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Effective Pincer Cobalt Precatalysts for Lewis Acid Assisted CO₂ Hydrogenation

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Supporting Information

ABSTRACT: The pincer ligand MeN[CH₂CH₂(PⁱPr₂)]₂ (^{iPr}PNP) was employed to support a series of cobalt(I) complexes, which were crystallographically characterized. A cobalt monochloride species, (^{iPr}PNP)CoCl, served as a precursor for the preparation of several cobalt precatalysts for CO₂ hydrogenation, including a cationic dicarbonyl cobalt complex, [(^{iPr}PNP)Co(CO)₂]⁺. When paired with the Lewis



acid lithium triflate, $[({}^{iPr}PNP)Co(CO)_2]^+$ affords turnover numbers near 30 000 (at 1000 psi, 45 °C) for CO₂-to-formate hydrogenation, which is a notable increase in activity from previously reported homogeneous cobalt catalysts. Though mechanistic information regarding the function of the precatalysts remains limited, multiple experiments suggest the active species is a molecular, homogeneous $[({}^{iPr}PNP)Co]$ complex.

■ INTRODUCTION

Growing realization of the deleterious effects of anthropogenic CO_2 emissions has provided considerable incentive to harness and store energy from carbon-neutral sources.¹ Solar energy driven H₂ production from water is one source that has the potential to provide a sustainable and economical fuel.² Along with further advances in water splitting, challenges associated with the storage and transportation of H₂ hinder broader application of this attractive energy vector.² Chemical hydrogen storage (CHS) based on the reversible fixation of H₂ into a lightweight liquid organic carrier molecule may provide a reliable method to surmount these H₂ utilization issues.³ The high gravimetric H₂ content produced from hydrogenation of CO_2 to formic acid (4.4%) and methanol (12.6%; eq 1) make this cheap and renewable carbon source an especially promising CHS target.⁴

$$CO_2 + 3H_2 \rightleftharpoons HCO_2H + 2H_2 \rightleftharpoons CH_3OH + H_2O$$
 (1)

The net hydrogenation of CO_2 to methanol is an exergonic reaction (-2.1 kcal/mol) under standard state conditions, but the hydrogenation to formic acid is slightly unfavorable (+7.6 kcal/mol).⁵ This endergonic intermediate step to formic acid has hindered many thermochemical catalysts in attempts to produce methanol directly from CO2; thus, catalytic hydrogenation to formic acid typically requires an exogenous base or alcohol to trap the product as formate salts, formamides, or esters.⁶ In a few cases, the formate species have been hydrogenated in situ to afford methanol using ruthenium catalysts.⁷ Homogeneous catalytic hydrogenations of CO₂-toformate have largely been the domain of precious metals such as ruthenium,⁸ iridium,⁹ and rhodium.¹⁰ The pincer iridium catalyst [2,6-(PⁱPr₂)₂C₅H₃N]IrH₃, reported by Nozaki and coworkers, is among the most active of these promotors, achieving turnover numbers (TONs) near 3.5×10^6 and

turnover frequencies (TOFs) near 150 000 h^{-1} (49–59 atm; 120–220 °C).¹¹ Though these numbers are impressive, widespread application of CHS methods would be greatly facilitated by the utilization of earth abundant metal catalysts, which are inexpensive and less toxic.

There have been several reports of first-row transition metal catalysts for CO₂-to-formate hydrogenation since the pioneering work of Inoue in 1976.¹² The earliest earth abundant metal catalysts displayed activities far inferior to their precious metal congeners (TON of 5-10) but clearly indicated that first-row transition metals were competent in promoting CO₂ reduction. More recent developments with iron¹³ and cobalt¹⁴ have produced catalysts with far improved activities, reaching TONs in excess of 5000 and 9000 for the two metals, respectively. Our own laboratory has participated in the development of iron pincer catalysts for CO2-to-formate hydrogenation, such as $(^{R}PNP)Fe(H)CO(BH_{4})$ $(^{R}PNP = MeN\{CH_{2}CH_{2}(PR_{2})\}_{2}, R =$ ⁱPr, Cy), which exhibited a modest TON of 2800.¹⁵ However, turnover increased dramatically upon application of Lewis acid (LA) cocatalysts, reaching a TON near 60 000 with the addition of lithium triflate (LiOTf; Figure 1). Mechanistic experiments suggest that the primary role of the LA is to assist



Figure 1. Iron pincer and Lewis acid cocatalyzed CO₂ hydrogenation.

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Figure 3. Synthesis of 1 and its reaction with carbon monoxide.

the dissociation of a formate anion from the iron center, although carboxylate extrusion is still implicated as the turnover limiting step.¹⁵ These insights prompted a new investigation into analogous cobalt catalysts, which may provide a reduced oxophilicity and accelerated formate loss. Herein, we describe the preparation of a family of cobalt pincer precatalysts for CO_2 hydrogenation. These new cobalt species provide TONs far surpassing the state-of-the-art for homogeneous cobalt promotors of CO_2 hydrogenation to formate and establish an important cocatalytic role for LAs in this transformation.

