Diborane(4) - metal bonding: Between Hydrogen Bridges and Frustrated Oxidative Addition

Supporting Information

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Experimental

The reactions were carried out under argon using standard Schlenk techniques. All solvents were rigorously dried by applying standard procedures and degassed prior to their use. The synthesis of $[HB(\mu-hpp)]_2$ was accomplished as reported previously.^[7] $[Rh(\mu-Cl)cod]_2$, $[Ir(\mu-Cl)cod]_2$, $[Cr(CO)_6]$, $[Mo(CO)_6]$ and $[W(CO)_{6]}$ were obtained from Acros, ABCR and Aldrich, respectively, and stored under argon.

$[Cr{HB(hpp)}_2(CO)_4]$

A mixture of dry [Cr(CO)₆] (44 mg, 0.20 mmol) and [HB(μ -hpp)]₂ (60 mg, 0.20 mmol) in dichloromethane (10 mL) stirred at room temperature was irradiated for 1 h with a 450 W medium pressure Hg lamp. The resulting solution was concentrated and the product precipitated by the addition of 10 mL of diethylether giving a red solid in 55 % yield (51 mg, 0.11 mmol). Crystals suitable for x-ray diffraction were obtained from a concentrated dichloromethane solution. C₁₈H₂₆B₂CrN₆O₄ (464.06): calcd. C 46.59, H 5.65, N 18.11; found C 46.46, H 5.78, N 17.80. ¹H{¹¹B} NMR (400 MHz, CD₂Cl₂): δ = 3.40-3.30 (m, 8 H, NCH₂), 3.13-3.05 (m, 4 H, NCH₂), 3.02-2.95 (m, 4 H, NCH₂), 1.91-1.83 (m, 8 H, CH₂), -4.84 (s, 2 H, BH) ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 234.7 (2 C, CO), 218.0 (2 C, CO), 156.8, (2 C, C_{quart}), 47.0 (4 C, NCH₂), 45.5 (4 C, NCH₂), 22.3 (4 C, CH₂) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂): δ = -8.76 (s, 2 B, BH) ppm. IR (KBr): v = 2953 (m, C-H val.), 2934 (m, C-H val.), 2858 (m, C-H val.), 2756 (w, C-H val.), 2010 (m, B-H val.), 1900 (s, C=O val.), 1865 (s, C=O val.), 1825 (s, C=O val.), 1584 (s, C=N val.), 1560 (s, C=N val.), 1508 (m), 1499 (m), 1474 (m), 1458 (m), 1439 (m), 1404 (m), 1396 (m), 1369 (w), 1348 (m), 1321 (m), 1306 (m), 1290 (m), 1275 (m), 1221 (m), 1186 (m), 1099 (w), 1045 (w) cm⁻¹. MS (LIFDI): m/z (%) = 464 (100) [M]⁺, 301 (13) [LH]⁺. Crystal data for C₁₈H₂₆B₂CrN₆O₄,

 $Mr = 464.07, 0.30 \ge 0.25 \ge 0.25 \text{ mm}^3$, orthorhombic, space group Pna2(1), a = 10.307(2), b = 15.475(3), c = 13.456(3) Å, V = 2146.2(7) Å^3, Z = 4, d_{calc} = 1.436 Mg·m⁻³, Mo-K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, Θ_{range} 2.82 to 29.50 °. Reflections measd. 21829, indep. 5928, R_{int} = 0.0762. Final R indices [I > 2 σ (I)]: R₁ = 0.0405, wR₂ = 0.0862.

