Organometallics **2007,** *26,* 4700−4701

Syntheses and Structure of Bridged Haloborylene Complexes

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Received May 16, 2007

Summary: The homodinuclear, bridged haloborylene transition metal complexes $[(\mu\text{-BCl})\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2]$ *and* $[(\mu\text{-BX})\{\text{Mn(CO)}_5\}_2]$ *(X = Cl, Br) were prepared by salt elimination reactions and characterized by single-crystal X-ray diffraction.*

Since the advent of the first structurally authenticated borylene complex,[1] the chemistry of this class of transition metal complexes of boron has received considerable interest.[2] In particular, complexes derived from fluoroborylene have been subject to numerous theoretical studies due to the close electronic relationship between BF and the ubiquitous CO ligand.[3] These studies revealed BF to possess enhanced σ-donor and π-acceptor properties with respect to CO, thus predicting an increased thermodynamic stability of BF complexes with respect to homolytic M−B dissociation. Due to the buildup of positive charge at the BF ligand, however, borylene complexes are known to be readily susceptible to nucleophilic attack at the boron center. Hence, the vast majority of experimentally realized species of that type have to rely both on electron-releasing substituents at boron and on sterically demanding groups, thus increasing their kinetic stability.[2] Indeed, corresponding complexes with boron-bound groups lacking π-donor properties are very rare and restricted to only two examples, namely, $[(\text{OC})_5\text{Cr}{=}\text{B}{-}\text{Si(SiMe}_3)_3]$[4] and $[(\mu\text{-B}t\text{Bu})\{(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn(CO)}_2\}_2]$ (R = H, Me).[1,5] Likewise, chloro- and bromoborylene complexes, which can be considered as the closest relatives of the elusive B−F species, represent peculiar cases, obviously due to the lack of steric protection provided by the small halide substituent. While terminal complexes of the type $[\text{L}_x\text{M}{=}\text{B}{-}\text{Hal}]$ are generally unknown, the bridged chloroborylene species $[(\mu\text{-BCl})\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn(CO)}_2\}_2]$, which was synthesized from its amino-substituted precursor $[(\mu\text{-BNMe}_2)\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn(CO)}_2\}_2]$ upon reaction with gaseous HCl,[6] represents the only fully characterized haloborylene complex.[7] Additionally, the heterodinuclear complex $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}\}(\mu\text{-BBr})(\mu\text{-CO})\{\text{Pd(Br)(PCy}_3)\}]$ was obtained by a salt elimination−oxidative addition sequence and characterized by multinuclear NMR spectroscopy and elemental analyses.[8] In the present paper we describe the direct synthesis of $[(\mu\text{-BCl})\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2]$ and of $[(\mu\text{-BX})\{\text{Mn(CO)}_5\}_2]$ (X = Cl, Br), the latter representing the first example of a structurally characterized bromoborylene complex.

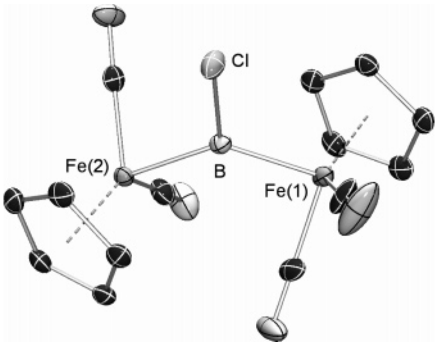

Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [deg]: Fe(1)−B = 2.019(2), Fe(2)−B = 2.006(2), B−Cl = 1.841(2); Fe(1)−B−Fe(2) = 131.27(12), Fe(1)−B−Cl = 113.91(12), Fe(2)−B−Cl = 114.82(12).

During the course of our studies about the reactivity of monoanionic transition metal carbonylates toward trihaloboranes, which recently led to a general access to dihaloboryl complexes,[9] we turned our attention to the preparation of bridged haloborylene complexes. From the reaction of 2 equiv of $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]$ with BCl_3, the bridged chloroborylene complex $[(\mu\text{-BCl})\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2]$ (**1**) is obtained. The synthesis is accompanied by the formation of an almost equimolar amount of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$, and therefore **1** was only isolated in 10% yield as an analytically pure red, air- and moisture-sensitive solid. The ^{11}B NMR resonance (δ = 146.6) shows the expected low-field shift in comparison to the dichloroboryl complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\text{BCl}_2)]$ (δ = 90.0).[9] The constitution of **1** was confirmed by single-crystal X-ray diffraction. Suitable crystals were grown from a solution of **1** in hexane at −35 °C.

The complex crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit contains one unique molecule. The Fe−B bond distances [2.019(2) and 2.006(2) Å] are elongated compared to that of the boryl species $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\text{BCl}_2)]$ [1.942(3) Å][9] but are still shorter than those of iron boryl

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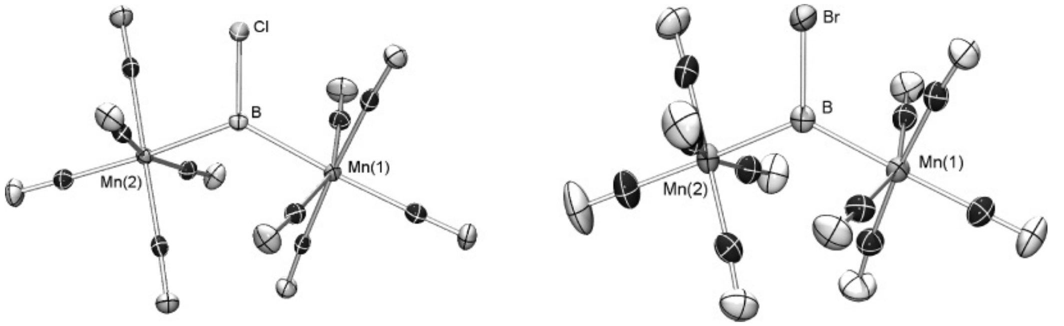
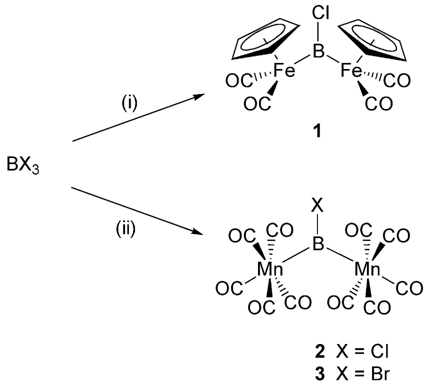


