Synthesis and Reactivity of Pincer-Type Cobalt Silyl and Silylene Complexes

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Supporting Information Placeholder

ABSTRACT: Preparation and characterization of a series of pincer-type $[P_2Si]Co$ complexes are reported, including a crystal structure of the first base-free cobalt silylene complex. The cationic silylene complex is strongly Lewis-acidic and oxophilic, readily coordinating Lewis bases such as triflate and pyridine and heterolytically cleaving the O–H bonds in ethanol and water.

Metal silylenes ($M{=}SiR_2$) have been shown to exhibit a variety of modes of reactivity, often quite distinct from their metal carbene congeners.[1] Though silylenes have been implicated as important intermediates in hydrosilylation catalysis,[2] their utilization in general has been limited by their high reactivity. Base-free silylene complexes featuring first-row transition metals are particularly unusual. Examples have been reported for titanium,[3] chromium,[4] manganese,[5] iron,[6] and nickel.[7] However, cobalt represents a notable absence from this series.

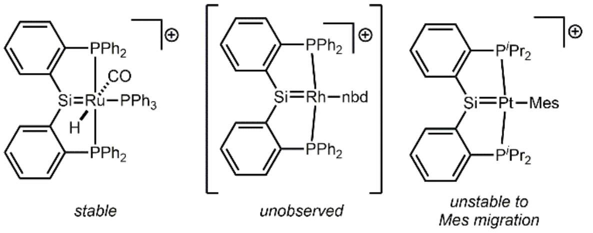
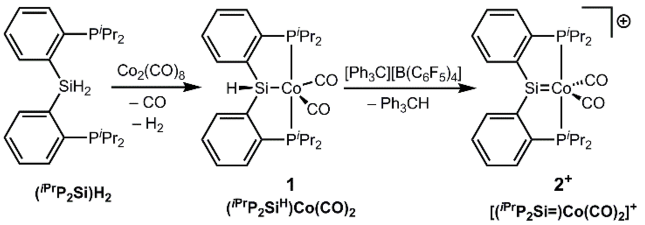


Chart 1. Previously reported silylene complexes supported by pincer-type $[P_2Si]$ ligands.

Our research groups have recently developed the coordination chemistry of a pincer-type $[P_2Si]$ ligand with an eye toward utilizing the chelate to approach silylene complexes for application in new stoichiometric and catalytic reactions (Chart 1).[8] The chemistry of $[P_2Si]$ complexes with a central silyl donor was originally explored by the Turculet, Iwasawa, and Milstein groups.[9] In one recent study, we showed that a cationic ruthenium(II) silylene supported by a $[P_2Si]$ ligand was quite stable, yet reactivity prospects were limited by the coordinatively saturated metal center.[8d] When related rhodium species were examined, the intermediacy of rhodium silylene cations was implicated in the formation of triflatosilyl rhodium diene complexes.[8b] In another study, we found that unsaturated cationic $(P_2Si{=})Pt$ silylene complexes are accessible yet prone to rearrangement via X-type ligand migration to the highly Lewis-acidic silylene unit, affording a T-shaped mesitylsilyl platinum cation from the complex shown in Chart 1.[8a] In an effort to attenuate such reactivity and maximize prospects for metal/silylene cooperativity, we have shifted our attention to group 9 metals. We envisioned that silylene complexes of monovalent group 9 metal centers may be more robust due to stronger M→Si π-backbonding and because the complex is designed not to carry X-type ligands on the metal. Here we report coordination of $[P_2Si]$ to cobalt, allowing synthesis, characterization, and preliminary reactivity studies of the first base-free cobalt silylene complex.

Cobalt Silylene Synthesis

Reaction of the $(^{iPr}P_2Si)H_2$ proligand[8a] with $Co_2(CO)_8$ afforded the diamagnetic hydrosilyl complex $(^{iPr}P_2Si^H)Co(CO)_2$ (**1**) with evolution of CO and H_2 (Scheme 1).[10] Complex **1** exhibits several spectroscopic features consistent with its formulation shown in Scheme 1, including prominent infrared bands for the Si–H (ν_{SiH} = 2048 cm^{-1}) and C≡O (ν_{CO} = 1958, 1908 cm^{-1}) stretching modes, with the Si–H stretch observed at similar energy to a related hydrosilyl ruthenium complex.[8d] The ^1H NMR (δ 6.15 ppm (s, $^1J_{SiH}$ = 182 Hz)) and ^{29}Si NMR (δ 54.8 ppm) resonances for the Si–H moiety in **1** are consistent with the expectations for a hydrosilyl complex of this type.[11] Complex **1** has been further characterized by X-ray crystallography, revealing a trigonal-bipyramidal geometry (τ parameter[12] of 0.84) with the silyl and one of the CO ligands in the axial positions (Figure 1).



Scheme 1. Preparation of $(^{iPr}P_2Si)Co$ hydrosilyl (**1**) and silylene complexes (**2**).

Hydride abstraction from **1** with trityl tetrakis(pentafluorophenyl)borate ($Ph_3C{\cdot}BAr^F_{20}$) was accomplished in high yield in fluorobenzene, affording the first example of a base-free cobalt silylene complex (**2**, $[(^{iPr}P_2Si{=})Co(CO)_2][BAr^F_{20}]$) (Scheme 1). The clearest spectroscopic evidence for the formation of **2** comes from its ^{29}Si chemical shift (δ 285 ppm), a significant downfield shift from the precursor consistent with what has been observed for related base-free metal silylenes (δ 200–370 ppm).[1b] The weaker donating nature of the formally neutral, π-accepting silylene ligand in **2** vs the anionic silyl in **1** leads to a ca. 70 cm^{-1} blue-shift in the C≡O stretching frequencies (ν_{CO} = 2028, 1983 cm^{-1}) relative to **1**.

