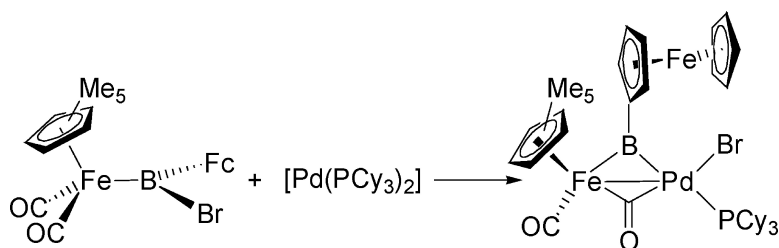Communication

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Heterodinuclear Bridged Borylene Complexes

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Incorporation into the coordination sphere of transition-metal complex fragments constitutes a successful strategy for the stabilization of the reactive borylene group, B−R, under mild conditions.[1] While isolation of transition-metal terminal borylene complexes[2] represents a numerically limited and chronologically recent achievement, bridged borylene species were the first instances in which the hypovalent B−R group could be linked via two-center two-electron bonds to a transition metal.[3] The privileged synthetic route to such compounds involved salt-elimination reactions between suitable anionic transition-metal complexes and appropriate diboranes(4)[3a−c] or, more commonly, dihaloboranes,[3d,f−h] leading invariably to formation of homodinuclear species. All attempts at accessing constitutionally more diverse systems, featuring a borylene group linking two *different* transition-metal complex fragments, were always frustrated by difficulties in limiting the extent of halide substitution by the more nucleophilic metal carbonylate.[4] Nonetheless, the expected increased reactivity associated with the uneven electronic situation of a heterodinuclear system, coupled with the structural novelty of the resulting species, prompted us to explore different synthetic approaches for the generation of heterodinuclear borylene complexes.

Our recent results in the chemistry of transition-metal haloboryl compounds[5] indicated a viable synthetic approach, whereby the boron atom of a suitable haloboryl complex could be linked to a second, electron-rich transition-metal complex fragment as a result of B−X (X = halogen) bond oxidative addition. Herein we report the synthesis of $[(\eta^5\text{-}C_5Me_5)(CO)Fe(\mu\text{-}CO)(\mu\text{-}BFc)Pd(Br)(PCy_3)]$ (**3**) [Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], the first structurally authentic heterodinuclear bridged borylene species, and the isolation and full analytical and spectroscopic characterization of $[(\eta^5\text{-}C_5Me_5)(CO)\text{-}Fe(\mu\text{-}CO)(\mu\text{-}BBr)Pd(Br)(PCy_3)]$ (**5**), which represents the only example of a transition-metal complex featuring the reactive B−Br group.

Monitoring the reaction of equimolar amounts of $[(\eta^5\text{-}C_5\text{-}Me_5)(OC)_2Fe\{B(Fc)Br\}]^{5a}$ (**1**) and $[Pd(PCy_3)_2]^6$ (**2**) in C_6D_6 by multinuclear NMR spectroscopy revealed gradual consumption of the starting materials and predominant formation of a new species, **3**, with concomitant liberation of PCy_3 (Scheme 1). Analytically pure orange crystals of **3** could be isolated by crystallization from a toluene/hexane solvent mixture at −30 °C. A single-crystal X-ray diffraction study clarified the atom connectivity within complex **3**. The molecular structure with relevant bond lengths and angles is shown in Figure 1. The study revealed the presence of a ferrocenylborylene group B−Fc that bridges, together with a CO ligand, the transition metals of the $[(\eta^5\text{-}C_5Me_5)(OC)Fe]$ and $[(Cy_3P)Pd\text{-}(Br)]$ complex fragments. Ignoring the metal−metal bond, the geometry at iron is that of a three-legged piano stool, with one terminal and one bridging carbonyl group, as commonly observed in homodinuclear bridged borylene complexes of iron.[3d,4]

