Pincer-Supported Carbonyl Complexes of Cobalt(I)

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General Methods

All experiments and manipulations were performed using standard Schlenk techniques under an argon atmosphere or in an argon or nitrogen filled glove box. 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_8, 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}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}C NMR shifts were referenced to solvent signals: benzene (128 ppm), dichloromethane (54.0 ppm) and THF (26.2 ppm). ^{31}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}H NMR spectroscopy using the Evans' method.[53] Infrared spectra were recorded on a Bruker Tensor 27 FTIR instrument. NMR spectra were recorded on either a Bruker AV-700, AV-500, DRX-500, or AV-300 NMR instrument. X-ray data was collected at -173^{o}C on a Bruker APEX II single crystal X-ray diffractometer, 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, GA. (^{tBu}POCOP)Rh(CO),[15] (^{tBu}POCOP)Ir(CO),[9] (^{iPr}POCOP)Ir(CO),[2] (^{iPr}PCP)Ir(CO),[2] (^{tBu}PCP)Ir(CO),[2] (^{tBu}PCP)Ir(H)(Cl),[11] (^{tBu}POCOP)I,[23] and (^{tBu}POCOP)Co(I)[23] were prepared according to literature procedures.

X-ray Crystallography

Using Olex2,[54] the structure was solved with the XS[55] structure solution program using direct methods and refined with the XL[55] refinement package using least squares minimisation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model, except 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 (^{tBu}POCOP)Co(BH_4) and (^{tBu}POCOP$^{(O)}$)Co(CO)$_3$ and can be found in the Cambridge Structural Database under CCDC 1555411 and 1555413, respectively.

Synthesis and Characterization of Compounds

*(^{tBu}POCOP)Co(CO) (**1**)*

(^{tBu}POCOP)Co(I) (100 mg, 0.173 mmol) was charged to 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 (^{tBu}POCOP)Co(I) was added via canula under Ar, causing the solution to turn brick red. CO (3.9 mL, 0.17 mmol) was bubbled through the solution using a gas-tight syringe and a long needle. The vessel was sealed and stirred for 1.5 hours, 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 hours to remove CO from trace (^{tBu}POCOP)Co(CO)$_2$. Yield: 60.8 mg (72 %). X-ray diffraction quality crystals of complex **1** were grown from a saturated pentane solution at -30ºC.

^{1}H NMR (C_6D_6, 300.0 MHz): δ 6.94 (1H, t, Ar*H*, $^2J_{HH}$ = 7.9 Hz), 6.74 (2H, d, Ar*H*, $^2J_{HH}$ = 7.9 Hz), 1.36 (36 H, vt, ^{t}Bu, $^5J_{PH}$ + $^3J_{PH}$ = 6.8 Hz). ^{31}P{^{1}H} (C_6D_6, 121.0 MHz): δ 228.2 (s). ^{13}C{^{1}H} NMR (C_6D_6, 175 MHz): δ 170.72 (vt, Ar, $^2J_{PC}$ + $^4J_{PC}$ = 10.6 Hz), 131.02 (s, Ar), 104.24 (vt, Ar, $^3J_{PC}$ + $^5J_{PC}$ = 6.4 Hz), 40.07 (vt, ^{t}Bu, $^1J_{PC}$ + $^3J_{PC}$ = 8.6 Hz), 28.73 (vt, ^{t}Bu, $^2J_{PC}$ + $^4J_{PC}$ = 3.2 Hz) Ir-*C*O and Ir-C_{ipso} not observed. IR (CH_2Cl_2, cm^{-1}): 1899. Anal. found (calcd for $C_{23}H_{39}CoO_3P_2$): C 57.2 (57.0), H 7.9 (8.1), N 0.2 (0.0) %.

*(^{tBu}POCOP)Co(CO)$_2$ (**2**)*

(^{tBu}POCOP)Co(CO) (**1**) (5.0 mg, 0.010 mmol) was dissolved in C_6D_6 and added to a J. Young NMR tube. The dark brown solution was subjected to three freeze-pump-thaw cycles and placed under 1 atm CO, resulting in an immediate color change to light brown. NMR spectroscopy revealed quantitative conversion to (^{tBu}POCOP)Co(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.

^{1}H NMR (C_6D_6, 300.0 MHz): δ 6.81 (1H, t, Ar*H*, $^2J_{HH}$ = 7.68 Hz), 6.70 (2H, d, Ar*H*, $^2J_{HH}$ = 7.63 Hz), 1.32 (36 H, vt, ^{t}Bu, $^5J_{PH}$ + $^3J_{PH}$ = 6.82). ^{31}P{^{1}H} (C_6D_6, 121.0 MHz): δ 240.5 (s). ^{13}C{^{1}H} NMR (C_6D_6, 175 MHz): δ 208.42 (m, Co-CO), 166.36 (vt, Ar, $^2J_{PC}$ + $^4J_{PC}$ = 7.7 Hz), 125.19 (s,

Ar), 104.70 (vt, Ar, $^{3}J_{PC} + {}^{5}J_{PC}$ = 5.3 Hz), 42.22 (vt, ^{t}Bu, $^{1}J_{PC} + {}^{3}J_{PC}$ = 7.8 Hz), 28.56 (vt, ^{t}Bu, $^{2}J_{PC} + {}^{4}J_{PC}$ = 2.3 Hz) Ir-C_{ipso} not observed. IR (CH_2Cl_2, cm^{-1}): 1915, 1969. Anal. found (calcd for $C_{24}H_{39}CoO_4P_2$): C 55.5 (56.3), H 7.7 (7.7), N 0.0 (0.0) %.

*(^{iPr}POCOP)Ir(CO)$_2$ (**3**)*

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

^{1}H NMR (C_6D_6, 300.1 MHz): δ 6.93 (3H, m, Ar*H*), 2.23 (4H, sept of vt, C*H*$(CH_3)_2$, $3J_{HH}$ = 7.0 Hz, $^{2}J_{PH} + {}^{4}J_{PH}$ = 2.1 Hz), 1.17 (24 H, m, CH(C*H*$_3$)$_2$. ^{31}P{^{1}H} (C_6D_6, 121.0 MHz): δ 172.6 (s). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz): δ 125.51 (s, Ar), 104.24 (vt, Ar, $^{3}J_{PC} + {}^{5}J_{PC}$ = 6.6 Hz), 32.39 (vt, *C*H$(CH_3)_2$, $^{1}J_{PC} + {}^{3}J_{PC}$ = 18.9 Hz), 16.94 (vt, CH(*C*H$_3$)$_2$, $^{2}J_{PC} + {}^{4}J_{PC}$ = 2.6 Hz), 16.59 (s, CH(*C*H$_3$)$_2$). Ir-*C*O, Ir-C_{ipso} and Ir-C_{ortho} not observed.

*(^{iPr}PCP)Ir(CO)$_2$ (**4**)*

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

^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.73 (2H, br s, Ar*H*), 7.16 (overlap with solvent, Ar*H*), 3.27 (4H, vt, ArC*H*$_2$PR$_2$, $^{2}J_{PH} + {}^{4}J_{PH}$ = 4.1 Hz), 1.95 (4H, m, C*H*$(CH_3)_2$), 1.21 (12H, app q, CH(C*H*$_3$)$_2$), 1.08 (12 H, app q, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} (C_6D_6, 121.0 MHz): δ 58.50 (s). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz): δ 184.03 (s, Ir-*C*O), 148.19 (s, Ar), 122.97 (s, Ar), 120.76 (t, Ar, $^{2}J_{PC}$ = 8.5 Hz), 42.36 (vt, Ar*C*H$_2$PR$_2$, $^{1}J_{PC} + {}^{3}J_{PC}$ = 16.8 Hz), 27.83 (vt, *C*H$(CH_3)_2$, $^{1}J_{PC} + {}^{3}J_{PC}$ = 12.7 Hz), 19.16 (s, CH(*C*H$_3$)$_2$), 18.63 (s, CH(*C*H$_3$)$_2$).

*(^{tBu}POCOP)Co(I)(CO) (**5**)*

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

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

*(^{tBu}POCOP)Co(H) (**6**)*

(^{tBu}POCOP)Co(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 (5 times) and pressurized with 10 atm H_2. The vessel was stirred for four days at room temperature, after which the pressure was released and the reactor transferred to a glovebox. The red solution was filtered and the solvent removed *in vacuo.* The resulting red solid was dissolved in benzene (3 mL), 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°C.

^{1}H NMR (THF-d_8, 500.0 MHz): δ 8.57 (36H, br s, ^{t}Bu), 5.10 (1H, br s, Ar*H*), -15.2 (2H, br s, Ar*H*). IR (KBr, cm^{-1}): 2026. Magnetic moment (THF-d_8, 296 K): 2.35 μ_B.

NMR Spectra

*(^{tBu}POCOP)Co(CO) (**1**)*

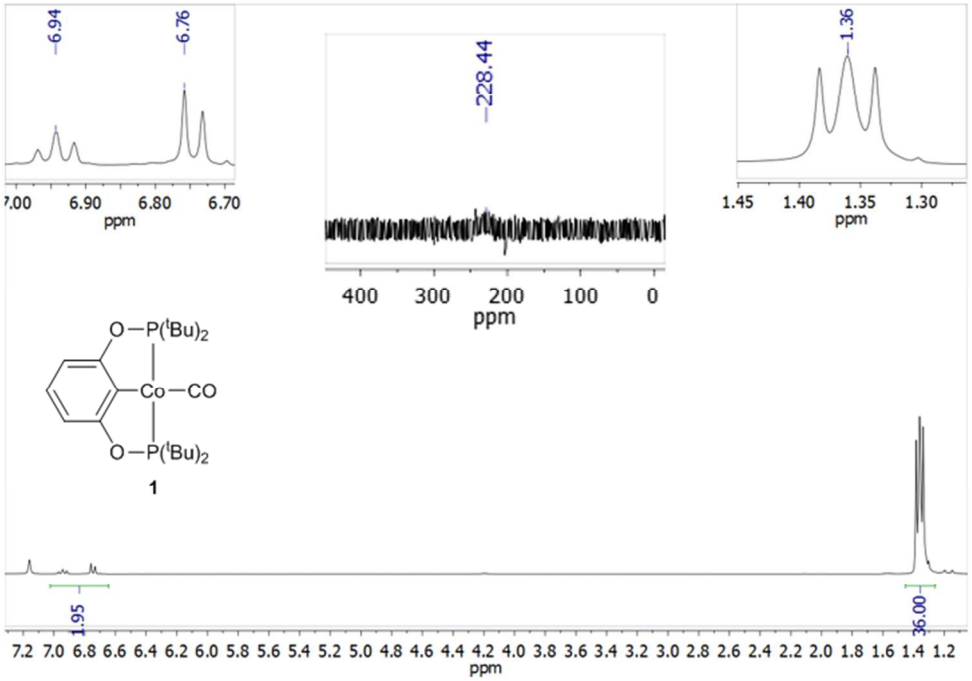
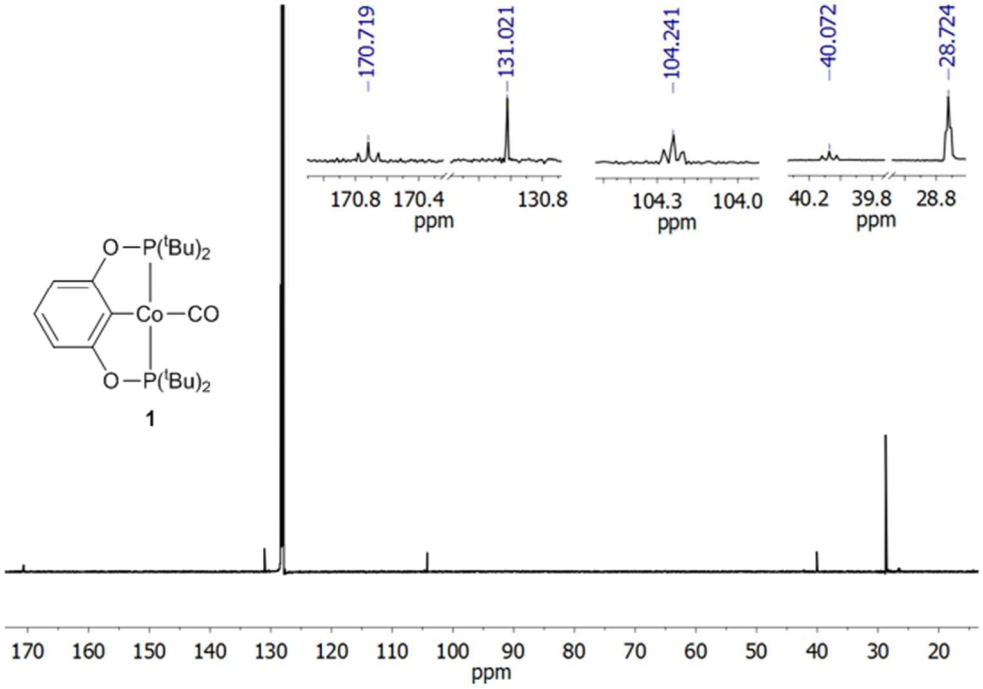


Figure S1: ^{1}H NMR spectrum (C_6D_6, 300 MHz) and $^{31}P\{^{1}H\}$ spectrum (C_6D_6, 121 MHz) (inset) of



(^{tBu}POCOP)Co(CO) (**1**).

Figure S2: $^{13}C\{^{1}H\}$ spectrum (C_6D_6, 175 MHz) (^{tBu}POCOP)Co(CO) (**1**).

