Electronic Supplementary Information for:

Protonation and electrochemical reduction of rhodium- and iridium-dinitrogen complexes in organic solution

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Supplementary Data and Spectra:

Fig. S1: FTIR spectrum of 1

\[ \nu_{NN} = 2125 \text{ cm}^{-1} \]

Fig. S2: FTIR spectrum of 2

\[ \nu_{NN} = 2078 \text{ cm}^{-1} \]
**Fig. S3:** $^1$H NMR spectra showing protonation of 1 with TFA in THF-$d_8$.

**Bottom (1, maroon):** 1.7 mg 1 (3.2 µmol) in THF-$d_8$. $^1$H NMR (500 MHz, THF-$d_8$): $\delta = 6.80$ (d, $^3J_{H,H} = 7.3$ Hz, 2H, m-Ph), 6.59 (t, $^3J_{H,H} = 7.3$ Hz, 1H, p-Ph), 3.23 (m, 4H, CH$_2$), 1.35 (m, $^2J_{P,H} = 6.2$ Hz, 36H, C(CH$_3$)$_3$).

**Top (2, teal):** 1.7 mg 1 in THF-$d_8$ with 1.1 eq. TFA added. $^1$H NMR (500 MHz, THF-$d_8$, 1a): $\delta = 6.85$ (d, $^3J_{H,H} = 7.3$ Hz, 2H, m-Ph), 6.72 (t, $^3J_{H,H} = 7.3$ Hz, 1H, p-Ph), 3.38 – 3.13 (m, 4H, CH$_2$), 1.32 (m, $^2J_{P,H} = 6.4$ Hz, 36H, C(CH$_3$)$_3$), -25.60 (dt, $^1J_{Rh,H} = 45.4$, $^2J_{P,H} = 11.8$ Hz, 1H, Rh-H). The spectrum describes a diamagnetic complex, and the loss of C$_{2v}$ symmetry is evident from splitting of methylene and tBu resonances. A hydride peak is visible at -25.60 ppm. The PMe$_3$ peak is from the internal standard in a capillary tube.
**Fig. S4:** $^{31}$P{^1}H NMR spectra showing protonation of 1 with TFA in THF-$d_8$

**Bottom (1, maroon):** 1.7 mg 1 (3.2 µmol) in THF-$d_8$. $^{31}$P{^1}H NMR (162 MHz, THF-$d_8$): $\delta = 81.48$ (d, $J_{P,Rh} = 158.2$ Hz). **Top (2, teal):** 1.7 mg 1 in THF-$d_8$ with 1.1 eq. TFA added. $^{31}$P{^1}H NMR (202 MHz, THF-$d_8$): $\delta = 77.61$ (dd, $J_{P,Rh} = 116.4$ Hz, $J_{P,H} = 6.8$ Hz, 1a). Referenced to PMe₃ in a capillary tube.
Fig. S5: $^{19}$F NMR spectra showing protonation of 1 with TFA in THF-$d_8$

Bottom (1, maroon): 3.0 µmol TFA in THF-$d_8$. $^{19}$F NMR (470 MHz, THF-$d_8$): $\delta = -80.67$ (s). Top (2, teal): 3.0 µmol TFA with 1.4 mg 1 (2.7 µmol, 0.9 eq.) added in THF-$d_8$. $^{19}$F NMR (470 MHz, THF-$d_8$): $\delta = -79.70$ (s), -80.28 (br. s).
**Fig. S6:** $^{31}$P($^1$H) NMR spectra showing protonation of 1 with pCAH-BF$_4$ and deprotonation of 1b with DBU under N$_2$.

**Bottom (1, maroon):** 1.2 mg 1 (2.3 µmol) in THF-$d_8$ under N$_2$. $^{31}$P($^1$H) NMR (202 MHz, THF-$d_8$): $\delta = 81.52$ (d, $^{1}J_{P,Rh} = 157.9$ Hz, 100%).

**Middle (2, green):** 1.2 mg 1 with 1 eq. pCAH-BF$_4$ in THF-$d_8$ under N$_2$. $^{31}$P($^1$H) NMR (202 MHz, THF-$d_8$): $\delta = 77.83$ (d, $^{1}J_{P,Rh} = 117.4$ Hz, 90%, 1b), 74.81 (d, $^{1}J_{P,Rh} = 112.7$ Hz, 10%).

