ACS Catalysis
Research Article
pubs.acs.org/acscatalysis

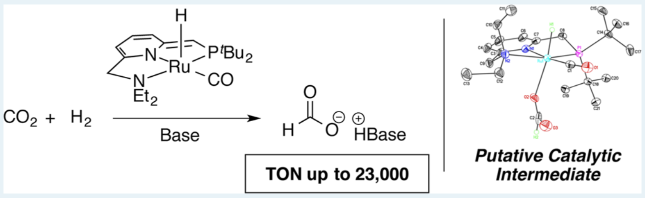
Catalytic CO_2 Hydrogenation to Formate by a Ruthenium Pincer Complex

Chelsea A. Huff and Melanie S. Sanford*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

S Supporting Information

ABSTRACT: This paper reports the hydrogenation of carbon dioxide to formate catalyzed by the Ru pincer complex Ru(PNN)CO(H) (PNN = 6-(di-*tert*-butylphosphinomethylene)-2-(*N*,*N*-diethylaminomethyl)-1,6-dihydropyridine). Stoichiometric studies are presented that support the feasibility of the individual steps in a proposed catalytic cycle for this transformation. The influence of base and solvent on catalyst performance is explored. Overall, under optimized conditions (using diglyme as the solvent and potassium carbonate as the base) up to 23,000 turnovers of formate and a turnover frequency of up to 2,200 h^{-1} can be achieved.



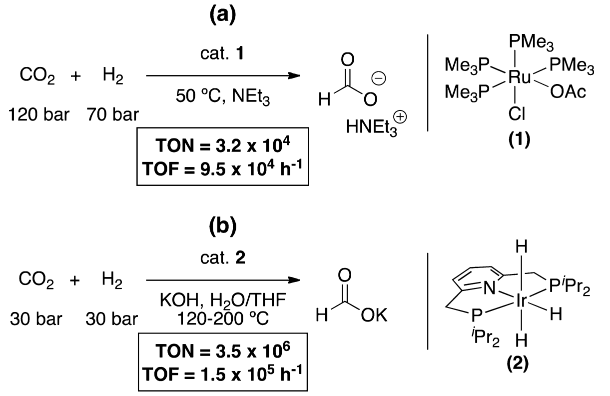
KEYWORDS: *hydrogenation, formic acid, homogeneous catalysis, pincer ligands, ruthenium*

INTRODUCTION

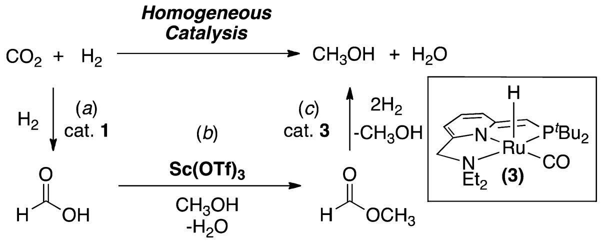
Formic acid (FA) is a commodity chemical that is widely used in agriculture and in the textile and leather industries.[1] The current commercial production of FA involves carbonylation of methanol to yield methyl formate, followed by hydrolysis of methyl formate to produce FA and regenerate MeOH.[1] An attractive alternative route to FA would involve the direct hydrogenation of CO_2. Indeed, significant effort has been directed toward the development of catalysts for CO_2 hydrogenation to FA,[2−4] formate salts,[2−11] formamides,[5−9,12−14] and formate esters.[5−7,12−16] Two of the most active homogeneous CO_2 hydrogenation catalysts reported to date are Jessop's $Ru(PMe_3)_4(Cl)(OAc)$ complex **1**[17] and Nozaki's $Ir(PNP)(H)_3$ [PNP = 2,6-bis-(diisopropylphosphinomethylene)pyridine] pincer catalyst **2** (Scheme 1).[18] Both complexes provide formate from CO_2 in yields representing >10^4 catalytic turnovers and with turnover frequencies in excess of 10^4 h^{-1}.

