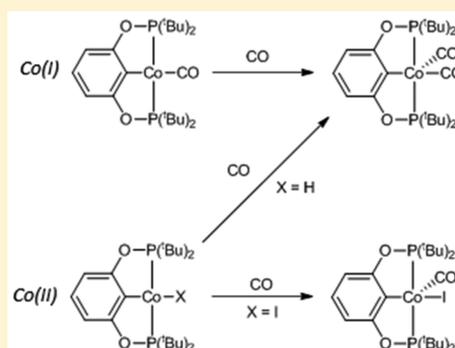


Pincer-Supported Carbonyl Complexes of Cobalt(I)

Louise M. Guard,[†] Travis J. Hebden,[†] Donald E. Linn, Jr.,[‡] and D. Michael Heinekey^{*,†}[†]Department of Chemistry, University of Washington, Seattle, Washington 98195-1700, United States[‡]Department of Chemistry, Indiana University-Purdue University Fort Wayne, 2101 Coliseum Boulevard, East Science Building 496, Fort Wayne, Indiana 46805-1499, United States

Supporting Information

ABSTRACT: A pair of POCOP-supported mono- and dicarbonyl complexes of Co have been prepared and crystallographically characterized. The reactivity of (^tBuPOCOP)Co(CO) with H₂, acids, and carbon monoxide has been compared to that of the previously reported Rh and Ir counterparts. Co is found to share reactivity traits with both Rh and Ir.



INTRODUCTION

Group 9 “pincer” complexes are ubiquitous in inorganic chemistry and have been studied extensively for a variety of reactions.^{1–23} POCOP (POCOP = κ^3 -C₆H₃-1,3-[OPR₂]₂, R = alkyl, aryl) is a commonly used subclass of these meridionally binding, chelating ligands and has been incorporated into frameworks such as (POCOP)M(CO) (where M = Ir,^{2,3,8,10} Rh^{14–16}), though direct Co analogues have remained elusive. Here we report the first example of a POCOP-supported four-coordinate monocarbonyl complex, (^tBuPOCOP)Co(CO), which allows for direct comparison, in terms of both structure and reactivity, with its second- and third-row metal counterparts. Of particular interest is the reaction of this monocarbonyl complex with carbon monoxide (CO) to form the dicarbonyl species (^tBuPOCOP)Co(CO)₂; we noted no similar reactivity with the analogous Rh and Ir complexes. Though both mono- and dicarbonyl Co complexes have been observed using the same PNP ligand,^{24,25} this is the first pair of POCOP-ligated Co carbonyl complexes and the first Co pincer system where both the mono- and dicarbonyl species have been crystallographically characterized.

RESULTS AND DISCUSSION

Pincer-Supported Monocarbonyl Group 9 Complexes. (^tBuPOCOP)Co(CO) (**1**) was prepared by the reduction of (^tBuPOCOP)Co(I)²³ using Na/Hg in the presence of 1 equiv of CO (eq 1). Solid-state characterization of **1** revealed a distorted-square-planar geometry where the bite angle of ^tBuPOCOP is 161.98(2)^o (Figure 1). This angle is in contrast with the Rh and Ir analogues, where the bite angles of the ^tBuPOCOP ligand are smaller and nearly identical (157.30(1)^o for Rh^{15,18} and 157.55(3)/157.51(4)^o for Ir^{8,26}). The C_{aryl}–M–CO angles are, however, essentially the same

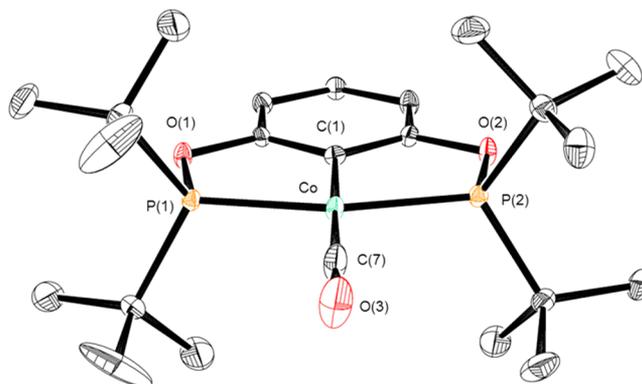


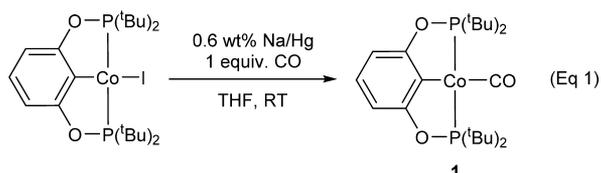
Figure 1. ORTEP³⁶ of **1** at 50% probability (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Co–C(1) 1.9353(16), Co–C(7) 1.7270(18), Co–P(1) 2.1587(5), Co–P(2) 2.1629(5), Co–O(3) 2.8662(14); P(1)–Co–P(2) 161.98(2), C(1)–Co–C(7) 179.30(8), P(1)–Co–C(1) 81.00(5), P(2)–Co–C(1) 80.99(5), P(1)–Co–C(7) 98.69(6), P(2)–Co–C(7) 99.33(6).

