Preparation and Structural Characterization of Transition Metal Complexes Featuring the Ferrocenyl(bromo)boryl Ligand[†]

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Transition metal complexes that feature the ferrocenyl(bromo)boryl ligand, −B(Fc)Br, were prepared utilizing salt-elimination and B−Br bond oxidative addition strategies. The stabilizing interaction that causes bending of the boron atom toward the ferrocenyl iron center in the $FcBBr_2$ precursor (**1**) weakens upon coordination of boron to the $[(\eta^5\text{-}C_5R_5)(OC)_2Fe]$ and *trans*-$[(Cy_3P)_2PtBr]$ fragments. The efficient π-back-bonding capability of the latter is reflected in the absence of any Fe−B interaction in crystalline *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (**7**), the first platinum haloboryl complex featuring a non-heteroatom-stabilized boryl ligand to be fully characterized and structurally authenticated. In the half-sandwich complexes $[(\eta^5\text{-}C_5R_5)(OC)_2Fe\{B(Fc)Br\}]$ (R = H, **2**; R = Me, **3**) different relative orientations of the $[(\eta^5\text{-}C_5R_5)(OC)_2Fe]$ and −B(Fc)Br groups are accompanied by different degrees of bending within the boryl ligand. The sensitivity of this parameter to the electronic environment at boron offers an indirect qualitative estimation of the π-bonding component of the TM−B bond.

Introduction

The nature of the metal−boron bond in transition metal boryl compounds has been the subject of intense structural and theoretical investigation.[1] Particular emphasis has been placed on attempts to quantify the relative contributions provided to the metal−boron linkage by σ- and π-bonding components.[2] The majority of the studies attribute strong σ-donor abilities to the boryl group. However, the π-acidity of the $-BR_2$ ligands appears to be highly dependent on the electronic properties of the transition metal complex fragment and of the substituents at boron. The effect of π-accepting ancillary ligands coordinated to the transition metal center and of π-donating groups linked to the boron atom generally predominates over any $[TM]\rightarrow BR_2$ π-back-donation. Consequently, such interaction is thought to provide a minor contribution to the overall stability of the metal−boron bond.[2]

On account of the electronic stabilization offered by π-donating groups to the Lewis acidic boron center, it is not surprising that the majority of transition metal boryl complexes reported to date feature oxy- or aminoboryl ligands.[1a] Alkyl or arylboryl compounds, including asymmetric aryl(halo)boryl species,[1c] still remain relatively rare. During the course of our studies on the synthesis and reactivity of haloboryl compounds,[3] we turned our attention to complexes featuring the ferrocenyl(bromo)boryl ligand −B(Fc)Br. In light of previous reports on the electronic stabilization provided by the iron center to the Lewis acidic boron atom in dibromoboryl-,[4b] 1,1′-bis(dibromoboryl)-,[4d] and 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene,[4e] we wondered to what extent this interaction would be affected by any $[TM]\rightarrow B(Fc)Br$ π-back-donation and, in particular, whether the ferrocenyl(bromo)boryl group could serve as a probe for the presence of any significant transition metal−boron π-bonding. Herein we report the synthesis and structural characterization of iron compounds $[(\eta^5\text{-}C_5H_5)(OC)_2Fe\{B(Fc)Br\}]$ (**2**) and $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{B(Fc)Br\}]$ (**3**), the synthesis of the ruthenium species $[(\eta^5\text{-}C_5H_4Me)(OC)_2Ru\{B(Fc)Br\}]$ (**4**), and the full characterization of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (**7**), the first structurally authenticated platinum haloboryl complex that features a non-heteroatom-stabilized boryl ligand.

[†] Dedicated to Prof. Dr. Johann Weis on the occasion of his 60th birthday.

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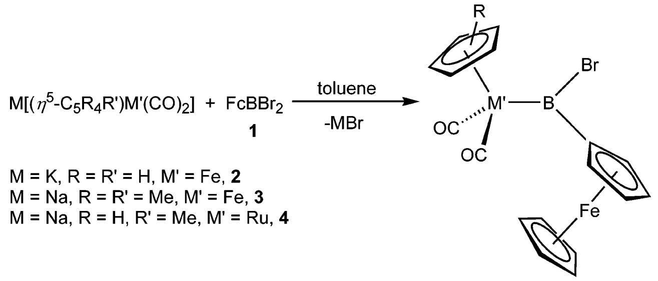
Scheme 1



Results and Discussion

Iron and Ruthenium Ferrocenyl(bromo)boryl Compounds. Iron and ruthenium boryl complexes **2**−**4** were synthesized in moderate to good yields (29−77%) via reaction of dibromoborylferrocene FcBBr$_2$ (**1**)[4a] with 1 equiv of the appropriate organometallic anion in toluene at room temperature (Scheme 1).

