Angewandte
Chemie

Coordination Modes of Boron

Proton-Induced Change of the Coordination Mode of a Boron Group: Boryl Complexes [$Mn(CO)_4(PR_3)(BH_2{\cdot}PMe_3)$] and Cationic Borane σ Complexes [$Mn(CO)_4(PR_3)(\eta^1\text{-}BH_3{\cdot}PMe_3)$]$^{+}$[**]

Takahiro Yasue, Yasuro Kawano,[*] and Mamoru Shimoi[*]

Protonation of hydrido complexes is one of the important synthetic methods in the chemistry of these interesting systems.[1–5] However, this methodology has been applied

---

[*] Dr. Y. Kawano, Prof. M. Shimoi, Dr. T. Yasue
Department of Basic Science
Graduate School of Arts and Sciences
University of Tokyo, Meguro-ku, Tokyo 153-8902 (Japan)
Fax: (+81) 3-5454-6567
E-mail: ykawano@jcom.home.ne.jp
cshimoi@mail.ecc.u-tokyo.ac.jp

[**] ($PR_3 = PMe_2Ph$, PEt_3).

DOI: 10.1002/ange.200219992

sparsely in the preparation of other types of mononuclear σ complexes.[6] We have explored the coordination chemistry of $BH_3{\cdot}PMe_3$ and reported base-stabilized boryl complexes (e.g., $[Cp^*M(CO)_3(BH_2{\cdot}PMe_3)]$ (M = Mo, W[7]) and $[Cp^*M(CO)_2(BH_2{\cdot}PMe_3)]$ (M = Fe, Ru[8])) and borane σ complexes (e.g., $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}PMe_3)]$ (M = Cr, Mo, W[9]) and $[CpMn(CO)_2(\eta^1\text{-}BH_3{\cdot}PMe_3)]$[10]). Herein, we report new manganese–boryl complexes, $[Mn(CO)_4(PR_3)(BH_2{\cdot}PMe_3)]$ (**1**) and their protonation to produce cationic borane σ complexes, $[Mn(CO)_4(PR_3)(\eta^1\text{-}BH_3{\cdot}PMe_3)]^+$ (**2**). Heterolytic cleavage of the metal-coordinated B–H bond of **2** is also described here.

Photolysis of $[MnMe(CO)_4(PR_3)]$ with $BH_3{\cdot}PMe_3$ resulted in the evolution of methane and gave an orange solution, from which boryl complexes $[Mn(CO)_4(PR_3)(BH_2{\cdot}PMe_3)]$ (**1a**: $PR_3 = PMe_2Ph$; **1b**: $PR_3 = PEt_3$) were isolated as pale yellow crystals in moderate yields (Scheme 1). The ^{11}B NMR spectra of complexes **1a** and **1b** display a boryl signal at lower field ($\delta = -29.4$ and -29.6 ppm, respectively) than that of $BH_3{\cdot}PMe_3$ ($\delta = -37.0$ ppm). The IR spectra of **1** show carbonyl bands shifted to lower energy in comparison to those of the precursor $[MnMe(CO)_4(PR_3)]$. These observations indicate polarization of the Mn–B bond in a Mn(−)–B(+) fashion and a resultant increase of electron density on the metal center. Similar polarization of the M–B bond has been found in phosphane-coordinated primary boryl complexes of Group 6 and 8 metals.[7,8] The solid-state structure of **1a** (Figure 1)[11] shows that this molecule adopts a highly distorted octahedral geometry. The phosphane ligand is located *cis* to the boryl group. The manganese–boron bond length (2.314(2) Å) is substantially longer than that in the catecholboryl complex $[Mn(CO)_5\{B(1,2\text{-}O_2C_6H_4)\}]$ (2.108(6) Å)[12] because of the absence of a vacant p orbital on the boron center that can be utilized for π interaction with the metal center. Two of the *cis*-carbonyl groups significantly tilt toward the boryl group. The C(2)-Mn-C(3) bond angle is 154.62(6)°. Owing to the pronounced Mn(−)–B(+) polarization mentioned above, the nature of compounds **1** closely resembles a contact ion pair composed of $[Mn(CO)_4(PR_3)]^-$ and $[BH_2{\cdot}PMe_3]^+$; the anion-like manganese moiety is isoelectronic with $Fe(CO)_5$. Consequently, the geometry of the $[Mn(CO)_4(PR_3)]$ moiety approaches a trigonal bipyramid, and the Mn–B bond becomes longer. Note that more π-acidic ligands prefer to be located at equatorial positions in trigonal-bipyramidal complexes. In the $[Mn(CO)_4(PR_3)]$ fragment, π-acidic carbonyl ligands occupy the equatorial positions, and a less π-acidic phosphane ligand is situated at an apical position, which is *cis* to the boryl group in **1**.