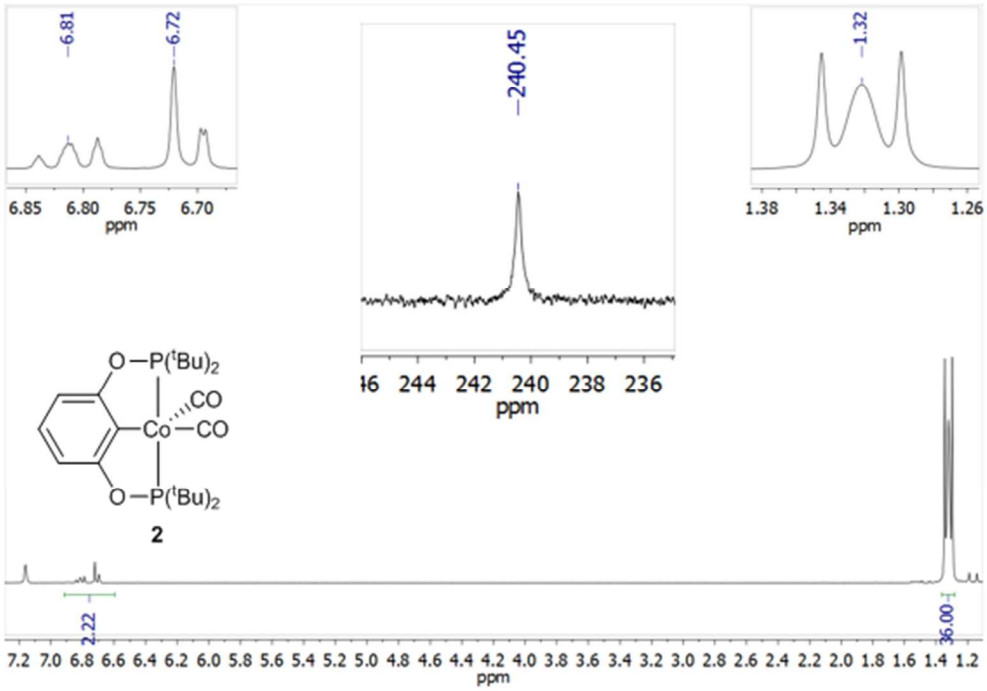


Figure S3: ^{1}H NMR spectrum (C_6D_6, 300 MHz) and $^{31}P\{^{1}H\}$ spectrum (C_6D_6, 121 MHz) (inset) of (^{tBu}POCOP)Co(CO)$_2$ (**2**).

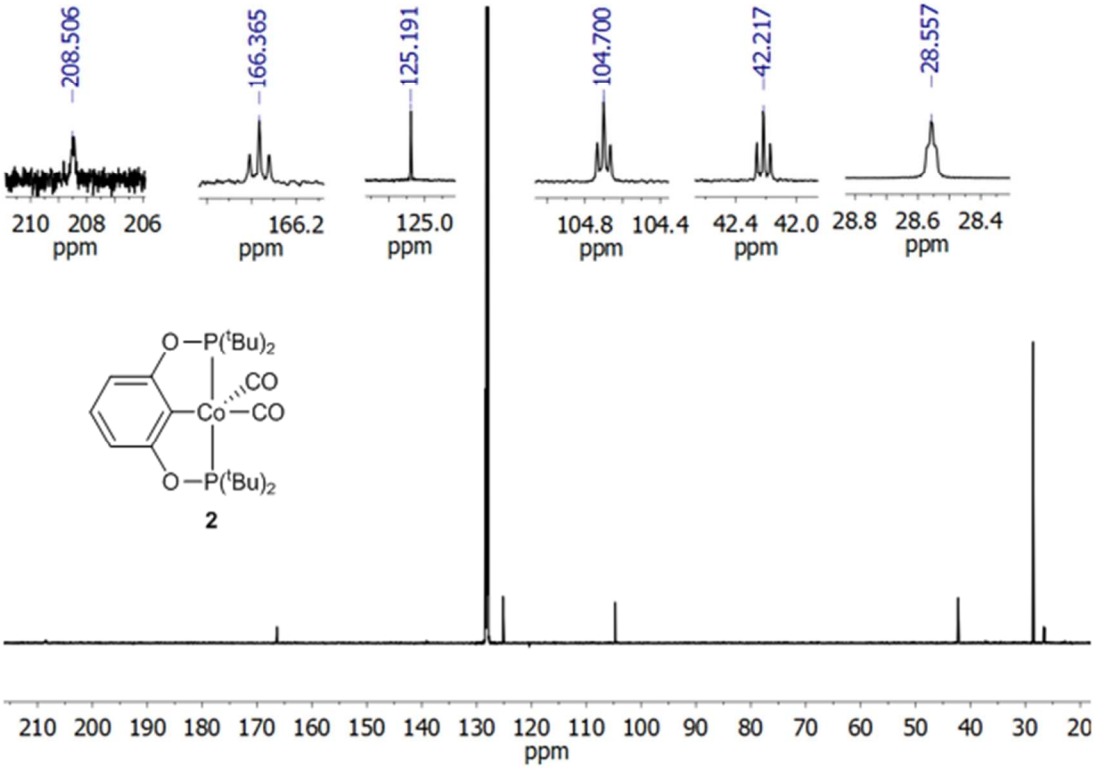


Figure S4: $^{13}C\{^{1}H\}$ spectrum (C_6D_6, 176 MHz) (^{tBu}POCOP)Co(CO)$_2$ (**2**).

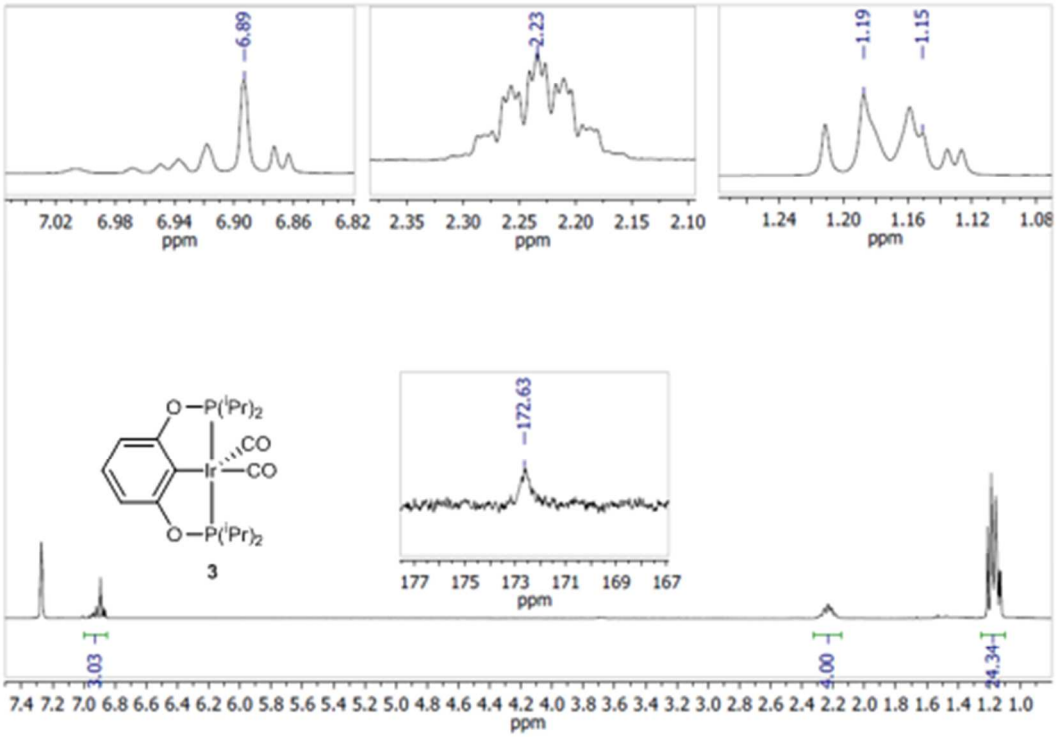
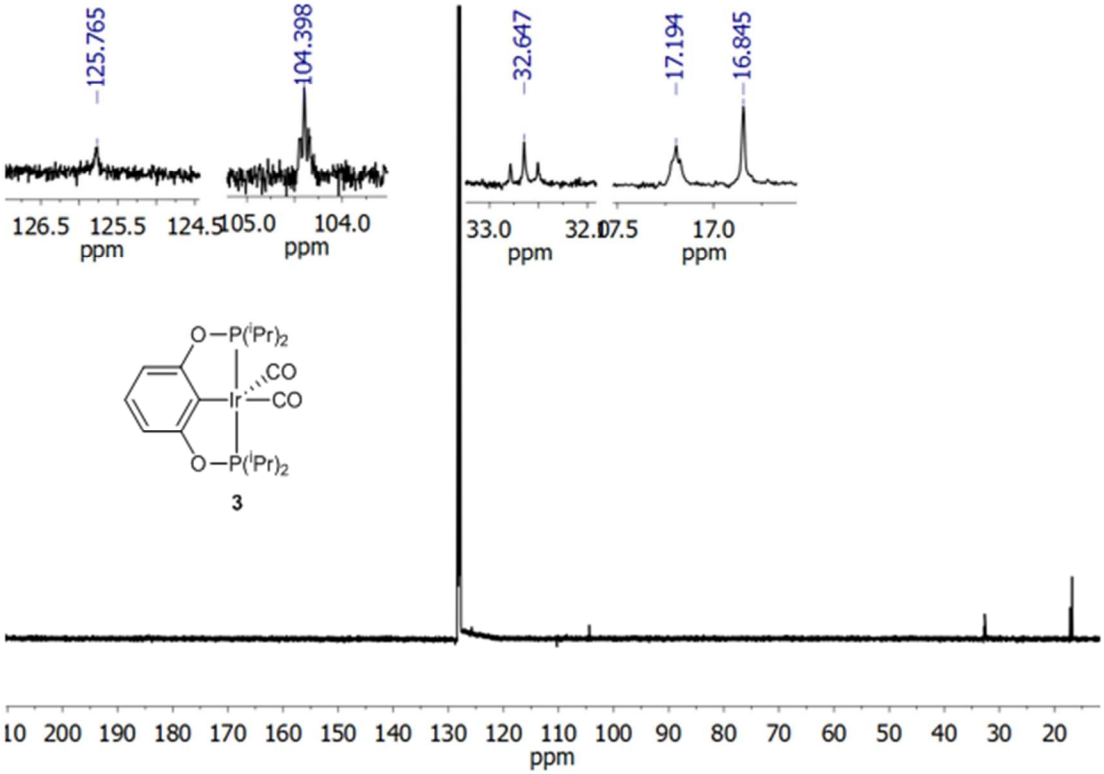


Figure S5: ^{1}H NMR spectrum (C_6D_6, 300 MHz) and $^{31}P\{^{1}H\}$ spectrum (C_6D_6, 121 MHz) (inset)



of (^{tBu}POCOP)Ir(CO)$_2$ (**3**).

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 126 MHz) of (^{tBu}POCOP)Ir(CO)$_2$ (**3**).

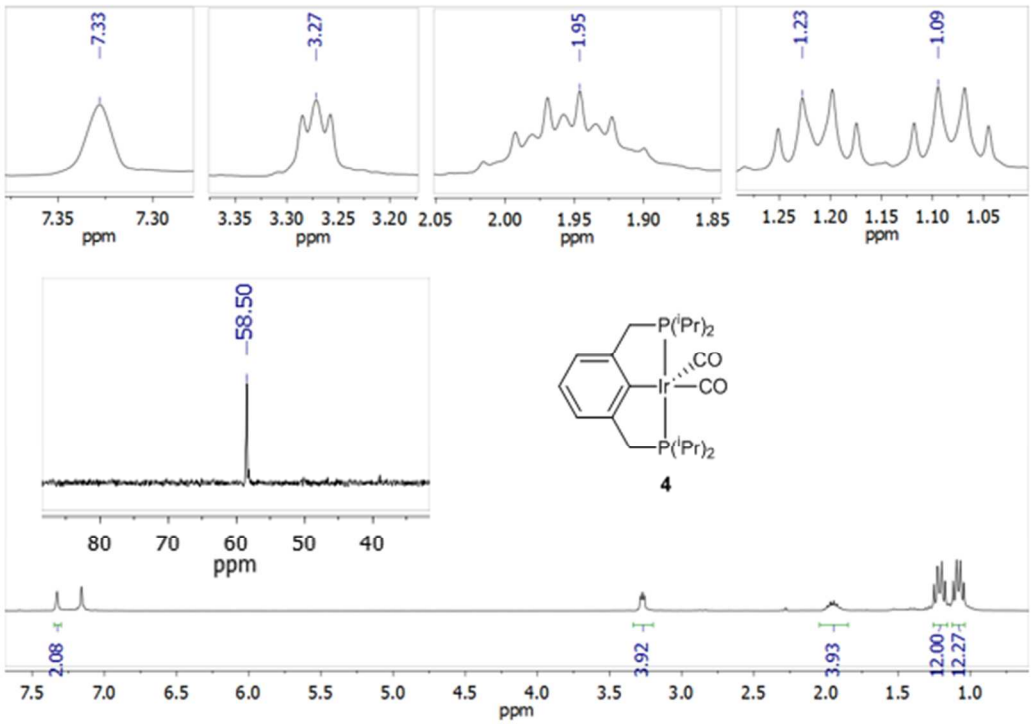


Figure S7: ^{1}H NMR spectrum (C_6D_6, 300 MHz) and $^{31}P\{^{1}H\}$ spectrum (C_6D_6, 121 MHz) (inset) of (^{tBu}PCP)Ir(CO)$_2$ (**4**).

