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Synthesis and Reactivity of Dihaloboryl Complexes

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Transition metal dihaloboryl complexes of the types $[(\eta^5\text{-}C_5R_5)Fe(CO)_2BX_2]$ (R = H, Me; X = F, Cl, Br), $[(\eta^5\text{-}C_5H_4Me)Ru(CO)_2BX_2]$ (X = Cl), and $[(OC)_5MnBX_2]$ (X = Cl, Br) were prepared via salt elimination reactions. Comparison of the CO stretching frequencies indicates a higher degree of Fe−B $d_\pi-p_\pi$ back-bonding in the dibromoboryl complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)_2BBr_2]$ with respect to their $-BCl_2$ and $-BF_2$ analogues. This finding is constistent with the $p_\pi-p_\pi$ back-bonding abilities of the halides (F > Cl > Br). Reactions of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX_2]$ (X = Cl, Br) with 4-methylpyridine were performed, leading to the formation of the corresponding Lewis-base adducts and, with base in excess, to the first metal-substituted boronium cation $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2BBr(NC_5H_4\text{-}4\text{-}Me)_2]^+$.

Introduction

In the last decade, transition metal complexes of boron, with defined 2c,2e M−B bonds, have become an area of great interest. Particularly boryl complexes $[L_nM-BR_2]$ are most prominent, and more than one hundred fully characterized examples have been reported.[1] Among these, monohaloboryl complexes $[L_nM-B(Hal)R]$ with an additional amino or aryl substituent at boron are well documented, while the knowledge about dihaloboryl complexes $[L_nM-BHal_2]$ is much more restricted. Examples include a few structurally characterized difluoroboryl complexes such as $[Pt(PPh_3)_2(BF_2)_2]$[2] and $[Ir(CO)(PPh_3)_2(BF_2)_3]$,[3] derived from the reactions of Pt^0 and Ir^I precursors with B_2F_4, and $[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(H)(BF_2)]$,[4] which was obtained via salt elimination. Very recently, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BF_2)]$ was reported as an unexpected side product from the reaction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2B(OMes)Cl]$ with $Na[BAr^f_4]$.[5] For these difluoroboryls, no subsequent substitution chemistry at the boron center was reported, presumably because of their reduced Lewis acidity due to strong $p_\pi-p_\pi$ back-bonding and the high thermodynamic stability of the B−F bond. As expected, complexes with $-BCl_2$ or $-BBr_2$ ligands show a significantly enhanced reactivity. The spectroscopically characterized dichloroboryl complex $[Os(Cl)(CO)(PPh_3)_2(BCl_2)]$ already served as a convenient precursor for extensive substitution chemistry,[6a−c] yielding, for example, the first base-stabilized borylene complex from the reaction with 8-aminoquinoline.[6a] Likewise, iron half-sandwich complexes of the type $[(\eta^5\text{-}C_5R_5)Fe(CO)_2BX_2]$ (R = Me, H; X = Cl, Br) demonstrated their propensity for boron-centered reactions, thus leading to a variety of novel and unusual coordination modes, including bridging boryl[7] and heterodinuclear borylene complexes,[8] metalloborylenes,[9] and metal-base-stabilized metalloborylenes,[10] the latter two featuring a "naked" boron atom in the coordination sphere of two or three transition metal centers, respectively. Spectroscopic data for the iron half-sandwich dichloroboryl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl_2]$ and $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2BCl_2]$, whose synthesis was interestingly accompanied by the formation of $[(\eta^5\text{-}C_5H_3MeBCl_3)Fe(CO)_3]$ as a side product, were initially reported by Aldridge et al.[11a,b]

In 2004 we communicated the structural characterization of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl_2]$ and its reaction with 4-methylpyridine, thus yielding the first Lewis-base adduct directly obtained from a boryl complex.[12] It should be noted that several examples for base-stabilized boryl complexes of molybdenum, tungsten, iron, and manganese were previously reported,[13a−c] which were, however, exclusively obtained from preformed borane adducts.

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(1) (a) Irvine, G. I.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685. (b) Smith, M. R., III. *Prog. Inorg. Chem.* **1999**, *48*, 505. (c) Braunschweig, H.; Colling, M. *J. Organomet. Chem.* **2000**, *614*−*615*, 18. (d) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1. (e) Braunschweig, H. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, New York, 2001; pp 213. (f) Braunschweig, H. *Adv. Organomet. Chem.* **2004**, *51*, 163. (g) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535. (h) Braunschweig, H.; Rais, D. *Heteroat. Chem.* **2005**, *16*, 566.

(2) Kerr, A.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Timms, P. L.; Whittell, G. R. *Chem. Commun.* **1998**, 319.

(3) Lu, N.; Norman, N. C.; Orpen, A. G.: Quayle, M. J.; Timms, P. L.; Whittell, G. R. *J. Chem. Soc., Dalton Trans.* **2000**, 4032.

(4) Peterson, T. H.; Golden, J. T.; Bergman, R. G. *Organometallics* **1999**, *18*, 2005.

(5) Kays, D. L.; Rossin, A.; Day, J. K.; Ooi, L.-L.; Aldridge, S. *Dalton Trans*. **2006**, 399.

(6) (a) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem.* **2000**, *112*, 978; *Angew. Chem., Int. Ed.* **2000**, *39*, 948. (b) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 4862. (c) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2003**, *680*, 81.

(7) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem.* **2005**, *117*, 1217; *Angew. Chem., Int. Ed.* **2005**, *44*, 1192.

(8) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F.; Uttinger, K. *J. Am. Chem. Soc.* **2005**, *127*, 1386.

(9) (a) Braunschweig, H.; Radacki, K.; Scheschkewitz, D.; Whittell, G. R. *Angew. Chem.* **2005**, *117*, 1685; *Angew. Chem. Int. Ed.* **2005**, *44*, 1658. (b) Braunschweig, H.; Whittell, G. R. *Chem. Eur. J.* **2005**, *11*, 6128.

(10) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem.* **2006**, *118*, 1087; *Angew. Chem., Int. Ed.* **2006**, *45*, 1066.

(11) (a) Aldridge, S.; Calder, R. J.; Baghurst, R. E.; Light, M. E.; Hursthouse, M. B. *J. Organomet. Chem.* **2002**, *649*, 9. (b) Aldridge, S.; Calder, R. J.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Crystallogr.* **2003**, *33*, 805.

(12) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2004**, *23*, 4178.

(13) (a) Kawano, Y.; Yasue, T.; Shimoi, M. *J. Am. Chem. Soc.* **1999**, *121*, 11744. (b) Yasue, T.; Kawano, Y.; Shimoi, M. *Chem. Lett.* **2000**, 58. (c) Yasue, T.; Kawano, Y.; Shimoi, M. *Angew. Chem.* **2003**, *115*, 1769; *Angew. Chem., Int. Ed.* **2003**, *42*, 1727.