across all three compounds (179.30(8)^o for Co, 178.80(6)^o for Rh, and 178.9(3)/179.47(18)^o for Ir). All bonds to the metal center are shorter for the Co-containing complex **1** than for the related Rh or Ir complexes, which is in line with the smaller covalent radius of Co.²⁷ Diamagnetic **1** is formally Co^I and exhibits only one virtual triplet at 1.36 ppm for the ^tBu protons in the ¹H NMR spectrum, indicating approximate C_{2v} symmetry in both the solution and solid state. In the infrared spectrum, a strong absorption at 1899 cm⁻¹ is attributable to the single

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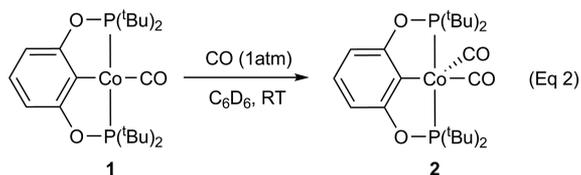
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carbonyl ligand. This is at a lower energy than both the Rh¹⁸ and Ir³ analogues (1956 and 1937 cm⁻¹, respectively), indicating strong back-donation from the metal center to the carbonyl ligand. This is likely explained by better orbital overlap between Co and the carbonyl ligand. The decreased electronegativity of first-row metals in comparison to their heavier congeners has also been invoked as an explanation,²⁸ and electrostatic effects could also play a role.^{29,30} The increased substitutional lability (or weaker M–CO bonds) of second-row metal complexes over analogous first- and third-row compounds is well-documented.^{28,31–35}



Pincer-Supported Dicarbonyl Group 9 Complexes.

The one-electron reduction of (^tBu₂POCOP)Co(I) in the presence of >2 equiv of CO, or exposure of **1** to 1 atm of CO (eq 2), resulted in the formation of (^tBu₂POCOP)Co(CO)₂



(**2**). In the latter case the reaction is instantaneous, resulting in quantitative spectroscopic yield. Complex **2** can be converted back to **1** by heating a solid sample of **2** under vacuum at 70 °C for prolonged periods (days). At 80 °C, decomposition of **1** is observed. Complex **2** has a distorted-square-pyramidal structure ($\tau = 0.08$)³⁷ with C(8) in the axial position (Figure 2). The Co atom is 0.473 Å above the plane formed by the equatorial atoms P(1)–C(1)–P(2)–C(7). Both Co–C(8) and Co–O(2) (1.7962(18) and 2.9406(13) Å) are elongated in comparison to Co–C(7) and Co–O(1) (1.7657(18) and 2.8681(14) Å) which is consistent with a weaker interaction between the axial

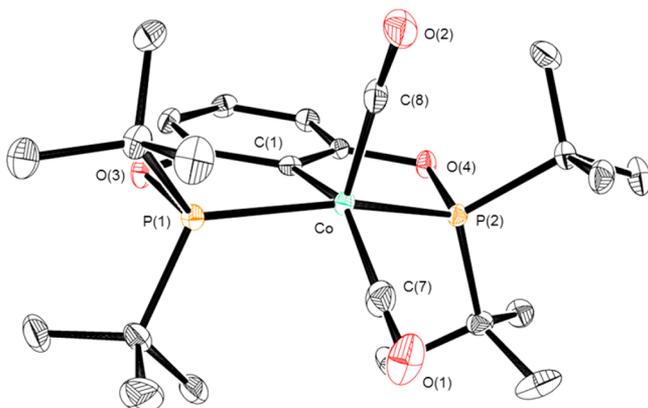


Figure 2. ORTEP³⁶ of **2** at 50% probability (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Co–C(1) 1.9776(16), Co–P(1) 2.2119(5), Co–P(2) 2.2112(5), Co–C(7) 1.7657(18), Co–O(1) 2.8681(14), Co–C(8) 1.7962(18), Co–O(2) 2.9406(13), P(1)–Co–P(2) 152.28(2), P(1)–Co–C(1) 79.54(4), P(2)–Co–C(1) 78.85(5), C(1)–Co–C(7) 147.76(8), C(1)–Co–C(8) 106.28(7), C(7)–Co–C(8) 105.96(8).

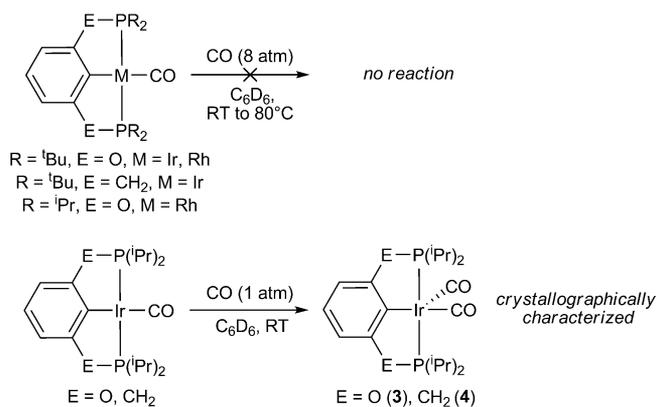
CO group and the metal center than the equatorial CO. There are two IR-active stretches at 1915 and 1969 cm⁻¹, as expected for the symmetric and antisymmetric stretches of the two carbonyl ligands bound to Co. The higher frequencies observed are consistent with diminished back-bonding in comparison to **1**.