**Top (3, blue):** 1.2 mg 1 with 1 eq. pCAH-BF$_4$ and 1.1 eq. DBU in THF-$d_8$ under N$_2$. $^{31}$P($^1$H) NMR (202 MHz, THF-$d_8$): $\delta = 81.53$ (d, $^{1}J_{P,Rh} = 157.9$ Hz, 90%), 74.80 (d, $^{1}J_{P,Rh} = 115.2$ Hz, 10%). Protonation of 1 with pCAH-BF$_4$ under N$_2$ gives 1b, and subsequent addition of DBU reforms complex 1 in 90% yield. Integrations are referenced to an internal standard of PMe$_3$ in a capillary tube, and yields are rounded to one significant figure.
Fig. S7: $^{31}\text{P}^{1}\text{H}$ NMR spectra showing protonation of 1 with $p$CAH-BF$_4$ and deprotonation of 1b with DBU under Ar.

**Bottom (1, maroon):** 1.3 mg 1 (2.5 µmol) in THF-$d_8$ under Ar. $^{31}\text{P}^{1}\text{H}$ NMR (202 MHz, THF-$d_8$): δ = 81.52 (d, $^1J_{\text{P,Rh}} = 158.0$ Hz, 100%).

**Middle (2, green):** 1.3 mg 1 with 1 eq. $p$CAH-BF$_4$ in THF-$d_8$ under Ar. $^{31}\text{P}^{1}\text{H}$ NMR (202 MHz, THF-$d_8$): δ = 81.52 (d, $^1J_{\text{P,Rh}} = 157.7$ Hz, 10%), 77.82 (br. d, $^1J_{\text{P,Rh}} = 121.2$ Hz, 70%, 1b), 75.45 (d, $^1J_{\text{P,Rh}} = 120.6$ Hz, 20%).

**Top (3, blue):** 1.3 mg 1 with 1 eq. $p$CAH-BF$_4$ and 1.1 eq. DBU in THF-$d_8$ under Ar. $^{31}\text{P}^{1}\text{H}$ NMR (202 MHz, THF-$d_8$): δ = 93.25 (d, $^1J_{\text{P,Rh}} = 154.0$ Hz, 10%), 81.54 (d, $^1J_{\text{P,Rh}} = 159.7$ Hz, 20%), 74.80 (d, $^1J_{\text{P,Rh}} = 115.0$ Hz, 10%), 74.28 (d, $^1J_{\text{P,Rh}} = 178.3$ Hz, 70%). Integrations are referenced to an internal standard of PMe$_3$ in a capillary tube, and yields are rounded to one significant figure.
**Fig. S8:** VT $^1$H NMR spectra upon protonation of 2 with DMAH-BF$_4$ to form 2a

**Bottom (1, maroon):** 3.4 mg 2 (5.5 µmol) in THF-$d_8$. $^1$H NMR (500 MHz, THF-$d_8$, 2): $\delta = 6.83$ (d, $^3$J$_{H,H} = 7.4$ Hz, 2H, m-Ph), 6.54 (t, $^3$J$_{H,H} = 7.4$ Hz, 1H, p-Ph), 3.25 (m, 4H, CH$_2$), 1.33 (m, $^3$J$_{P,H} = 6.4$ Hz, 36H, C(CH$_3$)$_3$).