We recently reported the catalytic reduction of CO_2 to methanol by a cascade sequence that begins with the conversion of CO_2 to FA (Scheme 2, step a).[15] This step is followed by Lewis-acid-catalyzed esterification to provide methyl formate (step b), with subsequent ester hydrogenation to liberate 2 equiv of CH_3OH (step c). We originally utilized Jessop's catalyst **1** for the CO_2 hydrogenation step, in concert with Milstein's Ru pincer complex Ru(PNN)(CO)(H) (**3**)[19−21] as the catalyst for ester hydrogenation. However, since **3** closely resembles Nozaki's Ir pincer catalyst **2**, we hypothesized that it might also be capable of catalyzing CO_2 hydrogenation. Herein, we demonstrate that **3** is an effective catalyst for the conversion of CO_2 to formate in the presence of an appropriate base. Furthermore, we provide insights into divergent mechanistic pathways by which catalyst **3** reacts with CO_2 and H_2.

Scheme 1. Hydrogenation of CO_2 to Formate with (a) Ru Catalyst 1 and (b) Ir Catalyst 2



Scheme 2. Cascade Catalytic Sequence for the Hydrogenation of CO_2 to CH_3OH[15]

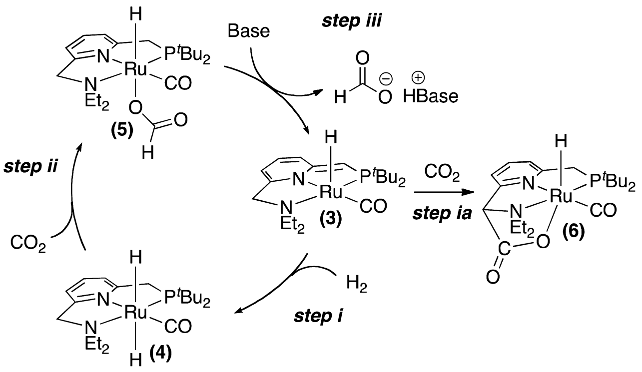


Received: July 26, 2013
Revised: September 5, 2013
Published: September 25, 2013

RESULTS AND DISCUSSION

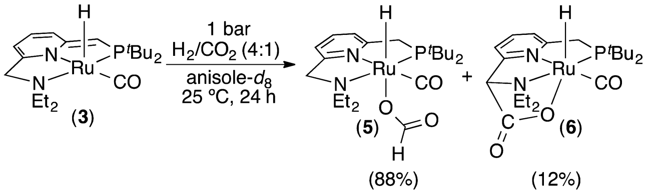
Proposed Catalytic Cycle. By analogy to iridium catalyst **2**,[18] a possible catalytic cycle for reducing CO_2 to formate at complex **3** (Scheme 3) would involve (i) heterolytic cleavage of H_2 to form ruthenium dihydride **4**, (ii) insertion of CO_2 to generate formate complex **5**, and (iii) deprotonation of the pincer ligand of **5** with concomitant release of formate to complete the catalytic cycle.[22−24] Step i of this cycle is well precedented, and has been studied in detail by Milstein and co-workers.[20] In contrast, the feasibility of steps ii and iii has not yet been established for this ruthenium system.

Scheme 3. Possible Catalytic Cycle for CO_2 Hydrogenation to Formate by Complex 3



We began our investigation by treating a solution of **3** in anisole-d_8 with a 4: 1 mixture of H_2 and CO_2 (Scheme 4). This resulted in the conversion of **3** to formate complex **5** in 88% NMR yield after 24 h at room temperature (see Supporting Information, Figure S1), thus establishing the feasibility of steps i and ii of the catalytic cycle proposed in Scheme 3. The identity of **5** was confirmed by independent synthesis, and this complex was characterized using standard one- and two-dimensional NMR spectroscopic techniques[25] as well as X-ray crystallography (Figure 1).[26] The CO_2 adduct **6** (formed by the direct reaction of **3** with CO_2, step ia of Scheme 3)[27−29] was detected as a minor side product in this reaction (12% yield, vide infra for further discussion).

