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Borylene Complexes

B^+ in the Coordination Sphere of Two Transition Metals **

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Borylenes B–R are of growing interest as ligands in organometallic chemistry because of their close relationship to CO.[1] Since the first reported example of a transition-metal borylene complex in 1995,[2] the number of compounds featuring bridging and, more rarely, terminal borylene ligands has continuously increased.[3] Especially for terminal borylene complexes, with a two-coordinate boron center, electronic stabilization or steric protection by the boron-bound group is essential. As a consequence, the number of terminally bound borylene ligands in neutral complexes is still restricted to a few examples, namely the aminoborylene $\mathrm{B{=}N(SiMe_3)_2}$,[4] the bulky, electronically unsaturated $\mathrm{BSi(SiMe_3)_3}$,[5] the metalloborylene $\mathrm{BFe(CO)_2(\eta^5\text{-}C_5Me_5)}$,[6] and most recently the alkylborylene B*t*Bu.[7] Additionally, cationic iron complexes of the type $[(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{OC})_2\mathrm{Fe(BR)}]^+$ (R = mesityl, N*i*Pr$_2$, NCy$_2$) were established by Aldridge et al. by halide abstraction from the corresponding bromoboryl complexes with $\mathrm{Na[BAr^f_4]}$.[8] Recently, this route was used to synthesize the first terminal platinum borylene complex *trans*-$[(\mathrm{Cy_3P})_2\mathrm{Pt(Br)(BMes)}]^+$.[9] We report herein on the halide abstraction from bridged haloborylene complexes[10] and the isolation of the first cationic metalloborylene complexes $[\{(\mathrm{OC})_5\mathrm{Mn}\}_2(\mu\text{-B})][\mathrm{BAr^f_4}]$ (**2**) and $[\{(\eta^5\text{-}\mathrm{C_5H_4R})(\mathrm{OC})_2\mathrm{Fe}\}_2(\mu\text{-B})][\mathrm{BAr^f_4}]$ (**4a**: R = H; **4b**: R = Me).

The reaction of $[\{(\mathrm{OC})_5\mathrm{Mn}\}_2(\mu\text{-BBr})]$ (**1**)[10] with one equivalent of $\mathrm{Na[BAr^f_4]}$ in dichloromethane resulted in the formation of a bright yellow solution and the appearance of a colorless NaBr precipitate within minutes. The ^{11}B NMR spectrum of the reaction mixture showed a broad signal at $\delta =$ 225 ppm, which is significantly shifted to low field with respect to the signal for the starting material ($\delta = 163$ ppm), indicating the formation of a new compound. After workup, the cationic metalloborylene complex $[\{(\mathrm{OC})_5\mathrm{Mn}\}_2(\mu\text{-B})][\mathrm{BAr^f_4}]$ (**2**) was obtained as a pale yellow solid in 11 % yield. The anticipated structure was confirmed by single-crystal X-ray diffraction (Figure 1). Suitable crystals were obtained from a solution of **2** in dichloromethane/hexane (1:1) at −35 °C.[10] Compound **2** crystallizes in the monoclinic space group *C*2/*c* and the cation exhibits approximately D_{4h} symmetry with a linear Mn-B-Mn arrangement. The Mn–B bond (1.9096(5) Å) is significantly shorter than those in **1** (2.149(3) and 2.163(3) Å)[11] or in the dichloroboryl complex $[(\mathrm{OC})_5\mathrm{Mn(BCl_2)}]$ (2.060(5) Å)[12] or other related boryl complexes.[13,14] The CO ligands *cis* to the boron atom show a noticeable umbrella effect that is indicated by the average C_{cis}-Mn-B (86.04°) and Mn-C_{cis}-O bond angles (176.6°). The Mn–C_{trans} distance (1.932(4) Å) is significantly longer than the corresponding Mn–C_{cis} distances (1.864(4)–1.884(4) Å), which is in agreement with the enhanced *trans*-influence of the boron ligand with respect to the CO ligand.[4e]

