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Boride Ligands

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Low-Coordinate Boride Ligands: A True Trimetalloborane[**]

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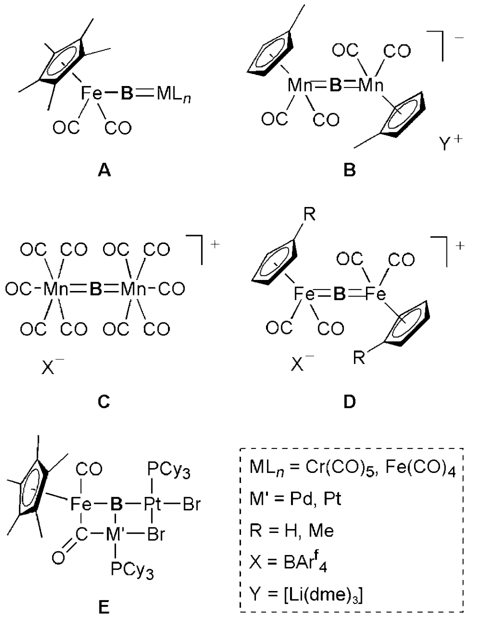
Dedicated to Professor Reinhold Tacke on the occasion of his 60th birthday

The development of boron–metal chemistry has roughly tracked that of carbon–metal (i.e., organometallic) chemistry, beginning with singly bound boryl (MBR_2) complexes, then doubly bound bridging (M_2BR) and terminal (MBR) borylene complexes.[1] In other words, the conceptual replacement of R groups from a borane BR_3 with metal fragments has been a gradual process, and full replacement to form a trimetalloborane is a lingering challenge.

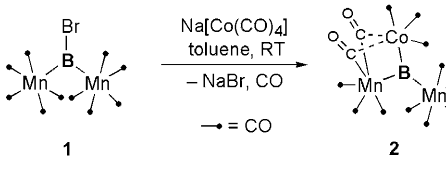
In organometallic chemistry, examples of multimetallic carbide complexes (formally C^{4-}) are very rare, and complexes with a non-hypercoordinate carbide ligand rarer still.[2] The steadily growing number of multimetallic boron complexes, such as M_2BR[3] and M_3BR,[4] encouraged our attempts towards the synthesis of complexes containing a single boron atom as a ligand. Consequently, the first di- (**A**)[5] and trimetallic (**E**)[6] complexes of low-coordinate boron were synthesized in 2005 and 2006, respectively (Scheme 1). Although the range of M_2B complexes has recently been elaborated upon with the synthesis of cationic (**C**, **D**)[5b] and anionic (**B**)[5c] examples, the only M_3B complexes currently known are $[(\eta^5\text{-}C_5Me_5)(OC)Fe(\mu\text{-}CO)M(PCy_3)(\mu\text{-}Br)Pt(PCy_3)Br(\mu_3\text{-}B)]$ (M = Pd, Pt; **E**).[6] These complexes were formed by the oxidative addition of two BBr bonds of the iron boryl complex $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\text{–}BBr_2]$ to two $\{M(PCy_3)\}$ fragments, and feature a distinct T-shaped configuration of the three metal centers around the boron atom thanks to bridging bromide and carbonyl ligands.

The T-shaped geometry of **E** means that although the complexes contain three metal–boron interactions, the label "trimetalloborane" is wholly inappropriate. Furthermore, density functional analysis revealed that the perpendicular attachment of the $\{M(PCy)_3\}$ fragment (M = Pd, Pt) to the linear Fe-B-Pt unit is not only due to strong interactions with the bridging Br and CO ligands, but also to a significant dative M–B bond. Thus, the overall bonding situation is that of a metal-base-stabilized metalloborylene complex.[6]



Scheme 1. Recently published neutral (**A**), anionic (**B**), and cationic (**C**, **D**) M_2B complexes, and M_3B complexes (**E**). $Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$.

