

Supporting Information for

Oxygen-Atom Transfer from Carbon Dioxide to a Fischer Carbene at (PNP)Ir

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Experimental Section

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with Ar gas followed by passage through an activated alumina column. Hexamethyldisiloxane and *t*-butyl methyl ether were distilled from CaH₂ and degassed prior to use. Phenyl isocyanate was distilled *in vacuo* from P₂O₅. (PNP)IrH₂ (**1**)¹ was prepared according to literature procedure. Other reagents were purchased from commercial vendors and used without further purification. Elemental analyses were carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz spectrometer. ¹H NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts are reported relative to an external standard of 85% H₃PO₄. Infrared spectra were recorded using a Perkin Elmer Spectrum BXII spectrometer. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

(PNP)Ir=C(H)O^tBu (2). To a red solution of (PNP)IrH₂ (**1**) (175.8 mg, 0.2823 mmol) in *t*-butyl methyl ether (6 mL) was added norbornylene (49.0 mg, 0.520 mmol) in *t*-butyl methyl ether (6 mL). After several hours, the solution gradually darkened and gained a purple hue. After 18 h,

¹ Fan, L.; Parkin, S.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 16772.

volatiles were removed *in vacuo* to yield a dark red film which was redissolved in pentane (10 mL), filtered and dried to yield **2** as a purple solid. Analytically pure crystals of **2** were obtained by slow evaporation of pentane from a concentrated solution at -35 °C (107.0 mg, 54%). Compound **2** was stored at -40 °C to prevent decomposition. ^1H NMR (C_6D_6): δ 13.78 (t, $^3J_{\text{PH}} = 7.5$ Hz, 1H, $-\text{C}(\text{H})\text{O}^t\text{Bu}$), 7.80 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar-*H*), 7.17 (s, 2H, Ar-*H*), 6.82 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar-*H*), 2.62 (m, 4H, $-\text{CH}(\text{CH}_3)_2$), 2.24 (s, 6H, Ar- CH_3), 1.30 (m, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.21 (m, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.10 (s, 9H, $-\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 40.8 (s). Anal. Calcd. for $\text{C}_{31}\text{H}_{50}\text{IrNOP}_2$: C, 52.67; H, 7.13; N, 1.98. Found: C, 52.74; H, 7.05; N, 2.04.

Independent preparation of (PNP)Ir-CO (3). In a sealed NMR tube, a red solution of **1** (40 mg, 0.064 mmol) in C_6D_6 was frozen and the headspace evacuated and backfilled with carbon monoxide. As the solution melted, an immediate color change to pale yellow was observed. The reaction was allowed to proceed 24 h and complete formation of **3** confirmed by NMR. Lyophilization of the solution yielded **3** as an analytically pure yellow powder (41 mg, 98%). X-ray quality crystals were grown at room temperature from a concentrated solution of **3** in benzene / hexamethyldisiloxane (1:1). ^1H NMR (C_6D_6): δ 7.72 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar-*H*), 6.92 (s, 2H, Ar-*H*), 6.83 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H, Ar-*H*), 2.27 (m, 4H, $-\text{CH}(\text{CH}_3)_2$), 2.18 (s, 6H, Ar- CH_3), 1.29 (m, 12H, $-\text{CH}(\text{CH}_3)_2$), 1.05 (m, 12H, $-\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 57.3 (s). IR (THF, KBr, cm^{-1}) $\nu(\text{CO})$: 1930. Anal. Calcd. for $\text{C}_{27}\text{H}_{40}\text{IrNOP}_2$: C, 49.98; H, 6.21; N, 2.16. Found: C, 49.97; H, 5.73; N, 2.05.

Independent preparation of (PNP)Ir- ^{13}C CO (3- ^{13}C). (PNP)Ir- ^{13}C CO was prepared by the same method as **3** using ^{13}CO (99%). ^1H NMR characterization data matched those for **3**. $^{13}\text{C}\{^1\text{H}\}$

NMR (C₆D₆): δ 187.6 (t, $^2J_{PC} = 7.5$ Hz, Ir- ^{13}C). $^{31}P\{^1H\}$ NMR (C₆D₆): δ 57.4 (d, $^2J_{PC} = 7.6$ Hz).
IR (THF, KBr, cm⁻¹) $\nu(^{13}CO)$: 1883.