Complexes **2**−**4** are highly oxygen- and moisture-sensitive red solids but are stable at room temperature for several days under an inert atmosphere. They are soluble in toluene but considerably less soluble in aliphatic hydrocarbons, such as hexane or heptane. The spectroscopic features of the new compounds are consistent with the presence of a ferrocenyl (bromo)boryl group directly linked to the transition metal center. In particular, the ^{11}B{^{1}H} NMR spectra of **2**−**4** display characteristic low-field resonances at δ 99.1, 103.0, and 90.1, respectively. Such values are similar to those of previously reported aryl(halo)boryl complexes, namely, [(η^5-C$_5$R$_4$R′)(CO)$_2$Fe{B(2,4,6-Me$_3$C$_6$H$_2$)Br}] [R = R′ = H, **5a**, δ 111.4; R = H, R′ = Me, **5b**, δ 111.3; R = R′ = Me, **5c**, δ 113.2][5] and [(η^5-C$_5$Me$_5$)(CO)$_2$Fe{B(Ph)Cl}] (**6**) [δ 111.0].[6] Compounds **2** and **4** exhibit carbonyl stretching bands at relatively high wavenumbers, 2015, 1955 cm^{-1} and 2021, 1958 cm^{-1}, respectively, which resemble those reported for **5a**−**c**. The analogous bands for compound **3** (1995, 1934 cm^{-1}) are moderately red-shifted and are very similar to those of **6** (1995, 1929 cm^{-1}).

Single crystals suitable for X-ray structural determination were obtained by layering heptane on a saturated solution of **2** in toluene at room temperature and from a toluene solution of **3** upon cooling to −30 °C. The molecular structures of **2** and **3** with relevant bond lengths are shown in Figures 1 and 2, respectively.

The asymmetric unit of **2** contains one unique molecule, while in that of **3** two independent molecules, **3a** and **3b**, are observed. The iron−boron bond distance in **2** [Fe(1)−B(1) = 1.997(2) Å] is slightly longer than that in **3** [Fe(12)−B(1) = 1.972(3) Å, **3a**; Fe(22)−B(2) = 1.985(3) Å, **3b**] but still in the range of those observed in mesityl(bromo)boryls **5a**−**c** [1.964(5) Å, **5a**; 1.962(4) Å, **5b**; 1.972(2) Å, **5c**][5] and in phenyl(chloro)boryl complex **6** [2.005(10) Å].[6] Interestingly, significant differences between the two structures arise when the relative orientations of the [(η^5-C$_5$R$_5$)(OC)$_2$Fe] (R = H, **2**; R = Me, **3**) fragments with respect to the boryl ligand are inspected. In **2**, the angle of intersection (θ = 15.2°) between the planes defined by the C$_5$H$_5$−ring centroid−Fe(1)−B(1) and Br(1)−B(1)−C(21) indicates a nearly coplanar arrangement of the two fragments. The corresponding angles for **3a** and **3b**, 88.8° and 89.0°, respectively, determine a virtually orthogonal disposition of the two groups. It has been previously argued that the relative orientation of the [(η^5-C$_5$R$_5$)(OC)$_2$Fe] and BX$_2$ units can serve as a probe of π-type interactions.[2e] These occur preferentially via overlap of the vacant boryl-based π-orbital with the HOMO of the transition metal fragment (θ = 0°) or, less favorably, with the lower lying perpendicular HOMO-2 (θ = 90°). On these grounds, the structural differences between **2** and **3** suggest the possibility for more significant [(η^5-C$_5$R$_5$)(OC)$_2$Fe]→B(Fc)Br π-back-donation in **2**. This hypothesis is corroborated by the analysis of relevant structural features within the boryl ligand.