Herein we present the first trimetallic complex of a boride ligand determined structurally to be a true trimetalloborane complex, which was formed by a salt elimination. Addition of an excess of $Na[Co(CO)_4]$ to a toluene solution of the bromoborylene complex $[\{(OC)_5Mn\}_2BBr]$ (**1**)[3o] at room temperature gave a brown solution (Scheme 2). The solvent was removed, and the crude solid was dissolved in hexane and filtered. Upon concentration and cooling, this solution provided orange crystals of complex **2** that has a signal in the ^{11}B NMR spectrum at $\delta = 195.8$ ppm that is shifted significantly downfield from the starting material **1** ($\delta = 163.6$ ppm). The position of this signal is consistent with the M_2B complexes **A** ($\delta = 191$, 205 ppm), **B** ($\delta = 195$ ppm), **C** ($\delta = 225$ ppm), and **D** ($\delta = 191$, 193 ppm), but is significantly different from trimetallic systems **E** ($\delta = 130$, 144 ppm). This discrepancy may be due to the differing nature of the metal



Scheme 2. Synthesis of **2** from **1** and $Na[Co(CO)_4]$.

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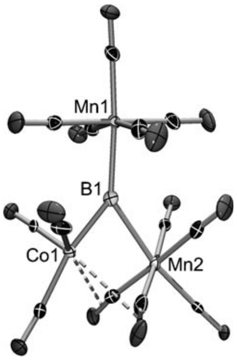

Figure 1. Molecular structure of **2**; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: B–Mn1 2.129(2), B–Mn2 2.290(2), B–Co1 1.903(2); Mn1-B-Mn2 140.0(1), Mn2-B-Co1 78.05(7), Co1-B-Mn1 142.0(1).

centers, as complexes **A**–**D** contain exclusively "mid-transition" metals, whereas **E** contains the late-transition metals Pd and Pt.

The IR spectrum of **2** has a complex carbonyl region, with no appreciable signals below 1980 cm^{-1}. Elemental analysis for carbon suggests a formulation [$M_3B(CO)_{13}$] ($M_3 = Mn_2Co$ or Mn_3). However, unmistakable evidence for the composition of **2** as [$(OC)_3Mn(\mu\text{-}CO)_2Co(CO)_3(\mu_3\text{-}B)Mn(CO)_5$] came from a single-crystal X-ray crystallographic analysis (Figure 1). Significant disorder involving the permutation of the {$Co(CO)_3$} fragment and its proximal {$Mn(CO)_5$} fragment was found; therefore, structural parameters discussed herein are those of the major (circa 70%) residue. (See the Supporting Information for further details of the disorder).

The structure shows a trigonal boron atom (sum of angles 359.3°) bound to the three metal fragments. One {$Mn(CO)_5$} fragment is independent, pseudooctahedral, and not associated with any other ligand apart from the boron atom itself (Mn–B 2.129(2) Å). The other {$Mn(CO)_5$} fragment is more loosely bound to the boron atom (Mn–B 2.290(2) Å), yet is closely associated with the {$Co(CO)_3$} fragment with which it partly shares two CO ligands (Mn–Co 2.6569(6) Å; Mn-C$_\mu$-O$_\mu$ 169.2(2) and 170.3(2)°, bent away from the Co atom). The C–O bond of the semi-bridging CO ligands appear to undergo statistically negligible lengthening compared to the non-bridging CO ligands, which suggests that their degree of bridging is low. The Co–B distance of **2** (1.903(2) Å) is very similar to that of the related complex [$(\eta^5\text{-}C_5H_5)(OC)Co\{\mu\text{-}BN(SiMe)_3\}W(CO)_5$] (1.913(3) Å).[3n] From this relationship, we can surmise that the electronic requirements of the formally unsaturated cobalt atom are very slightly satisfied by the proximal manganese atom and the two semi-bridging CO ligands. Given the short Co–B distance, significant multiple bonding may also be inferred.

Asymmetrical bridging carbonyl ligands are not uncommon, although in the case of **2** the degree of bridging of the "semi-bridging" CO ligands is unusually low. In 1974, Cotton and Troup addressed this issue by proposing that semi-bridging CO infrared stretching frequencies lie within the range 1800–1900 cm^{-1}; that is, between those of symmetrical bridging and terminal CO ligands.[7a] They presented the complex [$Fe_3(CO)_8(SC_4H_8)_2$], which contains bridging CO ligands with Fe-C$_\mu$-O$_\mu$ angles of 167°, and the IR band at the lowest wavelength is found at 1903 cm^{-1}. These ligands were described as "slightly disturbed terminal" CO ligands.