RESULTS AND DISCUSSION

Synthesis and Coordination Chemistry of Cobalt Precatalysts. Recent research reports have described the coordination chemistry and catalytic activity of numerous cobalt pincer complexes supported by formally neutral tridentate ligands.¹⁶ Catalysts derived from secondary amine ^RPN^HP ligands (^RPN^HP = HN{CH₂CH₂(PR₂)}₂) have been prominent among these reports, including the discovery of highly active cobalt promotors of borylation, *N*-alkylation, and reversible hydrogenation and dehydrogenation reactions.¹⁷ Tertiary amine ^RPNP cobalt species have received less investigation, and only a handful of species have been characterized (Figure 2).¹⁸

Our own synthetic experiments were directed toward obtaining ${}^{R}PNP$ cobalt(I) species bearing CO and hydride ligands, in analogy to the successful ^RPNP iron CO₂ hydrogenation catalysts (Figure 1).¹⁵ Initial chelation of ^{iPr}PNP to cobalt was achieved by ligand substitution with (Ph₃P)₃CoCl, affording the deep blue paramagnetic complex, (^{iPr}PNP)CoCl (1; Figure 3). The modest yield (46%) of 1 was primarily due to difficulties in separation from the copious amounts of free PPh₃ generated in the reaction. Complex 1 was characterized by ¹H NMR spectroscopy, combustion analysis, and single-crystal X-ray diffraction. The molecular structure of 1 is presented in Figure 4 with relevant metrical parameters noted in Table 1. The molecular geometry is best described as trigonal pyramidal $(\tau = 0.81)^{19}$ with P(1), P(2), and Cl(1) comprising the basal plane and N(1) as the apical site. This divergence from the more common tetrahedral geometry mirrors that observed for the secondary amine analogue, (^{iPr}PN^HP)CoCl, which was reported by Arnold and coworkers. 17b A solution magnetic moment of μ_{eff} = 2.52 μ_{B}



Figure 4. Molecular structure of $({}^{iPr}PNP)CoCl(1)$ at 30% ellipsoids. All hydrogen atoms were removed for clarity.

Table 1. Selected Bond Distances	(Å) for 1, 2-Cl, 3, and 4
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	1	2-Cl	3	4
Co(1) - N(1)	2.172(3)	2.117(2)	2.091(7)	
Co(1) - P(1)	2.2483(8)	2.2350(4)	2.162(2)	2.1927(5)
Co(1) - P(2)	2.2383(8)		2.166(2)	2.1935(5)
Co(1) - C(1)		1.764(2)	1.742(9)	1.752(2)
Co(1)-X	2.2483(8)	1.744(2)		1.749(2)
	X = Cl(1)	X = C(2)		X = C(2)
C(1) - O(1)		1.152(3)	1.16(1)	1.157(2)
C(2) - O(2)		1.155(3)		1.157(2)

was also measured for 1, which is consistent with a high-spin d^8 electronic structure.

With complex 1 in hand, incorporation of CO and hydride ligands into the cobalt coordination sphere was pursued. Initial attempts to substitute a hydride for the cobalt–chloride bond using various borohydride reagents afforded intractable mixtures of products along with metallic precipitate, suggesting that competing reduction and/or disproportionation reactions dominated. Alternatively, treatment of an ethereal solution of 1 with carbon monoxide rapidly produced a cationic complex, $[({}^{Pr}PNP)Co(CO)_2]Cl$ (2-Cl), as an orange precipitate (Figure 3). Incorporation of strong field carbon monoxide ligands enforced a low-spin, diamagnetic cobalt(I) environment and permitted characterization by NMR spectroscopy as well as

infrared and X-ray diffraction experiments. Samples of 2-Cl exhibited limited solubility in arene and ethereal solvents, but they dissolved well in acetonitrile. The ³¹P NMR spectrum of 2-Cl in this solvent displayed a single resonance at 89.62 ppm, and the ¹H NMR spectrum was highlighted by a singlet at 2.45 ppm assigned to the N-methyl substituent. Solid-state IR spectra exhibited two strong C–O stretching bands at 1913 and 1981 cm⁻¹, which shifted appropriately to 1866 and 1940 cm⁻¹ upon ¹³CO labeling. The molecular structure of 2-Cl was further elucidated by X-ray diffraction (Figure 5; Table 1) and



Figure 5. Molecular structure of $[({}^{iPr}PNP)Co(CO)_2]Cl$ (2-Cl) at 30% ellipsoids. All hydrogen atoms and an outer-sphere chloride anion were removed for clarity.

presented an approximate trigonal bipyramidal geometry with the chloride anion lying far outside the cobalt coordination sphere (>6 Å). The C-O bond distances (1.152(3) and 1.155(3) Å) for the bound carbon monoxide ligands suggest only a modest degree of π -backbonding, consistent with the high-frequency bands observed by infrared analysis. Mindiola and co-workers have reported a related PNP-pincer cobalt(I) dicarbonyl species that displays an analogous geometry and metrical parameters.²⁰ The poor solubility of 2-Cl in most organic solvents also motivated the preparation of a borate congener. This complex, $[({}^{iPr}PNP)Co(CO)_2]BAr_4^F$ (2-BAr₄^F) $(BAr_{4}^{F} = B(3,5-(CF_{3})_{2}C_{6}H_{3})_{4})$, was obtained via a straightforward salt metathesis with $Na[BAr_{4}^{F}]$. The spectroscopic features and X-ray diffraction results for 2-BAr^F₄ were analogous to those of 2-Cl and may be found in the Supporting Information.

The reactivity of **2-Cl** toward substitution of the outer-sphere chloride anion was explored with two borohydride reagents, sodium triethylborohydride and sodium tri-*sec*-butylborohydride (*N*-selectride; Figure 6). The use of either borohydride reagent produced a mixture of two new cobalt(I) hydrides species, (^{iPr}PNP)Co(CO)(H) (3) and (κ^{2-i} PrPNP)Co(CO)₂H (4), with complex 4 favored when employing the more sterically hindered hydride transfer reagent. The two cobalt

products may be separated from the initial reaction mixture through an arduous sequence of recrystallizations and a final Pasteur sorting of the dark orange specimens of 3 from the yellow-green crystals of 4. This method was successfully used to obtain small quantities of analytically pure material; however, the conversion of 3 to 4 through application of additional carbon monoxide is the preferable method to obtain the dicarbonyl cobalt hydride species.²¹ Conversion of 4 to 3 via thermolysis under vacuum occurred only with concurrent decomposition and was not synthetically useful.

