Supporting Information

Reversible Addition of Ethylene to a Pincer-Based Boryl-Iridium Unit with the Formation of a Bridging Ethylidene

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I. General Considerations.

General Considerations. Unless specified otherwise, all manipulations were performed under an Ar atmosphere using standard Schlenk line or glovebox techniques. Toluene, pentane was dried and deoxygenated (by purging) using a solvent purification system (Innovative Technology Pure Solv MD-5 Solvent Purification System) and stored over molecular sieves in an Ar-filled glove box. C₆D₆, toluene-d8, 1-hexene, trans-3-hexene, 1,4 dioxane was dried over NaK/Ph₂CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. (PBP)IrH₄ (1), (PBP)Ir(H₂)(CO) (2) and(PBP)Ir(CO)₂ (3) were prepared via literature procedures.¹ All other chemicals were used as received from commercial vendors.

Physical Methods. NMR spectra were recorded on a Varian Inova 400 (¹H NMR, 399.535 MHz; ¹¹B NMR, 128.185 MHz; ³¹P NMR, 161.734 MHz), Bruker 400 (¹H NMR, 399.535 MHz; ¹³C NMR, 100.500 MHz, ¹¹B NMR, 128.185 MHz; ³¹P NMR, 161.734 MHz) and Varian Inova 500 (¹H NMR, 499.703 MHz; ¹³C NMR, 125.697 MHz; ³¹P NMR, 202.265 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ¹H and ¹³C NMR spectra, the residual solvent peak was used as an internal reference (¹H NMR: δ 7.16 for C₆D₆; ¹³C NMR: δ 128.62 for C₆D₆). ¹¹B NMR spectra were referenced externally with BF₃ etherate at δ 0. ³¹P NMR spectra were referenced externally with 85% phosphoric acid at δ 0. Elemental analyses were performed by CALI Labs, Inc. (Highland Park, NJ)

II. Synthesis and characterization of iridium complexes.



 $(PB^{Vinyl}P)Ir(H)(C_2H_4)$ (4). In a 25 mL Teflon screw-capped round-bottomed flask, 1 (0.10 g, 0.10 mmol) was dissolved in toluene (2 mL). The solution was degassed twice via freeze-pump-thaw, and the flask was refilled with ethylene (1 atm). The reaction was stirred at room temperature

overnight. The volatiles were removed under vacuum, and the resulting solid was recrystallized in toluene/pentane 1:3, yielding a pale orange solid (82 mg, 72%).

¹H NMR (500 MHz, C₆D₆): δ 8.30 (d, J_{H-H} = 7.5 Hz, 1H), 8.09 (d, J_{H-H} = 7.5 Hz, 1H), 7.32 (td, J_{H-H} = 7.4 Hz, 1.0 Hz, 1H), 7.24 (m, 2H), 7.14 (m, 1H), 7.03 (m, 1H), 6.97 (m, 1H), 4.45 (m, 1H, B–CH=CH₂), 2.96-1.89 (br, 6H, CH₂=CH₂ B–CH=CH₂), 2.70 (br, 1H, CHMe₂), 2.40 (br, 1H, CHMe₂), 2.28 (br, 1H, CHMe₂), 1.98 (br, 1H, CHMe₂), 1.28 (dvt, J_{H-H} = 7.1 Hz, 3H, CHMe₂), 1.13 (m, 9H, CHMe₂), 0.83 (dvt, J_{H-H} = 6.4 Hz, 3H, CHMe₂), 0.73 (dvt, J_{H-H} = 6.9 Hz, 3H, CHMe₂), 0.55 (dvt, J_{H-H} = 7.7 Hz, 3H, CHMe₂), 0.35 (dvt, J_{H-H} = 7.3 Hz, 3H, CHMe₂), -13.70 (br, 1H, Ir–H). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 32.3 (br). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ 20.3 (br). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ 165.2 (br, C_q), 157.5 (br, C_q), 142.3 (br, C_q), 137.2 (br, C_q), 133.6 (t, J_{C-P} = 10.0 Hz, CH), 131.4 (t, J_{C-P} = 10.8 Hz, CH), 130.9 (s, CH), 129.9 (s, CH), 129.8 (s, CH), 129.3 (s, CH), 128.9 (s, CH), 125.6 (t, J_{C-P} = 3.0 Hz, CH), 125.5 (br, CH), 74.6 (br, Ir–CH=CH₂), 56.3 (br, CH₂=CH₂), 35.5 (m, CHMe₂), 32.0 (t, J_{C-P} = 14.1 Hz, CHMe₂), 27.5 (t, J_{C-P} = 17.0 Hz, CHMe₂), 27.1 (t, J_{C-P} = 14.6 Hz, CHMe₂), 22.1 (s, CH₃), 20.7 (s, CH₃), 20.4 (s, CH₃), 19.4 (s, CH₃), 19.0 (s, CH₃), 18.7 (s, CH₃), 18.6 (s, CH₃), 18.5 (s, CH₃). Elem. Anal. Calcd for C₂₈H₄₄BIrP₂: C, 52.09; H, 6.87. Found: C, 52.09; H, 6.58.



