

## Supporting Information

### **Selective cleavage of the C-C bond of aminoethyl groups, via a multi-step pathway, by a pincer iridium complex**

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**General Methods.** All reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or under argon using standard Schlenk techniques. Benzene and *p*-xylene were distilled from sodium/benzophenone under argon. Deuterated solvents for use in NMR experiments were dried as their protiated analogs, but were vacuum transferred from the drying agent. (PCP)IrH<sub>2</sub><sup>1</sup> and N-ethylidene-ethylamine<sup>2</sup> (CH<sub>3</sub>CH<sub>2</sub>N=CHCH<sub>3</sub>) were synthesized according to published methods. All other chemicals were used as received from commercial suppliers.

<sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained on a 300-MHz, Varian Mercury-300 spectrometer. <sup>1</sup>H chemical shifts are reported in ppm downfield from tetramethylsilane and were referenced to residual protiated (<sup>1</sup>H) or deuterated solvent. <sup>31</sup>P NMR chemical shifts are reported in ppm downfield from 85% H<sub>3</sub>PO<sub>4</sub> and were referenced to external (capillary) PMe<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>. Dodecahydrotriphenylene was employed as an internal standard when yields were determined by NMR spectroscopy.

**Ir(H)(cyclohexylisocyanide)(CH<sub>3</sub>) (1a).** 15 mg of (PCP)IrH<sub>2</sub> (0.026 mmol) was dissolved in 1 mL of *p*-xylene solution containing 5.0 mg of norbornene (0.053 mmol) at room temperature. To the resulting solution was added 6.5  $\mu$ L of N-ethyl cyclohexylamine (0.052 mmol). An orange solution was obtained within 10 min. at room temperature. Complex **1a** was formed in 91% yield; complex **1b** was formed in 3% yield (<sup>31</sup>P{<sup>1</sup>H} NMR). The solvent and organic volatiles were removed by vacuum. The resulting orange solid was redissolved in pentane which was allowed to slowly evaporate to give orange crystals. Two different crystalline phases were obtained; structure determination of both gave molecular structures without any significant differences. Both structures are shown in Figure S1. **1a**: <sup>31</sup>P NMR (121.4 MHz, *para*-xylene-*d*<sub>10</sub>):  $\delta$  53.45 (d,  $J_{\text{PH}} = 12.4$  Hz). <sup>1</sup>H NMR (300 MHz, *para*-xylene-*d*<sub>10</sub>):  $\delta$  7.18 (d,  $J_{\text{HH}} = 7.2$  Hz, 2H, PCP aromatic-*H*), 7.09 (t,  $J_{\text{HH}} = 7.2$  Hz, 1H, PCP aromatic-*H*), 3.37 (d of vt,  $J_{\text{PH}} = 3.75$  Hz,  $J_{\text{HH}} = 16.8$  Hz, 2H, CH<sub>2</sub>), 3.29 (d of vt,  $J_{\text{PH}} = 4.05$  Hz,  $J_{\text{HH}} = 16.8$  Hz, 2H, CH<sub>2</sub>), 1.68-0.90 (m, 11 H, cyclohexyl*H*), 1.35 (t,  $J_{\text{PH}} = 6.6$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.31 (t,  $J_{\text{PH}} = 5.7$  Hz, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.08 (t,  $J_{\text{PH}} = 3.2$  Hz, 3H, CH<sub>3</sub>), -11.98(t,  $J_{\text{PH}} = 15.9$  Hz, 1H, Ir-*H*).

**Ir(H)(CH<sub>3</sub>)(cyclohexylisocyanide) (1b).** <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, *para*-xylene-*d*<sub>10</sub>):  $\delta$

51.23 ppm (s).  $^1\text{H}$  NMR (300 MHz, *para*-xylene- $d_{10}$ ):  $\delta$  7.18 (d,  $J_{\text{HH}} = 7.2$  Hz, 2H, PCP aromatic- $H$ ), 7.09 (t,  $J_{\text{HH}} = 7.2$  Hz, 1H, PCP aromatic- $H$ ), 3.37 (d of vt,  $J_{\text{PH}} = 3.75$  Hz,  $J_{\text{HH}} = 16.8$  Hz, 2H,  $\text{CH}_2$ ), 3.29 (d of vt,  $J_{\text{PH}} = 4.05$  Hz,  $J_{\text{HH}} = 16.8$  Hz, 2H,  $\text{CH}_2$ ), 1.68-0.90 (m, 11 H, cyclohexyl $H$ ), 1.38 (t,  $J_{\text{PH}} = 6.6$  Hz, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.31 (t,  $J_{\text{PH}} = 5.7$  Hz, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 0.45 (t,  $J_{\text{PH}} = 3.2$  Hz, 3H,  $\text{CH}_3$ ), -11.84 (t,  $J_{\text{PH}} = 16.4$  Hz, 1H, Ir- $H$ ).

**Ir(H)(*t*Butylisocyanide)(CH<sub>3</sub>) (**2a**)**. 15 mg of (PCP)IrH<sub>2</sub> (0.026 mmol) was dissolved in 1 mL of *p*-xylene solution containing 5.0 mg of norbornene (0.053 mmol) at room temperature. To the resulting solution was added 7.2  $\mu\text{L}$  of N-ethyl-*tert*-butylamine (0.052 mmol). An orange solution was obtained at room temperature within 30 min. Complex **2a** was formed in 94% yield; complex **2b** was formed in <1% yield ( $^{31}\text{P}\{\text{H}\}$  NMR). The solvent and organic volatiles were removed by vacuum. The resulting orange solid was redissolved in pentane which was allowed to slowly evaporate to give orange crystals. Two different crystalline phases were obtained; structure determination of both gave molecular structures without any significant differences. Both structures are shown in Figure S2. **2a:**  $^{31}\text{P}$  NMR (121.4 MHz, *para*-xylene- $d_{10}$ ):  $\delta$  54.10 ppm (d,  $J_{\text{PH}} = 16.4$  Hz).  $^1\text{H}$  NMR (300 MHz, *para*-xylene- $d_{10}$ ):  $\delta$  7.08 (d,  $J_{\text{HH}} = 7.2$  Hz, 2H, PCP aromatic- $H$ ), 6.97 (t,  $J_{\text{HH}} = 7.2$  Hz, 1H, PCP aromatic- $H$ ), 3.29 (vt,  $J_{\text{PH}} = 4.05$  Hz, 4H,  $\text{CH}_2$ ), 1.35 (t,  $J_{\text{PH}} = 6.0$  Hz, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.33 (t,  $J_{\text{PH}} = 6.4$  Hz, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 1.25 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), -0.15 (t,  $J_{\text{PH}} = 3.4$  Hz, 3H,  $\text{CH}_3$ ), -12.03 (t,  $J_{\text{PH}} = 16.4$  Hz, 1H, Ir- $H$ ).

**Ir(H)(CH<sub>3</sub>)(*t*Butylisocyanide) (**2b**)**.  $^{31}\text{P}$  NMR (121.4 MHz, *para*-xylene- $d_{10}$ ):  $\delta$  56.57 ppm (d,  $J_{\text{PH}} = 16.4$  Hz).  $^1\text{H}$  NMR (300 MHz, *para*-xylene- $d_{10}$ ):  $\delta$  7.09 – 6.97 (m, 3H, PCP aromatic- $H$ ), 3.22 (vt,  $J_{\text{PH}} = 3.6$  Hz, 4H,  $\text{CH}_2$ ), 1.35 (t,  $J_{\text{PH}} = 6.4$  Hz, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 1.11 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), -0.07 (t,  $J_{\text{PH}} = 3.0$  Hz, 3H,  $\text{CH}_3$ ), -11.11 (t,  $J_{\text{PH}} = 16.4$  Hz, 1H, Ir- $H$ ).

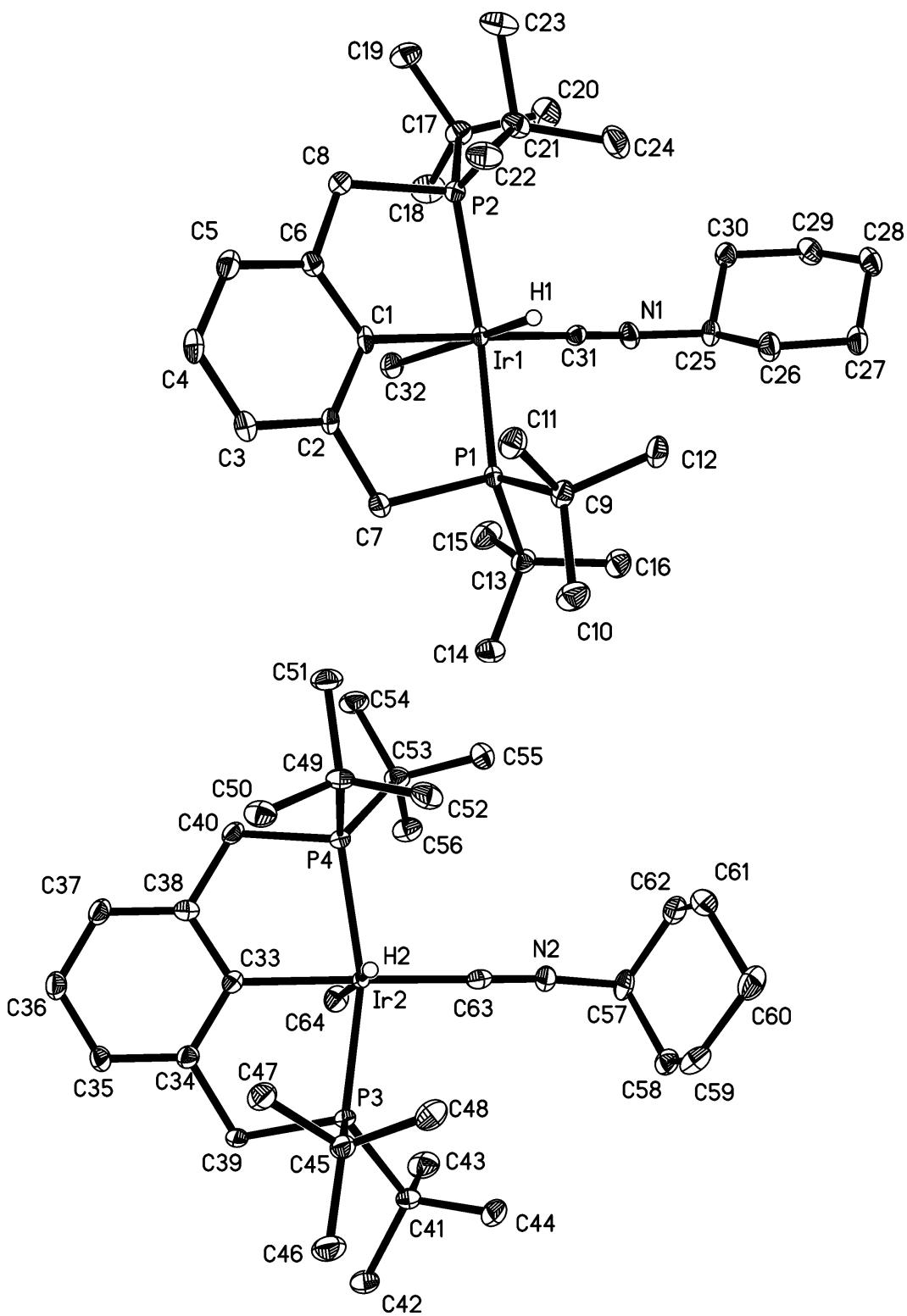
**Ir(H)(ethylisocyanide)(CH<sub>3</sub>) (**3a**)**. 15 mg of (PCP)IrH<sub>2</sub> (0.026 mmol) was dissolved in 1 mL of *p*-xylene solution containing 5.0 mg of norbornene (0.053 mmol) at room temperature. To the resulting solution was added 5.4  $\mu\text{L}$  of diethylamine (0.052 mmol). The solution was heated at 45 °C for 2 h and an orange solution was obtained. Complex **3a** was formed in 60% yield; complex **3b** was formed in 30% yield ( $^{31}\text{P}\{\text{H}\}$  NMR). The solvent and organic volatiles were removed by vacuum. The resulting orange solid was washed by pentane. Complex **3b** was