The cobalt(I) hydride products were each characterized by a combination of X-ray diffraction, combustion analysis, as well as NMR and IR spectroscopy. The upfield region of the ¹H NMR spectrum of the product mixture in benzene- d_6 exhibited two triplet Co–H resonances, one at -24.82 (for 3) and one at -12.18 ppm (for 4). The corresponding ³¹P {¹H} NMR spectrum displayed two singlet resonances, one each at 80.86 (for 3) and 65.17 ppm (for 4). Infrared analyses performed on isolated samples of 3 revealed strong bands at 1877 and 1836 cm⁻¹, which were assigned as the ν (CoH) and ν (CO) stretches, respectively, on the basis of ¹³CO labeling studies.²¹ Similarly, infrared spectra of 4 exhibited intense ν (CO) bands at 1961 and 1878 cm⁻¹ and a ν (CoH) stretch at 1937 cm⁻¹, with the assignments confirmed by isotopic substitution of the carbonyls.²¹

Single crystals of 3 and 4 suitable for X-ray diffraction were obtained from chilled solutions of hexamethyldisiloxane, and their molecular structures are depicted in Figure 7. Complex 3 exhibits a trigonal bipyramidal geometry similar to 2-Cl, but with the H(1)-Co(1)-N(1) angle $(175(3)^{\circ})$ now defining the central axis. The most notable feature of complex 4 is the change in hapticity of the chelate from κ^3 to κ^2 with dissociation of the N-donor. A closely related hapticity change has been observed by Gray and Wong in cobalt(II) dihalide species when employing a $(PhCH_2)N\{CH_2CH_2(PPh_2)\}_2$ ligand.^{18c} While the origin of the divergent synthesis of 3 and 4 from 2-Cl is uncertain, each species suggests that the amine and CO ligands possess some lability in this cobalt coordination environment. Such flexibility is likely to influence catalytic applications.

Cobalt Precatalyst Activity for CO₂ Hydrogenation. Preparation of a family of $[(^{iPr}PNP)Co]$ complexes provided an opportunity to explore the catalytic hydrogenation of CO₂-to-formate as well as to compare their activities to related iron and cobalt catalysts. Initial catalytic experiments were performed using conditions previously optimized for the iron catalyst (^{iPr}PNP)Fe(H)CO(BH₄), which attained a reported TON of 59 000. Each of the newly prepared $[(^{iPr}PNP)Co]$ complexes were screened using identical conditions with the formate production determined by ¹H NMR spectroscopy. The results are summarized in Table 2.



Figure 6. Preparation and product ratios of 3 and 4 from hydride transfer to 2-Cl.



Figure 7. Molecular structures of $({}^{iPr}PNP)Co(CO)(H)$ (3) (right) and $(\kappa^{2-iPr}PNP)Co(CO)_2H$ (4) (left) at 30% ellipsoids. All hydrogen atoms not attached to cobalt were removed for clarity.

Table 2. CO2 Hydrogenation Promoted by Cobalt Precatalysts^a



^{*a*}Reaction conditions: 1000 psi of CO_2/H_2 (1:1), 0.3 μ mol catalyst, 24 mmol DBU, 4.8 mmol LiOTf in 5 mL of THF at 80 °C for 16 h. ^{*b*}Reported conversions are based on a DBU/formate ratio of 1:1. ^{*c*}Average TON for three or more trials.

Although the conversions under these conditions were modest compared to iron catalysts, many of the precatalysts demonstrated TONs on par with state-of-the-art cobalt catalysts for CO_2 -to-formate hydrogenation.¹⁴ The cobalt(I) monochloride complex 1 was the weakest promotor (entry 1), showing a conversion only modestly above that observed without a catalyst (entry 6). The two dicarbonyl cation complexes 2-Cl and 2-BAr^F₄ exhibited comparable though distinct TONs (given the ± 350 TON standard deviations observed over multiple trials of these experiments). Still, the anion effect for the reaction was quite mild. More notably, removal of the LiOTf cocatalyst nearly inactivated the system (entry 7), indicating that the presence of a LA is critical for this CO₂-to-formate process. The cobalt(I) hydride species 3 and 4 also achieved significant TONs (entries 4 and 5). The relatively small variations in TON and conversion for the carbonylcontaining [(^{*i*Pr}PNP)Co] precatalysts may indicate each species promotes CO₂ hydrogenation through a common catalytic cycle; however, greater mechanistic study will be required to probe this possibility. Given the comparable precatalyst activities and its relative ease of preparation, 2-Cl was selected for further experiments to enhance and understand the conversion of CO₂-to-formate.

The modest yields observed in initial catalytic experiments prompted investigation into the conversion profile for the reaction. Several catalytic trials of varying length were conducted using 2-Cl and the conditions described in Table 2. After 1 h the reaction had produced a TON of 7800, roughly three-quarters of the maximum observed conversion under these conditions (Figure 8). Unfortunately, the prospect for



Figure 8. TON for formate vs time profile for CO₂ hydrogenation.

achieving higher conversion at longer reaction times appeared limited, as trials conducted for 24 h afforded little additional turnover compared to 16 h. These results indicate that degradation of the catalytically active species is a likely cause for the limited conversions.