Despite the asymmetric nature of **2** in the solid state (C(8) is clearly in the axial position), only one virtual triplet is observed for the ^tBu protons in the room-temperature NMR spectrum. The equilibration of the axial and equatorial CO ligands probably occurs through a pseudorotation. This type of observation, where CO groups appear inequivalent in the solid state and equivalent in solution, has been previously noted for other pincer group 9 complexes, including (^{Ph}PCP)Co(CO)₂,¹⁹ [(ⁱPrPC_{carbonyl}P)Ir(CO)₂]BARF₄,³⁸ (CF₃PCP)Ir(CO)₂,¹ and (ⁱPrPBP)Ir(CO)₂.³⁹

Previous examples of (pincer)Co^I(CO) complexes that add an additional 1 equiv of CO are restricted to two PNP complexes, where PNP = κ^3 -N-[2-P(ⁱPr)₂-4-Me-C₆H₃]₂²⁴ or κ^3 -N-[Si(Me)₂CH₂P(^tBu)₂]₂.²⁵ In the former system, the complex was isolated but not structurally characterized. In the latter case, the mono- and dicarbonyl Co species were proposed to be in an equilibrium that favors the monocarbonyl when under 1 atm of CO.²⁵ For a PNCNP case, Kirchner and co-workers calculated that the loss of CO from (PNCNP)Co(CO)₂ (PNCNP = κ^3 -C₆H₃-1,3-[N(Me)P(ⁱPr)₂]₂) is endergonic by 9.3 kcal mol⁻¹, and (PNCNP)Co(CO) is not observed experimentally.^{20,21} (PNCNP)Co(CO)₂ is slightly more electron rich than **2** (ν_{CO} 1906 and 1963 cm⁻¹ vs 1915 and 1969 cm⁻¹, respectively). This may explain why **1** can be prepared from **2**, but only by prolonged heating under dynamic vacuum. There are a few examples of (pincer)Co^I(CO) complexes that appear to be inert to the addition of a second CO ligand^{40–42} or (pincer)Co^I(CO)₂ complexes that do not lose a CO ligand under mild vacuum.^{19,24,43}

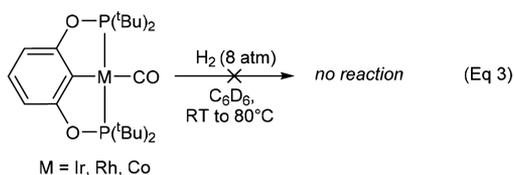
Following the formation of **2**, the reaction of (pincer)M(CO) (M = Ir, Rh) complexes with CO was investigated. No reaction was observed when benzene solutions of (^tBu₂PCP)Ir(CO), (^tBu₂POCOP)Ir(CO), (^tBu₂POCOP)Rh(CO), or (ⁱPr₂POCOP)Rh(CO) were pressurized with 8 atm of CO at either room temperature or 80 °C. In contrast, (ⁱPr₂POCOP)Ir(CO) and (ⁱPr₂PCP)Ir(CO) were observed to add 1 equiv of CO to form dicarbonyl complexes (Scheme 1). (ⁱPr₂POCOP)Ir(CO)₂ (**3**) and (ⁱPr₂PCP)Ir(CO)₂ (**4**) were found to be moderately stable and could be crystallized under CO. Immediate loss of CO to give (ⁱPr₂POCOP)Ir(CO) and

Scheme 1. Reaction of Rh and Ir Monocarbonyls with CO



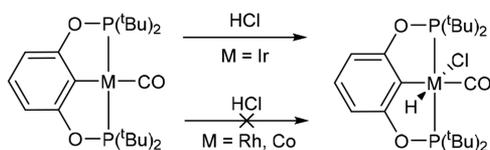
(^{iPr}PCP)Ir(CO) was observed when the solutions were degassed (see the Supporting Information for details). This differing reactivity among the three metals is apparently dictated by a subtle interplay of steric and electronic factors; the optimal orbital size of Co is enough to overcome the steric restraint imposed upon the metal by ^{tBu}POCOP. The differing reactivities of Ir versus Rh can also be rationalized by how electron rich the metal center is; the ν_{CO} value of (^{iPr}POCOP)-Ir(CO) is 1944 cm^{-1} ,³ whereas for (^{iPr}POCOP)Rh(CO) it is 1962 cm^{-1} .¹⁶ Several examples of (pincer)Ir(CO)₂ complexes have been reported.^{1,38,39,44,45}

Further Reactivity of (^{tBu}POCOP)Co(CO) (1). Though we had noted structural differences between ^{tBu}POCOP-supported group 9 monocarbonyl complexes, we were interested in investigating if the fundamental reactivity of these compounds was also distinct. The reaction of **1** with 8 atm of H₂ (at both room temperature and 80 °C) did not result in the formation of any hydride-containing Co species (eq 3), which is in line with observations made for Rh⁴⁶ and Ir,² both of which are inert to elevated pressures of hydrogen.



