

## Supporting Information

# Zwitterionic Half-Sandwich Rh and Ir Complexes Containing Diphosphine *Nido*-Carborane Ligand: Synthesis, Structure Transformation and Application on H<sub>2</sub> Activation

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## Experimental Details

**General Data.** All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, THF, or calcium hydride (dichloromethane) and methanol was distilled over Mg/I<sub>2</sub>. The starting materials 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>,<sup>1</sup> [Cp\*MC<sub>2</sub>]<sub>2</sub><sup>2</sup> (M = Ir, Rh) were synthesized according to the literature. D<sub>2</sub> gas was produced from the reaction of CD<sub>3</sub>OD and LiAlD<sub>4</sub> at -78°C. Other chemical reagents were obtained from commercial sources and used without further purification. <sup>1</sup>H NMR (400 MHz) and <sup>31</sup>P NMR (162 MHz) spectra were obtained on a VAVCE DMX-400 spectrometer. <sup>11</sup>B NMR (160 MHz) was obtained on a Bruker DMX-500 spectrometer. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

**Synthesis of 1a.** [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (197 mg, 0.25 mmol) was added to a solution of 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (256.3 mg, 0.5 mmol) in THF and CH<sub>3</sub>OH (5 mL/10 mL) at 0°C. Maintain this temperature for 0.5 h, NaHCO<sub>3</sub> (43.0 mg, 0.5 mmol) was then added to the solution and the mixture was stirred for 24 h at room temperature. After removal of the solvent under vacuum, **1a** was isolated by column chromatography on silica gel with elution CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (15:1). Yield: 76% (328.3 mg). Fine yellow crystals of **1a** were obtained through recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane at -18 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ = 1.84 (d, 15H, Cp\*, <sup>4</sup>J(PH) = 4.2 Hz), 7.41–7.91 ppm (m, 20H, phenyl); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25°C): δ = -6.8 (2B), -10.7 (1B), -11.2 (1B), -17.9 (2B), -22.0 (1B), -35.1 (1B), -37.6 ppm (1B); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, 25°C): δ = 75.98 ppm (s, PPh<sub>2</sub>); IR (KBr, disk): ν = 2567, 2535 (B–H), 1381 cm<sup>-1</sup> (C–H); elemental analysis calcd (%) for C<sub>36</sub>H<sub>45</sub>B<sub>9</sub>ClP<sub>2</sub>Ir: C 50.01, H 5.25; found: C 50.09, H 5.29.

**Synthesis of 1b.** A procedure analogous to the preparation of **1a** was used, [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (154.5 mg,

0.25 mmol) was added to a solution of 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (256.3 mg, 0.5 mmol) in THF and CH<sub>3</sub>OH (5 mL/10 mL) at 0°C. Maintain this temperature for 0.5 h, NaHCO<sub>3</sub> (43.0 mg, 0.5 mmol) was then added to the solution and the mixture was stirred for 24 h at room temperature. After removal of the solvent under vacuum, **1b** (244.1 mg) was obtained with the yield 63%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ = 1.41 (d, 15H, Cp\*, <sup>4</sup>J(P,H) = 3.0 Hz), 7.51–8.08 ppm (m, 20H, phenyl); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25°C): δ = -4.4 (1B), -7.2 (1B), -9.4 (2B), -11.7 (1B), -17.4 (2B), -32.5 (1B), -37.9 ppm (1B); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, 25°C): δ = 75.28 ppm (s, PPh<sub>2</sub>); IR (KBr, disk): ν = 2589, 2563 (B–H), 1381 cm<sup>-1</sup> (C–H); elemental analysis calcd (%) for C<sub>36</sub>H<sub>45</sub>B<sub>9</sub>ClP<sub>2</sub>Rh: C 55.65, H 5.84; found: C 55.61, H 5.88.

**Synthesis of 2a.** Et<sub>3</sub>N (11.1 mg, 0.1 mmol) was added to a solution of **1a** (86.5 mg, 0.1 mmol) in THF, and the mixture was refluxed for 4 h. The color gradually turned green from yellow and some white precipitate was formed, suggesting a formation of Cp\*Ir(7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>). The solvent was removed, and washed with hexane (5 mL). Finally the green solid was obtained with the yield 67% (55.5 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ = 1.87 (d, 15H, Cp\*, <sup>4</sup>J(P,H) = 2.6 Hz), 7.41–7.97 ppm (m, 20H, phenyl); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25°C): δ = -12.6 (1B), -16.9 (2B), -19.9 (2B), -25.7 (2B), -28.4 (1B), -42.5 ppm (1B); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, 25°C): δ = 58.84 ppm (s, PPh<sub>2</sub>); IR (KBr, disk): ν = 2550 (B–H), 1383 cm<sup>-1</sup> (C–H); elemental analysis calcd (%) for C<sub>36</sub>H<sub>44</sub>B<sub>9</sub>P<sub>2</sub>Ir: C 52.21, H 5.35; found: C 52.29, H 5.27.

