Supporting information for:

Dehydrogenation of Cyclic Amines by a Coordinatively Unsaturated Cp*Ir(III) Phosphoramidate Complex

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Experimental Section

General Considerations. All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents. [1][BAr^F₄],¹ [Cp*IrCl₂]₂,² and Na[BAr^F₄]³ were prepared using a literature procedure. CDCl₃ was dried over CaH₂ and degassed by three freeze-pump-thaw cycles. NMR spectra were recorded on a Bruker Avance 300, 400, or 600 MHz spectrometer. ¹H NMR spectra are reported in parts per million (ppm) and were referenced to residual solvent: ¹H(CDCl₃): δ 7.27; ¹³C(CDCl₃): δ 77.16 and ¹H(d₈-THF): δ 3.58; ¹³C(d₈-THF): δ 67.57; coupling constants are reported in Hz. ¹³C NMR spectra were performed as proton-decoupled experiments and are reported in ppm. The multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *dd* = doublet of doublets. ESI-MS, Infrared (IR), and microanalysis data were obtained at the University of British Columbia.



Figure S1. [2][BAr^F₄], ¹H NMR, THF-d₈, 300 MHz, 298 K

Figure S2. [2][BAr^F₄], ¹H NMR, THF-d₈, 300 MHz, 298 K (expansion of Figure S1)







Figure S4. [**3**][BAr^F₄], ¹H NMR, THF-d₈, 300 MHz, 298 K





Figure S5. [3][BAr^F₄], ¹H NMR, THF-d₈, 400 MHz, 298 K (expansion of Figure S4)

Figure S6. [**3**][BAr^F₄], ¹³C{¹H} NMR, THF-d₈, 150 MHz, 298 K



Figure S7. [4][Cl], 5, and pyrrolidine in a 1:3:3 ratio, ¹H NMR, CDCl₃, 400 MHz, 298 K



Figure S8. [4][C1], **5**, and pyrrolidine in a 1:3:3 ratio, ¹H NMR, CDCl₃, 400 MHz, 298 K (expansion of Figure S7; free pyrrolidine at δ = 2.87 and 1.68)





Figure S10. 6, ¹H NMR, CDCl₃, 400 MHz, 298 K



Figure S11. 6, ¹³C{¹H} NMR, CDCl₃, 100 MHz, 298 K



Figure S12. [7][BAr^F₄], ¹H NMR, CDCl₃, 400 MHz, 298 K





Figure S13. [7][BAr^F₄], ¹H NMR, CDCl₃, 400 MHz, 298 K (expanded view of Figure S12)

Crystallographic details

Crystals of [2][BAr^F₄], [3][BAr^F₄], [4][Cl], and 6 were mounted on a glass fiber loop. All measurements were made using graphite-monochromated Mo K_a radiation ($\lambda = 0.71073$ Å) on a Bruker APEX Duo diffractometer. The structures were solved by direct methods⁴ and refined by full-matrix least-squares procedures on F2 (SHELXL-2013)⁴ using the OLEX2 interface.⁵ All hydrogen atoms were placed in calculated positions and all non-hydrogen atoms were refined anisotropically. The hydride atoms in complexes [2][BAr^F₄] and [3][BAr^F₄] were not located.

Additional details:

[2][BAr^F₄]: The coordinated amine and imine were disordered and modeled over two positions [68/32]. One level A alert was found - PLAT971_ALERT_2_A: this electron density is potentially attributable to the terminal iridium(III) hydride that was intentionally not included in the model due to poor modeling (unsatisfactory statistics). The spectroscopic data, namely IR and NMR spectroscopy, are consistent with the presence of a terminal Ir-H moiety.

[3][BAr^F₄]: Rotational disorder about several of the $-CF_3$ groups of the BAr^F₄⁻ counterion was modeled. Additionally, one of the 3,5-(CF₃)₂C₆H₃ rings was completely modeled over two positions [53/47]. The coordinated amine and imine were disordered and modeled over two positions at N2 [53/47] and N1 [53/47]. An intense q-peak located 2.367 Å from Ir was assigned as a possible Cl⁻ ion impurity [allowed to refine freely - occupancy 21%].