Reaction of compound 2 with CO₂. In a sealed NMR tube, a purple solution of **2** (20 mg) in C₆D₆ was frozen and the headspace evacuated and backfilled with carbon dioxide (1 atm). As the solution thawed, a gradual change in color from purple to pale yellow was observed. After 30 min, the consumption of **2** and formation of **3** and *t*-butyl formate were confirmed by NMR, and the presence of **3** was confirmed by IR. 1H NMR (*t*-butyl formate, C₆D₆): δ 7.64 (s, 1H, -C(O)H), 1.24 (s, 9H, -C(CH₃)₃).

Reaction of compound 2 with carbonyl sulfide. In a sealed NMR tube, a purple solution of **2** (25 mg) in C₆D₆ was frozen and the headspace evacuated and backfilled with carbonyl sulfide (1 atm). As the solution thawed, a gradual change in color from purple to pale yellow was observed. After 30 min, the consumption of **2** and formation of **3** and *t*-butyl thioformate were confirmed by NMR. 1H NMR (*t*-butyl thioformate, C₆D₆): δ 9.50 (s, 1H, -C(S)H), 0.85 (s, 9H, -C(CH₃)₃).

Reaction of compound 2 with phenyl isocyanate. An NMR tube was charged with a purple solution of **2** (40.6 mg, 0.0574 mmol) in C₆D₆, and phenyl isocyanate (7.0 μ L, 0.064 mmol) was added by microsyringe. Over a period of 3 min, the solution lightened and adopted a golden hue. After 15 min, the consumption of **2** and formation of **3** and *N*-phenyl *t*-butylformimidate were confirmed by NMR. 1H NMR (*N*-phenyl *t*-butylformimidate, C₆D₆): δ 7.51 (s, 1H, -C(NPh)H), 7.15 – 7.05 (m, 2H, Ar-H), 7.00 – 6.90 (m, 3H, Ar-H), 1.38 (s, 9H, -C(CH₃)₃).

Thermolysis of compound 2 in *t*-butyl methyl ether in the presence of CO₂. In a sealed NMR tube, a purple solution of **2** (30 mg) in *t*-butyl methyl ether was frozen and the headspace evacuated and backfilled with carbon dioxide (1 atm). The sealed tube was heated at 70 °C for 4 days, and NMR (³¹P) analysis revealed **3** as the predominant product (> 70%). **3** is not formed by thermolysis of **2** in *t*-butyl methyl ether in the absence of CO₂.²

² Romero, P. E.; Whited, M. T.; Grubbs, R. H., submitted for publication in *Organometallics*.