**Second to bottom (2, gold):** 3.4 mg 2 (5.5 µmol) with 1 eq. DMAH-BF$_4$ in THF-$d_8$ at 25 °C. $^1$H NMR (500 MHz, THF-$d_8$, 2a) $\delta = 6.75$ (d, $^3$J$_{H,H} = 7.5$ Hz, 2H, m-Ph), 6.57 (t, $^3$J$_{H,H} = 7.5$ Hz, 1H, p-Ph), 3.50 – 3.15 (m, 4H, CH$_2$), 1.34 (m, $^3$J$_{P,H} = 6.7$ Hz, 18H, C(CH$_3$)$_3$), 1.27 – 1.15 (m, 18H, C(CH$_3$)$_3$). The spectrum describes a diamagnetic complex, and the loss of C$_2v$ symmetry is evident from splitting of methylene and tBu resonances; however, no hydride resonance is resolved at ambient temperature. **Third from bottom and upwards (3-7, green through plum):** 3.4 mg 2 (5.5 µmol) with 1 eq. DMAH-BF$_4$ in THF-$d_8$ at various temperatures. A hydride resonance resolves at low temperatures and is visible at -40 °C at $\delta = -36.7$ (br. s, 1H, Ir-H).
Fig. S9: VT $^{31}\text{P}^{1}\text{H}$ NMR spectra upon protonation of 2 with DMAH-BF$_4$ to form 2a

-40 °C

-30 °C

-20 °C

-10 °C

0 °C

25 °C

Bottom (1, maroon): 3.4 mg 2 (5.5 µmol) in THF-$d_8$. $^{31}\text{P}^{1}\text{H}$ NMR (202 MHz, THF-$d_8$, 2): $\delta = 72.80$ (s).

Second to bottom (2, gold): 3.4 mg 2 (5.5 µmol) with 1 eq. DMAH-BF$_4$ in THF-$d_8$ at 25 °C. No phosphorus resonance is visible for the diamagnetic complex described in the corresponding $^1$H NMR spectrum (see Fig. S8).

Third from bottom and upwards (3-7, green through plum): 3.4 mg 2 (5.5 µmol) with 1 eq. DMAH-BF$_4$ in THF-$d_8$ at various temperatures. A phosphorus resonance resolves at low temperatures and is visible at -40 °C at $\delta = 69.15$ (br. s).
Fig. S10: $^{31}$P{$^1$H} NMR spectra showing deprotonation of 2a with DBU under N$_2$.

Bottom (1, maroon): 2.8 mg 2 (4.6 µmol) in THF-$d_8$. $^{31}$P{$^1$H} NMR (202 MHz, THF-$d_8$, 2): $\delta = 72.80$ (s).

Middle (2, green): 2.8 mg 2 (4.6 µmol) with 1 eq. DMAH-BF$_4$ in THF-$d_8$. No phosphorus resonance is visible for the diamagnetic complex 2a at 25 °C (see Fig. S9).

Top (3, blue): 2.8 mg 2 (4.6 µmol) with 1 eq. DMAH-BF$_4$ and 1.1 eq. DBU in THF-$d_8$. $^{31}$P{$^1$H} NMR (202 MHz, THF-$d_8$): $\delta = 72.80$ (s). 2 is reformed in 97% yield upon deprotonation of 2a with DBU under N$_2$. Integrations are referenced to an internal standard of PMe$_3$ in a capillary tube.
**Fig. S11**: $^{31}$P{$^1$H} NMR spectra showing deprotonation of 2a with DBU under Ar

**Bottom (1, maroon)**: 1.3 mg 2 (2.1 µmol) in THF-$d_8$. $^{31}$P{$^1$H} NMR (202 MHz, THF-$d_8$, 2): δ = 72.80 (s).

**Middle (2, green)**: 1.3 mg 2 (2.1 µmol) with 1 eq. DMAH-BF$_4$ in THF-$d_8$. No phosphorus resonance is visible for the diamagnetic complex 2a at 25 °C (see Fig. S9).

**Top (3, blue)**: 1.3 mg 2 (2.1 µmol) with 1 eq. DMAH-BF$_4$ and 1.1 eq. DBU in THF-$d_8$. $^{31}$P{$^1$H} NMR (202 MHz, THF-$d_8$): δ = 72.60 (d, $J = 11.5$ Hz, 18%), 70.53 (d, $J = 11.1$ Hz, 42%), 69.00 (br. s, 38%), 67.62 (d, $J = 12.1$ Hz, 6%). Upon deprotonation under Ar, a number of unidentified products are formed. In contrast to deprotonation under N$_2$ (Figure S10), no 2 is reformed, indicating that N$_2$ is lost upon protonation with DMAH-BF$_4$. Integrations are referenced to an internal standard of PMe$_3$ in a capillary tube.
**Fig. S12:** $^1$H NMR spectrum showing formation of $\text{[(PCP)Ir(H)(py)]}^+$ from reaction of 2a with pyridine-$d_5$.

