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New Bidentate Cationic and Zwitterionic Relatives of Crabtree's Hydrogenation Catalyst

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- **General Protocol for Hydrogenation Experiments**
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Experimental Section

General Considerations. Unless stated otherwise, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite[®] (Aldrich) was oven dried (130 °C) for 5 d and then evacuated for 24 h prior to use. The non-deuterated solvents dichloromethane, tetrahydrofuran, diethyl ether, toluene, benzene, hexanes, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system provided by mBraun Inc.

Dichloromethane, tetrahydrofuran, and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, hexanes, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Purification of NEt₃ was achieved by stirring over KOH for 7 d, followed by distillation; the distilled NEt₃ was then refluxed over CaH₂ for 3 d under dinitrogen, followed by distillation. C₆D₆ and CD₂Cl₂ (Aldrich) were degassed by using three repeated freeze-pump-thaw cycles and CD₂Cl₂ was dried over CaH₂ for 7 d, and distilled *in vacuo*. All deuterated and non-deuterated solvents used within the glovebox were stored over activated 3 Å molecular sieves for 24h prior to use. Styrene, cyclohexene, and 1-methylcyclohexene (Aldrich) were degassed by using three repeated freeze-pump-thaw cycles and dried over activated 3 Å molecular sieves for 7 d prior to use. Compounds 1-PⁱPr₂-2-NMe₂-indene¹ and [(η⁴-1,5-cyclooctadiene)IrCl]₂² were prepared by employing published procedures. All other commercial reagents were obtained from Aldrich and were used as received, with the exception that all silver salts were dried *in vacuo* for 12 h prior to use, hydrogen (99.999%, UHP Grade) was obtained from Air Liquide, and [1]⁺PF₆⁻ was obtained from Strem. Unless otherwise stated, ¹H, ¹³C, and ³¹P NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe₄ (for ¹H and ¹³C) or 85% H₃PO₄ in D₂O (for ³¹P).

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In some cases slightly fewer than expected independent ^1H or ^{13}C NMR resonances were observed

(despite prolonged data acquisition times). ^1H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{13}C -DEPT, ^1H - ^1H COSY, ^1H - ^{13}C HSQC, and ^1H - ^{13}C HMBC NMR experiments.

Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

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2 J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth.* 1974, **15**, 18.

Preparation of $[\mathbf{2}]^+\text{SO}_3\text{CF}_3^-$. To a solution of $[\text{IrCODCl}]_2$ (0.10 g, 0.15 mmol) in THF (3 mL) was added a solution of AgSO_3CF_3 (0.076 g, 0.30 mmol) in THF (2 mL) via Pasteur pipette. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite to yield a clear bright yellow solution, to which a solution of 1- P^iPr_2 -2-NMe₂-indene (0.082 g, 0.30 mmol) in THF (1.5 mL) was added, with immediate formation of a dark red solution. After magnetically stirring the solution for 1 h, the supernatant was decanted from any precipitate that had formed and NEt₃ (0.4 mL, 3 mmol) was added via syringe to the solution to facilitate the rearrangement of 1- P^iPr_2 -2-NMe₂-indene to 3- P^iPr_2 -2-NMe₂-indene within the coordination sphere of Ir. After 30 min, the solvent and other volatile materials were removed *in vacuo* to leave a dark brown sticky solid. This solid was washed with toluene (2 x 2 mL) and pentane (2 mL) to leave $[\mathbf{2}]^+\text{SO}_3\text{CF}_3^-$ as an analytically pure orange solid (0.10 g, 0.14 mmol, 47 %). Anal. Calcd for C₂₆H₃₈PNIrOSF₃: C 43.08; H 5.28; N 1.93. Found: C 42.96; H 5.09; N 1.78. ^1H NMR (CD₂Cl₂): δ 7.52-7.48 (m, 2H, Ar-Hs), 7.38-7.34 (m, 2H, Ar-Hs), 4.81-4.76 (m, 2H, COD), 4.26-4.20 (m, 2H, COD), 3.80 (s, 2H, C1(H)₂), 3.13 (s, 6H, NMe₂), 3.06-2.99 (m, 2H, P(CHMe₂)₂), 2.32-2.26 (m, 4H, COD), 1.94-1.90 (m, 4H, COD), 1.38 (d of d, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{PH}} = 17.5$ Hz, 6H, P(CHMe_aMe_b)₂), 1.30 (d of d, $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{PH}} = 15.5$ Hz, 6H, P(CHMe_aMe_b)₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 195.9 (SO₃CF₃), 179.5 (d, $^2J_{\text{PC}} = 16.0$ Hz, C2), 144.2 (d, $^2J_{\text{PC}} = 6.0$ Hz, C3a), 136.9 (C7a), 130.7 (d, $^1J_{\text{PC}} = 34.8$ Hz, C3), 127.4, 127.2, 125.9, 122.6 (C4, C5, C6,