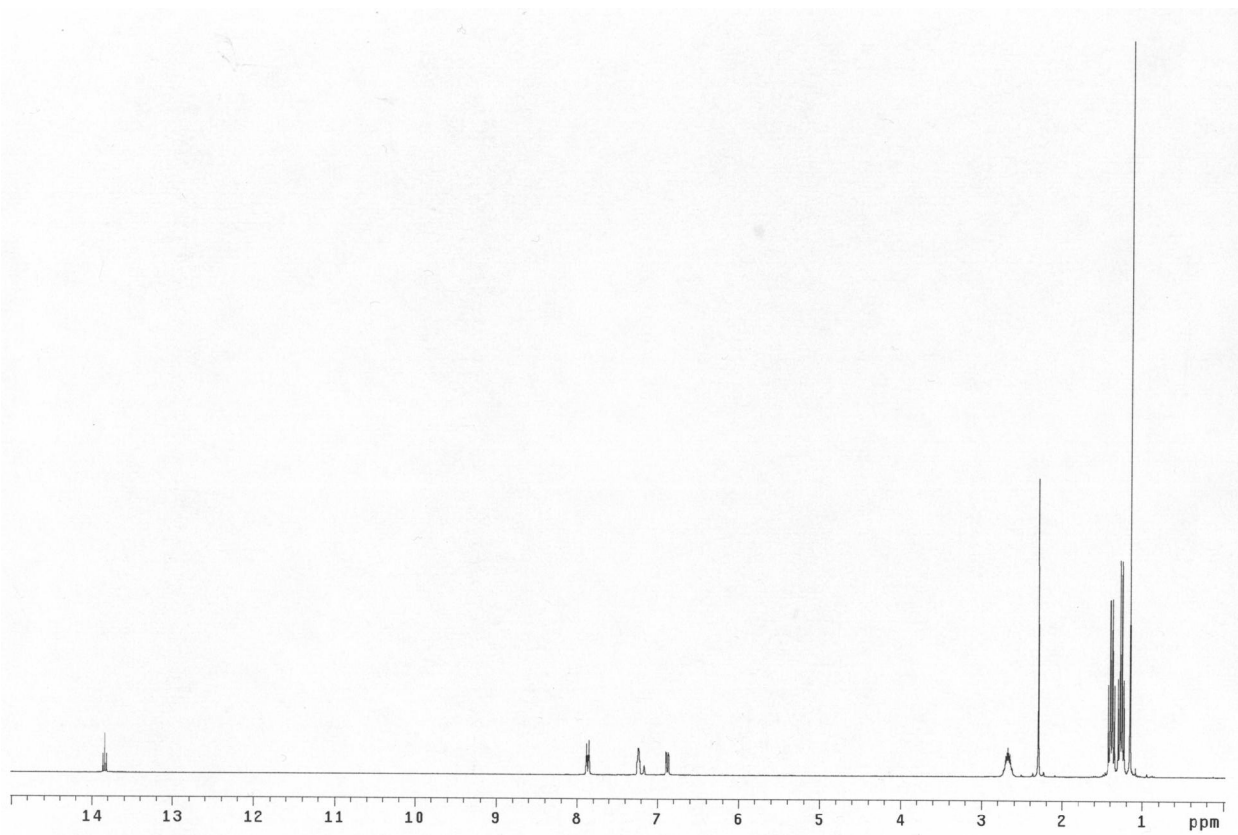


Figure S1. ^1H NMR spectrum of $(\text{PNP})\text{Ir}=\text{C}(\text{H})\text{O}'\text{Bu}$ (**2**) before reaction with CO_2

* = (PNP)Ir(CO)
▣ = t-butyl formate
S = residual solvent (benzene)