extracted in pentane solution. The resulting yellow solid **3a** was recrystallized from benzene solution as orange crystals. **3a**:  $^{31}\text{P}$  NMR (121.4 MHz, *para*-xylene-*d*<sub>10</sub>):  $\delta$  54.35 (s).  $^1\text{H}$  NMR (300 MHz, *para*-xylene-*d*<sub>10</sub>): 7.08 (d,  $J_{\text{HH}} = 7.2$  Hz, 2H, PCP aromatic-*H*), 6.97 (t,  $J_{\text{HH}} = 7.4$  Hz, 1H, PCP aromatic-*H*), 3.30 (vt,  $J_{\text{PH}} = 4.0$  Hz, 4H,  $\text{CH}_2$ ), 3.05 (q,  $J_{\text{HH}} = 7.2$  Hz, 2 H,  $\text{CH}_2$ ), 1.36 (t,  $J_{\text{PH}} = 6.2$  Hz, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.32 (t,  $J_{\text{PH}} = 6.2$  Hz, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 1.01 (t,  $J_{\text{HH}} = 7.2$  Hz, 3 H,  $\text{CH}_3$ ), -0.13 (d of t,  $J_{\text{PH}} = 3.4$  Hz,  $J_{\text{HH}} = 1.2$  Hz, 3 H,  $\text{CH}_3$ ), -11.95 (t,  $J_{\text{PH}} = 16.4$  Hz, 1H, Ir-*H*).

**Ir(H)(CH<sub>3</sub>)(ethylisocyanide) (3b)**.  $^{31}\text{P}$  NMR (121.4 MHz, *para*-xylene-*d*<sub>10</sub>):  $\delta$  52.20 (s).  $^1\text{H}$  NMR (300 MHz, *para*-xylene-*d*<sub>10</sub>): 7.09 (d,  $J_{\text{HH}} = 7.2$  Hz, 2H, PCP aromatic-*H*), 6.97 (t,  $J_{\text{HH}} = 7.4$  Hz, 1H, PCP aromatic-*H*), 3.35 (vt,  $J_{\text{PH}} = 3.0$  Hz, 4H,  $\text{CH}_2$ ), 2.83 (q,  $J_{\text{HH}} = 7.2$  Hz, 2 H,  $\text{CH}_2$ ), 1.38 (t,  $J_{\text{PH}} = 6.0$  Hz, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.33 (t,  $J_{\text{PH}} = 6.2$  Hz, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 0.78 (t,  $J_{\text{HH}} = 7.2$  Hz, 3 H,  $\text{CH}_3$ ), 0.44 (d of t,  $J_{\text{PH}} = 4.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, 3 H,  $\text{CH}_3$ ), -11.75 (t,  $J_{\text{PH}} = 17.8$  Hz, 1H, Ir-*H*).

**Reaction with N-ethylidene-ethylamine:** 14 mg of (PCP)IrH<sub>2</sub> (0.024 mmol) was dissolved in 1 mL of *p*-xylene solution containing 5.0 mg of norbornene (0.053 mmol) at room temperature. To the resulting solution was added 4.2  $\mu\text{L}$  of diethylamine (0.048 mmol). An orange solution was obtained within 10 min at room temperature. The ratio of **3a** and **3b** was found to be 1 : 0.48 ( $^1\text{H}$  NMR).

**Thermolysis of 1a-3a, 1b-3b.** All six methyl hydride isocyanide complexes were found to slowly lose methane at 90 °C to give the corresponding four-coordinate isocyanide complexes (PCP)Ir(CNR). Methane production was quantified in the case of a mixture of **2a** and **2b**. Conversion to (PCP)Ir(CNR) was taken to completion in a sealed NMR tube and 0.055 equiv methane was observed in solution by  $^1\text{H}$  NMR. Based upon the solubility of methane in toluene,<sup>3</sup> and the gas/solution volume ratio, we extrapolate that 0.7 equiv methane was present in the gas phase. While it is possible that the unaccounted-for methyl groups (ca. 0.25 equiv) led to products other than methane, we suspect the discrepancy is due to imprecision in either the measurement or literature data.



**Figure S-1.** ORTEP diagrams of the molecular structure of **1a** independently obtained by X-ray diffraction of two crystalline phases.

Table S-1. Crystal data and structure refinement for *trans*-(PCP)Ir(CH<sub>3</sub>)(H)(CNC<sub>6</sub>H<sub>11</sub>) (**1a**)

Identification code	irhcyhexylethylamine	
Empirical formula	C <sub>32</sub> H <sub>58</sub> IrN P2	
Formula weight	710.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9046(5) Å	α = 92.292(1)°.
	b = 17.4366(10) Å	β = 92.525(1)°.
	c = 20.8837(12) Å	γ = 92.968(1)°.
Volume	3232.1(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.461 Mg/m <sup>3</sup>	
Absorption coefficient	4.250 mm <sup>-1</sup>	
F(000)	1456	
Crystal size	0.38 x 0.20 x 0.075 mm <sup>3</sup>	
Theta range for data collection	1.95 to 30.53°.	
Index ranges	-12≤h≤12, -24≤k≤24, -29≤l≤29	
Reflections collected	39726	
Independent reflections	19438 [R(int) = 0.0239]	
Completeness to theta = 30.53°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.6242	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	19438 / 2 / 1111	
Goodness-of-fit on F <sup>2</sup>	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0623	
R indices (all data)	R1 = 0.0343, wR2 = 0.0649	
Largest diff. peak and hole	1.939 and -1.587 e.Å <sup>-3</sup>	

Table S-2. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for *trans*-(PCP)Ir(CH<sub>3</sub>)(H)(CNC<sub>6</sub>H<sub>11</sub>) (**1a**).

Ir(1)-C(31)	1.958(2)	C(11)-H(11C)	0.97(3)
Ir(1)-C(1)	2.084(2)	C(12)-H(12A)	0.99(4)
Ir(1)-C(32)	2.213(3)	C(12)-H(12B)	0.96(3)
Ir(1)-P(1)	2.3053(7)	C(12)-H(12C)	0.96(4)
Ir(1)-P(2)	2.3115(7)	C(13)-C(15)	1.528(4)
Ir(1)-H(1)	1.583(17)	C(13)-C(14)	1.532(4)
P(1)-C(7)	1.843(3)	C(13)-C(16)	1.533(4)
P(1)-C(13)	1.895(3)	C(14)-H(14A)	0.94(3)
P(1)-C(9)	1.901(3)	C(14)-H(14B)	0.94(4)
P(2)-C(8)	1.845(3)	C(14)-H(14C)	0.95(4)
P(2)-C(17)	1.894(3)	C(15)-H(15A)	1.00(3)
P(2)-C(21)	1.896(3)	C(15)-H(15B)	0.90(4)
C(1)-C(6)	1.399(3)	C(15)-H(15C)	0.95(4)
C(1)-C(2)	1.414(3)	C(16)-H(16A)	0.99(3)
C(2)-C(3)	1.397(3)	C(16)-H(16B)	0.99(3)
C(2)-C(7)	1.514(4)	C(16)-H(16C)	0.92(3)
C(3)-C(4)	1.390(4)	C(17)-C(18)	1.535(4)
C(3)-H(3)	0.89(3)	C(17)-C(20)	1.536(4)
C(4)-C(5)	1.383(4)	C(17)-C(19)	1.539(4)
C(4)-H(4)	0.98(3)	C(18)-H(18A)	0.96(4)
C(5)-C(6)	1.401(4)	C(18)-H(18B)	0.96(4)
C(5)-H(5)	0.92(4)	C(18)-H(18C)	0.98(3)
C(6)-C(8)	1.516(4)	C(19)-H(19A)	0.95(4)
C(7)-H(7A)	0.96(3)	C(19)-H(19B)	0.93(4)
C(7)-H(7B)	0.97(3)	C(19)-H(19C)	0.93(4)
C(8)-H(8A)	0.90(3)	C(20)-H(20A)	0.96(4)
C(8)-H(8B)	1.01(4)	C(20)-H(20B)	0.95(4)
C(9)-C(10)	1.533(4)	C(20)-H(20C)	1.02(4)
C(9)-C(11)	1.535(4)	C(21)-C(22)	1.536(4)
C(9)-C(12)	1.538(4)	C(21)-C(24)	1.539(4)
C(10)-H(10A)	0.99(4)	C(21)-C(23)	1.541(4)
C(10)-H(10B)	0.92(4)	C(22)-H(22A)	0.93(4)
C(10)-H(10C)	0.97(4)	C(22)-H(22B)	0.99(4)
C(11)-H(11A)	0.97(3)	C(22)-H(22C)	0.93(3)
C(11)-H(11B)	0.96(3)	C(23)-H(23A)	1.04(3)