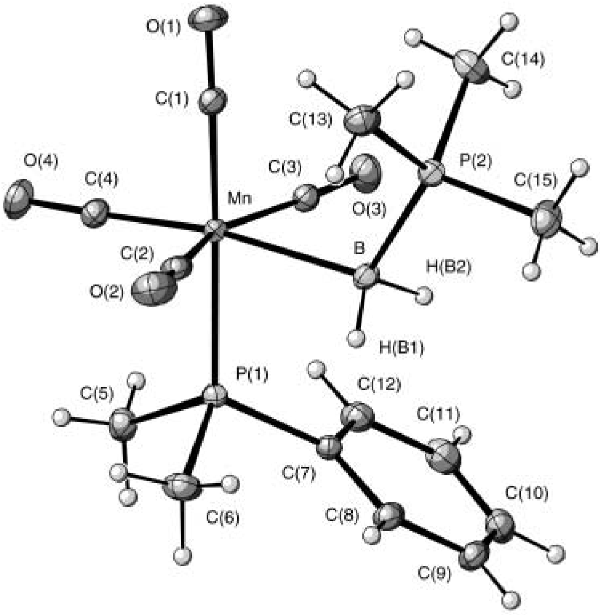
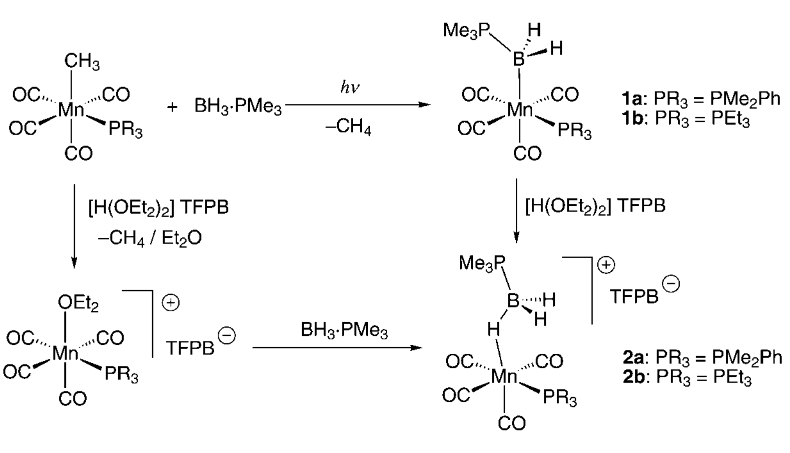


Figure 1. Structure of **1a** (ORTEP diagram; thermal ellipsoids at the 30% probability level). Selected interatomic distances [Å] and angles [°]: Mn-B 2.314(2), Mn-P(1) 2.302(1), B-P(2) 1.901(2), B-H(B1) 1.08(2), B-H(B2) 1.12(2), Mn-C(1) 1.792(2), Mn-C(2) 1.811(1), Mn-C(3) 1.814(1), Mn-C(4) 1.801(1); C(2)-Mn-C(3) 154.62(6), C(4)-Mn-B 171.76(6), Mn-B-P(2) 114.99(9).

The boryl complexes were protonated by treating **1** in [D$_2$]dichloromethane with the Brønsted acid $[H(OEt_2)_2](TFPB)$ (TFPB = $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$), which has a weakly coordinating anion.[13] The resulting pale yellow solutions showed a broad BH resonance signal around $\delta = -4.5$ ppm in the ^1H NMR spectra. The ^{11}B NMR spectrum of the product displayed a doublet of quartets at higher field ($\delta = -40.3$ to -40.4 ppm) than that of free $BH_3{\cdot}PMe_3$. The appearance of these signals clearly shows the formation of borane σ complexes $[Mn(CO)_4(PR_3)(\eta^1\text{-}BH_3{\cdot}PMe_3)](TFPB)$ (**2**, see Scheme 1). The value of the chemical shift of the ^{11}B NMR signal falls in the range of those for σ complexes of $BH_3{\cdot}PMe_3$.[9,10] The ^1H NMR signal around $\delta = -4.5$ ppm is assigned to the BH resonance; the ^1H NMR signals of the metal-coordinated and terminal BH protons are averaged through fast site-exchange. This process was not frozen out even at −80 °C. Similar fluxional behavior has been found in other complexes of phosphaneboranes.[9,10,14,15] Complexes **2** were also generated by methyl abstraction from $[MnMe(CO)_4(PR_3)]$ using $[H(OEt_2)_2](TFPB)$, followed by addition of $BH_3{\cdot}PMe_3$. These complexes have a lifetime of a few days, and can be observed by spectroscopy; however, they could not be isolated in pure forms.