The molecular structure of **2** was determined by X-ray crystallography (Figure 1), revealing a five-coordinate geometry about Co. Although the $\tau = 0.30$ for this structure, it is nonetheless best analyzed as trigonal bipyramidal, with the axial phosphines deviating slightly from linearity (∠PCoP = 156°) because of the chelate constraint. The structure possesses a rigorous crystallographic C_s symmetry (in the $Cmc2_1$ space group), which is unusual for structures of pincer complexes based on the bis(*o*-phosphinoaryl)element motif. This observed solid-state symmetry is related to the presence of a trigonal-planar silicon center with coplanar aromatic rings. The coplanarity of these rings with the central element is rare, even for sp^2-hybridized, planar central atoms,[13,14] and is presumably a consequence of the stabilization of the electron-deficient Si center via conjugation with the aromatic rings and the larger size of silicon versus C, N, and B. The possibility silicon conjugation with the aromatic rings in **2** is supported by a 0.05 Å shorter $Si–C_{Ar}$ bond relative to **1**, though the sp^2 hybridization in **2** also likely plays some role in this shortening. Only rotation of isopropyl groups about the P–C bond appears to be needed to attain the time-averaged C_{2v} symmetry observed by NMR in solutions of **2**. The Co–Si bond length in **2** (2.121(2) Å) is among the shortest reported, similar to those for amidinate-supported, base-stabilized CpCo(I) silylene complexes reported by Stalke and co-workers (2.114 Å)[15] and Driess and co-workers (2.125 Å and 2.120 Å).[16] Although no direct analogy is available for cobalt, the Si–Co bond shortening (ca. 7%) upon hydride abstraction is similar to what has been observed between Cp*Ru hydrosilyl and cationic silylene complexes.[17]

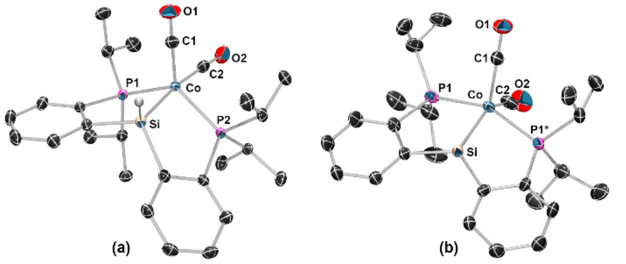
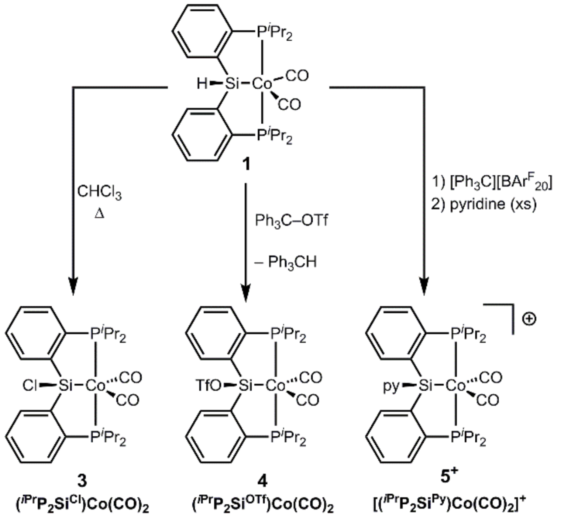


Figure 1. Solid-state structures of (a) hydrosilyl complex **1** and (b) silylene complex **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms (except for Si–*H* in **1**), the BAr^F_{20} anion of **2**, and co-crystallized toluene of **2** are omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Si–Co, 2.2671(7); Co–C1, 1.750(2); Co–C2, 1.760(2); Si–Co–C1, 85.20(7); P1–Co–P2, 128.20(3). For **2**: Si–Co, 2.1207(19); Co–C1, 1.790(8); Co–C2, 1.770(8); Si–Co–C1, 115.1(3); P1–Co–P1*, 156.19(7).

Structural and Electronic Properties of the $(P_2Si)Co$ Series

To build on our understanding of silylene complex **2**, we prepared a series of $(P_2Si^X)Co(CO)_2{}^{n+}$ complexes, with X representing anionic or neutral Lewis bases. The chlorosilyl complex $(^{iPr}P_2Si^{Cl})Co(CO)_2$ (**3**) was synthesized by heating hydrosilyl complex **1** in chloroform at 80 °C for 20 h. The related triflatosilyl complex **4** could be prepared by hydride abstraction from **1** using trityl triflate. Finally, the cationic, pyridine-stabilized silylene complex **5** was synthesized by addition of pyridine to silylene **2** (Scheme 2). Complexes **3**–**5** were isolated as single crystals and analyzed by X-ray crystallography (Figure 2). The Si center in **3**–**5** is pyramidalized (Table 1) to a similar degree, as it is in **1**, and the Co–Si bond lengths are also similar in these four compounds, consistent with a single Co–Si bond.



Scheme 2. Synthesis of complexes **3**–**5**

Complexes **1**–**5** compositionally differ by the nature of the donor attached to the silylene center (where **2** is donor-free). The relative influence of the nature of this donor is apparent from the comparison of the ν_{CO} values (Table 1). Introduction of stronger donors (triflate, pyridine, chloride, hydride) leads to the decrease in the CO stretching frequencies over a range of ca. 70 cm^{-1}, consistent with strong Co→Si π-backbonding in **2** that is progressively attenuated with stronger donors on Si.