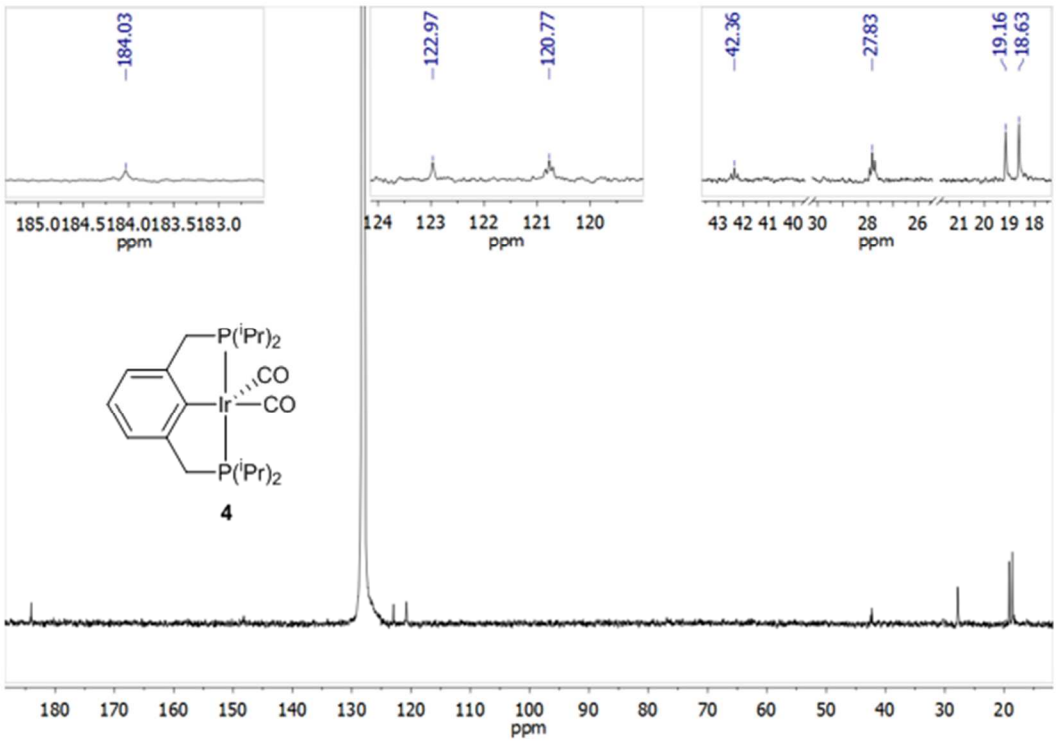
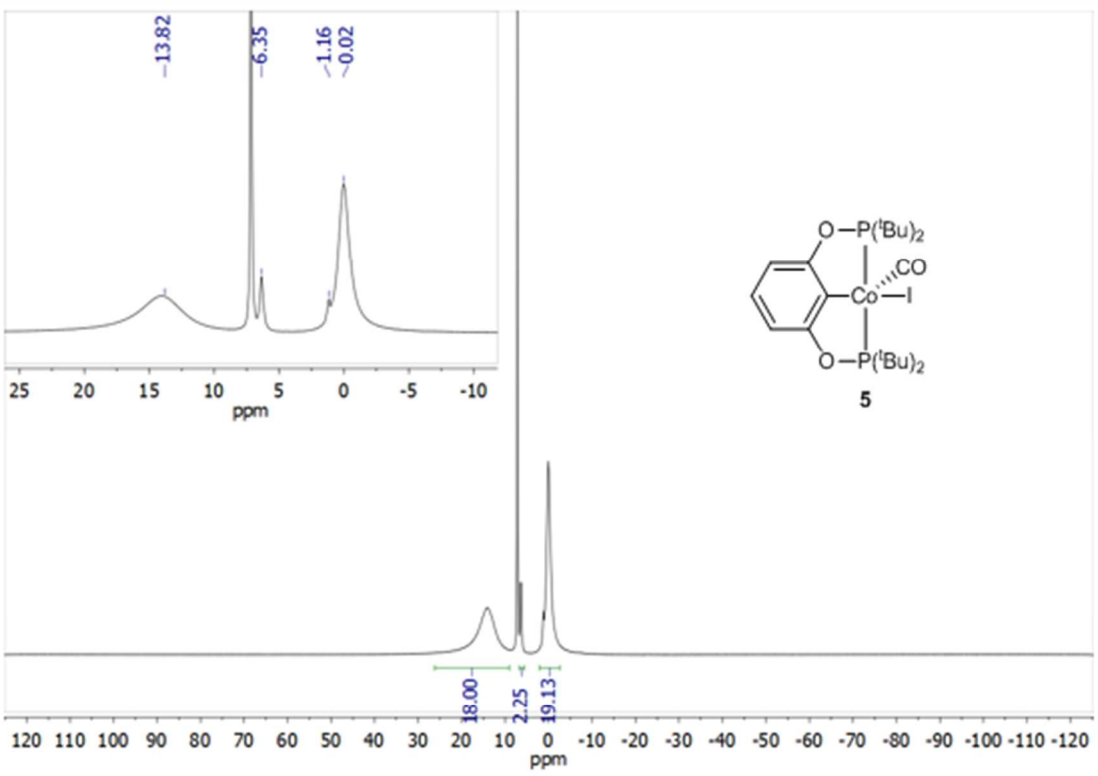


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 126 MHz) of (^{tBu}PCP)Ir(CO)$_2$ (4).



v

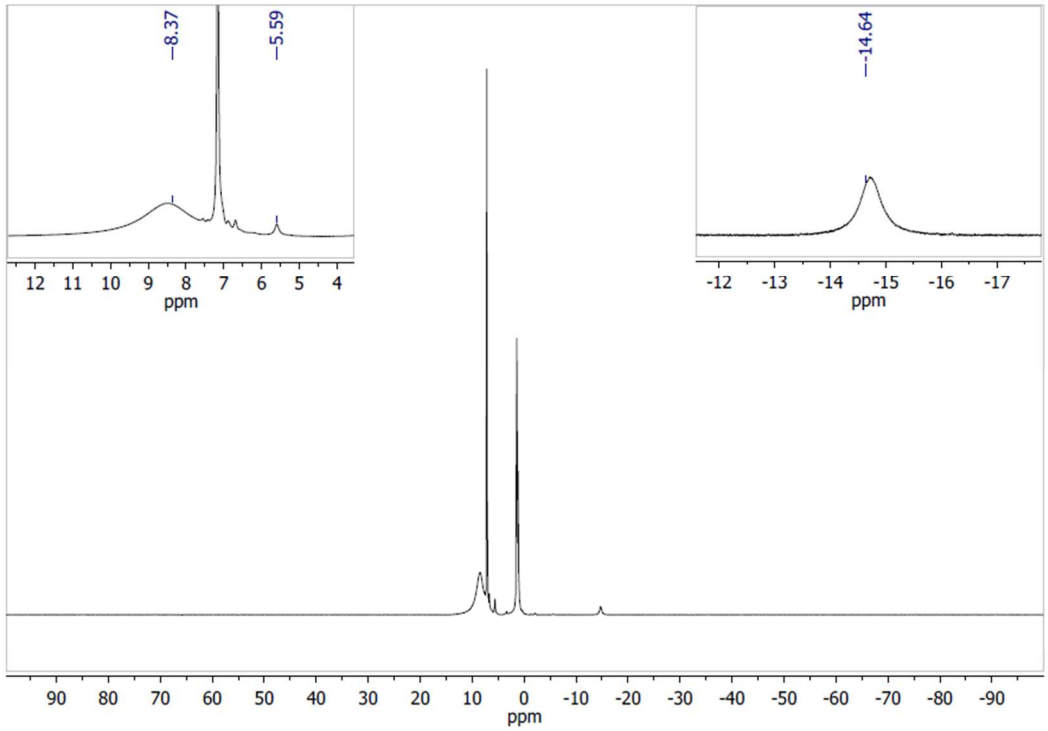


Figure S9: ^{1}H NMR spectrum (C_6D_6, 300 MHz) of (^{tBu}POCOP)Co(I)(CO) (**5**).

Figure S10: ^{1}H NMR spectrum (C_6D_6, 300 MHz) of (^{tBu}POCOP)Co(H) (**6**).

Experimental Details

*Reaction of (^{tBu}POCOP)Co(CO) (**1**) with H_2*

(^{tBu}POCOP)Co(CO) (**1**) (5 mg, 0.010 mmol) was dissolved in C_6D_6 (200 μL) and added to a 5 mm thick-walled NMR tube fitted with a Teflon valve. The brown solution was subjected to three freeze-pump-thaw cycles and pressurized with 8 atm H_2. No reaction was observed by ^{1}H or ^{31}P NMR spectroscopy after 4 days.

Reaction of (^{tBu}POCOP)Ir(CO) with CO

(^{tBu}POCOP)Ir(CO) (5.0 mg, 0.008 mmol) was dissolved in C_6D_6 and added to a J. Young NMR tube. The yellow solution was subjected to three freeze-pump-thaw cycles and pressurized with 8 atm CO. No color change or reaction was observed by ^{1}H and ^{31}P NMR spectroscopy. Similar lack of reactivity were noted when the reaction mixture was heated at 80°C for 3 days.

Reaction of (^{tBu}PCP)Ir(CO) with CO

(^{tBu}PCP)Ir(CO) (5.5 mg, 0.009 mmol) was dissolved in C_6D_6 and added to a J. Young NMR tube. The yellow solution was subjected to three freeze-pump-thaw cycles and pressurized with 8 atm CO. No color change or reaction was observed by ^{1}H and ^{31}P NMR spectroscopy. Similar lack of reactivity were noted when the reaction mixture was heated at 80°C for 3 days.

Reaction of (^{tBu}POCOP)Rh(CO) with CO

(^{tBu}POCOP)Rh(CO) (5.0 mg, 0.008 mmol) was dissolved in C_6D_6 and added to a J. Young NMR tube. The yellow solution was subjected to three freeze-pump-thaw cycles and pressurized with 8 atm CO. No color change or reaction was observed by ^{1}H and ^{31}P NMR spectroscopy. Similar lack of reactivity were noted when the reaction mixture was heated at 80°C for 3 days.

Reaction of (^{iPr}POCOP)Rh(CO) with CO

(^{iPr}POCOP)Rh(CO) (4.7 mg, 0.009 mmol) was dissolved in C_6D_6 and added to a J. Young NMR tube. The yellow solution was subjected to three freeze-pump-thaw cycles and pressurized with 1 atm CO. No color change or reaction was observed by ^{1}H and ^{31}P NMR spectroscopy. Similar lack of reactivity were noted when the reaction mixture was heated at 80°C for 3 days.

Reaction of (^{tBu}POCOP)Rh(CO) with H_2

(^{tBu}POCOP)Rh(CO) (5.6 mg, 0.01 mmol) was dissolved in C_6D_6 (200 μL) and added to a 5 mm thick-walled NMR tube fitted with a Teflon valve. The yellow solution was subjected to three freeze-pump-thaw cycles and pressurized with 8 atm H_2. No reaction was observed by ^{1}H or ^{31}P NMR spectroscopy after 2 days at room temperature or 3 days at 80ºC.

*Reaction of (^{tBu}POCOP)Co(CO) (**1**) with [H(Et$_2$O)]Cl*

(^{tBu}POCOP)Co(CO) (**1**) (9.8 mg, 0.02 mmol) was dissolved in diethyl ether (2 mL) in a 5 mL Schlenk flask. [H(Et$_2$O)]Cl (HCl) (10 μL, 2 M in diethyl ether, 0.02 mmol) was added to the brown solution using a gastight syringe. No color change was observed. No evidence of reaction or formation of hydride-containing species was noted by either ^{1}H or ^{31}P NMR spectroscopy.

*Reaction of (^{tBu}POCOP)Co(CO) (**1**) with [H(Et$_2$O)]BF$_4$*

(^{tBu}POCOP)Co(CO) (**1**) (11 mg, 0.023 mmol) was dissolved in 1,4-dichlorobenzene and C_6D_6 (4:1 mixture, 400 μL:100 μL) to give a brown solution. $H(Et_2O)BF_4$ (3.1 μL, 0.023 mmol) was added by micropipette causing a precipitate to form. The supernatant showed no evidence of a new product (by either ^{1}H and ^{31}P NMR spectroscopy) and the solid was either insoluble (Et_2O, C_6D_6, C_6H_5F, tol-d_8) or unstable (CD_2Cl_2).

X-ray Crystallography

Using Olex2,[7] the structure was solved with the XS[8] structure solution program using direct methods and refined with the XL[8] refinement package using least squares minimisation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model, except the Co-H in **6**, which was located in the electron density map and freely refined. Related structures for (^{tBu}POCOP)Co(BH_4) and (^{tBu}POCOP$^{(O)}$)Co$(CO)_3$ and can be found in the Cambridge Structural Database under CCDC 1555411 and 1555413, respectively.

*X-ray data for (^{tBu}POCOP)Co(CO) (**1**) (CCDC 1554616)*

Table S1: Crystal data and structure refinement for (^{tBu}POCOP)Co(CO) (**1**).

