Supporting Information

Alkane Dehydrogenation by C-H Activation at Ir^{III}

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General Experimental

Unless specified otherwise, all reactions were carried out under a dry nitrogen atmosphere using standard glovebox, Schlenk, or vacuum-line techniques. Octane, ≥ 98%, was used as received from Alfa Aesar. All other reagents were used as received. Solvents were purified before use: benzene and pentane were purified by passage through columns of activated alumina and molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Benzene-d_6, toluene-d_8 were dried over sodium/benzophenone and dichloromethane-d_2, chloroform-d_1 were dried over CaH_2. NMR spectra were obtained on Bruker AV300 or AV500 MHZ spectrometers with chemical shifts (δ) reported in ppm downfield of tetramethylsilane. Octane dehydrogenation reactions were quantified using Agilent 7890A gas chromatograph with a 30 m x 0.32 mm Agilent GASPRO capillary column. ^{dm}Phebox, ^{iPr}Phebox, and ^{R}PheboxIr(OAc)$_2$(OH$_2$) (**1a** (R = CH_3), **1b** (R = ^{i}Pr, H) were prepared according to published procedures.[1] Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA.

Synthesis and Characterization of Complexes

^{dm}PheboxIr(OAc)(C_6H_5) (2a). A 50 mL Teflon-stoppered reaction vessel was charged with a stir bar, **1a** (150 mg, 0.0239 mmol), and benzene (12.5 ml, 140 mmol). Oxygen was removed from the solution through three freeze-pump-thaw cycles and then heated at 100 °C. After 1.5 h the reaction mixture was cooled to room temperature and the volatiles were removed. The resulting bright orange solid was dried overnight *in vacuo*. Complex **2a** was isolated as a bright orange solid. Yield: 149 mg, 99%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.63 (1H, Phebox-aryl-H), 6.63 (t, 2H, 3-Ph), 6.55 (t, 1H, 4-Ph), 6.42 (d, 2H, 2-Ph), 4.44 (d, 2H, $J_{HH'}$ = 8.3 Hz, OCH_2), 4.36 (d, 2H, $J_{HH'}$= 8.3 Hz, OCH_2), 2.62 (s, 6H, Phebox-CH_3), 2.01 (s, 3H, OAc), 1.41 (s, 6H, CH_3), 1.04 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.31 (OAc), 179.16 (Ph), 177.08 (C=N),

140.39, 134.76 (2-Ph), 125.48 (Phebox-*C*H), 125.23 (3-Ph), 123.93, 121.95, 120.87 (4-Ph), 82.22 (O*C*H_2C(CH_3)$_2$), 66.29 (OCH_2*C*(CH_3)$_2$), 26.95 (CH_3), 26.85 (CH_3), 25.42 (OAc), 18.81 (Phebox-CH_3). Anal. Calcd for $C_{26}H_{31}N_2O_4Ir$: C, 49.74; H, 4.98; N, 4.46. Found: C, 48.92; H, 4.89; N, 4.36.

^{iPr}PheboxIr(OAc)(C_6H_5) (2b). Following the general procedure above **2b** was prepared from **1b** (106 mg, 0.162 mmol) and isolated as a bright orange solid. Yield: 85 mg, 78%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.66 (t, 2H, 3-Ph), 6.63 (s, 1H, Phebox-aryl-H), 6.58 (t, 1H, 4-Ph), 6.41 (d, 2H, 2-Ph), 4.72 (t, 1H, OCH$_2$C*H*), 4.57 (m, 2H, OC*H*$_2$CH), 4.51 (t, 1H, OCH$_2$C*H*), 3.95 (m, 2H, OC*H*$_2$CH), 2.65 (s, 3H, Phebox-CH_3), 2.58 (s, 6H, Phebox-CH_3), 2.49 (m, 1H, C*H*(CH_3)$_2$), 2.04 (s, 3H, OAc), 2.00 (m, 1H, C*H*(CH_3)$_2$), 0.94 (d, 3H, J_{HH}= 7.1 Hz, CH(C*H*$_3$)$_2$), 0.83 (d, 3H, J_{HH}= 6.8 Hz, CH(C*H*$_3$)$_2$), 0.77 (d, 3H, J_{HH}= 7.1 Hz, CH(C*H*$_3$)$_2$), 0.11 (d, 3H, J_{HH} = 6.7 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.00 (OAc), 179.55 (Ph), 178.46 (C=N), 178.18 (C=N), 140.75, 140.43, 134.35 (2-Ph), 125.64 (3-Ph), 125.35, 125.21, 123.90, 122.33 (Phebox-CH), 121.23 (4-Ph), 71.18 (OCH$_2$*C*H), 70.28 (OCH$_2$*C*H), 67.30 (O*C*H$_2$CH), 29.30 (*C*H(CH_3)$_2$), 29.17 (*C*H(CH_3)$_2$), 24.88 (OAc), 19.66 (CH(*C*H$_3$)$_2$), 19.60 (CH(*C*H$_3$)$_2$), 18.89 (Phebox-CH_3), 18.82 (Phebox-CH_3), 14.77 (CH(*C*H$_3$)$_2$), 14.28 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{28}H_{35}N_2O_4Ir$: C, 51.28; H, 5.39; N, 4.27. Found: C, 51.48; H, 5.68; N, 4.32.