Scheme 1. Syntheses of complexes **1** and **2**.

Figure 2 shows the DFT-optimized structure of the model compound $[Mn(CO)_4(PH_3)(\eta^1\text{-}BH_3{\cdot}PMe_3)]^+$ (**2c**).[16,17] It resembles the structure of $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}PMe_3)]$ (M = Cr, W) except for the metal-coordinated phosphane ligand. The Mn···B interatomic distance (2.780 Å) is far longer than that of **1a**, and the Mn-H-B bond angle is 133.44°. Thus, the mode of coordination for the borane ligand is essentially end-on. The B–H(1) bond length is 1.270 Å, and the B–H σ bond is elongated by about 6 % on coordination.

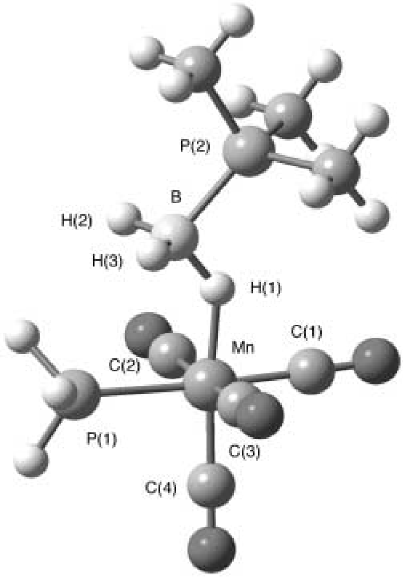
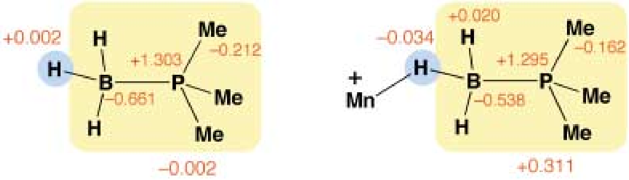


Figure 2. DFT-optimized structure of **2c**. Selected interatomic distances [Å] and angles [°]: Mn···B 2.780, Mn-H(1) 1.753, B-H(1) 1.270, B-H(2) 1.200, B-H(3) 1.200, B-P(2) 1.950, Mn-P(1) 2.380, Mn-C(1) 1.840, Mn-C(2) 1.880, Mn-C(3) 1.880, Mn-C(4) 1.840; Mn-H(1)-B 133.44, P(1)-Mn-C(1) 176.80.

Borane σ complexes **2** are formally the conjugate acids of **1**. However, deprotonation from **2** did not occur even when they were treated with bases such as NaH and diazabicycloundecene. On the other hand, a solution of **2** decomposed in a few days at room temperature to give a mixture containing $[MnH(CO)_4(PR_3)]$ and $[BH_2{\cdot}2PMe_3]^+$, although the decomposition process was not very clean. This suggests the coordinated B–H σ bond of complexes **2** cleaves heterolytically into H^- and "$[BH_2{\cdot}PMe_3]^+$".[18] Recently, Kubas and co-workers reported similar heterolytic cleavage of H_2 and silanes on the cationic manganese or rhenium fragments $[M(CO)_{5-n}(PR_3)_n]^+$ (M = Mn, Re, n = 1, 2).[19] The electron-deficient metal centers undergo strong σ donation from the H–H, Si–H, as well as B–H σ orbitals, but backdonation into the corresponding σ* orbitals hardly occurs. Therefore, the electron density of these σ ligands is significantly reduced and the metal-coordinated σ bond is activated heterolytically. The natural bond orbital (NBO) analysis based on the aforementioned DFT calculations on **2c** shows that the bridging hydrogen atom of the borane ligand becomes more hydridic on coordination to the cationic manganese center.[20] Its natural charge is −0.034, whereas that of the B–H hydrogen atom of free $BH_3{\cdot}PMe_3$ is +0.002. At the same time, that of the "$BH_2{\cdot}PMe_3$" group increases from −0.002 to +0.311 (Scheme 2). The electron density of the $BH_3{\cdot}PMe_3$ ligand is thus withdrawn toward the bridging hydrogen by the highly electrophilic $[Mn(CO)_4(PR_3)]^+$ ion in the cationic borane complexes.