Table 1. Key structural and spectroscopic parameters for silyl and silylene complexes **1**–**5**

	1	**2**	**3**	**4**	**5**
∑∠Si[a]	333.6°	360.0°	334.9°	341.7°	340.4°
$d_{Co–Si}$ (Å)	2.2671(7)	2.121(2)	2.2453(6)	2.216(1)	2.223(1)
[calcd]	*[2.276]*	*[2.114]*	*[2.262]*		
δ ^{29}Si	54.8	284.6	93.7	108.8	114.0
[calcd]	*[74]*	*[341]*	*[120]*		
ν_{CO} (cm^{-1})	1958	2028	1970	1987	1990
	1908	1983	1921	1938	1939

[a] ∑∠Si = sum of bond angles around silicon, excluding H (**1**), Cl (**3**), OTf (**4**), or N_{pyr} (**5**).

Since **2** is the first complex of its type on cobalt and a rare example of a stable group 9 silylene, we endeavored to understand the nature of Co–Si bonding and the electronics at silicon using computational methods (see details in the Experimental Section). The molecular structures calculated for **1**, **2** (with the counterion included), and **3** agreed reasonably well with the X-ray data. The calculated ^{29}Si NMR chemical shifts were somewhat higher than the experimental values (Table 1), but in a consistent fashion and confirming the strong downfield shift for **2**. It is common for silylene complexes obtained by abstraction of an α-X anion from a silyl precursor to be highly electrophilic at Si.[1b] In the extreme, these structures can be viewed as metal-substituted silylium cations. Examination of the calculated LUMO of **2** (Figure 2) shows that it is indeed centered primarily on Si, with delocalization into the aromatic rings and some contribution from Co. On the other hand, the Wiberg index[18] for the Co=Si bond in **2** was calculated to be 0.98, notably higher than the 0.74 value obtained for the $[(P_2Si{=})Pt\text{–mesityl}]^+$ complex.[8a] Thus our hypothesis that a monovalent Co should be more capable of π-bonding with the Si center is borne out at least to a modest extent.

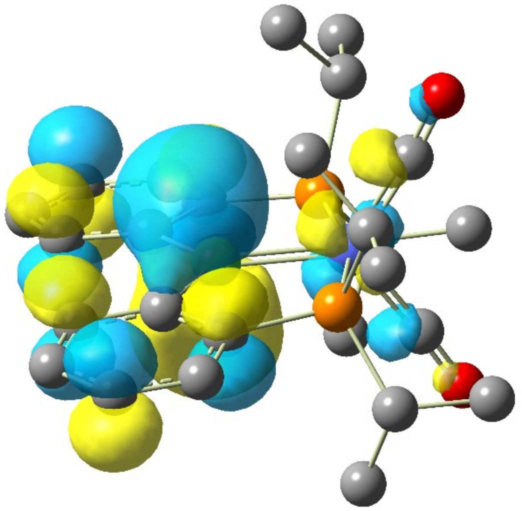


Figure 2. Depiction of the LUMO (isovalue 0.03) of **2**, calculated by M06/SDD/6-31G(d). Hydrogen atoms are omitted for clarity.

O–H Splitting at the Co=Si Bond

The theoretical and experimental studies presented above, combined with many studies on related metal silylene complexes, suggest that the silicon center in **2** should be very electrophilic. A side product was also frequently observed during the reactions **2**, which we attributed to reaction of the acidic silylene cation with trace water. Thus, we report here preliminary reactivity of **2** with ethanol and water in order to understand the interactions of silylene **2** with O–H bonds.

Exposure of **2** to ethanol results in a mixture of two hydride-containing products (^{31}P NMR: δ 96.9 ppm (major) and 99.0 ppm (minor); ^{1}H NMR δ −9.43 (t, $^3J_{PH}$ = 33.7 Hz, major) and −12.38 (t, $^3J_{PH}$ = 38.5 Hz, minor)). Heating the mixture at 50 °C for 1 h leads to complete conversion to the previously minor isomer, which was identified by X-ray crystallography as an ethoxysilyl cobalt hydride, $[(^{iPr}P_2Si^{OEt})CoH(CO)_2][BAr^F_{20}]$ (**6-anti**) with the ethoxy and hydride oriented *anti* to one another (dihedral angle of 178(2)°) (Figure 2). The silyl donor in **6-anti** is pyramidalized, in a manner similar to hydrosilyl complex **1**. The cobalt hydride, which was located in the difference map, bends significantly toward silicon (∠Si–Co–H = 72.3(15)°, d_{SiH} = 2.30(4) Å), consistent with the expected high Lewis acidity of the silyl donor and indicating a weak Si/Co–H interaction (SISHA).[19]

Based on the observations described above, the reaction of **2** with ethanol appears first to afford a complex with ethoxy and hydride oriented *syn* (**6-syn**) as a kinetic product, which isomerizes to the fully characterized *anti* isomer **6-anti** upon heating. Such a reaction course is consistent with the fact that the Lewis-acidic silylene would be expected to react first by coordination of ethanol to silicon, followed by fast proton transfer from ethanol to the cobalt center. Isomerization to **6-anti** occurs readily with only one equivalent of ethanol and thus does not require exogenous ethanol. The expected high acidity of the Co(III) hydride cation with π-accepting carbonyl co-ligands[20] suggests that isomerization may occur by proton transfer, perhaps mediated by solvent, though we cannot rule out Si/H reductive elimination followed by oxidative addition to give the *anti* isomer.