$[Mo{HB(hpp)}_2(CO)_4]$

A mixture of dry $[Mo(CO)_6]$ (53 mg, 0.20 mmol) and $[HB(\mu-hpp)]_2$ (60 mg, 0.20 mmol) in dichloromethane (10 mL) stirred at room temperature was irradiated for 1 h with a 450 W medium pressure Hg lamp. The resulting solution was concentrated and the product precipitated by the addition of 10 mL of diethylether giving a yellow solid in 80 % yield (81 mg, 0.16 mmol). Crystals suitable for x-ray diffraction were obtained from a concentrated dichloromethane solution. C₁₈H₂₆B₂MoN₆O₄ (508.02): calcd. C 42.56, H 5.16, N 16.54; found C 42.78, H 5.30, N 16.52. ¹H{¹¹B} NMR (400 MHz, CD₂Cl₂): δ = 3.37-3.31 (m, 8 H, NCH₂), 3.17-3.05 (m, 4 H, NCH₂), 3.05-2.95 (m, 4 H, NCH₂), 1.92-1.82 (m, 8 H, CH₂), -2.91 (s, 2 H, BH) ppm. ${}^{13}C{}^{1}H$ NMR (100 MHz, CD₂Cl₂): δ = 225.7 (2 C, CO), 208.1 (2 C, CO), 156.9, (2 C, C_{quart}), 47.1 (4 C, NCH₂), 45.1 (4 C, NCH₂), 22.8 (4 C, CH₂) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂): δ = -7.65 (s, 2 B, BH) ppm. IR (KBr): v = 2949 (m, C-H val.), 2928 (m, C-H val.), 2860 (m, C-H val.), 2758 (w, C-H val.), (2018) (m, B-H val.), 1904 (s, C=O val.), 1856 (s, C=O val.), 1834 (s, C=O val.), 1584 (s, C=N val.), 1560 (s, C=N val.), 1476 (m), 1462 (m), 1439 (m), 1404 (m), 1396 (m), 1371 (m), 1346 (m), 1319 (m), 1290 (m), 1275 (m), 1219 (m), 1186 (m), 1113 (m), 1097 (m), 1042 (m) cm⁻¹. MS (LIFDI): m/z (%) = 507 (100) [M]⁺, 301 (11) [LH]⁺. Crystal data for $C_{18}H_{26}B_2MON_6O_4$, Mr = 508.01, 0.40 x 0.35 x 0.35 mm³, monoclinic, space group C2/m, a = 17.260(3), b = 13.197(3), c = 17.260(3)10.373(2) Å, $\alpha = 115.40(3)^{\circ}$, V = 2134.4(9) Å³, Z = 4, d_{calc} = 1.581 Mg·m⁻³, Mo-K_{α} radiation (graphitemonochromated, $\lambda = 0.71073$ Å), T = 100 K, Θ_{range} 2.53 to 30.03 °. Reflections measd. 6054, indep. 3243, $R_{int} = 0.0274$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0308$, $wR_2 = 0.0806$.

$[W{HB(hpp)}_2(CO)_4]$

A mixture of dry $[W(CO)_6]$ (70 mg, 0.20 mmol) and $[HB(\mu-hpp)]_2$ (60 mg, 0.20 mmol) in dichloromethane (10 mL) stirred at room temperature was irradiated for 1 h with a 450 W medium pressure Hg lamp. The resulting solution was concentrated and the product precipitated by the addition of 10 mL of diethylether giving a yellow solid in 63 % yield (75 mg, 0.13 mmol). Crystals suitable for x-ray diffraction were obtained from a concentrated dichloromethane solution. C₁₈H₂₆B₂WN₆O₄ (595.90): calcd. C 36.28, H 4.40, N 14.10; found C 35.80, H 4.89, N 13.69. ¹H{¹¹B} NMR (400 MHz, CD_2Cl_2): $\delta = 3.35$ (t, ³J(H, H) = 5.8 Hz, 8 H, NCH₂), 3.16-3.10 (m, 4 H, NCH₂), 3.04-3.00 (m, 4 H, NCH₂), 1.93-1.85 (m, 8 H, CH₂), -3.26 (d, ${}^{1}J({}^{183}W, {}^{1}H) = 29.5$ Hz, 2 H, BH) ppm. ${}^{13}C{}^{1}H$ NMR (100 MHz, CD_2Cl_2): δ = 217.2 (2 C, CO), 203.9 (2 C, CO), 157.1, (2 C, C_{quart}), 47.0 (4 C, NCH₂), 45.0 (4 C, NCH₂), 22.7 (4 C, CH₂) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂): $\delta = -7.73$ (s, 2 B, BH) ppm. IR (KBr): v = 3287 (w), 3213 (w), 3157 (w), 2953 (m, C-H val.), 2934 (m, C-H val., 2858 (m, C-H val.), 2756 (w, C-H val.), 2041 (w, B-H val.}, 2012 (m, B-H val.), 1892 (s, C=O val.), 1856 (s, C=O val.), 1819 (s, C=O val.), 1638 (w), 1585 (s, C=N val.), 1560 (s, C=N val.), 1474 (m), 1458 (m), 1439 (m), 1404 (m), 1396 (m), 1371 (w), 1348 (m), 1321 (m), 1306 (m), 1290 (m), 1275 (m), 1221 (m), 1182 (m), 1099 (w), 1045 (w) cm⁻¹. MS (LIFDI): m/z (%) = 594 (100) [M]⁺, 301 (7) [LH]⁺. Crystal data for $C_{18}H_{26}B_2WN_6O_4$, Mr = 595.91, 0.20 x 0.10 x 0.10 mm³, monoclinic, space group C2/m, a = 17.166(3), b = 13.209(3), c = 10.321(2) Å, α = 115.06(3)°, V = 2119.9(9) Å³, Z = 4, d_{calc} = 1.867 Mg·m⁻³, Mo-K_g radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, Θ_{range} 2.53 to 30.06 °. Reflections measd. 5870, indep. 3210, R_{int} = 0.0285. Final R indices $[I > 2\sigma(I)]$: R₁ = 0.0281, wR₂ = 0.0717.