Scheme 2. NBO charge distribution in free $BH_3{\cdot}PMe_3$ (left) and **2c** (right).

Experimental Section

1a: A mixture of $[MnMe(CO)_4(PMe_2Ph)]$ (247 mg, 0.75 mmol) and $BH_3{\cdot}PMe_3$ (203 mg, 2.28 mmol) in hexane (10 mL) was photolyzed at 3 °C for 90 min using a 450 W medium-pressure Hg arc lamp. The resulting solution was evaporated and evacuated for 1 h to remove excess $BH_3{\cdot}PMe_3$. Recrystallization of the solid residue from hexane at −80 °C provided pale yellow crystals of **1a** (90 mg, 31 %). Compound **1b** was obtained in an analogous manner in 15 % yield.

Data for **1a**: ^1H NMR (500 MHz, [D$_6$]benzene, 23 °C, TMS): δ = 0.88 (d, $^2J(P,H)$ = 10.0 Hz, 9H; PMe$_3$), 1.49 (d, $^2J(P,H)$ = 8.5 Hz, 6H; P*Me*$_2$Ph), 7.02, 7.09, 7.36 ppm (m, 5H; PMe$_2$*Ph*), the BH proton signals were too broad to be observed; ^{11}B NMR (160.4 MHz, [D$_6$]benzene, 23 °C, BF$_3$·OEt$_2$): δ = −29.4 ppm (dt, $^1J(B,H)$ = 105.3 Hz, $^1J(B,P)$ = 73.5 Hz); ^{31}P NMR (202.4 MHz, [D$_6$]benzene, 23 °C, 85 % H$_3$PO$_4$): δ = 27.3 (br; PMe$_2$Ph), 0.9 ppm (br; PMe$_3$); ^{13}C NMR (125.7 MHz, [D$_6$]benzene, 23 °C, TMS): δ = 13.0 (d, $^1J(C,P)$ = 36.7 Hz; PMe$_3$), 16.6 (d, $^1J(C,P)$ = 29.3 Hz; P*Me*$_2$Ph), 129.0, 129.4 (d, $^1J(C,P)$ = 7.3 Hz), 140.7 (d, $^1J(C,P)$ = 38.1 Hz) (Ph), 219.9, 226.8, 227.9 ppm (CO); IR (KBr): $\tilde{\nu}$ = 1893.8 (vs), 1906.3 (vs), 1925.6 (vs), 2008.5 (s) (C≡O), 2357 (w) (BH) cm^{-1}; MS (EI, 70 eV): m/z (%): 394 (12) [M^+], 366 (89) [M^+−CO], 338 (24) [M^+−2 CO], 320 (60) [M^+−PMe$_3$], 310 (30) [M^+−3 CO], 282 (100) [M^+−4 CO]; elemental analysis (%) calcd for $C_{15}H_{22}BMnO_4P_2$: C 45.72, H 5.63; found: C 45.64; H, 5.57.

Data for **1b**: ^1H NMR (500 MHz, [D$_6$]benzene, 23 °C, TMS): δ = 0.91 (dt, $^3J(H,H)$ = 7.5 Hz, $^3J(P,H)$ = 15.5 Hz, 9H; P(CH$_2$C*H*$_3$)$_3$), 0.92 (d, $^2J(P,H)$ = 10.5 Hz, 9H; PMe$_3$), 1.59 ppm (dq, $^3J(H,H) \approx {}^2J(P,H)$ = 7.5 Hz, 6H; P(C*H*$_2$CH$_3$)$_3$), the BH proton signals were too broad to be observed; ^{11}B NMR (160.4 MHz, [D$_6$]benzene, 23 °C, BF$_3$·OEt$_2$): δ = −29.6 ppm (dt, $^1J(B,H)$ = 106.3 Hz, $^1J(B,P)$ = 71.2 Hz); ^{31}P NMR (202.4 MHz, [D$_6$]benzene, 23 °C, 85 % H$_3$PO$_4$): δ = 43.0 (br; PEt$_3$), 0.7 ppm (br; PMe$_3$); ^{13}C NMR (125.7 MHz, [D$_6$]benzene, 23 °C, TMS): δ = 7.5 (P(CH$_2$*C*H$_3$)$_3$), 12.9 (d, $^1J(C,P)$ = 37.1 Hz; PMe$_3$), 19.0 (d, $^1J(C,P)$ = 24.6 Hz; P(*C*H$_2$CH$_3$)$_3$), 129.0, 129.4 (d, $^1J(C,P)$ = 7.3 Hz), 140.7 (d, $^1J(C,P)$ = 38.1 Hz) (Ph), 220.5, 227.8, 228.0 ppm (br; CO); IR (KBr): $\tilde{\nu}$ = 1889 (vs), 1910 (vs), 2004 (vs) (C≡O), 2357 (w) (BH) cm^{-1}; MS (EI, 70 eV): m/z (%): 374 (5) [M^+], 346 (24) [M^+−CO], 318 (5) [M^+−2 CO], 290 (3) [M^+−3 CO], 262 (100) [M^+−4 CO], 173 (27) [Mn(PEt$_3$)$^+$], 144 (60) [Mn(BH$_2$·PMe$_3$)$^+$]; elemental analysis (%) calcd for $C_{13}H_{26}BMnO_4P_2$: C 41.74, H 7.01; found: C 41.57, H 6.85.