^{dm}PheboxIr(OAc)(C_6D_5) (2a-*d*$_5$). A resealable Teflon-capped NMR tube was charged with **1a** (5.3 mg, 0.0084 mmol) and 0.43 mL C_6D_6 were vacuum transferred to give a light green solution. Dioxane (0.8 μL, 0.0084 mmol) was added via microsyringe and the solution was degassed using three freeze/pump/thaw cycles. The mixture was heated at 100 °C for 2 h, resulting in a bright orange solution. Yield: 96%, determined by integration of Phebox-aryl-H signal against dioxane internal standard. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 6.58 (s, 1H,

Phebox-aryl-H), 3.68 (d, 2H, $J_{HH'}$ = 8.3 Hz, OCH_2), 3.57 (d, 2H, $J_{HH'}$ = 8.3 Hz, OCH_2), 2.68 (s, 6H, Phebox-CH_3), 2.08 (br s, 3H, OAc), 1.56 (br s, 3H, HOAc), 1.24 (s, 6H, CH_3), 0.95 (s, 6H, CH_3). ^{1}H NMR (C_6D_6, 500 MHz, 40 °C): δ 6.58 (s, 1H, Phebox-aryl-H), 3.68 (d, 2H, $J_{HH'}$ = 8.3 Hz, OCH_2), 3.57 (d, 2H, $J_{HH'}$ = 8.3 Hz, OCH_2), 2.68 (s, 6H, Phebox-CH_3), 1.79 (br s, 6H, OAc/HOAc), 1.24 (s, 6H, CH_3), 0.96 (s, 6H, CH_3).

Addition of HOAc to 2a. A resealable Teflon-capped NMR tube was charged with **2a** (2.0 mg, 0.0032 mmol) and benzene-*d*$_6$ (0.40 mL). All of the ^{1}H NMR signals described above in the characterization of **2a** were observed. HOAc (0.2 μL, 0.0035 mmol) was added via microsyringe and the mixture was degassed using three freeze/pump/thaw cycles. In the ^{1}H NMR spectrum after addition of HOAc all of the ^{dm}Phebox and phenyl ligand signals were observed. Notably, the acetate signal at 2.07 ppm was absent at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 6.95 (d, 2H, 2-Ph), 6.89 (t, 2H, 3-Ph), 6.76 (t, 1H, 4-Ph), 6.58 (s, 1H, Phebox-aryl-H), 3.67 (d, 2H, OCH_2), 3.57 (d, 2H, OCH_2), 2.68 (s, 6H, Phebox-CH_3), 1.23 (s, 6H, CH_3), 0.96 (s, 6H, CH_3).

General procedure for the reaction of 1a with octane. Five 25 mL resealable Teflon-stoppered reaction vessel were charged with **1a** and 1.5 mL of octane. Each vessel was sealed under a nitrogen atmosphere. Each vessel was heated at 200 °C for 20 minutes and then removed from heat and shaken to ensure complete solubility of **1a**. Each vessel was put back into the 200 °C bath and heated a specified amount of time (3, 6, 24, 48, or 72 h). After allowing the reaction to cool to room temperature, the volatiles were transferred to a 5 mL volumetric flask. The reaction vessel was washed twice with pentane and combined in the flask. Mesitylene (6 μL) was added as an internal standard and the mixture was diluted to a total volume of 5 mL using pentane. The volatile products were quantified by GC analysis.