Previously, (^{tBu}POCOP)Ir(CO) has been found to react with [H(Et₂O)]Cl (HCl) to give (^{tBu}POCOP)Ir(H)(Cl)(CO),³ though the analogous reaction with Rh was shown not to proceed.¹⁴ Due to the similar steric constraints at the metal in these cases,^{18,26} it was proposed that the weaker Rh–H bond in comparison to that of Ir–H was the cause for this lack of reactivity.^{14,47} Since first-row M–H bonds are expected to be weaker than those of their second- and third-row congeners, we anticipated that **1** would be inert to HCl. The addition of HCl to an Et₂O solution of **1** did not result in a reaction, similar to previous observations on the Rh system (Scheme 2).

Scheme 2. Differing Reactivities of (^{tBu}POCOP)Ir(CO)³ and (^{tBu}POCOP)M(CO) (M = Rh,¹⁴ Co) with HCl



Ir^I and Rh^I ^{tBu}POCOP monocarbonyl complexes also differ in their reactivity with acids containing noncoordinating counterions. While Ir is protonated at the metal by [H(Et₂O)]-BF₄ to give [(^{tBu}POCOP)Ir(H)(CO)]BF₄,³ the Rh complex is protonated at the carbon of the ligand aryl backbone to give an agostic complex, [(^{tBu}PO^HCOP)Rh(CO)]BF₄.¹⁴ While complex **1** reacts immediately with [H(Et₂O)]BF₄, the product has poor solubility in most solvents and decomposes rapidly in any solvent that it is soluble in, hampering characterization.

Reactivity of (^{tBu}POCOP)Co^{II} Complexes. Compound **2** could not be formed via the direct addition of CO to (^{tBu}POCOP)Co(I), as had been previously demonstrated by Peters⁴⁸ for a tetrahedral Co^{II} complex, κ^3 -[PhB(CH₂P-(^{iPr})₂)₃]Co(I), which formed a Co^I dicarbonyl upon exposure

to CO. This shows that (^{tBu}POCOP)Co(I) is not easily reduced, unlike the Peters system. Instead, upon addition of 1 atm of CO to a C₆D₆ solution of (^{tBu}POCOP)Co(I), a color change from yellow-green to dark green was noted and four new peaks in the paramagnetic region of the ¹H NMR spectrum were observed (between 13.82 and 0.02 ppm). Their relative integrations of 18:18:2:1 were suggestive of a five-coordinate Co species with inequivalent ^tBu groups above and below the P–Co–P plane. Crystallization under CO confirmed that the new compound was (^{tBu}POCOP)Co(I)(CO) (**5**) (Figure 3), where one molecule of CO has associated with the

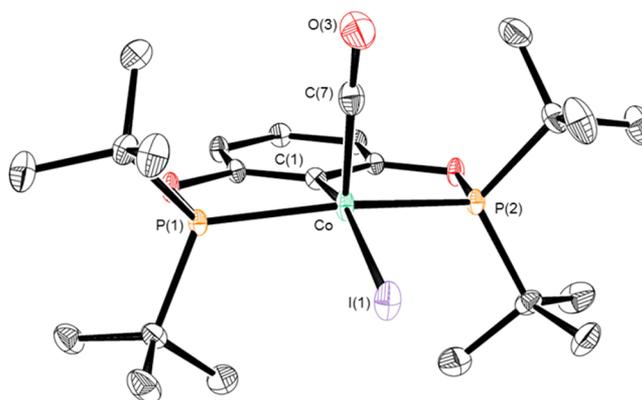
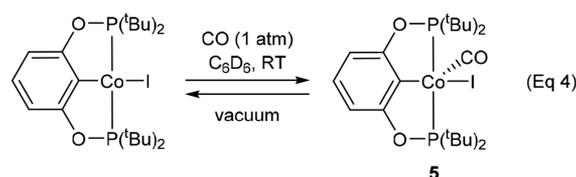
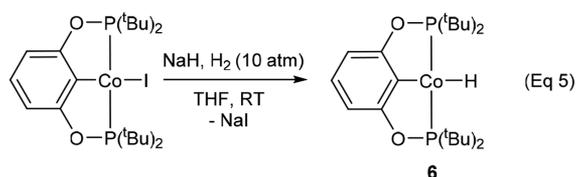


Figure 3. ORTEP³⁶ of complex **5** at 50% probability (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Co–C(1) 1.944(3), Co–P(1) 2.2646(8), Co–P(2) 2.2634(7), Co–C(7) 1.844(3), Co–O(3) 2.986(3), Co–I(1) 1.6199(5); P(1)–Co–P(2) 158.20(3), P(1)–Co–C(7) 97.70(9), P(2)–Co–C(7) 97.61(8), C(1)–Co–C(7) 106.80(11), C(1)–Co–I(1) 160.99(8), C(7)–Co–I(1) 92.21(9).