The corresponding Mn-C$_\mu$-O$_\mu$ angles of **2** are also slightly bent; however, no signal could be found in the 1800–1900 cm^{-1} range of the IR spectrum. Such a low degree of bridging was also found by Chen et al. in a number of bridging carbyne complexes in which a single CO ligand bridges an M–Co (M = Mn, Re) bond in an unsymmetrical fashion (M-C$_\mu$-O$_\mu$ 160–168°).[7b,c] In each of these complexes, one or two IR bands were observed between 1831–1889 cm^{-1}; however, the presence of other semi-bridging CO ligands in the molecules precludes their assignment. Another bridging {WCo_2} carbyne complex synthesized by Schenk et al. has W-C$_\mu$-O$_\mu$ angles of 166.1(7) and 170.3(7)°, with corresponding IR bands at 1880 and 1840 cm^{-1}.[7d] Like these systems, the degree of interaction of the {$Co(CO)_3$} fragment of **2** with each of the semi-bridging carbonyl ligands is minimal.

To gain some insight into the electronic structure of **2**, we computationally examined its Kohn–Sham orbitals (Figure 2).[8] The trigonal planar coordination of the metal atoms around the boron atom is incompatible with the spatial

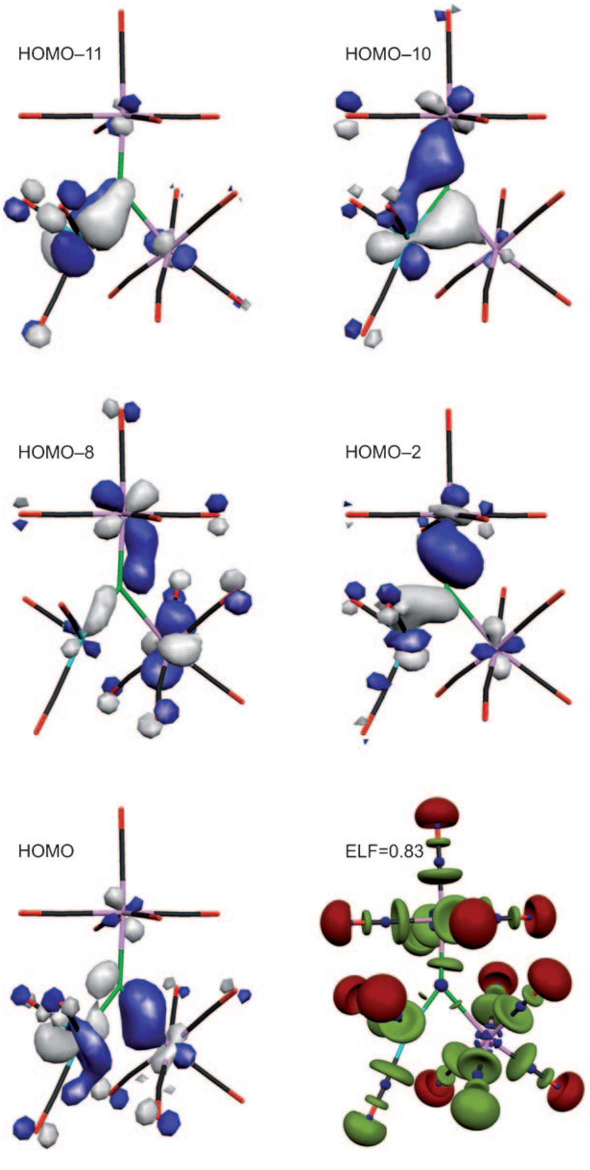

Figure 2. Kohn–Sham orbitals describing B–M bonding interactions in **2** and plot of ELF. B green, Mn pink, Co cyan, C black, O red; the ELF basins are colored green (disynaptic), red (monosynaptic), and blue (core basins).

orientation of p orbitals. Therefore, the boron orbitals that are involved in the bonding with metal fragments are mixtures of s and p orbitals. Both {Mn(CO)$_5$} units are bonded to boron by predominantly σ interactions (HOMO, HOMO−2, and HOMO−10). π bonding to the boron atom can be seen both in the M$_3$ plane (presumably a mixture of p_x and p_y orbitals at boron) and orthogonal to it (back-donation into the empty p_z orbital at boron). The former, in-plane interactions can be seen with all three metals (e.g., HOMO−8, HOMO−10), whereas an unmistakable orthogonal π interaction with the boron p_z orbital can be seen exclusively with cobalt (HOMO−11). As the cobalt atom has lost one of its carbonyl ligands and can be considered to be coordinatively unsaturated, the high degree of π bonding with the boron atom is unsurprising. The strong π bonding presumably alleviates the requirement for electron density by the cobalt atom from the potentially bridging proximal Mn−CO ligands, and may explain their almost terminal disposition with respect to the manganese atom.

