Ancillary Ligand Effects on C-H Bond Activation Reactions Promoted by β-Diiminate Iridium Complexes.

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-- Supporting Information --

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Additional Experimental Procedures

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[1] Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Hydrogen and argon gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. The following compounds were prepared according to literature procedures: (^{iPr}BDI)Ir(COE)N_2,[2] [Li(OEt $_2$)][BDI-**1**], [Li(OEt $_2$)][BDI-**2**], [Li(OEt $_2$)][BDI-**3**],[3] [Li(OEt_2)][BDI-**4**],[4] [Li(OEt_2)][BDI-**5**],[5] $[Ir(COE)_2Cl]_2$ and $[Ir(COD)Cl]_2$.[6]

^{1}H spectra were recorded on Varian Mercury 300, Inova 400 and 500 spectrometers operating at 299.763, 399.780 and 500.62 MHz, respectively. ^{13}C NMR spectra were obtained on Varian Mercury 300 and Inova 500 spectrometers operating at 75.37 and 100.52 MHz, respectively. All chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. ^{2}H NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 76.851 MHz and the spectra were referenced using an internal benzene-d_6 standard. ^{31}P NMR spectroscopy was carried out on a Varian Inova 400 spectrometer operating at 161.83 MHz and spectra were referenced to an external H_3PO_4 standard. ^{19}F NMR spectroscopy was conducted on

a Varian Inova 400 spectrometer operating at 376.127 MHz. Spectra were referenced to an external hexaflourobenzene standard. Infrared spectroscopy was conducted on a Mattson RS-10500 Research Series FT-IR spectrometer calibrated with a polystyrene standard.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD Area detector system or a Bruker X8 APEX2 system equipped with a molybdenum X-ray tube (λ = 0.71073 A). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Preparation of (BDI-2)Ir(COE)N_2. This molecule was prepared in a similar manner to (BDI-**1**)Ir(COE)N_2 with 0.050 g (0.056 mmol) of $[Ir(COE)_2Cl]_2$ and 0.049g (0.111 mmol) of Li[BDI-**2**]·Et_2O yielding 0.028 g (48%) of brown crystals identified as (BDI-**2**)Ir(COE)N_2. Anal. Calcd. for $C_{33}H_{47}IrN_4$: C, 57.28; H, 6.85; N, 8.10. Found: C, 57.62; H, 6.91; N, 7.75. ^{1}H NMR (benzene-d_6): δ = 1.00-1.22 (m, 8H, *CH_2* COE), 1.28 (t, 6H, 8 Hz, CH_2*Me*), 1.48 (t, 6H, 8 Hz, CH_2*Me*), 1.49 (s, 3H, *CH_3*), 1.72 (s, 3H, *CH_3*), 2.23 (br s, 2H, *CH_2* COE), 2.42 (m, 2H, C*H_2*Me), 2.67 (br d, 2H, *CH* COE), 2.79 (m, 2H, C*H_2*Me), 2.93 (m, 2H, C*H_2*Me), 3.17 (m, 2H, C*H_2*Me), 5.34 (s, 1H, *CH*), 7.19-7.26 (Ar*H*). ^{13}C

NMR (benzene-d_6): δ= 13.69, 14.35, 31.34 (*C*H_2 COE), 25.07, 25.92, (CH_2*Me*), 24.00, 24.10 (C*Me*), 26.75, 28.23 (*C*H_2Me), 59.16 (-*C*H COE), 101.30 (*C*H), 125.58, 126.31 (*p*-Ar), 126.57, 126.64 (*m*-Ar), 137.41, 138.30 (*o*-Ar). IR (benzene-d_6): $\nu_{N\text{-}N}$ = 2121 cm^{-1}.

Preparation of (BDI-1)Ir(COD). A 20 mL scintillation vial was charged with 0.093 g (0.14 mmol) of $[Ir(COD)Cl]_2$ in approximately 5 mL diethyl ether. The resulting orange slurry was chilled in a drybox freezer to –35 ºC for about 20 minutes after which time 0.105 g (0.280 mmol) Li[BDI-**1**]·Et_2O in approximately 5 mL diethyl ether was added. The orange mixture was stirred for 16 hrs at ambient temperature. Filtration through Celite followed by solvent removal *in vacuo* and subsequent recrystallization from pentane at -35 ºC affords 0.053g (37%) of a yellow solid identified as (BDI-**1**)Ir(COD). Anal. Calcd. for $C_{29}H_{37}IrN_2$: C, 57.49; H, 6.16; N, 4.62. Found: C, 57.40; H, 5.84; N, 4.36. ^{1}H NMR (benzene-d_6): δ = 1.42 (br d, 4H, COD), 1.56 (s, 6H, CH_3), 2.08 (br s, 4H, COD), 2.28 (s, 12H, ArMe) 3.04 (br s, 4H, COD), 5.39 (s, 1H, CH), 6.95-7.04 (Ar*H*). ^{13}C NMR (benzene-d_8): δ = 19.28 (Ar*Me*), 25.77 (C*Me*), 31.89, 63.22 (COD), 102.21 (*C*H), 126.07 (*p*-Ar), 129.00 (*m*-Ar), 132.97 (*o*-Ar).

Preparation of (BDI-3)Ir(COD). This molecule was prepared in a similar manner to (BDI-**1**)Ir(COD) with 0.101 g (0.150 mmol) of $[Ir(COD)Cl]_2$ and 0.151 g (0.30 mmol) Li[BDI-**3**]·Et_2O yielding 0.070g (65%) of orange solid identified as (BDI-**3**)Ir(COD). Single crystals suitable for X-ray diffraction were grown under similar conditions. Anal. Calcd. for $C_{37}H_{53}IrN_2$: C, 61.89; H, 7.44. Found: C, 61.67; H, 7.24. ^{1}H NMR (benzene-d_6): δ = 1.07 (d, 12H, 6Hz, CHMe_2), 1.41 (d, 12H, 6Hz, CHMe_2), 1.71 (s, 6H, CH_3), 2.06

(br s, 4H, COD), 3.18 (br s, 4H, COD), 3.50 (sept, 4H, 6Hz, C*H*Me$_2$), 5.33 (s, 1H, CH), 7.09-7.18 (Ar*H*). ^{13}C NMR (benzene-d_8): δ =24.46, 25.04 (CH*Me*$_2$), 26.56 (*C*HMe$_2$), 28.11 (C*Me*), 30.94, 62.36 (COD), 100.32 (*C*H), 123.90 (*p*-Ar), 126.49 (*m*-Ar), 142.56 (*o*-Ar).