Co center in the axial position to form a slightly distorted square pyramidal structure ($\tau = 0.05$).³⁷ The Co atom is 0.319 Å above the plane formed by the equatorial atoms, a shorter distance than in **2**, consistent with a lower τ value (less deviation from an idealized structure). In contrast to the previously reported complex (PNCNP)Co(Cl)(CO) (PNCNP = κ^3 -C₆H₃-1,3-[N(Me)P(^{iPr})₂]₂),²¹ the CO ligand in complex **5** does not significantly deviate from linearity (Co–C–O is 177.4(3)° in **5** and 170.0(1)° in (PNCNP)Co(Cl)(CO)). An IR stretch at 1983 cm^{-1} was also observed, indicating diminished back-bonding to the CO ligand in comparison to complexes **1** or **2**, which is expected for Co^{II} versus Co^I. This was mirrored in the solid-state structure, where the Co–CO distances are much longer in **5** than in either **1** or **2**. Under vacuum, a benzene solution of complex **5** showed partial regeneration of (^{tBu}POCOP)Co(I) by ¹H NMR spectroscopy (eq 4).



To probe the addition of CO to a POCOP-supported Co^{II} complex with a ligand smaller than iodide, (^{tBu}POCOP)Co(H)⁴⁹ (**6**) was prepared by the reaction of (^{tBu}POCOP)Co(I) with NaH in THF under H₂ (eq 5). The ¹H NMR spectrum



contains three paramagnetic resonances between 8.57 and -15.2 ppm, and the solid-state structure was confirmed by X-ray crystallography (Figure 4). The bite angle of the ${}^t\text{BuPOCOP}$

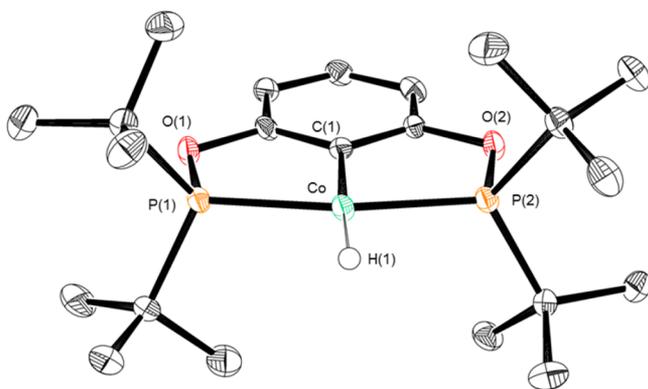
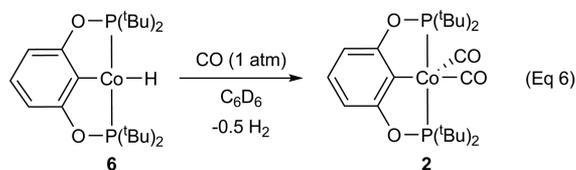


Figure 4. ORTEP³⁶ of complex **6** at 50% probability (hydrogen atoms, other than H1 which was freely located and refined, have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Co–C(1) 1.9294(19), Co–P(1) 2.1586(6), Co–P(2) 2.1651(6); P(1)–Co–P(2) 163.65(3).

ligand is $163.65(3)^\circ$, which is significantly larger than the analogous angles in **1**, **2**, and **5** and is presumably due to reduced steric clash between the ligand ${}^t\text{Bu}$ groups and the hydride ligand in comparison to either CO or I. The room-temperature addition of CO to a degassed C_6D_6 solution of **6** caused an instantaneous color change from red to green. Upon standing for 20 min, the solution turned red and ultimately brown. Formation of H_2 was observed by ${}^1\text{H}$ NMR spectroscopy. The final product was confirmed to be **2** by ${}^1\text{H}$ NMR spectroscopy (eq 6). As of yet, we do not have any evidence supporting a mechanism for the formation of **2**, though it is possible that a bimolecular pathway is operative.^{50–52}



CONCLUSION

We have prepared the first example of crystallographically characterized mono- and dicarbonyl Co complexes containing the same pincer ligand. This has also allowed direct comparison to the previously reported Ir and Rh complexes. In line with the lack of reactivity previously reported for $({}^t\text{BuPOCOP})\text{Ir}(\text{CO})$ and $({}^t\text{BuPOCOP})\text{Rh}(\text{CO})$, $({}^t\text{BuPOCOP})\text{Co}(\text{CO})$ does not react with elevated pressures of H_2 , at either ambient or elevated temperatures. As with its Rh counterpart, $({}^t\text{BuPOCOP})\text{Co}(\text{CO})$ is also found to be inert toward HCl. $({}^t\text{BuPOCOP})\text{Co}(\text{CO})$ is the only compound in the triad to

react with CO to form $({}^t\text{BuPOCOP})\text{M}(\text{CO})_2$, though using a ligand with a reduced steric profile allowed $(\text{pincer})\text{Ir}(\text{CO})_2$ (pincer = ${}^i\text{PrPOCOP}$ or ${}^i\text{PrPCP}$) complexes to be observed and characterized. Even with ${}^i\text{Pr}$ substituents on the POCOP ligand, the Rh complex does not react with CO, which we attribute to an electronic effect. The reactivity of $({}^t\text{BuPOCOP})\text{Co}^{\text{II}}$ complexes with CO was also investigated. $({}^t\text{BuPOCOP})\text{Co}(\text{I})$ was found to form $({}^t\text{BuPOCOP})\text{Co}(\text{I})(\text{CO})$, which was stable under a CO atmosphere, whereas $({}^t\text{BuPOCOP})\text{Co}(\text{H})$ ultimately eliminates H_2 to yield $({}^t\text{BuPOCOP})\text{Co}(\text{CO})_2$.