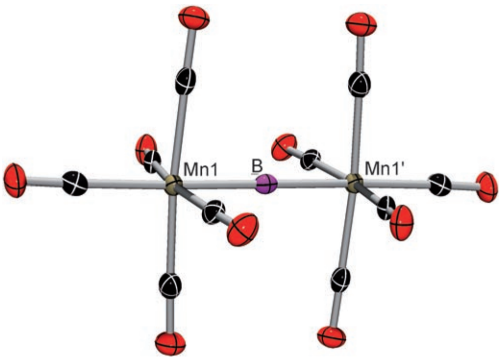

Figure 1. Molecular structure of **2**. The $[\mathrm{BAr^f_4}]^-$ ion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn–B 1.9096(5), Mn–C_{trans} 1.932(4), Mn–C_{cis}(av) 1.8748(4); Mn-B-Mn 180.0.

Complex **2** is very air- and moisture-sensitive and readily decomposes within a few days in the solid state at −35 °C under an atmosphere of argon. The stability of **2** in solution is even lower. Monitoring the decay of a sample of **2** in $\mathrm{CD_2Cl_2}$ by ^{11}B NMR spectroscopy revealed the formation of a new compound within 2 h with a doublet at $\delta = 123.9$ ($^1J_{\mathrm{B\text{-}F}} =$ 265 Hz). This is in the expected area for the bridged fluoroborylene complex $[\{(\mathrm{OC})_5\mathrm{Mn}\}_2(\mu\text{-BF})]$, which is obviously formed by fluoride abstraction from the $[\mathrm{BAr^f_4}]^-$ ion. Similar behavior was observed before by Aldridge et al. for the reaction of $[(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{OC})_2\mathrm{Fe\{B(Cl)OMes\}}]$ with $\mathrm{Na[BAr^f_4]}$.[8c]

The lability of **2** might be attributed to the highly unsaturated character of the boron atom in comparison to other cationic borylene complexes such as $[(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{OC})_2\mathrm{Fe(BN}i\mathrm{Pr_2)}]^+$, wherein the boron center is stabilized electronically by the amino substituent.[8b,c] In addition, the $[(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{OC})_2\mathrm{Fe}]$ fragment provides steric protection and is also more electron-rich than the $[(\mathrm{OC})_5\mathrm{Mn}]$ moiety. To synthesize a more stable cationic metalloborylene complex, we focused our attention on the reactivity of the iron chloroborylene complex $[\{(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{OC})_2\mathrm{Fe}\}_2(\mu\text{-BCl})]$ (**3a**).[11] Reaction of **3a** with $\mathrm{Na[BAr^f_4]}$ afforded after workup the analytically pure complex $[\{(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{OC})_2\mathrm{Fe}\}_2(\mu\text{-B})][\mathrm{BAr^f_4}]$ (**4a**) as a pale red, crystalline solid in 34 % yield. Under an atmosphere of argon, **4a** showed no propensity to

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decompose neither in the solid state nor in dichloromethane solution over a period of two weeks, and thus, its thermal stability is substantially higher than that of **2**. Single crystals of **4a** for X-ray diffraction studies were obtained from dichloromethane/toluene at −35 °C. Due to significant disorder of the Fe-B-Fe-moiety, a discussion of the structure parameters of **4a** is not meaningful. Hence, we subsequently synthesized the (C_5H_4Me)-substituted derivatives [{(η^5-C_5H_4Me)$(OC)_2$Fe}$_2$(μ-BCl)] (**3b**) and [{(η^5-C_5H_4Me)$(OC)_2$Fe}$_2$(μ-B)][BAr$^f_4$] (**4b**) by an analogous procedure. Compound **4b** crystallizes in the orthorhombic space group $Pca2_1$, and the unit cell contains two independent ion pairs (Figure 2). In one of the cations, the [(η^5-C_5H_4Me)$(OC)_2$Fe] moiety is rotationally disordered and therefore only the other molecule is discussed in the following.

