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Carbon Dioxide Hydrosilylation Promoted by Cobalt Pincer Complexes

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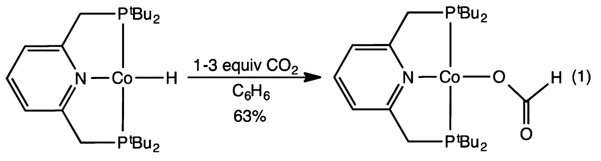
S *Supporting Information*

ABSTRACT: The addition of carbon dioxide to (^{tBu}PNP)CoH [^{tBu}PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine] resulted in rapid insertion into the Co−H bond to form the corresponding κ^1-formate complex, which has been structurally characterized. Treatment of (^{tBu}PNP)CoH with $PhSiH_3$ resulted in oxidative addition to form *trans*-(^{tBu}PNP)$CoH_2(SiH_2Ph)$, which undergoes rapid exchange with excess free silane. With 0.5 mol % (^{tBu}PNP)CoH, the catalytic hydrosilylation of CO_2 with $PhSiH_3$ to a mixture of oligomers containing silyl formate, bis(silyl)acetyl, and silyl ether subunits has been observed.

The hydrosilylation of carbon dioxide (CO_2) promoted by homogeneous transition-metal catalysts is of interest to exploit this renewable resource as a C1 carbon feedstock.[1] The formation of strong Si−O bonds renders CO_2 hydrosilylation more thermodynamically favorable than the analogous hydrogenation reaction.[2] CO_2 hydrosilylation has been promoted by a range of transition metals, including ruthenium,[3] rhodium,[4] iridium,[5] iron,[6] copper,[7] and zinc.[8] Lewis acid catalysts, often in combination with transition metals,[9] and organocatalytic methods[10] have also been reported for the hydrosilylation of CO_2.

Milstein and co-workers and our laboratory have been independently studying the synthesis,[11] oxidative addition reactivity,[12] hydrogen-atom-transfer chemistry,[13] and catalytic performance[14] of bis(phosphino)pyridine pincer-ligated cobalt alkyl and hydride complexes. The four-coordinate cobalt(I) hydride (^{tBu}PNP)CoH is a potentially interesting platform to study fundamental transformations such as insertion of unsaturates. The addition of 1−3 equiv of CO_2 to a benzene solution of (^{tBu}PNP)CoH followed by recrystallization from diethyl ether at −35 °C furnished red crystals identified as the cobalt κ^1-formate complex, (^{tBu}PNP)$Co(CO_2H)$, a rare example derived from the insertion of CO_2 into a Co−H bond (eq 1).[15]



(^{tBu}PNP)CoH **(^{tBu}PNP)Co(CO_2H)**

The benzene-d_6 ^{1}H NMR spectrum of (^{tBu}PNP)$Co(CO_2H)$ exhibited a singlet at 9.81 ppm assigned as the Co-CO_2*H* resonance. In the ^{13}C isotopologue, this peak splits into a doublet with a $^1J_{C-H}$ value of 189 Hz. The ^{13}C NMR resonance was located at 167.1 ppm. The solid-state IR spectrum (KBr) of (^{tBu}PNP)$Co(CO_2H)$ exhibits strong bands centered at 1618 and 1325 cm^{-1}, which shift appropriately to 1570 and 1304 cm^{-1} in (^{tBu}PNP)Co($^{13}CO_2H$). Crystallographic characterization of (^{tBu}PNP)$Co(CO_2H)$ also confirmed κ^1 coordination of the formate (Figure 1, left). The geometry about the cobalt center is best described as square planar with the bond angles about the metal summing to 362.68(18)°.

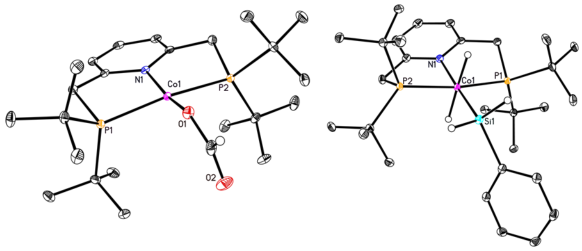


Figure 1. Representation of the molecular structures of (^{tBu}PNP)Co-(CO_2H) (left) and (^{tBu}PNP)$CoH_2(SiH_2Ph)$ (right) at 30% probability ellipsoids. Hydrogen atoms, except those bound to cobalt, silicon, and formate, are omitted for clarity.