^{dm}PheboxIr(OAc)(H) (3a). In a resealable Teflon-stoppered reaction vessel, complex **1a** (7.3 mg, 0.012 mmol) was heated in octane (2 mL) for 72 h. A bright orange powder was obtained after removing the volatiles in vacuo. Crystals were obtained at room temperature by layering a benzene solution of **3a** with pentane. Yield: 7.0 mg, 96%. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.49 (s, 1H, Phebox-aryl-H), 3.84 (d, 2H, $J_{HH'}$ = 8.3 Hz, OCH_2), 3.79 (d, 1H, $J_{HH'}$ = 8.3 Hz, OCH_2), 2.64 (s, 6H, Phebox-CH_3), 2.06 (s, 3H, OAc), 1.33 (s, 6H, CH_3), 1.29 (s, 6H, CH_3), -33.78 (s, 1H, Ir-H). ^{13}C NMR (C_6D_6, 125 MHz): δ 185.78 (OAc), 178.59 (Ph), 177.20 (C=N), 139.38, 126.93 (Phebox-CH), 123.04, 81.65 ($OCH_2C(CH_3)_2$), 65.71 ($OCH_2C(CH_3)_2$), 27.27 (CH_3), 26.57 (CH_3), 26.32 (OAc), 18.89 (Phebox-CH_3). Anal. Calcd for $C_{20}H_{27}N_2O_4Ir$: C, 43.55; H, 4.93; N, 5.08. Found: C, 42.94; H, 4.79; N, 4.45.

Isomerization of 1-octene using 3a. A sealable NMR tube was loaded with **3a** (2.0 mg, 0.0036 mmol) and 600 μL of a 0.11 M solution of 1-octene in octane was added. The solution was degassed using 3 freeze-pump-thaw cycles and the tube was flame sealed. The reaction was heated at 200 °C for 24 h and then cooled to room temperature. The tube was opened and then the mixture was transferred to a 5 mL volumetric flask. The tube was washed two times with pentane and the washes were combined in the flask. Mesitylene (6 μL) was added as an internal standard and the solution was diluted to a total volume of 5 mL with more pentane. The volatiles were analyzed by GC; 15 TON; 90% conversion.

Octane dehydrogenation in the presence of 1-hexene. A 25 mL resealable Teflon-stoppered reaction vessel was charged with **1a** (7.0 mg, 0.011 mmol) and 1.5 mL of octane. 1-Hexene (14 μL, 0.11 mmol) was added via microsyringe and the reaction was closed under a nitrogen atmosphere. The reaction was performed using the general procedure for octane dehydrogenation and the octene yield was determined by GC; 33(1)%.

Octane dehydrogenation in the presence of H_2O. A 25 mL resealable Teflon-stoppered reaction vessel was charged with **1a** (7.3 mg, 0.012 mmol) and 1.5 mL of octane. HPLC grade H_2O (25 μL, 1.4 mmol, 120 equiv.) was added via microsyringe and the reaction was closed under a nitrogen atmosphere. The reaction was performed using the general procedure for octane dehydrogenation and octene yield was determined by GC; 44(2)%

H/D exchange between octane and CD_3COOD using 1a. A sealable NMR tube was charged with **1a** (4.0 mg, 0.0064 mmol), octane (210 μL, 1.4 mmol), and acetic acid-d_4 (100 μL, 1.8 mmol). The solution was degassed using 3 freeze-pump-thaw cycles and the tube was flame sealed. After heating at 160 °C for 48 h the reaction was cooled to room temperature and opened. A 2 M dichloromethane-d_2 in benzene solution (50 μL, 0.10 mmol) was added and the reaction was analyzed by ^{2}H NMR spectroscopy; 1.5(1) % deuterium incorporation (determined by integration of the deuterated octane signal against CD_2Cl_2) into the terminal C-H bonds of octane.