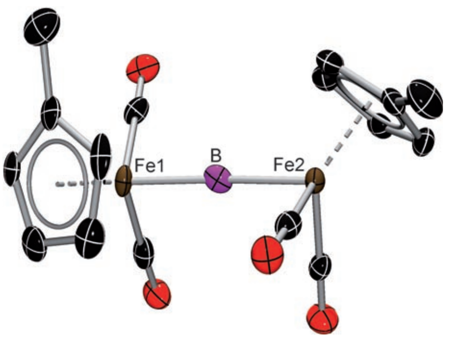

Figure 2. Molecular structure of **4b**. The [BAr$^f_4$]$^-$ ion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–B 1.828(5), Fe2–B 1.851(5); Fe1-B-Fe2 174.6(3).

In analogy to **2**, the cation in **4b** is characterized by a linear Fe-B-Fe moiety and the twist between the [(η^5-C_5H_5)$(OC)_2$Fe] fragments amounts to 107.2°. The Fe–B bond lengths (1.828(5), 1.851(5) Å) are significantly shorter than in the chloroborylene complex **3a** (2.018(2), 2.006(2) Å)[11] but are comparable to those in the cationic aminoborylene complex [(η^5-C_5H_5)$(OC)_2$Fe(BNCy$_2$)][BAr$^f_4$] (1.859(6) Å)[8d] and the neutral metallaborylene complex [{(η^5-C_5Me_5)$(OC)_2$Fe(μ-B)Fe$(CO)_4$] (1.867(2) Å).[6]

To elucidate the bonding situation, SCF calculations on **2** and **4a** were performed.[15] The energy surface of both cations was computed at the DFT/B3LYP level of theory. In the case of **2**, the D_{4h} transition state lies only 2.5 kJ mol^{-1} higher in energy than the minimum (D_{4d}). For **4a**, a minimum with C_{2h} symmetry was found, whereas the observed C_2 geometry in the crystal structure represents a low-lying transition state (+2.7 kJ mol^{-1}), and the C_{2v}-symmetric structure is a saddle point with a rotational barrier of 12.9 kJ mol^{-1}. These results indicate almost free rotation of the metal carbonyl moieties around the M-B-M axis in both cations. The experimental IR spectra of **4a** show two sharp signals in the CO stretching frequencies region at 2068 and 2048 cm^{-1} and a broad band at 2017 cm^{-1}. This is consistent with the presence of a C_2-symmetrical molecule in solution and thus, all further presented computational results for **4a** are restricted to this symmetry.

The IR spectroscopic data are well reproduced by computations. The scaled carbonyl stretching frequencies were found at 2127, 2098, and 2076 cm^{-1} for **2** and at 2068, 2048, 2029, and 2026 cm^{-1} for **4a**. The calculated ^{11}B NMR chemical shifts are in the expected low-field region, but are about 30 ppm low-field shifted in comparison to the experimental signals (**2**: 257 and **4a**: 230 ppm), which might be attributed to a low accuracy of the frontier orbitals energies in the conjugated M-B-M-moieties. The Wiberg bond index (WBI) for the metal–boron interaction has a magnitude comparable to this found in terminal aminoborylene complexes, which feature a distinctive metal–boron π-component (**2**: 0.66; **4a**: 0.76; [$(CO)_5$Cr=B=N(SiMe$_3$)$_2$]: 0.74 versus [(η^5-C_5H_5)$(OC)_2$Fe(^{t}BCl$_2$)]: 0.18).[4e] The most striking aspect of the canonical orbitals is the presence of a π-type orbital that describes the metal–boron-backbonding interactions (depending on the molecule and symmetry HOMO-3 to HOMO-9). These findings and the observed cylindrical distribution of the electron localization function (ELF) around the B–M bonds (Figure 3) also emphasize the delocalized nature of the M-B-M linkage.