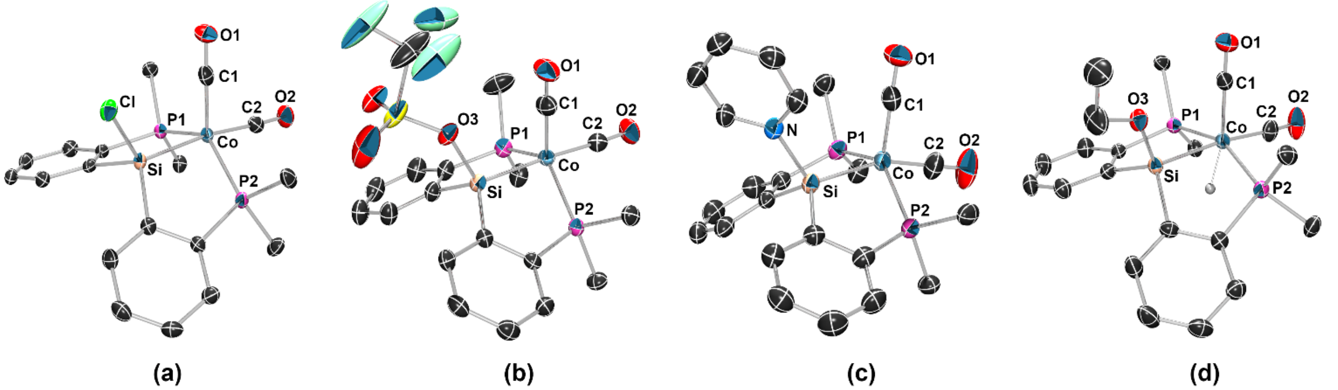
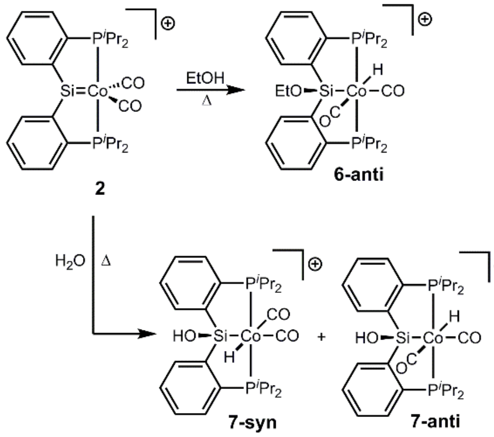


Figure 3. Molecular structures of complexes **3**–**6-anti** (a–d) with thermal ellipsoids at 50% probability and all hydrogen atoms (except for Co–*H* in **6-anti**), counterions (for **5** and **6-anti**), co-crystallized solvent molecules, and portions of the phosphine isopropyl substituents omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**: Co–Si, 2.2453(6); Co–C1, 1.762(2); Co–C2, 1.7715(19); Si–Cl, 2.1189(8); Si–Co–C1, 90.87(6); P1–Co–P2, 133.65(2). For **4**: Co–Si, 2.2163(11); Co–C1, 1.763(4); Co–C2, 1.777(4); Si–O3, 1.797(3); Si–Co–C1, 87.12(14); P1–Co–P2, 132.49(4). For **5**: Co–Si, 2.2229(14); Co–C1, 1.773(5); Co–C2, 1.761(5); Si–N, 1.920(4); Si–Co–C1, 99.71(15); P1–Co–P2, 138.27(5). For **6-anti**: Co–H, 1.43(4); Co–Si, 2.2885(9); Co–C1, 1.805(3); Co–C2, 1.824(3); Si–O3, 1.640(2); Si–Co–H, 72.4(15); Si–Co–C1, 91.20(10); P1–Co–P2, 156.46(4).



Scheme 3. Formation of ethoxy- and hydroxysilyl complexes from silylene **2**

Reaction of silylene **2** with water (≥1 equiv) proceeds with more complexity, initially forming a mixture of three as-yet unidentified hydride-containing intermediates and converging upon heating to a mixture represented by a single, broad ^{31}P NMR signal (δ 99.8 ppm). Further examination by ^{1}H NMR showed the presence of two overlapping Co–*H* signals in a 3:1 ratio. These signals are associated with two singlets (δ 2.86 (major) and 2.34 (minor) ppm) assigned as Si–O*H*, and the presence of silanol functionality is supported by a broad infrared peak at 3618 cm^{-1}.[21] Taking all the spectroscopic data into account, we assign the ultimate products from reacting **2** with water as *syn* and *anti* hydroxysilyl cobalt hydride complexes (Scheme 3). It is not clear at this time whether the *syn* or *anti* isomer is formed as the major product, though analogy with the corresponding ethanol reaction suggests that the *anti* isomer may be favored. The initial course of the reaction of silylene **2** with water is not clear at this point. It is somewhat surprising, based on findings with platinum,[8a] that a silanol (Si–OH) forms rather than a disiloxane (Si–O–Si). Although siloxane intermediates may be present in the reaction, the evidence suggests that under our conditions they are not the thermodynamic products, and they cannot be favored by utilizing less than 1 equiv of water.

Conclusions

In conclusion, we have presented syntheses of a series of pincer-type (P$_2$Si)Co silyl and silylene complexes. The cationic base-free silylene **2** is the first of its type on cobalt. It is isolable and crystallizable, and it reacts readily with pyridine, ethanol, and water. Reaction with ethanol and water leads to heterolytic cleavage of the O–H bond to form a cationic Co(III) hydride complex with alkoxy- or hydroxy-substituted silyl donor. These reactions suggest that further Co/Si cooperative reactivity may be realized for **2** and related pincer-supported silylenes. Such reactivity will be the subject of future studies.

Experimental Section

General Considerations. All manipulations were carried out in an argon- or nitrogen-filled glove box. Routine solvents were purchased from Sigma-Aldrich and were deoxygenated and dried using a Glass Contour Solvent Purification System or PureSolv MD-5 Solvent Purification System and were stored over 4Å molecular sieves in an inert-atmosphere glove box. Ethanol was purchased in dry and degassed form from Sigma-Aldrich and used as received. Fluorobenzene was dried via reflux over CaH$_2$, vacuum-transferred, and stored over 4Å molecular sieves. NMR solvents (Cambridge Isotope Labs) were degassed and vacuum-transferred from sodium/benzophenone (benzene-*d*$_6$ and toluene-*d*$_8$) or refluxed over and vacuum-transferred from CaH$_2$ (dichloromethane-*d*$_2$ and bromobenzene-*d*$_5$), then stored in an argon-filled glove box over 4Å molecular sieves prior to use. All other chemicals were used as received from commercial vendors. The (^{iPr}P$_2$Si)H$_2$ ligand,[8a] Ph$_3$C·BAr$^F_{20}$,[22] and Ph$_3$C·OTf[23] were prepared according to literature procedures. Other reagents were purchased from commercial vendors and used without further purification.