Empirical formula	$C_{23}H_{39}CoO_3P_2$
Formula weight	484.41
Temperature/K	100
Crystal system	triclinic

Space group	P-1
a/Å	8.3363(5)
b/Å	11.8213(7)
c/Å	13.4166(8)
α/°	100.151(3)
β/°	96.138(3)
γ/°	104.534(3)
Volume/Å^3	1243.85(13)
Z	2
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	0.839
F(000)	516.0
Crystal size/mm^3	0.05 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.124 to 57.094
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	45352
Independent reflections	6250 [R_{int} = 0.0509, R_{sigma} = 0.0360]
Data/restraints/parameters	6250/0/274
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0321, wR_2 = 0.0743
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.0794
Largest diff. peak/hole / e Å^{-3}	0.41/-0.44

Table S2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (^{tBu}POCOP)Co(CO) (**1**). $U_{eq}$is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Co01	4653.9(3)	2697.8(2)	2346.2(2)	10.82(7)
P2	6552.0(5)	4384.5(4)	2562.0(3)	9.92(9)
P1	3211.0(5)	998.7(4)	2575.5(3)	10.18(9)
O2	7886.9(14)	4510.7(10)	3615.2(8)	12.6(2)
C1	6003(2)	2620.1(14)	3585.9(12)	10.6(3)
C7	3456(2)	2751.9(16)	1232.0(14)	21.6(4)
O1	4165.4(14)	731.2(10)	3625.4(8)	13.6(2)
C16	8035(2)	4488.8(16)	1613.2(12)	15.2(3)
C3	6535(2)	1561.3(15)	4955.4(12)	13.9(3)
C6	7437(2)	3531.6(14)	4071.4(12)	10.4(3)
C5	8418(2)	3501.2(15)	4960.9(12)	12.8(3)
C20	5880(2)	5771.1(15)	2918.2(13)	15.3(3)
C2	5601(2)	1649.9(14)	4067.9(12)	11.5(3)
C12	1123(2)	972.1(16)	2961.8(13)	16.1(3)

C4	7951(2)	2502.9(15)	5391.2(12)	13.1(3)
C8	3180(2)	-371.6(15)	1632.2(12)	15.3(3)
O3	2669.8(19)	2781.4(13)	493.3(10)	33.5(4)
C10	2207(2)	-1535.4(16)	1883.4(14)	21.9(4)
C15	1378(3)	2233.5(18)	3608.5(15)	26.2(4)
C11	2478(3)	-283.4(18)	554.5(13)	28.3(5)
C9	5029(2)	-366.2(18)	1661.8(16)	27.5(4)
C17	8507(3)	3313(2)	1493.3(19)	39.4(6)
C21	7304(3)	6920.3(17)	3251.9(16)	27.4(4)
C14	-201(2)	766.1(18)	2019.0(15)	22.6(4)
C13	527(2)	62.4(19)	3621.1(15)	26.4(4)
C23	4985(3)	5591(2)	3842(2)	41.5(6)
C18	9653(3)	5493(2)	1962.4(18)	40.2(6)
C22	4643(3)	5886(2)	2046(2)	52.4(8)
C19	7163(3)	4582(3)	593.5(17)	61.6(10)

Table S3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (^{tBu}POCOP)Co(CO) (**1**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Co01	12.14(12)	8.97(12)	9.05(11)	3.02(8)	-2.15(8)	-0.42(8)
P2	11.8(2)	8.1(2)	8.99(18)	2.50(14)	0.28(15)	1.37(15)
P1	10.32(19)	9.6(2)	9.08(18)	2.00(14)	-0.33(15)	0.65(15)
O2	14.5(6)	10.2(6)	10.7(5)	4.2(4)	-2.1(4)	-0.6(5)
C1	11.4(7)	11.1(8)	10.0(7)	2.2(6)	1.5(6)	4.0(6)
C7	23.5(10)	13.0(9)	24.0(9)	5.9(7)	-1.0(8)	-2.2(7)
O1	12.7(6)	11.1(6)	13.6(5)	5.3(4)	-3.4(4)	-2.2(5)
C16	16.1(8)	16.4(9)	13.7(8)	4.5(6)	5.0(6)	3.5(7)
C3	14.6(8)	12.6(8)	14.0(7)	6.3(6)	-0.4(6)	1.3(6)
C6	11.7(7)	9.1(8)	11.1(7)	3.6(6)	3.4(6)	2.6(6)
C5	11.5(8)	13.3(8)	11.5(7)	2.3(6)	0.1(6)	0.7(6)
C20	16.4(8)	11.1(8)	18.3(8)	1.1(6)	1.5(7)	5.7(7)
C2	10.8(7)	9.8(8)	12.1(7)	1.3(6)	0.8(6)	1.1(6)
C12	13.2(8)	17.7(9)	18.1(8)	4.5(7)	3.9(7)	4.3(7)
C4	14.2(8)	14.4(8)	9.2(7)	3.9(6)	-1.8(6)	2.0(6)
C8	19.3(9)	11.5(8)	14.1(8)	1.2(6)	3.3(7)	3.6(7)
O3	42.1(9)	25.1(8)	23.4(7)	12.5(6)	-15.6(6)	-5.1(7)
C10	27.6(10)	10.7(9)	25.2(9)	2.1(7)	4.7(8)	2.6(7)
C15	24.8(10)	26.9(11)	27(1)	-2.0(8)	8.2(8)	11.0(8)
C11	48.6(13)	20.6(10)	13.0(8)	-0.8(7)	-0.2(8)	10.1(9)

C9	22.5(10)	22.8(10)	37.5(11)	0.4(8)	12.3(9)	7.7(8)
C17	49.6(14)	24.1(11)	55.3(15)	9(1)	36.4(12)	17.6(10)
C21	29.2(11)	12.3(9)	37.1(11)	-1.8(8)	6.5(9)	3.7(8)
C14	13.3(9)	22.5(10)	30.5(10)	7.1(8)	-1.6(7)	3.4(7)
C13	20.5(10)	35.7(12)	29.6(10)	17.2(9)	12.0(8)	9.1(9)
C23	52.0(15)	21.0(11)	60.7(15)	8.9(10)	41.4(13)	12.8(10)
C18	34.3(12)	29.1(12)	45.9(13)	-7.8(10)	27.0(11)	-9.7(10)
C22	63.6(17)	37.1(14)	51.1(15)	-14.3(11)	-33.5(13)	38.2(13)
C19	33.3(13)	145(3)	23.9(11)	44.4(16)	14.4(10)	33.6(16)

Table S4: Bond Lengths for (^{tBu}POCOP)Co(CO) (**1**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co01	P2	2.1629(5)	C16	C18	1.521(3)
Co01	P1	2.1587(5)	C16	C19	1.514(3)
Co01	C1	1.9352(16)	C3	C2	1.386(2)
Co01	C7	1.7270(19)	C3	C4	1.392(2)
P2	O2	1.6623(11)	C6	C5	1.384(2)
P2	C16	1.8654(17)	C5	C4	1.391(2)
P2	C20	1.8633(17)	C20	C21	1.523(2)
P1	O1	1.6617(11)	C20	C23	1.533(3)
P1	C12	1.8630(17)	C20	C22	1.523(3)
P1	C8	1.8644(17)	C12	C15	1.538(3)
O2	C6	1.3914(18)	C12	C14	1.528(2)
C1	C6	1.398(2)	C12	C13	1.532(2)
C1	C2	1.400(2)	C8	C10	1.525(2)
C7	O3	1.139(2)	C8	C11	1.532(2)
O1	C2	1.3903(19)	C8	C9	1.536(3)
C16	C17	1.524(3)			

Table S5: Bond Angles for (^{tBu}POCOP)Co(CO) (**1**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Co01	P2	161.977(18)	C19	C16	C18	110.33(19)
C1	Co01	P2	80.99(5)	C2	C3	C4	117.49(15)
C1	Co01	P1	81.00(5)	O2	C6	C1	117.02(14)
C7	Co01	P2	99.32(6)	C5	C6	O2	119.26(14)
C7	Co01	P1	98.69(6)	C5	C6	C1	123.72(15)
C7	Co01	C1	179.30(8)	C6	C5	C4	117.96(15)
O2	P2	Co01	107.37(4)	C21	C20	P2	115.03(13)

O2	P2	C16	99.61(7)	C21	C20	C23	107.55(16)
O2	P2	C20	99.92(7)	C21	C20	C22	109.78(17)
C16	P2	Co01	116.24(6)	C23	C20	P2	104.40(13)
C20	P2	Co01	117.07(6)	C22	C20	P2	110.50(13)
C20	P2	C16	113.26(8)	C22	C20	C23	109.30(19)
O1	P1	Co01	107.66(4)	O1	C2	C1	117.27(14)
O1	P1	C12	99.71(7)	C3	C2	C1	124.02(15)
O1	P1	C8	99.78(7)	C3	C2	O1	118.70(14)
C12	P1	Co01	115.61(6)	C15	C12	P1	104.21(12)
C12	P1	C8	113.08(8)	C14	C12	P1	110.55(12)
C8	P1	Co01	117.70(6)	C14	C12	C15	109.09(15)
C6	O2	P2	112.05(10)	C14	C12	C13	110.03(15)
C6	C1	Co01	122.56(12)	C13	C12	P1	114.38(13)
C6	C1	C2	115.11(14)	C13	C12	C15	108.31(15)
C2	C1	Co01	122.33(12)	C5	C4	C3	121.70(15)
O3	C7	Co01	179.5(2)	C10	C8	P1	114.17(12)
C2	O1	P1	111.74(10)	C10	C8	C11	109.96(15)
C17	C16	P2	104.38(12)	C10	C8	C9	108.82(15)
C18	C16	P2	114.69(13)	C11	C8	P1	109.77(12)
C18	C16	C17	107.32(18)	C11	C8	C9	108.77(15)
C19	C16	P2	110.33(13)	C9	C8	P1	105.15(12)
C19	C16	C17	109.5(2)				

*X-ray data for (^{tBu}POCOP)Co(CO)$_2$ (**2**) (CCDC 1554617)*

Table S6: Crystal data and structure refinement for (^{tBu}POCOP)Co(CO)$_2$ (**2**).

Empirical formula	$C_{24}H_{39}CoO_4P_2$
Formula weight	512.42
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.3587(9)
b/Å	10.4411(7)
c/Å	16.2681(10)
α/°	90
β/°	99.582(3)
γ/°	90
Volume/Å^3	2572.4(3)
Z	4

ρ_{calc}g/cm^3	1.323
μ/mm^{-1}	0.818
F(000)	1088.0
Crystal size/mm^3	0.03 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.69 to 57.018
Index ranges	-20 ≤ h ≤ 20, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21
Reflections collected	138446
Independent reflections	6432 [R_{int} = 0.0569, R_{sigma} = 0.0267]
Data/restraints/parameters	6432/0/292
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0660
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.0703
Largest diff. peak/hole / e Å^{-3}	0.92/-0.32

Table S7: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (^{tBu}POCOP)Co(CO)$_2$ (**2**). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Co1	2775.3(2)	9703.4(2)	1119.6(2)	11.05(6)
P1	2847.3(3)	7834.8(4)	493.8(2)	12.39(9)
P2	2035.8(3)	11354.4(4)	1504.1(2)	11.52(8)
O4	1269.5(7)	10764.4(10)	1999.5(7)	14.4(2)
O3	2100.4(7)	6898.7(10)	807.8(7)	16.1(2)
O2	4233.6(8)	9500.1(12)	2535.1(8)	31.7(3)
C11	3906.8(12)	5592.7(16)	340.8(11)	23.3(4)
O1	3572.7(9)	11096.5(12)	-80.9(9)	32.2(3)
C8	3637.5(11)	9544.1(15)	2006.4(11)	18.6(3)
C1	1726.4(10)	8841.2(14)	1421.7(9)	11.8(3)
C6	1134.8(10)	9460.3(14)	1852.4(9)	12.2(3)
C21	2643.8(10)	12437.7(15)	2328.3(10)	15.9(3)
C10	3876.9(11)	6479.4(16)	1740.1(10)	22.0(4)
C4	310.4(10)	7557.2(15)	1977.1(10)	16.0(3)
C5	435.4(10)	8862.5(15)	2132.3(9)	14.8(3)
C22	2794.5(12)	11679.0(17)	3150.8(10)	22.4(4)
C7	3241.4(12)	10565.4(16)	366.0(11)	22.8(4)
C17	1315.1(11)	12313.7(15)	680.6(10)	17.2(3)
C2	1550.8(10)	7549.6(14)	1265.7(9)	12.6(3)
C3	866.2(10)	6887.4(15)	1535.9(10)	15.7(3)
C9	3866.7(10)	6848.6(15)	825.2(10)	17.3(3)
C20	557.2(11)	13004.4(16)	1002.5(10)	20.2(3)

C23	3533.6(11)	12798.7(16)	2076.9(11)	19.8(3)
C13	2497.1(12)	7719.8(16)	-667.8(10)	21.2(4)
C24	2158.4(12)	13668.1(16)	2494.3(11)	24.4(4)
C19	1855.8(13)	13289.9(19)	270.2(12)	31.6(4)
C18	894.8(13)	11342.6(19)	31.6(11)	33.6(5)
C12	4685.6(11)	7655.9(18)	743.4(12)	26.5(4)
C16	1745.4(12)	8689.0(17)	-905(1)	25.1(4)
C14	2122.9(13)	6393.5(18)	-939.8(11)	31.5(4)
C15	3251.3(14)	8072(2)	-1139.3(12)	34.4(5)