(PB^{CHCH3}P)Ir(H)₂(CO) (5). In a 25 mL Teflon screw-capped roundbottomed flask, 2 (40 mg, 0.10 mmol) was dissolved in toluene (2 mL). The solution was degassed twice via freeze-pump-thaw, and the flask was refilled with ethylene (1 atm). The reaction was stirred at room

temperature overnight. The volatiles were removed under vacuum, and the resulting solid was recrystallized in pentane, yielding a colorless solid (25 mg, 60%).

¹H NMR (500 MHz, C₆D₆) δ 8.43 (dd, J_{H-H} = 7.5, 2.3 Hz, 1H), 8.34 (d, J_{H-H} = 7.6 Hz, 1H), 7.38 (t, J_{H-} н = 7.3 Hz, 1H), 7.25 (t, J_{H-H} = 7.4 Hz, 1H), 7.09 (m, 3H), 6.99 (t, J_{H-H} = 7.2 Hz, 1H), 3.37 (m, 1H, B– CH–CH₃), 2.17 (m, 2H, CHMe₂), 1.81 (m, 2H, CHMe₂), 1.75 (d, J_{H–H} = 7.0 Hz, 3H, B–CH–CH₃), 1.23 (dd, J_{H-P} = 15.1 Hz, J_{H-H} = 6.9 Hz, 3H, CH*Me*₂), 1.14 (dd, J_{H-P} = 15.3 Hz, J_{H-H} = 7.0 Hz, 3H, CH*Me*₂), 1.11 (dd, J_{H-P} = 14.6 Hz, J_{H-H} = 7.0 Hz, 3H, CH*Me*₂), 1.01 (dd, J_{H-P} = 15.6 Hz, J_{H-H} = 7.2 Hz, 3H, CHMe₂), 0.97 (dd, J_{H-P} = 16.0 Hz, J_{H-H} = 6.8 Hz, 3H, CHMe₂), 0.93 (dd, J_{H-P} = 15.7 Hz, J_{H-H} = 6.8 Hz, 3H, CHMe₂), 0.65 (dd, J_{H-P} = 14.5 Hz, J_{H-H} = 6.9 Hz, 3H, CHMe₂), 0.57 (dd, J_{H-P} = 15.3 Hz, J_{H-H} = 6.8 Hz, 3H, CH Me_2), -11.10 (ddd, J_{H-P} = 19.6, 13.3 Hz, J_{H-H} = 2.5 Hz, 1H, Ir–H), -12.88 (t, J_{H-P} = 14.5 Hz, 1H, Ir–*H*). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 42.6 (d, J_{P-P} = 257.4 Hz), 39.3 (d, J_{P-P} = 257.9 Hz). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ 17.8 (s). ¹³C{¹H} NMR (126 MHz, C₆D₆) δ 185.5 (dd, J_{C-P} = 14.8, 8.8 Hz, CO), 165.07 (br), 160.17 (br), 141.4 (dd, J_{C-P} = 50.3, 3.9 Hz), 138.4 (dd, J_{C-P} = 52.4, 2.9 Hz), 134.2 (d, J_{C-P} = 16.8 Hz), 131.4 (d, J_{C-P} = 15.6 Hz), 131.3 (br), 130.3 (d, J_{C-P} = 2.1 Hz), 130.2 (br), 129.5 (d, J_{C−P} = 2.2 Hz), 125.3 (d, J_{C−P} = 7.2 Hz), 124.5 (d, J_{C−P} = 7.5 Hz), 56.3 (s, B−*C*H−CH₃),32.4 (dd, J_{C−P} = 37.1, 2.6 Hz, CHMe₂), 30.0 (dd, J_{C-P} = 22.4, 3.9 Hz, CHMe₂), 29.6 (dd, J_{C-P} = 34.5, 3.6 Hz, CHMe₂), 27.6 (dd, J_{C-P} = 22.6, 4.5 Hz, CHMe₂), 22.3 (s, CH₃), 21.5 (s, CH₃), 21.0 (s, CH₃), 20.9 (d, J_{C-P} = 2.4 Hz, CHMe₂), 20.7 (d, J_{C-P} = 3.2 Hz, CHMe₂), 20.5 (s, CH₃), 20.4 (s, CH₃), 19.7 (s, CH₃), 19.6 (d, J_{C-P} =