Characterization Methods. NMR spectra were recorded at ambient temperature on a Bruker Avance III HD 400 (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz; ^{19}F, 376.50 MHz; ^{29}Si, 79.50 MHz; ^{31}P, 161.98 MHz) or Varian Inova 500 (^{1}H, 499.68 MHz; ^{13}C, 125.47 MHz; ^{19}F, 470.11 MHz; ^{29}Si, 99.32 MHz; ^{31}P, 202.29 MHz) NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent; ^{19}F, ^{29}Si, and ^{31}P NMR chemical shifts are reported relative to external standards of neat trifluoroacetic acid (−78.55 ppm), tetramethylsilane (0 ppm), and 85% H$_3$PO$_4$ (0 ppm), respectively. All chemical shifts are reported in δ (ppm). Infrared spectra were obtained on an Agilent CARY 630 ATR-FTIR, Mattson 4020 Galaxy Series, or Thermo Scientific Nicolet iS5 FTIR spectrometer. Elemental analyses were performed by CALI Labs, Inc. (Highland Park, NJ) or Midwest Microlab, LLC.

Computational Details. All computations were carried out with the Gaussian09 program.[24] All of the geometries were fully optimized by M06[25] functional. The Stuttgart basis set and the associated effective core potential (ECP) was used for Co atoms, and an all-electron 6-31G(d) basis set was used for the other atoms. Based on the optimized structures, B3LYP/SDD/6-311+G(2d,p) level of theory was then used for the NMR calculation using the GIAO method relative to TMS.

(^{iPr}P$_2$Si^H)Co(CO)$_2$ (1). A 20 mL scintillation vial was charged with Co$_2$(CO)$_8$ (50 mg, 0.15 mmol) and 8 mL toluene. To this was added a solution of the (^{iPr}P$_2$Si)H$_2$ ligand (0.81 mL, 0.36 M in toluene, 0.29 mmol) with stirring, causing a color change from dark brown to bright yellow with bubbling as CO and H$_2$ were evolved. The reaction was allowed to proceed with stirring for 1 h and the volatiles were removed *in vacuo*. The orange residue was dissolved in minimal pentane, filtered, and crystallized at –35 °C to give pure **1** as a crop of yellow/orange crystals suitable for X-ray diffraction. Yield: 92 mg (59%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.91 (d, J = 7.2 Hz, 2H), 7.23 (dd, J_1 = 7.7 Hz, J_2 = 3.0 Hz), 7.18 (td, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H), 7.07 (t, J = 7.5 Hz, 2H), 6.15 (s, $^{1}J_{\mathrm{SiH}}$ = 182 Hz, 1H, Si–*H*), 2.24 (m, 4H), 1.26 (dvt, J_1 = 8.8 Hz, J_2 = 7.0 Hz, 6H), 0.92 (dvt, J_1 = 8.1 Hz, J_2 = 6.8 Hz, 6H), 0.87–0.80 (overlapping dvt, 12H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 120 MHz): δ 220.4 (br s, Co–*C*O), 207.2 (br s, Co–*C*O), 154.1 (quin, J = 30 Hz), 145.2 (dd, J_1 = 22 Hz, J_2 = 20 Hz), 133.3 (t, J = 11 Hz), 129.7, 128.4 (br s, overlap with C$_6$D$_6$), 128.0 (overlap with C$_6$D$_6$), 31.7 (t, J = 15 Hz, P–*C*H–(CH$_3$)$_2$), 29.6 (t, J = 8.6 Hz, P–*C*H–(CH$_3$)$_2$), 19.0 (t, J = 2.4 Hz, *C*H$_3$), 18.84 (s, overlapping), 18.82 (t, J = 2.2 Hz, overlapping), 18.53 (t, J = 1.3 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz): δ 93.8 (br s). ^{29}Si{^{1}H} (C$_6$H$_5$F, 79 MHz): δ 54.8 (t, J_{SiP} = 22 Hz). IR (ATR, cm^{-1}): 2048 (SiH), 1958 (CO), 1908 (CO). Anal. calcd. for C$_{26}$H$_{37}$CoO$_2$P$_2$Si: C, 58.86; H, 7.03. Found: C, 59.16; H, 7.25.