Preparation of (BDI-4)Ir(COD). This molecule was prepared in a similar manner to (BDI-**1**)Ir(COD) with 0.100 g (0.149 mmol) of [Ir(COD)Cl]$_2$ and 0.181 g (0.298 mmol) of Li[BDI-**4**]·Et$_2$O yielding 0.027 g (11%) of red crystals identified as (BDI-**4**)Ir(COD). Anal. Calcd. for $C_{37}H_{45}IrN_2F_6$: C, 53.93; H, 5.50; N, 3.40. Found: C, 53.73; H, 5.78; N, 3.14. ^{1}H NMR (benzene-d_6): δ =1.21 (d, 12H, 7Hz, CH*Me*$_2$), 1.41 (br s, 4H, COD), 1.44 (d, 12H, 7Hz, CH*Me*$_2$), 1.99 (br s, 4H, COD), 3.33 (sept, 4H, 7Hz, C*H*Me$_2$), 3.38 (br s, 4H, COD), 6.52 (s, 1H, CH), 7.17 (br, 4H, *m*-Ar*H*), 7.24 (br, 2H, *p*-Ar*H*). ^{13}C NMR (benzene-d_8): δ =24.30, 24.90 (CH*Me*$_2$), 28.37 (*C*HMe$_2$), 30.44 (COD), 67.59 (COD), 94.45 (*C*H), 123.85 (*p*-Ar), 128.11 (*m*-Ar), 141.80 (*o*-Ar), 150.74 (*C*F$_3$). ^{19}F NMR (benzene-d_6): δ = 108.10 (s, C*F*$_3$).

Preparation of (BDI-5)Ir(COD). A 20 mL scintillation vial was charged with 0.044 g (0.066 mmol) of [Ir(COD)Cl]$_2$ and 0.075 g (0.132 mmol) of Li[BDI-**5**]·Et$_2$O in approximately 15 mL of diethyl ether. The yellow solution was stirred at ambient temperature for 2 days and the solvent removed *in vacuo* leaving a yellow solid. Extraction into pentane and filtration through a pad of Celite followed by solvent removal produced a yellow powder. Recrystallization from pentane or methylene chloride at -35 ºC afforded 0.020g (19%) of a yellow crystalline solid identified as (BDI-**5**)Ir(COD). Anal. Calcd. for $C_{43}H_{63}IrN_2$: C, 64.54; H, 7.94; N, 3.50. Found: C, 64.22; H, 7.65; N,

3.23. ^{1}H NMR (benzene-d_6): δ = 0.92 (s, 9H, C(CH_3)$_3$), 1.08 (d, 6H, 7Hz, CHMe_2), 1.15 (d, 6H, 7Hz, CHMe_2), 1.38 (d, 6H, 7Hz, CHMe_2), 1.41 (d, 6H, 7Hz, CHMe_2), 1.77 (br d, 4H, COD), 1.79 (s, 9H, C(CH_3)$_3$), 2.00 (br s, 4H, COD), 2.93 (sept, 2H, 7Hz, CHMe$_2$), 3.23 (sept, 2H, 7Hz, CHMe$_2$), 3.91 (br s, 4H, COD), 4.64 (t, 1H, 6Hz, η^6-*p*-Ar), 5.03 (d, 2H, 6Hz, η^6- *m*-Ar), 5.39 (s, 1H, CH), 7.15 (br, 4H, *m*-ArH), 7.30 (br s, 2H, *p*-ArH). ^{13}C NMR (benzene-d_8): δ =23.00, 23.32, 23.85, 25.19 (CHMe_2), 27.62, 28.74 (CHMe$_2$), 30.31, 31.41 (C(CH_3)$_3$), 33.73, 54.85 (COD), 79.47 (η^6-*p*-Ar), 93.04 (η^6-*m*-Ar), 98.58 (CH), 122.44 (*p*-Ar), 123.20 (*m*-Ar), 136.23 (*o*-Ar).

Preparation of (BDI-1)Ir(CO)$_2$. A J. Young NMR tube was charged with 8 mg (0.01 mmol) of (BDI-**1**)Ir(COE)N$_2$ and approximately 0.5 mL of benzene-d_6. On the vacuum line, the tube was submerged in liquid nitrogen, evacuated and 1 atm of CO admitted. The solution was quickly thawed and left to stand at ambient temperature for 24 hours.. The solvent and resulting cyclooctene was removed *in vacuo* to yielding a yellow foam. ^{1}H NMR (benzene-d_6): δ = 1.45 (s, 12H, ArMe), 2.03 (s, 6H, CH_3), 5.14 (s, 1H, CH), 6.91-7.01 (ArH). ^{13}C NMR (benzene-d_6): δ= 19.37 (ArMe), 22.32 (CH$_3$), 101.81 (CH), 126.66 (*p*-Ar), 128.71 (*m*-Ar), 131.59 (*o*-Ar). IR (pentane): ν_{CO} = 2054cm^{-1}, 1986 cm^{-1}.

Preparation of (BDI-2)Ir(CO)$_2$. This molecule was prepared in a similar manner to (BDI-**1**)Ir(CO)$_2$ with 10 mg (0.020 mmol) of (BDI-**2**)Ir(COE)N$_2$. ^{1}H NMR (benzene-d_6): δ = 1.25 (t, 12H, 8 Hz, CH$_2$$Me$), 1.53 (s, 6H, C$H_3$), 2.55 (m, 4H, C$H_2$Me), 2.69 (m, 4H, C$H_2$Me), 5.18 (s, 1H, CH), 7.07-7.18 (ArH). ^{13}C NMR (benzene-d_6): δ= 14.24 (CH$_2$$Me$),

22.99 (*C*H_3), 24.98 (*C*H_2Me), 101.43 (*C*H), 126.18 (*p*-Ar), 127.07 (*m*-Ar), 136.63 (*o*-Ar). IR (pentane): ν_{CO} = 2054cm^{-1}, 1985 cm^{-1}.