EXPERIMENTAL SECTION

General Methods. All experiments and manipulations were performed using standard Schlenk techniques under an argon atmosphere or in an argon- or nitrogen-filled glovebox. Glassware and Celite were dried in an oven maintained at 140°C for at least 24 h. Deuterated solvents were dried over calcium hydride or molecular sieves (CD_2Cl_2 , THF- d_6 , and C_6D_6) or sodium/benzophenone (toluene- d_8) and vacuum-transferred prior to use. Protio solvents were passed through columns of activated alumina and molecular sieves. All other reagents were used as received. ${}^1\text{H}$ NMR spectra were referenced to residual protio solvents: dichloromethane (5.32 ppm), THF (1.79 ppm), toluene (2.09 ppm), and benzene (7.16 ppm). ${}^{13}\text{C}$ NMR shifts were referenced to solvent signals: benzene (128 ppm), dichloromethane (54.0 ppm), and THF (26.2 ppm). ${}^{31}\text{P}$ NMR shifts were referenced to an 85% H_3PO_4 external standard (0 ppm). High-pressure NMR experiments were performed using a pressurization apparatus designed in our laboratory.² Solution magnetic susceptibilities were determined by ${}^1\text{H}$ NMR spectroscopy using the Evans method.⁵³ Infrared spectra were recorded on a Bruker Tensor 27 FTIR instrument. NMR spectra were recorded on a Bruker AV-700, AV-500, DRX-500, or AV-300 NMR instrument. X-ray data were collected at -173°C on a Bruker APEX II single-crystal X-ray diffractometer, with Mo radiation. Elemental analysis was performed under air-free conditions at the CENTC facility at the University of Rochester (funded by NSF CHE-0650456) and at Atlantic Microlab, Norcross, GA. $({}^t\text{BuPOCOP})\text{Rh}(\text{CO})$,¹⁵ $({}^t\text{BuPOCOP})\text{Ir}(\text{CO})$,⁹ $({}^i\text{PrPOCOP})\text{Ir}(\text{CO})$,² $({}^i\text{PrPCP})\text{Ir}(\text{CO})$,² $({}^t\text{BuPCP})\text{Ir}(\text{CO})$,² $({}^t\text{BuPCP})\text{Ir}(\text{H})(\text{Cl})$,¹¹ $({}^t\text{BuPOCOP})\text{I}$,²³ and $({}^t\text{BuPOCOP})\text{Co}(\text{I})$ ²³ were prepared according to literature procedures.

X-ray Crystallography. Using Olex2,⁵⁴ the structure was solved with the XS⁵⁵ structure solution program using direct methods and refined with the XL⁵⁵ refinement package using least-squares minimization. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model, except for the Co–H in **6**, which was located in the electron density map and freely refined. Details of the crystal and refinement data for **1–6** (CCDC 1554616, 1554617, 1555407, 1554618, 1554619, and 1554620, respectively) are given in the Supporting Information. Related structures for $({}^t\text{BuPOCOP})\text{Co}(\text{BH}_4)$ and $({}^t\text{BuPOCOP}^{\text{O}})\text{Co}(\text{CO})_3$ can be found in the Cambridge Structural Database under CCDC 1555411 and 1555413, respectively.

Synthesis and Characterization of Compounds. $({}^t\text{BuPOCOP})\text{Co}(\text{CO})$ (**1**). $({}^t\text{BuPOCOP})\text{Co}(\text{I})$ (100 mg, 0.173 mmol) was charged in a 50 mL Schlenk flask with a stir bar and dissolved in THF (15 mL) to yield a yellow-green solution. Na/Hg (40 mg/6.58 g, 0.6 wt %) was prepared in a separate 50 mL Schlenk flask. The THF solution of $({}^t\text{BuPOCOP})\text{Co}(\text{I})$ was added via cannula under Ar, causing the solution to turn brick red. CO (3.9 mL, 0.17 mmol) was bubbled through the solution using a gastight syringe and a long needle. The vessel was sealed, and the contents were stirred for 1.5 h, yielding a brown solution which was separated from the remaining mercury by filtration. The solvent was removed in vacuo to yield a brown solid. The residue was dissolved in pentane (20 mL) and filtered through Celite. Removal of the solvent gave a brown solid, which was heated under vacuum at 70°C for 15 h to remove CO from trace $({}^t\text{BuPOCOP})\text{Co}(\text{CO})_2$. Yield: 60.8 mg (72%). X-ray diffraction quality

crystals of complex **1** were grown from a saturated pentane solution at $-30\text{ }^{\circ}\text{C}$.