Table S8: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (^{tBu}POCOP)Co(CO)$_2$ (**2**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	10.32(11)	10.12(10)	13.04(10)	-0.04(7)	2.93(7)	-1.32(8)
P1	11.91(19)	12.08(18)	13.68(18)	-0.97(14)	3.60(14)	-0.32(14)
P2	12.39(19)	10.32(18)	12.00(17)	-0.51(14)	2.52(14)	-1.47(14)
O4	15.6(5)	11.6(5)	17.6(5)	-2.8(4)	7.5(4)	-2.0(4)
O3	13.7(5)	11.8(5)	24.4(6)	-3.4(4)	7.8(4)	-1.3(4)
O2	26.9(7)	24.6(7)	36.5(7)	-4.7(6)	-15.4(6)	2.1(5)
C11	20.2(9)	20.8(8)	30.4(9)	-3.3(7)	8.5(7)	5.7(7)
O1	29.0(7)	24.0(7)	51.2(9)	-2.0(6)	28.8(7)	-5.2(6)
C8	17.8(8)	12.1(7)	25.4(8)	-3.1(6)	1.7(7)	-1.2(6)
C1	11.3(7)	13.6(7)	10.2(6)	1.7(5)	1.2(5)	-0.7(6)
C6	13.6(7)	10.8(7)	11.5(7)	0.2(5)	0.2(6)	-1.1(6)
C21	16.3(8)	13.5(7)	17.6(7)	-3.0(6)	1.6(6)	-3.1(6)
C10	22.5(9)	18.4(8)	24.0(8)	2.8(7)	0.9(7)	5.6(7)
C4	12.8(8)	17.6(8)	17.8(7)	4.3(6)	3.3(6)	-3.0(6)
C5	14.2(8)	16.8(7)	14.2(7)	0.0(6)	5.0(6)	0.1(6)
C22	24.4(9)	27.4(9)	14.8(8)	-3.3(7)	2.0(7)	-4.5(7)
C7	24.3(9)	17.2(8)	26.7(9)	-2.8(7)	4.1(7)	5.4(7)
C17	18.6(8)	16.3(7)	16.5(7)	1.8(6)	2.1(6)	3.9(6)
C2	10.1(7)	13.4(7)	13.9(7)	-0.4(5)	1.1(6)	1.0(6)
C3	15.4(8)	11.2(7)	20.1(8)	1.8(6)	2.2(6)	-0.9(6)
C9	12.9(8)	15.9(7)	23.7(8)	-0.2(6)	4.8(6)	1.5(6)
C20	17.7(8)	19.7(8)	22.7(8)	-0.2(6)	1.8(7)	3.6(6)
C23	18.3(8)	15.4(8)	24.9(8)	-1.4(6)	1.3(7)	-4.6(6)
C13	28.9(9)	20.5(8)	13.9(7)	-4.4(6)	2.2(7)	4.6(7)
C24	22.5(9)	18.8(8)	31.5(9)	-11.3(7)	3.1(7)	-2.2(7)
C19	30.7(10)	34.2(10)	32.8(10)	19.2(8)	13.8(8)	12.2(8)
C18	38.1(11)	33.5(11)	23.0(9)	-10.2(8)	-13.5(8)	17.9(9)
C12	14.0(8)	26.6(9)	40.5(11)	-2.3(8)	9.0(7)	-0.2(7)
C16	33.3(10)	22.5(9)	16.4(8)	-4.3(7)	-4.8(7)	4.8(7)

C14	41.6(12)	24.0(9)	24.7(9)	-11.6(7)	-7.2(8)	6.6(8)
C15	47.8(13)	37.5(11)	21.5(9)	2.1(8)	16.8(9)	10.3(10)

Table S9: Bond Lengths for (^{tBu}POCOP)Co(CO)$_2$ (**2**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	P1	2.2118(4)	C1	C2	1.390(2)
Co1	P2	2.2113(4)	C6	C5	1.383(2)
Co1	C8	1.7962(17)	C21	C22	1.539(2)
Co1	C1	1.9775(15)	C21	C23	1.537(2)
Co1	C7	1.7657(19)	C21	C24	1.532(2)
P1	O3	1.6514(11)	C10	C9	1.535(2)
P1	C9	1.8766(16)	C4	C5	1.394(2)
P1	C13	1.8806(16)	C4	C3	1.392(2)
P2	O4	1.6522(11)	C17	C20	1.534(2)
P2	C21	1.8794(15)	C17	C19	1.536(2)
P2	C17	1.8787(16)	C17	C18	1.527(2)
O4	C6	1.3920(17)	C2	C3	1.390(2)
O3	C2	1.3924(18)	C9	C12	1.538(2)
O2	C8	1.148(2)	C13	C16	1.535(2)
C11	C9	1.536(2)	C13	C14	1.536(2)
O1	C7	1.104(2)	C13	C15	1.536(3)
C1	C6	1.395(2)			

Table S10: Bond Angles for (^{tBu}POCOP)Co(CO)$_2$ (**2**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P2	Co1	P1	152.277(17)	C22	C21	P2	107.19(11)
C8	Co1	P1	101.61(5)	C23	C21	P2	108.42(11)
C8	Co1	P2	100.94(5)	C23	C21	C22	110.23(13)
C8	Co1	C1	106.29(7)	C24	C21	P2	115.59(11)
C1	Co1	P1	79.51(4)	C24	C21	C22	106.60(14)
C1	Co1	P2	78.85(4)	C24	C21	C23	108.76(13)
C7	Co1	P1	94.19(6)	C3	C4	C5	120.47(14)
C7	Co1	P2	94.92(6)	C6	C5	C4	118.21(14)
C7	Co1	C8	105.95(8)	O1	C7	Co1	176.50(17)
C7	Co1	C1	147.76(7)	C20	C17	P2	113.43(11)
O3	P1	Co1	106.81(4)	C20	C17	C19	109.42(14)
O3	P1	C9	100.12(6)	C19	C17	P2	111.52(12)
O3	P1	C13	100.12(7)	C18	C17	P2	105.67(11)
C9	P1	Co1	117.07(5)	C18	C17	C20	106.90(14)

C9	P1	C13	109.82(7)	C18	C17	C19	109.70(15)
C13	P1	Co1	119.41(5)	C1	C2	O3	117.04(13)
O4	P2	Co1	106.77(4)	C3	C2	O3	118.97(13)
O4	P2	C21	100.72(6)	C3	C2	C1	123.99(14)
O4	P2	C17	99.42(7)	C2	C3	C4	118.32(14)
C21	P2	Co1	116.96(5)	C11	C9	P1	115.07(11)
C17	P2	Co1	118.90(5)	C11	C9	C12	108.68(14)
C17	P2	C21	110.59(7)	C10	C9	P1	106.84(11)
C6	O4	P2	112.23(9)	C10	C9	C11	106.75(13)
C2	O3	P1	113.00(9)	C10	C9	C12	110.18(14)
O2	C8	Co1	174.16(16)	C12	C9	P1	109.24(11)
C6	C1	Co1	122.65(11)	C16	C13	P1	106.72(11)
C2	C1	Co1	122.52(11)	C16	C13	C14	106.99(14)
C2	C1	C6	114.72(13)	C16	C13	C15	108.35(15)
O4	C6	C1	116.68(13)	C14	C13	P1	112.20(12)
C5	C6	O4	119.08(13)	C14	C13	C15	110.41(15)
C5	C6	C1	124.24(14)	C15	C13	P1	111.91(12)

*X-ray data for (^{iPr}POCOP)Ir(CO)$_2$ (**3**) (CCDC 1555407)*

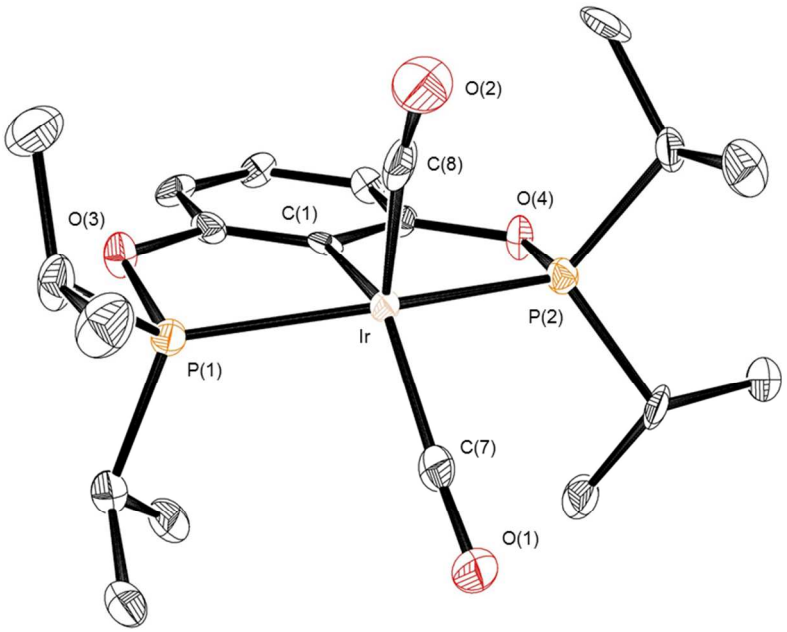


Figure S11: ORTEP[9] of (^{iPr}POCOP)Ir(CO)$_2$ (**3**) at 50% probability (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Ir-C(1) 2.114(8), Ir-P(1) 2.306(2), Ir-P(2) 2.219(2), Ir-C(7) 1.876(9), Ir-O(1) 3.040(6), Ir-C(8) 1.934(9), Ir-O(2) 3.053(7), P(1)-Ir-P(2) 152.22(8), P(1)-Ir-C(1) 76.5(2), P(2)-Ir-C(1) 77.4(2), C(1)-Ir-C(7) 134.2(3), C(1)-Ir-C(8) 112.2(3), C(7)-Co-C(8) 113.6(4).

Table S11: Crystal data and structure refinement for (^{iPr}POCOP)Ir(CO)$_2$ (**3**).

Empirical formula	$C_{20}H_{31}IrO_4P_2$
Formula weight	589.59
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.9573(10)
b/Å	10.2731(8)
c/Å	14.5271(10)
α/°	90
β/°	91.337(4)
γ/°	90
Volume/Å^3	2231.6(3)
Z	4
ρ_{calc}g/cm^3	1.755
μ/mm^{-1}	6.148
F(000)	1160.0
Crystal size/mm^3	0.05 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.724 to 50.79
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	4097
Independent reflections	4097 [R_{int} = 0.1189, R_{sigma} = 0.0590]
Data/restraints/parameters	4097/0/252
Goodness-of-fit on F^2	0.999
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0663, wR_2 = 0.1456
Largest diff. peak/hole / e Å^{-3}	2.59/-2.00

Table S12: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (^{iPr}POCOP)Ir(CO)$_2$ (**3**). U_{eq} is defined as 1/3 of of the trace of the

orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ir(1)	2893.1(2)	9354.3(3)	8159.2(2)	12.84(16)
P(1)	3350.6(14)	7220(2)	8028.5(14)	16.4(5)
P(2)	1838.7(15)	10908(2)	8452.1(14)	15.4(5)
O(4)	1016(4)	10201(6)	9003(4)	19.0(13)
O(3)	2826(4)	6410(6)	8831(4)	19.4(14)
C(2)	2072(5)	7024(9)	9158(5)	16.1(18)
O(1)	3038(4)	10173(7)	6157(4)	27.4(15)
C(1)	1948(5)	8313(8)	8930(5)	13.7(17)
C(7)	2973(5)	9820(9)	6915(6)	18.3(19)
O(2)	4452(5)	10520(7)	9275(5)	35.8(18)
C(8)	3869(6)	10011(9)	8923(6)	23(2)
C(18)	2110(6)	12252(8)	9244(5)	22(2)
C(5)	543(5)	8242(8)	9749(5)	16.3(18)
C(6)	1176(6)	8895(9)	9234(5)	17.3(18)
C(4)	709(5)	6953(9)	9971(5)	17.6(19)
C(3)	1470(6)	6315(9)	9674(5)	21(2)
C(9)	4515(5)	6739(9)	8246(6)	24(2)
C(17)	788(7)	10590(9)	6898(7)	31(3)
C(15)	1251(6)	11655(9)	7465(6)	23(2)
C(12)	2978(6)	6280(10)	7001(6)	24(2)
C(14)	3446(7)	6704(9)	6118(6)	29(2)
C(16)	608(7)	12711(9)	7702(7)	35(2)
C(19)	2362(6)	11748(10)	10212(6)	28(2)
C(13)	1963(6)	6349(11)	6892(6)	33(2)
C(10)	4745(7)	6697(11)	9277(6)	36(3)
C(11)	5166(6)	7627(11)	7750(7)	34(2)
C(20)	2809(6)	13157(10)	8834(7)	29(2)

Table S13: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (^{iPr}POCOP)Ir(CO)$_2$ (**3**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir(1)	16.5(2)	11.2(3)	10.8(2)	1.20(11)	1.37(13)	0.77(13)
P(1)	19.4(11)	16.6(14)	13.3(10)	1.8(8)	3.8(8)	4.2(10)
P(2)	19.0(11)	12.5(13)	14.7(11)	0.6(8)	2.8(8)	-0.7(9)
O(4)	23(3)	9(3)	26(3)	3(3)	7(2)	5(3)
O(3)	20(3)	14(4)	24(3)	3(2)	9(2)	1(3)
C(2)	20(4)	16(5)	13(4)	-4(3)	3(3)	3(4)
O(1)	38(4)	26(4)	18(3)	4(3)	5(3)	5(3)

C(1)	24(4)	11(5)	6(4)	-2(3)	4(3)	-9(4)
C(7)	13(4)	18(5)	24(5)	-1(4)	3(3)	13(4)
O(2)	36(4)	31(5)	40(4)	1(3)	-14(3)	-15(3)
C(8)	32(5)	15(6)	24(5)	10(4)	10(4)	8(5)
C(18)	38(6)	9(5)	19(5)	1(3)	7(4)	2(4)
C(5)	12(4)	17(5)	20(4)	-2(3)	2(3)	0(4)
C(6)	25(5)	15(5)	11(4)	2(3)	-1(3)	-2(4)
C(4)	14(4)	22(5)	17(4)	5(4)	0(3)	-3(4)
C(3)	28(5)	15(5)	18(4)	9(4)	-10(3)	-16(4)
C(9)	19(4)	22(5)	31(5)	3(4)	6(3)	11(4)
C(17)	41(6)	22(6)	30(6)	1(4)	-18(5)	5(4)
C(15)	33(5)	14(5)	22(5)	10(4)	1(4)	11(4)
C(12)	27(5)	19(6)	25(5)	-3(4)	-3(4)	11(4)
C(14)	48(6)	17(6)	22(5)	-3(4)	7(4)	6(5)
C(16)	58(7)	18(6)	29(5)	-1(4)	-4(4)	12(5)
C(19)	39(5)	26(6)	19(5)	-14(4)	-1(4)	-8(5)
C(13)	44(6)	23(7)	32(6)	-12(4)	-10(4)	6(5)
C(10)	41(6)	44(7)	22(5)	8(4)	-1(4)	11(5)
C(11)	23(5)	41(7)	37(6)	6(5)	1(4)	10(5)
C(20)	33(5)	20(6)	34(5)	-1(4)	7(4)	-12(5)

Table S14: Bond Lengths for (^{iPr}POCOP)Ir(CO)$_2$ (**3**).