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We herein report (i) the syntheses of a series of dihaloboryl complexes of iron, ruthenium, and manganese via salt elimination reactions and (ii) selected examples of their reactivity toward 4-methylpyridine, yielding corresponding Lewis-base adducts, and the first transition metal-substituted boronium cation [(η^5-C_5Me_5)Fe(CO)$_2$BBr(NC_5H_4-4-Me)$_2$]Br.

Results and Discussion

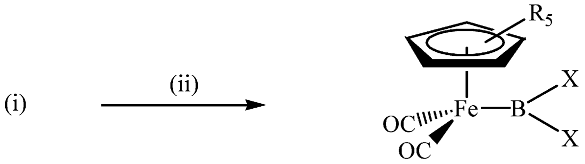
Iron Complexes. The salt elimination reaction of the highly nucleophilic[14] [(η^5-C_5R_5)Fe(CO)$_2$]$^-$ anion (R = H, Me) with haloboranes (e.g., ClB(1,2-$O_2C_6H_4$), $ClBPh_2$, $(ClBNH)_3$, Cl(Me_2N)-BB(NMe_2)Cl)[15a−c] or dihaloboranes (e.g., Br_2BMes, Cl_2-$BNMe_2$)[16,17] is a well-established and versatile route for the preparation of iron half-sandwich boryl complexes. Here, we studied the reactions between M[(η^5-C_5R_5)Fe(CO)$_2$] (M = K, R = H; M = Na, R = Me) and $BF_3{\cdot}OEt_2$ or BX_3 (X = Cl, Br), which provided a general access to dihaloboryl complexes of the type [(η^5-C_5R_5)Fe(CO)$_2$$BX_2$] (**1**−**6**).

In particular, the addition of excess $BF_3{\cdot}OEt_2$ to a suspension of K[(η^5-C_5H_5)Fe(CO)$_2$] or Na[(η^5-C_5Me_5)Fe(CO)$_2$] in toluene at 0 °C yields, as judged by ^{11}B NMR spectroscopy, [(η^5-C_5H_5)Fe(CO)$_2$$BF_2$] (**1**) ($\delta$ = 47.1 {J_{B-F} = 181 Hz}) and [(η^5-C_5Me_5)Fe(CO)$_2$$BF_2$] (**2**) ($\delta$ = 48.3 {J_{B-F} = 189 Hz}). Both compounds can be isolated by crystallization from hexane at −60 °C as analytically pure red solids in yields of 37−45%. The spectroscopic data of **2** are essentially identical to these, recently reported by Aldridge et al.[5]

The reactions of excess BX_3 (X = Cl, Br) with Na[(η^5-C_5R_5)-Fe(CO)$_2$] (R = H, Me) in toluene at −78 °C yield the dichloroboryl complexes [(η^5-C_5R_5)Fe(CO)$_2$$BCl_2$] (**3**: R = H; **4**: R = Me) and the dibromoboryl complexes [(η^5-C_5R_5)Fe(CO)$_2$-BBr_2] (**5**: R = H; **6**: R = Me), which display broad ^{11}B NMR signals at δ = 90.0 (**3**), 94.9 (**4**), 85.9 (**5**), and 91.0 (**6**). According to ^{1}H NMR spectroscopy, the reaction mixtures contain small amounts of [(η^5-C_5R_5)Fe(CO)$_2$X] (R = H, Me; X = Cl, Br), which are in the case of **5** and **6** highly dependent on the purity of BBr_3. Purification of the latter over mercury followed by condensation in vacuo prior to use significantly minimizes the amount of unwanted FeBr species. After removal of all volatiles in vacuo, extraction with hexane, and crystallization at −60 °C, analytically pure compounds **3**−**6** were isolated as red solids in yields of 31−48%.The complexes **1**−**6** are air- and moisture-sensitive but can be stored under argon at −30 °C for several weeks without decomposition. As for the corresponding trihaloboranes, **3**−**6** vaporize when exposed to air, due to hydrolysis of the B−X bonds. In solution, compound **5** shows decomposition after 1 day and **6** after a few hours, which is consistent with the enhanced stabilization of the bulky C_5Me_5 ligand in comparison to the parent C_5H_5 group. While **1**−**6** are all very soluble in toluene, the solubility in hexane varies from good (**1**−**4**) to moderate (**5**, **6**).

The nature of the metal−boron bond and in particular the role of Fe−B d_π−p_π back-bonding in boryl complexes of the type [(η^5-C_5R_5)Fe(CO)$_2$$BR_2$] have been extensively studied on the basis of structural and IR data.[1] The CO stretching frequencies of the dibromoboryl complexes **5** (2045, 2000) and **6** (2022, 1975) are shifted to significantly higher wavenumbers in comparison to their dichloro- and diflouroboryl analogues **1**−**4** (**1**: 2022, 1965; **3**: 2026, 1974; **2**: 2002, 1946; **4**: 2006, 1955) (Table 1). This is consistent with a higher degree of d_π−p_π back-bonding in **5** and **6** and is not surprising, when the p_π−p_π back-bonding abilities of the halides (F > Cl > Br) are considered. Comparison with [(η^5-C_5H_5)Fe(CO)$_2$B(1,2-$O_2C_6H_4$)] (2024, 1971)[15a] also indicates the presence of a relevant π-interaction in the case of **5**.

Scheme 1[a]



1 X=F, R=H **4** X=Cl, R=Me

2 X=F, R= Me **5** X=Br, R=H

3 X=Cl, R= H **6** X=Br, R= Me

[a] Reaction conditions: (i) $BF_3{\cdot}OEt_2$ or BX_3 (X = Cl, Br); (ii) K[(η^5-C_5H_5)Fe(CO)$_2$] or Na[(η^5-C_5Me_5)Fe(CO)$_2$] 1 equiv, toluene, 0 or −78 °C.