C(23)-H(23B)	0.95(4)	P(4)-C(49)	1.897(3)
C(23)-H(23C)	0.91(4)	C(33)-C(34)	1.407(4)
C(24)-H(24A)	0.97(4)	C(33)-C(38)	1.409(3)
C(24)-H(24B)	0.96(4)	C(34)-C(35)	1.396(4)
C(24)-H(24C)	1.02(3)	C(34)-C(39)	1.523(4)
N(1)-C(31)	1.163(3)	C(35)-C(36)	1.390(4)
N(1)-C(25)	1.444(3)	C(35)-H(35)	0.97(3)
C(25)-C(30)	1.524(4)	C(36)-C(37)	1.389(4)
C(25)-C(26)	1.527(4)	C(36)-H(36)	0.97(3)
C(25)-H(25)	0.98(3)	C(37)-C(38)	1.402(4)
C(26)-C(27)	1.524(4)	C(37)-H(37)	0.92(3)
C(26)-H(26A)	0.95(4)	C(38)-C(40)	1.522(4)
C(26)-H(26B)	0.91(3)	C(39)-H(39A)	0.99(3)
C(27)-C(28)	1.521(4)	C(39)-H(39B)	0.99(4)
C(27)-H(27A)	0.98(3)	C(40)-H(40A)	0.93(3)
C(27)-H(27B)	0.97(4)	C(40)-H(40B)	1.04(3)
C(28)-C(29)	1.529(4)	C(41)-C(44)	1.531(4)
C(28)-H(28A)	0.96(4)	C(41)-C(43)	1.534(4)
C(28)-H(28B)	0.96(4)	C(41)-C(42)	1.541(4)
C(29)-C(30)	1.529(4)	C(42)-H(42A)	1.01(4)
C(29)-H(29A)	0.90(3)	C(42)-H(42B)	0.91(3)
C(29)-H(29B)	0.96(3)	C(42)-H(42C)	1.00(4)
C(30)-H(30A)	1.01(4)	C(43)-H(43A)	0.98(3)
C(30)-H(30B)	0.97(3)	C(43)-H(43B)	0.93(4)
C(32)-H(32A)	1.08(4)	C(43)-H(43C)	1.01(3)
C(32)-H(32B)	0.97(3)	C(44)-H(44A)	0.98(4)
C(32)-H(32C)	1.00(3)	C(44)-H(44B)	0.96(4)
Ir(2)-C(63)	1.958(3)	C(44)-H(44C)	0.98(3)
Ir(2)-C(33)	2.072(2)	C(45)-C(47)	1.533(4)
Ir(2)-C(64)	2.207(3)	C(45)-C(46)	1.534(4)
Ir(2)-P(4)	2.3016(6)	C(45)-C(48)	1.542(4)
Ir(2)-P(3)	2.3035(7)	C(46)-H(46A)	0.99(4)
Ir(2)-H(2)	1.564(17)	C(46)-H(46B)	0.94(3)
P(3)-C(39)	1.839(3)	C(46)-H(46C)	0.97(4)
P(3)-C(45)	1.893(3)	C(47)-H(47A)	0.94(3)
P(3)-C(41)	1.894(3)	C(47)-H(47B)	0.91(3)
P(4)-C(40)	1.842(3)	C(47)-H(47C)	1.03(4)
P(4)-C(53)	1.890(3)	C(48)-H(48A)	0.94(3)

C(48)-H(48B)	0.93(4)	C(56)-H(56B)	0.92(4)
C(48)-H(48C)	0.94(4)	C(56)-H(56C)	0.94(4)
C(49)-C(50)	1.536(4)	N(2)-C(63)	1.160(3)
C(49)-C(51)	1.536(4)	N(2)-C(57)	1.449(3)
C(49)-C(52)	1.539(4)	C(57)-C(62)	1.526(4)
C(50)-H(50A)	0.92(3)	C(57)-C(58)	1.528(4)
C(50)-H(50B)	0.93(4)	C(57)-H(57)	0.95(3)
C(50)-H(50C)	0.93(4)	C(58)-C(59)	1.516(4)
C(51)-H(51A)	0.98(4)	C(58)-H(58A)	0.97(4)
C(51)-H(51B)	0.97(3)	C(58)-H(58B)	0.99(3)
C(51)-H(51C)	0.96(4)	C(59)-C(60)	1.517(5)
C(52)-H(52A)	0.93(4)	C(59)-H(59A)	1.02(4)
C(52)-H(52B)	0.98(3)	C(59)-H(59B)	0.86(4)
C(52)-H(52C)	0.95(4)	C(60)-C(61)	1.524(4)
C(53)-C(56)	1.533(4)	C(60)-H(60A)	0.99(3)
C(53)-C(55)	1.536(4)	C(60)-H(60B)	0.91(4)
C(53)-C(54)	1.548(4)	C(61)-C(62)	1.522(5)
C(54)-H(54A)	1.01(4)	C(61)-H(61A)	1.02(3)
C(54)-H(54B)	0.92(4)	C(61)-H(61B)	0.93(4)
C(54)-H(54C)	0.94(4)	C(62)-H(62A)	0.97(4)
C(55)-H(55A)	1.01(3)	C(62)-H(62B)	0.96(4)
C(55)-H(55B)	1.01(4)	C(64)-H(64A)	0.97(3)
C(55)-H(55C)	0.96(3)	C(64)-H(64B)	0.98(4)
C(56)-H(56A)	1.07(4)	C(64)-H(64C)	0.99(4)
C(31)-Ir(1)-C(1)	176.59(10)	P(1)-Ir(1)-H(1)	80.5(11)
C(31)-Ir(1)-C(32)	95.66(11)	P(2)-Ir(1)-H(1)	83.9(11)
C(1)-Ir(1)-C(32)	80.93(10)	C(7)-P(1)-C(13)	104.56(12)
C(31)-Ir(1)-P(1)	98.07(7)	C(7)-P(1)-C(9)	103.52(12)
C(1)-Ir(1)-P(1)	82.19(7)	C(13)-P(1)-C(9)	108.42(12)
C(32)-Ir(1)-P(1)	95.70(8)	C(7)-P(1)-Ir(1)	102.36(9)
C(31)-Ir(1)-P(2)	98.23(7)	C(13)-P(1)-Ir(1)	121.54(9)
C(1)-Ir(1)-P(2)	82.38(7)	C(9)-P(1)-Ir(1)	114.16(9)
C(32)-Ir(1)-P(2)	96.73(8)	C(8)-P(2)-C(17)	104.10(12)
P(1)-Ir(1)-P(2)	158.39(2)	C(8)-P(2)-C(21)	103.51(13)
C(31)-Ir(1)-H(1)	95.3(11)	C(17)-P(2)-C(21)	108.28(12)
C(1)-Ir(1)-H(1)	88.1(11)	C(8)-P(2)-Ir(1)	102.51(9)
C(32)-Ir(1)-H(1)	168.8(11)	C(17)-P(2)-Ir(1)	122.21(9)