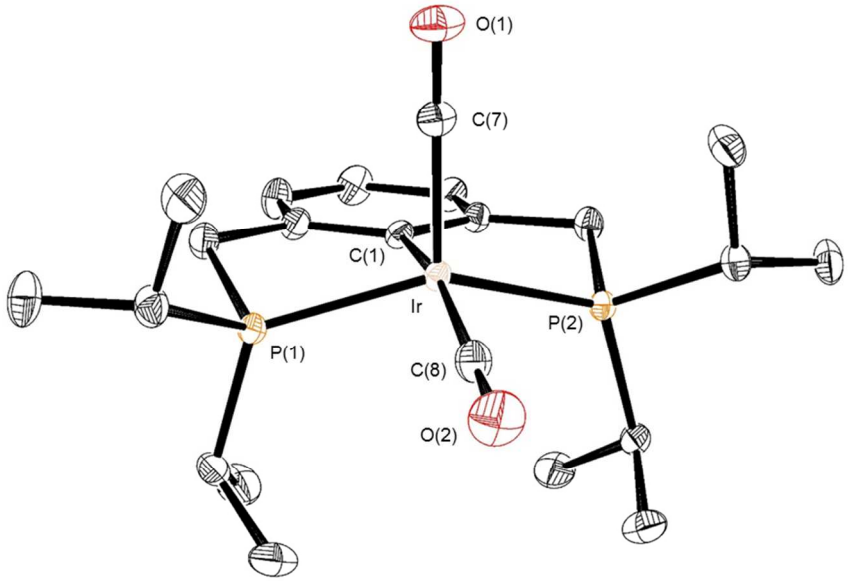
Ir(1)	P(1)	2.306(2)	O(1)	C(7)	1.166(10)
Ir(1)	P(2)	2.291(2)	C(1)	C(6)	1.381(11)
Ir(1)	C(1)	2.115(7)	O(2)	C(8)	1.129(11)
Ir(1)	C(7)	1.876(9)	C(18)	C(19)	1.537(12)
Ir(1)	C(8)	1.934(10)	C(18)	C(20)	1.530(11)
P(1)	O(3)	1.646(6)	C(5)	C(6)	1.392(11)
P(1)	C(9)	1.831(8)	C(5)	C(4)	1.385(12)
P(1)	C(12)	1.853(9)	C(4)	C(3)	1.391(12)
P(2)	O(4)	1.652(6)	C(9)	C(10)	1.529(12)
P(2)	C(18)	1.836(9)	C(9)	C(11)	1.526(13)
P(2)	C(15)	1.833(9)	C(17)	C(15)	1.526(13)
O(4)	C(6)	1.402(11)	C(15)	C(16)	1.495(12)
O(3)	C(2)	1.385(9)	C(12)	C(14)	1.538(12)
C(2)	C(1)	1.377(12)	C(12)	C(13)	1.524(12)
C(2)	C(3)	1.391(11)			

Table S15: Bond Angles for (^{iPr}POCOP)Ir(CO)$_2$ (**3**).

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**

P(2)	Ir(1)	P(1)	152.22(8)	C(1)	C(2)	O(3)	117.5(7)
C(1)	Ir(1)	P(1)	76.5(2)	C(1)	C(2)	C(3)	123.2(8)
C(1)	Ir(1)	P(2)	77.4(2)	C(2)	C(1)	Ir(1)	121.7(6)
C(7)	Ir(1)	P(1)	97.9(3)	C(2)	C(1)	C(6)	116.7(7)
C(7)	Ir(1)	P(2)	93.5(3)	C(6)	C(1)	Ir(1)	121.7(6)
C(7)	Ir(1)	C(1)	134.2(3)	O(1)	C(7)	Ir(1)	176.5(8)
C(7)	Ir(1)	C(8)	113.5(4)	O(2)	C(8)	Ir(1)	170.4(8)
C(8)	Ir(1)	P(1)	99.1(3)	C(19)	C(18)	P(2)	111.4(6)
C(8)	Ir(1)	P(2)	99.4(3)	C(20)	C(18)	P(2)	110.9(6)
C(8)	Ir(1)	C(1)	112.2(3)	C(20)	C(18)	C(19)	114.0(8)
O(3)	P(1)	Ir(1)	106.0(2)	C(4)	C(5)	C(6)	117.8(8)
O(3)	P(1)	C(9)	102.1(4)	C(1)	C(6)	O(4)	118.4(7)
O(3)	P(1)	C(12)	99.6(4)	C(1)	C(6)	C(5)	123.2(8)
C(9)	P(1)	Ir(1)	121.7(3)	C(5)	C(6)	O(4)	118.4(7)
C(9)	P(1)	C(12)	105.4(4)	C(5)	C(4)	C(3)	121.4(8)
C(12)	P(1)	Ir(1)	118.5(3)	C(2)	C(3)	C(4)	117.7(8)
O(4)	P(2)	Ir(1)	107.9(2)	C(10)	C(9)	P(1)	111.6(6)
O(4)	P(2)	C(18)	100.6(3)	C(11)	C(9)	P(1)	111.8(6)
O(4)	P(2)	C(15)	102.3(4)	C(11)	C(9)	C(10)	110.4(8)
C(18)	P(2)	Ir(1)	119.8(3)	C(17)	C(15)	P(2)	109.0(6)
C(15)	P(2)	Ir(1)	117.8(3)	C(16)	C(15)	P(2)	115.0(6)
C(15)	P(2)	C(18)	105.7(4)	C(16)	C(15)	C(17)	111.0(8)
C(6)	O(4)	P(2)	114.3(5)	C(14)	C(12)	P(1)	113.0(7)
C(2)	O(3)	P(1)	114.7(5)	C(13)	C(12)	P(1)	109.9(6)
O(3)	C(2)	C(3)	119.2(8)	C(13)	C(12)	C(14)	111.9(8)

X-ray data *for*



*(^{iPr}PCP)Ir(CO)$_2$ (**4**) (CCDC 1554618)*

Figure S12: ORTEP[9] of (^{iPr}PCP)Ir(CO)$_2$ (**4**) at 50% probability (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Ir-C(1) 2.119(3), Ir-P(1) 2.3117(9), Ir-P(2) 2.3055(9), Ir-C(7) 1.921(3), Ir-O(1) 3.060(3), Ir-C(8) 1.894(3), Ir-O(2) 3.037(3), P(1)-Ir-P(2) 142.86(3), P(1)-Ir-C(1) 80.18(8), P(2)-Ir-C(1) 80.17(9), C(1)-Ir-C(7) 91.26(12), C(1)-Ir-C(8) 163.47(12), C(7)-Ir-C(8) 105.27(13).

Table S16: Crystal data and structure refinement for (^{iPr}PCP)Ir(CO)$_2$ (**4**).

Empirical formula	$C_{22}H_{35}IrO_2P_2$
Formula weight	585.64
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.6059(10)
b/Å	14.2148(8)
c/Å	20.9243(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4641.7(5)
Z	8
ρ_{calc}g/cm^3	1.676
μ/mm^{-1}	5.905
F(000)	2320.0
Crystal size/mm^3	0.1 × 0.1 × 0.05

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.894 to 56.72
Index ranges	$-20 \le h \le 20$, $-18 \le k \le 18$, $-27 \le l \le 27$
Reflections collected	228967
Independent reflections	5786 [R_{int} = 0.0681, R_{sigma} = 0.0185]
Data/restraints/parameters	5786/0/252
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0227, wR_2 = 0.0443
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0491
Largest diff. peak/hole / e Å^{-3}	3.31/-1.26

Table S17: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for (^{iPr}PCP)Ir(CO)$_2$ (**4**). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ir1	1047.5(2)	7132.3(2)	1707.7(2)	12.32(4)
P1	-38.2(5)	6495.5(5)	2322.3(4)	14.44(15)
C1	9.9(19)	7986(2)	1406.9(15)	14.2(6)
C15	-800(2)	7475(2)	2385.8(16)	19.5(7)
C3	-1428(2)	8614(2)	1581.6(16)	22.9(7)
C4	-1372(2)	9129(2)	1017.4(17)	23.7(7)
C5	-635(2)	9084(2)	651.8(16)	19.6(7)
C2	-751(2)	8043(2)	1773.2(15)	17.6(6)
C6	52(2)	8528(2)	844.3(14)	14.9(6)
P2	1455.5(5)	7419.0(5)	666.8(4)	12.67(15)
O2	1817.6(16)	8713.1(17)	2517.6(13)	29.7(6)
C16	875(2)	8501(2)	464.9(15)	16.7(6)
O1	2263.8(18)	5489.9(18)	1904.8(14)	34.8(6)
C20	2597(2)	7675(2)	495.4(15)	17.7(6)
C17	1182(2)	6573(2)	30.8(15)	17.6(6)
C19	1589(2)	5617(2)	165.5(17)	25.6(7)
C9	-666(2)	5476(2)	2045.2(16)	20.6(7)
C7	1510(2)	8142(2)	2210.6(16)	18.9(7)
C12	209(2)	6124(2)	3152.4(15)	21.3(7)
C21	2752(2)	8075(3)	-172.5(16)	24.8(7)
C14	920(3)	6705(3)	3457.5(16)	30.7(9)
C11	-1285(3)	5730(3)	1504.8(19)	32.3(9)
C10	-62(3)	4687(2)	1837.7(19)	30.9(9)
C18	211(2)	6477(3)	-41.4(17)	26.6(8)
C22	2986(2)	8317(2)	1005.6(17)	23.5(7)

C13	-578(2)	6094(3)	3585.2(17)	29.4(8)
C8	1808(2)	6110(2)	1830.8(15)	20.9(7)

Table S18: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (^{iPr}PCP)Ir(CO)$_2$ (**4**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	13.69(6)	12.85(5)	10.41(6)	1.13(4)	0.57(5)	1.18(4)
P1	17.7(4)	15.3(3)	10.3(4)	0.6(3)	0.7(3)	-1.4(3)
C1	15.1(14)	13.7(14)	13.9(14)	-1.1(11)	1.1(11)	2.2(11)
C15	19.7(16)	20.2(14)	18.6(16)	1.7(13)	4.7(13)	1.2(13)
C3	15.5(15)	29.4(17)	23.7(18)	1.1(14)	3.6(13)	4.6(14)
C4	17.6(16)	27.2(17)	26.2(18)	1.1(14)	-1.9(14)	9.2(14)
C5	22.6(17)	19.6(15)	16.6(16)	1.7(12)	0.1(13)	4.3(13)
C2	20.7(15)	17.0(15)	15.1(15)	0.2(12)	2.5(13)	2.5(12)
C6	15.7(15)	15.8(14)	13.3(15)	0.8(11)	1.2(12)	1.1(12)
P2	12.5(4)	14.0(3)	11.5(4)	0.9(3)	0.5(3)	0.1(3)
O2	27.4(13)	25.8(12)	36.0(14)	-11.0(11)	-8.3(12)	1.1(11)
C16	18.3(16)	17.2(14)	14.8(15)	5.1(12)	1.5(12)	2.6(12)
O1	34.9(15)	28.9(14)	40.7(16)	6.6(12)	-2.5(13)	13.4(12)
C20	13.5(14)	20.8(16)	18.8(16)	1.2(12)	1.6(12)	0.1(12)
C17	20.1(16)	19.8(15)	12.8(15)	-2.8(12)	1.6(12)	-3.3(12)
C19	32.0(19)	20.0(16)	24.7(18)	-6.4(14)	-0.7(15)	0.8(14)
C9	25.6(17)	19.3(15)	16.8(16)	0.6(12)	1.2(14)	-8.0(13)
C7	16.3(16)	18.8(15)	21.5(17)	-1.5(13)	-2.6(13)	2.9(12)
C12	25.2(17)	22.1(16)	16.5(17)	4.0(12)	2.4(13)	-0.3(13)
C21	19.4(17)	34.9(19)	20.0(17)	2.3(14)	5.4(14)	-5.3(14)
C14	41(2)	39(2)	12.0(16)	3.1(14)	-5.3(15)	-10.7(18)
C11	34(2)	36(2)	27.0(19)	-2.1(16)	-7.3(16)	-12.4(17)
C10	40(2)	18.9(16)	34(2)	-5.6(15)	0.6(17)	-6.0(16)
C18	24.1(18)	31.3(18)	24.3(18)	-7.4(15)	-5.2(15)	-5.0(15)
C22	19.4(17)	27.5(17)	23.8(18)	2.8(14)	-0.3(14)	-7.1(14)
C13	32(2)	42(2)	14.1(17)	7.4(15)	3.2(15)	0.9(17)
C8	21.7(16)	23.3(16)	17.6(17)	3.3(12)	1.1(13)	0.1(14)