Scheme 4. Reaction of 3 with CO_2 and H_2



We next sought to identify conditions for promoting the final step (iii) of the proposed catalytic cycle. Based on precedent by Nozaki with Ir catalyst **2**,[18] we hypothesized that a strong base could deprotonate the pincer ligand of **5** and induce formate release. Indeed, the treatment of a solution of **5** in anisole-d_8 with 1 equiv of KO^{t}Bu resulted in quantitative formation of **3** and potassium formate as determined by ^{1}H NMR spectroscopic analysis (Scheme 5 and Supporting Information, Figures S2−S3).

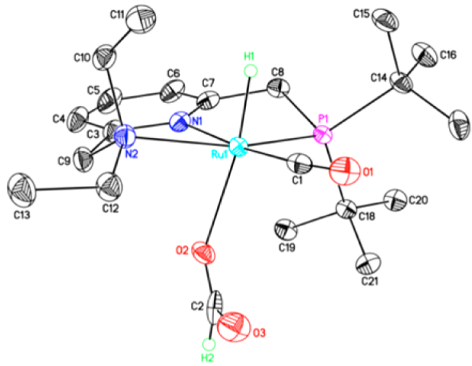
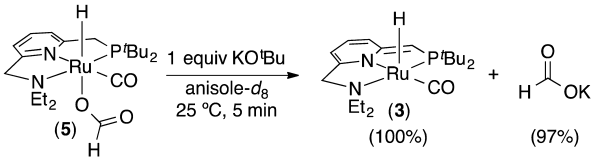


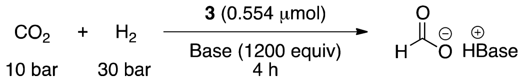
Figure 1. ORTEP diagram (50% probability level) of the molecular drawing of **5**. The packing solvent (benzene) as well as all H atoms (other than the Ru−H and H−COO) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−H1 = 1.45(3), Ru1−N1 = 2.0983(18), Ru1−N2 = 2.2535(18), Ru1−O2 = 2.2497(16), Ru1−C1 = 1.834(2), Ru1−P1 = 2.2626(5), O2−C2 = 1.203(3), O3−C2 = 1.283(3); H1−Ru1−O2 = 169.2(10); P1−Ru1−N2 = 158.83(5); N1−Ru1−O2 = 82.67(7), N2−Ru1−O2 = 83.88(6).

Scheme 5. Deprotonation of 5 by KO^{t}Bu to Form 3 and HCOOK



Catalytic Hydrogenation of CO_2. The results in Schemes 4 and 5 demonstrate the feasibility of all three individual steps of the proposed **3**-catalyzed hydrogenation of CO_2 to formate. To combine these steps to achieve catalysis, we initially treated **3** with 10 bar CO_2 and 30 bar H_2 in the presence of 1200 equiv of KO^{t}Bu in anisole at room temperature, conditions analogous to those of the stoichiometric reactions in Schemes 4 and 5 (Table 1, entry 1). The turnover number (TON) for this reaction was determined based on the yield of formate after 4 h as a preliminary estimate of catalyst reactivity (see Supporting Information, Figure S4 for a representative ^{1}H NMR spectrum). Catalysis was sluggish under these initial conditions,

Table 1. Hydrogenation of CO_2 to Formate Catalyzed by 3[a]



entry	solvent	temp (°C)	base	TON formate
1	anisole	25	KO^{t}Bu	7
2	anisole	120	KO^{t}Bu	270
3	diglyme	120	KO^{t}Bu	800
4	diglyme	120	K_2CO_3	1,100
5[b]	diglyme	120	KOH	510
6	diglyme	120	K_3PO_4	900
7	diglyme	120	$KHCO_3$	550
8	diglyme	120	NEt_3	<5
9[b]	diglyme	120	K_2CO_3	660
10[b,c]	diglyme	120	K_2CO_3	1,400
11[b]	diglyme	200	K_2CO_3	9,000
12[b,d]	diglyme	200	K_2CO_3	23,000