Interestingly, the Fe1−B1 bond distance [1.903(3) Å] is, to our knowledge, the shortest reported for a bond between iron and any
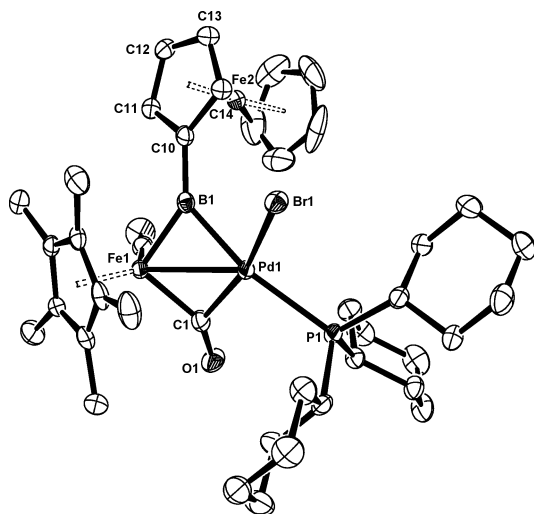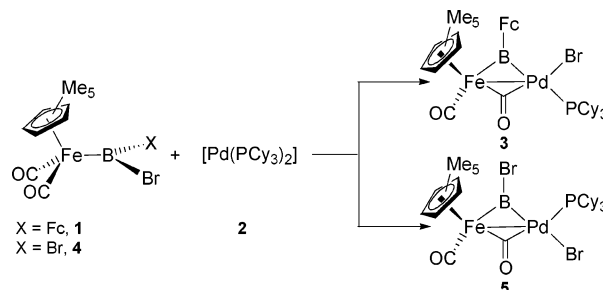

Figure 1. Molecular structure of **3·C₇H₈**. Toluene has been omitted for clarity. Bond lengths (Å) and angles (deg): Fe1−B1: 1.903(3), Pd1−B1: 2.090(3), Pd1−P1: 2.4297(7), Pd1−Br1: 2.5457(4), Fe1−Pd1: 2.5684(5), Fe1−B1−Pd1: 79.92(11), Fe1−B1−C10: 140.7(1), Pd1−B1−C10: 138.87(19).

Scheme 1. Synthesis of Heterodinuclear Bridged Borylene Complexes

three-coordinate boron ligand system. In particular, this distance is moderately shorter than that found in bromoboryl precursor **1** [1.985(3) and 1.972(3) Å][5a] or in $[(\eta^5\text{-}C_5R_5)(OC)Fe]_2(\mu\text{-}CO)\text{-}(\mu\text{-}BAr)$ [R = H, Ar = 2,4,6-Me₃C₆H₂, 1.956(5) and 1.966(5) Å;[4] R = Me, Ar = Ph, 1.934(6) and 1.936(6) Å][3h] and considerably shorter than that in $[(\eta^5\text{-}C_5H_5)(OC)_2Fe]_2[\mu\text{-}B(2,4,6\text{-}Me_3C_6H_2)]$ [2.090(10) and 2.091(10) Å],[3g] featuring an unsupported bridging mesitylborylene group.

The Fe1−Pd1 bond distance [2.5684(5) Å] is within the range [2.544(4)−2.850(2) Å] of those reported for heterodinuclear compounds containing Fe−Pd bonds.[7] The Pd1−B1 bond distance [2.090(3) Å] is longer than the ones reported for the only two structurally characterized complexes that feature bonds between palladium and a three-coordinate boron [2.006(9)−2.077(6) Å][8a,b] and comparable to the ones found in the boryl bridged complex $[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)_2(\mu\text{-}BCl_2)Pd(PCy_3)]$ [2.062(4) and 2.090(4)