3.6 Hz, CH*Me*₂). ATR-IR: v_{co} = 1977 cm⁻¹. Elem. Anal. Calcd. for C₂₇H₄₂BIrOP₂: C, 50.08; H, 6.54. Found: C, 50.05; H, 6.46.



 $(PB^{CHCH3}P)Ir(CO)_2$ (6). In a J. Young tube, 3 (21 mg, 0.030 mmol) was dissolved in C₆D₆ (0.50 mL). The solution was degassed twice via freeze-pump-thaw, and the tube was refilled with ethylene (1 atm). After heating at 50 °C for 36 hours, the volatiles were removed under vacuum,

the resulting solid was recrystallized in pentane, yielding pale yellow solid (18 mg, 79%).

¹H NMR (500 MHz, C₆D₆): δ 8.40 (m, 1H), 8.12 (d, J_{H-H} = 7.6 Hz, 1H), 7.40 (m, 1H), 7.28 (m, 1H), 7.18 (m, 1H), 7.05 (m, 2H), 6.92 (t, J_{H-H} = 7.4 Hz, 1H), 2.72 (m, 1H, IrC*H*(B)Me), 2.31 (m, 1H), 2.21 (m, 3H), 1.39 (dd, J_{H-H} = 7.0, J_{P-H} = 0.7 Hz, 3H, IrCH(B)*Me*), 1.15 (m, 6H, CH*Me*₂), 1.08 (dd, J_{H-H} = 16.1, J_{P-H} = 6.8 Hz, 3H, CH*Me*₂), 0.87 (m, 12H, CH*Me*₂), 0.75 (dd, J_{H-H} = 16.4, J_{P-H} = 7.0 Hz, 3H, CH*Me*₂). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 32.6 (d, J_{P-P} = 184 Hz), 27.6 (d, J_{P-P} = 184 Hz). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ 20.4. ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 182.0 (dd, J_{P-C} = 13.2, J_{P-C} = 10.9 Hz, CO), 181.4 (dd, J_{P-C} = 12.1, J_{P-C} = 9.5 Hz, CO), 165.0 (br, B-*C*), 159.7 (br, B-*C*), 133.5 (d, J_{P-C} = 48.7 Hz), 132.8 (d, J_{P-C} = 22.7 Hz), 131.3 (d, J_{P-C} = 48.5 Hz), 130.6 (m, 3C), 129.8 (s), 129.2 (s), 125.2 (d, J_{P-C} = 7.5 Hz), 125.1 (d, J_{P-C} = 23.7 Hz, CHMe₂), 24.1 (dd, J_{P-C} = 25.7, 5.2 Hz, CHMe₂), 29.0 (d, J_{P-C} = 4.7 Hz, IrCH(B)*Me*), 19.9 (s, MeCH*Me*), 19.5 (s, MeCH*Me*), 19.2 (s, MeCH*Me*), 18.5 (s, MeCH*Me*), 18.3 (s, MeCH*Me*), 17.5(s, MeCH*Me*, 2C), 16.8 (d, J_{P-C} = 5.0 Hz, MeCH*Me*). ATR-IR: v_{CO} = 1987 cm⁻¹, 1942 cm⁻¹. Elem. Anal. Calcd. for C₂₈H₄₀BIrO₂P₂: C, 49.93; H, 5.99. Found: C, 50.28; H, 5.97.