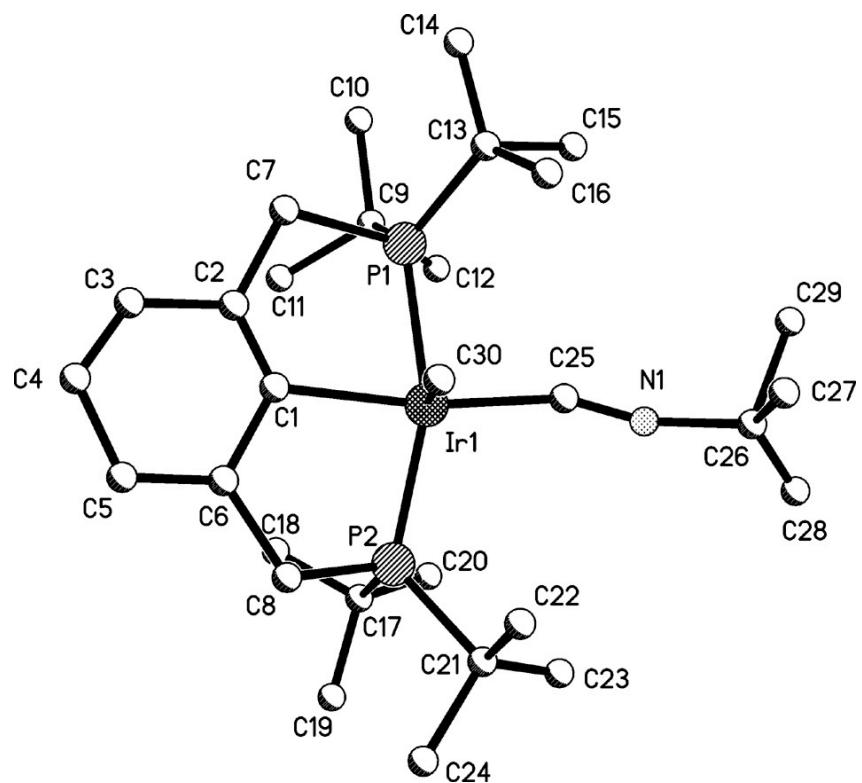
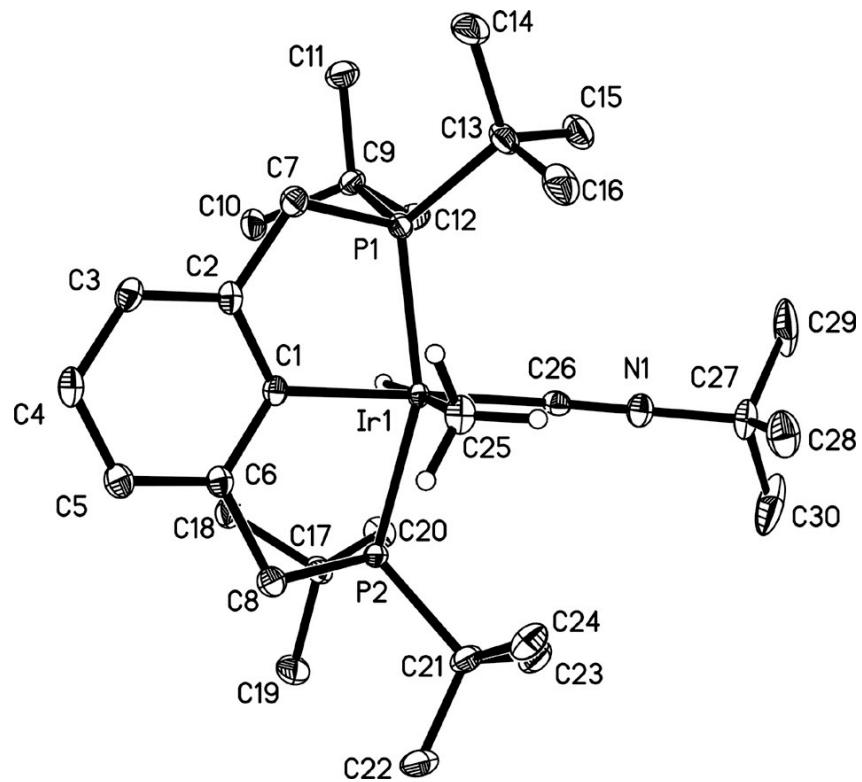
C(21)-P(2)-Ir(1)	113.85(9)	C(9)-C(10)-H(10B)	114(2)
C(6)-C(1)-C(2)	116.9(2)	H(10A)-C(10)-H(10B)	108(3)
C(6)-C(1)-Ir(1)	121.72(19)	C(9)-C(10)-H(10C)	113(2)
C(2)-C(1)-Ir(1)	121.08(18)	H(10A)-C(10)-H(10C)	106(3)
C(3)-C(2)-C(1)	121.4(2)	H(10B)-C(10)-H(10C)	107(3)
C(3)-C(2)-C(7)	120.0(2)	C(9)-C(11)-H(11A)	110.9(19)
C(1)-C(2)-C(7)	118.5(2)	C(9)-C(11)-H(11B)	114.6(19)
C(4)-C(3)-C(2)	120.1(3)	H(11A)-C(11)-H(11B)	110(3)
C(4)-C(3)-H(3)	121(2)	C(9)-C(11)-H(11C)	110.2(19)
C(2)-C(3)-H(3)	118(2)	H(11A)-C(11)-H(11C)	107(3)
C(5)-C(4)-C(3)	119.6(2)	H(11B)-C(11)-H(11C)	104(3)
C(5)-C(4)-H(4)	118.2(18)	C(9)-C(12)-H(12A)	116(2)
C(3)-C(4)-H(4)	122.2(18)	C(9)-C(12)-H(12B)	112.3(18)
C(4)-C(5)-C(6)	120.4(3)	H(12A)-C(12)-H(12B)	110(3)
C(4)-C(5)-H(5)	118(2)	C(9)-C(12)-H(12C)	107(2)
C(6)-C(5)-H(5)	121(2)	H(12A)-C(12)-H(12C)	104(3)
C(1)-C(6)-C(5)	121.4(2)	H(12B)-C(12)-H(12C)	107(3)
C(1)-C(6)-C(8)	118.6(2)	C(15)-C(13)-C(14)	107.6(2)
C(5)-C(6)-C(8)	119.8(2)	C(15)-C(13)-C(16)	107.0(2)
C(2)-C(7)-P(1)	109.29(18)	C(14)-C(13)-C(16)	110.0(2)
C(2)-C(7)-H(7A)	109.3(17)	C(15)-C(13)-P(1)	107.97(19)
P(1)-C(7)-H(7A)	105.2(17)	C(14)-C(13)-P(1)	113.7(2)
C(2)-C(7)-H(7B)	114(2)	C(16)-C(13)-P(1)	110.42(19)
P(1)-C(7)-H(7B)	111(2)	C(13)-C(14)-H(14A)	109(2)
H(7A)-C(7)-H(7B)	107(3)	C(13)-C(14)-H(14B)	110(2)
C(6)-C(8)-P(2)	109.82(18)	H(14A)-C(14)-H(14B)	110(3)
C(6)-C(8)-H(8A)	114.6(19)	C(13)-C(14)-H(14C)	113(2)
P(2)-C(8)-H(8A)	108.0(19)	H(14A)-C(14)-H(14C)	105(3)
C(6)-C(8)-H(8B)	111.5(19)	H(14B)-C(14)-H(14C)	110(3)
P(2)-C(8)-H(8B)	102.1(19)	C(13)-C(15)-H(15A)	109.4(19)
H(8A)-C(8)-H(8B)	110(3)	C(13)-C(15)-H(15B)	113(3)
C(10)-C(9)-C(11)	107.0(2)	H(15A)-C(15)-H(15B)	106(3)
C(10)-C(9)-C(12)	109.0(2)	C(13)-C(15)-H(15C)	108(2)
C(11)-C(9)-C(12)	108.0(2)	H(15A)-C(15)-H(15C)	114(3)
C(10)-C(9)-P(1)	114.3(2)	H(15B)-C(15)-H(15C)	106(3)
C(11)-C(9)-P(1)	107.06(18)	C(13)-C(16)-H(16A)	109.6(18)
C(12)-C(9)-P(1)	111.19(18)	C(13)-C(16)-H(16B)	114.7(18)
C(9)-C(10)-H(10A)	108.5(19)	H(16A)-C(16)-H(16B)	104(2)

C(13)-C(16)-H(16C)	112(2)	H(22B)-C(22)-H(22C)	110(3)
H(16A)-C(16)-H(16C)	106(3)	C(21)-C(23)-H(23A)	113.1(18)
H(16B)-C(16)-H(16C)	111(3)	C(21)-C(23)-H(23B)	115(2)
C(18)-C(17)-C(20)	106.7(2)	H(23A)-C(23)-H(23B)	105(3)
C(18)-C(17)-C(19)	106.8(2)	C(21)-C(23)-H(23C)	109(2)
C(20)-C(17)-C(19)	110.0(2)	H(23A)-C(23)-H(23C)	106(3)
C(18)-C(17)-P(2)	108.14(19)	H(23B)-C(23)-H(23C)	109(3)
C(20)-C(17)-P(2)	110.7(2)	C(21)-C(24)-H(24A)	109(2)
C(19)-C(17)-P(2)	114.1(2)	C(21)-C(24)-H(24B)	112(2)
C(17)-C(18)-H(18A)	113(2)	H(24A)-C(24)-H(24B)	108(3)
C(17)-C(18)-H(18B)	110(2)	C(21)-C(24)-H(24C)	111.4(19)
H(18A)-C(18)-H(18B)	109(3)	H(24A)-C(24)-H(24C)	108(3)
C(17)-C(18)-H(18C)	112(2)	H(24B)-C(24)-H(24C)	107(3)
H(18A)-C(18)-H(18C)	105(3)	C(31)-N(1)-C(25)	155.9(3)
H(18B)-C(18)-H(18C)	107(3)	N(1)-C(25)-C(30)	109.7(2)
C(17)-C(19)-H(19A)	108(2)	N(1)-C(25)-C(26)	108.6(2)
C(17)-C(19)-H(19B)	111(2)	C(30)-C(25)-C(26)	111.3(2)
H(19A)-C(19)-H(19B)	104(3)	N(1)-C(25)-H(25)	106.0(19)
C(17)-C(19)-H(19C)	114(2)	C(30)-C(25)-H(25)	113.1(19)
H(19A)-C(19)-H(19C)	111(3)	C(26)-C(25)-H(25)	108(2)
H(19B)-C(19)-H(19C)	109(3)	C(27)-C(26)-C(25)	111.1(2)
C(17)-C(20)-H(20A)	113(2)	C(27)-C(26)-H(26A)	107(2)
C(17)-C(20)-H(20B)	110(2)	C(25)-C(26)-H(26A)	109(2)
H(20A)-C(20)-H(20B)	110(3)	C(27)-C(26)-H(26B)	112(2)
C(17)-C(20)-H(20C)	111(2)	C(25)-C(26)-H(26B)	108(2)
H(20A)-C(20)-H(20C)	104(3)	H(26A)-C(26)-H(26B)	109(3)
H(20B)-C(20)-H(20C)	109(3)	C(28)-C(27)-C(26)	111.2(2)
C(22)-C(21)-C(24)	108.2(2)	C(28)-C(27)-H(27A)	107.7(18)
C(22)-C(21)-C(23)	107.0(2)	C(26)-C(27)-H(27A)	106.7(18)
C(24)-C(21)-C(23)	108.6(2)	C(28)-C(27)-H(27B)	109(2)
C(22)-C(21)-P(2)	107.23(19)	C(26)-C(27)-H(27B)	108(2)
C(24)-C(21)-P(2)	111.1(2)	H(27A)-C(27)-H(27B)	114(3)
C(23)-C(21)-P(2)	114.4(2)	C(27)-C(28)-C(29)	111.8(2)
C(21)-C(22)-H(22A)	107(2)	C(27)-C(28)-H(28A)	109(2)
C(21)-C(22)-H(22B)	112(2)	C(29)-C(28)-H(28A)	110(2)
H(22A)-C(22)-H(22B)	107(3)	C(27)-C(28)-H(28B)	110(2)
C(21)-C(22)-H(22C)	112(2)	C(29)-C(28)-H(28B)	109(2)
H(22A)-C(22)-H(22C)	110(3)	H(28A)-C(28)-H(28B)	106(3)

C(30)-C(29)-C(28)	110.7(2)	C(45)-P(3)-Ir(2)	114.35(9)
C(30)-C(29)-H(29A)	111(2)	C(41)-P(3)-Ir(2)	121.18(9)
C(28)-C(29)-H(29A)	106(2)	C(40)-P(4)-C(53)	104.81(12)
C(30)-C(29)-H(29B)	109.8(18)	C(40)-P(4)-C(49)	103.74(12)
C(28)-C(29)-H(29B)	112(2)	C(53)-P(4)-C(49)	108.56(12)
H(29A)-C(29)-H(29B)	107(3)	C(40)-P(4)-Ir(2)	102.58(9)
C(25)-C(30)-C(29)	110.1(2)	C(53)-P(4)-Ir(2)	120.87(9)
C(25)-C(30)-H(30A)	108(2)	C(49)-P(4)-Ir(2)	114.19(8)
C(29)-C(30)-H(30A)	108(2)	C(34)-C(33)-C(38)	116.4(2)
C(25)-C(30)-H(30B)	109.9(19)	C(34)-C(33)-Ir(2)	121.63(18)
C(29)-C(30)-H(30B)	110.6(18)	C(38)-C(33)-Ir(2)	121.66(19)
H(30A)-C(30)-H(30B)	110(3)	C(35)-C(34)-C(33)	121.7(2)
N(1)-C(31)-Ir(1)	178.9(2)	C(35)-C(34)-C(39)	119.9(2)
Ir(1)-C(32)-H(32A)	112.8(19)	C(33)-C(34)-C(39)	118.3(2)
Ir(1)-C(32)-H(32B)	110.2(19)	C(36)-C(35)-C(34)	120.3(3)
H(32A)-C(32)-H(32B)	104(3)	C(36)-C(35)-H(35)	118(2)
Ir(1)-C(32)-H(32C)	108(2)	C(34)-C(35)-H(35)	122(2)
H(32A)-C(32)-H(32C)	112(3)	C(37)-C(36)-C(35)	119.5(2)
H(32B)-C(32)-H(32C)	110(3)	C(37)-C(36)-H(36)	120.0(18)
C(63)-Ir(2)-C(33)	170.89(10)	C(35)-C(36)-H(36)	120.4(18)
C(63)-Ir(2)-C(64)	91.46(11)	C(36)-C(37)-C(38)	120.0(2)
C(33)-Ir(2)-C(64)	79.45(10)	C(36)-C(37)-H(37)	118(2)
C(63)-Ir(2)-P(4)	98.21(7)	C(38)-C(37)-H(37)	122(2)
C(33)-Ir(2)-P(4)	82.47(7)	C(37)-C(38)-C(33)	121.8(2)
C(64)-Ir(2)-P(4)	96.40(8)	C(37)-C(38)-C(40)	119.9(2)
C(63)-Ir(2)-P(3)	99.21(7)	C(33)-C(38)-C(40)	118.2(2)
C(33)-Ir(2)-P(3)	82.26(7)	C(34)-C(39)-P(3)	108.98(17)
C(64)-Ir(2)-P(3)	95.24(8)	C(34)-C(39)-H(39A)	109.9(19)
P(4)-Ir(2)-P(3)	158.74(2)	P(3)-C(39)-H(39A)	105.5(19)
C(63)-Ir(2)-H(2)	94.9(11)	C(34)-C(39)-H(39B)	113(2)
C(33)-Ir(2)-H(2)	94.2(11)	P(3)-C(39)-H(39B)	111(2)
C(64)-Ir(2)-H(2)	173.0(11)	H(39A)-C(39)-H(39B)	108(3)
P(4)-Ir(2)-H(2)	85.7(11)	C(38)-C(40)-P(4)	109.31(17)
P(3)-Ir(2)-H(2)	80.8(11)	C(38)-C(40)-H(40A)	113.3(19)
C(39)-P(3)-C(45)	102.78(13)	P(4)-C(40)-H(40A)	114.1(19)
C(39)-P(3)-C(41)	105.31(12)	C(38)-C(40)-H(40B)	112.2(16)
C(45)-P(3)-C(41)	108.39(12)	P(4)-C(40)-H(40B)	102.0(16)
C(39)-P(3)-Ir(2)	102.54(9)	H(40A)-C(40)-H(40B)	105(2)