Å],^{9} which features a four-coordinate boron atom. Such values indicate a pronounced asymmetry in the bridging coordination of the B–Fc group that appears to interact more strongly with iron than with palladium. The high trans influence of the borylene ligand causes elongation of the Pd1–P1 bond distance [2.4297(7) Å], which is longer than the one found, for instance, in *trans*-[(Cy$_3$P)$_2$-PdBr$_2$] [2.3631(10) Å].^{8c} The ferrocenylborylene and bromide ligands are in a mutual cis disposition, while the open coordination site liberated upon dissociation of the PCy$_3$ ligand is occupied by a bridging carbonyl group. Severe steric constraints imposed by the bulky tricyclohexylphosphine are likely to be partially responsible for the relatively long Pd–B bond distance and the ligand disposition around palladium, which is such as to preclude any unfavorable interaction between the B–Fc and PCy$_3$ groups.

The spectroscopic features of complex **3** are in full agreement with its solid state formulation. In particular, the ^{11}B{^{1}H} NMR spectrum of **3** in toluene-d_8 shows a broad signal at $\delta = 136$ ($\omega_{1/2}$ = 1780 Hz), significantly downfield shifted with respect to that of the bromoboryl precursor **1**, at $\delta = 103$.^{5a}

In the ^{31}P{^{1}H} NMR spectrum, the mutual trans disposition of the phosphorus and boron atoms causes broadening of the singlet resonance at $\delta = 23.9$ because of unresolved coupling of phosphorus with the quadrupolar boron nucleus. The ^{1}H NMR spectrum of **3** is temperature-dependent. Broad resonances are observed at 25 °C for the protons of the boron-substituted cyclopentadienyl ring. A strongly downfield shifted resonance, integrating for one proton, is found at $\delta = 6.16$, while the remaining three protons give rise to a broad unresolved signal at $\delta = 4.40{-}4.36$. Heating at 45 °C causes coalescence of the signals for two of the protons and sharpening of the resonance due to the remaining two protons. Two distinct resonances at $\delta = 5.17$ and 4.41, each integrating for two protons, are finally observed at 105 °C, along with minor signals due to thermal decomposition of the sample. Gradual sharpening of the resonances occurs upon cooling, and three distinct signals for the boron-substituted cyclopentadienyl protons are observed at $\delta = 6.30$, 4.33, and 4.24, in a 1:2:1 integral ratio, at −65 °C. Hindered rotation of the ferrocenyl group around the B–C10 bond is likely responsible for the broadness of the signals, while the downfield shift of one of the resonances is puzzling. However, careful inspection of the solid-state structural parameters suggests the presence of a long-range C14–H···Br interaction (C14–H···Br distance = 2.776 Å; cf. sum of the van der Waals radii for Br and H = 3.05 Å = 1.85 + 1.20 Å) that would account for the observed deshielded ^{1}H NMR resonance. The propensity of transition-metal-bound halides to take part in hydrogen bond-type interactions has previously been highlighted.^{10}

The successful synthesis of complex **3** confirmed the viability of our synthetic approach. To establish its generality, we turned our attention to the synthesis of more challenging systems, particularly those that had proven inaccessible by other routes, such as compounds featuring the bromoborylene group. Treatment of dibromoboryl complex [(η^5-C$_5$Me$_5$)(OC)$_2$Fe(BBr$_2$)]^{5c} (**4**) with an equimolar amount of **2** in C$_6$D$_6$ yielded a bright red solution that, as judged by multinuclear NMR spectroscopy, contained a new species, **5**, along with free PCy$_3$. All attempts at obtaining crystals of **5** suitable for an X-ray diffraction study were unsuccessful. However, the spectroscopic and analytical data are in full agreement with a formulation of compound **5** as the heterodinuclear bridged bromoborylene complex [(η^5-C$_5$Me$_5$)(CO)Fe(μ-CO)(μ-BBr)Pd(Br)-(PCy$_3$)]. In particular, the ^{11}B{^{1}H} NMR spectrum shows a