Preparation of (BDI-3)Ir(CO)$_2$. A thick walled glass vessel was charged with 0.012 g (0.020 mmol) of (BDI-**3**)IrH_4 and approximately 15 mL of pentane. On the vacuum line, the vessel was submerged in liquid nitrogen, evacuated and one atmosphere of CO added. The contents of the vessel were thawed and the resulting solution stirred for 24 hours at ambient temperature. The pentane was removed *in vacuo* and the resulting yellow solid recrystallized from pentane at –35 ºC yielding 0.009g (71%) of (BDI-**3**)Ir$(CO)_2$. Anal. Calcd. for $C_{31}H_{41}IrN_2O_2$: C, 55.92; H, 6.21; N, 4.21. Found: C, 55.44; H, 5.69; N, 3.94. ^{1}H NMR (benzene-d_6): δ =1.08 (d, 12H, 7Hz, CH*Me*$_2$), 1.47 (d, 12H, 7Hz, CH*Me*$_2$), 1.64 (s, 6H, CH_3), 3.30 (sept, 4H, 7Hz, C*H*Me$_2$), 5.24 (s, 1H, CH), 7.10 (br s, 4H, *m*-Ar*H*), 7.11 (br s, 2H, *p*-Ar*H*). ^{13}C NMR (benzene-d_8): δ =23.44, 24.49 (CH*Me*$_2$), 24.57 (C*Me*), 28.05 (*C*HMe$_2$), 100.97 (*C*H), 124.14 (*p*-Ar), 127.70 (*m*-Ar), 141.35 (*o*-Ar), 154.62 (N-*C*), 160.47 (*C*Me), 198.50 (*C*O). IR (pentane): ν_{CO} =1985cm^{-1}, 2053cm^{-1}.

Preparation of (BDI-4)Ir(CO)$_2$. A thick walled glass vessel was charged with 0.014 g (0.017 mmol) of (BDI-**4**)Ir(COD) and approximately 15 mL of pentane. On the vacuum line, the vessel was submerged in liquid nitrogen, evacuated and one atmosphere of CO added. The contents of the vessel were thawed and the resulting solution stirred for 24 hours at ambient temperature. The pentane was removed *in vacuo* yielding 0.011 g (82%) of a yellow powder identified as (BDI-**4**)Ir$(CO)_2$. Anal. Calcd. for $C_{31}H_{35}IrN_2O_2F_6$: C, 48.12; H, 4.56; N, 3.62. Found: C, 48.55; H, 5.01; N, 3.66. ^{1}H NMR (benzene-d_6): δ =1.32 (d, 12H, 7Hz, CH*Me*$_2$), 1.60 (d, 12H, 7Hz, CH*Me*$_2$), 3.13 (sept, 4H, 7Hz, C*H*Me$_2$),

6.75 (s, 1H, CH), 7.15 (br s, 4H, *m*-Ar*H*), 7.25 (br s, 2H, *p*-Ar*H*). ^{13}C NMR (benzene-d_8): δ =23.82, 25.26 (CH*Me*$_2$), 29.15 (*C*HMe$_2$), 92.32 (*C*H), 123.82 (*p*-Ar), 128.88 (*m*-Ar), 141.18 (*o*-Ar), 148.70 (*C*F$_3$), 153.76 (N-*C*), 170.18 (*C*O). ^{19}F NMR (benzene-d_6): δ = 102.62 (s, C*F*$_3$). IR (pentane): ν_{CO} =2005cm^{-1}, 2069cm^{-1}.

Preparation of (BDI-1)IrH$_2$N$_2$. A thick walled glass vessel was charged with 0.098 g (0.15 mmol) of (BDI-**1**)Ir(COE)N$_2$ and approximately 10 mL of pentane. On the vacuum line, the vessel was submerged in liquid nitrogen, evacuated and one atmosphere of H$_2$ admitted. The contents of the vessel were then thawed and the resulting yellow solution stirred at ambient temperature for 8 hours. The resulting dark purple solution was transferrd into the dry box and filtered through a glass frit. The filtrate was collected and the pentane removed *in vacuo* yielding a dark foam. Recrystallization from pentane at –35 ºC yielded 0.024 g (30 %) of a black solid identified as (BDI-**1**)IrH$_2$N$_2$. Anal. Calcd. for CHIrN: C,; H,; N,. Found: C,; H,; N,. ^{1}H NMR (cyclohexane-d_{12}): δ = 1.59 (s, 6H, Ar*Me*), 1.80 (s, 6H, Ar*Me*), 2.18 (s, 3H, *CH*$_3$), 2.26 (s, 3H, *CH*$_3$), 5.36 (s, 1H, *CH*), 6.93-7.08 (Ar*H*), -20.45 (s, 2H, Ir-*H*), -20.09 (t, 3.6Hz, 1H, Ir-*H*D in benzene-d_6). ^{13}C NMR (cyclohexane-d_{12}): δ= 19.03, 19.27 (Ar*Me*), 22.29, 22.46 (C*Me*), 101.97 (*C*H), 124.76, 125.85 (*p*-Ar), 128.41 (*m*-Ar), 130.91, 131.51 (*o*-Ar). IR (benzene-d_6): $\nu_{N\text{-}N}$ = 2167 cm^{-1}; IR (KBr): $\nu_{N\text{-}N}$ = 2170 cm^{-1}.

Thermolysis of (BDI-1)Ir(COE)N$_2$. A J. Young NMR tube was charged with 8 mg (0.013 mmol) of (BDI-**1**)Ir(COE)N$_2$ and approximately 0.5 mL of cyclohexane-d_{12}. On the vacuum line, the tube was submerged in liquid nitrogen and evacuated. The contents of the tube were thawed and the procedure repeated. The resulting reaction mixture was

thermolyzed in a 50 ºC oil bath for 8 hours and monitored by ^{1}H NMR spectroscopy. The tube was periodically evacuated to remove the N_2 product. The spectra collected over time revealed formation of (BDI-**1**)Ir(η^3-C_8H_{13})H followed by the appearance of (BDI-**1**)Ir(COE)H_2 and two iridium cyclooctadiene complexes in a 14:1 ratio. The major product was identified as (BDI-**1**)Ir(1,4-COD). **(BDI-1)Ir(1,4-COD)**: ^{1}H NMR (cyclohexane-d_{12}): δ = 1.47 (m, 1,4-COD), 1.52 (s, 12H, Ar*Me*), 1.63 (s, 6H, CH_3), 1.94 (m, 1,4-COD), 2.65 (m, 1,4-COD), 2.45 (m, 1,4-COD), 4.07 (dt, 2H, 1,4-COD), 5.32 (s, 1H, *CH*), 6.82-7.11 (Ar*H*).

Preparation of 3. This molecule was prepared in a manner similar to **2** with 10 mg (0.02 mmol) of (BDI-**2**)Ir(COE)N_2 in 0.5 mL of benzene-d_6 resulting in a red solution of **3** identified in approximately 85% yield by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ = 1.15 (t, 3H, 12Hz, CH_2*Me*), 1.25 (t, 3H, 12Hz, CH_2*Me*), 1.26 (t, 3H, 12Hz, CH_2*Me*), 1.67 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.26 (m, 2H, CH_2Me), 2.48 (m, 2H, CH_2Me), 2.75 (m, 2H, CH_2Me), 4.12 (dd, 1H, ^1J= 11, ^2J= 1.2 Hz, olefinic CH), 4.25 dd, 1H, ^1J= 11, ^2J= 1.2 Hz, olefinic CH), 2.34 (dd, 1H, olefinic CH), 4.78 (s, 1H, CH), 6.65- 7.18 (Ar*H*).