Having reduced CO_2 to formate, removal of the [CO_2H] fragment from the coordination sphere of the cobalt was explored. The treatment of a benzene-d_6 solution of (^{tBu}PNP)-$Co(CO_2H)$ with 1 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene under 4 atm of H_2 produced no new resonances over the course of 3 h at 60 °C, as judged by ^{1}H NMR spectroscopy. Likewise, the addition of either Et_3SiH or $(Me_3SiO)_2MeSiH$ to (^{tBu}PNP)Co-(CO_2H) produced no reaction at ambient temperature; heating to 70 °C for 3 h resulted in decomposition. The addition of 3 equiv of the primary silane, $PhSiH_3$ to (^{tBu}PNP)Co($^{13}CO_2H$), resulted in the formation of $PhH_2SiO^{13}CH_2{-}OSiH_2Ph$, identified by its diagnostic ^{13}C NMR resonance at 85.6 ppm and a new cobalt product.[5a] The observation of a broad ^{31}P NMR resonance at 105 ppm along with a triplet at −9.12 ppm in the ^{1}H NMR spectrum identified the cobalt product as *trans*-(^{tBu}PNP)-$CoH_2(SiH_2Ph)$.[12−14] This compound was independently synthesized by the addition of $PhSiH_3$ to (^{tBu}PNP)CoH (eq 2), and the solid-state structure was determined by X-ray diffraction (Figure 1, right).

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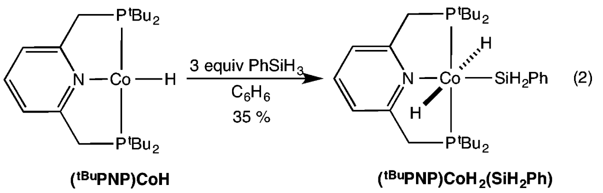
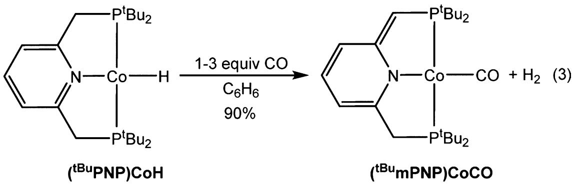


The isolation of *trans*-(^{tBu}PNP)CoH$_2$(SiH$_2$Ph) is noteworthy in light of previous observations with (^{tBu}PNP)CoH. In the presence of 4 atm of H$_2$, broadening of the hydride resonance was observed, establishing the accessibility of (^{tBu}PNP)CoH$_3$; however, sufficiently high H$_2$ pressures were not achieved to fully characterize the putative cobalt(III) species. Thus, silane oxidative addition with (^{tBu}PNP)CoH provides definitive evidence for the accessibility of cobalt(III) with the [(^{tBu}PNP)-Co] platform.

To explore the reversibility of Si−H oxidative addition, reductive coupling, and elimination, exchange spectroscopy experiments were performed. In the presence of 1 equiv of PhSiH$_3$, a 0.04 M benzene-d_6 solution of *trans*-(^{tBu}PNP)-CoH$_2$(SiH$_2$Ph) exhibited cross peaks (295 K, 1.5 s mixing time) between the resonances for the Co−H, Co−SiH$_2$Ph, and free PhSiH$_3$. In the absence of excess silane, the cross peaks between Co−H and Co−SiH$_2$Ph were maintained. These data establish facile Si−H reductive coupling, elimination, and exchange on the NMR time scale at 295 K.

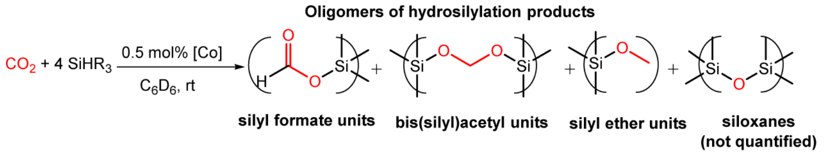
The facile removal of formate from the cobalt coordination sphere with PhSiH$_3$ prompted evaluation of (^{tBu}PNP)CoH as a precatalyst for CO$_2$ hydrosilylation. With 0.5 mol % (^{tBu}PNP)-CoH (relative to ^{13}CO$_2$) and 4 equiv of phenylsilane in benzene-d_6, complete consumption of the ^{13}CO$_2$ gas was observed in 2 h accompanied by the formation of oligomers containing silyl formate, bis(silyl)acetyl, and silyl ether subunits (Table 1). The presence of multiple Si−H bonds per silane molecule resulted in mixtures of oligomeric reduction products.[5c] In an attempt to reduce this complication, PhSiH$_3$ was replaced with Ph$_2$SiH$_2$ and slower catalytic hydrosilyation was observed (entry 2). Use of the cobalt precursor, (^{iPr}PNP)CoNs (Ns = CH$_2$SiMe$_3$) where the phosphorus substituents have been changed from ^{t}Bu to ^{i}Pr, increased the activity and selectivity of the catalytic reaction (entries **3** and **4**).