2a: Compound **1a** (41 mg, 0.10 mmol) and [H(OEt$_2$)$_2$](TFPB) (362 mg, 0.36 mmol) were combined in dichloromethane (10 mL) under vacuum. After the mixture had been stirred for 3 h, volatiles were evaporated to dryness. The ^1H, ^{11}B, and ^{31}P NMR spectra of the resulting yellow residue indicated complete consumption of **1a** and displayed new signals assignable to **2a**. Alternatively, **2a** was cleanly generated by addition of $BH_3{\cdot}PMe_3$ to a solution of $[Mn(CO)_4(PMe_2Ph)(OEt_2)]^+$, which was produced by the reaction of $[MnMe(CO)_4(PMe_2Ph)]$ with $[H(OEt_2)_2](TFPB)$ in diethyl ether. The PEt_3 derivative **2b** was prepared by similar methods.

Data for **2a**: ^1H NMR (500 MHz, [D$_2$]dichloromethane, 23 °C, TMS): $\delta = -4.48$ (br, 3H; BH), 1.32 (d, $^2J(P,H) = 11.5$ Hz, 9H; PMe_3), 1.98 (d, $^2J(P,H) = 9.0$ Hz, 6H; $P\mathit{Me}_2Ph$), 7.57, 7.72 ppm (s, 1H, 2H; $[B\{C_6\mathit{H}_3(CF_3)_2\}_4]$); ^{11}B NMR (160.4 MHz, [D$_2$]dichloromethane, 23 °C, $BF_3{\cdot}OEt_2$): $\delta = -40.4$ (dq, $^1J(B,H) = 81$ Hz, $^1J(B,P) = 70$ Hz; $BH_2{\cdot}PMe_3$), −6.7 ppm (s; TFPB); ^{31}P NMR (202.4 MHz, [D$_2$]dichloromethane, 23 °C, 85% H_3PO_4): $\delta = -4.0$ (br; PMe_3), 15.0 ppm (br; PMe_2Ph); MS (FAB, sulfolane): m/z (%): 367 (10) $[M^+-CO]$, 193 (100) $[Mn(PMe_2Ph)^+]$, 139 (43) $[PHMe_2Ph^+]$.

Data for **2b**: ^1H NMR (500 MHz, [D$_2$]dichloromethane, 23 °C, TMS): $\delta = -4.43$ (br, 3H; BH), 1.10–1.22 (m, 9H; $P(CH_2C\mathit{H}_3)_3$), 1.35 (d, $^2J(P,H) = 11.5$ Hz, 9H; PMe_3), 1.72–1.80 (m, 6H; $P(C\mathit{H}_2CH_3)_3$), 7.57, 7.72 ppm (s, 1H, 2H; $[B\{C_6\mathit{H}_3(CF_3)_2\}_4]$); ^{11}B NMR (160.4 MHz, [D$_2$]dichloromethane, 23 °C, $BF_3{\cdot}OEt_2$): $\delta = -40.3$ (br), −6.7 ppm (s; TFPB); ^{31}P NMR (202.4 MHz, [D$_2$]dichloromethane, 23 °C, 85% H_3PO_4): $\delta = -5.3$ (br; PMe_3), 48.7 ppm (br; PEt_3); MS (FAB, sulfolane): m/z (%): 173 (100) $[Mn(PEt_3)^+]$, 120 (28) $[PHEt_3^+]$.