Preparation of 4. This molecule was prepared in a similar manner to (BDI-**1**)Ir$(CO)_2$ with approximately 10 mg of **4** prepared *in situ* from (BDI-**2**)Ir(COE)N_2 in approximately 0.5 mL of benzene-d_6. On the vacuum line, the solution was frozen at 77 K one atmosphere of CO was admitted. The solution was thawed and the resulting yellow solution was left to stand at ambient temperature for 1 day. ^{1}H NMR (benzene-d_6): δ = 1.24 (t, 3H, 12Hz, CH_2*Me*), 1.26 (t, 3H, 12Hz, CH_2*Me*), 1.27 (t, 3H, 12Hz, CH_2*Me*), 1.51 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.53 (m, 2H, CH_2Me), 2.59 (m, 2H, CH_2Me), 2.96 (m,

2H, C*H*$_2$Me), 5.11 (dd, 1H, ^1J= 17, ^2J= 1.4 Hz, olefinic CH), 5.18 (dd, 1H, olefinic CH), 5.61 dd, 1H, ^1J= 17, ^2J= 1.4 Hz, olefinic CH), 5.17 (s, 1H, CH), 6.98- 7.41 (Ar*H*). IR (pentane): ν_{CO} = 2055 cm^{-1}, 1986 cm^{-1}.

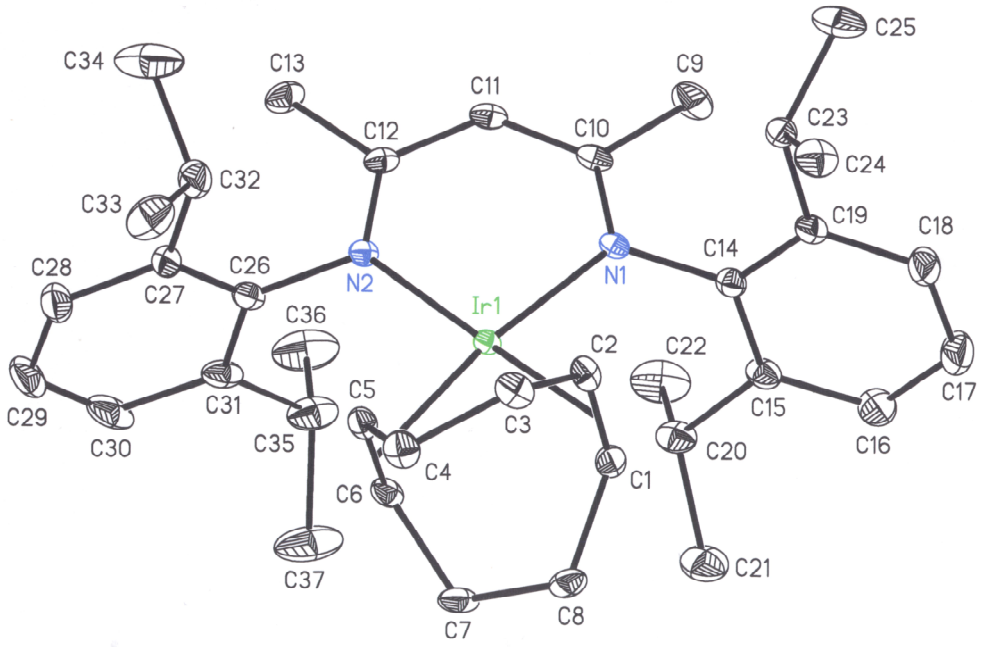

Figure S1. Fully labeled view of the molecular structure of (BDI-**3**)Ir(COD) at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S1. Crystal data and structure refinement for (BDI-**3**)Ir(COD).

Identification code	cb3	
Empirical formula	C37 H53 Ir N2	
Formula weight	718.01	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.2170(8) Å	α= 90°.
	b = 13.0464(3) Å	β= 110.693(1)°.
	c = 16.0041(3) Å	γ = 90°.
Volume	6488.1(2) $Å^3$	
Z	8	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	4.143 mm^{-1}	
F(000)	2928	
Crystal size	0.30 x 0.20 x 0.15 mm^3	
Theta range for data collection	1.31 to 33.14°.	
Index ranges	-50<=h<=39, -19<=k<=15, -23<=l<=23	
Reflections collected	37846	
Independent reflections	10890 [R(int) = 0.0464]	
Completeness to theta = 33.14°	88.0 %	
Absorption correction	SADABS	
Max. and min. transmission	0.5754 and 0.3696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10890 / 0 / 361	
Goodness-of-fit on F^2	0.999	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0712	
R indices (all data)	R1 = 0.0544, wR2 = 0.0795	
Largest diff. peak and hole	2.298 and -1.570 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for (BDI-**3**)Ir(COD).