Three maxima are found around the boron atom in **2** in the electron localization function (ELF) distribution (Figure 2). As expected for the independent, σ-bound {Mn(CO)$_5$} moiety, the Mn−B valence basins have similar dimensions both in and perpendicular to the BM$_3$ plane. Its bias towards Mn2 can be rationalized by the greater distance from boron to {Mn(CO)$_5$} than to the {Co(CO)$_3$} moiety. Thus there exists smaller Pauli repulsion in this area, which leads to slightly higher ELF values. The elongation of the Co−B valence basin perpendicular to the BM$_3$ plane again emphasizes the importance of the Co→B π-back-donation in **2**.

Four signals were observed in the ^{13}C NMR spectrum of **2**: two broad signals at $\delta = 216.1$ and 212.9 ppm, and two sharp signals at $\delta = 209.2$ and 208.6 ppm. The two sharp signals appear roughly in a ratio of approximately 4:1, which can be tentatively assigned to the {Mn(CO)$_5$} carbonyl ligands, whereas the broadness of the remaining two signals could be explained by the coordinative unsaturation (and hence fluxionality) of the {Co(CO)$_3$} fragment and/or the quadrupolar nature of the cobalt nucleus.

In conclusion, an unusual trimetallic boride complex **2** has been synthesized. Conceptually, complex **2** is the first example of a trimetalloborane, as it contains three covalent M−B bonds, in contrast to the previously reported trimetallic complexes in which significant dative M→B bonding was present.[6] Boron transition metal chemistry has historically suffered from a perceived synthetic difficulty, which is partly related to the absence of nucleophilic boron reagents (recently remedied[9]). To create the first M−B bonds, pioneers in the field of transition metal boryl complexes[1a] were forced to use the opposite strategy: that of nucleophilic attack of an anionic metal species on a haloborane. With a judicious selection of first-row transition metal complex anions, we have successfully pushed this protocol to its limits within hypovalent boron chemistry with the formal threefold metallation of a borane.

Experimental Section

5b: A mixture of [(OC)$_5$Mn]$_2$BBr (90.0 mg, 0.187 mmol) and a large excess of Na[Co(CO)$_4$] (72.6 mg, 0.374 mmol) were stirred in toluene (5 mL) at room temperature for 12 h. All volatiles were removed under vacuum, and hexane (20 mL) was added. The mixture was filtered, concentrated, and cooled to −60 °C overnight. The resulting bright red crystals were collected by filtered and dried under vacuum. Yield 34.0 mg (0.062 mmol, 33 %). ^{13}C{^{1}H} NMR (13 °C, 150.9 MHz, C$_6$D$_6$): $\delta = 216.1$ (br), 212.9 (br), 209.2, 208.6 ppm. ^{11}B NMR (25 °C, 160.5 MHz, C$_6$D$_6$): $\delta = 195.8$ ppm. IR (hexane): $\tilde{\nu} = 2083$, 2063, 2056, 2044, 2025, 2015, 2007, 1984, 1980 cm^{-1}. Anal. calcd (%) for C$_{13}$BCoMn$_2$O$_{13}$: C 28.71; found: C 28.39.

The crystal data for **2** was collected on a Bruker X8 APEX diffractometer with a CCD area detector and multi-layer mirror with monochromated Mo$_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically.

Crystal data for **2**: C$_{13}$BCoMn$_2$O$_{13}$, $M_r = 543.75$, orange needles, $0.32 \times 0.05 \times 0.05$ mm^3, monoclinic space group $P2_1/n$, $a = 8.5432(14)$, $b = 16.650(3)$, $c = 12.896(2)$ Å, $\beta = 97.623(7)°$, $V = 1818.2(5)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.986$ g cm^{-3}, $\mu = 2.338$ mm^{-1}, $F(000) = 1056$, $T = 100(2)$ K, $R_1 = 0.0365$, $wR^2 = 0.0754$, 4992 independent reflections ($2\sigma \leq 61.18°$), and 329 parameters.

CCDC 721478 contains 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.

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