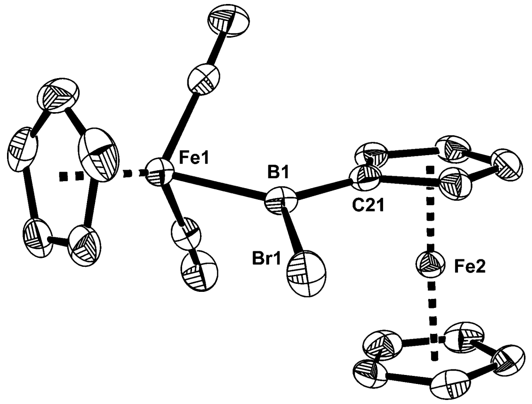


Figure 1. Molecular structure of [(η^5-C$_5$H$_5$)(OC)$_2$-Fe{B(Fc)Br}] (**2**). Relevant bond lengths (Å): Fe(1)−B(1) = 1.997(2), Br(1)−B(1) = 1.9892(22), C(21)−B(1) = 1.5461(31).

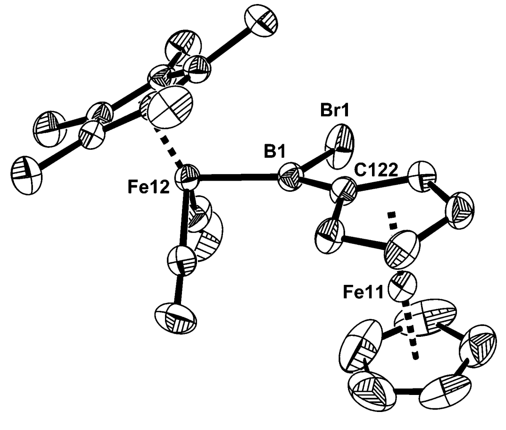


Figure 2. Molecular structure of [(η^5-C$_5$Me$_5$)(OC)$_2$-Fe{B(Fc)Br}] (**3a**). Relevant bond lengths (Å): Fe(12)−B(1) = 1.972(3), Br(1)−B(1) = 2.0158(27), C(122)−B(1) = 1.5384(36).

The geometry and electronic properties of borylferrocenes have been the subject of structural and theoretical investigations.[4b] A common feature of the molecular structure of FcBBr$_2$ (**1**),[4b] 1,1′-bis(dibromoboryl)ferrocene,[4d] and 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene[4e] is the bending of the −BBr$_2$ substituent(s) toward the ferrocenyl iron center. The degree of substituent bending was estimated analyzing the values of the dip angle α*, which is defined as the angle between the centroid of the C$_5$H$_5$ ring, the *ipso*-carbon, and the boron atom. Such values decrease with increasing number of boryl substituents on the ferrocenyl moiety,

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[5] Coombs, D. L.; Aldridge, S.; Jones, C. *Dalton Trans.* **2002**, 3851.

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going from 17.7° and 18.9° for **1** (two crystallographically independent molecules were present in the asymmetric unit of **1**)[4b] to 9.1° for 1,1′-bis(dibromoboryl)ferrocene[4d] and 6.8° (0.1°) for 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene.[4e] This evidence was interpreted in terms of an interaction between filled d-type orbitals at iron and the empty p-orbital on boron, capable of relieving, at least partially, the electron deficiency of the latter. Such reasoning found further support in the molecular structure of $FcB(N^{i}Pr_2)_2$, where electronic stabilization of the boron center is achieved by N−B π-bonding and no bending of the boryl substituent toward the iron atom is observed.[4b]

Upon coordination of the −B(Fc)Br unit to a transition metal complex fragment, the electronic deficiency of the boron center could be expected to be partially relieved by any π-component of the overall TM−B bond. Inspection of the molecular structures of **2** and **3** reveals smaller values of the dip angle α^* than in **1**, namely, 4.2° for **2** and 8.0° and 7.6° for **3a**,**b**, respectively. When considered in conjunction with the values of θ discussed above for π-back-donation arguments, the α^* values suggest, consistently, that a more significant $[(\eta^5\text{-}C_5R_5)(OC)_2Fe]\rightarrow B(Fc)Br$ π-interaction occurs in **2** than in **3**. This conclusion may seem counterintuitive at first, on account of the stronger σ-donating properties of the $(\eta^5\text{-}C_5Me_5)$ ligand with respect to those of $(\eta^5\text{-}C_5H_5)$. However, the attainment of a coplanar arrangement of the $[(\eta^5\text{-}C_5R_5)(OC)_2Fe]$ and BX_2 units, which would allow optimal π-orbital overlap, might be disfavored in **3** on steric grounds, due to the increased bulk of the pentamethyl(cyclopentadienyl) ligand. The diminished Fe→B π-back-donation would then be reflected in a higher degree of bending within the ferrocenylboryl substituent in **3**.