[(^{iPr}P$_2$Si=)Co(CO)$_2$][BAr$^{F}_{20}$] (2). (^{iPr}P$_2$Si^{H})Co(CO)$_2$ (**1**) (31 mg, 0.058 mmol) and trityl tetrakis(pentafluorophenyl)borate (Ph$_3$C•BAr$^{F}_{20}$) (55 mg, 0.060 mmol) were separately dissolved in fluorobenzene (2 mL each), and the Ph$_3$C•BAr$^{F}_{20}$ solution was added dropwise to the solution of **1** with stirring, causing an immediate color change from yellow to red. Pentane (10 mL) was added to precipitate the desired product. The supernatant was removed and the resulting red/orange powder was washed with pentane (3 × 3 mL). Residual pentane was removed *in vacuo* to afford [(^{iPr}P$_2$Si=)Co(CO)$_2$][BAr$^{F}_{20}$] (**2**). Crude yield: 68 mg (94%). The solid could be further purified by crystallization from a toluene:fluorobenzene (3:1) solution at –35 °C. Recrystallized yield (as toluene solvate): 37 mg (49%). ^{1}H NMR (C$_6$D$_5$Br, 500 MHz): δ 7.96 (m, 2H), 7.47 (m, 4H), 2.46 (m, 4H), 0.88-0.75 (m, 24H). ^{13}C{^{1}H} NMR (C$_6$H$_5$F, 120 MHz): For cation portion only. δ 202.0 (br s, Co–*C*O), 149.0 (t, *J* = 22 Hz), 148.0 (t, *J* = 25 Hz), 132.9 (t, *J* = 9 Hz), 132.5 (s), 132.3 (s), 130.4 (s), 28.0 (t, *J* = 12.9 Hz, P–*C*H–(CH$_3$)$_2$), 17.2 (s, *C*H$_3$), 16.3 (s, *C*H$_3$). ^{19}F NMR (C$_6$D$_5$Br, 470 MHz): δ –133.1 (br s, 2F), –163.5 (t, *J* = 21 Hz, 1F), –167.3 (br s, 2F). ^{29}Si{^{1}H} NMR (C$_6$H$_5$F, 99 MHz): δ 284.6 (br s). ^{31}P{^{1}H} NMR (C$_6$D$_5$Br, 202 MHz): δ 105.1. IR (ATR, cm^{-1}): 2028 (CO), 1983 (CO). Anal. calcd. for C$_{50}$H$_{36}$BCoF$_{20}$O$_2$P$_2$Si: C, 49.69; H, 3.00. Found: C, 51.00; H, 2.99. *NOTE:* Microanalysis showed high values for C due to the presence of co-crystallized toluene evident in NMR spectra and the crystal structure of **2**.

(^{iPr}P$_2$Si^{Cl})Co(CO)$_2$ (3). A 20 mL scintillation vial was charged with (^{iPr}P$_2$Si^{H})Co(CO)$_2$ (**1**) (65 mg, 0.12 mmol), 5 mL C$_6$D$_6$, and CDCl$_3$ (ca. 300 μL). The mixture was heated in the sealed vial at 85 °C for 20 h, leading to a gradual change in solution color from yellow to green. Volatiles were removed *in vacuo* and the resulting pale-green powder was washed with cold pentane (3 × 3 mL). The solid was then dried *in vacuo* to afford pure **3**. Yield: 62 mg (90%). Single crystals suitable for X-ray diffraction were grown from a 3:1 pentane:toluene solution at –35 °C. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 8.16 (d, *J* = 7.3 Hz, 2H), 7.22 (m, 4H), 7.08 (t, *J* = 7.3 Hz, 2H), 2.29 (m, 4H), 1.26 (dvt, J_1 = 8.6 Hz, J_2 = 6.8 Hz, 6H), 0.96 (dvt, J_1 = 8.2 Hz, J_2 = 6.9 Hz, 6H), 0.88-0.74 (overlapping dvt, 12H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 120 MHz): δ 219.4 (Co–*C*O), 205.9 (Co–*C*O), 156.0 (m), 144.2 (m), 133.1 (t, *J* = 11 Hz), 130.5 (s), 128.9 (t, *J* = 2 Hz), 32.0 (t, *J* = 15 Hz, P–*C*H–(CH$_3$)$_2$), 29.8 (t, *J* = 10 Hz, P–*C*H–(CH$_3$)$_2$), 19.4 (t, *J* = 2 Hz, *C*H$_3$), 19.0 (s, *C*H$_3$), 18.97 (t, *J* = 2 Hz, *C*H$_3$), 18.8 (br s, *C*H$_3$). ^{29}Si{^{1}H} (C$_6$D$_6$, 99 MHz): δ 93.7 (t, J_{SiP} = 30 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 202 MHz): δ 95.2 (br s). IR (ATR, cm^{-1}): 1970 (CO), 1921 (CO). Anal. calcd. for C$_{36}$H$_{36}$ClCoO$_2$P$_2$Si: C, 55.27; H, 6.42. Found: C, 55.74; H, 6.45.

(^{iPr}P$_2$Si^{OTf})Co(CO)$_2$ (4). (^{iPr}P$_2$Si^{H})Co(CO)$_2$ (**1**) (50 mg, 0.094 mmol) and trityl trifluoromethanesulfonate (Ph$_3$C•OTf; 37 mg, 0.094 mmol) were separately dissolved in dichloromethane (2 mL each), and the Ph$_3$C•OTf solution was added dropwise to the stirring solution of **1**. The reaction mixture was stirred for 5 min and all volatiles were removed *in vacuo*. The resulting oil was washed with cold pentane (3 mL) to remove most of the triphenylmethane byproduct (desired product **4** also has some pentane solubility, so some **4** was lost in this step). The resulting powder was dissolved in minimal pentane and crystallized at −35 °C, affording yellow crystals of analytically pure **4**. Recrystallized yield: 24 mg (38%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 8.55 (dt, J_1 = 7.5 Hz, J_2 = 1.1 Hz, 2H), 7.26 (tdd, J_1 = 7.4 Hz, J_2 = 2.5 Hz, J_3= 1.0 Hz, 2H), 7.20 (m, 2H), 7.07 (m, 2H), 2.25 (m, 4H), 1.24 (dvt, J_1 = 9.5 Hz, J_2 = 6.9 Hz, 6H), 0.93 (dvt, J_1 = 9.1 Hz, J_2 = 6.9 Hz, 6H), 0.83 – 0.66 (m, 12H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 218.1 (br s, Co–*C*O), 204.3, (br s, Co–*C*O), 151.4 (t, *J* = 27 Hz), 145.6 (t, *J* = 22 Hz), 133.6 (t, *J* = 11 Hz), 131.0, 129.8 (t, *J* = 2.7 Hz), 119.4 (q, *J* = 318 Hz, –*C*F$_3$), 31.5 (t, *J* = 15 Hz), 30.3 (t, *J* = 10 Hz), 19.33, 18.91, 18.79, 18.23. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 376.3 MHz): δ –77.3. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 79.5 MHz): δ 108.8 (t, *J* = 34 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 161.9 MHz): δ 96.0. IR (CH$_2$Cl$_2$, cm^{-1}): 1987 (CO), 1938 (CO). Anal. calcd. for C$_{27}$H$_{36}$CoF$_3$O$_5$P$_2$SSi: C, 47.79; H, 5.35. Found: C, 47.73; H, 5.20.