Ir(1)-N(2)	2.088(2)	C(26)-C(27)	1.404(5)
Ir(1)-N(1)	2.096(2)	C(26)-C(31)	1.419(5)
Ir(1)-C(6)	2.116(3)	C(27)-C(28)	1.390(5)
Ir(1)-C(2)	2.117(3)	C(27)-C(32)	1.528(5)
Ir(1)-C(5)	2.143(3)	C(28)-C(29)	1.391(6)
Ir(1)-C(1)	2.165(3)	C(29)-C(30)	1.378(7)
N(1)-C(10)	1.352(3)	C(30)-C(31)	1.396(5)
N(1)-C(14)	1.443(4)	C(31)-C(35)	1.522(6)
N(2)-C(12)	1.340(4)	C(32)-C(33)	1.525(6)
N(2)-C(26)	1.444(4)	C(32)-C(34)	1.523(6)
C(1)-C(2)	1.413(5)	C(35)-C(36)	1.532(6)
C(1)-C(8)	1.513(4)	C(35)-C(37)	1.542(6)
C(2)-C(3)	1.514(4)		
C(3)-C(4)	1.532(5)	N(2)-Ir(1)-N(1)	90.14(10)
C(4)-C(5)	1.529(4)	N(2)-Ir(1)-C(6)	93.25(11)
C(5)-C(6)	1.414(5)	N(1)-Ir(1)-C(6)	151.12(12)
C(6)-C(7)	1.513(5)	N(2)-Ir(1)-C(2)	152.57(12)
C(7)-C(8)	1.528(5)	N(1)-Ir(1)-C(2)	93.36(11)
C(9)-C(10)	1.512(4)	C(6)-Ir(1)-C(2)	96.62(12)
C(10)-C(11)	1.383(5)	N(2)-Ir(1)-C(5)	92.32(11)
C(11)-C(12)	1.392(5)	N(1)-Ir(1)-C(5)	169.57(11)
C(12)-C(13)	1.519(4)	C(6)-Ir(1)-C(5)	38.79(13)
C(14)-C(19)	1.410(5)	C(2)-Ir(1)-C(5)	79.86(12)
C(14)-C(15)	1.409(4)	N(2)-Ir(1)-C(1)	168.54(12)
C(15)-C(16)	1.390(5)	N(1)-Ir(1)-C(1)	91.69(11)
C(15)-C(20)	1.529(5)	C(6)-Ir(1)-C(1)	79.78(12)
C(16)-C(17)	1.389(6)	C(2)-Ir(1)-C(1)	38.53(13)
C(17)-C(18)	1.374(6)	C(5)-Ir(1)-C(1)	87.90(12)
C(18)-C(19)	1.398(5)	C(10)-N(1)-C(14)	114.4(2)
C(19)-C(23)	1.524(5)	C(10)-N(1)-Ir(1)	124.5(2)
C(20)-C(21)	1.520(5)	C(14)-N(1)-Ir(1)	120.18(18)
C(20)-C(22)	1.530(5)	C(12)-N(2)-C(26)	114.0(2)
C(23)-C(24)	1.525(5)	C(12)-N(2)-Ir(1)	125.6(2)
C(23)-C(25)	1.536(5)	C(26)-N(2)-Ir(1)	120.20(17)

C(2)-C(1)-C(8)	123.4(3)	C(18)-C(19)-C(14)	118.6(3)
C(2)-C(1)-Ir(1)	68.91(17)	C(18)-C(19)-C(23)	118.2(3)
C(8)-C(1)-Ir(1)	114.2(2)	C(14)-C(19)-C(23)	123.2(3)
C(1)-C(2)-C(3)	124.3(3)	C(21)-C(20)-C(15)	112.8(3)
C(1)-C(2)-Ir(1)	72.57(17)	C(21)-C(20)-C(22)	109.7(3)
C(3)-C(2)-Ir(1)	113.1(2)	C(15)-C(20)-C(22)	112.1(3)
C(2)-C(3)-C(4)	112.0(3)	C(19)-C(23)-C(24)	112.3(3)
C(5)-C(4)-C(3)	110.9(2)	C(19)-C(23)-C(25)	111.8(3)
C(6)-C(5)-C(4)	124.3(3)	C(24)-C(23)-C(25)	107.3(3)
C(6)-C(5)-Ir(1)	69.60(18)	C(27)-C(26)-C(31)	121.5(3)
C(4)-C(5)-Ir(1)	115.2(2)	C(27)-C(26)-N(2)	121.1(3)
C(5)-C(6)-C(7)	125.4(3)	C(31)-C(26)-N(2)	117.4(3)
C(5)-C(6)-Ir(1)	71.61(18)	C(28)-C(27)-C(26)	118.2(4)
C(7)-C(6)-Ir(1)	112.4(2)	C(28)-C(27)-C(32)	120.0(4)
C(6)-C(7)-C(8)	111.4(3)	C(26)-C(27)-C(32)	121.7(3)
C(1)-C(8)-C(7)	111.2(2)	C(29)-C(28)-C(27)	121.4(4)
N(1)-C(10)-C(11)	124.9(3)	C(30)-C(29)-C(28)	119.5(4)
N(1)-C(10)-C(9)	120.2(3)	C(29)-C(30)-C(31)	122.0(4)
C(11)-C(10)-C(9)	114.9(3)	C(30)-C(31)-C(26)	117.3(4)
C(10)-C(11)-C(12)	129.7(3)	C(30)-C(31)-C(35)	121.5(4)
N(2)-C(12)-C(11)	124.1(3)	C(26)-C(31)-C(35)	121.2(3)
N(2)-C(12)-C(13)	121.8(3)	C(33)-C(32)-C(34)	108.6(3)
C(11)-C(12)-C(13)	114.1(3)	C(33)-C(32)-C(27)	113.3(3)
C(19)-C(14)-C(15)	120.5(3)	C(34)-C(32)-C(27)	111.5(4)
C(19)-C(14)-N(1)	121.6(3)	C(36)-C(35)-C(31)	112.8(3)
C(15)-C(14)-N(1)	117.8(3)	C(36)-C(35)-C(37)	109.4(3)
C(16)-C(15)-C(14)	118.6(3)	C(31)-C(35)-C(37)	112.3(4)
C(16)-C(15)-C(20)	120.3(3)		
C(14)-C(15)-C(20)	121.1(3)		
C(17)-C(16)-C(15)	121.3(4)		
C(18)-C(17)-C(16)	119.8(4)		
C(17)-C(18)-C(19)	121.2(4)		

Symmetry transformations used to generate equivalent atoms:

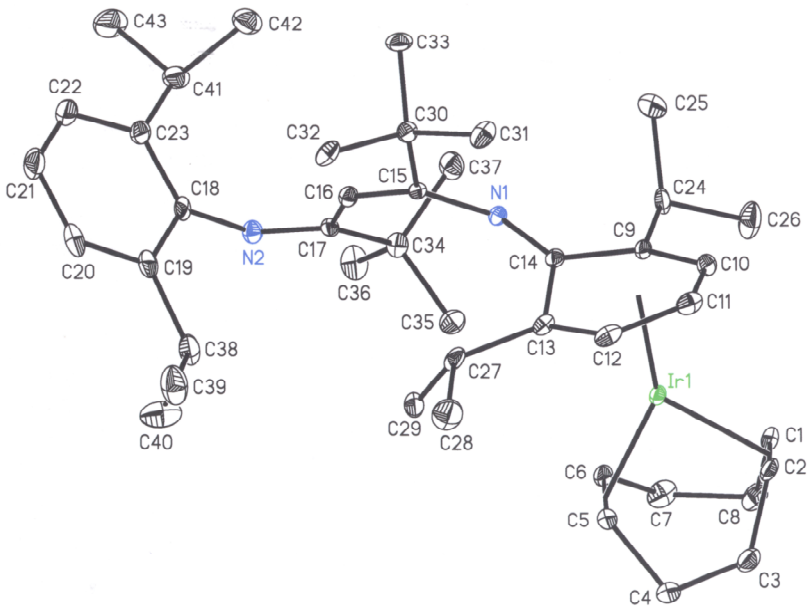

Figure S2. Fully labeled view of the molecular structure of (BDI-**5**)Ir(COD) at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S3. Crystal data and structure refinement for (BDI-**5**)Ir(COD).