3.4 mg 2 (5.5 µmol) with 1 eq. DMAH-BF$_4$ added in THF-$d_8$, subsequently spiked with excess (one drop) pyridine-$d_5$. $^1$H NMR (500 MHz, THF-$d_8$): δ = 6.91 (d, $^3J_{H,H} = 7.3$ Hz, 2H, m-Ph), 6.55 (t, $^3J_{H,H} = 7.3$ Hz, 1H, p-Ph), 3.17 (m, 4H, C$_2$H$_2$), 1.23 (m, 18H, C(C$_3$H$_3$)$_3$), 1.07 (m, 18H, C(C$_3$H$_3$)$_3$), -22.78 (br. s, 1H, Ir-H). While the number of bound pyridine molecules was not confirmed, the relatively downfield hydride resonance is characteristic of a weak donor bound *trans* to the hydride, suggesting a six-coordinate species in the presence of excess pyridine. This matches the reported $^1$H NMR spectrum of $\text{[(PCP)Ir(H)(THF)]}^+$ in excess pyridine.$^1$ The PMe$_3$ peak is from the internal standard in a capillary tube.
**Fig. S13:** $^{31}\text{P}[^1\text{H}]$ NMR spectrum showing formation of $[(\text{PCP})\text{Ir(H)(py)}]^{+}$ from reaction of 2a with pyridine-$d_5$.

3.4 mg 2 (5.5 µmol) with 1 eq. DMA-BF$_4$ added in THF-$d_8$, subsequently spiked with excess (one drop) pyridine-$d_5$. $^{31}\text{P}[^1\text{H}]$ NMR (202 MHz, THF-$d_8$) $\delta = 46.53$ (s). This matches the reported $^{31}\text{P}$ NMR spectrum of $[(\text{PCP})\text{Ir(H)(THF)}]^{+}$ in excess pyridine.$^1$ Referenced to PMe$_3$ in a capillary tube.
Fig. S14: ATR-IR spectra of 2, DMAH-BF₄, and 2a

ATR-IR spectrum of 2 (red, top), DMAH-BF₄ (blue, middle), and after the addition of 1 eq. DMAH-BF₄ to 3.4 mg 2 (5.5 µmol) in THF-d₈ to form 2a (green, bottom). The bottom spectrum was taken using the crude residue obtained after removing THF-d₈ under vacuum. The N-N stretch from 2 is no longer visible, indicating that 2a does not contain N₂ in the solid state. Loss of the N-H stretch from DMAH-BF₄ confirms proton transfer from the anilinium to the metal complex occurred.
**Fig. S15:** CV of 1 in THF with added equiv TFA

CV of 1.2 mg 1 in 5 mL THF (0.46 mM) with 0.1 M TBA-PF$_6$ and 1 eq. Fc added (black, solid) taken at 50 mV/s. Upon addition of 1 eq. TFA, an irreversible one-electron reduction occurs at -2.63 V vs. Fc (red, solid). IR compensation was set to 3200 Ω. Control experiments of 1 equiv Fc in THF with 0.1 M TBA-PF$_6$ without (black, dashed) and with (red, dashed) 1 eq. TFA confirm that this reduction event is dependent on the presence of both 1 and TFA.
Fig. S16: CV of 2 in THF with added equiv TFA