$[Rh(cod){HB(hpp)}_2Cl]$

A mixture of dry $[Rh(\mu-Cl)cod]_2$ (49 mg, 0.10 mmol) and $[HB(\mu-hpp)]_2$ (60 mg, 0.20 mmol) in acetone (10 mL) was stirred at room temperature for 1.5 h developing a yellow suspension. The solvent was removed and the residue washed with 3 mL of acetone and diethylether giving the product in 84 % yield (92 mg, 0.17 mmol). Yellow crystals suitable for x-ray diffraction were obtained from a concentrated acetone solution. C₂₂H₃₈B₂ClN₆Rh (635.87): calcd. C 41.55, H 6.02, N 13.22; found C 42.08, H 6.19, N 12.87. 1 H 11 B NMR (400 MHz, CD₂Cl₂): δ = 3.50 (s, 4 H, CH), 3.38-3.26 (m, 8 H, NCH₂), 3.09-3.03 (m, 4 H, NCH₂), 3.01-2.95 (m, 4 H, NCH₂), 2.43-2.35 (m, 4 H, CH₂), 2.09 (s, 2 H, BH), 1.90-1.78 (m, 8 H, CH₂), 1.93-1.85 (m, 8 H, CH₂), 1.69-1.63 (dd, 4 H, ³J(H, H) = 7.9 Hz, ³J(H, H) = 7.3 Hz, CH₂) ppm. ${}^{13}C{}^{1}H{}$ NMR (100 MHz, CD₂Cl₂): $\delta = 73.2$ (4 C, CH), 47.3 (4 C, NCH₂), 46.4 (4 C, NCH₂), 31.9 (4 C, CH₂), 22.9 (4 C, CH₂) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂): δ = -7.59 (s, 2 B, BH) ppm. ¹⁰³Rh NMR (13 MHz, CD₂Cl₂): δ = -7327 (s, Rh) ppm. IR (KBr): v = 2999 (m, C-H val.), 2981 (m, C-H val.), 2951 (m, C-H val.), 2930 (m, C-H val.), 2857 (m, C-H val.), 2843 (m, C-H val.), 2828 (m, C-H val.), 2752 (m, C-H val.), 2367 (w), 2258 (w, B-H val.), 1576 (s, C=N val.), 1497 (m), 1476 (m), 1468 (m), 1458} (m), 1439 (m), 1396 (m), 1366 (m), 1325 (m), 1319 (m), 1306 (m), 1287 (m), 1271 (m), 1219 (m), 1180 (m), 1115 (m), 1099 (m), 1065 (m), 1045 (m) cm⁻¹. MS (LIFDI): m/z (%) = 546 (2) $[M-H]^+$, 512 (4) $[M-CI]^+$, 511 (9) $[M-H]^+$ $HCI]^{+}$, 301 (100) $[LH]^{+}$, 300 (49) $[LH]^{+}$. Crystal data for $C_{22}H_{38}B_2CIN_6Rh$, Mr = 546.56, 0.20 x 0.05 x 0.05 mm³, orthorhombic, space group P2(1)2(1)2(1), a = 7.8430(16), b = 15.131(3), c = 19.384(4) Å, V = 2300.3(8) Å³, Z = 4, d_{calc} = 1.578 Mg·m⁻³, Mo-K_a radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, Θ_{range} 2.50 to 27.52 °. Reflections measd. 43594, indep. 5288, R_{int} = 0.0985. Final R indices [I > $2\sigma(I)$]: R₁ = 0.0399, wR₂ = 0.0728.