Identification code	wb5	
Empirical formula	C43 H65 Ir N2	
Formula weight	802.17	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.8294(10) Å	α= 90°.
	b = 19.1650(17) Å	β= 91.796(2)°.
	c = 16.9639(15) Å	γ = 90°.
Volume	3844.0(6) $Å^3$	
Z	4	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	3.504 mm^{-1}	
F(000)	1656	
Crystal size	0.25 x 0.05 x 0.03 mm^3	
Theta range for data collection	2.07 to 30.51°.	
Index ranges	-16<=h<=16, -26<=k<=26, -23<=l<=23	
Reflections collected	44018	
Independent reflections	11320 [R(int) = 0.0782]	
Completeness to theta = 30.51°	96.5 %	
Absorption correction	SADABS	
Max. and min. transmission	0.9175 and 0.4745	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11320 / 0 / 651	
Goodness-of-fit on F^2	0.953	
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0701	
R indices (all data)	R1 = 0.0738, wR2 = 0.0807	
Largest diff. peak and hole	1.307 and -0.841 $e.Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for (BDI-**5**)Ir(COD).

Ir(1)-C(5)	2.108(4)	C(18)-C(19)	1.418(5)
Ir(1)-C(6)	2.113(4)	C(19)-C(20)	1.383(6)
Ir(1)-C(1)	2.137(4)	C(19)-C(38)	1.522(6)
Ir(1)-C(2)	2.142(4)	C(20)-C(21)	1.400(7)
Ir(1)-C(10)	2.231(4)	C(21)-C(22)	1.363(7)
Ir(1)-C(11)	2.241(4)	C(22)-C(23)	1.386(6)
Ir(1)-C(12)	2.245(4)	C(23)-C(41)	1.518(6)
Ir(1)-C(13)	2.292(4)	C(24)-C(26)	1.521(6)
Ir(1)-C(9)	2.373(4)	C(24)-C(25)	1.532(6)
N(1)-C(14)	1.295(4)	C(27)-C(29)	1.517(6)
N(1)-C(15)	1.366(4)	C(27)-C(28)	1.519(6)
N(2)-C(17)	1.288(4)	C(30)-C(32)	1.538(5)
N(2)-C(18)	1.418(5)	C(30)-C(31)	1.532(5)
C(1)-C(2)	1.431(6)	C(30)-C(33)	1.537(5)
C(1)-C(8)	1.516(6)	C(34)-C(35)	1.527(6)
C(2)-C(3)	1.504(6)	C(34)-C(37)	1.531(6)
C(3)-C(4)	1.526(6)	C(34)-C(36)	1.543(6)
C(4)-C(5)	1.529(5)	C(38)-C(40)	1.524(7)
C(5)-C(6)	1.426(6)	C(38)-C(39)	1.527(6)
C(6)-C(7)	1.511(6)	C(41)-C(43)	1.521(6)
C(7)-C(8)	1.536(6)	C(41)-C(42)	1.536(6)
C(9)-C(10)	1.413(5)		
C(9)-C(14)	1.468(5)	C(5)-Ir(1)-C(6)	39.50(15)
C(9)-C(24)	1.516(5)	C(5)-Ir(1)-C(1)	88.62(16)
C(10)-C(11)	1.404(6)	C(6)-Ir(1)-C(1)	80.30(16)
C(11)-C(12)	1.399(6)	C(5)-Ir(1)-C(2)	80.19(15)
C(12)-C(13)	1.434(5)	C(6)-Ir(1)-C(2)	97.52(15)
C(13)-C(14)	1.479(5)	C(1)-Ir(1)-C(2)	39.07(16)
C(13)-C(27)	1.534(5)	C(5)-Ir(1)-C(10)	175.04(16)
C(15)-C(16)	1.372(5)	C(6)-Ir(1)-C(10)	144.60(15)
C(15)-C(30)	1.567(5)	C(1)-Ir(1)-C(10)	94.96(16)
C(16)-C(17)	1.464(5)	C(2)-Ir(1)-C(10)	100.45(15)
C(17)-C(34)	1.543(5)	C(5)-Ir(1)-C(11)	138.63(16)
C(18)-C(23)	1.414(5)	C(6)-Ir(1)-C(11)	168.76(15)