In situ observation of (PB^{CH(CH2)4CH3}P)Ir(CO)₂ (6'). To a J. Young tube was added 3 (13 mg, 0.020 mmol) and 1-hexene (0.40 mL, 1.6 mmol). The tube was placed into a 50 °C oil bath for 16 h. Following the thermolysis, all volatiles were removed under vacuum and the solid was redissolved in C₆D₆, ¹H NMR, ³¹P{¹H} NMR and ¹¹B{¹H} NMR spectra were recorded, showing complete consumption of **3** to generate **6'**. ¹H NMR (500 MHz, C₆D₆): δ 8.42 (d, J_{H-H} = 7.6 Hz, 1H), 8.20 (d, J_{H-H} = 7.6 Hz, 1H), 7.38 (tdd, J_{H-H} = 7.5, 2.4, 1.0 Hz, 1H), 7.28 (m, 1H), 7.17 (m, 1H), 7.04 (m, 2H), 6.93 (t, J_{H-H} = 7.4 Hz, 1H), 2.67(m, 1H, B–C–Ir), 2.29 (m, 4H, (CH₂)₄Me and CHMe₂), 1.92 (m, 1H, CHMe₂), 1.22 (dd, J_{H-H} = 15.2, 7.1 Hz, 3H, CHMe₂), 1.18 (dd, J_{H-H} = 15.9, 6.8 Hz, 3H, CHMe₂), 1.10 (dd, J_{H-H} = 16.1, 6.8 Hz, 3H, CH*Me*₂), 1.02 (m, 4H, (CH₂)₄Me), 0.95 (dd, J_{H-H} = 16.8, 6.8 Hz, 3H, СН*Me*₂), 0.87 (m, 6H, CH*Me*₂), 0.81 (dd, J_{H-H} = 16.4, 7.0 Hz, 3H, CH*Me*₂), 0.76 (dd, J_{H-H} = 16.4, 7.0 Hz, 3H, CHMe₂), 0.70 (t, J_{H-H} = 7.0 Hz, 3H, CH₂Me). ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 31.7 (d, J_{P-P} = 187 Hz), 27.7 (d, $J_{P-P} = 187$ Hz). ¹¹B{¹H} NMR (128 MHz, C₆D₆): δ 20.5. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 182.5 (dd, J_{C-P} = 14.1, 10.2 Hz, CO), 181.5 (dd, J_{C-P} = 12.1, 8.5 Hz, CO), 166.0 (br, B–C_{sp2}), 159.8 (br, B–C_{sp2}), 134.2 (d, J_{C-P} = 48.9 Hz, P–C_{sp2}), 131.7 (d, J_{C-P} = 48.6 Hz, P–C_{sp2}), 131.7 (d, J_{C-P} = 22.5 Hz, $C_{sp2}H$), 131.7 (d, $J_{C-P} = 48.6$ Hz, $P-C_{sp2}$), 131.1 (d, $J_{C-P} = 2.2$ Hz, $C_{sp2}H$), 131.0 (d, $J_{C-P} = 20.6$ Hz, $C_{sp2}H$), 130.5 (d, $J_{C-P} = 2.2 Hz$, $C_{sp2}H$), 130.4 (d, $J_{C-P} = 3.0 Hz$, $C_{sp2}H$), 129.5 (d, $J_{C-P} = 2.4 Hz$, $C_{sp2}H$), 125.8 (d, J_{C-P} = 7.8 Hz, C_{sp2}H), 125.7 (d, J_{C-P} = 7.8 Hz, C_{sp2}H), 52.6 (br, IrCH(B)Me), 39.0 (d, J_{C-P} = 5.0 Hz, (CH₂)₄Me), 35.7 (s, (CH₂)₄Me), 32.9 (s, (CH₂)₄Me), 30.8 (d, J_{C-P} = 32.8 Hz, CHMe₂), 29.7 (d, J_{C-P} = 30.5 Hz, CHMe₂), 27.8 (dd, J_{C-P} = 23.8, 4.3 Hz, CHMe₂), 24.6 (dd, J_{C-P} = 25.8, 5.7 Hz, CHMe₂), 23.4 (s, (CH₂)₄Me), 20.6 (s, CHMe₂), 20.0 (d, J_{C-P} = 2.3 Hz, CHMe₂), 19.8 (d, J_{C-P} = 3.3 Hz, CHMe₂), 19.0 (d, J_{C-P} = 4.3 Hz, CHMe₂), 18.9 (d, J_{C-P} = 2.9 Hz, CHMe₂), 18.2 (d, J_{C-P} = 3.8 Hz, CHMe₂), 18.0 (d, J_{C-P}

= 3.7 Hz, CH*Me*₂), 17.4 (d, J_{C-P} = 5.6 Hz, CH*Me*₂), 14.9 (s, CH₂*Me*). ATR-IR: ν_{CO} = 1989 cm⁻¹, 1945 cm⁻¹