Platinum Ferrocenyl(bromo)boryl Compound *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$. With the results obtained on the synthesis of compounds **2**−**4** in hand, we turned our attention to the possibility of introducing the ferrocenyl(bromo)boryl group into a more electron-rich system. Preparation of a platinum(II) compound seemed to be a potentially rewarding target, particularly given the paucity of structurally characterized monoboryl complexes of platinum[7] and the absence of any such compound featuring a non-heteroatom-stabilized (halo)boryl ligand.

Reaction of $FcBBr_2$ (**1**) with the Pt^0 precursor $[Pt(PCy_3)_2]$[8a] in benzene at room temperature led to oxidative addition of one B−Br bond of **1** and subsequent isomerization to the bright orange Pt^{II} ferrocenyl(bromo)boryl complex *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (**7**) (Scheme 2).

Complex **7** is soluble in benzene, methylene chloride, and, to a lesser extent, hexane. It is only moderately oxygen-sensitive but extremely moisture-sensitive, being rapidly decomposed by traces of water to *trans*-$[(Cy_3P)_2Pt(H)(Br)]$ (as judged by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy) and unidentified boron-containing products. The $^{11}B\{^1H\}$ NMR spectrum of **7** is characterized by an extremely broad resonance ($\omega_{1/2}$ = ~1980 Hz) centered at δ 82, while the $^{31}P\{^1H\}$ NMR spectrum exhibits a sharp singlet at δ 21.51 ($^1J_{P-Pt}$ = 2892 Hz), significantly upfield shifted when compared to that of $[Pt(PCy_3)_2]$ [δ 62.28, $^1J_{P-Pt}$ = 4161 Hz].[8b] The presence of the ferrocenyl(bromo)boryl ligand is confirmed in the ^1H NMR spectrum by two multiplets at 4.94 and 4.32 ppm, each integrating 2H, that are assigned to the protons of the boron-substituted cyclopentadienyl ring. The protons of the unsubstituted cyclopentadienyl ring resonate as a singlet at 4.22 ppm.

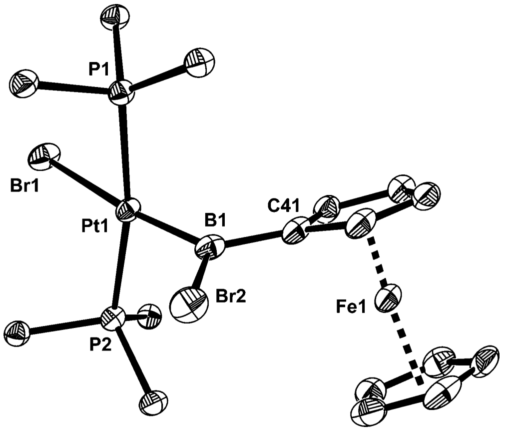
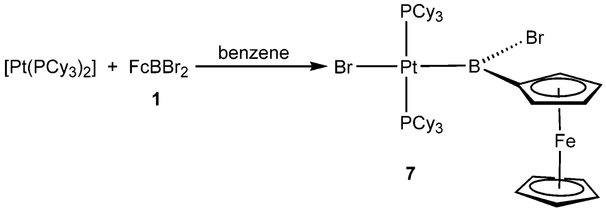


Figure 3. Molecular structure of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (**7**). Cyclohexyl groups have been omitted for clarity. Relevant bond lengths (Å): Pt(1)−B(1) = 1.9963(34), Br(2)−B(1) = 2.0040(35), C(41)−B(1) = 1.5487(49).