Solvent effects are often significant for reactions that contain highly polar transition structures, such as CO_2 functionalization or LA components.²² This influence motivated solvent screening for 2-CI/LiOTf catalyzed CO_2 hydrogenation (Table 3). Given the need to dissolve the LiOTf cocatalyst, relatively polar solvents were selected for examination. 1,4dioxane and ethyl acetate both performed well as solvents for CO_2 hydrogenation, providing TONs comparable to those obtained in tetrahydrofuran (THF). The use of a polar protic solvent, ethanol, was highly detrimental to the reaction, as was the use of dichloromethane. Significantly, acetonitrile afforded a more robust TON of 14 000 under these conditions. This activity in acetonitrile was further enhanced by empirical optimization of the LA loading to 3.2 mmol of LiOTf, and Table 3. Solvent Screening for 2-Cl/LiOTf Catalyzed CO_2 Hydrogenation^{*a*}

solvent	TON
THF	10 000 ^b
1,4-dioxane	8600 ^b
acetonitrile	14000^{b}
ethanol	<100
ethyl acetate	8300
dichloromethane	110

^{*a*}Reaction conditions: 1000 psi of CO_2/H_2 (1:1), 0.3 μ mol catalyst, 24 mmol DBU, 4.8 mmol LiOTf in 5 mL of solvent at 80 °C for 16 h. ^{*b*}Average TON for two or more trials.

yielded a TON of 18 000. A nearly complete conversion of >98% (based on a 1,8-diazabicycloundec-7-ene (DBU)/ formate ratio of 1:1) can also be achieved by lowering the DBU to 3 mmol (see Supporting Information).

Having empirically optimized several reagents in the CO_2 hydrogenation reaction, the optimum temperature and pressure were investigated. Unfortunately, all attempts to lower the pressure of CO_2/H_2 below 1000 psi produced inferior TONs, and trials at greater pressure were obviated by safety concerns. However, varying the reaction temperature afforded more favorable results (Table 4). Raising the reaction temperature

 Table 4. Influence of Temperature on 2-Cl/LiOTf Catalyzed

 CO2 Hydrogenation^a

temperature (°C)	TON	TOF $(h^{-1})^{b}$
25	17 000	
45	29 000 ^c	5700 (±280)
60	23 000	
80	18 000 ^c	$12\ 000\ (\pm 280)$
100	10 000	

^{*a*}Reaction conditions: 1000 psi of CO_2/H_2 (1:1), 0.3 μ mol 2-Cl, 24 mmol DBU, 3.2 mmol LiOTf in 5 mL of MeCN for 16 h. ^{*b*}TOF measured after the first hour including temperature equilibration. ^{*c*}Average TON for three or more trials.

had only deleterious effects, but cooling the reaction improved the TON considerably, reaching a maximum of 29 000 at 45

°C. This temperature dependence likely reflects the limited lifetime of the active catalyst (Figure 8), wherein the rate of decomposition is slowed to a greater degree than that of catalysis. At 25 °C the balance between catalyst lifetime and catalytic rate shifts, with the production of formate slowed sufficiently to negate the effects of enhanced catalyst lifetime. The activity of 2-Cl/LiOTf catalyzed CO₂ hydrogenation more than triples the highest previously reported TON for cobalt (9400) described by Linehan and co-workers for (dmpe)₂CoH $(dmpe = Me_2PCH_2CH_2PMe_2)$, though that system operated at ambient temperature using Verkade's base.^{14c,d} The TOF of 2-Cl/LiOTf at 45 °C (5700 \pm 280 h⁻¹) is an order of magnitude lower than the 74 000 \pm 7500 h⁻¹ TOF reported for (dmpe)₂CoH.^{14d} Though these two TOF values were measured over different time scales (which can greatly effect TOF values) it is likely that 2-Cl/LiOTf produces formate more slowly than (dmpe)₂CoH, but does so for a longer time period.

Following our efforts to empirically enhance the 2-Cl/LiOTf catalyzed CO₂-to-formate reaction, some consideration was given to the mechanism of catalysis in hopes of guiding more rationale-based improvements. One possible mechanism based largely on studies of related iron and cobalt catalysts is illustrated in Figure 9.^{14d,15} In this mechanism, CO_2 reduction would occur from insertion into the Co-H bond of 4 (or indirectly from 3), followed by dissociation of the formate anion to generate a cobalt dicarbonyl cation, 2. This insertion could occur from either a direct Co-H nucleophilic attack by the 18-electron complex or via transient dissociation of an ancillary ligand and coordination of CO2. Both insertion pathways have been implicated in transition metal-mediated formate generation.²³ Subsequent coordination of dihydrogen to 2 and deprotonation by DBU would close the cycle.^{13d} This mechanistic hypothesis is appealing, as it combines several elementary reactions that have considerable precedent,^{13,14} proposes two intermediates that have been well-characterized, and would be consistent with the similar TONs observed for precatalysts 2, 3, and 4 (Table 2). Nevertheless, additional evidence for this mechanism has remained elusive.