Received: August 19, 2002
Revised: December 3, 2002 [Z19992]

Keywords: boranes · boron · coordination modes · manganese · protonation

---

[1] R. H. Crabtree, *Acc. Chem. Res.* **1990**, *23*, 95.

[2] R. H. Morris, P. G. Jessop, *Coord. Chem. Rev.* **1992**, *121*, 155.

[3] D. M. Heinkey, W. J. Oldham, Jr., *Chem. Rev.* **1993**, *93*, 913.

[4] R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 823; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

[5] G. J. Kubas, *Metal Dihydrogen and σ-Bond Complexes*, Kluwer Academic/Plenum Publishers, New York, **2001**.

[6] a) Protonation of a silyl complex $[CpRu(PMe_3)_2SiCl_3]$: F. R. Lemke, *J. Am. Chem. Soc.* **1994**, *116*, 11183; S. T. N. Freeman, F. R. Lemke, L. Brammer, *Organometallics* **2002**, *21*, 2030; b) protonation of $[CpFe(CO)(PEt_3)SiEt_3]$: E. Scharrer, S. Chang, M. Brookhart, *Organometallics* **1995**, *14*, 5686.

[7] Y. Kawano, T. Yasue, M. Shimoi, *J. Am. Chem. Soc.* **1999**, *121*, 11744.

[8] T. Yasue, Y. Kawano, M. Shimoi, *Chem. Lett.* **2000**, 58.

[9] M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi, H. Ogino, *J. Am. Chem. Soc.* **1999**, *121*, 11704.

[10] T. Kakizawa, Y. Kawano, M. Shimoi, *Organometallics* **2001**, *20*, 3211.

[11] Crystal data for **1a**: pale yellow crystals, triclinic, space group $P\bar{1}$ (no. 2); $T = 150$ K; $a = 10.5746(8)$, $b = 10.6779(9)$, $c = 9.0029(7)$ Å; $\alpha = 109.026(2)$, $\beta = 96.043(3)$, $\gamma = 88.092(2)°$; $V = 955.69(13)$ Å^3; $Z = 2$, $R = 0.024$, $wR2 = 0.060$ for 4070 reflections with $|F_o| > 3\sigma(F_o)$, 296 parameters, GoF = 1.110. The boron-attached hydrogen atoms were found by the difference Fourier syntheses and their positions were refined. CCDC-190001 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] K. M. Waltz, H. He, C. N. Muhoro, J. F. Hartwig, *J. Am. Chem. Soc.* **1995**, *117*, 11357.

[13] M. Brookhart, B. Grant, A. F. Vople, Jr., *Organometallics* **1992**, *11*, 3920.

[14] R. Macías, N. P. Rath, L. Barton, *Angew. Chem.* **1999**, *111*, 203; *Angew. Chem. Int. Ed.* **1999**, *38*, 162.

[15] M. Ingleson, N. J. Patmore, G. D. Ruggiero, C. G. Frost, M. F. Mahon, M. C. Willis, A. S. Weller, *Organometallics* **2001**, *20*, 4434.

[16] The stationary point was located at the B3LYP level of theory, by using density functional theory calculations based on hybrid functionals. A double ζ plus polarization valence basis set, 6-31G(d) was employed for all the atoms except manganese. For Mn, a basis set with an approximation of effective core potentials, LANL2DZ was applied. The NBO analysis was carried out on the resulting structure at the B3LYP level using a 6–311+G(2d,p) basis set.[20] All calculations were performed with the Gaussian 98W package of programs.[17]

[17] Gaussian98 (Revision A.11), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2001**.

[18] Several boryl cations with the formula $[BX_2{\cdot}L]^+$ (L = neutral Lewis base) have been reported: P. Kölle, H. Nöth, *Chem. Rev.* **1985**, *85*, 399.

[19] a) J. Huhmann-Vincent, B. L. Scott, G. J. Kubas, *Inorg. Chim. Acta* **1999**, *294*, 240; b) J. Huhmann-Vincent, B. L. Scott, G. J. Kubas, *J. Am. Chem. Soc.* **1998**, *120*, 6808; c) X. Fang, J. Huhmann-Vincent, B. L. Scott, G. J. Kubas, *J. Organomet. Chem.* **2000**, *609*, 95; d) J. Huhmann-Vincent, B. L. Scott, G. J. Kubas, *Inorg. Chem.* **1999**, *38*, 115; e) X. Fang, B. L. Scott, K. D. John, G. J. Kubas, *Organometallics* **2000**, *19*, 4141.

[20] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO version 3.1.