	¹¹ B{ ¹ H} NMR	³¹ P{ ¹ H} NMR	¹³ C{ ¹ H} NMR and	Vco
			for B ^{CHR} P	
6	20.4 ppm	32.6 (d, J _{P-P} = 184 Hz)	45.4 ppm	1987 cm ⁻¹
		27.6 (d, J _{P-P} = 184 Hz)		1942 cm ⁻¹
6'	20.5 ppm	31.7 (d, J _{P-P} = 187 Hz)	52.6 ppm	1989 cm ⁻¹
		27.7 (d, J _{P-P} = 187 Hz)		1945 cm ⁻¹

Table S1. Selected spectral data of 6 and 6'.

In situ NMR study of the reaction of 3 with *trans*-3-hexene. To a J. Young tube was added 3 (13 mg, 0.020 mmol), *trans*-2-hexene (10 μ L, 0.080 mmol) and 0.40 mL C₆D₆. The tube was placed into a 100 °C oil bath; it was retrieved four times to collect NMR spectra at room temperature (Figure S1). The major new product after 127 h was compound **6'**. At intermediate times, another product displaying an AB pattern in the ³¹P{¹H} NMR spectrum was observed (46.7 ppm (d, J_{P-P} = 163.2 Hz), 44.9 ppm (d, J_{P-P} = 225.2 Hz)). It was not unambiguously identified, but it is likely to be an isomer of **6'** possessing a non-terminal bridging hexylidene.



Figure S1. ³¹P{¹H} NMR spectra at room temperature of in situ internal hexene addition experiment after heating at 100 °C for certain time in C_6D_6 .

III. In situ NMR study of olefin addition

Addition of 1-Hexene with and without CO. Two J. Young NMR tubes (A and B) were loaded with identical solutions under argon: **3** (0.20 mL 0.10 M in C₆D₆, 0.020 mmol), 1-hexene (50 μ L 2.0M in C₆D₆, 0.10 mmol), ¹Bu₂PhP=O (0.10 mL, 0.20 M in C₆D₆, 0.020 mmol), and 1,4 dioxane (50 μ L 0.20 M in C₆D₆, 0.010 mmol). ¹Bu₂PhP=O was added as ³¹P{¹H} NMR internal standard and 1,4 dioxane was added as ¹H NMR internal standard, although ¹H NMR spectra were not useful in analyzing the mixture due to extensive overlap. Tube **B** was degassed twice using the freeze-pump-thaw method, followed by introduction of 1 atm of CO. NMR spectra of solutions in both tube **A** and tube **B** were recorded, and then both tubes were placed into the same 50 °C oil bath at the same time. After 90 h, 73% **6'** was generated in tube **A** while 0% generation of the desired product was observed in tube **B** (³¹P{¹H} NMR evidence). Traces of water adduct (at 54.6 ppm) was observed in tube **B** due to the reaction of **3** with adventitious water in CO to form (PB^{OH}P)Ir(H)(CO)₂.²



Figure S2. A. ³¹P{¹H} NMR spectra of the reaction of 1-hexene with **3** under argon atmosphere. **B.** ³¹P{¹H} NMR spectra of in situ addition of 1-hexene to **3** experiment under CO atmosphere.

Reaction rate comparison for 3 reacted with increased amounts of 1-hexene. To three J.

Young tubes was added solutions according to Table S2. All tubes were placed into the same 50 °C oil bath at the same time, and all ${}^{31}P{}^{1}H{}$ NMR spectra were recorded at room temperature after periodically taking the tubes out of the oil bath simultaneously. Concentration of **3** was calculated by ${}^{31}P{}^{1}H{}$ NMR spectra using 0.020 mmol ${}^{t}Bu_{2}PhP=O$ as internal standard. The reaction rate displays positive dependence on [1-hexene] and [**3**].

	3	1-Hexene	^t Bu ₂ PhP=O	C ₆ D ₆	Total
	0.10 M in $C_6 D_6$		0.20 M in C ₆ D ₆		Volume
Tube	0.20 mL, 0.020	25 μL, 0.20 mmol,	0.10 mL, 0.020 mmol,	75 μL	0.40
с	mmol, 0.050 M	0.50 M	0.050 M		mL
Tube	0.20 mL, 0.020	50 μL, 0.40 mmol,	0.10 mL, 0.020 mmol,	50 μL	0.40
D	mmol, 0.050 M	1.0 M	0.050 M		mL
Tube	0.20 mL, 0.020	0.10 mL, 0.80	0.10 mL, 0.020 mmol,	0 μL	0.40
E	mmol, 0.050 M	mmol, 2.0 M	0.050 M		mL

Table S2. Constituents in tubes C, D and E



Figure S3. Consumption of **3** over time for **3** (0.050 M) and 1-hexene (0.50 M) addition reaction showing disappearance of **3** on a log scale.



