Supporting Information for

Agostic BH interaction in a Rh(I)-Complex of an Anionic bis phosphine-borane Ligand.

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Experimental Section

General: All experiments were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under nitrogen from Na/benzophenone (diethylether, pentane). Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.130 MHz for ^{1}H, 121.495 MHz for ^{31}P, 155.505 MHz for ^{7}Li and 75.768 MHz for ^{11}B, and on a Bruker Avance 400 spectrometer operating at 100.613 MHz for ^{13}C. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P shifts are relative to a 85% H_3PO_4 external reference. ^{7}Li shifts are relative to a lithium chloride in D_2O external reference and ^{11}B shifts relative to a $BF_3 \bullet Et_2O$ external reference. Selectively decoupled ^{1}H NMR spectra were recorded on a Bruker Avance 500 Spectrometer. Coupling constants are given in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet, m, multiplet. Elemental analysis was performed by the "Service de Microanalyse du LCC". $RhCl_3$ hydrate was purchased from Strem. $dppm(BH_3)_2$[1] and $[Rh(COD)Cl]_2$[2] were prepared according to literature procedures.

Experimental procedures

$(H_3B)Ph_2P$-CHLi-$PPh_2(BH_3)$, Et_2O (**2**) :

A 1.6 M ethereal solution of MeLi (0.819 mL, 1.310 mmol) was added to a dry ether (5 mL) solution of $dppm(BH_3)_2$ (0.270g, 0.655 mmol) and stirred for 36 h at room temperature. The solvent was then removed under vacuum and the resulting solid washed copiously with dry pentane and dried under vacuum. The resulting compound was obtained as 1/1 lithium salt/diethylether adduct **1** as a white solid in nearly quantitative yield.

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.495 Hz): δ 8.95 (m); $^{11}B\{^1H\}$ NMR (C_6D_6, 75.768 Hz): δ -33.2 (bd, $^1J_{BP}$ = 64 Hz, BH_3); ^7Li (C_6D_6, 155.505 MHz): δ 0.95; ^1H (C_6D_6, 300.130 Hz): δ 7.83-7.96 (m, 8H, CH arom.), 7.00-7.13 (m, 12H, CH arom.), 4.00 (q, 4H, $^3J_{HH}$ = 7.06 Hz, CH_2 Et_2O), 1.45 (bs, BH_3), 1.33 (t, 1H, $^2J_{HP}$ = 13.60 Hz, PCH(Li)P), 0.87 (t, 6H, $^3J_{HH}$ = 7.06 Hz, CH_3 Et_2O); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.613 MHz): δ 140.59 (d, $^1J_{CP}$ = 68.63 Hz, C arom.), 132.25 (pt, J_{CP} = 4.79 Hz, CH arom.), 129.44 (s, CH arom.), 128.47 (pt, J_{CP} = 5.03 Hz, CH arom.), 66.67 (s, CH_2, Et_2O), 14.97 (s, CH_3 Et_2O), 8.53 (t, $^1J_{CP}$ = 70.46 Hz, CHLi).

$[(H_3B)Ph_2P]_2$CH-Rh(COD) (**3**):