Initial experiments to probe the proposed mechanism focused on evaluating the interconversion of 2 and 4 though reactions with H₂ and CO₂. To this end, a J. Young NMR tube



Figure 9. Hypothetical mechanism for [(^{iPr}PNP)Co] catalyzed CO₂ hydrogenation.

was charged with 2-Cl in acetronitrile- d_3 and treated with LiOTf (3 equiv) and DBU (8 equiv) under an H_2 atmosphere. The sample was monitored by NMR spectroscopy at ambient temperature over 1 d, where 2-Cl persists as the major diamagnetic species, along with some free ligand (vide infra) and other minor ³¹P NMR resonances. Notably, a set of paramagnetic peaks was also observed in the ¹H NMR spectrum, though no evidence of 4 was found. Heating the sample at 50 °C for several days did afford trace amounts of 4, but this occurred along with general sample decomposition. Likewise, the reduction of CO_2 by 4 was investigated by treating an acetronitrile- d_3 solution of 4 with LiOTf (3 equiv) and a CO₂ atmosphere. However, no evidence of formate formation was observed by NMR spectroscopy even after extended heating. This inability to identify a high-fidelity route for interconversion between 2 and 4 obviates more meaningfully mechanistic conclusions at this time. The proposed mechanism in Figure 9 cannot be discounted with the observations in hand, but clearly more extensive studies, including high-pressure experiments to better mimic catalytic conditions, will be required to further elucidate the catalytic pathway. These investigations are the focus of ongoing work in our laboratory.

Observation of nontrivial amounts of free ^{iPr}PNP ligand during our mechanistic experiments using 2-Cl and 4 brought immediate questions regarding the speciation of the active cobalt catalyst. In particular, it raised the possibility that the $[(^{iPr}PNP)Co]$ precatalysts simply serve as a source of metallic cobalt for a heterogeneous catalytic species instead of a homogeneous molecular catalyst. Distinguishing between homo- or heterogeneous catalytic speciation is rarely a straightforward process.²⁴ Nonetheless, several widely used experiments were conducted to test for evidence of heterogeneity. These experiments were conducted at 80 °C with the expectation that should decomposition to a heterogeneous catalyst occur, it would be more pronounced at higher temperature and thus easier to detect. The results of these experiments are summarized in Table 5. Initial tests

Table 5. Tests for Speciation of Cobalt Catalyzed CO₂ Hydrogenation^{*a*}

CO ₂ +	0.3 μmol	catalyst	H⁺ DBU	
2				
80 °C, 16 h				
entry	catalyst	adulterant	TON	
1	2-Cl		18 000	
2	2-Cl	~1500 equiv of Hg	16 000	
3	2-Cl	0.2 equiv of PMe ₃	16 000	
4	2-Cl	20 equiv of PMe ₃	7000	
5	Co ₂ CO ₈		410	
6	2-Cl	1 equiv of ^{iPr} PNP	21 000	

 a Reaction conditions: 1000 psi of CO_2/H2 (1:1), 0.3 μmol catalyst, 24 mmol DBU, 3.2 mmol LiOTf in 5 mL of MeCN at 80 °C for 16 h.

focused on poisoning experiments using Hg and PMe₃. The addition of excess Hg (~1500 equiv) failed to produce a significant inhibition in catalysis (entry 2) compared to the control reaction (entry 1). This is often consistent with a homogeneous catalyst, though it cannot be taken as irrefutable given the low solubility of cobalt in liquid mercury.²⁵ To augment this test, substoichiometric amounts of PMe₃ were

added as a poison and found to reduce TONs by only a small fraction (entry 3). This suggests that the number of active catalyst sites is nearly equal with the 2-Cl loading, as expected for a homogeneous catalyst. If a particulate catalyst was operative, extensive inhibition would be expected from a substoichiometric poison, as only a small fraction of surface metal sites would be active. In fact, significant amounts of added PMe₃ were required to effect a dramatic reduction in TON (entry 4).

The nature of the active catalytic cobalt species was further probed with additional comparative catalysis. One such experiment employed an alternate cobalt source, Co2CO8 (entry 5), which is a common precursor for the synthesis of various cobalt nanoparticles.²⁶ It is also possible that loss of the chelating ligand from a precatalyst would generate a soluble $H_rCo(CO)_{\nu}$ active species, similar to species invoked in catalytic hydroformylation.²⁷ While Co₂CO₈ produced some turnover for the CO2-to-formate reaction, the TON is far inferior to that observed for 2-Cl and suggests the two systems do not share a common active species.²⁸ Perhaps the strongest evidence that catalysis occurs via a molecular [(^{*i*Pr}PNP)Co] complex came from doping 2-Cl with extra ^{iPr}PNP ligand (entry 6). Supplementing the reaction with 1 equiv of ^{iPr}PNP ligand increased activity, achieving a TON of 21 000. A similar enhancement has been described by Beller and co-workers for related formate dehydrogenation catalysis and presumably originates from stabilization of the chelate-metal complex.² While the precise mechanism of 2-Cl/LiOTf catalyzed CO₂ hydrogenation to formate remains the object of ongoing investigation, the experiments described above strongly suggest that the cobalt precatalysts give rise to a molecular $\left[\left(^{iPr}PNP\right)\right]$ Co] active species.