C(1)-Ir(1)-C(11)	110.86(16)	C(4)-C(5)-Ir(1)	115.6(3)
C(2)-Ir(1)-C(11)	92.39(15)	C(5)-C(6)-C(7)	123.5(4)
C(10)-Ir(1)-C(11)	36.60(15)	C(5)-C(6)-Ir(1)	70.1(2)
C(5)-Ir(1)-C(12)	109.68(16)	C(7)-C(6)-Ir(1)	113.1(3)
C(6)-Ir(1)-C(12)	133.41(16)	C(6)-C(7)-C(8)	111.8(4)
C(1)-Ir(1)-C(12)	143.84(16)	C(1)-C(8)-C(7)	111.1(3)
C(2)-Ir(1)-C(12)	111.75(15)	C(10)-C(9)-C(14)	117.6(3)
C(10)-Ir(1)-C(12)	65.47(16)	C(10)-C(9)-C(24)	121.0(3)
C(11)-Ir(1)-C(12)	36.34(16)	C(14)-C(9)-C(24)	119.0(3)
C(5)-Ir(1)-C(13)	100.51(14)	C(10)-C(9)-Ir(1)	66.7(2)
C(6)-Ir(1)-C(13)	103.48(14)	C(14)-C(9)-Ir(1)	86.0(2)
C(1)-Ir(1)-C(13)	169.54(14)	C(24)-C(9)-Ir(1)	131.7(3)
C(2)-Ir(1)-C(13)	147.29(15)	C(11)-C(10)-C(9)	122.2(4)
C(10)-Ir(1)-C(13)	76.26(14)	C(11)-C(10)-Ir(1)	72.1(2)
C(11)-Ir(1)-C(13)	65.30(14)	C(9)-C(10)-Ir(1)	77.7(2)
C(12)-Ir(1)-C(13)	36.83(13)	C(12)-C(11)-C(10)	119.4(4)
C(5)-Ir(1)-C(9)	146.09(13)	C(12)-C(11)-Ir(1)	72.0(2)
C(6)-Ir(1)-C(9)	111.96(14)	C(10)-C(11)-Ir(1)	71.3(2)
C(1)-Ir(1)-C(9)	106.21(14)	C(11)-C(12)-C(13)	119.4(4)
C(2)-Ir(1)-C(9)	130.09(14)	C(11)-C(12)-Ir(1)	71.7(2)
C(10)-Ir(1)-C(9)	35.57(13)	C(13)-C(12)-Ir(1)	73.4(2)
C(11)-Ir(1)-C(9)	64.53(14)	C(12)-C(13)-C(14)	118.3(3)
C(12)-Ir(1)-C(9)	76.06(14)	C(12)-C(13)-C(27)	119.4(3)
C(13)-Ir(1)-C(9)	63.33(12)	C(14)-C(13)-C(27)	118.8(3)
C(14)-N(1)-C(15)	133.0(3)	C(12)-C(13)-Ir(1)	69.8(2)
C(17)-N(2)-C(18)	123.2(3)	C(14)-C(13)-Ir(1)	88.9(2)
C(2)-C(1)-C(8)	122.5(4)	C(27)-C(13)-Ir(1)	128.9(3)
C(2)-C(1)-Ir(1)	70.7(2)	N(1)-C(14)-C(9)	118.3(3)
C(8)-C(1)-Ir(1)	115.0(3)	N(1)-C(14)-C(13)	128.7(3)
C(1)-C(2)-C(3)	124.3(4)	C(9)-C(14)-C(13)	112.5(3)
C(1)-C(2)-Ir(1)	70.3(2)	N(1)-C(15)-C(16)	125.4(3)
C(3)-C(2)-Ir(1)	112.2(3)	N(1)-C(15)-C(30)	117.0(3)
C(2)-C(3)-C(4)	112.2(3)	C(16)-C(15)-C(30)	115.9(3)
C(5)-C(4)-C(3)	111.1(3)	C(15)-C(16)-C(17)	137.2(4)
C(6)-C(5)-C(4)	123.4(4)	N(2)-C(17)-C(16)	119.6(3)
C(6)-C(5)-Ir(1)	70.4(2)	N(2)-C(17)-C(34)	115.2(3)

C(16)-C(17)-C(34)	124.7(3)	C(32)-C(30)-C(31)	107.8(3)
C(23)-C(18)-C(19)	120.4(4)	C(32)-C(30)-C(33)	108.8(3)
C(23)-C(18)-N(2)	117.0(3)	C(31)-C(30)-C(33)	107.7(3)
C(19)-C(18)-N(2)	121.9(3)	C(32)-C(30)-C(15)	112.1(3)
C(20)-C(19)-C(18)	118.4(4)	C(31)-C(30)-C(15)	113.6(3)
C(20)-C(19)-C(38)	121.5(4)	C(33)-C(30)-C(15)	106.7(3)
C(18)-C(19)-C(38)	119.9(4)	C(35)-C(34)-C(37)	110.6(3)
C(19)-C(20)-C(21)	120.8(4)	C(35)-C(34)-C(17)	112.6(3)
C(22)-C(21)-C(20)	120.3(4)	C(37)-C(34)-C(17)	107.8(3)
C(21)-C(22)-C(23)	121.5(4)	C(35)-C(34)-C(36)	107.0(4)
C(22)-C(23)-C(18)	118.6(4)	C(37)-C(34)-C(36)	108.6(4)
C(22)-C(23)-C(41)	122.0(4)	C(17)-C(34)-C(36)	110.2(3)
C(18)-C(23)-C(41)	119.3(4)	C(19)-C(38)-C(40)	110.3(4)
C(9)-C(24)-C(26)	113.2(4)	C(19)-C(38)-C(39)	114.0(4)
C(9)-C(24)-C(25)	110.6(4)	C(40)-C(38)-C(39)	110.2(4)
C(26)-C(24)-C(25)	110.2(4)	C(23)-C(41)-C(43)	114.1(4)
C(29)-C(27)-C(28)	108.8(4)	C(23)-C(41)-C(42)	111.1(4)
C(29)-C(27)-C(13)	114.5(3)	C(43)-C(41)-C(42)	109.5(4)
C(28)-C(27)-C(13)	114.6(4)		

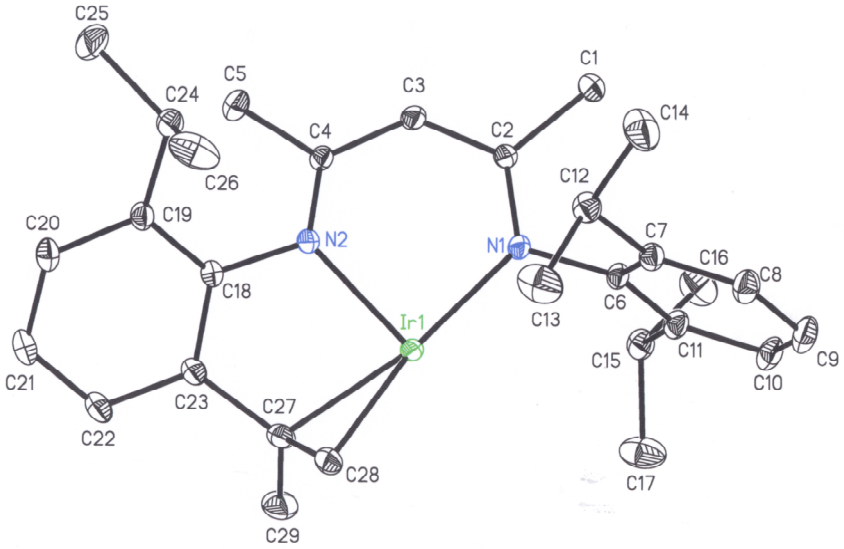

Figure S3. Fully labeled view of the molecular structure of **2** at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S5. Crystal data and structure refinement for **2**.

Identification code	wb17	
Empirical formula	C29 H39 Ir N2	
Formula weight	607.82	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7968(4) Å	α= 70.603(2)°.
	b = 11.7022(5) Å	β= 69.381(2)°.
	c = 12.7810(5) Å	γ = 66.310(2)°.
Volume	1349.37(9) $Å^3$	
Z	2	
Density (calculated)	1.496 Mg/m^3	
Absorption coefficient	4.965 mm^{-1}	
F(000)	608	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.75 to 39.67°.	
Index ranges	-19<=h<=19, -20<=k<=20, -22<=l<=19	
Reflections collected	52539	
Independent reflections	15437 [R(int) = 0.0231]	
Completeness to theta = 39.67°	94.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6366 and 0.4367	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15437 / 0 / 339	
Goodness-of-fit on F^2	0.875	
Final R indices [I>2sigma(I)]	R1 = 0.0212, wR2 = 0.0513	
R indices (all data)	R1 = 0.0298, wR2 = 0.0550	
Largest diff. peak and hole	2.250 and -0.957 $e.Å^{-3}$	

Table 3. Bond lengths [Å] and angles [°] for wb17.