[(^{iPr}P$_2$Si^{Py})Co(CO)$_2$][BAr$^{F}_{20}$] (5). (^{iPr}P$_2$Si^{H})Co(CO)$_2$ (**1**) (60 mg, 0.11 mmol) and trityl tetrakis(pentafluorophenyl)borate (Ph$_3$C•BAr$^{F}_{20}$; 104 mg, 0.11 mmol) were separately dissolved in fluorobenzene (2 mL each), and the Ph$_3$C•BAr$^{F}_{20}$ solution was added dropwise to the stirring fluorobenzene solution of **1**, causing an immediate color change form yellow to red. After 5 min, excess pyridine (ca. 15 μL) was added to the reaction mixture via pipette, causing a color change from red to yellow. Pentane (10 mL) was added with stirring to precipitate the desired product, which was isolated by filtration and washed with pentane (3 × 3 mL) and dried *in vacuo*, affording pure **5**. Yield: 131 mg (89%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 8.23 (tt, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H, pyr *para* C–*H*), 7.99–7.89 (m, 4H), 7.86–7.77 (m, 2H), 7.74–7.61 (m, 6H), 2.91 (m, 2H), 2.59 (m, 2H), 1.38 (dvt, J_1 = 9.9 Hz, J_2 = 6.8 Hz, 6H), 1.15 (dvt, J_1 = 7.4 Hz, J_2 = 6.3 Hz, 6H), 0.91 (overlapping dvt, 12H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz): For cation portion only. δ 215.7 (Co–*C*O), 204.8 (Co–*C*O), 148.9–147.7 (m), 146.7, 145.4, 133.2 (t, *J* = 10 Hz), 132.6, 132.0 , 130.6, 127.6, 31.8 (t, *J* = 11 Hz), 31.4 (t, *J* = 15 Hz), 19.8, 19.3, 19.2, 19.0. ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 376.3 MHz): δ −133.0 (br), –163.5 (t, *J* = 20.4 Hz), –167.4 (t, *J* = 19.6 Hz). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 79.5 MHz): δ 114.0 (t, $^{3}J_{SiP}$ = 34 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161.9 MHz): δ 97.5. IR (CH$_2$Cl$_2$, cm^{-1}): 1990 (CO), 1939 (CO). Anal. calcd. for C$_{55}$H$_{41}$BCoF$_{20}$NO$_2$P$_2$Si: C, 51.30; H, 3.21. Found: C, 51.09; H, 3.21.

[(^{iPr}P$_2$Si^{OEt})Co(H)(CO)$_2$][BAr$^{F}_{20}$] (6). (^{iPr}P$_2$Si^{H})Co(CO)$_2$ (**1**) (40 mg, 0.075 mmol) and trityl tetrakis(pentafluorophenyl)borate (Ph$_3$C•BAr$^{F}_{20}$; 69.6 mg, 0.075 mmol) were separately dissolved in fluorobenzene (2 mL each), and the Ph$_3$C•BAr$^{F}_{20}$ solution was added dropwise to the stirring fluorobenzene solution of **1**. After 5 min, excess ethanol (ca. 15 μL) was added to the reaction mixture via pipette and the mixture was heated at 55 °C for 1 h. Pentane (10 mL) was added to precipitate the desired product, which was isolated by filtration as a pale yellow powder, washed with pentane (3 × 3 mL), and dried *in vacuo* to give pure **6**. Yield: 87 mg (92%). Single crystals suitable for X-ray diffraction were grown from a 3:1 diethyl ether:fluorobenzene solution at −35 °C. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 8.14 (d, *J* = 7.4 Hz, 2H), 7.79 (m, 2H), 7.73 (t, *J* = 7.3 Hz, 2H), 7.66 (t, *J* = 6.7 Hz, 2H), 3.56 (q, *J* = 7.0 Hz, 2H, –OC*H*$_2$CH$_3$), 2.91 (m, 2H), 2.79 (m, 2H), 1.44 (dvt, J_1 = 10.6 Hz, J_2 = 7.4 Hz, 6H), 1.25 (dvt, J_1 = 8.8 Hz, J_2 = 7.4 Hz, 6H), 1.16 (dvt, J_1 = 10.4 Hz, J_2 = 7.0 Hz, 6H), 1.09 (dvt, J_1 = 10.4 Hz, J_2 = 7.1 Hz, 6H), 1.05 (t, *J* = 6.9 Hz, 3H, –OCH$_2$C*H*$_3$), −12.25 (t, *J* = 38.6 Hz, 1H, Co–*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz): For cation portion only (NOTE: Co–*C*O not visible). δ 150.5 (t, *J* = 20 Hz), 139.86 (t, *J* = 27 Hz), 133.4 (t, *J* = 10 Hz), 132.7, 131.5 (t, *J* = 3.9 Hz), 130.0 (t, *J* = 2.9 Hz), 61.5, 31.6 (t, *J* = 16 Hz), 30.8 (t, *J* = 11 Hz), 19.2, 18.8, 18.7, 18.2, 18.1. ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 79.5 MHz): δ 62.4 (t, $^{3}J_{SiP}$ = 9.1 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161.9 MHz): δ 99.2. IR (CH$_2$Cl$_2$, cm^{-1}): 2067 (CO), 2041 (CO). *Note:*

Samples of **6** routinely failed microanalysis, even after recrystallization. However, multinuclear NMR spectroscopy indicates high purity (>97%) for this material.