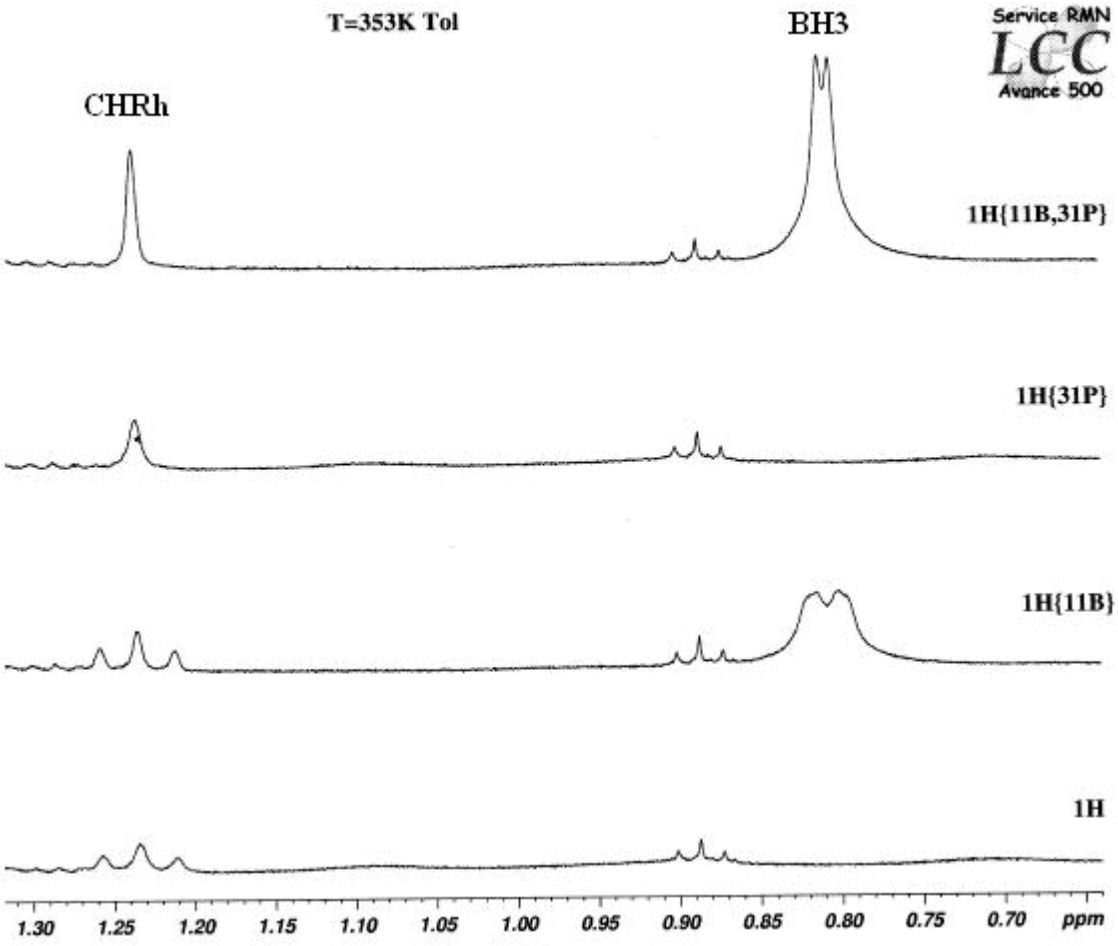
A C_6D_6 solution of **2** (0.067g, 0.136 mmol) was added to a room temperature C_6D_6 stirred solution of $[(COD)RhCl]_2$ (0.0336g, 0.068 mmol) and the reaction was monitored by ^{31}P NMR spectroscopy. After completion, the solvent was removed under vacuum. Pentane was added and the resulting suspension was filtered over cellite®. Removal of the solvent and drying under vacuum lead to complex **3** that was obtained as a greenish powder (0.040g) in 47% yield.

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.495 Hz): δ 4.88 (bs); $^{11}B\{^1H\}$ NMR (C_7D_8, 353 K, 160.526 Hz): δ -40.62 (d, $^1J_{PB}$ = 73 Hz, B); ^1H NMR (C_6D_6, 300.130 Hz): δ 8.10-8.20 and 7.50-7.60 (2 x m, 4H,