Table 1. Spectroscopic Data of 1−12

	^{11}B NMR [ppm]	IR (toluene) [cm^{-1}]
[(η^5-C_5H_5)Fe(CO)$_2$$BF_2$] (**1**)	47.1 (J_{B-F} = 181 Hz)	2022, 1965
[(η^5-C_5Me_5)Fe(CO)$_2$$BF_2$] (**2**)	48.3 (J_{B-F} = 189 Hz)	2002, 1946
[(η^5-C_5H_5)Fe(CO)$_2$$BCl_2$] (**3**)	90.0	2026, 1974
[(η^5-C_5Me_5)Fe(CO)$_2$$BCl_2$] (**4**)	94.9	2006, 1955
[(η^5-C_5H_5)Fe(CO)$_2$$BBr_2$] (**5**)	85.9	2045, 2000
[(η^5-C_5Me_5)Fe(CO)$_2$$BBr_2$] (**6**)	91.0	2022, 1975
[(η^5-C_5Me_5)Fe(CO)$_2$$BCl_2$-($NC_5H_4$-4-Me)] (**7**)	21.3	1958, 1899
[(η^5-C_5Me_5)Fe(CO)$_2$$BBr_2$-($NC_5H_4$-4-Me)] (**8**)	14.3	1963, 1904
[(η^5-C_5Me_5)Fe(CO)$_2$BBr-(NC_5H_4-4-Me)$_2$]Br (**9**)	21.0	1977, 1918
[(η^5-C_5H_4Me)Ru(CO)$_2$-BCl_2] (**10**)	81.0	2021, 1958
[$(OC)_5MnBCl_2$] (**11**)	94.2	2115, 2052, 2012
[$(OC)_5MnBBr_2$] (**12**)	92.9	2116, 2051, 2013

We recently compared **3** with its Lewis-base adduct [(η^5-C_5H_5)Fe(CO)$_2$$BCl_2$($NC_5H_4$-4-Me)], thus gaining valuable information about the degree of Fe−B d_π−p_π back-bonding in the former.[12] Analogously to the reported preparation, the addition of 1 equiv of 4-methylpyridine to **4** and **6** in toluene yields the corresponding base-stabilized boryl complexes [(η^5-C_5Me_5)Fe(CO)$_2$$BX_2$($NC_5H_4$-4-Me)] (**7**: X = Cl; **8**: X = Br). Crystals suitable for X-ray diffraction were obtained from solutions of **7** and **8** in benzene (Figure 1). Both compounds crystallize in the orthorhombic space group *Pnma*, and the asymmetric unit contains half a molecule with a crystallographic mirror plane bisecting the N, *ipso*-C, B, Fe atoms and the C_5-Me_5 ring. The geometry around boron is that of a slightly distorted tetrahedron, in agreement with its sp^3-hybridization. The Fe(1)−B(1) (**7**: 2.129(3) Å; **8**: 2.106(7) Å), B(1)−N(1) (**7**: 1.623(4) Å; **8**: 1.628(9) Å), and B(1)−Cl(1) (**7**: 1.884(2) Å) bond distances are similar to those in [(η^5-C_5H_5)Fe(CO)$_2$-BCl_2(NC_5H_4-4-Me)] (Fe−B = 2.1326(14) Å; B−N = 1.6103(17) Å; B−Cl = 1.8814(14) Å).[12] Unfortunately, all attempts to grow single crystals of the corresponding boryl complexes **4**

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[14] Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121.

[15] (a) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908. (b) Braunschweig, H.; Kollann, C.; Müller, M. *Eur. J. Inorg. Chem.* **1998**, 291. (c) Braunschweig, H.; Ganter, B.; Koster, M.; Wagner, T. *Chem. Ber.* **1996**, *129*, 1099.

[16] Aldridge, S.; Coombs, D. L.; Jones, C. *Chem. Commun.* **2002**, 856.

[17] Braunschweig, H.; Kollann, C.; Englert, U. *Eur. J. Inorg. Chem.* **1998**, *4*, 465.

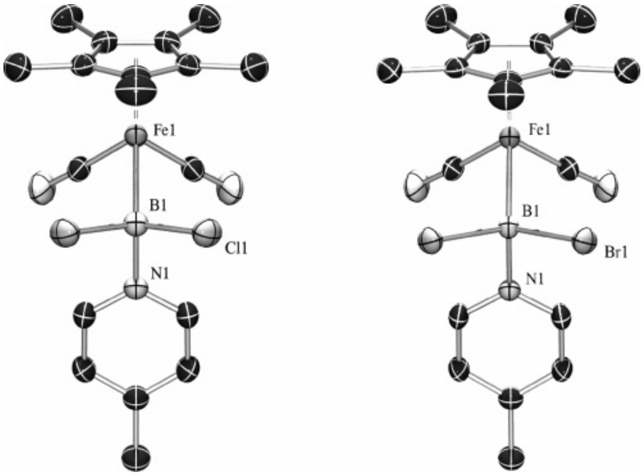


Figure 1. Molecular structures of **7** and **8**. Selected bond lengths [Å] and angles [deg]: **7**: Fe1−B1 = 2.129(3), B1−Cl1 = 1.884(2), B1−N1 = 1.623(4), Fe1−B1−N1 = 115.77(19), Fe1−B1−Cl1 = 111.85(11), N1−B1−Cl1 = 104.50(13); **8**: Fe1−B1 = 2.106(7), B1−Br1 = 2.069(4), B1−N1 = 1.628(9), Fe1−B1−N1 = 117.1(4), Fe1−B1−Br1 = 112.3(2), N1−B1−Br1 = 104.1(3).

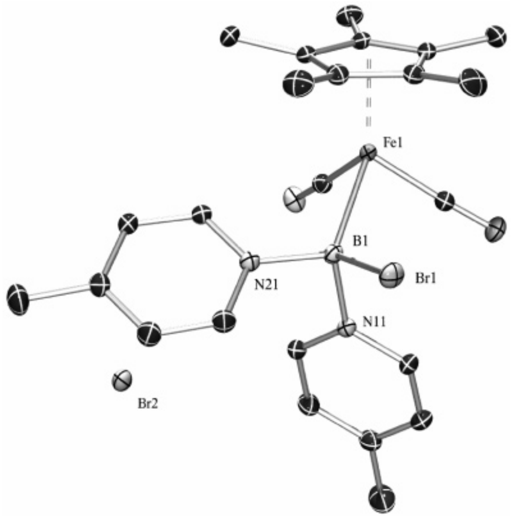
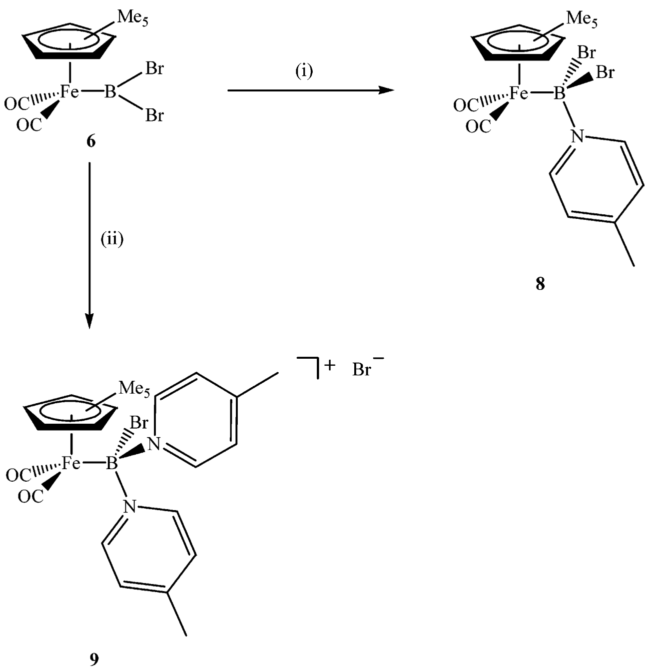


