs of decomposition after several days at ambient temperature, and in the solid state both compounds can be even handled under air for short periods.



1a M(CO)n = Ru(CO)2

1b M(CO)n = Mo(CO)3

The structure of **1a** and **1b** in solution derives from multinuclear NMR and IR spectra. The ^{11}B NMR spectra show two signals at $\delta = 39.7$ and 63.3 (**1a**), and $\delta = 38.2$ and 65.6 (**1b**), respectively. The resonances at higher field, which are ascribed to the bromine substituted boron atoms, are in the same region as the shift of the starting material ($\delta = 37.3$), while the signals of the transition metal substituted boron atoms show a significant low field shift of about 25 ppm, as expected. Due to a restricted rotation with respect to the boron nitrogen double bond the four methyl groups of each compound exhibit four signals in the ^1H and ^{13}C NMR spectra. The IR spectra of both compounds give no evidence for a metal boron π-interaction, since the CO stretching frequencies (**1a**, 2005, 1945 cm^{-1}; **1b**, 1985, 1901, 1887 cm^{-1}) exhibit a considerable red shift with respect to those of the corresponding methyl complexes of ruthenium[12] (2028, 1960 cm^{-1}) and molybdenum[13] (2018, 1950, 1946 cm^{-1}).

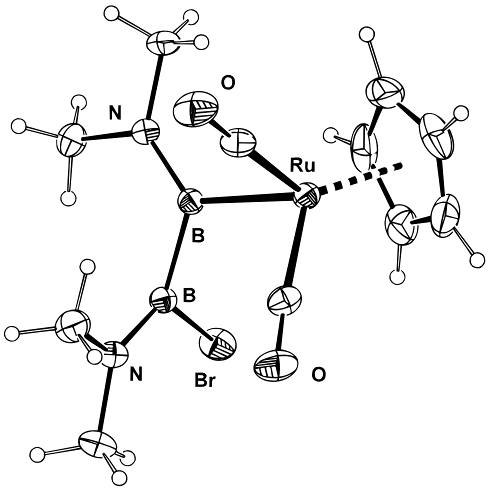


Figure 1. PLATON drawing of molecular structure of **1a** (displacement ellipsoids at 30% probability).[14]

An X-ray structure analysis was carried out for the ruthenium derivative **1a** (Figure 1). This complex crystallizes in the triclinic space group $P\bar{1}$ and the molecule adopts C_1 symmetry.

The boron and nitrogen atoms are trigonal planar coordinated and both boryl groups are almost perpendicular to each other, including a dihedral angle of 92.52(7)°. The ruthenium boron distance was found to be 217.3(3) pm, thus resembling the corresponding ruthenium carbon ($CH_2Si(CH_3)_3$ ligand) distance in $[(C_5H_5)Ru(CO)_2\{CH_2Si(CH_3)_3\}]$.[15] These findings together with the almost perpendicular orientation of the Cp_c−Ru−B1 (Cp_c = ring centroid) plane with respect to the Ru−B1−N1 plane (103.37(7)°) provide no evidence for a metal boron π-interaction in the solid state.[16] The lack of any metal boron back-bonding was already established for several corresponding boryl complexes of iron. [2a,17a,b] Boron nitrogen double bonds, already established for both compounds in solution, were also found for $[Br(Me_2N)B{-}B(NMe_2)Ru(C_5H_5)(CO)_2]$ **1a** in the crystal, as indicated by boron nitrogen distances of 139.3(4) pm (B1−N1), and 138.0(4) pm (B2−N2), respectively.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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