Scheme 2



Single crystals of **7** suitable for X-ray structural determination were obtained by slow evaporation of a 1:1 mixture of benzene and hexane at room temperature. The molecular structure of **7** with relevant bond lengths is displayed in Figure 3. It reveals a square planar platinum center (maximum deviation from the PtP_2BBr plane = 0.1274 Å), with the ferrocenyl(bromo)boryl and the bromide ligands adopting a mutually *trans* arrangement. Such a configuration is consistent with the high *trans* influence of the boryl ligand and is common to the other structurally authentic monoboryl platinum complexes, namely, *trans*-$[(Ph_3P)_2Pt(Cl)\{B(cat)\}]$ (**8**)[7b] and *trans*-$[(Ph_3P)_2Pt(Cl)\{BCl(NMe_2)\}]$ (**9**).[7a] Accordingly, the Pt(1)−Br(1) bond distance [2.6183(8) Å] in **7** is considerably longer than, for instance, the analogous distance in *trans*-$[(Cy_3P)_2PtBr_2]$ [2.435(1) Å].[9]

The ferrocenyl(bromo)boryl group is oriented in a nearly orthogonal position (85.0°) with respect to the mean square plane containing the platinum center. It has been previously noted that such an orientation allows for maximum overlap between the filled platinum

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(7) (a) Curtis, D.; Lesley, M. G. J.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *Dalton Trans.* **1999**, 1687. (b) Clegg, W.; Lawlor, F. J.; Lesley, G.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Scott, A. J.; Souza, F. E. S. *J. Organomet. Chem.* **1998**, *550*, 183.

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d_{xy}-orbital and the empty p-orbital on boron, accounting for any platinum to boron π-back-donation.[1a] Although steric arguments are likely to be of some importance in determining the relative ligand orientations, the platinum–boron bond distance Pt(1)–B(1) [1.9963(34) Å] in **7**, being shorter than that found in **8** [2.008(8) Å] and **9** [2.075(10) Å], corroborates the presence of a π-contribution to the bonding between the electron-rich [$(Cy_3P)_2PtBr$] fragment and the Lewis acidic boron center. Further qualitative evidence is provided by a comparison of the estimated and experimentally determined Pt–B bond distance in **7**. The absence of any structurally authentic alkyl derivative containing the *trans*-[$(Cy_3P)_2PtBr$] fragment unfortunately prevents a more accurate comparison. However, given the poor π-acidic properties of the bromide ligand, an estimated value for the covalent radius of the *trans*-[$(Cy_3P)_2PtBr$] fragment (1.295 Å) can be derived by subtraction of the covalent radius for bromine (1.14 Å) from the Pt–Br bond distance in *trans*-[$(Cy_3P)_2PtBr_2$].[9] A similar procedure, applied to $FcBBr_2$ (**1**),[10] yields a value of 0.792 Å for the covalent radius of the –B(Fc)Br group. The sum of the covalent radii for **7** then amounts to 2.09 Å, which is considerably larger than the experimental value of 1.9963(34) Å, consistent with the presence of a π-component to the platinum–boron bond.

This hypothesis is confirmed by analysis of the structural parameters within the ferrocenylboryl group. The value of the α* angle in **7** (−6.5°) indicates the absence of any interaction between the boron and the iron atoms, in line with sufficient electronic stabilization of the boron center provided by the *trans*-[$(Cy_3P)_2PtBr$] fragment. However, even if any direct steric interaction between the bulky tricyclohexylphosphine and the boryl ligand is not immediately apparent upon inspection of the crystal structure, the possibility of a more subtle influence of the phosphine over the intrinsic orientation of the ferrocenylboryl group must be borne in mind.

Conclusions

Coordination of the ferrocenyl(bromo)boryl ligand –B(Fc)Br to different transition metal complex fragments provides some insight into their π-back-bonding abilities, thanks to the intrinsic orientational dependence of the ferrocenylboryl ligand on the electronic situation at boron. The crystal structures of iron compounds **2** and **3** suggest that differences in the steric bulk of the (η^5-C_5R_5) ligand are likely to affect the relative orientations of the transition metal and boryl units, limiting the degree of π-bonding in the (η^5-C_5Me_5) derivative **3**. This is accompanied by a more pronounced bending of the boron atom toward the iron of the ferrocenyl moiety in **3**, a feature that has been previously interpreted in terms of a stabilizing interaction between filled d-type orbitals at iron and the electron-deficient boron center.

Upon oxidative addition of a B–Br bond of **1** to [$Pt(PCy_3)_2$], complex **7** is synthesized, the first haloboryl platinum compound containing a non-heteroatom-stabilized boryl ligand to be fully characterized and structurally authenticated. Its crystal structure reveals no bending of the boron atom toward the iron center within the boryl group, in line with the presence of a significant π-component to the overall Pt–B bond.