downfield shifted resonance at $\delta = 118$ {for [(η^5-C$_5$Me$_5$)(OC)$_2$-FeBBr$_2$] (**4**), δ(^{11}B) = 94},^{5c} while in the ^{31}P{^{1}H} NMR spectrum the phosphorus of the PCy$_3$ group resonates as a sharp singlet at δ = 45.6. The discrepancy between this and the corresponding value for ferrocenylborylene complex **3**, although surprising at first, might find an explanation in a different disposition of the ligands around palladium. In analogy with complex **3**, it is reasonable to infer stereoselective formation of *cis*-**5**, featuring mutually *cis*-borylene and bromide ligands, as the kinetic product of the reaction. Isomerization to the less sterically congested *trans*-**5** isomer would then account for the different value of the phosphorus resonance with respect to that of **3**.

In conclusion, heterodinuclear bridged borylene complexes, including the first example of a transition-metal compound featuring the reactive B–Br borylene group, have been synthesized via oxidative addition of the B–Br bond of bromoboryl precursors to [Pd(PCy$_3$)$_2$]. The study of the reactivity of these and analogous species is currently underway in our laboratories.

Supporting Information Available: Details of the synthesis and characterization of **3** and **5** and crystallographic data for **3** (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1787. (b) Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 771. (c) Braunschweig, H.; Colling, M. *J. Organomet. Chem.* **2000**, *614–615*, 18. (d) Braunschweig, H.; Colling, M. *Eur. J. Inorg. Chem.* **2003**, 393. (e) Braunschweig, H. *Adv. Organomet. Chem.* **2004**, *51*, 163.

(2) (a) Braunschweig, H.; Kollann, C.; Englert, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 3179. (b) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 948. (c) Braunschweig, H.; Kollann, C.; Englert, U. *Angew. Chem., Int. Ed.* **2001**, *40*, 4198. (d) Braunschweig, H.; Colling, M.; Kollann, C.; Stammler, H. G.; Neumann, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2298. (e) Braunschweig, H.; Colling, M.; Hu, C.; Radacki, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 215. (f) Coombs, D. L.; Aldridge, S.; Jones, C.; Willock, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6356.

(3) (a) Braunschweig, H.; Wagner, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 825. (b) Braunschweig, H.; Ganter, B. *J. Organomet. Chem.* **1997**, *545*, 163. (c) Braunschweig, H.; Müller, M. *Chem. Ber./Recl.* **1997**, *130*, 1295. (d) Braunschweig, H.; Kollann, C.; Englert, U. *Eur. J. Inorg. Chem.* **1998**, 465. (e) Shimoi, M.; Ikubo, S.; Kawano, Y.; Yasuro, K.; Katoh, K.; Ogino, H. *J. Am. Chem. Soc.* **1998**, *120*, 4222. (f) Braunschweig, H.; Kollann, C.; Klinkhammer, W. *Eur. J. Inorg. Chem.* **1999**, 1523. (g) Aldridge, S.; Coombs, D. L.; Jones, C. *Chem. Commun.* **2002**, 856. (h) Coombs, D. L.; Aldridge, S.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **2003**, *22*, 4213.

(4) Coombs, D. L.; Aldridge, S.; Jones, C. *J. Chem. Soc., Dalton Trans.* **2002**, 3851.

(5) (a) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Organometallics* **2004**, *23*, 5545. (b) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2004**, *23*, 4178. (c) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. Manuscript in preparation.

(6) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187.

(7) Braunstein, P.; Durand, J.; Morise, X.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **2000**, *14*, 444 and references therein.

(8) (a) Onozawa, S.-Y.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450. (b) Onozawa, S.-Y.; Tanaka, M. *Organometallics* **2001**, *20*, 2956. (c) Clarke, M. L.; Orpen, G. A.; Pringle, P. G.; Turley, E. *J. Chem. Soc., Dalton Trans.* **2003**, 4393.

(9) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem., Int. Ed.*, in press.

(10) (a) Aullon, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, 653. (b) Cini, R.; Cavaglioni, A. *Inorg. Chem.* **1999**, *38*, 3751. (c) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 11822.

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