**Synthesis of 2b.** The synthetic procedure is analogous to that of **2a**. **1b** (77.5, 0.1 mmol) and Et<sub>3</sub>N (11.1 mg, 0.1 mmol) were charged into a schlenk tube in THF. The mixture was refluxed for 4 h. And the color gradually turned purple and some white precipitate was formed. Then the solvent was removed, and washed with hexane (5 mL). Finally, purple solid was isolated with the yield 72% (53.2 mg). Crystals suitable for X-ray crystallography were grown from a CH<sub>2</sub>Cl<sub>2</sub> / hexane solution

at room temperature.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 1.60$  (d, 15H,  $\text{Cp}^*$ ,  $^4J(\text{P,H}) = 2.2$  Hz), 7.33–7.82 ppm (m, 20H, phenyl);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = -13.0$  (1B),  $-17.2$  (2B),  $-20.6$  (2B),  $-26.8$  (2B),  $-28.6$  (1B),  $-43.5$  (1B), ppm;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $25^\circ\text{C}$ ):  $\delta = 57.61$  ppm (s,  $\text{PPh}_2$ ); IR (KBr, disk):  $\nu = 2568$  (B–H),  $1381$   $\text{cm}^{-1}$  (C–H); elemental analysis calcd (%) for  $\text{C}_{36}\text{H}_{44}\text{B}_9\text{P}_2\text{Rh}$ : C 58.52, H 6.00; found: C 58.47, H 6.09.

**Synthesis of 3a.** **2a** (77.5 mg, 0.1 mmol) were charged into a schlenk tube in  $\text{CH}_3\text{OH}$  (10 mL). The mixture was refluxed in dark for 16 h. The color of the solution was changed to yellow from green. The solution was filtrated and the solvent was removed under reduced pressure. After washing with hexane (5 mL), the yellow **3a** was quantitatively obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 1.59$  (d, 15H,  $\text{Cp}^*$ ,  $^4J(\text{P,H}) = 5.0$  Hz), 7.42–7.84 ppm (m, 20H, phenyl).  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 20.7$  (1B), 13.9 (1B), 6.1 (1B), 4.6 (2B), 2.2(1B),  $-2.4$ (1B),  $-6.2$ (1B),  $-18.7$  ppm (1B);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $25^\circ\text{C}$ ):  $\delta = 91.70$  ppm (s,  $\text{PPh}_2$ ); IR (KBr, disk):  $\nu = 2562$  (B–H),  $1380$   $\text{cm}^{-1}$  (C–H); elemental analysis calcd (%) for  $\text{C}_{36}\text{H}_{44}\text{B}_9\text{P}_2\text{Ir}$ : C 52.21, H 5.35; found: C 52.14, H 5.37.

**Synthesis of 3b.** The synthetic procedure is analogous to that of **3a**. **2b** (77.5 mg, 0.1 mmol) were charged into a schlenk tube in  $\text{CH}_3\text{OH}$  (10 mL). The mixture was refluxed in dark for 16 h. The color of the solution was changed to orange-red from purple. After washing with hexane (5 mL), the yellow solid was quantitatively obtained.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 1.45$  (d, 15H,  $\text{Cp}^*$ ,  $^4J(\text{P,H}) = 3.8$  Hz), 7.53–8.12 ppm (m, 20H, phenyl);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 18.7$  (1B), 12.3 (2B), 11.6 (1B),  $-0.9$ (1B),  $-3.1$  (2B),  $-6.7$  (1B),  $-17.9$  ppm (1B);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $25^\circ\text{C}$ ):  $\delta 92.53$  ppm (s,  $\text{PPh}_2$ ); IR (KBr, disk):  $\nu = 2586$ , 2554 (B–H),  $1379$   $\text{cm}^{-1}$  (C–H); elemental analysis calcd (%) for  $\text{C}_{36}\text{H}_{44}\text{B}_9\text{P}_2\text{Rh}$ : C 58.52, H 6.00%; found: C 58.61, H 6.06.