[a]Conditions: CO_2 (10 bar), H_2 (30 bar), **3** (0.554 μmol, 1 equiv), base (0.6648 mmol, 1200 equiv), solvent (2 mL), 4 h. [b]With 100,000 equiv of K_2CO_3, 5 mL of diglyme. [c]24 h. [d]48 h.

and only 7 turnovers were observed after 4 h (max possible TON = 1200 based on equiv of base). However, raising the temperature to 120 °C resulted in a dramatic improvement in the performance of catalyst **3**, as it afforded 270 turnovers under otherwise analogous conditions (entry 2). We reasoned that replacing the nonpolar solvent anisole with diglyme should better solubilize KO^{t}Bu.[30] This change resulted in a 3-fold improvement in TON (to 800) after the same period of time (entry 3).

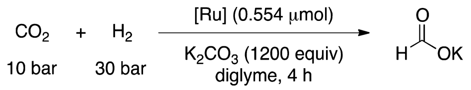
A variety of different bases were next evaluated for the reaction in diglyme. K_2CO_3, KOH, K_3PO_4, and $KHCO_3$ were all effective in promoting this transformation, with TONs ranging from 510 to 1,100 (entries 4–7).[31] The best base for this reaction was K_2CO_3, yielding a TON of 1,100 and a TOF of 1,600 h^{-1}.[32,33] These data stand in contrast to Nozaki's results with Ir pincer complex **2**. In that system, moving from KOH to a weaker base like K_3PO_4 resulted in a significant decrease in the TON (>7-fold).[18] The diversity of bases effective in the reaction of **3** suggests that deprotonation of intermediate **5** may be more facile than deprotonation of the analogous Ir−formate intermediate. Notably, however, the neutral amine base NEt_3, which has been frequently employed in CO_2 hydrogenation reactions,[5−9,12−14,17] resulted in <5 turnovers in this system (entry 8).

Because the best results were obtained using K_2CO_3 as the base (entry 4), we next examined the effect of increasing the equivalents of K_2CO_3, which would correspondingly increase the theoretical maximum TON of **3**. The use of 100,000 equiv of K_2CO_3 at 120 °C provided 660 turnovers after 4 h (entry 9) and 1,400 turnovers after 24 h. Notably, based on the stoichiometry of K_2CO_3, the maximum possible turnovers is 200,000.[32] Furthermore, increasing the temperature to 200 °C provided 9,000 and 23,000 turnovers after 4 and 48 h, respectively, with a TOF of 2,200 h^{-1} at this temperature.[33]

Preliminary Mechanistic Considerations. As discussed above, we originally envisioned the catalytic cycle in Scheme 3 as a plausible pathway for this transformation. If this mechanism is operative, formate complex **5** should display similar catalytic activity as **3**. Indeed, under otherwise identical conditions, this catalyst provided a comparable TON after 4 h (compare Table 1, entry 4 and Table 2, entry 1) and reaction rate profiles (see Supporting Information, Figures S5 and S6).

The mechanism as drawn in Scheme 3 implicates Ru-CO_2 complex **6** as an off-cycle side product. Previous studies from our group showed that the formation of **6** is irreversible at room temperature,[27] suggesting it may serve as a catalyst deactivation pathway. To test this possibility, we also examined the reactivity of **6** as a catalyst for CO_2 hydrogenation under our standard reaction conditions. Unexpectedly, we found that this Ru−CO_2 adduct afforded a TON of formate comparable to that of **3** and **5** after 4 h at 120 °C (Table 2, entry 2).