CONCLUDING REMARKS

The significant activity of 2-Cl and the related cobalt precatalysts provides a substantial step forward in cobaltpromoted CO₂ hydrogenation. Just as significant, these catalytic systems demonstrate yet another example of the remarkable enhancement possible from LA cocatalysts in reversible CO2 hydrogenation catalysis and are the first such example using cobalt.^{15,30} In comparison to prior cobalt catalysis with (dmpe)₂CoH, 2-Cl/LiOTf provides a marked increase in TON (29 000) using a more attractive base (DBU) in contrast to a maximum TON of 9400 using Verkade's base. It should, however, be noted that the 2-Cl/LiOTf system requires more forcing temperature and pressures conditions (1000 psi; 45 °C) when compared to the mild 290 psi; 21 °C conditions employed for (dmpe)₂CoH. In comparison to the ~60 000 TON obtained with [(^{iPr}PNP)Fe] catalyst congeners, 2-Cl/ LiOTf is clearly less productive. Yet the 2-Cl/LiOTf catalysis results do suggest great potential for cobalt in CO2 hydrogenation. The TOF of 5700 (± 280) h⁻¹ (45 °C) observed after the first hour of catalysis and the improved performance at lower temperature suggests the native activity of 2-Cl/LiOTf is quite high, but the system chiefly suffers from poor stability, which limits its overall production. Additionally, further elucidation of the catalytic mechanism could permit improved targeting of precatalysts that activate with higher efficiency and provide enhanced CO₂ hydrogenation. Efforts to achieve these mechanistic insights and further develop [(^RPNP)Co] catalysts are the focus of current work in our laboratory.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using standard vacuum, Schlenk, cannula, or glovebox techniques. Hydrogen, carbon dioxide, and high-purity carbon monoxide were purchased from Airgas and used as received. (Ph₂P)₂CoCl, MeN- $\{CH_2CH_2(P'Pr_2)\}_{2}$, and sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate were prepared as previously described.³¹ All other chemicals were purchased from Aldrich, Fisher, VWR, Strem, or Cambridge Isotope Laboratories. Nonvolatile solids were dried under vacuum at 60 °C for 2 d. DBU was dried over CaH2 and twice distilled prior to use. Solvents were dried and deoxygenated using literature procedures.³² ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker 300 MHz DRX, 500 MHz DRX, or 600 MHz spectrometers at ambient temperature, unless otherwise noted. ¹H and ¹³C chemical shifts are referenced to residual solvent signals; ³¹P chemical shifts are referenced to an external standard of H₃PO₄. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.³³ IR spectra were recorded on a Thermo-Nicolet FTIR. X-ray crystallographic data were collected on a Bruker CCD diffractometer with Mo K α radiation or Cu K α radiation. Samples were collected in inert oil and quickly transferred to a cold gas stream. The structures were solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic calculations were performed using the SHELX programs. Highpressure catalytic CO₂ hydrogenation reactions were performed using a Parr 5500 series compact reactor with glass insert. Elemental analyses were performed at Robertson Microlit Laboratory in Ledgewood, NJ.

Preparation of (^{*Pr*}*PNP*)*CoCl* (1). A 200 mL round-bottom flask was charged with 1.49 g (1.69 mmol) of (Ph₃P)₃CoCl, 649 mg (2.04 mmol, 1.2 equiv) of ^{*Pr*}*PNP*, and ~30 mL of diethyl ether. The reaction was stirred for 1 h at ambient temperature. The resulting green-black solution was filtered through a pad of Celite. The filtrate solution was reduced by half and chilled to -35 °C. After it was cooled for 30 min, an initial crop of royal blue crystals was obtained. The solid was washed with cold pentane (ca. 5 mL) until the eluent was no longer green. A second recrystallization from diethyl ether at -35 °C yielded 323 mg (46%) of analytically pure 1 as blue plates. Higher yields of less pure material may be obtained from extended recrystallization times and subsequent crops of solid. These samples typically contain significant amounts of free PPh₃. ¹H NMR (C₆D₆): δ 64.3, 42.2, 30.4, 15.7, 12.3, 9.8, -0.24, -1.4, -11.7. Anal. Calcd for C₁₇H₃₉ClCoNP₂: C, 49.34; H, 9.50; N, 3.38. Found: C, 49.37; H, 9.61; N, 3.33%. Magnetic susceptibility (Evans method) $\mu_{eff} = 2.52 \mu_{B}$. *Preparation of [(^{Pr}PNP)Co(CO)₂]Cl* (2-Cl). *Method* A: A heavy-

walled glass vessel was charged with 219 mg (0.53 mmol) of (^{iPr}PNP)CoCl and ~15 mL of diethyl ether. On a high-vacuum line, the solution was frozen at -196 °C, and the vessel was pressurized to 400 torr with carbon monoxide. The solution was warmed to ambient temperature and stirred for 1 h giving an orange precipitate with a colorless supernatant. The vessel was degassed, and the precipitate collected by filtration and then washed with \sim 5 mL of diethyl ether. The orange powder was dried in vacuo yielding 242 mg (98%) of 2-Cl. Method B: A heavy-walled glass vessel was charged with 658 mg (0.75 mmol) of (Ph₃P)₃CoCl and ~6 mL of diethyl ether. The brown-green suspension was frozen in a liquid nitrogen chilled cold well, and a solution of 287 mg (0.90 mmol, 1.2 equiv) of "PrPNP in ~3 mL of diethyl ether was slowly added, ensuring that the suspension remained frozen. The vessel was quickly removed from the glovebox and kept frozen at -196 °C. The vessel was evacuated and pressurized to 400 torr with carbon monoxide. The suspension was thawed and stirred at ambient temperature for 4 h, during which time the precipitate changed from brown-green to a vibrant orange. The suspension was filtered through a glass frit and washed with copious amounts of diethyl ether (ca. 12 mL). The orange solid was then washed with ~8 mL of cold THF, or until the filtrate was no longer a dark orange, and then finally with a small quantity of pentane to aid drying. This method yielded 327 mg (93%) of 2-Cl. Anal. Calcd for C19H39ClCoNO2P2: C, 48.57; H, 8.37; N, 2.98. Found: C, 48.29; H,

8.52; N, 2.85%. ¹H NMR (CD₃CN): δ 1.29–1.38 (m, 24H, PCH(CH₃)₂), 2.37–2.43 (m, 2H, PCH₂CH₂N), 2.45 (s, 3H, NCH₃), 2.49–2.54 (m, 2H, PCH₂CH₂N), 2.49–2.54 (m, 2H, PCH(CH₃)₂), 2.77–2.91 (m, 4H, PCH₂CH₂N). ³¹P{¹H} NMR (CD₃CN): δ 89.62 (s). ¹³C{¹H} (CD₃CN): δ 17.59 (PCH(CH₃)₂), 17.83 (PCH(CH₃)₂), 18.36 (PCH(CH₃)₂), 18.55 (PCH(CH₃)₂), 25.75 (NCH₃), 27.26 (t, PCH(CH₃)₂), 27.49 (t, PCH(CH₃)₂), 52.75 (NCH₃), 65.36 (PCH₂CH₂N), 198.28 (CO), 199.12 (CO). IR (KBr): ν_{CO} = 1940, 1866 cm⁻¹.