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C7), 93.4 (d, $^2J_{PC} = 11.3$ Hz, COD), 59.8 (COD), 52.2 (NMe₂), 33.0 (d, $^3J_{PC} = 2.6$ Hz, COD), 31.6 (d,

$^3J_{PC} = 9.5$ Hz, C1), 28.8 (COD), 25.4 (d, $^1J_{PC} = 30.4$ Hz, P(CHMe₂)₂), 19.7 (P(CHMe_aMe_b)₂), 18.5

(P(CHMe_aMe_b)₂); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): δ 35.9. Crystals suitable for single crystal X-ray diffraction

analysis were obtained from a concentrated THF solution of [2]⁺SO₃CF₃⁻ at room temperature (0.22

mm x 0.14 mm x 0.08 mm).

Preparation of [2]⁺BF₄⁻. To a solution of [IrCODCl]₂ (0.050 g, 0.075 mmol) in THF (3 mL) was added a solution of AgBF₄ (0.032 g, 0.16 mmol) in THF (2 mL) via Pasteur pipette. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite to yield a clear bright yellow solution, to which a solution of 1-P^{*i*}Pr₂-2-NMe₂-indene (0.041 g, 0.149 mmol) in THF (1.5 mL) was added, with formation of a yellow-red solution. After 1.5 h, the solvent and volatile materials were removed *in vacuo* to leave a sticky brown solid. The solid was washed with toluene (2 mL) and subsequently with pentane (2 mL) to leave [2]⁺BF₄⁻ as an analytically pure orange powder (0.037 g, 0.056 mmol, 37 %). Anal. Calcd for C₂₅H₃₈PNIrBF₄: C 45.32; H 5.78; N 2.11. Found: C 45.39; H 5.70; N 2.15. All ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR data for the cation were identical to those reported for [2]⁺SO₃CF₃⁻.

Preparation of [2]⁺PF₆⁻. To a solution of [IrCODCl]₂ (0.060 g, 0.090 mmol) in THF (3 mL) was added a solution of AgPF₆ (0.045 g, 0.18 mmol) in THF (2 mL) via Pasteur pipette. Immediate formation of a white precipitate was observed. After 5 min, a solution of 1-P^{*i*}Pr₂-2-NMe₂-indene (0.049 g, 0.18 mmol) in THF (3 mL) was added, with immediate formation of a dark red solution. The reaction vial was then sealed and shaken vigorously for 30 s, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite, and to the filtrate was added NEt₃ (0.075 mL, 0.54 mmol) to facilitate the rearrangement of 1-P^{*i*}Pr₂-2-NMe₂-indene to 3-P^{*i*}Pr₂-2-NMe₂-indene within the coordination sphere of Ir. The reaction mixture sealed and manually shaken for 10 s, and then was left to settle. After 5 min, the solvent and other volatile materials were removed *in vacuo*

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to leave a sticky orange-brown solid. The product was extracted into CH₂Cl₂ (5 mL) and the mixture filtered over Celite in order to remove any insoluble materials. The filtrate was then pumped to dryness and the resulting sticky orange solid was washed once with pentane (2 mL). The solid was dried *in vacuo* to leave [2]⁺PF₆⁻ as an analytically pure orange powder (0.101 g, 0.140 mmol, 78 %). Anal. Calcd for C₂₅H₃₈P₂NIrF₆: C 41.66; H 5.31; N 1.94. Found: C 41.44; H 5.41; N 2.11. All ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR data for the cation were identical to those reported for [2]⁺SO₃CF₃⁻.