Table S19: Bond Lengths for (^{iPr}PCP)Ir(CO)$_2$ (**4**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	P1	2.3117(8)	C6	C16	1.510(4)
Ir1	C1	2.120(3)	P2	C16	1.835(3)
Ir1	P2	2.3055(8)	P2	C20	1.853(3)
Ir1	C7	1.920(3)	P2	C17	1.844(3)

Ir1	C8	1.894(3)	O2	C7	1.141(4)
P1	C15	1.836(3)	O1	C8	1.143(4)
P1	C9	1.843(3)	C20	C21	1.528(4)
P1	C12	1.856(3)	C20	C22	1.530(5)
C1	C2	1.416(4)	C17	C19	1.525(4)
C1	C6	1.408(4)	C17	C18	1.529(4)
C15	C2	1.517(4)	C9	C11	1.530(5)
C3	C4	1.392(5)	C9	C10	1.528(5)
C3	C2	1.391(5)	C12	C14	1.524(5)
C4	C5	1.383(5)	C12	C13	1.526(5)
C5	C6	1.391(4)			

Table S20: Bond Angles for (^{iPr}PCP)Ir(CO)$_2$ (**4**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Ir1	P1	80.18(8)	C3	C2	C15	121.1(3)
C1	Ir1	P2	80.16(8)	C1	C6	C16	117.7(3)
P2	Ir1	P1	142.86(3)	C5	C6	C1	121.1(3)
C7	Ir1	P1	105.27(10)	C5	C6	C16	121.1(3)
C7	Ir1	C1	91.26(12)	C16	P2	Ir1	103.26(10)
C7	Ir1	P2	106.36(10)	C16	P2	C20	105.42(14)
C8	Ir1	P1	94.78(10)	C16	P2	C17	105.47(15)
C8	Ir1	C1	163.48(13)	C20	P2	Ir1	118.88(10)
C8	Ir1	P2	95.22(10)	C17	P2	Ir1	120.18(10)
C8	Ir1	C7	105.25(14)	C17	P2	C20	102.15(14)
C15	P1	Ir1	102.59(11)	C6	C16	P2	108.7(2)
C15	P1	C9	105.96(16)	C21	C20	P2	113.7(2)
C15	P1	C12	106.42(15)	C21	C20	C22	110.7(3)
C9	P1	Ir1	121.50(11)	C22	C20	P2	111.3(2)
C9	P1	C12	100.42(15)	C19	C17	P2	110.6(2)
C12	P1	Ir1	118.69(11)	C19	C17	C18	110.6(3)
C2	C1	Ir1	120.8(2)	C18	C17	P2	111.0(2)
C6	C1	Ir1	121.7(2)	C11	C9	P1	112.5(2)
C6	C1	C2	117.4(3)	C10	C9	P1	109.8(2)
C2	C15	P1	108.1(2)	C10	C9	C11	110.7(3)
C2	C3	C4	120.3(3)	O2	C7	Ir1	176.7(3)
C5	C4	C3	119.8(3)	C14	C12	P1	112.9(2)
C4	C5	C6	120.5(3)	C14	C12	C13	110.6(3)
C1	C2	C15	118.0(3)	C13	C12	P1	113.4(2)
C3	C2	C1	120.9(3)	O1	C8	Ir1	179.7(3)

*X-ray data for (^{tBu}POCOP)Co(I)(CO) (**5**) (CCDC 1554619)*

Table S21: Crystal data and structure refinement for (^{tBu}POCOP)Co(I)(CO) (**5**).

Empirical formula	$C_{23}H_{39}CoIO_3P_2$
Formula weight	611.31
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	8.3917(5)
b/Å	12.5946(8)
c/Å	13.1771(8)
α/°	100.647(3)
β/°	94.311(4)
γ/°	105.546(3)
Volume/Å^3	1307.15(14)
Z	2
ρ_{calc}g/cm^3	1.553
μ/mm^{-1}	1.981
F(000)	622.0
Crystal size/mm^3	0.07 × 0.03 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.172 to 56.906
Index ranges	$-11 \leq h \leq 11$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected	44046
Independent reflections	6481 [R_{int} = 0.0371, R_{sigma} = 0.0284]
Data/restraints/parameters	6481/0/283
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0720
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0768
Largest diff. peak/hole / e Å^{-3}	2.45/-1.21

Table S22: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (^{tBu}POCOP)Co(I)(CO) (**5**). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I(1)	2928.2(2)	2554.8(2)	5612.4(2)	20.89(6)
Co(1)	4318.8(4)	2746.7(3)	7510.7(3)	14.03(8)
P(2)	3081.4(8)	966.0(5)	7676.7(5)	11.61(13)
P(1)	6397.9(8)	4347.2(5)	7589.3(5)	11.34(13)
O(2)	4145(2)	808.8(15)	8716.2(14)	14.1(4)
O(1)	7656(2)	4469.6(15)	8660.2(14)	14.4(4)
O(3)	1811(3)	3807.2(19)	8410(2)	30.5(5)
C(1)	5832(3)	2656(2)	8661.5(19)	11.3(5)

C(12)	7901(3)	4328(2)	6606(2)	16.6(5)
C(5)	6515(3)	1672(2)	10009(2)	14.8(5)
C(14)	7252(4)	4570(3)	5584(2)	25.5(7)
C(3)	8295(3)	3528(2)	9976(2)	14.6(5)
C(16)	3334(4)	-236(2)	6698(2)	17.5(5)
C(6)	5522(3)	1724(2)	9137(2)	11.7(5)
C(8)	5928(4)	5736(2)	7888(2)	17.0(5)
C(2)	7259(3)	3535(2)	9108(2)	12.1(5)
C(4)	7890(3)	2586(2)	10423(2)	15.6(5)
C(17)	2032(4)	-571(3)	5737(2)	25.9(7)
C(20)	949(3)	640(3)	8081(2)	20.4(6)
C(10)	4482(4)	5731(3)	7100(3)	24.9(6)
C(11)	5482(4)	5914(3)	9001(2)	25.2(6)
C(7)	2793(4)	3410(2)	8088(2)	20.1(6)
C(13)	9660(4)	5129(3)	7019(2)	23.7(6)
C(9)	7417(4)	6757(3)	7861(3)	27.2(7)
C(18)	5079(4)	243(3)	6378(3)	27.5(7)
C(15)	8031(4)	3108(3)	6411(3)	27.2(7)
C(22)	223(4)	-608(3)	8147(3)	31.0(7)
C(21)	1088(4)	1335(3)	9194(3)	29.0(7)
C(19)	3381(5)	-1271(3)	7140(3)	31.1(8)
C(23)	-250(4)	921(3)	7313(3)	31.4(8)

Table S23: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (^{tBu}POCOP)Co(I)(CO) (**5**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
I(1)	22.75(10)	18.6(1)	17.36(9)	8.58(7)	-7.73(7)	-1.06(7)
Co(1)	13.34(17)	10.87(17)	16.61(17)	7.75(14)	-3.94(14)	-0.31(14)
P(2)	11.5(3)	9.4(3)	13.6(3)	5.1(2)	-0.9(2)	1.3(2)
P(1)	11.8(3)	9.8(3)	12.4(3)	5.9(2)	-1.0(2)	1.5(2)
O(2)	14.3(9)	10.2(8)	15.8(9)	6.2(7)	-2.7(7)	-0.8(7)
O(1)	16.2(9)	10.5(9)	15.2(9)	7.7(7)	-3.4(7)	-0.4(7)
O(3)	25.4(12)	24.8(12)	46.6(14)	12.1(10)	10.4(11)	11.6(10)
C(1)	11.9(11)	12.6(12)	11.6(11)	5.7(9)	0.7(9)	5.3(10)
C(12)	15.1(13)	19.0(13)	15.8(12)	5.6(10)	3.7(10)	3.5(11)
C(5)	18.1(13)	12.2(12)	15.4(12)	6.4(10)	0.6(10)	4.5(10)
C(14)	23.6(15)	34.3(17)	18.4(14)	13.2(13)	3.6(12)	2.6(13)
C(3)	13.7(12)	12.8(12)	16.2(12)	5.6(10)	-1.3(10)	1.3(10)
C(16)	24.3(14)	14.5(13)	14.1(12)	2.9(10)	1.7(11)	6.5(11)
C(6)	11.6(12)	11.1(11)	12.9(11)	4.0(9)	0.9(10)	3.3(10)
C(8)	19.4(13)	12.8(12)	19.9(13)	4.8(10)	-0.4(11)	6.6(11)
C(2)	13.9(12)	9.7(11)	14.4(11)	6.8(9)	2(1)	3(1)

C(4)	15.8(13)	17.5(13)	13.1(12)	5(1)	-1.2(10)	4.1(11)
C(17)	34.7(17)	17.8(14)	18.5(14)	-1.2(11)	-4.1(13)	1.7(13)
C(20)	13.4(13)	22.2(14)	26.7(15)	7.9(12)	3.7(11)	4.7(11)
C(10)	26.2(16)	17.7(14)	32.0(16)	8.9(12)	-6.4(13)	8.7(12)
C(11)	29.2(16)	18.7(14)	27.8(15)	1.8(12)	5.4(13)	8.6(13)
C(7)	18.3(14)	15.8(13)	26.2(14)	8.0(11)	0.4(12)	3.2(11)
C(13)	16.1(14)	29.4(16)	24.5(15)	7.2(12)	4.4(12)	2.9(12)
C(9)	25.9(16)	15.2(14)	37.9(18)	6.4(13)	-0.4(14)	2.1(12)
C(18)	29.4(17)	27.2(16)	26.5(16)	3.0(13)	6.1(13)	10.4(14)
C(15)	28.4(16)	21.2(15)	32.8(17)	2.5(13)	10.7(14)	8.8(13)
C(22)	27.3(16)	23.4(16)	41.9(19)	15.0(14)	7.5(15)	0.3(13)
C(21)	30.1(17)	25.7(16)	36.1(18)	11.8(14)	17.2(15)	9.1(14)
C(19)	53(2)	17.6(15)	27.5(16)	8.1(13)	8.5(16)	16.0(15)
C(23)	15.0(14)	36.4(19)	47(2)	23.6(16)	0.1(14)	5.6(13)

Table S24: Bond Lengths for (^{tBu}POCOP)Co(I)(CO) (**5**).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
I(1)	Co(1)	2.6200(4)	C(12)	C(14)	1.527(4)
Co(1)	P(2)	2.2634(7)	C(12)	C(13)	1.540(4)
Co(1)	P(1)	2.2647(7)	C(12)	C(15)	1.544(4)
Co(1)	C(1)	1.944(2)	C(5)	C(6)	1.390(3)
Co(1)	C(7)	1.844(3)	C(5)	C(4)	1.384(4)
P(2)	O(2)	1.6503(19)	C(3)	C(2)	1.386(4)
P(2)	C(16)	1.869(3)	C(3)	C(4)	1.394(4)
P(2)	C(20)	1.867(3)	C(16)	C(17)	1.525(4)
P(1)	O(1)	1.6548(19)	C(16)	C(18)	1.548(4)
P(1)	C(12)	1.876(3)	C(16)	C(19)	1.532(4)
P(1)	C(8)	1.874(3)	C(8)	C(10)	1.535(4)
O(2)	C(6)	1.387(3)	C(8)	C(11)	1.531(4)
O(1)	C(2)	1.386(3)	C(8)	C(9)	1.542(4)
O(3)	C(7)	1.142(4)	C(20)	C(22)	1.546(4)
C(1)	C(6)	1.404(3)	C(20)	C(21)	1.542(5)
C(1)	C(2)	1.396(4)	C(20)	C(23)	1.528(4)

Table S25: Bond Angles for (^{tBu}POCOP)Co(I)(CO) (**5**).