Figure 2. Molecular structure of **9**. Selected bond lengths [Å] and angles [deg]: Fe1−B1 = 2.1465(19), B1−Br1 = 2.061(2), B1−N11 = 1.626(2), B1−N22 = 1.596(2); Fe1−B1−N11 = 112.56(12), Fe1−B1−N21 = 118.44(12), Fe1−B1−Br1 = 111.51(9), Br1−B1−N11 = 104.83(11), Br1−B1−N21 = 105.67(11).

and **6** failed, thus precluding a structural comparison between these species.

Scheme 2[a]



[a] Reaction conditions: (i) 4-methylpyridine, 1 equiv, toluene, 0 °C; (ii) 4-methylpyridine, ca. 2 equiv, toluene, 0 °C.

Interestingly, in the case of **6**, the addition of excess 4-methylpyridine leads to a yellow precipitate, which is poorly soluble in toluene but well soluble in dichloromethane. The ^{11}B NMR spectrum indicates the formation of a new species **9** with a signal at $\delta = 21.0$, which is slightly low-field shifted with respect to that of **8** ($\delta = 14.3$). Recrystallization of **9** from hot toluene afforded crystals suitable for X-ray diffraction (Figure 2). **9** crystallizes in the triclinic space group $P\bar{1}$ and represents, to the best of our knowledge, the first metal-substituted boronium species.[19] The boron center is tetrahedrally coordinated by two neutral 4-methylpyridine donors, bromine, and iron. In comparison to **8** (Fe−B = 2.106(7) Å, B−N = 1.628(9) Å), the Fe(1)−B(1) (2.1465(19) Å) distance is elongated, while the B(1)−N(11)/N(21) (average 1.611(2) Å) contacts are slightly shortened. The B(1)−Br(1) (2.061(2) Å) bond distance is longer than that in the, however only slightly related, boronium ion $[\{C_6H_4(Ph_2P)_2\}BBrH]^+$ (B−Br = 1.975(7) Å).[20] Obviously, the presence of 4-methylpyridine in excess induces the liberation of one boron-bound bromide with addition of the neutral base to the boron center. It should be noted that we recently observed a similar bromide−pyridine exchange at a platinum-coordinated boryl ligand, which led to a cationic, base-stabilized borylene complex.[21]**Ruthenium and Manganese Complexes.** Although to a lesser extent than the aforementioned iron-based nucleophile $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]^-$, corresponding anionic ruthenium and manganese species, in particular $[(\eta^5\text{-}C_5R_5)Ru(CO)_2]^-$,[22a−d] $[(\eta^5\text{-}C_5R_5)Mn(H)(CO)_2]^-$,[23] and $[(OC)_5Mn]^-$,[24a,b] have been successfully utilized for the preparation of various boryl compexes.

To prove the generality of the synthesis of dihaloboryl complexes via salt elimination reactions, anionic Ru- and Mn-based carbonylates were employed. $Na[(\eta^5\text{-}C_5H_4Me)Ru(CO)_2]$ was reacted with BCl_3 in toluene at −78 °C, yielding, as indicated by ^{11}B NMR data, the dihaloboryl complex $[(\eta^5\text{-}C_5H_4Me)Ru(CO)_2BCl_2]$ (**10**) ($\delta = 81.0$). After workup, **10** is obtained as a green oil, which, according to multinuclear NMR spectroscopy, is free of accompanying impurities.

The reactions of $K[Mn(CO)_5]$ with excess BCl_3 in toluene and BBr_3 in hexane yield the dihaloboryl complexes $[(OC)_5Mn$-

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[18] Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911.

[19] For a recent review about cationic boron compounds see: Piers, W.; Conrey, K.; Bourke, S. *Angew. Chem.* **2005**, *117*, 5142; *Angew. Chem., Int. Ed.* **2005**, *44*, 5016.

[20] Sigl, M.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1411.

[21] Braunschweig, H.; Radacki, K.; Rais, D.; Scheschkewitz, D. *Angew. Chem.* **2005**, *117*, 5796; *Angew. Chem. Int. Ed.* **2005**, *44*, 5651.

[22] (a) Braunschweig, H.; Koster, M.; Wang, R. *Inorg. Chem.* **1999**, *38*, 415. (b) Hartwig, J. F.; Waltz, K. M. *Science* **1997**, *277*, 211. (c) Braunschweig, H.; Kollann, C.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 1523. (d) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Organometallics* **2004**, *23*, 5545.

[23] Braunschweig, H.; Colling, M.; Kollann, C.; Englert, U. *J. Chem. Soc., Dalton Trans.* **2002**, 2289.

[24] (a) Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357. (b) Coombs, D. L.; Aldridge, S.; Jones, C. *J. Chem. Soc., Dalton Trans.* **2002**, 3851.

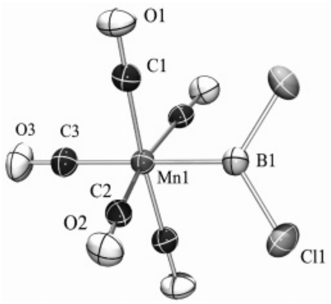

Figure 3. Molecular structure of **11**. Selected bond lengths [Å] and angles [deg]: Mn1−B1 = 2.060(5), B1−Cl1 = 1.777(3); Mn1−B1−Cl1 = 124.46(14), Mn1−C1−O1 = 179.2(3), Mn1−C2−O2 = 177.1(3), C1−Mn1−C2 = 89.85(11), C1−Mn1−B1 = 87.50(10), C2−Mn1−B1 = 83.68(9).