General procedure for the reaction of 1a and octane in the presence of base. Following literature procedure,[2] a 25 mL resealable Teflon-stoppered a reaction vessel was charged with **1a**, base (1 equiv.) and octane (2 mL). The reaction was sealed under nitrogen and heated at 160 °C for 48 h. After cooling to room temperature, the volatiles were removed in vacuo. The orange residue was dissolved in benzene and transferred to a resealable NMR tube. After removal of the volatiles, C_6D_6 was transferred to give a dark orange solution. An internal standard solution was added to the NMR tube and yields were determined by ^{1}H NMR spectroscopy.

Reaction of 1a with octane in the presence of K_2SO_4. Following the general procedure, **1a** (13 mg, 0.021 mmol), K_2SO_4 (3.6 mg, 0.021 mmol) were heated in octane. At the end of the

reaction 20 μL of a dioxane internal standard solution (0.23 M in C_6D_6) was added. Integration of dioxane signal vs Phebox-aryl-H or Ir-H signal was used to obtain yields: 34% **4a**, ~1% **3a**, 41% **1a**.

Reaction of 1a with octane in the presence of $KHCO_3$. Following the general procedure, **1a** (13 mg, 0.021 mmol) $KHCO_3$ (2.1 mg, 0.021 mmol) were heated in octane. At the end of the reaction 20 μL of a dioxane internal standard solution was (0.23 M in C_6D_6). Integration of dioxane signal vs Phebox-aryl-H or Ir-H signal was used to obtain yields: 50% **4a**, 11% **3a**, 11% **1a**.

Reaction of 1a with octane in the presence of 18-crown-6. Following the general procedure, **1a** (13 mg, 0.021 mmol), K_2CO_3 (2.9 mg, 0.21 mmol), 18-crown-6 (11 mg, 0.042 mmol) were heated in octane. At the end of the reaction 20 μL of a hexamethyldisiloxane internal standard solution was (0.094 M in C_6D_6). Integration of dioxane signal vs Phebox-aryl-H or Ir-H signal was used to obtain yields: 37% **4a**, 31% **3a**; total yield of Ir products 68%.

Crystallographic Information for 3a

Table S1. Crystal data and structure refinement for **3a**.

Empirical formula	C_{23} H_{30} Ir N_2 O_4	
Formula weight	590.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 14.5034(9) Å	α = 90°
	b = 10.1858(6) Å	β = 103.835(3)°
	c = 15.4427(10) Å	γ = 90°
Volume	2215.1(2) $Å^3$	
Z	4	
Density (calculated)	1.771 Mg/m^3	
Absorption coefficient	6.059 mm^{-1}	
F(000)	1164	
Crystal size	0.17 x 0.07 x 0.02 mm^3	
Theta range for data collection	2.42 to 28.55°	
Index ranges	$-19 \leq h \leq 19$,	
	$-13 \leq k \leq 13$,	
	$-20 \leq l \leq 20$	
Reflections collected	83959	
Independent reflections	5620 [R(int) = 0.0472]	
Completeness to θ = 25.00°	100.0 %	
Max. and min. transmission	0.8884 and 0.4257	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5620 / 6 / 287	
Goodness-of-fit on F^2	1.048	
Final R indices [I > 2σ (I)]	R_1 = 0.0188, wR_2 = 0.0363	
R indices (all data)	R_1 = 0.0288, wR_2 = 0.0394	
Largest diff. peak and hole	0.794 and -0.598 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6913(2)	3939(2)	713(2)	17(1)
C(2)	6398(2)	4663(2)	-19(2)	16(1)
C(3)	6437(2)	6043(2)	-5(2)	19(1)
C(4)	6980(2)	6641(2)	763(2)	21(1)
C(5)	7497(2)	5949(2)	1504(2)	20(1)
C(6)	7467(2)	4578(2)	1464(2)	17(1)
C(7)	7973(2)	3590(2)	2075(2)	19(1)
C(8)	5932(2)	3763(2)	-710(2)	18(1)
C(9)	5950(2)	6863(2)	-785(2)	27(1)
C(10)	8061(2)	6693(3)	2297(2)	30(1)
C(11)	4999(2)	2931(2)	-1957(2)	27(1)
C(12)	5526(2)	1791(2)	-1389(2)	21(1)
C(13)	6221(2)	1111(3)	-1839(2)	28(1)
C(14)	4854(2)	803(3)	-1142(2)	26(1)
C(15)	8880(2)	2565(3)	3265(2)	36(1)
C(16)	8423(2)	1519(3)	2567(2)	23(1)
C(17)	9158(2)	745(3)	2232(2)	34(1)
C(18)	7757(2)	606(3)	2900(2)	40(1)
C(19)	7955(2)	256(2)	90(2)	23(1)
C(20)	8559(2)	-778(3)	-184(2)	35(1)
C(21)	9178(2)	5600(3)	75(2)	36(1)
C(22)	9816(2)	6273(3)	-300(2)	35(1)
C(23)	10635(2)	5671(3)	-375(2)	33(1)
N(1)	7858(2)	2360(2)	1845(1)	19(1)
N(2)	6056(2)	2511(2)	-581(1)	19(1)
O(1)	8561(1)	3848(2)	2867(1)	25(1)
O(2)	5370(1)	4139(2)	-1494(1)	22(1)
O(3)	8152(1)	1456(2)	22(1)	23(1)
O(4)	7257(1)	-59(2)	406(1)	25(1)
Ir(1)	6950(1)	2057(1)	628(1)	16(1)