^1H NMR (C_6D_6 , 300.0 MHz): δ 6.94 (1H, t, ArH, $^2J_{\text{HH}} = 7.9$ Hz), 6.74 (2H, d, ArH, $^2J_{\text{HH}} = 7.9$ Hz), 1.36 (36 H, vt, ^1Bu , $^5J_{\text{PH}} + ^3J_{\text{PH}} = 6.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.0 MHz): δ 228.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 175 MHz): δ 170.72 (vt, Ar, $^2J_{\text{PC}} + ^4J_{\text{PC}} = 10.6$ Hz), 131.02 (s, Ar), 104.24 (vt, Ar, $^3J_{\text{PC}} + ^5J_{\text{PC}} = 6.4$ Hz), 40.07 (vt, ^1Bu , $^1J_{\text{PC}} + ^3J_{\text{PC}} = 8.6$ Hz), 28.73 (vt, ^1Bu , $^2J_{\text{PC}} + ^4J_{\text{PC}} = 3.2$ Hz), Ir-CO and Ir-C_{ipso} not observed. IR (CH_2Cl_2 , cm^{-1}): 1899. Anal. Found (calcd for $\text{C}_{23}\text{H}_{39}\text{CoO}_3\text{P}_2$): C, 57.2 (57.0); H, 7.9 (8.1); N, 0.2 (0.0).

$(^{\text{tBu}}\text{POCOP})\text{Co}(\text{CO})_2$ (**2**). $(^{\text{tBu}}\text{POCOP})\text{Co}(\text{CO})$ (**1**; 5.0 mg, 0.010 mmol) was dissolved in C_6D_6 and placed in a J. Young NMR tube. The dark brown solution was subjected to three freeze–pump–thaw cycles and placed under 1 atm of CO, resulting in an immediate color change to light brown. NMR spectroscopy revealed quantitative conversion to $(^{\text{tBu}}\text{POCOP})\text{Co}(\text{CO})_2$ (**2**). Removal of the CO atmosphere resulted in partial conversion back to **1**. X-ray diffraction quality crystals were grown from a saturated pentane solution of **2** under an atmosphere of CO.

^1H NMR (C_6D_6 , 300.0 MHz): δ 6.81 (1H, t, ArH, $^2J_{\text{HH}} = 7.68$ Hz), 6.70 (2H, d, ArH, $^2J_{\text{HH}} = 7.63$ Hz), 1.32 (36 H, vt, ^1Bu , $^5J_{\text{PH}} + ^3J_{\text{PH}} = 6.82$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.0 MHz): δ 240.5 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 175 MHz): δ 208.42 (m, Co-CO), 166.36 (vt, Ar, $^2J_{\text{PC}} + ^4J_{\text{PC}} = 7.7$ Hz), 125.19 (s, Ar), 104.70 (vt, Ar, $^3J_{\text{PC}} + ^5J_{\text{PC}} = 5.3$ Hz), 42.22 (vt, ^1Bu , $^1J_{\text{PC}} + ^3J_{\text{PC}} = 7.8$ Hz), 28.56 (vt, ^1Bu , $^2J_{\text{PC}} + ^4J_{\text{PC}} = 2.3$ Hz), Ir-C_{ipso} not observed. IR (CH_2Cl_2 , cm^{-1}): 1915, 1969. Anal. Found (calcd for $\text{C}_{24}\text{H}_{39}\text{CoO}_4\text{P}_2$): C, 55.5 (56.3); H, 7.7 (7.7); N, 0.0 (0.0).

$(^{\text{iPr}}\text{POCOP})\text{Ir}(\text{CO})_2$ (**3**). $(^{\text{iPr}}\text{POCOP})\text{Ir}(\text{CO})$ (5 mg, 0.009 mmol) was dissolved in C_6D_6 and placed in a J. Young NMR tube. The yellow solution was subjected to three freeze–pump–thaw cycles and placed under 1 atm of CO, resulting in an immediate lightening of the solution color. NMR spectroscopy revealed quantitative conversion to $(^{\text{iPr}}\text{POCOP})\text{Ir}(\text{CO})_2$ (**3**). Removal of the CO atmosphere resulted in conversion back to $(^{\text{iPr}}\text{POCOP})\text{Ir}(\text{CO})$. X-ray diffraction quality crystals were grown from a saturated pentane solution of **3** under an atmosphere of CO at $-20\text{ }^{\circ}\text{C}$.

^1H NMR (C_6D_6 , 300.1 MHz): δ 6.93 (3H, m, ArH), 2.23 (4H, sept of vt, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}} = 7.0$ Hz, $^2J_{\text{PH}} + ^4J_{\text{PH}} = 2.1$ Hz), 1.17 (24 H, m, $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.0 MHz): δ 172.6 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz): δ 125.51 (s, Ar), 104.24 (vt, Ar, $^3J_{\text{PC}} + ^5J_{\text{PC}} = 6.6$ Hz), 32.39 (vt, $\text{CH}(\text{CH}_3)_2$, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 18.9$ Hz), 16.94 (vt, $\text{CH}(\text{CH}_3)_2$, $^2J_{\text{PC}} + ^4J_{\text{PC}} = 2.6$ Hz), 16.59 (s, $\text{CH}(\text{CH}_3)_2$), Ir-CO, Ir-C_{ipso} and Ir-C_{ortho} not observed.