Preparation of [(^{iPr}PNP)Co(CO)₂]Cl (**2-BAr^F**₄). A 20 mL scintillation vial was charged with 37 mg (0.08 mmol) of 2-Cl and a solution of 70 mg (0.08 mmol) of NaBAr $^{\rm F}_4$ in 5 mL of THF. A clear orange solution was immediately formed and allowed to stir for 1 h at ambient temperature. The solvent was removed in vacuo, and the residue was triturated with pentane to remove traces of ethereal solvent, giving a red-orange solid. The solid was washed with ~3 mL of pentane and then extracted with diethyl ether. The solution was reduced to 2 mL and chilled at -35 °C overnight yielding 47 mg (56%) of 2-BAr^F₄ as large scarlet blocks. Additional recrystallizations from the original supernatant gave a total of 68 mg (82%). Anal. Calcd for C₅₁H₅₁BCoNO₂P₂F₂₄: C, 47.21%; H, 3.96%; N, 1.08%. Found: C, 47.73%; H, 3.84%; N, 1.01% ¹H NMR (CD₂Cl₂): δ 1.31–1.39 (m, 24H, PCH(CH₃)₂), 2.24-2.28 (m, 2H, PCH₂CH₂N), 2.31-2.36 (m, 2H, PCH₂CH₂N), 2.39 (s, 3H, NCH₃), 2.42-2.46 (m, 2H, PCH(CH₃)₂), 2.50–2.56 (m, 2H, PCH(CH₃)₂), 2.71–2.80 (m, 4H, PCH_2CH_2N), 7.56 (s, 4H, $p-CH BAr^{F_4}$), 7.72 (s, 8H, $o-CH BAr^{F_4}$). ¹³C{¹H} NMR (CD₂Cl₂): δ 17.58 (PCH(CH₃)₂), 17.84 (PCH- $(CH_3)_2$, 18.29 (PCH $(CH_3)_2$), 18.58 (PCH $(CH_3)_2$), 24.71 (t, PCH₂CH₂N), 27.09 (m, PCH(CH₃)₂), 52.51 (NCH₃), 65.21 (PCH₂CH₂N), 117.86 (*p*-CH BAr^F₄), 124.99 (q, CF₃), 129.25 (q, *m*-CH BAr^F₄), 135.19 (*o*-CH BAr^F₄), 162.14 (q, C-B), CO resonances not located. ³¹P{¹H} NMR (CD₂Cl₂): δ 88.50 (s). IR (KBr): ν_{CO} = 1996, 1937 cm⁻

Preparation of (^{iPr}PNP)Co(CO)(H) (3). A 20 mL scintillation vial was charged with 105 mg (0.22 mmol) of [(^{iPr}PNP)Co(CO)₂]Cl and ~8 mL of diethyl ether and then frozen in a liquid nitrogen chilled cold well. 225 μ L (0.23 mmol) of 1.0 M Na(Et)₃BH in THF was quickly added to the frozen solution. The reaction was thawed and stirred at ambient temperature for 30 min. The orange suspension initially lightened to yellow-orange before darkening to a cloudy brown-green solution. The diethyl ether was removed in vacuo leaving a brown residue. The residue was triturated with pentane to remove traces of ethereal solvent followed by extraction of a lime-green solution with additional pentane. The removal of solvent in vacuo afforded a dark green oil. Recrystallization with hexamethyldisiloxane yielded 26 mg (29%) of 3 as small dark orange crystals, which often must be manually separated from green crystals of 4. The crystals were quickly washed with minimal amounts of cold hexamethyldisiloxane. Subsequent recrystallization with additional hexamethyldisiloxane may be required to remove all traces of 4. Anal. Calcd for C₁₈H₄₀CoNOP₂: C, 53.07; H, 9.90; N, 3.44. Found: C, 52.90; H, 9.95; N, 3.35%. ¹H NMR (C_6D_6): δ –24.82 (t, 57.1 Hz, 1H, Co-H), 1.06-1.12 (m, 12H, PCH(CH₃)₂), 1.14-1.19 (m, 2H, PCH₂CH₂N), 1.25-1.32 (m, 12H, PCH(CH₃)₂), 1.47-1.53 (m, 2H, PCH₂CH₂N), 1.61–1.67 (m, 2H, PCH(CH₃)₂), 1.77–1.89 (m, 4H, (PCH₂CH₂N), 2.00–2.06 (m, 2H, PCH(CH₃)₂), 2.42 (s, 3H, NCH₃). $^{13}C{^{1}H}$ NMR (C_6D_6) : δ 18.64 (PCH(CH₃)₂), 19.06 (t, (PCH(CH₃)₂), 20.15 (t, (PCH(CH₃)₂), 20.32 (t, (PCH(CH₃)₂), 26.00 (t, PCH₂CH₂N) 26.41 (t, PCH(CH₃)₂) 29.93 (q, PCH(CH₃)₂), 55.06 (NCH₃), 62.96 (t, (t) FCH(CH₃)₂) 25.55 (q) FCH(CH₃)₂), 55.66 (NCH₃), 62.56 (t), PCH₂CH₂N), 211.26 (CO). ³¹P{¹H} NMR (C₆D₆): δ 80.86 (s). IR (KBr): $\nu_{C_0-H} = 1877 \text{ cm}^{-1}$, $\nu_{CO} = 1836 \text{ cm}^{-1}$. Selected data for (^{iPr}PNP)Co(¹³CO)H. ¹H NMR (C₆D₆): -24.82 (dt, ²J_{C-H} = 13.9 Hz, ${}^{2}J_{\rm P-H}$ = 57.1 Hz, 1H, Co-H). IR (KBr): $\nu_{\rm Co-H}$ = 1865 cm⁻¹, $\nu_{\rm CO}$ = 1802 cm^{-1} .