[($^{iPr}P_2Si^{OH}$)Co(H)(CO)$_2$][BAr$^F_{20}$] (7-syn and 7-anti, mixture of isomers**).** ($^{iPr}P_2Si^H$)Co(CO)$_2$ (**1**) (40 mg, 0.075 mmol) and trityl tetrakis(pentafluorophenyl)borate (Ph$_3$C•BAr$^F_{20}$; 69.6 mg, 0.075 mmol) were separately dissolved in fluorobenzene (2 mL each), and the Ph$_3$C•BAr$^F_{20}$ solution was added dropwise to the stirring fluorobenzene solution of **1**. After 5 min, excess water (ca. 15 μL) was added via pipette and the mixture was heated at 80 °C overnight. Pentane (10 mL) was added to precipitate the desired product, which was isolated by filtration, washed with pentane (3 × 3 mL), and dried *in vacuo* to afford **7** as a pale yellow powder consisting of an approximately 3:1 mixture of two isomers. Analysis of the mixture by ^{1}H NMR (see Figure S30) showed mostly overlapping peaks for the major and minor isomers, so only diagnostic peaks are reported for the minor isomer. ^{1}H NMR of major isomer (CD$_2$Cl$_2$, 400 MHz): δ 8.17 (d, *J* = 7.4 Hz, 2H), 7.83–7.57 (m, 6H), 2.97–2.84 (m, 2H, PC*H*(CH$_3$)$_2$), 2.86 (s, 1H, Si–O*H*), 2.88–2.76 (m, 2H, PC*H*(CH$_3$)$_2$), 1.42 (m, 6H, PCH(C*H*$_3$)$_2$), 1.28 (m, 6H, PCH(C*H*$_3$)$_2$), 1.19 (m, 6H, PCH(C*H*$_3$)$_2$), 1.06 (m, 6H, PCH(C*H*$_3$)$_2$), −12.16 (t, $^2J_{PH}$ = 38.7 Hz, 1H, Co–*H*). Distinct ^{1}H NMR peaks for minor isomer: 2.80–2.68 (m, PC*H*(CH$_3$)$_2$), 2.55–2.42 (m, PC*H*(CH$_3$)$_2$), 2.34 (s, 1H, Si–O*H*), −12.11 (t, $^2J_{PH}$ = 35.8 Hz, 1H, Co–*H*). ^{29}Si{^{1}H} NMR for mixture of isomers (CD$_2$Cl$_2$, 161.9 MHz): δ 62.4 (t, $^3J_{SiP}$ = 9.6 Hz). ^{31}P{^{1}H} NMR for mixture of isomers (CD$_2$Cl$_2$, 161.9 MHz): δ 99.8 (br). IR for mixture of isomers (CH$_2$Cl$_2$, cm^{-1}): 3618 (br, OH of silanol), 2068 (CO), 2038 (CO).

X-ray Crystallography. Single-crystal X-ray diffraction data for compounds **1**–**3** were collected on a Bruker APEX 2 diffractometer using Mo Kα radiation (λ = 0.71073 Å), cooled to 110 K using a cold nitrogen stream (Oxford). Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[26] The integration method employed a three-dimensional profiling algorithm and all data were corrected for *Lp* and decay. Finally, the data were merged and scaled to produce a suitable data set. The absorption correction program SADABS[27] was employed to correct the data for absorption effects. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[28]

Single-crystal X-ray diffraction data for compounds **4**–**6** were collected on a Rigaku XtaLAB mini diffractometer using Mo Kα radiation (λ = 0.71073 Å), cooled to 173 K using a cold air stream provided by an Oxford Cryosystems desktop cooler (Oxford Cryosystems Ltd, Oxford). The crystals were mounted on a MiTeGen micromount (MiTeGen, LLC, Ithaca, NY) using STP oil. The frames were integrated using CrystalClear-SM Expert 3.1 b27[29] to give the *hkl* files corrected for *Lp* and decay. Data were corrected for absorption effects using a multiscan method (REQAB).[29] Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[28]

All structures were solved using SHELXS-2013 and refined using SHELXL-2013 with the Olex2 software package.[30] All non-hydrogen atoms were refined with anisotropic thermal parameters. Cobalt and silicon hydrides were located in the Fourier difference maps and refined isotropically; all other hydrogen atoms were inferred geometrically from neighboring sites and refined with riding thermal parameters. Crystallographic parameters of all complexes are summarized in Table S1. ORTEP drawings were prepared using ORTEP-3 for Windows V2013.1[31] and POV-Ray for Windows v3.6.[32] Crystallographic data for the complexes have been deposited at the Cambridge Crystallographic Data Centre (Nos. 1845823–1845828) and can be obtained free of charge via www.ccdc.cam.ac.uk.

Special Crystallographic Refinement Details. Triflatosilyl complex **4** contained two approximately equivalent molecules in the asymmetric unit, one of which exhibited a triflate that was disordered over two positions. In order to allow suitable refinement, the two triflates were subjected to EADP restraints.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Tabulated X-ray parameters, NMR and IR spectra (PDF)
Computed structures for all compounds studied (ZIP)
Crystallographic information (CIF)

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Notes

The authors declare no competing financial interests.

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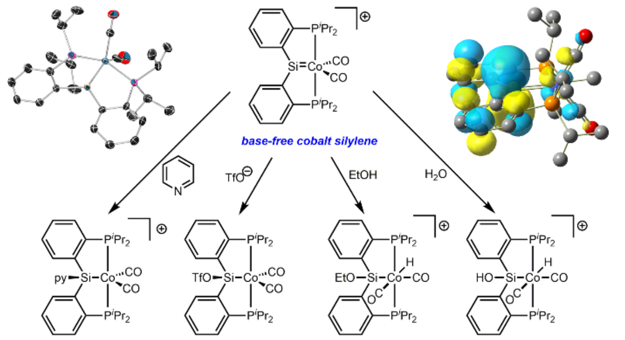
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H2O
py
TfO
EtO
HO
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