CH arom.), 7.00-7.13 and 6.60-6.80 (2 x m, 6H, CH arom.), 4.90 (m, 4H, CH=CH COD), 2.72 and 1.29 (bm, COD), 1.11 (t, $^{2}J_{HP}$ = 11.07 Hz, PCH(Rh)P), 1.09 (bm, BH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.613 Hz): δ 135.70 (d, $^{1}J_{PC}$ = 33.40 Hz, C_{ipso} Ar), 134.37 (dd, $^{1}J_{PC}$ = 66.04 Hz, $^{3}J_{PC}$ = 9.68 Hz, C_{ipso} Ar), 132.63 and 131.75 (2 x d, J_{PC} = 9.5 Hz, CH Ar), 130.78 and 130.11 (2 x d, $^{4}J_{PC}$ = 2.01 Hz, CH Ar), 128.82 and 128.35 (2 x d, J_{PC} = 9.85 Hz, CH Ar), 89.35 and 72.32 (2 x bs, CH COD), 31.88 and 29.04 (2 x bs, CH_2 COD), -3.72 (td, $^{1}J_{PC}$ = 15.42 Hz, $^{1}J_{RhC}$ = 18.89 Hz, CHRh).

Anal. calcd for $C_{33}H_{39}B_2P_2Rh$: C, 63.71; H, 6.32. Found: C, 63.51; H, 6.65.

Selectively decoupled ^{1}H NMR spectra of 3 in C_7D_8 at 353 K



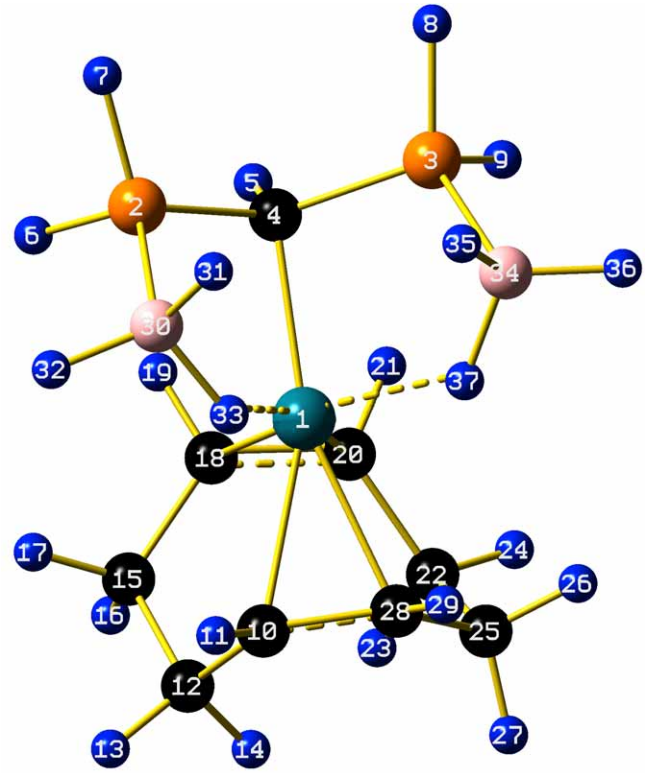
X-Ray crystal structure analysis

Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. The crystal structures were solved using SIR 97[3] and Shelxl-97.[4] ORTEP drawings were made using ORTEP III for Windows.[5] CCDC 725320 - 725321 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at **www.ccdc.cam.ac.uk/conts/** retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk

Theoretical Calculations

Calculations were performed with the GAUSSIAN 03 series of programs.[6] The B3PW91 functional [7] was used in combination with the 6-31+G* basis set for all non-metal-bound atoms (C, H, P), the 6-311+G* for all metal-bound-atoms (C, H, P, S) and the LANL2DZ basis[8] for iridium with an additional f-polarization function (exponent = 1.350).[9] The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency).