BX_2] (**11**: X = Cl; **12**: X = Br), which are characterized by a broad ^{11}B NMR signal at δ = 94.2 (**11**) and 92.9 (**12**), respectively. Interestingly, the formation of **12** is not observed when toluene is used as a solvent, and the ^{11}B NMR spectrum of the dark orange reaction mixture shows several signals of unidentified species in the area δ = 0−10. Pure **11** is obtained as a bright yellow solid by sublimation at room temperature and **12** as a yellow solid by crystallization from hexane at −30 °C. Both compounds are well soluble in toluene and hexane, vaporize when exposed to air, and show decomposition in solution at room temperature after a few hours, but can be stored under argon at −30 °C for several weeks. Single crystals suitable for X-ray diffraction of **11** were obtained from a toluene solution at −60 °C. **11** crystallizes in the orthorhombic space group *Fdd*2 and adopts C_{2v} symmetry (Figure 3). The Mn(1)−B(1) (2.060(5) Å) distance is shorter than in [$(OC)_5MnB(1,2\text{-}O_2C_6H_4)$] (Mn−B = 2.108(6) Å),[24a] indicating stronger Mn−B $d_\pi-p_\pi$ back-bonding in **11**. This is, however, as reflected by the average C_{eq}−Mn(1)−B(1) (85.6°) and Mn−C_{eq}−O (178.2°) angles, which are equivalent within experimental error in both compounds, not accompanied by a more pronounced umbrella effect, which was observed for a corresponding pair of structurally related borylene complexes of the type [$(OC)_5Cr{=}B{-}R$] (R = $N(SiMe_3)_2$, $Si(SiMe_3)_3$).[25]

All attempts of growing single crystals of **12** from toluene, hexane, or mixtures of both at various temperatures failed. However, a few yellow crystals suitable for X-ray diffraction were obtained from a solution of **12** in toluene/hexane after three weeks at −30 °C, which show a broad signal in the ^{11}B NMR spectrum at δ = 63.1 and turned out to be the bisboryloxide [$\{(OC)_5MnBBr\}_2O$] (**13**) (Figure 4). **13** crystallizes in the monoclinic space group *C*2/*c*. The boron atoms are slightly distorted trigonal planar coordinated by the manganese, chlorine, and oxygen atoms. The Mn(1)−B(1) (2.093(2) Å) bond distance is slightly longer than in **11** (2.060(5) Å). The B−O−B (159.3(3)°) angle is significantly widened compared to the, to our knowledge, only structurally characterized halosubstituted bisboryloxide [$(i\text{-}Pr_2N)BCl]_2O$ (134.2(2)°)[26] or $(CatB)_2O$ (134.2(2)°) (Cat = 1,2-$O_2C_6H_4$).[27] These data provide evidence for an increased O−B $p_\pi-p_\pi$ interaction in **13**, which can be assigned to the weaker π-donating abilities of the −Mn(CO)$_5$ fragment in comparison to −NR$_2$ or −OR substituents. Due to slow diffusion of water into the flask, **13** is obviously formed by partial hydrolysis of **12** and subsequent condensation. Several attempts for a direct preparation of **13** from **12**, in particular by treatment with water vapor, by controlled hydrolysis with different water-containing solvents, or by reactions with $Me_3SiOSiMe_3$ or Li_2O,[28] failed. In all cases, ^{11}B NMR spectroscopy of the reaction mixtures gave evidence for the formation of **13**, which then, however, could not be isolated in the desired purity and yield.

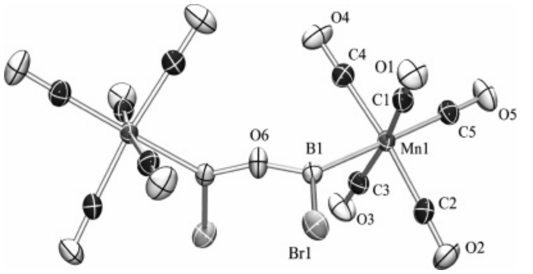

Figure 4. Molecular structure of **13**. Selected bond lengths [Å] and angles [deg]: Mn1−B1 = 2.093(2), B1−Br1 = 1.981(2), B1−O6 = 1.342(2); B1−O6−B1A = 159.3(3), Mn1−B1−Br1 = 121.91(10), Mn1−B1−O6 = 126.03(15), C1−Mn1−C3 = 169.40(8), C2−Mn1−C4 = 173.70(8), C1−Mn1−C2 = 90.48(9), C3−Mn1−C4 = 89.79(9), C3−Mn1−B1 = 84.75(8), C3−Mn1−C5 = 94.62(8).

Conclusion

A wide variety of dihaloboryl complexes were obtained via salt elimination reactions from suitable Fe-, Ru-, and Mn-based carbonylates. In particular, the properties of the iron complexes of the type [$(\eta^5\text{-}C_5R_5)(OC)_2Fe{-}BHal_2$] (R = H, Me) are in agreement with the trend expected for a series of compounds with B−F, B−Cl, and B−Br bonds. IR data indicate an increase in $d_\pi-p_\pi$ back-bonding along the series $Fe{-}BF_2 < Fe{-}BCl_2 < Fe{-}BBr_2$, reflecting the decreasing potential of the halide for an effective $p_\pi-p_\pi$ overlap with the small boron center. Thus, the Fe center appears to compensate, at least to some extent, for the reduced electronic stabilization of the boron atom provided by the heavier halides. Nevertheless, dibromoboryls proved to be far more reactive than their flouro- and chloro-substituted counterparts. This is for example indicated by the labilility of the complex [$(\eta^5\text{-}C_5H_5)Fe(CO)_2BBr_2$] (**5**) or the facile hydrolysis of [$(OC)_5MnBBr_2$] (**12**) yielding the bisboryloxo species [$\{(OC)_5MnBBr\}_2O$] (**13**). The boron centers in the complexes [$(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX_2$] (**4**: X = Cl; **6**: X = Br) proved to be sufficiently Lewis-acidic to readily add 4-methylpyridine, thus forming the corresponding base adducts [$(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX_2(NC_5H_4\text{-}4\text{-}Me)$] (**7**: X = Cl; **8**: X = Br). Here again, the bromo complex **6** displayed its enhanced reactivity and formed, in the presence of excess base, the unprecedented metal-substituted boronium species **9**.

Experimental Section

1. General Considerations. All manipulations were conducted either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Solvents (toluene, benzene, and hexane) were purified by distillation from appropriate drying agents (sodium and sodium wire) under dry argon, immediately prior to use. Deuterated solvents (C_6D_6 and CD_2Cl_2) were degassed

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(25) (a) Braunschweig, H.; Colling, M.; Kollann, C.; Merz, K.; Radacki, K. *Angew. Chem.* **2001**, *113*, 4327; *Angew. Chem., Int. Ed.* **2001**, *40*, 4198. (b) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H.-G.; Neumann, B. *Angew. Chem.* **2001**, *113*, 2359; *Angew. Chem., Int. Ed.* **2001**, *40*, 2298.

(26) Maringgele, W.; Noltemeyer, M.; Meller, A. *Organometallics* **1997**, *16*, 2276.

(27) Lang A.; Khizek J.; Nöth H.; Schur S.; Thomann M *Z. Anorg. Allg. Chem.* **1997**, *623*, 901.

(28) Paetzold, P.; Geret-Baumgarten, L.; Boese, R. *Angew. Chem.* **1992**, *104*, 1071.

by three freeze−pump−thaw cycles and stored over molecular sieves in the glovebox. IR spectra were recorded as toluene (**1**−**8**, **10**−**12**) or dichloromethane (**9**) solutions between KBr plates on a Bruker Vector 22 FT-IR-spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were acquired on a Bruker AMX 400 NMR spectrometer at 400.14 and 100.63 MHz (**3**, **10**−**12**) and a Bruker Avance 500 NMR spectrometer at 500.13 and 125.76 MHz (**1**, **2**, **4**−**9**), respectively, and referenced to external TMS via the residual protio solvent (^{1}H) or the solvent itself (^{13}C). ^{19}F{^{1}H} NMR spectra were recorded on a Bruker DRX 300 NMR spectrometer at 282.40 MHz and referenced to external CFCl$_3$. ^{11}B{^{1}H} NMR spectra were recorded on a Bruker Avance 200 NMR spectrometer at 64.22 MHz and referenced to external BF$_3$·OEt$_2$. Microanalyses for C, H, and N were performed by Mrs. L. Michels (University of Wuerzburg) on a Leco CHNS-932 instrument.

2. Synthetic Procedures. Synthesis of [(η^5-C$_5$H$_5$)Fe(CO)$_2$BF$_2$] (1). A Schlenk tube containing a suspension of K[(η^5-C$_5$H$_5$)Fe(CO)$_2$] (0.23 g, 1.06 mmol) in toluene (10 mL) was cooled to 0 °C, and BF$_3$·Et$_2$O (0.15 mL, 0.17 g, 1.21 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 15 min, resulting in the formation of a cloudy, red solution. Subsequent removal of all volatiles in vacuo at room temperature afforded a red solid. Hexane (20 mL) was added, and residual solids were separated by centrifugation. The clear, red supernatant liquors were then decanted, reduced in volume by ca. 50%, and cooled to −60 °C. After a period of ca. 6 h, the red-colored crystals of pure **1** that had formed were isolated and dried in vacuo (yield 0.090 g, 37%). IR: 2022, 1965 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 3.99 (s, C$_5$H$_5$); ^{13}C{^{1}H} 83.72 (s, C$_5$H$_5$), 213.0 (s, CO); ^{11}B{^{1}H} 47.1 (t, $J_{\mathrm{B-F}} = 181$ Hz); ^{19}F{^{1}H} 2.72 (q, $J_{\mathrm{B-F}} = 181$ Hz). Anal. Calcd for C$_7$H$_5$O$_2$BF$_2$Fe: C 37.24; H 2.23. Found: C 37.16; H 2.22.

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BF$_2$] (2). A Schlenk tube containing a suspension of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (0.15 g, 0.56 mmol) in toluene (10 mL) was cooled to 0 °C, and BF$_3$·Et$_2$O (0.10 mL, 0.12 g, 0.81 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 15 min, resulting in the formation of a cloudy, red solution. Subsequent removal of all volatiles in vacuo at room temperature afforded a dark red solid. Hexane (10 mL) was added and residual solids were separated by centrifugation. The clear, red supernatant liquors were then decanted, reduced in volume by ca. 50%, and cooled to −60 °C. After a period of ca. 14 h, the red-colored crystals of pure **2** that had formed were isolated and dried in vacuo (yield 0.067 g, 40%). IR: 2002, 1946 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 1.45 (s, C$_5$Me$_5$); ^{13}C{^{1}H} 10.20 (s, C$_5$*Me*$_5$), 96.62 (s, *C*$_5$Me$_5$), 215.7 (s, CO); ^{11}B{^{1}H} 48.3 (t, $J_{\mathrm{B-F}} = 189$ Hz); ^{19}F{^{1}H} −3.77 (q, $J_{\mathrm{B-F}} = 187$ Hz). Anal. Calcd for C$_7$H$_5$O$_2$BFeF$_2$: C 48.71; H 5.11. Found: C 48.72; H 4.96.

Synthesis of [(η^5-C$_5$H$_5$)Fe(CO)$_2$BCl$_2$] (3) was already reported.[12]

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BCl$_2$] (4). A Schlenk tube containing a suspension of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (1.43 g, 7.15 mmol) in toluene (20 mL) was cooled to −78 °C and evacuated, and gaseous BCl$_3$ (2.88 g, 24.6 mmol) introduced. The reaction mixture was slowly allowed to warm to −30 °C, at which point the orange-colored suspension began to darken. Stirring was continued at this temperature for ca. 1 h, resulting in the formation of a cloudy, dark red solution. Subsequent removal of all volatiles in vacuo at room temperature afforded a dark red oil. Hexane (20 mL) was added, and residual solids were separated by centrifugation. The clear, red supernatant liquors were then decanted, reduced in volume by ca. 50%, and cooled to −60 °C. After a period of ca. 16 h, the red-colored crystals of pure **4** that had formed were isolated and dried in vacuo (yield 0.58 g, 31%). IR: 2006, 1955 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 1.43 (s, C$_5$Me$_5$); ^{13}C{^{1}H} 9.29 (s, C$_5$*Me*$_5$), 96.31 (s, *C*$_5$Me$_5$), 215.2 (s, CO); ^{11}B{^{1}H} 94.9 (br s, $\omega_{1/2} = 137$ Hz). Anal. Calcd for C$_{12}$H$_{15}$O$_2$BFeCl$_2$: C 43.83; H 4.60. Found: C 44.07; H 4.50.

Synthesis of [(η^5-C$_5$H$_5$)Fe(CO)$_2$BBr$_2$] (5). A Schlenk tube containing a suspension of Na[(η^5-C$_5$H$_5$)Fe(CO)$_2$] (0.40 g, 2.00 mmol) in toluene (15 mL) was cooled to −78 °C, and BBr$_3$ (0.30 mL, 0.79 g, 3.16 mmol) was added dropwise. The reaction mixture was slowly allowed to warm to −30 °C, at which point the orange-colored suspension began to darken. Stirring was continued at this temperature for ca. 1 h, resulting in the formation of a cloudy, dark red solution. Subsequent removal of all volatiles in vacuo at room temperature afforded a dark red oil. Hexane (20 mL) was added, and residual solids were separated by centrifugation. The clear, red supernatant liquors were then decanted, reduced in volume by ca. 50%, and cooled to −60 °C. After a period of ca. 16 h, the red-colored crystals of pure **5** that had formed were isolated and dried in vacuo (yield 0.33 g, 48%). IR: 2045, 2000 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 4.01 (s, C$_5$H$_5$); ^{13}C{^{1}H} 87.40 (s, C$_5$H$_5$), 212.7 (s, CO); ^{11}B{^{1}H} 85.9 (br s). Anal. Calcd for C$_7$H$_5$O$_2$BFeBr$_2$: C 24.19; H 1.45. Found: C 24.03; H 1.57.