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 by three freeze–pump–thaw cycles and stored over molecular sieves in the glovebox. IR spectra for compounds **2**–**4** were recorded as toluene solutions between KBr plates on a Bruker Vector 22 FT-IR-spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were acquired on a Bruker AMX 400 NMR spectrometer at 400.14 and 100.63 MHz, respectively, and referenced to external TMS via the residual protio solvent (^1H) or the solvent itself (^{13}C). $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance 200 NMR spectrometer at 64.22 and 81.02 MHz, respectively, and referenced to external $BF_3{\cdot}OEt_2$ and 85% H_3PO_4. Microanalyses for C, H, and N were performed by Mr. C. P. Kneis (University of Wuerzburg) on a Leco CHNS-932 instrument.

2. Synthetic Procedures. [(η^5-C_5H_5)$(OC)_2$Fe{B(Br)Fc}] (2). K[(η^5-C_5H_5)Fe$(CO)_2$] (0.43 g, 1.99 mmol) was suspended in toluene (5 mL), and a solution of dibromoborylferrocene (**1**) (0.70 g, 1.97 mmol) in toluene (10 mL) was added. After stirring for 30 min, all volatiles were removed in vacuo and the residue was treated with hexane (20 mL). The remaining solid was removed by centrifugation. The red supernatant solution was concentrated in vacuo to 10 mL and stored at −30 °C for 2 days, yielding **2** as a red solid (0.69 g, 77%). ^1H NMR (C_6D_6): δ 4.74 (m, 2H, C_5H_4B), 4.46 (m, 2H, C_5H_4B), 4.17 (s, 5H, C_5H_5), 4.13 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 215.3 (CO), 85.1 (C_5H_5), 77.3 ($C_5H_5FeC_5H_4B$), 75.2 ($C_5H_5Fe\mathit{C}_5H_4B$), 69.8 ($\mathit{C}_5H_5FeC_5H_4B$). $^{11}B\{^1H\}$ NMR (C_6D_6): δ 99.1 (br, $\omega_{1/2}$ = ~340 Hz, s). IR ν(C═O) 2015 (vs), 1955 (vs) cm^{-1}. Anal. Calcd for $C_{17}H_{14}BBrFe_2O_2$: C, 45.10; H, 3.12. Found: C, 45.17; H, 3.33.

[(η^5-C_5Me_5)$(OC)_2$Fe{B(Br)Fc}] (3). Na[(η^5-C_5Me_5)Fe$(CO)_2$] (0.48 g, 1.78 mmol) was suspended in toluene (5 mL), and a solution of dibromoborylferrocene (**1**) (0.63 g, 1.77 mmol) in toluene (10 mL) was added. After stirring for 30 min, all volatiles were removed in vacuo and the residue was treated with hexane (20 mL). The remaining solid was removed by centrifugation. The red supernatant solution was concentrated in vacuo to 10 mL and stored at −30 °C for 2 days, yielding **3** as a red solid (0.27 g, 29%). ^1H NMR (C_6D_6): δ 4.80 (m, 2H, C_5H_4B), 4.46 (m, 2H, C_5H_4B), 4.22 (s, 5H, C_5H_5), 1.51 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 217.3 (CO), 95.7 (C_5Me_5), 77.5 ($C_5H_5Fe\mathit{C}_5H_4B$), 75.1 ($C_5H_5Fe\mathit{C}_5H_4B$), 69.8 ($\mathit{C}_5H_5FeC_5H_4B$), 9.5 ($C_5\mathit{Me}_5$). $^{11}B\{^1H\}$ NMR (C_6D_6): δ 103.0 (br, $\omega_{1/2}$ = ~500 Hz, s). IR ν(C═O) 1995 (vs), 1934 (vs) cm^{-1}. Anal. Calcd for $C_{22}H_{24}BBrFe_2O_2$: C, 50.54; H, 4.63. Found: C, 50.64; H, 4.72.