Figure S4. Consumption of **3** over time for **3** (0.050 M) and 1-hexene (1.0 M) addition reaction showing disappearance of **3** on a log scale.



Figure S5. Consumption of 3 over time for 3 (0.050 M) and 1-hexene (2.0 M) addition reaction

showing disappearance of **3** on a log scale.

Table S3.	Results	of Tube C ,	D and E
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Tube number	1-hexene concentration/M	k _{obs} * 10 ⁴ /min ⁻¹ M ⁻¹
Tube C	0.50	6.0
Tube D	1.0	16
Tube E	2.0	29



Figure S6. Experimental rate constant is positively related to 1-hexene concentration.

Ethylene observation in the thermolysis of 5. 5 (0.020 mmol, 14 mg) was dissolved in 0.40 mL C₆D₆, and heated inside the Varian Inova 500 instrument. The spectra were recorded after 10 min when the temperature was stabilized at 80 °C. Free ethylene and hydrides of 2 was observed in the spectra recorded at 80 °C (ca. 1%).



Figure S7. ¹H NMR spectra recorded for the thermolysis of 5.

Ethylene observation in the thermolysis of 6. 6 (0.020 mmol, 14 mg) was dissolved in 0.40 mL C₆D₆/toluene-d₈, and heated with Varian Inova 400 instrument. The spectra were recorded after the temperature was stabilized at 75 °C, 90 °C and 100 °C for 10 min. Free ethylene was observed in the spectra recorded at 90 °C and 100 °C, but not at 75 °C.



Figure S8. ¹H NMR spectra recorded for the thermolysis of 6.

Thermolysis of 6 at 100 °C with and without CO. Two J. Young NMR tubes (F and G) were loaded with identical solutions under argon: 6 (12 mg, 0.020 mmol), ^tBu₂PhP=O (0.10 mL, 0.20 M in C₆D₆, 0.020 mmol) and C₆D₆ 0.30 mL. Tube G was degassed twice using the freeze-pump-thaw method, followed by introduction of 1 atm of CO. Both tubes were placed into the same 100 °C oil bath at the same time. All ³¹P{¹H} NMR spectra were recorded at room temperature after periodically taking the tubes out of the oil bath simultaneously. The content of **3** and **6** was calculated from ³¹P{¹H} NMR spectra vs 0.020 mmol ^rBu₂PhP=O as the internal standard. Slower generation of **3** was observed in Tube **G**.

Table S4. Moles of **3**, **6** in tubes **F** and **G**, calculated by³¹P{¹H} NMR spectra with ^tBu₂PhP=O as internal standard.

Time (min)	Tube F (mmol)		Tube G	(mmol)
	3	6	3	6
0	0	0.019	0	0.019
16	0.003	0.016	0.001	0.018
48	0.006	0.013	0.003	0.016
123	0.008	0.012	0.004	0.015



Figure S9. A. ³¹P{¹H} NMR spectra recorded for thermolysis of **6** to generate **3** at 100 °C without CO in tube **F. B.** ³¹P{¹H} NMR spectra recorded for thermolysis of **6** to generate **3** at 100 °C with 1 atm CO in tube **G**.

IV. X-Ray structural determination details.

X-Ray data collection, solution, and refinement for 4. A yellow, multi-faceted block of suitable size (0.32 x 0.25 x 0.05 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (150 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_{α} = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.³ An absorption correction was applied using SADABS.⁴ The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2 . The structure was solved in the orthorhombic P bca space group using XS⁵ (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model with the exception of the hydrogen bound to iridium which was located from the difference map. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.⁶ CCDC: 1858843 contain the supplementary crystallographic data.