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BBr$_2$] (6). A Schlenk tube containing a suspension of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (0.51 g, 1.88 mmol) in toluene (15 mL) was cooled to −78 °C, and BBr$_3$ (0.18 mL, 0.47 g, 1.88 mmol) was added dropwise. The reaction mixture was slowly allowed to warm to −30 °C, at which point the orange-colored suspension began to darken. Stirring was continued at this temperature for ca. 1 h, resulting in the formation of a cloudy, dark red solution. Subsequent removal of all volatiles in vacuo at room temperature afforded a dark red oil. Hexane (20 mL) was added, and residual solids were separated by centrifugation. The clear, red supernatant liquors were then decanted, reduced in volume by ca. 50%, and cooled to −60 °C. After a period of ca. 16 h, the red-colored crystals of pure **6** that had formed were isolated and dried in vacuo (yield 0.28 g, 35%). IR: 2022, 1975 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 1.40 (s, C$_5$Me$_5$); ^{13}C{^{1}H} 9.11 (s, C$_5$*Me*$_5$), 96.46 (s, *C*$_5$Me$_5$), 214.2 (s, CO); ^{11}B{^{1}H} 91.0 (br s). Anal. Calcd for C$_{12}$H$_{15}$O$_2$BFeBr$_2$: C 34.50; H 3.62. Found: C 34.88; H 3.60.

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BCl$_2$·NC$_5$H$_4$-4-Me] (7). A solution of **4** (0.49 g, 1.89 mmol) in toluene (15 mL) was cooled to 0 °C, and a solution of 4-methylpyridine (0.18 g, 1.89 mmol) in further toluene (5 mL) added dropwise. The reaction mixture was allowed to warm, with stirring, to room temperature, and all volatiles were removed in vacuo to afford pure **7** in quantitative yield. IR: 1958, 1899 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 1.27 (s, 3H, NC$_5$H$_4$-4-*Me*), 1.90 (s, 15H, C$_5$Me$_5$), 6.19 (m, 2H, NC$_5$H$_2$-3,5-*H*$_2$-4-Me), 9.26 (m, 2H, NC$_3$H$_4$-2,6-*H*$_2$-4-Me); ^{13}C{^{1}H} 10.11 (s, C$_5$*Me*$_5$) 20.34 (s, NC$_5$H$_4$-4-*Me*), 97.06 (s, *C*$_5$Me$_5$), 124.8 (s, NC$_4$-4-*C*-H$_4$-4-Me), 144.0 (s, N*C*$_4$H$_4$-4-Me), 215.2 (s, CO); ^{11}B{^{1}H} 21.3 (s). Anal. Calcd for C$_{18}$H$_{22}$O$_2$NBFeCl$_2$: C 51.24; H 5.26; N 3.32. Found: C 50.47; H 5.37; N 3.68.

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BBr$_2$·NC$_5$H$_4$-4-Me] (8). A solution of **6** (0.16 g, 0.38 mmol) in toluene (5 mL) was cooled to 0 °C and a solution of 4-methylpyridine (0.036 g, 0.38 mmol) in further toluene (2 mL) added dropwise. The reaction mixture was allowed to warm, with stirring, to room temperature. The clear red solution was reduced in volume by ca. 50%, hexane (3 mL) was added, and cooling to −30 °C over a period of 16 h afforded yellow crystals of **8** (0.16 g, 81%). IR: 1963, 1904 cm^{-1}, ν(CO). NMR (C$_6$D$_6$): ^{1}H 1.28 (s, 3H, NC$_5$H$_4$-4-*Me*), 1.85 (s, 15H, C$_5$Me$_5$), 6.11 (m, 2H, NC$_5$H$_2$-3,5-*H*$_2$-4-Me), 9.62 (m, 2H, NC$_3$H$_4$-2,6-*H*$_2$-4-Me); ^{13}C{^{1}H} 9.99 (s, C$_5$*Me*$_5$) 20.30 (s, NC$_5$H$_4$-4-*Me*), 97.49 (s, *C*$_5$Me$_5$), 124.5 (s, NC$_4$-4-*C*-H$_4$-4-Me), 145.1 (s, N*C*$_4$H$_4$-4-Me), 221.1 (s, CO); ^{11}B{^{1}H} 14.3 (s). Anal. Calcd for C$_{18}$H$_{22}$O$_2$NBFeBr$_2$·C$_6$H$_6$: C 48.94; H 4.79; N 2.38. Found: C 48.76; H 4.87; N 2.52.

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BBr(NC$_5$H$_4$-4-Me)$_2$]Br (9). **6** (0.31 g, 0.74 mmol) and 4-methylpyridine (0.14 g, 1.54 mmol) in toluene (7 mL) were stirred for 5 min. Hexane (5 mL) was added, and the yellow precipitate was collected by centrifugation, washed