CV of 1.4 mg 2 in 5 mL THF (0.46 mM) with 0.1 M TBA-PF₆ and 1 eq. Fc added (black, solid) taken at 50 mV/s. Upon addition of 1 eq. TFA, an irreversible one-electron reduction occurs at -2.42 V vs. Fc (red, solid), followed by a substoichiometric reversible reduction at -2.88 V vs. Fc. IR compensation was set to 3200 Ω. Control experiments of 1 equiv Fc in THF with 0.1 M TBA-PF₆ without (black, dashed) and with (red, dashed) 1 equiv TFA confirm that these redox events are dependent on the presence of both 2 and TFA.
CV of 1.2 mg 1 in 5 mL THF (0.46 mM) with 0.1 M TBA-PF$_6$ and 1 eq. Fc added (black, solid) taken at 50 mV/s. Upon addition of 25 eq. TFA, a large irreversible reduction occurs with peak current at -1.93 V vs Fc (red, solid) followed by a second reduction at -2.59 V vs Fc. IR compensation was set to 3200 Ω. The large current of the first irreversible reduction upon flooding with acid (compare to 1 equiv TFA in Fig. S15) is characteristic of electrocatalytic proton reduction. Control experiments of 1 eq. Fc with 25 equiv TFA (red, dashed) confirm that the catalytic current is dependent on the presence of 1.
**Fig. S18:** CV of 2 in THF with large excess of TFA

CV of 1.4 mg 2 in 5 mL THF (0.46 mM) with 0.1 M TBA-PF₆ and 1 eq. Fc added (black, solid) taken at 50 mV/s. Upon addition of 25 eq. TFA, a large irreversible reduction occurs with peak current at -2.53 V vs Fc (red, solid). IR compensation was set to 3200 Ω. The large current enhancement of this irreversible reduction upon flooding with acid (compare to 1 equiv TFA in Fig. S16) is characteristic of electrocatalytic proton reduction. Control experiments of 1 equiv Fc with 25 equiv TFA (red, dashed) confirm that the catalytic current is dependent on the presence of 2.
Fig. S19: CV of 2 in THF with added DMAH-BF₄

CV of 1.3 mg 2 in 5 mL THF (0.42 mM) with 0.1 M TBA-PF₆ and 1 equiv Fc added (black, solid) taken at 50 mV/s. Upon addition of 1 eq. DMAH-BF₄, an irreversible one-electron reduction occurs at -1.82 V vs. Fc (red, solid), followed by a reversible reduction at -2.89 V vs. Fc. IR compensation was set to 3000 Ω. Control experiments of 1 equiv Fc in THF with 0.1 M TBA-PF₆ without (black, dashed) and with (red, dashed) 1 equiv DMAH-BF₄ confirm that these redox events are dependent on the presence of both 2 and DMAH-BF₄.
**Fig. S20:** $^1$H NMR spectra showing reduction of 2a with CoCp$_2^*$

*Bottom (1, maroon):* 2.9 mg 2 (4.7 µmol) in THF-$d_8$. $^1$H NMR (500 MHz, THF-$d_8$): $\delta = 6.83$ (d, $J = 7.4$ Hz, 2H), 6.54 (t, $J = 7.4$ Hz, 1H), 3.25 (m, $J = 3.9$ Hz, 4H), 1.33 (m, $J = 6.4$ Hz, 36H). *Second (2, light green):* 2.9 mg 2 with 1 eq. DMA-BF$_3$ added in THF-$d_8$ to form 2a. *Third (3, blue-green):* Reduction of 2a with 1.1 eq. CoCp$_2^*$ in THF-$d_8$, showing hydride resonances at -9.42 ppm and -19.52 ppm characteristic of (PCP)IrH$_4$ and (PCP)IrH$_2$, respectively. Aromatic resonances at 6.83 ppm (d, $J = 7.4$ Hz) and 6.54 ppm (t, $J = 7.4$ Hz) correspond to 2. *Top (4, purple):* $^1$H NMR spectrum after one week showing full conversion to 2 and (PCP)IrH$_4$. The PMe$_3$ peak is from the internal standard in a capillary tube.
Fig. S21: $^1$H NMR spectrum of mixture of (PCP)IrH$_2$ and (PCP)IrH$_4$

Mixture of (PCP)IrH$_2$ and (PCP)IrH$_4$ in THF-$d_8$, which were prepared according to literature procedures and match reported spectra. The PMe$_3$ peak is from the internal standard in a capillary tube.
Fig. S22: $^{31}$P$^1$H NMR spectrum of mixture of (PCP)IrH$_2$ and (PCP)IrH$_4$

Mixture of (PCP)IrH$_2$ and (PCP)IrH$_4$ in THF-$_d_8$, which were prepared according to literature procedures and match reported spectra. Referenced to PMe$_3$ in a capillary tube.
References: