# **Inorganic Chemistry**

## Hydrogenation of CO<sub>2</sub> at Room Temperature and Low Pressure with a Cobalt Tetraphosphine Catalyst

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**S** Supporting Information

**ABSTRACT:** Large-scale implementation of carbon neutral energy sources such as solar and wind will require the development of energy storage mechanisms. The hydrogenation of CO<sub>2</sub> into formic acid or methanol could function as a means to store energy in a chemical bond. The catalyst reported here operates under low pressure, at room temperature, and in the presence of a base much milder (7 pK<sub>a</sub> units lower) than the previously reported CO<sub>2</sub> hydrogenation catalyst, Co(dmpe)<sub>2</sub>H. The Co(I) tetraphosphine complex, [Co(L3)-(CH<sub>3</sub>CN)]BF<sub>4</sub>, where L3 = 1,5-diphenyl-3,7-bis(diphenylphosphino)-propyl-1,5-diaza-3,7-diphosphacyclooctane (0.31 mM), catalyzes CO<sub>2</sub> hydrogenation with an initial turnover frequency of 150(20) h<sup>-1</sup> at 25 °C, 1.7 atm of a 1:1 mixture of H<sub>2</sub> and CO<sub>2</sub>, and 0.6 M 2-*tert*-butyl-1,1,3,3-tetramethylguanidine.

## INTRODUCTION

The development of catalysts that promote the transformation of  $CO_{22}$  a greenhouse gas, to a chemical fuel or carbon feedstock would help to reduce dependence on fossil fuels. Conversion of renewable hydrogen to a carbon-based fuel could be achieved through the hydrogenation of  $CO_2$  to formate.<sup>1–7</sup> Numerous examples of precious second- and thirdrow transition metal catalysts for  $CO_2$  hydrogenation have been reported.<sup>3,4,8–21</sup> There are fewer known examples of first-row transition metal catalysts for  $CO_2$  hydrogenation; however, this number has been increasing in recent years.<sup>22–45</sup>

Our group is particularly interested in cobalt catalysts for CO<sub>2</sub> hydrogenation. Previously reported cobalt catalysts for CO<sub>2</sub> hydrogenation, in addition to the catalyst reported in this work, are shown in Figure 1. Known examples of cobalt catalysts include a cobalt tetraphosphine catalyst reported by Beller and co-workers.<sup>33,45</sup> This catalyst gave close to 4000 turnovers [turnover number (TON)] of formate after 20 h at 120 °C and 60 atm of a 1:1 H<sub>2</sub>/CO<sub>2</sub> mixture. The cobalt tetraphosphine catalyst can operate at lower temperatures (<100 °C) and pressures (<60 atm), albeit with a reduction in the turnover number. For example, at a 20 atm total pressure and 100 °C, 60 turnovers to formate were obtained after 20 h. More recently, Beller and co-workers reported that a mixture of  $[Co(acac)_3]$  (acac = acetylacetonate), triphos [1,1,1-tris-(diphenylphosphinomethyl)ethane], and  $HNTf_2$  (Tf = trifluoromethanesulfonyl) generates an active catalyst for the hydrogenation of CO2 to methanol at 100 °C.43 Himeda and Fujita have reported a cobalt analogue of their Cp\*Ir(III) catalysts bearing hydroxyl-substituted N donor ligands.<sup>34,46</sup> Though less active than the iridium analogue, a maximal turnover frequency





Figure 1. Previously reported cobalt catalysts for  $CO_2$  hydrogenation and the cobalt catalyst described in this work.

(TOF) of formate of 39 h<sup>-1</sup> at 80–100 °C was obtained using Cp\*Co(4DHBP)L (L = Cl or OH<sub>2</sub>, and DHBP = 6,6'-dihydroxy-2,2'-bipyridine) in 1 M NaHCO<sub>3</sub>.<sup>34</sup> Bernskoetter and co-workers recently reported CO<sub>2</sub> hydrogenation to



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formate using  $[({}^{iP}PNP)Co(CO)_2]^+$   $\{{}^{iP}PNP = MeN-[CH_2CH_2(P^iPr_2)]_2\}$  in the presence of a Lewis acid co-catalyst (lithium triflate).<sup>47</sup> With activity that is similar to that of some of the best precious metal catalysts for CO<sub>2</sub> hydrogenation,<sup>48,49</sup> this catalyst produced >30000 equiv of formate at 1000 psi (68 atm) and 45 °C.

Unlike the cobalt catalysts described above,  $HCo(dmpe)_2$  [dmpe = 1,2-bis(dimethylphosphino)ethane] can hydrogenate CO<sub>2</sub> to formate at 1 atm of pressure and room temperature in the presence of Verkade's base (2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane).<sup>35,36</sup> Turnover frequencies (TOFs) of 3400 h<sup>-1</sup> were achieved with the  $HCo(dmpe)_2$  system, making it one of the fastest catalysts under ambient conditions.<sup>35,36</sup> Though the activity of this catalyst was encouraging, we sought to investigate other potential cobalt—hydride compounds for catalytic CO<sub>2</sub> hydrogenation as Verkade's base is very strong and not compatible with some solvent systems ( $pK_a = 33.6$  for protonated Verkade's base in CH<sub>3</sub>CN).<sup>50</sup>

In this study, we show that a cobalt complex containing a tetradentate phosphine ligand, [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]<sup>+</sup> (Figure 1), is an active catalyst for hydrogenation of  $CO_2$  under ambient conditions. This complex was previously studied for electrocatalytic hydrogen production,<sup>51,52</sup> and the rigid coordination geometry of the tetradentate phosphine ligands was found to play an important role in modulating the thermodynamic properties of the various cobalt-hydride species formed during electrocatalysis. Density functional theory (DFT) calculations predict the hydricity ( $\Delta G^{\circ}_{H^{-}}$ ) of  $HCo^{I}(L3)$  is ~41 kcal/mol in acetonitrile.<sup>52</sup> The hydricity  $(\Delta G^{\circ}_{H^{-}})$  of formate in acetonitrile has been estimated to be 44 kcal/mol,<sup>41,53,54</sup> suggesting that transfer of a hydride from  $HCo^{I}(L3)$  to  $CO_{2}$  should be favorable by 3 kcal/mol. Additionally, the  $pK_{a}$  for  $[(H)_{2}Co^{III}(L3)]^{+}$  was calculated to be ~23 in acetonitrile, which is much lower than the  $pK_a$  of *cis*-[(H)<sub>2</sub>Co(dmpe)<sub>2</sub>]<sup>+</sup> ( $pK_a = 33.7$ ).<sup>52,55</sup> Therefore, we predicted that it should be possible to use a base weaker than Verkade's base for catalytic  $CO_2$  hydrogenation using  $[Co^I(L3) (CH_3CN)$ <sup>+</sup> as a catalyst precursor to HCo<sup>1</sup>(L3). Herein, we report that  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is an active catalyst precursor for the hydrogenation of CO<sub>2</sub> to formate under ambient conditions.

#### RESULTS

**Reactivity and Thermodynamic Studies.**  $[Co^{I}(L3)-(CH_{3}CN)]^{+}$  was synthesized using the reported procedure.<sup>51</sup> In previously reported calculations, the free energy for addition of H<sub>2</sub> ( $\Delta G^{\circ}_{H_2}$ ) to  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  was estimated to be 4– 5 kcal/mol.<sup>52</sup> The ability of  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  to add H<sub>2</sub> was investigated experimentally by pressurizing a CD<sub>3</sub>CN solution of  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  with H<sub>2</sub> (1 atm). An equilibrium between  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  and *trans*- $[(H)_{2}Co^{III}(L3)]^{+}$  was observed by <sup>1</sup>H and <sup>31</sup>P{H} nuclear magnetic resonance (NMR) spectroscopy (eq 1). The



equilibrium constant for the reaction was determined to be 2.1 atm<sup>-1</sup>, corresponding to a  $\Delta G^{\circ}_{H_2}$  of -0.44 kcal/mol (see the Supporting Information for calculations and experimental details). All attempts to isolate *trans*-[(H)<sub>2</sub>Co<sup>III</sup>(L3)]<sup>+</sup> were unsuccessful, as the complex was observed to revert back to [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]<sup>+</sup> upon removal of the H<sub>2</sub> atmosphere.

NMR spectroscopic data are consistent with assignment of the H<sub>2</sub> addition product as *trans*- $[(H)_2Co^{III}(L3)]^+$ , as opposed to a *cis*-dihydride or a dihydrogen complex. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of  $[(H)_2 Co^{III}(L3)]^+$  contains two multiplets at 40.3 and 31.1 ppm, both of which are shifted downfield of [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]<sup>+</sup>. A single upfield resonance is observed as a quintet at -10.09 ppm (2H,  ${}^{2}J_{P-H} = 37.7$  Hz) in the  ${}^{1}H$ NMR spectrum, corresponding to two magnetically equivalent hydride ligands having a similar scalar interaction with the inequivalent phosphorus groups. As noted by Heinekey,<sup>5</sup> dihydrogen ligands display very weak coupling to phosphine ligands  $({}^{2}J_{P-H} < 10 \text{ Hz})$ , a trend that is observed in authentic examples of cobalt dihydrogen complexes.<sup>57-60</sup> No H-D coupling was observed when  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is pressurized with 1 atm of HD instead of H<sub>2</sub>, providing further evidence that the compound is a dihydride complex and not a dihydrogen complex.<sup>61,62</sup> A single resonance is observed in the <sup>1</sup>H NMR spectrum for the PCH<sub>2</sub>N groups of the L3 ligand (see Figure S9), indicating that both six-membered rings of the P<sub>2</sub>N<sub>2</sub> macrocycle are identical on the <sup>1</sup>H NMR time scale. If  $[(H)_2 Co^{III}(L3)]^+$  were a *cis*-dihydride, then the hydride ligands would need a mechanism for rapid interconversion between the top and bottom faces of the L3 macrocycle. A likely mechanism for hydride exchange is rapid loss of  $H_2$  from  $[(H)_2Co^{III}(L3)]^+$ , followed by binding of H<sub>2</sub> on the opposite face of  $[Co^{I}(L3)]$ -(CH<sub>3</sub>CN)]<sup>+</sup>. However, separate resonances are observed for  $[(H)_2Co^{III}(L3)]^+$  and  $[Co^I(L3)(CH_3CN)]^+$ , indicating that these complexes do not exchange rapidly on the NMR time scale. In contrast to a *cis*-dihydride complex, both faces of *trans*- $[(H)_2Co^{III}(L3)]^+$  will be magnetically equivalent, and this complex is most consistent with the observed spectroscopic data

An equilibrium is observed among  $[Co^{I}(L3)(CH_{3}CN)]^{+}$ , trans- $[(H)_2 Co^{III}(L3)]^+$ , and  $HCo^{I}(L3)$  when an  $CD_3 CN$ solution of  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is pressurized with H<sub>2</sub> (1.7 atm) in the presence of 1 equiv of 'BuTMG (2-tert-butyl-1.1.3.3-tetramethylguanidine) (pK, BH<sup>+</sup> in CH<sub>2</sub>CN = 26.5)<sup>37</sup> (Scheme 1).  $HCo^{I}(L3)$  was independently synthesized by addition of potassium triethylborohydride to [Co<sup>I</sup>(L3)-(CH<sub>3</sub>CN)]<sup>+</sup> in tetrahydrofuran (THF). The hydride resonance for HCo<sup>I</sup>(L3) appears as an overlapping doublet of triplets  $(^{2}J_{P-H} = 56 \text{ Hz}, 43 \text{ Hz})$ , indicating that it is coupled to only three of the four phosphorus atoms in the L3 ligand (Figure 2, top). The  ${}^{31}P{}^{1}H$  NMR spectrum of HCo<sup>I</sup>(L3) shows that all four phosphorus atoms of the L3 ligand are inequivalent. Three of the phosphines are coupled to each other (47.4, 34.9, and 12.7 ppm), while one phosphine (33.0 ppm) does not show appreciable coupling to the other phosphines (Figure 2, bottom). Strong coupling is observed between the hydride resonance and the other three phosphorus resonances.

The unusual coupling patterns observed for  $HCo^{I}(L3)$  suggest the complex is distorted due to the geometric constraints of the tetradentate L3 ligand. Previous DFT calculations on  $HCo^{I}(L3)$  indicate the complex is best described as a square pyramidal geometry with one of the terminal PPh<sub>2</sub> groups in the axial position,<sup>52</sup> as indicated by its

Scheme 1. Equilibria between  $[Co^{I}(L3)(CH_{3}CN)]^{+}$ ,  $[Co^{III}(L3)(CH_{3}CN)]^{+}$ , and  $HCo^{I}(L3)$  in the Presence of  $H_{2}$  and  $^{t}BuTMG$ 





**Figure 2.** Hydride region of the <sup>1</sup>H NMR spectrum of HCo<sup>I</sup>(L3) in THF- $d_8$  (top). <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of HCo<sup>I</sup>(L3) in THF- $d_8$  (bottom).

 $\tau_5$  value of 0.12 ( $\tau_5 = 0$  for an ideal square pyramid, and  $\tau_5 = 1$  for an ideal trigonal bipyramid).<sup>63</sup> The calculated H–Co–P<sub>cis</sub> angles are typical for a square pyramid (83–93°), while the H– Co–P<sub>trans</sub> angle of 143° is substantially smaller than the angle of 180° expected for an ideal square pyramid. These geometric parameters suggest the phosphorus *trans* to the hydride ligand is raised out of the equatorial plane, thereby diminishing its level of bonding overlap with the d<sub>z</sub><sup>2</sup> and d<sub>x</sub><sup>2</sup>-y<sup>2</sup></sup> orbitals on cobalt. This geometric effect could account for the lack of coupling between this phosphorus atom and the other ligands in the complex.

The observation of the chemical equilibrium shown in Scheme 1 allows us to determine both the thermodynamic hydricity of HCo<sup>I</sup>(L3) and the  $pK_a$  of *trans*-[(H)<sub>2</sub>Co<sup>III</sup>(L3)]<sup>+</sup> from the equilibrium constants measured by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Using a well-established thermochemical cycle, <sup>53,64</sup> the hydricity of HCo<sup>I</sup>(L3) was determined to be 40.6(4) kcal/mol in CD<sub>3</sub>CN by measuring the equilibrium constant for the formation of HCo(L3) from [Co<sup>I</sup>(L3)-(CH<sub>3</sub>CN)]<sup>+</sup> and H<sub>2</sub> in the presence of two different concentrations of <sup>t</sup>BuTMG (see the Supporting Information for more details). The hydricity of formate in CH<sub>3</sub>CN has been determined to be 44 kcal/mol.<sup>41,53,54</sup> As a result, the transfer of hydride from HCo<sup>I</sup>(L3) to CO<sub>2</sub> is favorable by 3 kcal/mol. The  $pK_a$  of [(H)<sub>2</sub>Co<sup>III</sup>(L3)]<sup>+</sup> was determined to be 26.3(2) from the ratio of HCo<sup>I</sup>(L3) to [(H)<sub>2</sub>Co<sup>III</sup>(L3)]<sup>+</sup> and H[<sup>t</sup>BuTMG]<sup>+</sup> to <sup>t</sup>BuTMG (see the Supporting Information for more details).

**Catalytic CO<sub>2</sub> Hydrogenation.** The CO<sub>2</sub> hydrogenation reactions described in this paper were performed at 25 °C. All reaction mixtures were pressurized with 1.7 atm of a 1:1 H<sub>2</sub>/ CO<sub>2</sub> mixture unless otherwise noted. The activity of  $[Co^{I}(L3)-(CH_{3}CN)]^{+}$  for catalytic CO<sub>2</sub> hydrogenation was examined using several different bases. No reaction was observed with NEt<sub>3</sub> (pK<sub>a</sub> BH<sup>+</sup> in CH<sub>3</sub>CN = 18.8)<sup>65</sup> at 1.7 or 34 atm of a 1:1 H<sub>2</sub>/CO<sub>2</sub> mixture. Catalysis was observed with DBU (1,8diazabicyclo[5.4.0]undec-7-ene), 'BuTMG, and Verkade's base (Table S3). Catalysis using 'BuTMG resulted in more turnovers of formate than using DBU, upon examination under identical conditions in CD<sub>3</sub>CN {0.62 mM  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  and 0.6 M base}. The L3 ligand dissociates in the presence of DBU (see below) prior to the addition of gas and is a likely reason for the inferiority of catalysis in the presence of DBU as the base. The activity in the presence of Verkade's base versus 'BuTMG was examined in THF-*d*<sub>8</sub> under identical conditions {0.62 mM  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  and 0.6 M base}. Again, 'BuTMG was found to be the superior base, though fewer catalytic turnovers were obtained in THF-*d*<sub>8</sub> than in CD<sub>3</sub>CN. All subsequent catalytic reactions were performed in CD<sub>3</sub>CN using 'BuTMG.

The concentration of catalyst was varied from 0.18 to 2.5 mM at a constant concentration of 'BuTMG (0.6 M) and 1.7 atm of a 1:1  $H_2/CO_2$  mixture (Figure S1). Catalysis appears to be limited by mass transfer (gas/liquid mixing) in the NMR tube at catalyst concentrations of >0.31 mM. The catalytic activity was observed to decrease at catalyst concentrations of <0.31 mM, and no catalysis was observed at 0.18 mM due to catalyst deactivation. As a result, we are unable to deduce the reaction order in catalyst.

The dependence on <sup>t</sup>BuTMG was investigated at 1.7 atm of a 1:1  $H_2/CO_2$  mixture with  $[Co^I(L3)(CH_3CN)]^+$  (0.31 mM) by varying the concentration of <sup>t</sup>BuTMG from 0.1 to 0.6 M. The turnover frequency (TOF) for formate production was observed to increase from 43(2)  $h^{-1}$  at 0.1 M base to



Figure 3. Plot showing TOF to formate vs <sup>t</sup>BuTMG concentration (0.1-0.6 M) with 0.31 mM [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]<sup>+</sup> and 1.7 atm of a 1:1 H<sub>2</sub>/CO<sub>2</sub> mixture at 25 °C.

152(17)  $h^{-1}$  at 0.6 M base (Figure 3). From 0.3 to 0.6 M <sup>t</sup>BuTMG, the TOF essentially doubles when deviations are taken into account [from 75(14)  $h^{-1}$  at 0.3 M to 152(17)  $h^{-1}$  at 0.6 M]. This is consistent with a first-order dependence on base concentration. However, a plot of log(TOF) versus log-(concentration of <sup>t</sup>BuTMG) displays a slope of 0.67, which suggests the order in base is less than first-order (Figure S2). These experiments are complicated by the slow, but observable, dissociation of the L3 ligand.

To determine the effect of  $H_2$  and  $CO_2$  on the reaction, catalysis was performed with several different  $H_2/CO_2$  mixtures (1:1, 3:1, and 15:85) (Table 1). The reaction appears to be

Table 1. Average TOFs for Formate Production at Various  $H_2/CO_2$  Ratios<sup>*a*</sup>

entry	$H_2/CO_2$	$H_2 \text{ pressure} \ (atm)$	CO <sub>2</sub> pressure (atm)	average TOF $(h^{-1})$
1	15:85	0.3	1.4	87(6)
2	50:50	0.85	0.85	150(20)
3	75:25	1.3	0.43	180(5)
<sup>a</sup> Using	0.31 mM	$\begin{bmatrix} Co^{I}(I 3) \end{bmatrix} C$	H(CN) <sup>+</sup> and 0.60	M <sup>t</sup> BuTMC in

"Using 0.31 mM  $[Co^{4}(L3)(CH_{3}CN)]^{+}$  and 0.60 M 'BuTMG :  $CD_{3}CN$  at 25 °C and 1.7 atm total pressure.

limited by  $H_2$  at lower  $H_2$  concentrations because the TOF is lower with a 15:85  $H_2/CO_2$  mixture than with the 1:1 or 3:1 mixture. The reaction is accelerated with an increasing  $H_2$ concentration (Figure S3). Gas chromatography (GC) analysis of the headspace gas for catalytic reactions with all  $H_2/CO_2$ ratios showed no presence of CO.

Under optimized conditions {0.31 mM  $[Co^{1}(L3)-(CH_{3}CN)]^{+}$  and 0.6 M <sup>t</sup>BuTMG}, ~270 turnover numbers (TON) of formate were obtained in 3.8 h before catalysis leveled off (Figure 4). To follow the reaction by <sup>31</sup>P{H} NMR



**Figure 4.** Representative kinetic plot showing the formation of formate at 25 °C and 1.7 atm of a 1:1  $H_2/CO_2$  mixture, 0.31 mM  $[Co^1(L3)(CH_3CN)]^+$ , and 0.6 M 'BuTMG in CD<sub>3</sub>CN. The concentration of the formate was determined using <sup>1</sup>H NMR spectroscopy by integrating the formate resonance relative to the residual HOD resonance of the CoCl<sub>2</sub> in D<sub>2</sub>O internal standard. The line is the best linear fit and was used to determine TOF ( $R^2 = 0.99$ ).

spectroscopy, the concentration of  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  had to be increased to 13 mM to allow for adequate signal to noise within a reasonable time frame. When the catalytic reaction was followed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy,  $[Co^{I}(L3)(CH_{3}CN)]^{+}$ and free ligand were the only species observed until all of the base had been consumed, at which point *trans*- $[(H)_{2}Co^{III}(L3)]^{+}$  was also observed. HCo<sup>I</sup>(L3) is detected during catalysis only when using a catalyst concentration of >12 mM and a 3:1 H<sub>2</sub>/CO<sub>2</sub> mixture.

**Catalysis with a Rhodium Analogue.** The prevalence of precious metal CO<sub>2</sub> hydrogenation catalysts<sup>3,4,8–21,46,66,67</sup> prompted us to synthesize a rhodium analogue of  $[Co^{I}(L3)-(CH_{3}CN)]^{+}$ .  $[Rh^{I}(L3)]BF_{4}$  was prepared by slow addition of  $[(\mu-Cl)Rh(COD)]_{2}$  to a stirring suspension of L3 in CH<sub>3</sub>CN (eq 2). The chloride was removed in a salt metathesis reaction with NaBF<sub>4</sub>, affording  $[Rh^{I}(L3)]BF_{4}$  in an overall 91% yield. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of  $[Rh^{I}(L3)]^{+}$  contains two multiplets at 9.78 and -4.81 ppm. Crystals of  $[Rh^{I}(L3)]^{+}$ 



suitable for X-ray diffraction were grown by diffusion of  $Et_2O$  into a  $CH_3CN$  solution of  $[Rh^I(L3)]^+$  (Figure 5). Complex



**Figure 5.** X-ray crystal structure of [Rh<sup>I</sup>(L3)]BF<sub>4</sub>. All hydrogen atoms have been omitted for the sake of clarity. The thermal ellipsoids are shown at 50% probability levels. Selected bond lengths (angstroms): Rh–P1, 2.3079(5); Rh–P2, 2.2486(5); Rh–P3, 2.2598(5); Rh–P4, 2.3044(5). Selected bond angles (degrees): P1–Rh–P2, 87.96(2); P3–Rh–P4, 94.9(2); P1–Rh–P4, 97.57(2); P2–Rh–P3, 80.49(2).

 $[Rh^{I}(L3)]^{+}$  possesses a distorted square planar geometry, with the P02–Rh01–P03 angle being the most acute. The solidstate structure of  $[Rh^{I}(L3)]^{+}$  is similar to that reported for  $[Co^{II}(L3)(CH_{3}CN)]^{2+}$  in that each arm of the L3 ligand forms a six-membered chelate that consists of a phosphorus atom from the P<sub>2</sub>N<sub>2</sub> fragment and one terminal diphenylphosphine.<sup>51</sup> One of the formed P<sub>2</sub>N<sub>2</sub> chelate rings adopts a chair conformation, and the other adopts a boat conformation.

The activity of  $[Rh^{I}(L3)]^{+}$  as a CO<sub>2</sub> hydrogenation catalyst was investigated. HRh(dmpe)<sub>2</sub> was previously determined to be less active as a CO<sub>2</sub> hydrogenation catalyst than HCo(dmpe)<sub>2</sub> is.<sup>36</sup> We anticipated that the same trend would hold for  $[Rh^{I}(L3)]BF_{4}$  and  $[Co^{I}(L3)(NCMe)]^{+}$ . When solutions of  $[Rh^{I}(L3)]^{+}$  (0.32 mM) and either 'BuTMG (0.6 M) or DBU (0.6 M) in CD<sub>3</sub>CN were pressurized with a 1:1 H<sub>2</sub>/CO<sub>2</sub> mixture (1.7–34 atm), more than two turnovers of formate were generated with each base, indicating that  $[Rh^{I}(L3)]^{+}$  is a catalyst (see Table S4). However, the activity of  $[Rh^{I}(L3)]^{+}$  is much lower than that of the cobalt analogue. An initial TOF of 3 h<sup>-1</sup> was observed when using 0.31 mM  $[Rh^{I}(L3)]^{+}$ , 0.6 M



<sup>t</sup>BuTMG, and 1.7 atm of a 1:1  $H_2/CO_2$  mixture, which is ~50 times slower than that with  $[Co^I(L3)(CH_3CN)]^+$  under the same conditions. The activity of  $[Rh^I(L3)]^+$  was also lower than that of  $[Co^I(L3)(CH_3CN)]^+$  when Verkade's base (0.6 M) was utilized in THF- $d_8$  (see Table S4).

Neither the Rh<sup>I</sup> hydride, HRh<sup>I</sup>(L3), nor the Rh<sup>III</sup> dihydride, [(H)<sub>2</sub>Rh<sup>III</sup>(L3)]<sup>+</sup>, was observed by <sup>1</sup>H or <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy during catalysis. Efforts to independently synthesize either of these species by pressurizing [Rh<sup>I</sup>(L3)]<sup>+</sup> with H<sub>2</sub> (1–34 atm) either with or without <sup>t</sup>BuTMG (5 equiv) were unsuccessful. This suggests that addition of H<sub>2</sub> to [Rh<sup>I</sup>(L3)]<sup>+</sup> is energetically uphill. Presumably, both HRh<sup>I</sup>(L3) and [(H)<sub>2</sub>Rh<sup>III</sup>(L3)]<sup>+</sup> are generated during catalysis; however, these species are at concentrations too low to be detected by NMR spectroscopy.

#### DISCUSSION

Several factors should be considered when developing a catalyst for  $CO_2$  hydrogenation. First, the catalyst must have sufficient hydride donor strength (hydricity) to transfer a hydride to  $CO_2$ . The hydricity of formate (the conjugate hydride donor of  $CO_2$ ) has been estimated to be ~44 kcal/mol in acetonitrile.<sup>64</sup> Second, the barrier for H<sub>2</sub> activation needs to be accessible under the reaction conditions employed. Finally, the product of H<sub>2</sub> activation (e.g., a dihydride or dihydrogen complex) must be deprotonated to yield the active hydride donor, which requires a base of suitable strength.

Previously reported DFT calculations<sup>52</sup> suggested that the hydricity of HCo<sup>I</sup>(L3) and the  $pK_a$  of  $[(H)_2Co^{III}(L3)]^+$  would poise this system to be an active catalyst for CO<sub>2</sub> hydrogenation. The experimental results reported in this work confirm this prediction. The hydricity of HCo<sup>I</sup>(L3) was determined experimentally to be 40.6(4) kcal/mol, which is in excellent agreement with the calculated value of 41 kcal/mol. In contrast, the experimentally determined  $pK_a$  of 26.3(2) for *trans*- $[(H)_2Co^{III}(L3)]^+$  is significantly, but not unreasonably, larger than the previously calculated  $pK_a$  of 23.<sup>52</sup>

Spectroscopic evidence suggests that addition of hydrogen to  $[Co^{1}(L3)]^{+}$  results in the formation of *trans*- $[(H)_{2}Co^{III}(L3)]^{+}$ . A *trans*-dihydride configuration is generally less stable than a *cis*-

dihydride geometry in  $[(H)_2 Co^{III}(diphosphine)_2]^+$  complexes;<sup>68</sup> however, the rigid tetradentate L3 ligand precludes formation of *cis*- $[(H)_2 Co^{III}(L3)]^+$  as a stable species. This raises an interesting mechanistic question regarding the formation of *trans*- $[(H)_2 Co^{III}(L3)]^+$ , because oxidative addition of H<sub>2</sub> to square planar d<sup>8</sup> metal complexes normally proceeds by initial formation of a *cis*-dihydride complex.<sup>69</sup> One possibility is that an arm of the tetradentate phosphine can dissociate from the strained *cis*- $[(H)_2 Co^{III}(L3)]^+$  intermediate, thereby allowing the hydride ligands to rearrange to a *trans* configuration.

We believe the catalytic reaction proceeds by the same mechanism as proposed for  $HCo^{I}(dmpe)_{2}$ .<sup>35,36</sup> With  $[Co^{I}(L3)-(CH_{3}CN)]^{+}$  as a starting point,  $H_{2}$  addition gives the  $Co^{III}$  dihydride complex *trans*- $[(H)_{2}Co^{III}(L3)]^{+}$  (Scheme 2). The base then deprotonates the dihydride complex to give  $HCo^{I}(L3)$ , which then transfers a hydride to  $CO_{2}$  to give formate and regenerate  $[Co^{I}(L3)(CH_{3}CN)]^{+}$ . The kinetic studies suggest that the reaction is accelerated with increasing concentrations of base; however, the dependence seems to be less than first order. The catalytic reaction also appears to be limited by  $H_{2}$  addition.

The pendant amines are not likely to serve as proton relays in this reaction because they are not basic enough to deprotonate either *trans*- $[(H)_2Co^{III}(L3)]^+$  or  $HCo^I(L3)$ .<sup>52</sup> However, the presence of the P2N2 ligand in the backbone of the L3 ligand does offer several advantages over other linear tetradentate phosphine ligands such as Ph<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>P(Ph)C<sub>2</sub>H<sub>4</sub>P-(Ph)C<sub>2</sub>H<sub>4</sub>PPh<sub>2</sub>. First, the central phosphorus atoms of classical linear tetraphosphines are chiral, leading to two different ligand diastereomers.<sup>70</sup> Incorporation of the  $P_2N_2$  macrocycle into the L3 ligand removes the chirality of the central phosphines, thereby simplifying the isolation of pure metal complexes. Second, other linear tetraphosphines can easily adopt a trigonal bipyramidal coordination geometry.<sup>70</sup> In the L3 ligand, the  $P_2N_2$  ring fixes the central phosphines in a conformation that disfavors the formation of trigonal bipyramidal metal complexes. This latter feature directly impacts the structure and thermodynamic properties of the cobalt hydride complexes reported in this study. The geometric constraints of the L3 ligand force  $[(H)_2Co^{III}(L3)]^+$  to adopt a *trans*-dihydride

geometry, as opposed to the *cis*-dihydride geometry that is commonly observed in  $[(H)_2Co^{III}(diphosphine)_2]^+$  complexes. Additionally, the rigid L3 ligand causes a distortion of the axial phosphine in HCo<sup>I</sup>(L3).

The use of DBU as a base is deleterious to the catalytic activity of the cobalt system presented here. This is in direct contrast to CO<sub>2</sub> hydrogenation using a copper triphosphine system,  $LCu(CH_3CN)PF_6$ , where L = 1,1,1-tris-(diphenylphosphinomethyl)ethane. In the copper system, the binding of DBU to the metal center enhances catalyst performance.<sup>37,38</sup> The dissociation of the tetradentate L3 ligand was a recurring problem throughout the current CO<sub>2</sub> hydrogenation experiments and appears to be promoted by DBU and by adventitious water. Removal of water from the solvent and the base can be accomplished using standard procedures. The gas mixture being used was found to contain significant water, and an additional drying regime was needed. At low pressures, the gas mixture was dried by passing the gas through a metal loop chilled to -42 °C. However, this approach for drying the gas worked at low pressures only because of the potential for condensing CO<sub>2</sub> at elevated pressures and thereby changing the  $H_2/CO_2$  ratio.

We do not believe that ligand dissociation is leading to the formation of a heterogeneous catalyst because ligand loss shuts down catalysis. Loss of a ligand from cobalt during CO<sub>2</sub> hydrogenation has literature precedent. Bernskoetter and coworkers recently reported a cobalt pincer complex, (<sup>*i*Pr</sup>PNP)-CoCl, that acts as a precatalyst for Lewis acid-assisted CO<sub>2</sub> hydrogenation.<sup>47</sup> Free ligand was observed during mechanistic studies, though heterogeneity tests suggested that the active catalyst is indeed homogeneous.<sup>47</sup> Similarly, ligand loss also contributed to a reduction in the catalytic activity for electrocatalytic hydrogen production using  $[Co^{II}(L3)-(CH_3CN)]^{2+.51,52}$ 

The pK<sub>a</sub> of trans- $[(H)_2 Co^{III}(L3)(NCMe)]^+$  was experimentally determined to be 26.3(2), suggesting that we would be able to at least partially deprotonate trans-[(H)<sub>2</sub>Co<sup>III</sup>(L3)-(NCMe)]<sup>+</sup> with DBU (pK<sub>a</sub> BH<sup>+</sup> = 24.3).<sup>65</sup> DBU is much weaker as a base than Verkade's base  $(pK_a BH^+ = 33.6)$ ,<sup>50</sup> the base necessary for rapid CO<sub>2</sub> hydrogenation with HCo-(dmpe)<sub>2</sub>.<sup>35,36</sup> The results reported in this paper confirm that DBU is of adequate strength to deprotonate trans- $[(H)_2 Co^{III}(L3)]^+$  and allow for catalysis. No catalysis was observed using NEt<sub>3</sub>, which is consistent with the experimentally determined  $pK_a$ . We found that more turnovers of formate were observed when using <sup>t</sup>BuTMG ( $pK_a BH^+ = 26.5$ in CH<sub>3</sub>CN),<sup>37</sup> a base that is stronger than DBU. <sup>t</sup>BuTMG is still a weaker base than Verkade's base, confirming that through careful catalyst system design we can achieve catalytic CO2 hydrogenation under milder conditions.

No carbon monoxide was observed during the catalytic reactions with  $[Co^{I}(L3)(CH_{3}CN)]^{+}$ , denoting that the reverse water gas shift reaction did not occur with this catalyst. Deactivation of  $HCo(dmpe)_2$  to  $[(\mu-dmpe)(Co(dmpe)_2)_2]^{2+}$  and  $[Co(dmpe)_2CO]^{+}$  was observed in catalytic reactions with  $CO_2$ :H<sub>2</sub> ratios of >1.<sup>36</sup> We did not observe these transformations in reaction mixtures containing  $[Co^{I}(L3)-(CH_{3}CN)]^{+}$ .

The observation that  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is a better catalyst than  $[Rh^{I}(L3)]^{+}$  is not entirely unexpected because catalytic CO<sub>2</sub> hydrogenation with HRh(dmpe)<sub>2</sub> was found to be an order of magnitude slower than catalysis with HCo(dmpe)<sub>2</sub>.<sup>36</sup> This difference was attributed to the decrease

in the acidity of the dihydride complex because the  $pK_1$  of rhodium dihydride is higher than that of cobalt dihydride. A second reason why rhodium may not be as good as a catalyst as cobalt is that the hydrogen addition step is much less favorable for rhodium than for cobalt. Unlike for the cobalt complex, we do not observe any hydride products in reactions of  $[Rh^{I}(L3)]^{+}$  with H<sub>2</sub>. Another observation is that we do not detect any ligand dissociation with rhodium as we did for cobalt. One could hypothesize from this observation that  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is a more effective catalyst than the rhodium analogue because one of the arms of the ligand L3 needs to dissociate from the metal during catalysis, but we have no evidence to support or rule out this possibility. Most likely, the higher  $pK_a$  of the rhodium dihydride and the lower reactivity of rhodium with H<sub>2</sub> both contribute to the lower catalytic activity observed for rhodium.

#### SUMMARY AND CONCLUSIONS

We have demonstrated that through careful choice of ligand we were able to design an active CO<sub>2</sub> hydrogenation catalyst. The choice of ligand afforded a decrease in the  $pK_a$  of the cobalt(III) dihydride by 7 p $K_a$  units relative to the values of the previously quantified and reported cobalt catalysts. The Co(I) tetraphosphine complex  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is an active catalyst precursor for CO<sub>2</sub> hydrogenation at room temperature and low pressure in the presence of a base of suitable strength. The reaction appears to be limited by H<sub>2</sub> addition and deprotonation of the resulting cobalt(III) dihydride complex. Consequently, increasing concentrations of base and hydrogen accelerate the reaction. The activity of the catalyst is hampered by the loss of the tetraphosphine ligand and sensitivity to adventitious water. In the presence of [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]<sup>+</sup> (0.31 mM), <sup>t</sup>BuTMG (0.6 M), and 1.7 atm of a 1:1  $H_2/CO_2$ mixture, an initial TOF of 150(20) h<sup>-1</sup> was observed at room temperature. Approximately 270 turnovers were observed under these conditions before death of the catalyst through ligand loss. The catalyst is less active than HCo(dmpe)<sub>2</sub>, but a weaker base can be used. For HCo(dmpe)<sub>2</sub> (0.28 mM), a TOF of 3400 h<sup>-1</sup> was observed when using 1 atm of a 1:1  $H_2/CO_2$ mixture at room temperature in the presence of Verkade's base (570 mM).<sup>35</sup> However, the activity of  $[Co^{I}(L3)(CH_{3}CN)]^{+}$  is comparable to that of  $HCo(dmpe)_2$  in the presence of a weaker base and at higher pressures. When DBU (960 mM) is used instead of Verkade's base, a TOF of 140 h<sup>-1</sup> is observed with  $HCo(dmpe)_2$  (40 mM) and 20 atm of a 1:1  $H_2/CO_2$  mixture at room temperature.<sup>35</sup> A continued focus of our laboratory is the development of transition metal complexes, with an emphasis on first-row metals, for catalysis through analysis of the thermodynamics for each step of the catalytic reaction. In particular, we are using this method to design more efficient catalysts for the catalytic hydrogenation of CO<sub>2</sub>.

## EXPERIMENTAL SECTION

**General Considerations.** Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen using standard Schlenk line and glovebox techniques. Tetrahydrofuran (THF), acetonitrile, diethyl ether, and absolute ethanol were passed through neutral alumina columns using an Innovative Technology, Inc., Pure Solvent solvent purification system, and no further drying techniques were employed. All other reaction solvents were purified and dried according to the literature.<sup>71</sup> Deuterated solvents were purchased from Cambridge Isotope Laboratories. CD<sub>3</sub>CN was dried over P<sub>2</sub>O<sub>5</sub>. THF-*d*<sub>8</sub> was dried over NaK. <sup>t</sup>BuTMG was purchased from Aldrich and dried over BaO. DBU was dried over P<sub>2</sub>O<sub>5</sub> and stored

over activated 3 Å molecular sieves. Karl Fischer titration of DBU dried in this manner contained 20 ppm water. HD was purchased from Cambridge Isotopes Laboratories and used as received. H<sub>2</sub>/CO<sub>2</sub> gas mixtures were purchased from Oxarc and Matheson at the highest quality available. H<sub>2</sub>/CO<sub>2</sub> gas mixtures were passed through an Agilent Oxygen moisture trap (model OT-2-SS) followed by a stainless steel loop in a -42 °C bath before use. All commercially obtained reagents were used as received unless otherwise specified.  $[Co^{II}(L3) (CH_3CN)][BF_4]_2$  and  $[Co^I(L3)(CH_3CN)]BF_4$  were prepared according to the literature.<sup>51</sup> <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Varian Oxford AS500 NMR spectrometer (operating frequency of 126 MHz for <sup>13</sup>C NMR and 202 MHz for <sup>31</sup>P{H} NMR). <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported relative to deuterated solvent signals or an internal reference. <sup>31</sup>P{H} NMR spectra were referenced against an external standard of 0.1% H<sub>2</sub>PO<sub>4</sub> in D<sub>2</sub>O ( $\delta$  = 0 ppm). Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift ( $\delta$ ), multiplicity, coupling constant (hertz), and relative integration. <sup>19</sup>F NMR spectra were recorded on a Varian 500 MHz instrument (470 MHz operating frequency) and are reported relative to the external standard of  $C_6H_5CF_3$  ( $\delta = -63.72$  ppm).

**Caution:** Operators of high-pressure equipment such as that required for these experiments should take proper precautions to minimize the risk of personal injury.

A single crystal of  $[Rh^{I}(L3)]BF_{4}$  was mounted on the tip of a 0.1 mm optical fiber CryoLoop and mounted on a Bruker SMART APEX II CCD Platform diffractometer for data collection at 100.0(2) K.<sup>72</sup> A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was performed using Mo K $\alpha$ radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 4.00 cm. The structure was determined using SHELXS-2013<sup>73</sup> and refined using SHELXL-2014/7.<sup>74</sup> Space group  $P2_1/n$  was determined on the basis of systematic absences and intensity statistics. A direct-methods solution that provided most nonhydrogen atoms from the E-map was calculated. Full matrix leastsquares/difference Fourier cycles that located the remaining nonhydrogen atoms were performed. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least-squares refinement converged to  $R_1 = 0.0370 [F^2, I > 2\sigma(I)]$  and  $wR_2 = 0.0873$  $(F^2$ , all data).

Hydricity and  $pK_a$  Measurement. [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]BF<sub>4</sub> (0.008 g,  $8 \times 10^{-3}$  mmol) was weighed into a J. Young NMR tube. CD<sub>3</sub>CN (400  $\mu$ L) and <sup>t</sup>BuTMG (1.0  $\mu$ L, 8.5 × 10<sup>-3</sup> mmol, 21 mM) were added to the tube to yield a  $[Co^{I}(L3)(CH_{3}CN)]BF_{4}$ concentration of 21 mM. A second tube containing [Co<sup>I</sup>(L3)- $(CH_3CN)$ ]BF<sub>4</sub> (10.1 mM), <sup>t</sup>BuTMG (13.4 mM), and CD<sub>3</sub>CN (400  $\mu$ L) was prepared using a CD<sub>3</sub>CN stock solution of [Co<sup>I</sup>(L3)-(CH<sub>3</sub>CN)]BF<sub>4</sub> and <sup>t</sup>BuTMG. Each tube was subjected to one freezepump-thaw cycle before pressurizing with H<sub>2</sub> (1 atm). The tubes were vortexed for 30 s after addition of  $H_2$ . The reactions were periodically monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy until equilibrium among [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]BF<sub>4</sub>, trans-[(H)<sub>2</sub>Co<sup>III</sup>(L3)]-BF<sub>4</sub>, and HCo<sup>I</sup>(L3) and had been reached. The first tube required 25 days to reach equilibrium, and the second tube required 21 days. The ratios of the three cobalt species were determined from the integration of a quantitative <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, taking into account the number of phosphines per resonance. The <sup>1</sup>H NMR resonances for <sup>t</sup>BuTMG and its conjugate acid are in rapid exchange, which results in full coalescence. The value of [BH<sup>+</sup>]/[B] was determined by the equation  $[BH^+]/[B] = (\delta_{obs} - \delta_B)/(\delta_{BH^+} - \delta_{obs})$ , where  $\delta_{obs}$  is the observed chemical shift,  $\delta_{\rm B}$  is the shift for pure <sup>t</sup>BuTMG, or 2.594 ppm in CD<sub>3</sub>CN, and  $\delta_{BH^+}$  is the shift for pure H[<sup>t</sup>BuTMG]<sup>+</sup>, or 2.937 ppm in  $CD_3CN$ .<sup>37</sup> The heterolysis constant for  $H_2$  is 76.0 kcal/mol in  $CH_3CN$ ,<sup>64</sup> and the pK<sub>a</sub> of H[<sup>t</sup>BuTMG]<sup>+</sup> is 26.5 in CH<sub>3</sub>CN.<sup>37</sup> These equilibrium ratios are listed in Table S2 and were used to calculate a  $\Delta G^{\circ}_{H^{-}}$  of 40.6(4) kcal/mol for HCo<sup>I</sup>(L3) and a pK<sub>a</sub> of 26.3(2) for trans-[(H)<sub>2</sub>Co<sup>III</sup>(L3)]BF<sub>4</sub>. See the Supporting Information for more details.

 $[Rh^{I}(L3)]BF_{4}$ . A solution of  $[(\mu-Cl)Rh(COD)]_{2}$  in CH<sub>3</sub>CN (10 mL) was added dropwise over the course of ~15 min to a suspension of L3 (0.200 g, 0.265 mmol) in CH<sub>3</sub>CN (5 mL). L3 had completely dissolved upon completion of the addition of  $[(\mu-Cl)Rh(COD)]_2$ . The yellow solution was stirred at room temperature for 40 min before the volume of the solvent was decreased to 5 mL under vacuum. Et<sub>2</sub>O (20 mL) was added to precipitate a yellow solid, [Rh(L3)]Cl, that was collected over a frit, washed with Et<sub>2</sub>O (~5 mL), and dried under vacuum. A solution of NaBF<sub>4</sub> (0.023 g, 0.21 mmol) in CH<sub>3</sub>CN (10 mL) was added dropwise to a solution of [Rh(L3)]Cl (0.197 g, 0.221 mmol) in CH<sub>3</sub>CN (15 mL). The slightly turbid yellow solution was left to stir at room temperature for 1 h before the volume of the solvent was decreased to ~5 mL under vacuum. The solution was filtered through a frit containing Celite. Et<sub>2</sub>O (~20 mL) was added to the filtrate. The resulting yellow solid was collected over a frit, washed with Et<sub>2</sub>O (~5 mL), and dried under vacuum (0.181 g, 91% yield). Xray quality crystals were grown at room temperature by vapor diffusion of Et<sub>2</sub>O into a solution of the complex in CH<sub>3</sub>CN. <sup>1</sup>H NMR (499 Hz, 4H, PCH<sub>2</sub>CN), 4.13 (d,  ${}^{2}J_{PH} = 14.4$  Hz, 4H, PCH<sub>2</sub>CN), 2.36 [s, 8H, P(CH<sub>2</sub>)<sub>3</sub>P], 2.20–2.13 [m, 5H, P(CH<sub>2</sub>)<sub>3</sub>P]. <sup>31</sup>P{<sup>1</sup>H} NMR (202) MHz, CD<sub>3</sub>CN): δ 9.78 (m, 2P), -4.81 (m, 2P). <sup>19</sup>F NMR (470 MHz, CD<sub>3</sub>CN):  $\delta$  -152.31 (s, BF<sub>4</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN):  $\delta$ 150.4 (s), 134.8-134.4 (m), 134.0-133.4 (m), 130.7 (s), 130.3 (s), 128.8-128.4 (m), 120.8 (s), 117.3 (s), 54.6-52.2 (m), 31.6-30.9 (m), 23.7-22.5 (m), 20.2 (s). Anal. Calcd For C46H50BF4N2P4Rh. NaCl: C, 58.50; H, 5.34; N, 2.97; Cl, 3.53. Found: C, 54.30; H, 5.40; N, 2.84; Cl, 3.48.

Standard Conditions for Catalysis Using [Co<sup>I</sup>(L<sub>3</sub>)(CH<sub>3</sub>CN)]<sup>+</sup> and <sup>t</sup>BuTMG. In a standard experiment, an 11 mM [Co<sup>I</sup>(L3)-(CH<sub>3</sub>CN)]BF<sub>4</sub> stock solution was prepared by dissolving [Co<sup>I</sup>(L3)-(CH<sub>3</sub>CN)]BF<sub>4</sub> (0.005 g,  $5 \times 10^{-3}$  mmol) in CD<sub>3</sub>CN (500  $\mu$ L). Thirteen microliters of this stock solution was combined with <sup>t</sup>BuTMG (31  $\mu$ L, 2.6 × 10<sup>-1</sup> mmol, 0.6 M) and CD<sub>3</sub>CN (387  $\mu$ L) in a J. Young tube to give a total sample volume of 431  $\mu$ L and a final [Co<sup>I</sup>(L3)(CH<sub>3</sub>CN)]BF<sub>4</sub> concentration of 0.31 mM. A sealed capillary containing a solution of CoCl<sub>2</sub> in D<sub>2</sub>O was added as an integration standard. A <sup>1</sup>H NMR spectrum was acquired before addition of gas. The following parameters were used for all <sup>1</sup>H NMR spectra acquired during the experiment: four transients, 5 s delay time, 2 s acquisition time, 45° pulse width, and a gain of 2. The delay time used for collection of <sup>1</sup>H NMR data was increased until the integration of the same peaks remains unchanged. A 5 s delay time was determined to be sufficient. The gas addition line was purged three times with a  $1:1 \text{ H}_2/$  $CO_2$  mixture (1.7 atm total pressure). The J. Young tube was opened to static vacuum before being pressurized to 1.7 atm. To ensure adequate gas liquid mixing, the tube was vortexed for 30 s after each gas addition. A <sup>1</sup>H NMR spectrum was acquired, and the tube was subsequently repressurized and vortexed. This procedure was repeated at every time point to ensure a constant concentration of the gases over the course of the experiment. Formate production was quantified by integrating the formate resonance (8.7 ppm) relative to the residual HOD in the CoCl<sub>2</sub> in the D<sub>2</sub>O capillary. The concentration of HOD was calibrated by integrating the HOD resonance in a <sup>1</sup>H NMR spectrum of the reaction mixture prior to the addition of the  $H_2/CO_2$ mixture against a selected resonance of base. The TOF was calculated from the linear region of the concentration formate versus time plots. Representative plots of the linear region used to calculate TOF can be found in the Supporting Information. Triplicate data collection was performed.

**Dependence on H<sub>2</sub> and CO<sub>2</sub> Pressure.** The standard CO<sub>2</sub> hydrogenation experiment procedure was performed as described above using a  $3:1 H_2/CO_2$  mixture or a  $15:85 H_2/CO_2$  mixture instead of a  $1:1 H_2/CO_2$  mixture. The total gas pressure was kept at 1.7 atm. The samples were pressurized and monitored by <sup>1</sup>H NMR spectroscopy using the same procedure described above. Triplicate data were collected for each gas mixture.

**Dependence on 'BuTMG.** The standard  $CO_2$  hydrogenation experiment was followed as described above with the following modifications. Thirteen microliters of the  $[Co^{1}(L3)(CH_{3}CN)]BF_{4}$  stock solution was combined with 'BuTMG (0.1, 0.3, or 0.6 M) and  $CD_3CN$  in a J. Young tube to give a total sample volume of 431  $\mu$ L and a final  $[Co^{1}(L3)(CH_{3}CN)]BF_{4}$  concentration of 0.31 mM. The samples were pressurized and monitored by <sup>1</sup>H NMR spectroscopy as described above. Triplicate data were collected at each concentration of 'BuTMG investigated.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01391.

Experimental details, equations used to calculate  $\Delta G^{\circ}$  for  $H_2$  addition,  $\Delta G^{\circ}_{H^{-}}$ , and  $pK_{a}$ , tables and figures of catalytic performance, representative kinetic plots, representative NMR data, and crystallographic data for  $[Rh^{I}(L3)]BF_4$  (PDF)

#### Accession Codes

CCDC 1549802 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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