Preparation of 3: To a solution of 1-P^tPr₂-2-NMe₂-indene (0.081 g, 0.29 mmol) in THF (4 mL) (pre-cooled to -35 °C) was added *n*-BuLi (0.19 mL of 1.6 M hexanes solution, 0.30 mmol) via syringe. After 1 h at room temperature, the solvent and other volatile materials were removed *in vacuo* to leave an off-white solid, which was washed with Et₂O (2 x 2 mL) to remove any unreacted *n*-BuLi. The resulting white solid was dissolved in toluene (3 mL), and to this solution was added [IrCODCl]₂ (0.099 g, 0.15 mmol) in toluene (3 mL) via Pasteur pipette; the solution instantly darkened to ruby red. After 40 min, the reaction mixture was filtered through Celite to remove any precipitate. The solvent and any other volatile materials were then removed *in vacuo* to yield **3** as an analytically pure dark orange solid (0.16 g, 0.27 mmol, 93 %). Anal. Calcd for C₂₅H₃₇PNi: C 52.24; H 6.49; N 2.44. Found: C 52.53; H 6.44; N 2.68. ¹H NMR (C₆D₆): δ 7.98 (d, ³J_{HH} = 11.0, 1H, C7-H), 7.80 (d, ³J_{HH} = 8.0, 1H, C4-H), 7.39-7.32 (m, 2H, C6-H and C5-H), 6.30 (d, *J* = 3.7 Hz, 1H, C1-H), 3.88-3.84 (m, 4H, COD), 2.75 (s, 6H, NMe₂), 2.74-2.68 (m, 2H, P(CHMe₂)₂), 1.95-1.79 (m, 4H, COD), 1.41-1.36 (m, 2H, COD), 1.33-1.26 (m, 2H, COD), 1.18 (d of d, ³J_{HH} = 7.0 Hz, ³J_{PH} = 15.1 Hz, 6H, P(CHMe_aMe_b)₂), 1.05 (d of d, ³J_{HH} = 7.2 Hz, ³J_{PH} = 15.9 Hz, 6H, P(CHMe_aMe_b)₂); ¹³C{¹H} NMR (C₆D₆): δ 164.5 (d, ²J_{PC} = 22.8 Hz, C2), 139.3 (d, *J* = 10.2 Hz, C3, C3a, or C7a), 130.6 (C3, C3a, or C7a), 121.5, 119.8, 116.9, 116.7 (C4, C5, C6, and C7), 87.3 (d, ³J_{PC} = 11.2 Hz, C1), 84.7 (d, *J*_{PC} = 11.8 Hz, COD), 54.8 (NMe₂), 54.6 (COD), 32.8 (d, *J*_{PC} = 2.3 Hz, COD), 28.7 (COD), 26.4 (d, ¹J_{PC} = 33.8 Hz, P(CHMe₂)₂), 19.6 (P(CHMe_aMe_b)₂), 19.1 (P(CHMe_aMe_b)₂); ³¹P{¹H} NMR (C₆D₆): δ 25.0. Crystals suitable for single crystal X-ray

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diffraction analysis were grown from a concentrated toluene solution of **3** at room temperature (0.36 mm x 0.18 mm x 0.13 mm).

General Protocol for Hydrogenation Experiments. The protocol used for hydrogenation reactions employing 0.5 mol% catalyst loading in CH₂Cl₂ is provided as a representative procedure. A solution of catalyst compound in CH₂Cl₂ (0.002 M in 7 mL solvent) was allowed to equilibrate for 5 min, at which point the alkene (0.4 M in 7 mL) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously. Subsequently, 1 mL aliquots of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and degassed by use of three freeze-pump-thaw cycles employing liquid nitrogen. Magnetic stirring of the solutions was initiated and the evacuated cells were backfilled with hydrogen gas (~ 1atm, UHP grade). With the exception of the noted experiments in which the catalyst was not fully soluble, clear yellow homogeneous solutions were observed throughout. At the desired sampling time, the reactor cell was opened to air and 2 mL of hexanes (or pentane in the case of the hydrogenation of cyclohexene) was added via Pasteur pipette. The resultant slurries were then filtered through a short Al₂O₃ column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS and quantitative data were obtained from GC-FID analysis; tabulated data represent the average of two runs.

Crystallographic Solution and Refinement Details

Both crystallographic data sets were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. The structures were solved by use of direct methods and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic

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displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen-
atoms were added at calculated positions and refined by use of a riding model employing isotropic
displacement parameters based on the isotropic displacement parameter of the attached atom.