$(^{\text{iPr}}\text{PCP})\text{Ir}(\text{CO})_2$ (**4**). $(^{\text{iPr}}\text{PCP})\text{Ir}(\text{CO})$ (5 mg, 0.009 mmol) was dissolved in C_6D_6 and placed in a J. Young NMR tube. The orange solution was subjected to three freeze–pump–thaw cycles and placed under 1 atm of CO, resulting in an immediate lightening of the solution color. NMR spectroscopy revealed quantitative conversion to $(^{\text{iPr}}\text{PCP})\text{Ir}(\text{CO})_2$ (**4**). Removal of the CO atmosphere resulted in conversion back to $(^{\text{iPr}}\text{PCP})\text{Ir}(\text{CO})$. X-ray diffraction quality crystals were grown from a saturated pentane solution of **4** under an atmosphere of CO at room temperature.

^1H NMR (C_6D_6 , 300.1 MHz): δ 7.73 (2H, br s, ArH), 7.16 (overlap with solvent, ArH), 3.27 (4H, vt, ArCH_2PR_2 , $^2J_{\text{PH}} + ^4J_{\text{PH}} = 4.1$ Hz), 1.95 (4H, m, $\text{CH}(\text{CH}_3)_2$), 1.21 (12H, app q, $\text{CH}(\text{CH}_3)_2$), 1.08 (12 H, app q, $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.0 MHz): δ 58.50 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz): δ 184.03 (s, Ir-CO), 148.19 (s, Ar), 122.97 (s, Ar), 120.76 (t, Ar, $^2J_{\text{PC}} = 8.5$ Hz), 42.36 (vt, ArCH_2PR_2 , $^1J_{\text{PC}} + ^3J_{\text{PC}} = 16.8$ Hz), 27.83 (vt, $\text{CH}(\text{CH}_3)_2$, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 12.7$ Hz), 19.16 (s, $\text{CH}(\text{CH}_3)_2$), 18.63 (s, $\text{CH}(\text{CH}_3)_2$).

$(^{\text{tBu}}\text{POCOP})\text{Co}(\text{I})(\text{CO})$ (**5**). $(^{\text{tBu}}\text{POCOP})\text{Co}(\text{I})$ (5 mg, 0.009 mmol) was dissolved in C_6D_6 and placed in a J. Young NMR tube. The yellow-green solution was subjected to three freeze–pump–thaw cycles and placed under 1 atm of CO, resulting in an immediate color change to forest green. NMR spectroscopy revealed quantitative conversion to $(^{\text{tBu}}\text{POCOP})\text{Co}(\text{I})(\text{CO})$ (**5**). Removal of the CO atmosphere resulted in partial conversion back to $(^{\text{tBu}}\text{POCOP})\text{Co}(\text{I})$. X-ray diffraction quality crystals were grown from a saturated benzene solution of **5** under an atmosphere of CO.

^1H NMR (C_6D_6 , 300.0 MHz): δ 13.8 (18H, br s, ^1Bu), 6.36 (2H, br s, ArH), 1.68 (1H, br s, ArH), 0.02 (18H, br s, ^1Bu). IR (CH_2Cl_2 , cm^{-1}): 1983.

$(^{\text{tBu}}\text{POCOP})\text{Co}(\text{H})$ (**6**). $(^{\text{tBu}}\text{POCOP})\text{Co}(\text{I})$ (60 mg, 0.10 mmol) was placed in a Teflon-lined, stainless steel Parr reactor with NaH (47 mg, 2.07 mmol), THF (5 mL), and a stir bar. The yellow-green solution/suspension was sealed in the reactor, in a nitrogen-filled glovebox, flushed with H_2 (five times), and pressurized with 10 atm of H_2 . The vessel was stirred for 4 days at room temperature, after which the pressure was released and the reactor transferred to a glovebox. The resulting red solid was dissolved in benzene (3 mL) and filtered and the solvent removed under reduced pressure to give a red solid. Yield: 43 mg (94%). X-ray diffraction quality crystals were grown from a saturated THF solution of **6** at $-15\text{ }^{\circ}\text{C}$.

^1H NMR ($\text{THF}-d_8$, 500.0 MHz): δ 8.57 (36H, br s, ^1Bu), 5.10 (1H, br s, ArH), -15.2 (2H, br s, ArH). IR (KBr, cm^{-1}): 2026. Magnetic moment ($\text{THF}-d_8$, 296 K): $2.35\ \mu_{\text{B}}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00434.

Crystallographic data and ^1H , $^{13}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for **1–6**, as well as additional experimental procedures (PDF)

Accession Codes

CCDC 1554616–1554620 and 1555407 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for D.M.H.: heinekey@chem.washington.edu.

ORCID

Louise M. Guard: 0000-0002-5679-1900

Notes

The authors declare no competing financial interest.

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