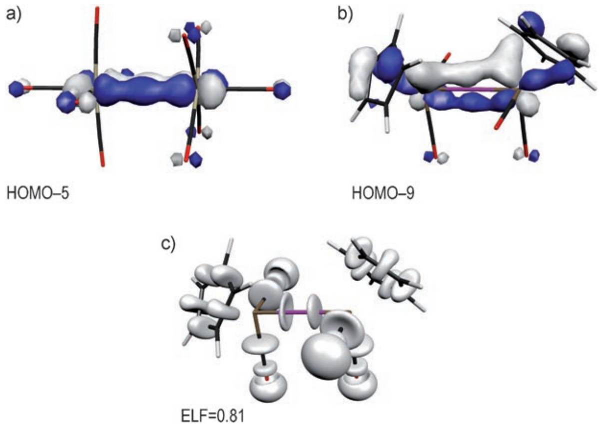

Figure 3. a, b) Kohn–Sham orbitals describing M-B-M π-interactions in **2** (a) and **4a** (b); c) the isosurface of the ELF of **4a**. The envelopes of core basins and valence C–H basins are omitted for clarity.

In conclusion, cationic metallaborylene complexes with a boron atom in the coordination sphere of two transition-metal centers were synthesized by halide abstraction from bridged haloborylene complexes and structurally characterized. The highly unsaturated boron center in these cationic species is expected to exhibit a broad and very interesting reactivity that will be the subject of further investigations.

Experimental Section

All manipulations were performed under an atmosphere of dry argon, using standard Schlenk line and glove-box techniques. See Supporting Information for details on the crystal data collection and the computations.

Synthesis of **2**: In a glove box, [{$(OC)_5$Mn}$_2$(μ-BBr)] (**1**) (111 mg, 240 μmol) and Na[BAr$^f_4$] (223 mg, 240 μmol) were allowed to react in dichloromethane (3 mL) over a period of 5 min. The yellow solution was filtered and all volatiles were subsequently removed in vacuo.

The yellow solid was washed with hexane (3 × 1 mL) and dried in vacuo to afford **2** as a pale yellow solid (yield: 32 mg, 11 %). IR: $\tilde{\nu} = 2127$ (s), 2098 (w), 2061 cm^{-1} (s), ν(CO); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 117.4$ (m, C^4, BAr$^f_4$), 125.8 (q, $^1J_{C\text{-}F} = 273$ Hz, CF_3), 129.0 (q, $^2J_{C\text{-}F} = 32$ Hz, C^{3,5}, BAr$^f_4$), 135.0 (s, C^{2,6}, BAr$^f_4$), 162.1 (q, $^1J_{C\text{-}B} = 50$ Hz, C$_1$, BAr$^f_4$), 211.4 (s, CO), 211.6 ppm (s, CO); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta = 224.9$ ppm (br s); elemental analysis calcd (%) for $C_{42}H_{12}B_2F_{24}Mn_2O_{10}$: C 39.91, H 0.96; found: C 39.10, H 1.29.