$[Ir(cod){HB(hpp)}_2CI]$

A mixture of dry $[Ir(\mu-CI)cod]_2$ (69 mg, 0.10 mmol) and $[HB(\mu-hpp)]_2$ (60 mg, 0.20 mmol) in acetone (10 mL) was stirred at room temperature for 1.5 h developing a pale yellow suspension. The solvent was removed and the residue washed with 3 mL of acetone and diethylether giving the product in 72 % yield (92 mg, 0.14 mmol). Pale yellow crystals suitable for x-ray diffraction were obtained from a concentrated dichloromethane solution. $C_{22}H_{38}B_2CIN_6Ir$ (635.87): calcd. C 41.55, H 6.02, N 13.22; found C 41.98, H 6.27, N 13.03. ¹H{¹¹B} NMR (400 MHz, CD₂Cl₂): δ = 3.40-3.25 (m, 8 H, NCH₂), 3.18-2.95 (m, 12 H, NCH₂, CH₂), 2.17 (s, 4 H, CH₂), 1.93-1.74 (m, 8 H, CH₂), 1.53-1.43 (m, 4 H, CH₂), 0.67 (s, 2 H, BH) ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 158.9 (2 C, C_{quart}), 59.5 (4 C, CH₂), 47.2 (4 C, NCH₂), 46.7 (4 C, NCH₂), 33.0 (4 C, CH) 22.8 (4 C, CH₂) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂): δ = -4.69 (s, 2 B, BH) ppm. IR (KBr): v = 2976 (m, C-H val.), 2955 (m, C-H val.), 2951 (m, C-H val.), 2922 (m, C-H val.), 2855 (m, C-H val.), 2841 (m, C-H val.), 2828 m, (C-H val.), 2820 m, (C-H val.), 2749 w, (C-H val.), 2681 w, (C-H val.), 2282 w, (B-H val.), 1711 (w), 1584 s, (C=N val.), 1477 (m), 1468 (m), 1456 (m), 1437 (m), 1395 (m), 1396 (m), 1364 (m), 1350 (m), 1321 (m), 1306 (m), 1288 (m), 1271 (m), 1221 s, 1211 (m), 1182 (m), 1152 (m), 1119 (m), 1099 (m), 1047 (m), 1001 (m) cm⁻¹. MS (LIFDI): m/z (%) = 636 (100) [M]⁺, 301 (8) [LH]⁺. Crystal data for $C_{22}H_{38}B_2$ ClIrN₆, Mr = 635.85, 0.20 x 0.15 x 0.10 mm³, orthorhombic, space group P2(1)2(1)2(1), a = 7.9180(16), b = 15.021(3), c = 19.356(4) Å, V = 2302.1(8) Å³, Z = 4, d_{calc} = 1.835 Mg·m⁻³, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, Θ_{range} 2.50 to 31.26°. Reflections measd. 48045, indep. 7392, R_{int} = 0.0999. Final R indices [I > 2σ(I)]: R₁ = 0.0409, wR₂ = 0.0728.

NMR-Experiments

NMR spectra were recorded at 298 K on a Bruker AVII 400 spectrometer. ¹H NMR and ¹³C NMR chemical shifts are reported relative to residual resonances of the d_2 -dichloromethane solvent. ¹¹B NMR chemical shifts are referenced to BF₃·Et₂O.

The ¹J(B-H) coupling constants for the group 6 complexes and $[M(cod){HB(hpp)}_2]$ (M = Ir) were derived from the ¹H NMR spectrum at ambient temperature. Due to the overlap with other signals the coupling constant for M = Rh could not be determined in a similar fashion. The value given in Table 1 was estimated from a high-temperature ¹¹B NMR in d₈-toluene. However the coupling could not be fully resolved at elevated temperatures. This could explain the unexpected low value of ¹J(B-H) for the rhodium complex.

X-ray Crystallographic Studies

Crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. The measurement was made on a Nonius-Kappa CCD diffractometer with a low temperature unit using graphite-monochromated Mo- K_{α} radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.¹¹ All

calculations were performed using the SHELXT-PLUS software package. The structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.¹² Graphical handling of the structural data during solution and refinement was performed with XPMA.¹³ Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.

Details of the Quantum Chemical Calculations

Turbomole V. 6.1^{14} was used for all quantum chemical calculations. A combination of the BP86¹⁵ functional and the def2-SV(P)¹⁶ basis set in RI-approximation¹⁷ was applied for the optimization process. The program Multiwfn 2.2.1 Rev. 1^{18} was used to evaluate the topology of the electron-density and the laplacian for [Cr{HB(hpp)}₂(CO)₄].

A comparison between the bond distances and angles determined by x-ray diffraction and quantum chemical calculations is shown in tables S1 and S2.