[(η^5-C_5H_4Me)$(OC)_2$Ru{B(Br)Fc}] (4). Na[(η^5-C_5H_4Me)Ru$(CO)_2$] (0.26 g, 1.00 mmol) were suspended in toluene (5 mL), and a solution of dibromoborylferrocene (**1**) (0.36 g, 1.01 mmol) in toluene (10 mL) was added. After stirring for 30 min, all volatiles were removed in vacuo and the residue was treated with hexane (10 mL). The remaining solid was removed by centrifugation. The orange supernatant solution was concentrated in vacuo to 10 mL and stored at −30 °C for 2 days, yielding **4** as a bright red solid (0.19 g, 37%). ^1H NMR (C_6D_6): δ 4.73 (m, 2H, C_5H_4B), 4.62 (m, 4H, $C_5\mathit{H}_4CH_3$), 4.38 (br s, 2H, C_5H_4B), 4.20 (s, 5H, C_5H_5), 1.55 (s, 3H, $C_5H_4C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 202.5 (CO), 108.0 (C_i, $\mathit{C}_5H_4CH_3$), 89.1 ($\mathit{C}_5H_4CH_3$), 88.2 ($\mathit{C}_5H_4CH_3$), 77.7 ($C_5H_5Fe\mathit{C}_5H_4B$), 75.2 ($C_5H_5Fe\mathit{C}_5H_4B$), 69.8 ($\mathit{C}_5H_5FeC_5H_4B$), 13.1 ($C_5H_4\mathit{C}H_3$). $^{11}B\{^1H\}$ NMR (C_6D_6): δ 90.1 (br, $\omega_{1/2}$ = ~410 Hz, s). IR ν(C═O) 2021

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[10] Br–B π-bonding is known to be very weak: Muetterties, E. L. *The Chemistry of Boron and Its Compounds*; Wiley: New York, 1967.

(vs), 1958 (vs) cm^{-1}. Anal. Calcd for $C_{18}H_{16}BBrFeO_2Ru$: C, 42.22; H, 3.15. Found: C, 42.13; H, 3.35.

***trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)Fc}] (7).** A colorless solution of [Pt(PCy$_3$)$_2$] (0.055 g, 0.073 mmol) in benzene (0.5 mL) was added to an orange solution of dibromoborylferrocene (**1**) (0.026 g, 0.073 mmol) in benzene (0.5 mL). The bright orange solution was stirred for 1 h at room temperature, after which time it was layered with hexane (1 mL). Slow evaporation of the resulting solution afforded **7** as bright orange crystals (0.053 g, 66%). ^{1}H NMR (CD_2Cl_2): δ 4.69 (m, 2H, C_5H_4B), 4.46 (m, 2H, C_5H_4B), 4.16 (s, 5H, C_5H_5), 2.62 (m, 6H, Cy), 2.13−1.22 (m, 60H, Cy). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 77.9 ($C_5H_5Fe\mathit{C}_5H_4B$), 72.1 ($C_5H_5Fe\mathit{C}_5H_4B$), 69.4 ($\mathit{C}_5H_5FeC_5H_4B$), 36.0 (t, $^1J_{C-P}$ = 27 Hz, C_i, Cy), 31.0 (s, Cy), 30.6 (s, Cy), 28.0 (t, $^2J_{C-P}$ = 11 Hz, Cy), 27.9 (t, $^2J_{C-P}$ = 11 Hz, Cy), 26.8 (s, Cy). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 82 ($\omega_{1/2}$ = ~1980 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.5 (s, $^1J_{P-Pt}$ = 2892 Hz). Anal. Calcd for $C_{46}H_{75}BBr_2FeP_2Pt$: C, 49.77; H, 6.67. Found: C, 50.26; H, 6.92.

General Procedure for X-ray Crystallography. A crystal of appropriate size was mounted on a glass fiber with silicone grease. The crystal was transferred to a Bruker SMART APEX diffractometer with CCD area detector, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus to −80 °C. Preliminary orientation matrix and cell constants were determined by collection of 100 frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected.[11] The raw data were integrated with SAINT.[12] Cell dimensions were calculated from the all reflections. Data analysis was performed with XPREP.[13] The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on comparison of redundant and equivalent reflections was applied with SADABS.[14] The structures were solved via direct methods and refined with the SHELX software package and expanded using Fourier techniques.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, with codes XXXXX. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ [fax +44-1223-336033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

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Supporting Information Available: Text detailing the structural determinations of **2**, **3**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] *SMART NT ver.5.63*, Area-Detector Software Package; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 1997−2001.

[12] *Saint+ NT ver. 6.45*, Area-Detector Integration Program; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 1997−2003.

[13] *XPREP ver. 6.10*, Part of the SHELXTL Crystal Structure Determination Package; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 1997−2001.

[14] Sheldrick, G. *SADABS ver. 2.10*, Area Detector Absorption Correction Program; 2002.

[15] Sheldrick, G. *SHELXS-97*: structure solution and *SHELXL-97*: structure refinement programs; 1997.