Cartesian coordinates, three lower frequencies and thermochemistry of I



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22	6	0	0.215851	1.527101	-2.618442
23	1	0	-0.665599	2.042947	-3.014340
24	1	0	1.073211	2.013424	-3.094075
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27	1	0	-0.265228	-0.097830	-3.998759
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33	1	0	-0.641276	-1.550276	0.975666
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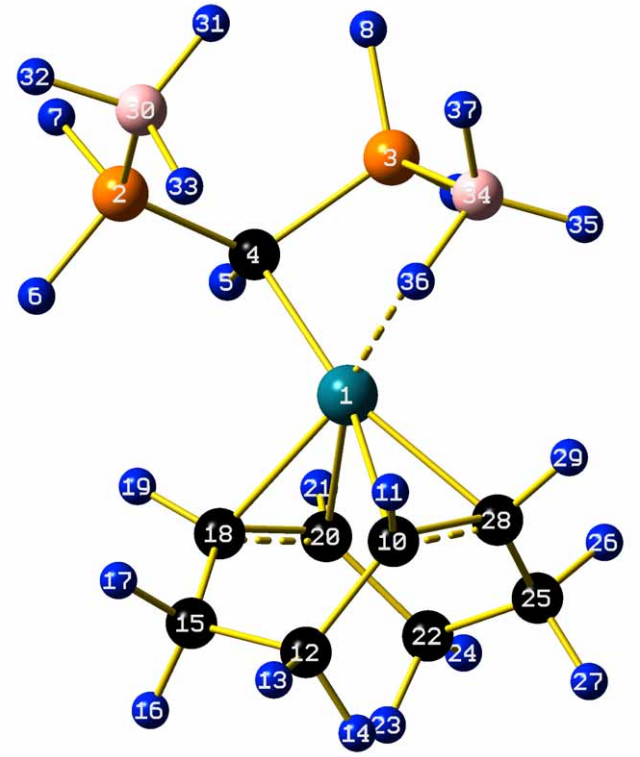
Cartesian coordinates, three lower frequencies and thermochemistry of II



Input orientation:

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27	1	0	-0.806344	0.692473	-3.737121
28	6	0	-0.312741	-0.502702	-2.010366
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35	1	0	2.719075	-1.030253	-0.787788
36	1	0	0.962790	-1.541237	0.173383
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	A	A	A
Frequencies --	32.5912	44.8499	52.3678
Red. masses --	3.2132	4.2388	3.1577
Frc consts --	0.0020	0.0050	0.0051
IR Inten --	4.5389	1.8882	4.1545

Sum of electronic and zero-point Energies= -1199.396470
Sum of electronic and thermal Energies= -1199.378530
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Sum of electronic and thermal Free Energies= -1199.442059

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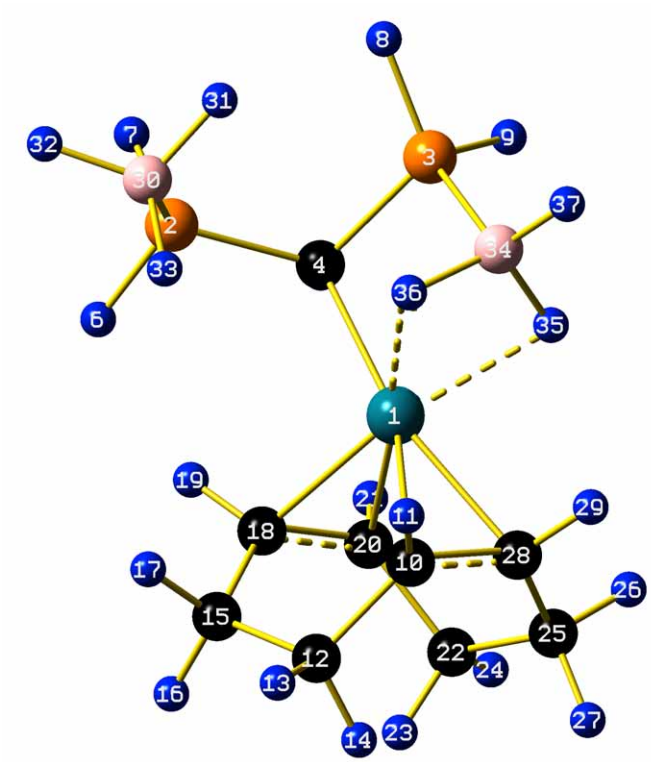
Cartesian coordinates, three lower frequencies and thermochemistry of III



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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IR Inten --	2.1237	7.2823	1.5845

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HF=-1199.6951394

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