Table S3. Bond lengths [Å] and angles [°] for **3a**.

C(1)-C(6)	1.403(3)
C(1)-C(2)	1.405(3)
C(1)-Ir(1)	1.923(2)
C(2)-C(3)	1.406(3)
C(2)-C(8)	1.447(3)
C(3)-C(4)	1.397(3)
C(3)-C(9)	1.497(3)
C(4)-C(5)	1.399(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.398(3)
C(5)-C(10)	1.504(3)
C(6)-C(7)	1.453(3)
C(7)-N(1)	1.302(3)
C(7)-O(1)	1.339(3)
C(8)-N(2)	1.297(3)
C(8)-O(2)	1.344(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(2)	1.460(3)
C(11)-C(12)	1.543(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-N(2)	1.493(3)
C(12)-C(14)	1.512(3)
C(12)-C(13)	1.520(4)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800

C(14)-H(14C)	0.9800
C(15)-O(1)	1.471(3)
C(15)-C(16)	1.548(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-N(1)	1.487(3)
C(16)-C(17)	1.514(4)
C(16)-C(18)	1.516(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-O(3)	1.266(3)
C(19)-O(4)	1.266(3)
C(19)-C(20)	1.495(4)
C(19)-Ir(1)	2.600(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(23)#1	1.380(4)
C(21)-C(22)	1.385(4)
C(21)-H(21)	0.9500
C(22)-C(23)	1.366(4)
C(22)-H(22)	0.9500
C(23)-C(21)#1	1.380(4)
C(23)-H(23)	0.9500
N(1)-Ir(1)	2.043(2)
N(2)-Ir(1)	2.055(2)
O(3)-Ir(1)	2.2509(18)
O(4)-Ir(1)	2.2432(17)
Ir(1)-H(1)	1.50(3)

C(6)-C(1)-C(2)	120.6(2)
C(6)-C(1)-Ir(1)	119.92(17)

C(2)-C(1)-Ir(1)	119.16(17)
C(1)-C(2)-C(3)	120.1(2)
C(1)-C(2)-C(8)	108.9(2)
C(3)-C(2)-C(8)	130.9(2)
C(4)-C(3)-C(2)	117.4(2)
C(4)-C(3)-C(9)	120.1(2)
C(2)-C(3)-C(9)	122.4(2)
C(3)-C(4)-C(5)	123.9(2)
C(3)-C(4)-H(4)	118.1
C(5)-C(4)-H(4)	118.1
C(6)-C(5)-C(4)	117.5(2)
C(6)-C(5)-C(10)	123.0(2)
C(4)-C(5)-C(10)	119.5(2)
C(5)-C(6)-C(1)	120.4(2)
C(5)-C(6)-C(7)	131.1(2)
C(1)-C(6)-C(7)	108.4(2)
N(1)-C(7)-O(1)	116.8(2)
N(1)-C(7)-C(6)	118.5(2)
O(1)-C(7)-C(6)	124.8(2)
N(2)-C(8)-O(2)	116.8(2)
N(2)-C(8)-C(2)	119.1(2)
O(2)-C(8)-C(2)	124.1(2)
C(3)-C(9)-H(9A)	109.5
C(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(2)-C(11)-C(12)	106.36(19)
O(2)-C(11)-H(11A)	110.5