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P(2)	Co(1)	I(1)	97.41(2)	C(13)	C(12)	C(15)	107.7(2)
P(2)	Co(1)	P(1)	158.20(3)	C(15)	C(12)	P(1)	103.90(19)
P(1)	Co(1)	I(1)	97.41(2)	C(4)	C(5)	C(6)	118.1(2)
C(1)	Co(1)	I(1)	160.99(8)	C(2)	C(3)	C(4)	118.0(2)
C(1)	Co(1)	P(2)	80.44(8)	C(17)	C(16)	P(2)	112.3(2)

C(1)	Co(1)	P(1)	80.33(8)	C(17)	C(16)	C(18)	108.9(2)
C(7)	Co(1)	I(1)	92.23(9)	C(17)	C(16)	C(19)	110.5(3)
C(7)	Co(1)	P(2)	97.60(9)	C(18)	C(16)	P(2)	103.49(19)
C(7)	Co(1)	P(1)	97.71(9)	C(19)	C(16)	P(2)	114.1(2)
C(7)	Co(1)	C(1)	106.79(12)	C(19)	C(16)	C(18)	107.1(3)
O(2)	P(2)	Co(1)	104.99(7)	O(2)	C(6)	C(1)	118.2(2)
O(2)	P(2)	C(16)	99.39(11)	O(2)	C(6)	C(5)	118.3(2)
O(2)	P(2)	C(20)	99.53(12)	C(5)	C(6)	C(1)	123.5(2)
C(16)	P(2)	Co(1)	118.56(9)	C(10)	C(8)	P(1)	109.6(2)
C(20)	P(2)	Co(1)	118.49(10)	C(10)	C(8)	C(9)	107.9(2)
C(20)	P(2)	C(16)	111.50(13)	C(11)	C(8)	P(1)	107.88(19)
O(1)	P(1)	Co(1)	104.44(7)	C(11)	C(8)	C(10)	111.2(3)
O(1)	P(1)	C(12)	99.89(11)	C(11)	C(8)	C(9)	106.3(2)
O(1)	P(1)	C(8)	99.77(11)	C(9)	C(8)	P(1)	113.9(2)
C(12)	P(1)	Co(1)	117.93(9)	O(1)	C(2)	C(1)	118.0(2)
C(8)	P(1)	Co(1)	118.82(9)	O(1)	C(2)	C(3)	118.2(2)
C(8)	P(1)	C(12)	111.72(13)	C(3)	C(2)	C(1)	123.7(2)
C(6)	O(2)	P(2)	113.72(15)	C(5)	C(4)	C(3)	121.5(2)
C(2)	O(1)	P(1)	113.79(16)	C(22)	C(20)	P(2)	113.7(2)
C(6)	C(1)	Co(1)	122.26(19)	C(21)	C(20)	P(2)	107.5(2)
C(2)	C(1)	Co(1)	122.47(18)	C(21)	C(20)	C(22)	105.8(3)
C(2)	C(1)	C(6)	115.2(2)	C(23)	C(20)	P(2)	109.8(2)
C(14)	C(12)	P(1)	112.2(2)	C(23)	C(20)	C(22)	108.2(3)
C(14)	C(12)	C(13)	110.1(2)	C(23)	C(20)	C(21)	111.9(3)
C(14)	C(12)	C(15)	109.3(3)	O(3)	C(7)	Co(1)	177.4(3)
C(13)	C(12)	P(1)	113.2(2)				

*X-ray data for (^{tBu}POCOP)Co(H) (**6**) (CCDC 1554620)*

Table S26: Crystal data and structure refinement for (^{tBu}POCOP)Co(H) (**6**).

Empirical formula	$C_{22}H_{40}O_2P_2Co$
Formula weight	457.41
Temperature/K	130.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.4261(2)
b/Å	27.1408(7)
c/Å	10.7755(3)
α/°	90
β/°	102.6589(11)
γ/°	90

Volume/Å^3	2404.36(11)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.861
F(000)	980.0
Crystal size/mm^3	0.5 × 0.5 × 0.5
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.154 to 56.596
Index ranges	-10 ≤ h ≤ 10, -33 ≤ k ≤ 36, -14 ≤ l ≤ 14
Reflections collected	9848
Independent reflections	5715 [R_{int} = 0.0471, R_{sigma} = 0.0867]
Data/restraints/parameters	5715/0/260
Goodness-of-fit on F^2	0.941
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0759
Final R indexes [all data]	R_1 = 0.0768, wR_2 = 0.0841
Largest diff. peak/hole / e Å^{-3}	0.54/-0.36

Table S27: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (^{tBu}POCOP)Co(H) (**6**). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Co(1)	630.9(3)	1376.6(2)	3977.1(3)	14.65(9)
P(1)	2389.5(7)	1132.1(2)	5641.4(5)	15.04(13)
P(2)	-892.4(7)	1433.1(2)	2090.6(5)	15.43(13)
O(1)	3387.8(16)	665.5(5)	5159.5(13)	18.0(3)
O(2)	-339.5(17)	977.3(5)	1234.4(13)	18.1(3)
C(1)	1518(2)	831.2(7)	3201.2(19)	14.2(5)
C(2)	2781(2)	542.7(7)	3879.3(19)	15.2(5)
C(3)	3444(2)	145.7(7)	3358(2)	19.0(5)
C(4)	2829(3)	42.9(8)	2084(2)	20.2(5)
C(5)	1580(2)	320.5(8)	1351(2)	18.2(5)
C(6)	955(2)	704.4(8)	1937(2)	16.9(5)
C(7)	4122(3)	1559.9(8)	6251(2)	19.6(5)
C(8)	5736(3)	1296.2(8)	6772(2)	26.6(6)
C(9)	3726(3)	1910.6(8)	7250(2)	25.1(5)
C(10)	4285(3)	1854.2(9)	5076(2)	31.7(6)
C(11)	1618(2)	823.0(8)	6931.4(19)	17.3(5)
C(12)	586(3)	1176.4(8)	7529(2)	26.9(6)
C(13)	499(3)	414.5(8)	6248(2)	23.5(5)
C(14)	2952(3)	588.9(8)	7948(2)	24.3(5)

C(15)	-3051(3)	1261.1(8)	2003(2)	22.2(5)
C(16)	-4060(3)	1713.5(9)	2190(2)	30.6(6)
C(17)	-3849(3)	992.7(9)	785(2)	34.2(6)
C(18)	-2967(3)	910.5(9)	3132(2)	30.6(6)
C(19)	-646(3)	1963.0(8)	1071(2)	19.4(5)
C(20)	1125(3)	1946.6(8)	939(2)	26.3(6)
C(21)	-913(3)	2445.1(8)	1736(2)	27.8(6)
C(22)	-1760(3)	1946.3(8)	-255(2)	27.5(6)

Table S28: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (^{tBu}POCOP)Co(H) (**6**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Co(1)	12.68(16)	16.48(16)	13.79(17)	-1.13(13)	0.72(12)	0.92(12)
P(1)	12.9(3)	16.9(3)	14.4(3)	-1.6(2)	0.9(2)	0.1(2)
P(2)	12.4(3)	19.0(3)	13.7(3)	-0.4(2)	0.5(2)	0.3(2)
O(1)	15.4(8)	21.8(8)	14.7(8)	-2.1(6)	-1.3(7)	3.8(6)
O(2)	16.2(8)	22.6(8)	13.6(8)	-0.8(7)	-1.0(7)	3.7(6)
C(1)	13.1(11)	16.8(11)	13.2(11)	-0.6(9)	3.6(9)	-0.3(9)
C(2)	13.1(11)	18.6(11)	13.3(12)	-1.5(9)	1.5(9)	-2.5(9)
C(3)	14.3(11)	17.0(11)	24.8(13)	0.3(10)	2.2(10)	1.4(9)
C(4)	17.6(12)	20.6(12)	23.2(13)	-3.2(10)	6(1)	2.3(9)
C(5)	17.3(12)	22.8(12)	14.4(12)	-5.9(10)	3(1)	-4.1(9)
C(6)	11.3(11)	19.4(12)	18.5(12)	1.9(10)	-0.2(10)	-3.5(9)
C(7)	16.0(11)	21.1(12)	20.0(13)	-2.2(10)	0.3(10)	-2.3(9)
C(8)	16.7(12)	30.2(14)	30.1(14)	-3.0(11)	-1.1(11)	-2.2(10)
C(9)	23.5(13)	19.0(12)	29.9(15)	-7.0(11)	-0.3(11)	-6.1(10)
C(10)	30.3(15)	34.4(14)	31.5(15)	4.4(12)	9.2(12)	-9.7(11)
C(11)	16.6(12)	20.4(12)	14.1(12)	-0.7(10)	1.5(9)	-0.7(9)
C(12)	28.6(13)	28.1(13)	28.2(14)	-1.1(11)	15.6(12)	0.7(11)
C(13)	17.9(12)	23.7(13)	28.1(14)	3.9(11)	3.1(11)	-5.3(10)
C(14)	25.5(13)	29.0(13)	17.9(13)	5.4(11)	3.6(11)	-0.6(11)
C(15)	13.0(11)	33.8(14)	19.6(13)	4(1)	3.1(10)	-2(1)
C(16)	18.2(13)	44.1(16)	30.9(15)	6.9(12)	8.8(11)	6.9(11)
C(17)	17.0(13)	48.1(16)	34.7(16)	-3.5(13)	-0.3(12)	-10.2(11)
C(18)	23.5(14)	34.6(15)	33.4(15)	6.7(12)	5.8(12)	-9.0(11)
C(19)	18.8(12)	21.6(12)	17.5(12)	1.3(10)	3(1)	-1.1(10)
C(20)	26.1(13)	26.2(13)	28.5(15)	0.6(11)	9.9(12)	-5.9(10)
C(21)	39.4(16)	19.4(12)	26.4(14)	4.2(11)	11.0(12)	0.8(11)
C(22)	29.5(14)	31.5(14)	20.7(13)	7.6(11)	3.8(11)	-0.5(11)

Table S29: Bond Lengths for (^{tBu}POCOP)Co(H) (**6**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co(1)	P(1)	2.1651(6)	C(4)	C(5)	1.391(3)
Co(1)	P(2)	2.1586(6)	C(5)	C(6)	1.381(3)
Co(1)	C(1)	1.929(2)	C(7)	C(8)	1.531(3)
P(1)	O(1)	1.6649(14)	C(7)	C(9)	1.528(3)
P(1)	C(7)	1.869(2)	C(7)	C(10)	1.528(3)
P(1)	C(11)	1.859(2)	C(11)	C(12)	1.528(3)
P(2)	O(2)	1.6694(14)	C(11)	C(13)	1.535(3)
P(2)	C(15)	1.860(2)	C(11)	C(14)	1.526(3)
P(2)	C(19)	1.849(2)	C(15)	C(16)	1.532(3)
O(1)	C(2)	1.402(2)	C(15)	C(17)	1.523(3)
O(2)	C(6)	1.396(2)	C(15)	C(18)	1.534(3)
C(1)	C(2)	1.393(3)	C(19)	C(20)	1.530(3)
C(1)	C(6)	1.384(3)	C(19)	C(21)	1.532(3)
C(2)	C(3)	1.388(3)	C(19)	C(22)	1.529(3)
C(3)	C(4)	1.385(3)			

Table S30: Bond Angles for (^{tBu}POCOP)Co(H) (**6**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P(2)	Co(1)	P(1)	163.65(2)	C(5)	C(6)	O(2)	118.87(18)
C(1)	Co(1)	P(1)	82.18(6)	C(5)	C(6)	C(1)	123.7(2)
C(1)	Co(1)	P(2)	81.56(6)	C(8)	C(7)	P(1)	113.67(15)
O(1)	P(1)	Co(1)	106.00(5)	C(9)	C(7)	P(1)	111.13(14)
O(1)	P(1)	C(7)	99.96(9)	C(9)	C(7)	C(8)	110.28(18)
O(1)	P(1)	C(11)	99.99(8)	C(9)	C(7)	C(10)	109.35(18)
C(7)	P(1)	Co(1)	116.17(7)	C(10)	C(7)	P(1)	103.79(15)
C(11)	P(1)	Co(1)	118.01(7)	C(10)	C(7)	C(8)	108.34(18)
C(11)	P(1)	C(7)	113.08(10)	C(12)	C(11)	P(1)	110.89(15)
O(2)	P(2)	Co(1)	106.71(6)	C(12)	C(11)	C(13)	108.04(17)
O(2)	P(2)	C(15)	100.04(9)	C(13)	C(11)	P(1)	104.22(14)
O(2)	P(2)	C(19)	99.59(8)	C(14)	C(11)	P(1)	113.64(14)
C(15)	P(2)	Co(1)	113.76(7)	C(14)	C(11)	C(12)	110.90(17)
C(19)	P(2)	Co(1)	119.59(7)	C(14)	C(11)	C(13)	108.79(18)
C(19)	P(2)	C(15)	113.65(10)	C(16)	C(15)	P(2)	110.91(15)
C(2)	O(1)	P(1)	112.80(12)	C(16)	C(15)	C(18)	108.86(17)
C(6)	O(2)	P(2)	111.88(12)	C(17)	C(15)	P(2)	113.96(15)
C(2)	C(1)	Co(1)	121.88(15)	C(17)	C(15)	C(16)	110.1(2)

C(6)	C(1)	Co(1)	122.39(16)	C(17)	C(15)	C(18)	108.76(19)
C(6)	C(1)	C(2)	115.73(19)	C(18)	C(15)	P(2)	103.96(15)
C(1)	C(2)	O(1)	117.02(17)	C(20)	C(19)	P(2)	105.75(15)
C(3)	C(2)	O(1)	119.39(18)	C(20)	C(19)	C(21)	108.32(18)
C(3)	C(2)	C(1)	123.59(19)	C(21)	C(19)	P(2)	109.81(14)
C(4)	C(3)	C(2)	117.5(2)	C(22)	C(19)	P(2)	113.97(15)
C(3)	C(4)	C(5)	121.7(2)	C(22)	C(19)	C(20)	108.94(17)
C(6)	C(5)	C(4)	117.7(2)	C(22)	C(19)	C(21)	109.84(18)
C(1)	C(6)	O(2)	117.40(18)				

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