C(44)-C(41)-C(43)	107.3(3)	H(47A)-C(47)-H(47B)	109(3)
C(44)-C(41)-C(42)	109.6(2)	C(45)-C(47)-H(47C)	111.4(19)
C(43)-C(41)-C(42)	107.0(3)	H(47A)-C(47)-H(47C)	107(3)
C(44)-C(41)-P(3)	110.35(19)	H(47B)-C(47)-H(47C)	106(3)
C(43)-C(41)-P(3)	108.28(19)	C(45)-C(48)-H(48A)	109.3(19)
C(42)-C(41)-P(3)	114.1(2)	C(45)-C(48)-H(48B)	112(2)
C(41)-C(42)-H(42A)	111(2)	H(48A)-C(48)-H(48B)	113(3)
C(41)-C(42)-H(42B)	111(2)	C(45)-C(48)-H(48C)	106(2)
H(42A)-C(42)-H(42B)	103(3)	H(48A)-C(48)-H(48C)	108(3)
C(41)-C(42)-H(42C)	117(2)	H(48B)-C(48)-H(48C)	108(3)
H(42A)-C(42)-H(42C)	106(3)	C(50)-C(49)-C(51)	106.8(2)
H(42B)-C(42)-H(42C)	107(3)	C(50)-C(49)-C(52)	108.1(2)
C(41)-C(43)-H(43A)	112(2)	C(51)-C(49)-C(52)	109.0(2)
C(41)-C(43)-H(43B)	114(2)	C(50)-C(49)-P(4)	106.50(18)
H(43A)-C(43)-H(43B)	110(3)	C(51)-C(49)-P(4)	114.33(19)
C(41)-C(43)-H(43C)	105.0(19)	C(52)-C(49)-P(4)	111.75(19)
H(43A)-C(43)-H(43C)	109(3)	C(49)-C(50)-H(50A)	110(2)
H(43B)-C(43)-H(43C)	106(3)	C(49)-C(50)-H(50B)	115(2)
C(41)-C(44)-H(44A)	108(2)	H(50A)-C(50)-H(50B)	101(3)
C(41)-C(44)-H(44B)	115(2)	C(49)-C(50)-H(50C)	111(2)
H(44A)-C(44)-H(44B)	103(3)	H(50A)-C(50)-H(50C)	108(3)
C(41)-C(44)-H(44C)	111.9(18)	H(50B)-C(50)-H(50C)	112(3)
H(44A)-C(44)-H(44C)	107(3)	C(49)-C(51)-H(51A)	112(2)
H(44B)-C(44)-H(44C)	111(3)	C(49)-C(51)-H(51B)	113.0(18)
C(47)-C(45)-C(46)	106.9(2)	H(51A)-C(51)-H(51B)	107(3)
C(47)-C(45)-C(48)	107.9(2)	C(49)-C(51)-H(51C)	107(2)
C(46)-C(45)-C(48)	108.7(2)	H(51A)-C(51)-H(51C)	107(3)
C(47)-C(45)-P(3)	107.86(18)	H(51B)-C(51)-H(51C)	111(3)
C(46)-C(45)-P(3)	114.2(2)	C(49)-C(52)-H(52A)	110(2)
C(48)-C(45)-P(3)	111.04(19)	C(49)-C(52)-H(52B)	111.6(17)
C(45)-C(46)-H(46A)	106(2)	H(52A)-C(52)-H(52B)	110(3)
C(45)-C(46)-H(46B)	115(2)	C(49)-C(52)-H(52C)	109(2)
H(46A)-C(46)-H(46B)	108(3)	H(52A)-C(52)-H(52C)	109(3)
C(45)-C(46)-H(46C)	112(2)	H(52B)-C(52)-H(52C)	107(3)
H(46A)-C(46)-H(46C)	109(3)	C(56)-C(53)-C(55)	107.4(2)
H(46B)-C(46)-H(46C)	107(3)	C(56)-C(53)-C(54)	107.1(2)
C(45)-C(47)-H(47A)	111(2)	C(55)-C(53)-C(54)	109.8(2)
C(45)-C(47)-H(47B)	111(2)	C(56)-C(53)-P(4)	108.19(19)

C(55)-C(53)-P(4)	109.80(19)	H(59A)-C(59)-H(59B)	100(3)
C(54)-C(53)-P(4)	114.4(2)	C(59)-C(60)-C(61)	111.0(2)
C(53)-C(54)-H(54A)	107.2(19)	C(59)-C(60)-H(60A)	112(2)
C(53)-C(54)-H(54B)	114(2)	C(61)-C(60)-H(60A)	109(2)
H(54A)-C(54)-H(54B)	111(3)	C(59)-C(60)-H(60B)	105(2)
C(53)-C(54)-H(54C)	112(2)	C(61)-C(60)-H(60B)	114(2)
H(54A)-C(54)-H(54C)	108(3)	H(60A)-C(60)-H(60B)	106(3)
H(54B)-C(54)-H(54C)	104(3)	C(62)-C(61)-C(60)	111.1(3)
C(53)-C(55)-H(55A)	112.4(19)	C(62)-C(61)-H(61A)	109.1(18)
C(53)-C(55)-H(55B)	113(2)	C(60)-C(61)-H(61A)	106.2(18)
H(55A)-C(55)-H(55B)	106(3)	C(62)-C(61)-H(61B)	108(3)
C(53)-C(55)-H(55C)	111(2)	C(60)-C(61)-H(61B)	113(2)
H(55A)-C(55)-H(55C)	110(3)	H(61A)-C(61)-H(61B)	109(3)
H(55B)-C(55)-H(55C)	104(3)	C(61)-C(62)-C(57)	111.9(2)
C(53)-C(56)-H(56A)	108(2)	C(61)-C(62)-H(62A)	109(2)
C(53)-C(56)-H(56B)	112(2)	C(57)-C(62)-H(62A)	106(2)
H(56A)-C(56)-H(56B)	106(3)	C(61)-C(62)-H(62B)	113(2)
C(53)-C(56)-H(56C)	111(2)	C(57)-C(62)-H(62B)	111(2)
H(56A)-C(56)-H(56C)	114(3)	H(62A)-C(62)-H(62B)	106(3)
H(56B)-C(56)-H(56C)	105(3)	N(2)-C(63)-Ir(2)	174.0(2)
C(63)-N(2)-C(57)	174.2(3)	Ir(2)-C(64)-H(64A)	114(2)
N(2)-C(57)-C(62)	109.9(2)	Ir(2)-C(64)-H(64B)	110(2)
N(2)-C(57)-C(58)	109.3(2)	H(64A)-C(64)-H(64B)	107(3)
C(62)-C(57)-C(58)	111.6(2)	Ir(2)-C(64)-H(64C)	113(2)
N(2)-C(57)-H(57)	106.1(19)	H(64A)-C(64)-H(64C)	104(3)
C(62)-C(57)-H(57)	109.8(19)	H(64B)-C(64)-H(64C)	108(3)
C(58)-C(57)-H(57)	110.0(19)		
C(59)-C(58)-C(57)	111.8(2)		
C(59)-C(58)-H(58A)	113(2)		
C(57)-C(58)-H(58A)	109(2)		
C(59)-C(58)-H(58B)	109(2)		
C(57)-C(58)-H(58B)	108(2)		
H(58A)-C(58)-H(58B)	106(3)		
C(58)-C(59)-C(60)	111.3(3)		
C(58)-C(59)-H(59A)	110(2)		
C(60)-C(59)-H(59A)	115(2)		
C(58)-C(59)-H(59B)	111(3)		
C(60)-C(59)-H(59B)	110(3)		



**Figure S-2.** ORTEP diagrams of the molecular structure of **2a** independently obtained by X-ray diffraction of two crystalline phases.