Table 2. Complexes 3, 5, and 6 as Catalysts for CO_2 Hydrogenation[a]

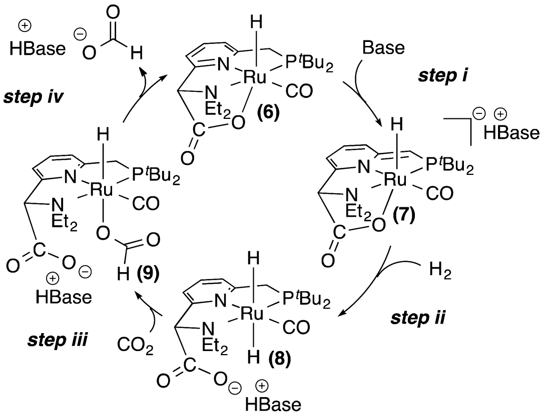


entry	[Ru]	temp (°C)	TON formate
1	**5**	120	1,000
2	**6**	120	1,100
3	**6**	70	<5
4	**3**	70	340
5	**5**	70	430

[a] Conditions: CO_2 (10 bar); H_2 (30 bar); Ru catalyst **3**, **5**, or **6** (0.554 μmol, 1 equiv), K_2CO_3 (0.6648 mmol, 1200 equiv), diglyme (2 mL), 4 h.

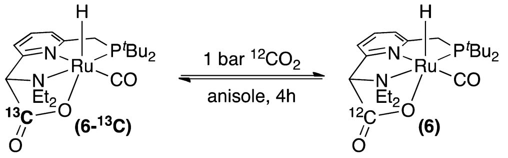
The observed catalytic activity of **6** can be explained by at least two mechanistic possibilities. A first is that CO_2 binding at **6** (step ia of Scheme 3) could be reversible at the elevated temperatures used for catalysis. This would enable the regeneration of **3**, which could then participate in CO_2 hydrogenation. Alternatively, **6** could potentially be capable of directly catalyzing CO_2 hydrogenation. As outlined in Scheme 6, a possible mechanism for this latter transformation could involve deprotonation of **6** to generate the unsaturated complex **7** (step i), followed by H_2 heterolysis (step ii), CO_2 insertion (step iii), and base-promoted product release (step iv).[34]

Scheme 6. Possible Catalytic Cycle for CO_2 Hydrogenation at Complex 6



To test the first possibility (reversible formation of **3** from **6** at elevated temperatures), we treated a $^{13}CO_2$-labeled sample of **6** with 1 bar of $^{12}CO_2$ at 120 °C. After 4 h, >98% exchange was observed (Supporting Information, Figure S8), indicating essentially complete reversibility under our standard catalysis conditions (Table 3, entry 1). Notably, the extent of exchange decreased sharply with temperature. At 100 °C, <45% exchange was observed after 4 h, and minimal (3%) exchange was detected after 4 h at 70 °C (entries 2–3). To probe the relevance of this reversibility to CO_2 hydrogenation catalysis, we examined the **6**-catalyzed hydrogenation of CO_2 to formate at 70 °C (slow exchange conditions). As shown in Table 2,

Table 3. Quantification of Reversible Binding of CO_2 at 6-^{13}C at Varied Temperatures[a]



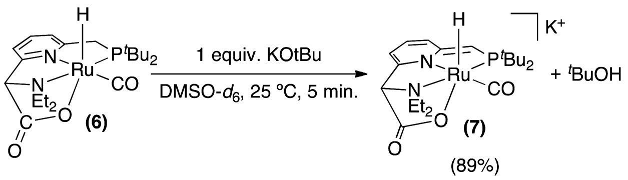
entry	temp (°C)	%6-^{13}C remaining
1	120	1.2
2	100	54
3	70	97

[a] Conditions: CO_2 (1 bar), **6**-^{13}**C** (1.8 mg, 3.63 μmol), anisole (0.45 mL), 4 h.

entry 3, less than 5 turnovers were observed after 4 h. In contrast, **3** and **5** provided 340 and 430 turnovers under these conditions at 70 °C (entries 4−5). The efficiency of **6** as a catalyst for hydrogenation at higher temperatures (fast exchange conditions), but not at lower temperatures (slow exchange conditions), suggests that the reversible binding of CO_2 is likely relevant to catalysis by **6** at elevated temperatures.