**Synthesis of 4a. Method 1** A solution of **2a** (41.4 mg, 0.05 mmol) in  $\text{CH}_2\text{Cl}_2$  was bubbled with

excess H<sub>2</sub> gas for 20 h at room temperature. Then the solvent and the volatile substances were removed under reduced pressure. After washing with hexane (5 mL), the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane to the concentrated extract gave **4a** as a yellow crystal with the yield 79% (32.8 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ = -13.95 (d, Ir-H, <sup>2</sup>J(HP) = 28.0 Hz), 1.89 (d, 15H, Cp\*, <sup>4</sup>J(P,H) = 2.2 Hz), 7.40–7.62 ppm (m, phenyl); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25°C): δ -2.5 (1B), -9.4(2B), -13.2(2B), -19.6(2B), -24.8(1B), -38.7ppm (1B); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, 25°C): δ: 69.87 ppm (s, PPh<sub>2</sub>); IR (KBr, disk): ν = 2583, 2560, 2529 (B-H), 2129 (Ir-H), 1381 cm<sup>-1</sup> (C-H); elemental analysis calcd (%) for C<sub>36</sub>H<sub>46</sub>B<sub>9</sub>P<sub>2</sub>Ir: C 52.08, H 5.58; found: C 52.15, H 5.63.

**Method 2** The mixture of **1a** (86.5 mg, 0.1 mmol) and AgOTf (28.2 mg, 0.11 mmol) were charged into a schlenk tube in CH<sub>3</sub>OH. After stirring 4 h, the solution was filtrated and was treated with excess H<sub>2</sub> gas for 20 h at room temperature. Then the solvent and the volatile substances were removed under reduced pressure. After washing with hexane (5 mL), the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane to the concentrated extract gave **4a** a yellow crystal with the yield 52% (43.2 mg).

**Synthesis of 4b. Method 1** The synthetic procedure is analogous to that of **4a**. A solution of **2b** (36.9 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was treated with excess H<sub>2</sub> gas for 10 h at room temperature. Then the solvent and the volatile substances were removed under reduced pressure. After washing with hexane (5 mL), the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane to the concentrated extract gave **4b** as a red crystal with the yield 83% (30.75 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ = -13.88 (d, 1H, Rh-H, <sup>2</sup>J(H,P) = 22.0 Hz), 1.87 (d, 15H, Cp\*, <sup>4</sup>J(P,H) = 2.4 Hz), 7.43–7.82 ppm (m, phenyl); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25°C): δ = -4.5 (1B), -8.7 (1B), -11.7 (1B), -15.3 (1B), -19.8 (2B), -22.5 (1B), -35.3 (1B), -38.7 ppm (1B); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>,

H<sub>3</sub>PO<sub>4</sub>, 25°C):  $\delta$  = 68.86 ppm (s, PPh<sub>2</sub>); IR (KBr, disk):  $\nu$  = 2588, 2562, 2520 (B–H), 2120 (Rh–H), 1383 cm<sup>-1</sup> (C–H); elemental analysis calcd (%) for C<sub>36</sub>H<sub>46</sub>B<sub>9</sub>P<sub>2</sub>Rh: C 58.36, H 6.26; found: C 58.35, H 6.29.

**Method 2** The synthetic procedure is analogous to that of **4a**. The mixture of **1b** (77.5, 0.1 mmol) and AgOTf (28.2 mg, 0.11 mmol) were charged into a schlenk tube in CH<sub>3</sub>OH. After stirring 4 h, the solution was filtrated and was treated with excess H<sub>2</sub> gas for 10 h at room temperature. After washing with hexane (5 mL), the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane to the concentrated extract gave **4b** as a red crystal with the yield 46% (34.1 mg).

**Synthesis of Cp\*Rh(D)(7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>D).** A solution of **2b** (36.9 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was treated with excess D<sub>2</sub> gas for 10 h at room temperature. Then the solvent and the volatile substances were removed under reduced pressure. After washing with hexane (5 mL), the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane to the concentrated extract gave a red crystal. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.81 (d, 15H, Cp\*, <sup>4</sup>J(P,H) = 2.8 Hz), 7.27–7.75 ppm (m, phenyl).