Table S-3. Crystal data and structure refinement for *trans*-(PCP)Ir(CH<sub>3</sub>)(H)(CN-*tert*-C<sub>4</sub>H<sub>9</sub>) (**2a**)

Identification code	irhcn-t-bu		
Empirical formula	C <sub>30</sub> H <sub>56</sub> IrN P2		
Formula weight	684.90		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/c		
Unit cell dimensions	a = 9.3998(7) Å	α = 90°.	
	b = 31.751(2) Å	β = 113.128(1)°.	
	c = 11.3603(8) Å	γ = 90°.	
Volume	3118.0(4) Å <sup>3</sup>		
Z	4		
Density (calculated)	1.459 Mg/m <sup>3</sup>		
Absorption coefficient	4.403 mm <sup>-1</sup>		
F(000)	1400		
Crystal size	0.11 x 0.08 x 0.025 mm <sup>3</sup>		
Theta range for data collection	2.05 to 30.59°.		
Index ranges	-13<=h<=13, -45<=k<=45, -16<=l<=16		
Reflections collected	37261		
Independent reflections	9585 [R(int) = 0.0345]		
Completeness to theta = 30.59°	99.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9999 and 0.8298		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	9585 / 1 / 531		
Goodness-of-fit on F <sup>2</sup>	1.004		
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0459		
R indices (all data)	R1 = 0.0322, wR2 = 0.0484		
Largest diff. peak and hole	1.373 and -1.106 e.Å <sup>-3</sup>		

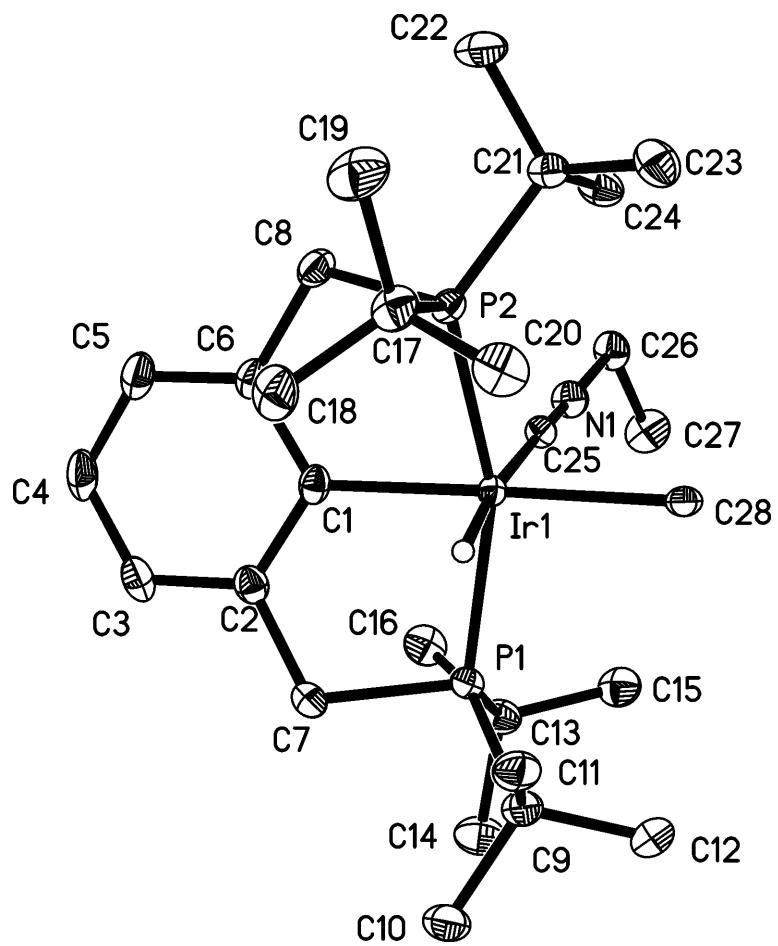
Table S-4. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for *trans*-(PCP)Ir(CH<sub>3</sub>)(H)(CN-*tert*-C<sub>4</sub>H<sub>9</sub>) (**2a**)

Ir(1)-C(26)	1.956(2)	C(11)-H(11B)	0.98(3)
Ir(1)-C(1)	2.081(2)	C(11)-H(11C)	0.92(3)
Ir(1)-C(25)	2.217(2)	C(12)-H(12A)	0.97(3)
Ir(1)-P(1)	2.3065(6)	C(12)-H(12B)	0.91(3)
Ir(1)-P(2)	2.3067(6)	C(12)-H(12C)	1.01(3)
Ir(1)-H(1)	1.567(17)	C(13)-C(16)	1.528(4)
P(1)-C(7)	1.844(2)	C(13)-C(15)	1.537(3)
P(1)-C(13)	1.893(2)	C(13)-C(14)	1.539(4)
P(1)-C(9)	1.902(2)	C(14)-H(14A)	0.94(3)
P(2)-C(8)	1.841(2)	C(14)-H(14B)	0.92(3)
P(2)-C(21)	1.890(2)	C(14)-H(14C)	0.98(3)
P(2)-C(17)	1.894(2)	C(15)-H(15A)	0.96(3)
C(1)-C(2)	1.411(3)	C(15)-H(15B)	0.95(3)
C(1)-C(6)	1.414(3)	C(15)-H(15C)	0.97(3)
C(2)-C(3)	1.395(3)	C(16)-H(16A)	0.96(3)
C(2)-C(7)	1.511(3)	C(16)-H(16B)	0.93(3)
C(3)-C(4)	1.389(3)	C(16)-H(16C)	0.93(3)
C(3)-H(3)	0.91(3)	C(17)-C(19)	1.535(3)
C(4)-C(5)	1.385(3)	C(17)-C(20)	1.535(3)
C(4)-H(4)	0.95(3)	C(17)-C(18)	1.542(3)
C(5)-C(6)	1.395(3)	C(18)-H(18A)	1.00(3)
C(5)-H(5)	0.92(3)	C(18)-H(18B)	0.97(3)
C(6)-C(8)	1.519(3)	C(18)-H(18C)	0.98(3)
C(7)-H(7A)	0.93(3)	C(19)-H(19A)	0.95(3)
C(7)-H(7B)	0.90(3)	C(19)-H(19B)	0.95(3)
C(8)-H(8A)	0.96(3)	C(19)-H(19C)	0.98(3)
C(8)-H(8B)	0.96(3)	C(20)-H(20A)	1.01(3)
C(9)-C(11)	1.532(3)	C(20)-H(20B)	0.98(3)
C(9)-C(12)	1.535(3)	C(20)-H(20C)	0.90(3)
C(9)-C(10)	1.539(3)	C(21)-C(24)	1.527(4)
C(10)-H(10A)	0.98(3)	C(21)-C(22)	1.535(4)
C(10)-H(10B)	0.98(3)	C(21)-C(23)	1.535(3)
C(10)-H(10C)	0.98(3)	C(22)-H(22A)	0.94(3)
C(11)-H(11A)	0.96(3)	C(22)-H(22B)	0.95(3)

C(22)-H(22C)	0.97(3)	C(27)-C(30)	1.512(4)
C(23)-H(23A)	0.99(3)	C(27)-C(28)	1.517(4)
C(23)-H(23B)	1.04(3)	C(27)-C(29)	1.520(4)
C(23)-H(23C)	0.93(3)	C(28)-H(28A)	0.95(3)
C(24)-H(24A)	1.00(3)	C(28)-H(28B)	0.97(3)
C(24)-H(24B)	0.96(3)	C(28)-H(28C)	0.94(3)
C(24)-H(24C)	0.99(3)	C(29)-H(29A)	0.97(4)
C(25)-H(25A)	1.01(3)	C(29)-H(29B)	0.96(4)
C(25)-H(25B)	1.00(3)	C(29)-H(29C)	0.90(4)
C(25)-H(25C)	0.97(3)	C(30)-H(30A)	0.94(4)
C(26)-N(1)	1.169(3)	C(30)-H(30B)	1.02(4)
N(1)-C(27)	1.455(3)	C(30)-H(30C)	0.93(5)
C(26)-Ir(1)-C(1)	168.90(9)	C(21)-P(2)-C(17)	109.01(11)
C(26)-Ir(1)-C(25)	89.31(9)	C(8)-P(2)-Ir(1)	102.59(8)
C(1)-Ir(1)-C(25)	79.59(9)	C(21)-P(2)-Ir(1)	120.36(8)
C(26)-Ir(1)-P(1)	99.59(6)	C(17)-P(2)-Ir(1)	114.63(8)
C(1)-Ir(1)-P(1)	82.26(6)	C(2)-C(1)-C(6)	116.8(2)
C(25)-Ir(1)-P(1)	96.94(7)	C(2)-C(1)-Ir(1)	121.62(16)
C(26)-Ir(1)-P(2)	98.97(6)	C(6)-C(1)-Ir(1)	121.05(16)
C(1)-Ir(1)-P(2)	82.06(6)	C(3)-C(2)-C(1)	121.1(2)
C(25)-Ir(1)-P(2)	96.23(7)	C(3)-C(2)-C(7)	120.3(2)
P(1)-Ir(1)-P(2)	157.31(2)	C(1)-C(2)-C(7)	118.4(2)
C(26)-Ir(1)-H(1)	95.5(10)	C(4)-C(3)-C(2)	121.0(2)
C(1)-Ir(1)-H(1)	95.6(10)	C(4)-C(3)-H(3)	121.1(17)
C(25)-Ir(1)-H(1)	175.1(11)	C(2)-C(3)-H(3)	117.9(17)
P(1)-Ir(1)-H(1)	82.5(11)	C(5)-C(4)-C(3)	118.9(2)
P(2)-Ir(1)-H(1)	82.8(11)	C(5)-C(4)-H(4)	122.2(17)
C(7)-P(1)-C(13)	104.47(11)	C(3)-C(4)-H(4)	118.9(16)
C(7)-P(1)-C(9)	103.56(11)	C(4)-C(5)-C(6)	120.8(2)
C(13)-P(1)-C(9)	108.91(11)	C(4)-C(5)-H(5)	119.5(19)
C(7)-P(1)-Ir(1)	102.60(8)	C(6)-C(5)-H(5)	119.7(19)
C(13)-P(1)-Ir(1)	121.00(8)	C(5)-C(6)-C(1)	121.2(2)
C(9)-P(1)-Ir(1)	114.08(7)	C(5)-C(6)-C(8)	119.8(2)
C(8)-P(2)-C(21)	104.75(11)	C(1)-C(6)-C(8)	118.8(2)
C(8)-P(2)-C(17)	103.29(11)	C(2)-C(7)-P(1)	109.99(16)