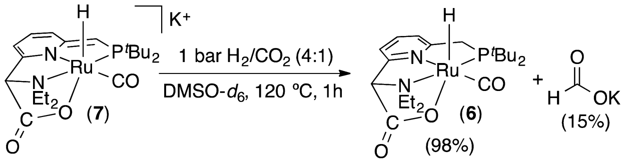
Importantly, the reversible formation of **3** from **6** under the conditions for catalysis does not rule out the possibility of direct CO_2 hydrogenation at **6** (catalytic cycle shown in Scheme 6). To explore this latter possibility, we first examined the stoichiometric reaction of **6** with 1 equiv of KO^{t}Bu in dimethylsulfoxide (DMSO) at 25 °C. After 5 min, a color change from yellow to bright orange was observed, accompanied by the complete conversion of **6** to a new Ru−H species, **7** (Scheme 7). This complex proved challenging to isolate in high purity,[35] as it is extremely moisture sensitive; however, an in situ-generated sample of **7** was fully characterized by ^1H and ^{13}C NMR spectroscopy.

Scheme 7. Formation of Anionic Ru Complex 7 by Deprotonation of 6



To probe whether **7** can participate in steps ii and iii of the catalytic cycle proposed in Scheme 6, a sample of **7**[35] was heated in DMSO-d_6 in the presence of 1 bar of a 4:1 mixture of H_2:CO_2 at 120 °C for 1 h in the absence of exogenous base (Scheme 8). Under these conditions, 15% yield of HCOOK was detected.[36] This result suggests that the **6**-catalyzed hydrogenation of CO_2 (Scheme 6) is a potentially viable route to formate, albeit a likely minor pathway relative to that depicted in Scheme 3.

Scheme 8. Stoichiometric Conversion of CO_2 to Formate with 7



In summary, this paper has shown that Ru(PNN)(CO)(H) (**3**), a known ester hydrogenation catalyst, can also catalyze the hydrogenation of CO_2 to formate in the presence of a base. The transformation is proposed to proceed through a mechanism involving (i) heterolytic cleavage of H_2 at **3** to form a Ru−dihydride species, (ii) CO_2 insertion to generate a Ru−formate complex, and (iii) base-promoted release of formate. The feasibility of each of these proposed mechanistic steps has been demonstrated through stoichiometric studies of organometallic intermediates. Ongoing work in this area aims to exploit this newfound reactivity of **3**, in combination with its ester hydrogenation activity, to accomplish **3**-catalyzed production of MeOH from CO_2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. Further details are given in Figures S1−S7 and Tables S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mssanfor@umich.edu. Phone: 734 615 0451.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation under the CCI Center for Enabling New Technologies Through Catalysis (CENTC) Phase II Renewal, CHE-1205189. C.A.H. was supported by a NSF Graduate Research Fellowship and by a Rackham Merit Fellowship. We also acknowledge funding from NSF Grant CHE-0840456 for X-ray instrumentation and the contribution of Dr. Jeff Kampf in collecting and refining crystallographic data. Finally, we thank Dr. Alex Miller (UNC) and Dr. Karen Goldberg (UW) for helpful discussions.

■ REFERENCES

(1) Reutemann, W.; Kieczka, H. Formic Acid. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2011.

(2) Schaub, T.; Paciello, R. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7278.

(3) Wesselbaum, S.; Hintermair, U.; Leitner, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 8585.

(4) Zhang, Z.; Xie, Y.; Li, W.; Hu, S.; Song, J.; Jiang, T.; Han, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 1127.

(5) Leitner, W. *Angew. Chem., Int. Ed.* **1995**, *34*, 2207.

(6) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.

(7) Jessop, P. G. Homogeneous Hydrogenation of Carbon Dioxide. In *Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, Germany, 2007; p 489.

(8) Jessop, P. G.; Joo, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, *248*, 2425.

(9) Wang, W.; Wang, S.; Ma, X.; Gong, J. *Chem. Soc. Rev.* **2011**, *40*, 3703.

(10) Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. *J. Am. Chem. Soc.* **2013**, *135* (31), 11533−11536.

(11) Langer, R.; Disken-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 9948.

(12) Federsel, C.; Ziebart, C.; Jackstell, R.; Baumann, W.; Beller, M. *Chem.—Eur. J.* **2012**, *18*, 72.

(13) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9777.

(14) Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 20701.

(15) Huff, C. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18122.

(16) Wesselbaum, S.; vom Stein, T.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 7499.

(17) Munshi, P.; Main, A. D.; Linehan, J. C.; Tai, C.-C.; Jessop, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 7963.

(18) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168.

(19) PNN = 6-(di-*tert*-butylphosphinomethylene)-2-(*N*,*N*-diethylaminomethyl)-1,6-dihydropyridine).

(20) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840.

(21) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113.

(22) Computational studies on similar systems suggest against a mechanism involving dissociation of one arm of the pincer ligand. See also refs 23 and 24. However, we can not rule out hemilability of a pincer ligand arm in the current system.

(23) For a computational study of CO_2 hydrogenation catalyzed by **1** see: Li, J.; Yoshizawa, K. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1039.

(24) For a computational study of the hydrogenation of dimethyl carbonate catalyzed by **3** see: Yang, X. *ACS Catal.* **2012**, *2*, 964.

(25) See the Supporting Information for full details on the synthesis and characterization of **5**.

(26) For an analogous FePNP complex see: Zell, T.; Butschke, B.; Ben-David, Y.; Milstein, D. *Chem.—Eur. J.* **2013**, *19*, 8068.

(27) For details on the synthesis and characterization of **6**, see: Huff, C. A.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2012**, *31*, 4643.

(28) For binding of CO_2 at a related RuPNP complex see: Vogt, M.; Gargir, M.; Iron, M. A.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *Chem.—Eur. J.* **2012**, *18*, 9194.

(29) For binding of other carbonyl compounds at **3** see: Huff, C. A.; Kampf, J. W.; Sanford, M. S. *Chem. Commun.* **2013**, *49*, 7147.

(30) Szmant, H. H. *Organic Building Blocks of the Chemical Industry*; Wiley: New York, 1989; p 222.

(31) Control reactions were peformed to probe the direct hydrogenation of K_2CO_3 and $KHCO_3$ to HCOOK catalyzed by **3** *in the absence of* CO_2. TONs of <5 for K_2CO_3 and 65 for $KHCO_3$ were observed under the standard conditions "a" described in Table 1.

(32) This value assumes that both K_2CO_3 and $KHCO_3$ can act as bases in the reaction.

(33) In all cases, the TOF was calculated using the number of turnovers of formate detected at ~35% conversion. The time required to reach ~35% conversion varied with the catalyst and conditions. Importantly, 35% conversion represents 35% of the maximum observed conversion rather than 35% of the maximum possible conversion.

(34) Alternative structures for **8** and **9** involve dissociation of the hemilabile NEt_2 arm, where the anionic oxygen tethered to the ligand could then coordinate to the Ru metal center. Our data do not allow us to distinguish these structures from those proposed in Scheme 6.

(35) The product was isolated in 89% yield, but the isolated material contained ~10% of starting material **6** (presumably generated by protonation).

(36) We believe that the low yield is due to the water sensitivity of **7**.