Monitoring of the catalytic hydrosilylation reactions revealed a dramatic reduction in the catalyst performance over time, suggesting a competing deactivation pathway. To gain insight into this process, a benzene-d_6 solution of (^{tBu}PNP)Co(^{13}CO$_2$H) was heated to 60 °C in the presence of 1 equiv of Ph$_2$SiH$_2$. After filtration to remove cobalt solids formed from decomposition, the ^{1}H NMR spectrum exhibited the number of peaks consistent with a C_s-symmetric compound with inequivalent phosphines. A single methylene resonance was observed along with a vinylic [C−H] doublet at 3.65 ppm, signaling modification of the pincer ligand.[11,13] Analysis by ^{13}C NMR spectroscopy revealed a broad resonance at 208 ppm. Solid-state (KBr) IR spectra exhibited a band at 1880 cm^{-1} in (^{tBu}PNP)Co(CO$_2$H), which shifts to 1836 cm^{-1} in the ^{13}C isotopologue. The combined spectroscopic data establish the formation of (^{tBu}mPNP)Co(CO), a compound that was also independently prepared from carbonylation of (^{tBu}mPNP)Co(N$_2$)[13] or by the addition of 1−3 equiv of CO gas to (^{tBu}PNP)CoH (eq 3).[12] Similar CO-promoted ligand modification has been observed in iridium complexes reported by Milstein and co-workers.[16]



With the spectroscopic signatures of a potential deactivation product in hand, the hydrosilylation reaction mixtures were analyzed by ^{13}C NMR spectroscopy after 26 h of reaction time. A broad ^{13}C NMR resonance signaling the formation of (^{tBu}mPNP)Co(^{13}CO) was observed, identifying ligand modification and CO coordination as a catalyst deactivation pathway.

Table 1. Evaluation of Cobalt and Silane Sources for Catalytic CO$_2$ Hydrosilylation[a]



entry	precatalyst	silane	time (h)	silyl formates[b] (%)	bis(silyl)acetyls[b] (%)	silyl ethers[b] (%)
1	(^{tBu}PNP)CoH	PhSiH$_3$	2	68	27	9
			26	19	63	24
			50	17	62	25
			120	15	63	27
2	(^{tBu}PNP)CoH	Ph$_2$SiH$_2$	2	5[c]	0	0
			26	88	4	11
3	(^{iPr}PNP)CoCH$_2$SiMe$_3$	PhSiH$_3$	2	>99	0	0
			26	>99	0	0
4	(^{iPr}PNP)CoCH$_2$SiMe$_3$	Ph$_2$SiH$_2$	2	>99[c]	0	0
			26	>99	0	0
5	(^{iPr}PNP)CoCH$_2$SiMe$_3$	MD′M[d]	26	0[c]	0	0

[a] See the Supporting Information for detailed experimental conditions. [b] % represents the fraction of the initial ^{13}CO$_2$ in the specified environment, and the values were determined by integration of quantitative ^{13}C NMR spectra relative to a known amount of a mesitylene internal standard. Error bars of approximately ±4% are estimated; see the Supporting Information for full details. [c] Free ^{13}CO$_2$ was also detected. [d] MD′M = (Me$_3$SiO)$_2$MeSiH.

Under catalytic conditions, CO could be generated by formate decarbonylation, as was proposed in iridium catalysis.[5a] To evaluate whether $({}^{tBu}$PNP)CoH also promotes formate decarbonylation, a benzene-d_6 solution of $({}^{tBu}$PNP)CoH was treated with 1 equiv of ethyl formate. With an internal standard, 75% conversion to $({}^{tBu}$mPNP)Co(CO) and ethanol was observed after 24 h. The use of $({}^{tBu}$mPNP)CoN_2 as a CO_2 hydrosilylation precatalyst produced activity similar to that of $({}^{tBu}$PNP)CoH; however, the addition of 2 equiv of CO to the reaction mixture inhibited turnover, producing 13% conversion in 26 h.

In summary, $({}^{tBu}$PNP)CoH has proven to be an effective platform for CO_2 insertion and the oxidative addition of $PhSiH_3$. This complex is also an active precatalyst for CO_2 hydrosilylation, with formate decarbonylation and concomitant pincer modification serving as a catalyst deactivation pathway. These findings should prove useful in the context of catalyst design.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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