Table 2. Crystallographic Data for Compounds 7−9, 11, and 13

	7	**8**	**9**	**11**	**13**
empirical formula	$C_{24}H_{28}BCl_2FeNO_2$	$C_{24}H_{28}BBr_2FeNO_2$	$C_{31}H_{37}BBr_2FeN_2O_2$	$C_5BCl_2MnO_5$	$C_{10}B_2Br_2Mn_2O$
CCDC deposit number	605969	605970	605971	610520	605972
fw ($g{\cdot}mol^{-1}$)	500.03	588.95	696.11	276.70	587.42
temperature (K)	193(2)	193(2)	100(2)	173(2)	173(2)
radiation, λ (Å)	Mo Kα 0.71073	Mo Kα 0.71073	Mo Kα 0.71073	Mo Kα 0.71073	Mo Kα 0.71073
cryst syst	orthorhombic	orthorhombic	triclinic	orthorhombic	monoclinic
space group	*Pnma*	*Pnma*	$P\bar{1}$	*Fdd*2	*C*2/*c*
a (Å)	8.1062(12)	8.1006(4)	9.5242(3)	23.778(5)	25.022(3)
b (Å)	12.5379(18)	12.6176(7)	11.6613(4)	6.7756(15)	6.3286(8)
c (Å)	23.605(3)	23.7893(13)	14.0952(4)	12.024(3)	13.1563(16)
α (deg)	90.0	90.0	92.027(2)	90.0	90.0
β (deg)	90.0	90.0	94.800(2)	90.0	120.051(2)
γ (deg)	90.0	90.0	99.939(2)	90.0	90.0
volume ($Å^3$)	2399.0(6)	2431.5(2)	1534.59(8)	1937.3(7)	1803(4)
Z	4	4	2	8	4
calcd density ($Mg{\cdot}m^{-3}$)	1.384	1.609	1.506	1.897	2.164
absorp coeff (mm^{-1})	0.872	3.928	3.125	1.901	5.884
F(000)	1040	1184	708	1072	1112
θ range for collection (deg)	2.66 to 26.50	1.83 to 26.09	2.56 to 33.98	3.43 to 26.12	1.88 to 26.06
no. of reflns collected	32 028	27 387	54 201	9195	14 341
no. of indep reflns	2595	2519	12 763	981	1784
min./max. transmn	0.695/0.888	0.509/0.760	0.622/0.901	0.663/0.890	0.281/0.490
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/params/restraints	2595/147/7	2519/147/9	12 763/352/0	981/67/1	1784/123/0
goodness-of-fit on F^2	1.057	1.236	1.032	1.249	1.063
final *R* indices [$I > 2\theta(I)$]	$R_1 = 0.0381$ $wR_2 = 0.0954$	$R_1 = 0.0497$, $wR_2 = 0.1016$	$R_1 = 0.0364$, $wR_2 = 0.0924$	$R_1 = 0.0263$, $wR_2 = 0.0645$	$R_1 = 0.0187$, $wR_2 = 0.0497$
R indices (all data)	$R_1 = 0.0426$, $wR_2 = 0.0991$	$R_1 = 0.0566$, $wR_2 = 0.1042$	$R_1 = 0.0516$, $wR_2 = 0.0990$	$R_1 = 0.0267$, $wR_2 = 0.0646$	$R_1 = 0.0199$, $wR_2 = 0.0503$
max./min. residual electron density ($e{\cdot}Å^{-3}$)	0.523/−0.365	1.162/−0.961	1.925/−0.727	0.359/−0.207	0.595/−0.396

with hexane (2×, 5 mL), and dried in vacuo. **9** was obtained as a bright yellow solid (0.34 g, 76%). IR: 1977, 1918 cm^{-1}, ν(CO). NMR (CD_2Cl_2): ^1H 1.73 (s, 15H, C_5Me_5), 2.62 (s, 6H, NC_5H_4-4-Me), 7.71 (m, 4H, NC_5H_2-3,5-H_2-4-Me), 8.79 (m, 2H, NC_3H_4-2,6-H_2-4-Me); $^{13}C\{^1H\}$ 9.94 (s, C_5*Me*$_5$), 21.30 (s, NC_5H_4-4-*Me*), 97.33 (s, *C*$_5$Me$_5$), 125.4 (s, NC_4-4-*C*-H_4-4-Me), 128.2 (s, NC_3-3,5-*C*$_2$-H_4-4-Me), 128.3 (s, NC_3-2,6-*C*$_2$-H_4-4-Me), 219.5 (s, CO); $^{11}B\{^1H\}$ 21.0 (s). Anal. Calcd for $C_{24}H_{29}O_2N_2BFeBr_2$: C 47.73; H 4.84; N 4.64. Found: C 47.64; H 4.78; N 4.34.

Synthesis of [(η^5-C_5H_4Me)Ru(CO)$_2$BCl$_2$] (10). A Schlenk tube containing a suspension of Na[(η^5-C_5H_5)Ru(CO)$_2$] (0.60 g, 2.31 mmol) in toluene (15 mL) was cooled to −78 °C and evacuated, and gaseous BCl_3 (1.44 g, 12.3 mmol) introduced. The reaction mixture was slowly allowed to warm to −30 °C and stirred for ca. 1 h, resulting in the formation of a cloudy, dark green solution. Subsequent removal of all volatiles in vacuo, at room temperature, afforded a dark green oil. Hexane (20 mL) was added, and residual solids were separated by centrifugation. All volatiles were removed in vacuo, yielding **10** as a pale green oil (yield 0.17 g, 23%). IR: 2021, 1958 cm^{-1}, ν(CO). NMR (C_6D_6): ^1H 1.57 (s, 3H, C_5H_4-*Me*) 4.54 (m, 2H, C_5*H*$_4$-Me) 4.60 (m, 2H, C_5*H*$_4$-Me); $^{13}C\{^1H\}$ 13.82 (s, C_5H_4-*Me*) 84.09 (s, *C*$_4$-1-C- H_4-1-Me) 84.80 (s, *C*$_4$-1-C- H_4-1-Me) 105.6 (s, C_4-1-*C*- H_4-1-Me) 200.7 (s, CO); $^{11}B\{^1H\}$ 81.0 (br s).

Synthesis of [(OC)$_5$MnBCl$_2$] (11). A Schlenk tube containing a suspension of K[Mn(CO)$_5$] (1.20 g, 5.12 mmol) in toluene (15 mL) was cooled to −78 °C and evacuated, and gaseous BCl_3 (1.44 g, 12.3 mmol) introduced. The reaction mixture was slowly allowed to warm to room temperature. Stirring was continued at this temperature for ca. 1 h, resulting in the formation of an orange solution and a white solid. The solid was separated by centrifugation, and the clear, orange solution was decanted and cooled to −30 °C. After a period of ca. 12 h, pale yellow crystals of **11** had formed, which were isolated and purified by sublimation at room temperature and 10^{-3} Torr (yield 0.92 g, 65%). IR: 2115, 2052, 2012 cm^{-1}, ν(CO). NMR (C_6D_6): $^{13}C\{^1H\}$ 208.8 (s, CO); $^{11}B\{^1H\}$ 94.2 (br s). Anal. Calcd for $C_5O_5MnBCl_2$: C 21.70. Found: C 21.79.

Synthesis of [(OC)$_5$MnBBr$_2$] (12). A Schlenk tube containing a suspension of K[Mn(CO)$_5$] (0.21 g, 0.90 mmol) in hexane (20 mL) was cooled to 0 °C, and BBr_3 (0.20 mL, 0.53 g, 2.10 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 15 min, resulting in the formation of an orange solution and a white solid. The solid was separated by centrifugation, and the clear, orange solution was decanted, reduced in volume by ca. 50%, and cooled to −30 °C. After a period of ca. 16 h, the yellow-colored crystals of pure **12** that had formed were isolated and dried in vacuo (yield 0.33 g, 50%). IR: 2116, 2051, 2013 cm^{-1}, ν(CO). NMR (C_6D_6): $^{13}C\{^1H\}$ 208.5 (s, CO); $^{11}B\{^1H\}$ 92.9 (br s). Anal. Calcd for $C_5O_5MnBBr_2$: C 16.43. Found: C 16.68.

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Supporting Information Available: Text detailing the structural determinations for **7**, **8**, **9**, **11**, and **13** (including CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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