Preparation of ($\kappa^{2-iPr}PNP)Co(CO)_2H$ (4). A 20 mL scintillation vial was charged with 70 mg (0.15 mmol) of [(^{iPr}PNP)Co(CO)_2]Cl and ~5 mL of diethyl ether and then frozen in a liquid nitrogen chilled cold well. 149 μL (0.15 mmol) of 1.0 M in Na(*sec*-butyl)₃BH in THF

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was quickly added to the frozen solution and then allowed to warm to ambient temperature over 20 min. The reaction initially formed an orange-brown suspension, cleared to a dark orange solution, and then finally became a green-brown solution with a white precipitate. The diethyl ether was removed in vacuo, affording a brown residue. The residue was triturated with pentane (ca. 3 mL) to remove traces of ethereal solvent followed by extraction of a light-green solution with additional pentane. Removal of solvent in vacuo afforded a dark green oil, which was dissolved in ~3 mL of diethyl ether and transferred to heavy-walled glass vessel. The green solution was frozen at -196 °C, and the vessel was pressurized with 130 torr of carbon monoxide. The reaction was allowed to thaw and stirred for 2 min, turning a pale orange. The carbon monoxide and diethyl ether were immediately removed in vacuo, and the residue was extracted with pentane to give a yellow solid. Recrystallization with hexamethyldisiloxane at -35 °C overnight initially afforded 31 mg (41%) of 4 as yellow-green crystals of analytically pure material. Prolonged recrystallizations gave a total of 38 mg (58%) with slightly lower purity. Anal. Calcd for C19H40CoNO2P2: C, 52.41; H, 9.26; N, 3.22. Found: C, 52.53; H, 9.09; N, 3.17%. ¹H NMR (C_6D_6): δ –12.18 (t, 41.7 Hz, 1H, Co-H), 1.06 (q, 12H, PCH(CH₃)₂), 1.12 (q, 12H, PCH(CH₃)₂), 1.30-1.34 (m, 4H, (PCH₂CH₂N), 1.76-1.82 (m, 4H, PCH(CH₃)₂), 1.88 (s, 3H, NCH₃), 2.26–2.30 (m, 4H, (PCH₂CH₂N). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): δ 18.52 (PCH(CH₃)₂, 23.54 (t, PCH₂CH₂N), 28.31 (t, PCH(CH₃)₂), 42.73 (NCH₃), 51.47 (PCH₂CH₂N), 214.60 (CO)₂. ³¹P{¹H} NMR $(C_6D_6): \delta 65.17 \text{ (s). IR (KBr)}: \nu_{C_0-H} = 1937 \text{ cm}^{-1}, \nu_{CO} = 1961 \text{ cm}^{-1}, 1878 \text{ cm}^{-1}. \text{ Selected data for } ({}^{1P}\text{PN}^{M}\text{P})\text{Co}({}^{13}\text{CO})_2\text{H}. {}^{1}\text{H} \text{ NMR}$ (C_6D_6) : 12.17 (tt, ${}^2J_{C-H} = 3.7$ Hz, ${}^2J_{P-H} = 41.6$ Hz, 1H, Co-H). IR (KBr): $\nu_{Co-H} = 1932$ cm⁻¹, $\nu_{CO} = 1912$, 1842 cm⁻¹.

General Methods for Catalytic CO₂ Hydrogenation Studies. In a drybox, a 50 mL glass reactor liner was charged with catalyst as a stock solution in acetonitrile (ca. 0.0017 M), a corresponding amount of DBU, LA, and 5 mL of solvent. The cylinder liner was placed into the Parr reactor, and the vessel was sealed. The reactor was removed from the drybox and pressurized with 500 psi of CO₂ followed by an additional 500 psi of H₂ at ambient temperature. The reactor was then heated to the indicated temperature and stirred for the indicated time. The reaction was stirred at an estimated 1000 rmp, based on the manufacturer's indicated maximum stir rate for the vessel. The reaction was stopped by placing the reactor in an ice bath and venting the gases. Using THF (ca. 5 mL) and a minimum of D_2O to rinse, the contents of the reactor were transferred to a 100 mL round-bottom flask, and the volatiles were removed under reduced pressure. Enough D_2O to ensure a freely flowing suspension (ca. 3–5 mL) and 100 μL of dimethylformamide were added as an internal standard for quantification of the formate product by ¹H NMR spectroscopy. The NMR sample was prepared from an aliquot of the cloudy suspension, which was diluted with D2O until fully dissolved.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01454.

Illustrated molecular structure, Lewis acid and DBU data for hydrogenation reactions, time versus TON data for hydrogenation reaction (PDF) X-ray CIF information (TXT)

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Notes

The authors declare no competing financial interest.

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