CCDC **1537026-1537029** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Compound	[2][BAr ^F ₄]	[3][BAr ^F ₄]
Empirical formula	$C_{50}H_{44}BN_2F_{24}Ir$	C ₅₂ H ₄₇ BCl _{0.22} F ₂₄ IrN ₂
Formula weight	1331.88	1366.72
Temperature/K	90.0	90.0
Crystal system	Triclinic	Triclinic
Space group	P-1	<i>P-1</i>
a/Å	12.7119(15)	12.7608(13)
b/Å	12.8605(16)	13.3680(15)
c/Å	17.518(2)	17.2480(18)
$lpha/^{\circ}$	94.122(3)	93.337(2)
β/°	110.854(3)	110.084(2)
$\gamma/^{\circ}$	103.523(3)	103.367(2)
\dot{V}/\dot{A}^3	2563.8(5)	2657.8(5)
Ζ	2	2
$\rho/g/cm^{-3}$	1.725	1.708
$\mu/\text{ mm}^{-1}$	2.729	2.646
F(000)	1312.0	1349.0
Crystal size/ mm ³	0.48 imes 0.11 imes 0.08	$0.48 \times 0.11 \times 0.08$
Radiation	MoKa ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2θ range for	2 206 to 59 129	2544 to 58338
datacollection/°	5.500 to 58.458	2.344 10 38.338
	$-17 \le h \le 17, -17 \le k \le 17, -$	$-17 \le h \le 17, -18 \le k \le 18, -18$
Index ranges	$24 \le l \le 23$	$23 \le l \le 23$
	13832 [$R_{int} = 0.0326$, $R_{sigma} =$	14303 [$R_{int} = 0.0390, R_{sigma}$
Independent reflections	0.0315]	= 0.0400]
Data/restraints/paramet	13832/705/701	14303/1666/1008
ers	15652 1951 191	14303/1000/1000
Goodness-of-fit on F^2	1.073	1.033
$\begin{array}{ll} R & [I \ge 2\theta & (I)] & (R1, \\ wR2) \end{array}$	$R_1 = 0.0443, wR_2 = 0.1141$	$R_1 = 0.0443, wR_2 = 0.1079$
R (all data) (R1, wR2)	$R_1 = 0.0504, wR_2 = 0.1177$	$R_1 = 0.0560, wR_2 = 0.1145$
Largest diff. peak/hole / (e Å ⁻³)	3.86/-1.55	1.97/-1.03

Table S1. Crystallographic data for [2	2][BAr ^F ₄] and $[3]$ [BAr ^F ₄]	

 $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$

Compound	[4][C1]	6
Empirical formula	$C_{20}H_{37}Cl_6IrN_2$	C ₁₅ H ₂₆ Cl ₂ IrN
Formula weight	710.41	483.47
Temperature/K	90(2)	90(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_{I}/n$	Pnma
a/Å	10.744(3)	12.981(3)
b/Å	13.537(3)	13.452(3)
c/Å	18.633(4)	9.6850(13)
$lpha/^{\circ}$	90	90
β/°	96.263(6)	90
γ/°	90	90
$V/Å^3$	2693.9(10)	1691.2(5)
Ζ	4	4
$\rho/g/cm^{-3}$	1.752	1.899
$\mu/\text{ mm}^{-1}$	5.562	8.199
F(000)	1400.0	936.0
Crystal size/ mm ³	$0.41 \times 0.22 \times 0.12$	0.18 x 0.11 x 0.09
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2θ range for datacollection/°	3.726 to 58.412	5.182 to 58.312
	$-14 \le h \le 14, -18 \le k \le 18, -$	$-14 \le h \le 17, -16 \le k \le 18, -10$
Index ranges	$25 \le 1 \le 24$	$13 \le l \le 13$
-	7267 [$R_{int} = 0.0366, R_{sigma} =$	2353 $[R_{int} = 0.0572, R_{sigma} =$
Independent reflections	0.0312]	0.0569]
Data/restraints/paramet	7267/0/267	2353/0/97
Goodness-of-fit on F^2	1.037	1.032
$\begin{array}{l} R [I \ge 2\theta (I)] (R1, \\ wR2) \end{array}$	$R_1 = 0.0226, wR_2 = 0.0574$	$R_1 = 0.0320, wR_2 = 0.0630$
R (all data) (R1, wR2)	$R_1 = 0.0254, wR_2 = 0.0588$	$R_1 = 0.0446, wR_2 = 0.0675$
Largest diff. peak/hole / (e Å ⁻³)	1.33/-2.53	1.86/-2.12

 Table S2. Crystallographic data for [4][Cl] and 6

 $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$



Figure S14. ORTEP depiction of the solid-state molecular structure of [4][Cl] (displacement ellipsoids are shown at the 50% probability) showing H--Cl hydrogen bond contacts of H(1)-Cl(2) 2.2362(7) Å and H(2)-Cl(2) 2.3018(7) Å.

References

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