C(12)-C(11)-H(11A)	110.5
O(2)-C(11)-H(11B)	110.5
C(12)-C(11)-H(11B)	110.5
H(11A)-C(11)-H(11B)	108.6
N(2)-C(12)-C(14)	110.5(2)
N(2)-C(12)-C(13)	109.9(2)
C(14)-C(12)-C(13)	110.5(2)
N(2)-C(12)-C(11)	101.05(18)
C(14)-C(12)-C(11)	112.5(2)
C(13)-C(12)-C(11)	112.1(2)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(1)-C(15)-C(16)	106.3(2)
O(1)-C(15)-H(15A)	110.5
C(16)-C(15)-H(15A)	110.5
O(1)-C(15)-H(15B)	110.5
C(16)-C(15)-H(15B)	110.5
H(15A)-C(15)-H(15B)	108.7
N(1)-C(16)-C(17)	110.5(2)
N(1)-C(16)-C(18)	109.0(2)
C(17)-C(16)-C(18)	110.7(2)
N(1)-C(16)-C(15)	101.2(2)
C(17)-C(16)-C(15)	112.2(2)
C(18)-C(16)-C(15)	112.8(2)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5

H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(3)-C(19)-O(4)	119.6(2)
O(3)-C(19)-C(20)	119.9(3)
O(4)-C(19)-C(20)	120.5(2)
O(3)-C(19)-Ir(1)	59.97(13)
O(4)-C(19)-Ir(1)	59.63(13)
C(20)-C(19)-Ir(1)	177.72(19)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(23)#1-C(21)-C(22)	120.5(3)
C(23)#1-C(21)-H(21)	119.7
C(22)-C(21)-H(21)	119.7
C(23)-C(22)-C(21)	119.6(3)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(22)-C(23)-C(21)#1	119.9(3)
C(22)-C(23)-H(23)	120.1
C(21)#1-C(23)-H(23)	120.1
C(7)-N(1)-C(16)	109.7(2)
C(7)-N(1)-Ir(1)	114.15(16)
C(16)-N(1)-Ir(1)	136.11(16)
C(8)-N(2)-C(12)	109.2(2)
C(8)-N(2)-Ir(1)	113.29(16)