Ir(1)-N(1)	2.0431(12)	C(22)-C(23)	1.394(2)
Ir(1)-N(2)	2.0528(12)	C(23)-C(27)	1.500(2)
Ir(1)-C(28)	2.1260(15)	C(24)-C(26)	1.522(3)
Ir(1)-C(27)	2.1627(15)	C(24)-C(25)	1.530(3)
Ir(1')-N(1)	2.191(4)	C(27)-C(28)	1.416(2)
Ir(1')-C(13)	2.351(5)	C(27)-C(29)	1.505(2)
Ir(1')-C(12)	2.373(5)		
Ir(1')-N(2)	2.392(4)	N(1)-Ir(1)-N(2)	89.44(5)
N(1)-C(2)	1.3284(18)	N(1)-Ir(1)-C(28)	158.64(6)
N(1)-C(6)	1.4451(18)	N(2)-Ir(1)-C(28)	100.18(6)
N(2)-C(4)	1.3418(18)	N(1)-Ir(1)-C(27)	162.62(6)
N(2)-C(18)	1.4208(17)	N(2)-Ir(1)-C(27)	79.73(5)
C(1)-C(2)	1.508(2)	C(28)-Ir(1)-C(27)	38.54(6)
C(2)-C(3)	1.404(2)	N(1)-Ir(1')-C(13)	106.63(16)
C(3)-C(4)	1.3869(19)	N(1)-Ir(1')-C(12)	78.60(13)
C(4)-C(5)	1.512(2)	C(13)-Ir(1')-C(12)	37.60(10)
C(6)-C(7)	1.402(2)	N(1)-Ir(1')-N(2)	77.81(13)
C(6)-C(11)	1.406(2)	C(13)-Ir(1')-N(2)	171.5(2)
C(7)-C(8)	1.393(2)	C(12)-Ir(1')-N(2)	150.47(18)
C(7)-C(12)	1.519(2)	C(2)-N(1)-C(6)	117.45(12)
C(8)-C(9)	1.388(3)	C(2)-N(1)-Ir(1)	125.64(10)
C(9)-C(10)	1.380(3)	C(6)-N(1)-Ir(1)	116.90(9)
C(10)-C(11)	1.396(2)	C(2)-N(1)-Ir(1')	103.07(14)
C(11)-C(15)	1.510(2)	C(6)-N(1)-Ir(1')	107.49(13)
C(12)-C(14)	1.518(3)	Ir(1)-N(1)-Ir(1')	59.13(13)
C(12)-C(13)	1.523(3)	C(4)-N(2)-C(18)	120.52(12)
C(15)-C(16)	1.520(3)	C(4)-N(2)-Ir(1)	123.11(9)
C(15)-C(17)	1.526(3)	C(18)-N(2)-Ir(1)	113.57(9)
C(18)-C(23)	1.397(2)	C(4)-N(2)-Ir(1')	108.49(14)
C(18)-C(19)	1.404(2)	C(18)-N(2)-Ir(1')	117.59(12)
C(19)-C(20)	1.395(2)	Ir(1)-N(2)-Ir(1')	55.55(11)
C(19)-C(24)	1.521(2)	N(1)-C(2)-C(3)	123.48(13)
C(20)-C(21)	1.384(3)	N(1)-C(2)-C(1)	120.30(13)
C(21)-C(22)	1.390(3)	C(3)-C(2)-C(1)	116.20(13)

C(4)-C(3)-C(2)	128.36(13)	C(16)-C(15)-C(17)	110.15(16)
N(2)-C(4)-C(3)	122.97(12)	C(23)-C(18)-C(19)	120.86(13)
N(2)-C(4)-C(5)	120.82(13)	C(23)-C(18)-N(2)	114.42(12)
C(3)-C(4)-C(5)	116.07(12)	C(19)-C(18)-N(2)	124.48(13)
C(7)-C(6)-C(11)	121.86(13)	C(20)-C(19)-C(18)	116.94(15)
C(7)-C(6)-N(1)	118.74(12)	C(20)-C(19)-C(24)	120.52(14)
C(11)-C(6)-N(1)	119.37(13)	C(18)-C(19)-C(24)	122.00(13)
C(8)-C(7)-C(6)	118.07(14)	C(21)-C(20)-C(19)	121.86(15)
C(8)-C(7)-C(12)	120.28(15)	C(20)-C(21)-C(22)	119.92(14)
C(6)-C(7)-C(12)	121.63(13)	C(21)-C(22)-C(23)	119.47(16)
C(9)-C(8)-C(7)	121.04(17)	C(22)-C(23)-C(18)	119.33(15)
C(10)-C(9)-C(8)	119.93(15)	C(22)-C(23)-C(27)	122.68(14)
C(9)-C(10)-C(11)	121.41(16)	C(18)-C(23)-C(27)	117.22(12)
C(10)-C(11)-C(6)	117.68(15)	C(26)-C(24)-C(19)	108.47(15)
C(10)-C(11)-C(15)	120.18(14)	C(26)-C(24)-C(25)	110.14(19)
C(6)-C(11)-C(15)	122.14(13)	C(19)-C(24)-C(25)	114.53(15)
C(14)-C(12)-C(7)	112.57(15)	C(28)-C(27)-C(23)	113.13(14)
C(14)-C(12)-C(13)	111.45(19)	C(28)-C(27)-C(29)	120.93(16)
C(7)-C(12)-C(13)	110.53(16)	C(23)-C(27)-C(29)	118.01(15)
C(14)-C(12)-Ir(1')	143.74(18)	C(28)-C(27)-Ir(1)	69.33(9)
C(7)-C(12)-Ir(1')	99.23(14)	C(23)-C(27)-Ir(1)	108.11(9)
C(13)-C(12)-Ir(1')	70.40(18)	C(29)-C(27)-Ir(1)	117.20(12)
C(12)-C(13)-Ir(1')	71.99(17)	C(27)-C(28)-Ir(1)	72.13(9)
C(11)-C(15)-C(16)	111.92(15)		
C(11)-C(15)-C(17)	111.90(17)		

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