Synthesis of **4a**: In a glove box, $[\{(\eta^5\text{-}C_5H_5)(OC)_2Fe\}_2(\mu\text{-}BCl)]$ (**3a**) (20 mg, 50 μmol) and Na[BAr$^f_4$] (44 mg, 50 μmol) were allowed to react in dichloromethane (0.5 mL) over a period of 5 min. The red solution was filtered, hexane (2 mL) was added, and the mixture was stored at −35 °C overnight. The pale red crystals that separated were washed with hexane (3 × 1 mL) and dried in vacuo to afford **4a** as a pale red solid (yield: 21 mg, 34 %). IR: $\tilde{\nu} = 2068$ (s), 2048 (w), 2017 cm^{-1} (s), ν(CO); ^{1}H NMR (CD_2Cl_2): $\delta = 7.72$ (s, 8 H, BAr$^f_4$), 7.57 (s, 4 H, BAr$^f_4$), 5.27 ppm (s, 10 H, C_5H_5); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 87.04$ (s, C_5H_5), 117.9 (m, C$_4$, BAr$^f_4$), 125.0 (q, $^1J_{C\text{-}F} = 272$ Hz, CF_3), 129.2 (q, $^2J_{C\text{-}F} = 29$ Hz, C^{3,5}, BAr$^f_4$), 135.2 (s, C^{2,6}, BAr$^f_4$), 162.2 (q, $^1J_{C\text{-}B} = 50$ Hz, C^1, BAr$^f_4$), 205.9 ppm (s, CO); ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta = 191.2$ (br s), −7.19 ppm (s, BAr$^f_4$); elemental analysis calcd (%) for $C_{46}H_{22}B_2F_{24}Fe_2O_4$: C 44.99, H 1.81; found: C 45.29, H 1.15.

Synthesis of **4b**: In a glove box, $[\{(\eta^5\text{-}C_5H_4Me)(OC)_2Fe\}_2(\mu\text{-}BCl)]$ (**3b**) (10 mg, 25 μmol) and Na[BAr$^f_4$] (22 mg, 25 μmol) were allowed to react in dichloromethane (3 mL) over a period of 5 min. The red solution was filtered and all volatiles were subsequently removed in vacuo. The red solid was washed with hexane (3 × 1 mL) and recrystallized from dichloromethane/toluene (1:2) to afford **4b** as a pale red solid (yield: 21 mg, 66 %). IR: $\tilde{\nu} = 2063$ (s), 2043 (w), 2011 cm^{-1} (s), ν(CO); ^{1}H NMR (CD_2Cl_2): $\delta = 7.72$, 7.57 (s, 12 H, BAr$^f_4$), 5.33 (s, 4 H, C_5H_4Me), 5.12 (s, 4 H, C_5H_4Me), 2.05 ppm (s, 6 H, CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 12.7$ (s, CH_3), 84.5, 86.2 (s, C_5H_4Me), 117.2 (m, C^4, BAr$^f_4$), 124.2 (q, $^1J_{C\text{-}F} = 272$ Hz, CF_3), 128.3 (q, $^2J_{C\text{-}F} = 32$ Hz, C^{3,5}, BAr$^f_4$), 135.0 (s, C^{2,6}, BAr$^f_4$), 205.5 ppm (s, CO); no signals for the boron-bound carbon atoms were observed due to an adversarial signal-noise ratio; ^{11}B{^{1}H} NMR (CD_2Cl_2): $\delta = 193.7$ (br s), −7.20 ppm (s, BAr$^f_4$); elemental analysis calcd (%) for $C_{48}H_{26}B_2F_{24}Fe_2O_4$: C 45.90, H 2.09; found: C 45.79, H 2.09.

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[1] a) F. M. Bickelhaupt, U. Radius, A. W. Ehlers, R. Hoffmann, E. J. Baerends, *New J. Chem.* **1998**, *22*, 1–3; b) U. Radius, F. M. Bickelhaupt, A. W. Ehlers, N. Goldberg, R. Hoffmann, *Inorg. Chem.* **1998**, *37*, 1080–1090; c) A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U. Radius, *Chem. Eur. J.* **1998**, *4*, 210–221; d) J. Uddin, C. Boehme, G. Frenking, *Coord. Chem. Rev.* **2000**, *197*, 249–276; e) J. Uddin, C. Boehme, G. Frenking, *Organometallics* **2000**, *19*, 571–582.

[2] H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904–905; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825–826.

[3] For reviews see: a) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882–1898; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786–1801; b) H. Braunschweig, M. Colling, *Eur. J. Inorg. Chem.* **2003**, 393–403; c) H. Braunschweig, *Adv. Organomet. Chem.* **2004**, *51*, 163–192; d) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559; e) H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566–571; f) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380–5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254–5274; g) H. Braunschweig, M. Colling, *J. Organomet. Chem.* **2000**, *614–615*, 18–26.

[4] a) H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355–3357; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179–3180; b) H. Braunschweig, M. Colling, C. Kollann, H. G. Stammler, B. Neumann, *Angew. Chem.* **2001**, *113*, 2359–2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2298–2300; c) H. Braunschweig, M. Colling, C. Hu, K. Radacki, *Angew. Chem.* **2003**, *115*, 215–218; *Angew. Chem. Int. Ed.* **2003**, *42*, 205–208; d) H. Braunschweig, M. Forster, K. Radacki, *Angew. Chem.* **2006**, *118*, 2187–2189; *Angew. Chem. Int. Ed.* **2006**, *45*, 2132–2134; e) B. Blank, M. Colling-Hendelkens, C. Kollann, K. Radacki, D. Rais, K. Uttinger, G. R. Whittell, *Chem. Eur. J.* **2007**, *13*, 4770–4781.

[5] H. Braunschweig, M. Colling, C. Kollann, K. Merz, K. Radacki, *Angew. Chem.* **2001**, *113*, 4327–4329; *Angew. Chem. Int. Ed.* **2001**, *40*, 4198–4200.

[6] a) H. Braunschweig, K. Radacki, D. Scheschkewitz, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1685–1688; *Angew. Chem. Int. Ed.* **2005**, *44*, 1658–1661; b) H. Braunschweig, G. R. Whittell, *Chem. Eur. J.* **2005**, *11*, 6128–6133.

[7] H. Braunschweig, M. Burzler, T. Kupfer, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 7932–7934; *Angew. Chem. Int. Ed.* **2007**, *46*, 7785–7787.

[8] a) D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356–6357; b) D. L. Kays, J. K. Day, L. L. Ooi, S. Aldridge, *Angew. Chem.* **2005**, *117*, 7623–7626; *Angew. Chem. Int. Ed.* **2005**, *44*, 7457–7460; c) D. L. Kays, A. Rossin, J. K. Day, L. L. Ooi, S. Aldridge, *Dalton Trans.* **2006**, 399–410; d) S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, D. L. Kays, N. D. Coombs, D. J. Willock, *Angew. Chem.* **2006**, *118*, 6264–6268; *Angew. Chem. Int. Ed.* **2006**, *45*, 6118–6122; e) G. A. Pierce, S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, N. D. Coombs, D. J. Willock, *Angew. Chem.* **2007**, *119*, 2089–2092; *Angew. Chem. Int. Ed.* **2007**, *46*, 2043–2046.

[9] H. Braunschweig, K. Radacki, K. Uttinger, *Angew. Chem.* **2007**, *119*, 4054–4057; *Angew. Chem. Int. Ed.* **2007**, *46*, 3979–3982.

[10] The crystal data for **2** and **4b** were collected on a Bruker X8APEX diffractometer and the structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen 1997). CCDC-676477 (**2**) and CCDC-676478 (**4b**) contain 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.

[11] P. Bissinger, H. Braunschweig, F. Seeler, *Organometallics* **2007**, *26*, 4700–4701.

[12] H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics* **2006**, *25*, 4605–4610.

[13] K. M. Waltz, X. He, C. Muhoro, J. F. Hartwig, *J. Am. Chem. Soc.* **1995**, *117*, 11357–11358.

[14] H. Braunschweig, M. Colling, C. Kollann, U. Englert, *J. Chem. Soc. Dalton Trans.* **2002**, 2289–2296.

[15] Electronic structure calculations reported in this work were performed with Gaussian 03 (Revision B.04), Gaussian, Inc., Pittsburgh, PA, **2003**. The electron localization function (ELF) and its properties were computed with the TopMoD package of S. Noury, X. Krokidis, F. Fuster, B. Silvi, **1997**. The charges and the Wiberg bond indices were calculated with the NBO 5 program of E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, **2001**.