**X-Ray Crystallography.** Diffraction data of **1a**, **1b**, **3b**, and **4b** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on  $F^2$  by using full-matrix least-squares techniques (SHELXL),<sup>3</sup> SADABS<sup>4</sup> absorption corrections were applied to the data. All the non-hydrogen atoms except those disordered ones were refined anisotropically. In complex **3b**, pentamethylcyclopentadienyl ligand in the asymmetric unit was disordered because of rotation in room temperature. It was refined to two idealized positions (46:54) and 20 ISOR instructions were used to restrain atoms of it. As a result, there were 20 Uiso/Uij restrained atom sites and 120 least-squares restraints in the refinement. Most

hydrogen atoms were located at calculated positions but some one (H9, H10A,B and H11' in 1a and 1b; H4A, H6A, H7A, H8A in 3b; H1A, H3A, H3B, H6A in 4b) were found by difference Fourier method. A summary of the crystallographic data and selected experimental information are given in Table 1.

## References

- 1 R. P. Alexander, H. A. Schroeder, *Inorg. Chem.* 1963, 2, 1107–1110.
- 2 C. A. White, P. M. Yates, Maitlis, *Inorg. Synth.* 1992, 29, 228–234.
- 3 Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*, Universität Göttingen: Germany, 1997.
- 4 Sheldrick, G. M. *SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program*; Bruker AXS: Madison, WI, 1998.

**Table 1. Crystallographic Data and Structure Refinement Parameters for 1a, 1b, 3b, 4b.**

	<b>1a</b> ·CH <sub>2</sub> Cl <sub>2</sub>	<b>1b</b> ·CH <sub>2</sub> Cl <sub>2</sub>	<b>3b</b>	<b>4b</b>
empirical formula	C <sub>37</sub> H <sub>47</sub> B <sub>9</sub> C <sub>13</sub> P <sub>2</sub> Ir	C <sub>37</sub> H <sub>47</sub> B <sub>9</sub> C <sub>13</sub> P <sub>2</sub> Rh	C <sub>36</sub> H <sub>44</sub> B <sub>9</sub> P <sub>2</sub> Rh	C <sub>36</sub> H <sub>46</sub> B <sub>9</sub> P <sub>2</sub> Rh
formula weight	949.53	860.24	738.85	740.87
crystal syst, space group	Triclinic, P-1	Triclinic, P-1	Monoclinic, P2(1)/n	Monoclinic, P2(1)/m
<i>a</i> (Å)	10.584(4)	10.556(3)	11.469(4)	9.646(3)
<i>b</i> (Å)	11.279(4)	11.240(4)	19.555(7)	19.419(6)
<i>c</i> (Å)	18.270(6)	18.262(6)	17.854(7)	10.436(3)
<i>α</i> (deg)	76.059(4)	76.758(4)	90	90
<i>β</i> (deg)	74.745(4)	74.904(4)	104.924(5)	110.175(3)
<i>γ</i> (deg)	84.583(4)	84.873(3)	90	90
volume (Å <sup>3</sup> ), Z	2041.1(12), 2	2035.3(11), 2	3869(3), 4	1835.0(10), 2
Dc(g cm <sup>-3</sup> )	1.545	1.404	1.268	1.341
<i>μ</i> (Mo Kα) (mm <sup>-1</sup> )	3.573	0.723	0.549	0.579
<i>F</i> (000)	944	880	1520	764
<i>θ</i> range (deg)	1.86 - 26.01	1.86 - 26.01	1.57 - 27.01	2.08 - 27.00
limited indices	-12,13;-13,12; -22,18	-13,10;-13,13; -22,12	-14,14;-24,23; -22,15	-9,12;-24,22; -13,12
Reflections/unique [R(int)]	9254/7782 [0.0392]	9221/7761 [0.0292]	18585/8205 [0.0531]	8864/4022 [0.0305]
completeness to <i>θ</i> (deg)	26.01(97.0%)	26.01(96.9%)	27.01(97.1 %)	27.00(97.3%)
data/restraints/parameters	7782/0/496	7761/0/496	8205/122/500	4022/0/245
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.963	1.004	0.904	1.065
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>a</sup> [I>2σ(I)]	0.0429, 0.1000	0.0387, 0.0996	0.0514, 0.1260	0.0488, 0.1288
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0522, 0.1032	0.0480, 0.1041	0.0880, 0.1352	0.0588, 0.1358

[a]  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum F_o^2}$  (based on reflections with  $F_o^2 > 2\sigma F^2$ ).  $wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]]^{1/2}}{[\sum w(F_o^2)^2]^{1/2}}$ ;  $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  (also with  $F_o^2 > 2\sigma F^2$ )