C(2)-C(7)-H(7A)	110.8(18)	C(16)-C(13)-C(14)	106.9(2)
P(1)-C(7)-H(7A)	103.8(18)	C(15)-C(13)-C(14)	109.3(2)
C(2)-C(7)-H(7B)	113.0(19)	C(16)-C(13)-P(1)	107.72(17)
P(1)-C(7)-H(7B)	114(2)	C(15)-C(13)-P(1)	110.12(17)
H(7A)-C(7)-H(7B)	104(2)	C(14)-C(13)-P(1)	114.98(18)
C(6)-C(8)-P(2)	108.96(16)	C(13)-C(14)-H(14A)	113.8(19)
C(6)-C(8)-H(8A)	110.2(18)	C(13)-C(14)-H(14B)	114.3(18)
P(2)-C(8)-H(8A)	111.9(18)	H(14A)-C(14)-H(14B)	104(3)
C(6)-C(8)-H(8B)	109.0(18)	C(13)-C(14)-H(14C)	105.9(18)
P(2)-C(8)-H(8B)	104.1(18)	H(14A)-C(14)-H(14C)	110(3)
H(8A)-C(8)-H(8B)	112(2)	H(14B)-C(14)-H(14C)	109(3)
C(11)-C(9)-C(12)	108.5(2)	C(13)-C(15)-H(15A)	109.0(19)
C(11)-C(9)-C(10)	107.5(2)	C(13)-C(15)-H(15B)	113.1(18)
C(12)-C(9)-C(10)	108.3(2)	H(15A)-C(15)-H(15B)	104(3)
C(11)-C(9)-P(1)	114.11(17)	C(13)-C(15)-H(15C)	112.3(18)
C(12)-C(9)-P(1)	110.96(16)	H(15A)-C(15)-H(15C)	109(3)
C(10)-C(9)-P(1)	107.29(16)	H(15B)-C(15)-H(15C)	109(3)
C(9)-C(10)-H(10A)	109.1(16)	C(13)-C(16)-H(16A)	113.8(18)
C(9)-C(10)-H(10B)	111.8(18)	C(13)-C(16)-H(16B)	112(2)
H(10A)-C(10)-H(10B)	106(2)	H(16A)-C(16)-H(16B)	101(3)
C(9)-C(10)-H(10C)	111.7(17)	C(13)-C(16)-H(16C)	109(2)
H(10A)-C(10)-H(10C)	109(2)	H(16A)-C(16)-H(16C)	110(3)
H(10B)-C(10)-H(10C)	109(2)	H(16B)-C(16)-H(16C)	111(3)
C(9)-C(11)-H(11A)	114.7(17)	C(19)-C(17)-C(20)	108.3(2)
C(9)-C(11)-H(11B)	111.2(17)	C(19)-C(17)-C(18)	107.5(2)
H(11A)-C(11)-H(11B)	105(2)	C(20)-C(17)-C(18)	108.0(2)
C(9)-C(11)-H(11C)	107.2(19)	C(19)-C(17)-P(2)	114.32(18)
H(11A)-C(11)-H(11C)	107(2)	C(20)-C(17)-P(2)	112.11(16)
H(11B)-C(11)-H(11C)	112(2)	C(18)-C(17)-P(2)	106.30(16)
C(9)-C(12)-H(12A)	108.5(18)	C(17)-C(18)-H(18A)	112.5(18)
C(9)-C(12)-H(12B)	111.0(19)	C(17)-C(18)-H(18B)	111.5(16)
H(12A)-C(12)-H(12B)	110(3)	H(18A)-C(18)-H(18B)	106(2)
C(9)-C(12)-H(12C)	112.5(16)	C(17)-C(18)-H(18C)	107.3(16)
H(12A)-C(12)-H(12C)	109(2)	H(18A)-C(18)-H(18C)	110(2)
H(12B)-C(12)-H(12C)	106(2)	H(18B)-C(18)-H(18C)	109(2)
C(16)-C(13)-C(15)	107.4(2)	C(17)-C(19)-H(19A)	109.1(18)

C(17)-C(19)-H(19B)	111.5(18)	Ir(1)-C(25)-H(25B)	116.7(17)
H(19A)-C(19)-H(19B)	107(2)	H(25A)-C(25)-H(25B)	107(2)
C(17)-C(19)-H(19C)	114.2(15)	Ir(1)-C(25)-H(25C)	109.2(19)
H(19A)-C(19)-H(19C)	105(2)	H(25A)-C(25)-H(25C)	107(2)
H(19B)-C(19)-H(19C)	110(2)	H(25B)-C(25)-H(25C)	105(2)
C(17)-C(20)-H(20A)	109.7(18)	N(1)-C(26)-Ir(1)	172.1(2)
C(17)-C(20)-H(20B)	111.9(18)	C(26)-N(1)-C(27)	168.8(2)
H(20A)-C(20)-H(20B)	108(3)	N(1)-C(27)-C(30)	108.4(2)
C(17)-C(20)-H(20C)	109.2(19)	N(1)-C(27)-C(28)	107.2(2)
H(20A)-C(20)-H(20C)	104(3)	C(30)-C(27)-C(28)	110.8(3)
H(20B)-C(20)-H(20C)	113(3)	N(1)-C(27)-C(29)	107.9(2)
C(24)-C(21)-C(22)	107.4(2)	C(30)-C(27)-C(29)	111.5(3)
C(24)-C(21)-C(23)	107.7(2)	C(28)-C(27)-C(29)	110.9(3)
C(22)-C(21)-C(23)	109.7(2)	C(27)-C(28)-H(28A)	109(2)
C(24)-C(21)-P(2)	107.99(17)	C(27)-C(28)-H(28B)	110.8(19)
C(22)-C(21)-P(2)	114.51(18)	H(28A)-C(28)-H(28B)	108(3)
C(23)-C(21)-P(2)	109.27(17)	C(27)-C(28)-H(28C)	109.1(18)
C(21)-C(22)-H(22A)	109(2)	H(28A)-C(28)-H(28C)	112(3)
C(21)-C(22)-H(22B)	112.5(19)	H(28B)-C(28)-H(28C)	108(3)
H(22A)-C(22)-H(22B)	113(3)	C(27)-C(29)-H(29A)	108(2)
C(21)-C(22)-H(22C)	112.2(18)	C(27)-C(29)-H(29B)	109(3)
H(22A)-C(22)-H(22C)	108(3)	H(29A)-C(29)-H(29B)	106(3)
H(22B)-C(22)-H(22C)	102(3)	C(27)-C(29)-H(29C)	112(2)
C(21)-C(23)-H(23A)	111.5(18)	H(29A)-C(29)-H(29C)	113(3)
C(21)-C(23)-H(23B)	112.4(17)	H(29B)-C(29)-H(29C)	109(3)
H(23A)-C(23)-H(23B)	105(2)	C(27)-C(30)-H(30A)	111(3)
C(21)-C(23)-H(23C)	106(2)	C(27)-C(30)-H(30B)	109.3(19)
H(23A)-C(23)-H(23C)	112(3)	H(30A)-C(30)-H(30B)	107(3)
H(23B)-C(23)-H(23C)	110(3)	C(27)-C(30)-H(30C)	110(3)
C(21)-C(24)-H(24A)	112.5(19)	H(30A)-C(30)-H(30C)	112(4)
C(21)-C(24)-H(24B)	112.9(19)	H(30B)-C(30)-H(30C)	107(3)
H(24A)-C(24)-H(24B)	107(3)		
C(21)-C(24)-H(24C)	106.4(17)		
H(24A)-C(24)-H(24C)	110(3)		
H(24B)-C(24)-H(24C)	108(3)		
Ir(1)-C(25)-H(25A)	110.9(17)		



**Figure S-3.** ORTEP diagram of the molecular structure of **3b**.

Table S-5. Crystal data and structure refinement for *cis*-(PCP)Ir(CH<sub>3</sub>)(H)(CNC<sub>2</sub>H<sub>5</sub>) (**3b**)

Identification code	iriso2	
Empirical formula	C <sub>28</sub> H <sub>52</sub> IrN <sub>2</sub> P <sub>2</sub>	
Formula weight	656.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.2568(17) Å b = 21.2282(16) Å c = 14.2049(10) Å	α = 90°. β = 123.311(1)°. γ = 90°.
Volume	5860.7(7) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.489 Mg/m <sup>3</sup>	
Absorption coefficient	4.681 mm <sup>-1</sup>	
F(000)	2672	
Crystal size	0.10 x 0.05 x 0.03 mm <sup>3</sup>	
Theta range for data collection	1.73 to 30.56°.	
Index ranges	-33<=h<=33, -30<=k<=30, -20<=l<=20	
Reflections collected	35557	
Independent reflections	8976 [R(int) = 0.0278]	
Completeness to theta = 30.56°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.5545	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8976 / 0 / 307	
Goodness-of-fit on F <sup>2</sup>	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0189, wR2 = 0.0409	
R indices (all data)	R1 = 0.0259, wR2 = 0.0432	
Largest diff. peak and hole	1.117 and -0.417 e.Å <sup>-3</sup>	

Table S-6. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for *cis*-(PCP)Ir(CH<sub>3</sub>)(H)(CNC<sub>2</sub>H<sub>5</sub>) (**3b**).

Ir(1)-C(25)	1.979(2)	C(11)-H(11B)	0.9800
Ir(1)-C(1)	2.0962(19)	C(11)-H(11C)	0.9800
Ir(1)-C(28)	2.2241(19)	C(12)-H(12A)	0.9800
Ir(1)-P(1)	2.3062(5)	C(12)-H(12B)	0.9800
Ir(1)-P(2)	2.3064(5)	C(12)-H(12C)	0.9800
Ir(1)-H(1)	1.58(3)	C(13)-C(15)	1.536(3)
P(1)-C(7)	1.842(2)	C(13)-C(14)	1.538(3)
P(1)-C(13)	1.888(2)	C(13)-C(16)	1.546(3)
P(1)-C(9)	1.894(2)	C(14)-H(14A)	0.9800
P(2)-C(8)	1.8494(19)	C(14)-H(14B)	0.9800
P(2)-C(17)	1.893(2)	C(14)-H(14C)	0.9800
P(2)-C(21)	1.896(2)	C(15)-H(15A)	0.9800
C(1)-C(2)	1.408(3)	C(15)-H(15B)	0.9800
C(1)-C(6)	1.416(3)	C(15)-H(15C)	0.9800
C(2)-C(3)	1.394(3)	C(16)-H(16A)	0.9800
C(2)-C(7)	1.509(3)	C(16)-H(16B)	0.9800
C(3)-C(4)	1.389(3)	C(16)-H(16C)	0.9800
C(3)-H(3)	0.9500	C(17)-C(18)	1.536(3)
C(4)-C(5)	1.382(3)	C(17)-C(19)	1.540(3)
C(4)-H(4)	0.9500	C(17)-C(20)	1.544(3)
C(5)-C(6)	1.397(3)	C(18)-H(18A)	0.9800
C(5)-H(5)	0.9500	C(18)-H(18B)	0.9800
C(6)-C(8)	1.509(3)	C(18)-H(18C)	0.9800
C(7)-H(7A)	0.9900	C(19)-H(19A)	0.9800
C(7)-H(7B)	0.9900	C(19)-H(19B)	0.9800
C(8)-H(8A)	0.9900	C(19)-H(19C)	0.9800
C(8)-H(8B)	0.9900	C(20)-H(20A)	0.9800
C(9)-C(11)	1.536(3)	C(20)-H(20B)	0.9800
C(9)-C(12)	1.537(3)	C(20)-H(20C)	0.9800
C(9)-C(10)	1.543(3)	C(21)-C(24)	1.534(3)
C(10)-H(10A)	0.9800	C(21)-C(23)	1.534(3)
C(10)-H(10B)	0.9800	C(21)-C(22)	1.539(3)
C(10)-H(10C)	0.9800	C(22)-H(22A)	0.9800
C(11)-H(11A)	0.9800	C(22)-H(22B)	0.9800