Figure 2. Molecular structures of **2** and **3**. Selected bond lengths [Å] and angles [deg]: **2**: Mn(1)−B = 2.164(2), Mn(2)−B = 2.161(2), B−Cl = 1.804(2); Mn(1)−B−Mn(2) = 131.65(10), Mn(1)−B−Cl = 113.87(11), Mn(2)−B−Cl = 114.48(11); **3**: Mn(1)−B = 2.149(3), Mn(2)−B = 2.163(3), B−Br = 1.997(3); Mn(1)−B−Mn(2) = 132.98(15), Mn(1)−B−Br = 114.20(15), Mn(2)−B−Br = 112.82(15).

Scheme 1[a]



[a] Reaction conditions: (i) 2 equiv of K[(η^5-C_5H_5)Fe(CO)$_2$], toluene, −60 °C; (ii) 2 equiv of Na[Mn(CO)$_5$], toluene (X = Cl) or hexane (X = Br), −30 °C.

complexes with π-stabilizing nitrogen substituents at boron.[10] The Fe−Fe distance [3.667 Å] is shorter than in [(μ-BMes){(η^5-C_5H_5)Fe(CO)$_2$}$_2$] [3.802 Å],[11] but significantly longer than in [{μ-BN(SiMe$_3$)$_2$}{μ-CO}{(η^5-C_5H_5)Fe(CO)}$_2$] [2.548(1) Å], which in contrast to the aforementioned homodinuclear iron species is characterized by the presence of only two terminal but one bridging CO ligand,[12] and therefore precludes any Fe−Fe interaction.

The reaction of 2 equiv of Na[Mn(CO)$_5$] with BX$_3$ (X = Cl, Br) leads to the formation of the homodinuclear haloborylene complexes [(μ-BX){Mn(CO)$_5$}$_2$] (**2**, X = Cl; **3**, X = Br), which were isolated as orange, air- and moisture-sensitive solids in 38% and 65% yield, respectively. The ^{11}B NMR resonances (**2**, δ = 160.1; **3**, δ = 163.6) are significantly low-field shifted with respect to those of the corresponding dihaloboryl species [(OC)$_5$Mn(BX$_2$)] (X = Cl, δ = 94.2; X = Br, δ = 92.9).[9] Recrystallization of **2** from hexane and **3** from toluene/hexane (1:1) afforded yellow crystals suitable for X-ray structure determination.

Both compounds crystallize in the monoclinic space group $P2_1/c$. While the asymmetric unit of **2** contains one unique molecule, two independent molecules are present in the case of **3**, which differ only marginally in the arrangement of the borylene ligand with respect to the (OC)$_5$Mn fragments. The difference between the Br−B−Mn−C$_{cis}$ torsion angles amounts to approximately 6°, and for simplicity reasons only one of the molecular structures is discussed below. In both compounds, the boron centers display distorted trigonal-planar coordination geometries with Mn−B−Mn angles of 131.65(10)° and 132.98(15)°. The Mn−B bond distances [**2**, 2.164(2) and 2.161(2) Å; **3**, 2.149(3) and 2.163(3) Å] are longer than in the boryl complexes [(OC)$_5$Mn(BCl$_2$)] [2.060(5) Å][9] and [(OC)$_5$MnB-(1,2-O$_2$C$_6$H$_4$)] [2.108(6) Å][13] and even exceed the Mn−B separation in the half-sandwich complex [(η^5-C$_5$H$_4$Me)(OC)$_2$-(H)Mn−B(Cl){Si(SiMe$_3$)$_3$}] [2.138(16) Å], which is characterized by a hydrogen atom adopting a bridging position between the metal and boron centers.[14] The B−Cl bond length [1.804(2) Å] in **2** is slightly longer than those found in [(OC)$_5$Mn(BCl$_2$)] [1.777(3) Å],[9] while the B−Br bond length [1.997(3) Å] in **3** is almost identical to that found in the bisboryloxide [{(OC)$_5$Mn-(BBr)}$_2$O] [1.981(2) Å].[9] The Mn−Mn distances [3.945 and 3.954 Å] are significantly longer than in [(μ-BNMe$_2$){(η^5-C_5H_5)-Mn(CO)$_2$}$_2$] [2.03(1) Å],[1] clearly indicating the absence of any Mn−Mn interactions. The Mn−C$_{trans}$ bond distances [**2**, 1.862(2) and 1.864(2) Å; **3**, 1.862(3) and 1.863(3) Å] are within the range of the Mn−C$_{cis}$ bond distances [**2**, 1.844(2)−1.874(2) Å; **3**, 1.848(3)−1.872(3) Å], and thus the *trans* influence of the borylene ligand is similar to that of CO.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-646830 (**1**), CCDC-646829 (**2**), and CCDC-622966 (**3**). Copies of these 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).

Acknowledgment. This work was supported by the DFG and the Fonds der Chemischen Industrie.

Supporting Information Available: Text detailing the synthetic procedures, spectroscopic data, and structural determinations for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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