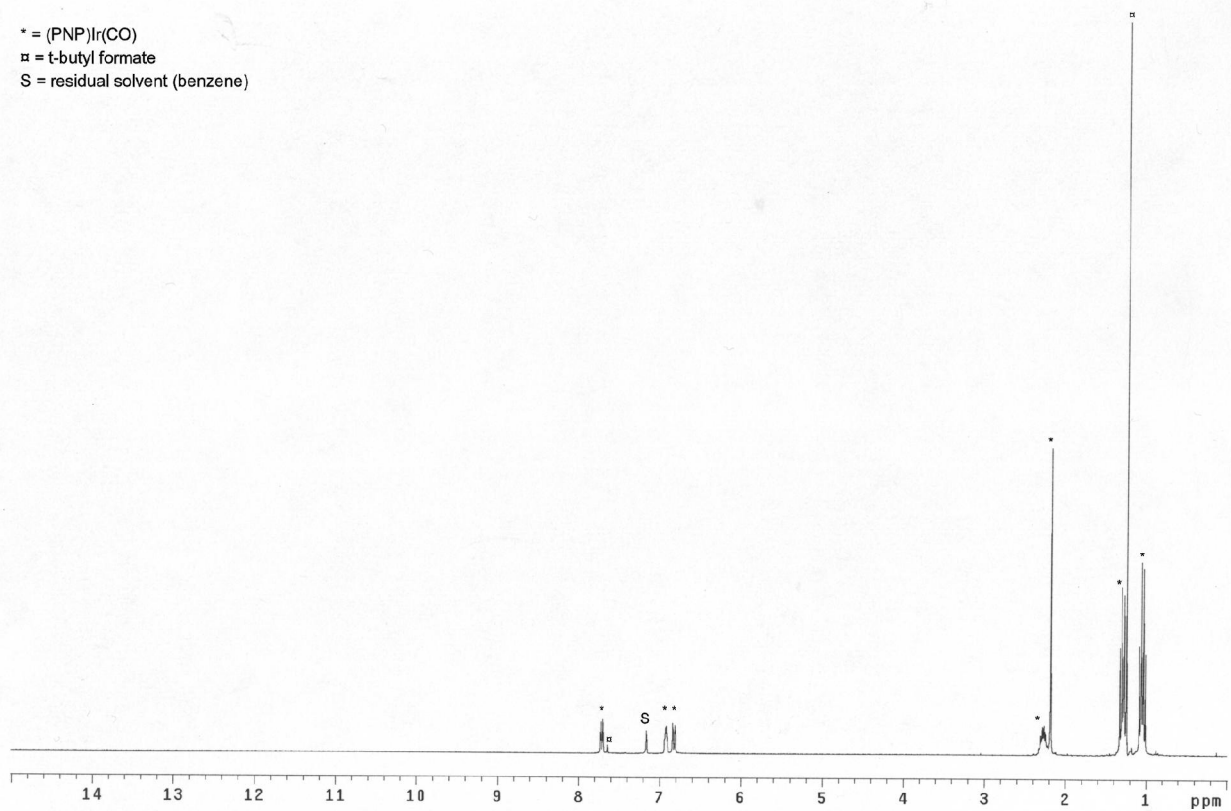


Figure S2. ^1H NMR spectrum of crude mixture from reaction of **2** with CO_2 (45 min)

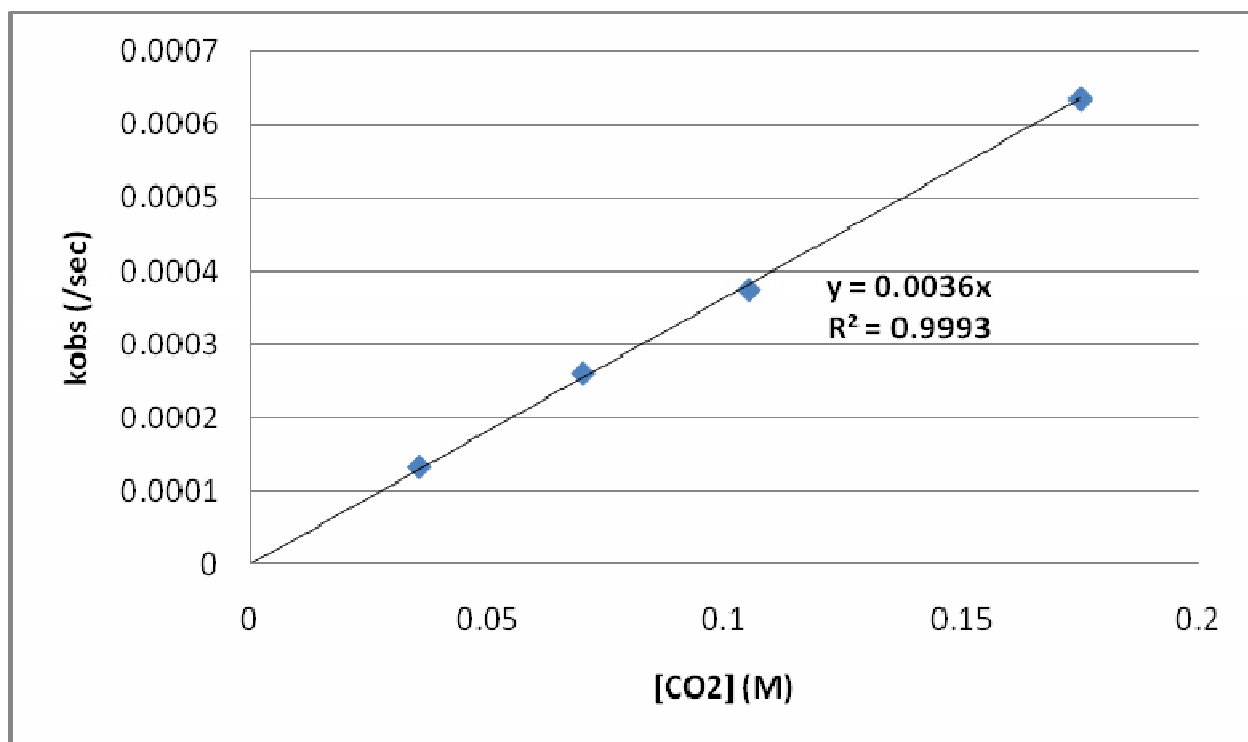


Figure S3. Plot of k_{obs} vs. $[\text{CO}_2]$ for the reaction of **2** with CO_2 at $-20\text{ }^\circ\text{C}$

Experimental Details. NMR tubes were charged with **2** (600 μL , 0.0034 M in toluene- d_8) and sealed with rubber septa, CO_2 (≥ 10 eq.) was added to the frozen sample in liquid N_2 *via* a gas-tight microsyringe. Reactions were monitored by ^1H NMR at $-20\text{ }^\circ\text{C}$ and were typically allowed to proceed through 3 half-lives (88% completion).

Full listing for reference 2a:

Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.