Parameter	M =	Cr	M = Mo		M = W	
	exp.	calc.	exp.	calc.	exp.	calc.
d(B-B)	1.739(4)	1.730	1.742(3)	1.742	1.749(6)	1.745
d(B-H) ^a	1.24(9)	1.282	1.17(2)	1.287	1.28(6)	1.289
d(B…M) ^a	2.391(3)	2.379	2.051(2)	2.519	2.483(4)	2.524
d(H…M) ^a	1.94(3)	1.919	2.06(2)	2.056	1.99(5)	2.065
d(M-C) ^a	1.888(3)	1.855	2.011(3)	2.005	2.007(4)	2.023
d(C-O) ^a	1.166(3)	1.172	1.154(3)	1.173	1.158(6)	1.174
d(B-N) ^a	1.557(4)	1.558	1.543(2)	1.558	1.541(5)	1.556
a(B-B-H) ^a	122.2(12)	122.3	124.4(11)	124.2	122.2(18)	124.4
a(B-B-M) ^a	68.7(1)	68.7	69.6(9)	69.8	69.4(2)	69.8
a(B-H-M) ^a	95.1(20)	93.8	97.5(14)	95.0	96.2(28)	94.8

Table S1Experimental and theoretical parameters of the group 6 $[M{HB(hpp)}_2(CO)_4]$ (M = Cr,
Mo, or W) complexes. Bond distances (d) are given in Å, angles (a) in °. The
geometries were optimized in C_{2v} symmetry.

^a Averaged value.

Parameter	M = Rh		M = Ir		
	exp.	calc.	exp.	calc.	
d(B-B)	1.811(6)	1.796	1.836(8)	1.805	
Ч(р ц)	1.15(4)	1.246	1.21(5)	1.243	
u(b-11)	1.28(3)	1.284	1.29(4)	1.300	
d(P. M)	2.369(5)	2.369	2.289(6)	2.356	
u(BIVI)	2.498(4)	2.607	2.558(6)	2.645	
d(HM)	1.99(4)	1.930	1.91(6)	1.909	
u(n…wi)	2.29(3)	2.442	2.42(5)	2.531	
d(M-C) ^a	2.121(4)	2.136	2.117(6)	2.154	
d(M-Cl) ^a	2.403(1)	2.420	2.495(1)	2.439	
d(B-N) ^a	1.547(6)	1.565	1.543(7)	1.563	
a(B-B-H)	129.5(10)	130.5	129.7(21)	131.6	
$\gamma(\mathbf{P} \mathbf{P} \mathbf{M})$	64.4(2)	61.9	60.2(3)	60.5	
a(b-b-ivi)	72.0(2)	76.2	79.8(3)	77.7	
2(B-H-N4)	83.6(16)	83.2	80.9(21)	81.3	
a(b-m-ivi)	94.4(21)	92.8	91.7(32)	92.5	

Table S2Experimental and theoretical parameters of the group 9 $[M(cod){HB(hpp)}_2Cl]$ (M =
Rh, or Ir) complexes. Bond distances (d) are given in Å, angles (a) in °. The geometries
were optimized in C1 symmetry.

^a Averaged value.

The quantum chemical calculations on all complexes are in good agreement with the structures determined by x-ray diffraction. An AIM analysis was performed for $[Cr{HB(hpp)}_2(CO)_4]$ and $[Rh(cod){HB(hpp)}_2CI]$ however imputable to the known difficulties concerning electron density studies on compounds containing heavy elements the results for the group 9 complex should be interpreted with care.

For the Rh complex the AIM analysis shows that the electron density in the B-B bond is strongly decreased (0.130 e Å⁻³) while the value of the average electron density of the two B-H bonds (0.147 e Å⁻³) is close to the free ligand. These findings indicate a dominant B_2 -Rh interaction which is in good agreement with the IR and NMR data.

Literature

- 11 DENZO-SMN, Data processing software; Nonius: 1998; http://www.nonius.com.
- 12 SHELX G. M. Sheldrick, *Acta Cryst A*, 2008, **A64**, 112-122.
- Zsolnai, L.; Huttner, *G. XPMA*; University of Heidelberg: Heidelberg, Germany,
 1994; http://www.uniheidelberg.de/institute/fak12/AC/huttner/software/software.html.
- 14 TURBOMOLE V6.1 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007.
- 15 A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098.
- 16 F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.
- 17 K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* 1995, **242**, 652.
- 18 T. Lu, Multiwfn: A multifunctional wavefunction analyzer, Version 2.1.1.