Figure S10. ORTEP drawings showing selected atom labeling of 5

X-ray data collection, solution, and refinement for 5. A Leica MZ 7₅ microscope was used to identify a suitable colorless block with very well-defined faces with dimensions (max, intermediate, and min) 0.395 x 0.299 x 0.098 mm³ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite, v2017.3-0.⁷ The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α = 0.70173Å with a potential of 40 kV and a current of 40 mA). 45 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (5 sets) was initiated using omega scans. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.⁷ The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS⁴ was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests of the data suggested the space group Pca2₁. A solution was obtained readily (with two slightly different molecules in the asymmetric unit) using XT/XS in APEX2.^{5,7-8} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated ellipsoids and the residual electron densities in both the molecules indicated disorder. In the molecule with Ir1 (and Ir1a) shown above the configuration shown in Figure S10-A was found to be the major component (93 %). Whereas in the molecule with Ir2 (and Ir2a) the configuration shown in Figure S10-B was found to be the major component (70%). The structure was refined (weighted least squares refinement on F^2) to convergence.^{5,8-9} Olex2 was employed for the final data presentation and structure plots.⁹ CCDC: 1858844 contain the supplementary crystallographic data.

X-Ray data collection, solution, and refinement for 6. A pale yellow, multi-faceted block of suitable size (0.23 x 0.12 x 0.05 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (150 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, $K_{\alpha} = 0.71073$ Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.³ An absorption correction was applied using SADABS.⁴ The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2 . The structure was solved in the monoclinic P 2₁/c space group using XS⁵(incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.⁶ CCDC: 1858845 contain the supplementary crystallographic data.



Figure S11. ${}^{31}P{}^{1}H$ NMR spectrum of 4 in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S12. ${}^{11}B{}^{1}H{}$ NMR spectrum of 4 in C₆D₆ at RT measured on a 400 MHz Varian NMR.



Figure S13. ¹H NMR spectrum of **4** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S14. ¹³C ^{1}H NMR spectrum of **4** in C₆D₆ at RT measured on a 400 MHz Bruker NMR.



Figure S15. DEPT NMR spectra of **4** in C₆D₆ at RT measured on a 400 MHz Bruker NMR. From top to bottom: 45°, 90°, and 135°.



Figure S16. gHSQC spectrum of **4** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S17. ¹H NMR spectrum of **5** in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S18. ${}^{31}P{}^{1}H$ NMR spectrum of 5 in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S19. ¹¹B{¹H} NMR spectrum of **5** in C_6D_6 at RT measured on a 400 MHz Varian NMR.



Figure S20. ¹³C ^{1}H NMR spectrum of 5 in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S21. ATR-IR spectrum of 5.



Figure S22. gHSQC spectrum of **5** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S23. gDQCOSY spectrum of **5** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S24. ¹H NMR spectrum of **6** in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S25. DEPT NMR spectra of 6 in C₆D₆ at RT measured on a 400 MHz Bruker NMR. From top to bottom: 135°, 90°, and 45°.



Figure S26. ${}^{31}P{}^{1}H$ NMR spectrum of 6 in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S27. ¹¹B{¹H} NMR spectrum of **6** in C_6D_6 at RT measured on a 400 MHz Varian NMR.



Figure S28. gHSQC spectrum of **6** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S29. gDQCOSY spectrum of **6** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S30. ATR-IR spectrum of 6.



Figure S31. ¹H NMR spectrum of **6'** in C_6D_6 at RT measured on a 500 MHz Varian NMR.



Figure S32. ${}^{31}P{}^{1}H$ NMR spectrum of **6'** in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S33. ${}^{11}B{}^{1}H{}$ NMR spectrum of G' in C₆D₆ at RT measured on a 400 MHz Varian NMR.



Figure S34. ${}^{13}C{}^{1}H$ NMR of **6'** in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S35. gHSQC spectrum of 6' in C₆D₆ at RT measured on a 500 MHz Varian NMR.



Figure S36. ATR-IR spectrum of 6'.

VI. SI References.

³ APEX, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

⁴ G. M. Sheldrick, *SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames.*, University of Göttingen, 2008.

⁵ G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.

⁶ A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University: Utrecht, The Netherlands, 1998.

⁷ APEX3 "Program for Data Collection on Area Detectors" BRUKER AXS Inc., 5465 East Cheryl
Parkway, Madison, WI 53711-5373 USA.

⁸ G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122. G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8.

XT, XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

⁹ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

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¹ W.-C. Shih; O. V. Ozerov, Organometallics 2017, **36**, 228-233.

² Y. Cao; W.-C. Shih; O. V. Ozerov, *Organometallics* 2019, **38**, 4076-4081.