C(22)-H(22C)	0.9800	C(26)-C(27)	1.507(3)
C(23)-H(23A)	0.9800	C(26)-H(26A)	0.9900
C(23)-H(23B)	0.9800	C(26)-H(26B)	0.9900
C(23)-H(23C)	0.9800	C(27)-H(27A)	0.9800
C(24)-H(24A)	0.9800	C(27)-H(27B)	0.9800
C(24)-H(24B)	0.9800	C(27)-H(27C)	0.9800
C(24)-H(24C)	0.9800	C(28)-H(28A)	0.9800
C(25)-N(1)	1.159(3)	C(28)-H(28B)	0.9800
N(1)-C(26)	1.438(2)	C(28)-H(28C)	0.9800
C(25)-Ir(1)-C(1)	96.17(7)	C(21)-P(2)-Ir(1)	123.12(6)
C(25)-Ir(1)-C(28)	88.02(8)	C(2)-C(1)-C(6)	116.63(17)
C(1)-Ir(1)-C(28)	175.77(7)	C(2)-C(1)-Ir(1)	121.84(14)
C(25)-Ir(1)-P(1)	99.81(6)	C(6)-C(1)-Ir(1)	121.44(14)
C(1)-Ir(1)-P(1)	82.26(6)	C(3)-C(2)-C(1)	121.69(19)
C(28)-Ir(1)-P(1)	97.67(5)	C(3)-C(2)-C(7)	120.73(18)
C(25)-Ir(1)-P(2)	96.02(6)	C(1)-C(2)-C(7)	117.30(17)
C(1)-Ir(1)-P(2)	80.73(6)	C(4)-C(3)-C(2)	120.2(2)
C(28)-Ir(1)-P(2)	98.26(5)	C(4)-C(3)-H(3)	119.9
P(1)-Ir(1)-P(2)	157.853(18)	C(2)-C(3)-H(3)	119.9
C(25)-Ir(1)-H(1)	173.7(10)	C(5)-C(4)-C(3)	119.56(18)
C(1)-Ir(1)-H(1)	89.2(10)	C(5)-C(4)-H(4)	120.2
C(28)-Ir(1)-H(1)	86.7(10)	C(3)-C(4)-H(4)	120.2
P(1)-Ir(1)-H(1)	77.6(9)	C(4)-C(5)-C(6)	120.5(2)
P(2)-Ir(1)-H(1)	88.0(9)	C(4)-C(5)-H(5)	119.7
C(7)-P(1)-C(13)	103.65(10)	C(6)-C(5)-H(5)	119.7
C(7)-P(1)-C(9)	102.44(9)	C(5)-C(6)-C(1)	121.15(19)
C(13)-P(1)-C(9)	109.33(9)	C(5)-C(6)-C(8)	121.12(18)
C(7)-P(1)-Ir(1)	102.24(7)	C(1)-C(6)-C(8)	117.73(17)
C(13)-P(1)-Ir(1)	117.66(7)	C(2)-C(7)-P(1)	110.60(13)
C(9)-P(1)-Ir(1)	118.74(7)	C(2)-C(7)-H(7A)	109.5
C(8)-P(2)-C(17)	105.02(10)	P(1)-C(7)-H(7A)	109.5
C(8)-P(2)-C(21)	102.61(9)	C(2)-C(7)-H(7B)	109.5
C(17)-P(2)-C(21)	108.93(10)	P(1)-C(7)-H(7B)	109.5
C(8)-P(2)-Ir(1)	102.04(7)	H(7A)-C(7)-H(7B)	108.1
C(17)-P(2)-Ir(1)	112.76(7)	C(6)-C(8)-P(2)	108.67(13)

C(6)-C(8)-H(8A)	110.0	C(13)-C(14)-H(14B)	109.5
P(2)-C(8)-H(8A)	110.0	H(14A)-C(14)-H(14B)	109.5
C(6)-C(8)-H(8B)	110.0	C(13)-C(14)-H(14C)	109.5
P(2)-C(8)-H(8B)	110.0	H(14A)-C(14)-H(14C)	109.5
H(8A)-C(8)-H(8B)	108.3	H(14B)-C(14)-H(14C)	109.5
C(11)-C(9)-C(12)	107.80(17)	C(13)-C(15)-H(15A)	109.5
C(11)-C(9)-C(10)	106.84(17)	C(13)-C(15)-H(15B)	109.5
C(12)-C(9)-C(10)	109.24(17)	H(15A)-C(15)-H(15B)	109.5
C(11)-C(9)-P(1)	108.94(13)	C(13)-C(15)-H(15C)	109.5
C(12)-C(9)-P(1)	110.92(14)	H(15A)-C(15)-H(15C)	109.5
C(10)-C(9)-P(1)	112.90(14)	H(15B)-C(15)-H(15C)	109.5
C(9)-C(10)-H(10A)	109.5	C(13)-C(16)-H(16A)	109.5
C(9)-C(10)-H(10B)	109.5	C(13)-C(16)-H(16B)	109.5
H(10A)-C(10)-H(10B)	109.5	H(16A)-C(16)-H(16B)	109.5
C(9)-C(10)-H(10C)	109.5	C(13)-C(16)-H(16C)	109.5
H(10A)-C(10)-H(10C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(10B)-C(10)-H(10C)	109.5	H(16B)-C(16)-H(16C)	109.5
C(9)-C(11)-H(11A)	109.5	C(18)-C(17)-C(19)	107.11(18)
C(9)-C(11)-H(11B)	109.5	C(18)-C(17)-C(20)	107.83(18)
H(11A)-C(11)-H(11B)	109.5	C(19)-C(17)-C(20)	108.72(19)
C(9)-C(11)-H(11C)	109.5	C(18)-C(17)-P(2)	108.79(15)
H(11A)-C(11)-H(11C)	109.5	C(19)-C(17)-P(2)	114.30(15)
H(11B)-C(11)-H(11C)	109.5	C(20)-C(17)-P(2)	109.87(14)
C(9)-C(12)-H(12A)	109.5	C(17)-C(18)-H(18A)	109.5
C(9)-C(12)-H(12B)	109.5	C(17)-C(18)-H(18B)	109.5
H(12A)-C(12)-H(12B)	109.5	H(18A)-C(18)-H(18B)	109.5
C(9)-C(12)-H(12C)	109.5	C(17)-C(18)-H(18C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(12B)-C(12)-H(12C)	109.5	H(18B)-C(18)-H(18C)	109.5
C(15)-C(13)-C(14)	108.98(18)	C(17)-C(19)-H(19A)	109.5
C(15)-C(13)-C(16)	109.05(17)	C(17)-C(19)-H(19B)	109.5
C(14)-C(13)-C(16)	106.64(17)	H(19A)-C(19)-H(19B)	109.5
C(15)-C(13)-P(1)	110.05(14)	C(17)-C(19)-H(19C)	109.5
C(14)-C(13)-P(1)	115.52(15)	H(19A)-C(19)-H(19C)	109.5
C(16)-C(13)-P(1)	106.36(14)	H(19B)-C(19)-H(19C)	109.5
C(13)-C(14)-H(14A)	109.5	C(17)-C(20)-H(20A)	109.5

C(17)-C(20)-H(20B)	109.5	H(26A)-C(26)-H(26B)	108.0
H(20A)-C(20)-H(20B)	109.5	C(26)-C(27)-H(27A)	109.5
C(17)-C(20)-H(20C)	109.5	C(26)-C(27)-H(27B)	109.5
H(20A)-C(20)-H(20C)	109.5	H(27A)-C(27)-H(27B)	109.5
H(20B)-C(20)-H(20C)	109.5	C(26)-C(27)-H(27C)	109.5
C(24)-C(21)-C(23)	106.97(17)	H(27A)-C(27)-H(27C)	109.5
C(24)-C(21)-C(22)	107.39(17)	H(27B)-C(27)-H(27C)	109.5
C(23)-C(21)-C(22)	109.59(18)	Ir(1)-C(28)-H(28A)	109.5
C(24)-C(21)-P(2)	108.14(14)	Ir(1)-C(28)-H(28B)	109.5
C(23)-C(21)-P(2)	110.73(14)	H(28A)-C(28)-H(28B)	109.5
C(22)-C(21)-P(2)	113.74(15)	Ir(1)-C(28)-H(28C)	109.5
C(21)-C(22)-H(22A)	109.5	H(28A)-C(28)-H(28C)	109.5
C(21)-C(22)-H(22B)	109.5	H(28B)-C(28)-H(28C)	109.5
H(22A)-C(22)-H(22B)	109.5		
C(21)-C(22)-H(22C)	109.5		
H(22A)-C(22)-H(22C)	109.5		
H(22B)-C(22)-H(22C)	109.5		
C(21)-C(23)-H(23A)	109.5		
C(21)-C(23)-H(23B)	109.5		
H(23A)-C(23)-H(23B)	109.5		
C(21)-C(23)-H(23C)	109.5		
H(23A)-C(23)-H(23C)	109.5		
H(23B)-C(23)-H(23C)	109.5		
C(21)-C(24)-H(24A)	109.5		
C(21)-C(24)-H(24B)	109.5		
H(24A)-C(24)-H(24B)	109.5		
C(21)-C(24)-H(24C)	109.5		
H(24A)-C(24)-H(24C)	109.5		
H(24B)-C(24)-H(24C)	109.5		
N(1)-C(25)-Ir(1)	178.21(17)		
C(25)-N(1)-C(26)	172.3(2)		
N(1)-C(26)-C(27)	111.61(18)		
N(1)-C(26)-H(26A)	109.3		
C(27)-C(26)-H(26A)	109.3		
N(1)-C(26)-H(26B)	109.3		
C(27)-C(26)-H(26B)	109.3		

**References:**

- (1) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C. *Chem. Commun.* **1996**, 2083.
- (2) Manganey, P.; Tejero, T.; Alexakis, A.; Grosjean, F.; Normant, J. *Synthesis* **1988**, 255.
- (3) Srivatsan, S.; Gao, W.; Gasem, K. A. M.; Robinson, R. L., Jr. *J. Chem. Eng. Data* **1998**, *43*, 623-625.