C(12)-N(2)-Ir(1)	137.41(16)
C(7)-O(1)-C(15)	106.0(2)
C(8)-O(2)-C(11)	105.91(18)
C(19)-O(3)-Ir(1)	90.90(16)
C(19)-O(4)-Ir(1)	91.24(14)
C(1)-Ir(1)-N(1)	79.01(9)
C(1)-Ir(1)-N(2)	79.37(9)
N(1)-Ir(1)-N(2)	158.30(8)
C(1)-Ir(1)-O(4)	167.92(9)
N(1)-Ir(1)-O(4)	100.25(7)
N(2)-Ir(1)-O(4)	100.52(7)
C(1)-Ir(1)-O(3)	109.66(8)
N(1)-Ir(1)-O(3)	91.76(7)
N(2)-Ir(1)-O(3)	93.83(7)
O(4)-Ir(1)-O(3)	58.26(6)
C(1)-Ir(1)-C(19)	138.78(9)
N(1)-Ir(1)-C(19)	96.51(8)
N(2)-Ir(1)-C(19)	98.55(8)
O(4)-Ir(1)-C(19)	29.13(7)
O(3)-Ir(1)-C(19)	29.13(7)
C(1)-Ir(1)-H(1)	85.2(12)
N(1)-Ir(1)-H(1)	87.3(12)
N(2)-Ir(1)-H(1)	92.6(12)
O(4)-Ir(1)-H(1)	106.8(12)
O(3)-Ir(1)-H(1)	164.6(12)
C(19)-Ir(1)-H(1)	135.8(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	20(1)	17(1)	1(1)	6(1)	1(1)
C(2)	18(1)	17(1)	15(1)	-1(1)	5(1)	2(1)
C(3)	20(1)	18(1)	20(1)	3(1)	7(1)	5(1)
C(4)	24(1)	13(1)	28(1)	-1(1)	10(1)	2(1)
C(5)	20(1)	18(1)	22(1)	-3(1)	7(1)	-1(1)
C(6)	17(1)	17(1)	17(1)	0(1)	7(1)	0(1)
C(7)	19(1)	25(1)	16(1)	-2(1)	6(1)	0(1)
C(8)	17(1)	21(1)	16(1)	2(1)	4(1)	3(1)
C(9)	34(2)	20(1)	26(1)	4(1)	6(1)	7(1)
C(10)	36(2)	20(1)	30(2)	-6(1)	-1(1)	-1(1)
C(11)	32(2)	21(1)	21(1)	0(1)	-5(1)	-2(1)
C(12)	21(1)	21(1)	19(1)	-4(1)	1(1)	-2(1)
C(13)	26(2)	34(2)	24(1)	-10(1)	6(1)	-3(1)
C(14)	25(2)	26(1)	26(1)	-3(1)	5(1)	-4(1)
C(15)	51(2)	26(1)	24(2)	2(1)	-6(1)	11(1)
C(16)	27(2)	24(1)	16(1)	4(1)	-1(1)	7(1)
C(17)	30(2)	41(2)	26(1)	-1(1)	-2(1)	16(1)
C(18)	41(2)	40(2)	38(2)	22(1)	9(2)	6(1)
C(19)	32(2)	18(1)	18(1)	1(1)	3(1)	4(1)
C(20)	45(2)	26(1)	34(2)	0(1)	11(1)	12(1)
C(21)	27(2)	47(2)	37(2)	-11(1)	13(1)	4(1)
C(22)	38(2)	34(2)	37(2)	-7(1)	14(1)	3(1)
C(23)	31(2)	39(2)	34(2)	-13(1)	16(1)	-8(1)
N(1)	20(1)	17(1)	18(1)	3(1)	2(1)	4(1)
N(2)	19(1)	18(1)	18(1)	-2(1)	1(1)	-1(1)
O(1)	31(1)	25(1)	16(1)	-1(1)	-3(1)	3(1)
O(2)	25(1)	22(1)	17(1)	1(1)	-1(1)	3(1)
O(3)	26(1)	20(1)	24(1)	2(1)	6(1)	3(1)
O(4)	33(1)	15(1)	27(1)	2(1)	6(1)	0(1)
Ir(1)	18(1)	12(1)	16(1)	1(1)	2(1)	1(1)
H(1)	32(15)	73(18)	41(16)	-9(14)	14(13)	-2(14)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3a**.

	x	y	z	U(eq)
H(4)	7000	7573	784	25
H(9A)	6110	7789	-659	40
H(9B)	5261	6746	-892	40
H(9C)	6160	6590	-1316	40
H(10A)	7729	6663	2780	45
H(10B)	8131	7608	2128	45
H(10C)	8690	6292	2500	45
H(11A)	5117	2914	-2562	32
H(11B)	4306	2862	-2011	32
H(13A)	6666	1759	-1974	43
H(13B)	5871	698	-2394	43
H(13C)	6573	439	-1440	43
H(14A)	5219	128	-755	39
H(14B)	4474	392	-1685	39
H(14C)	4432	1250	-827	39
H(15A)	8673	2438	3825	43
H(15B)	9581	2502	3400	43
H(17A)	8838	109	1783	51
H(17B)	9572	278	2731	51
H(17C)	9539	1346	1964	51
H(18A)	7316	1125	3153	60
H(18B)	8127	24	3359	60
H(18C)	7397	78	2402	60
H(20A)	8816	-447	-674	52
H(20B)	8175	-1562	-381	52
H(20C)	9083	-1003	324	52
H(21)	8607	6016	126	44
H(22)	9684	7149	-504	43
H(23)	11075	6127	-632	40
H(1)	6160(20)	2080(30)	1100(20)	48(10)

GC Method

GC analyses (FID detection) were performed on an Agilent 7890A GC instrument fitted with an Agilent GS-GASPRO column (30 m length x 0.32 mm ID) using the following GC method:

Detector: FID

Starting temperature: 100 °C

Time at starting temp: 0 min

Ramp1: 10 °C/min up to 260 °C; hold for 5 min

Flow rate (carrier): 2 mL/min (He)

Split ratio: 25:1

Inlet temperature: 250 °C

Detector temperature: 250 °C

References

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2. Ito, J.; Kaneda, T; Nishiyama, H. *Organometallics* **2012**, *31*, 4442.