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Formylation of Amines by CO_2 Hydrogenation Using Preformed Co(II)/Nickel(II) Complexes

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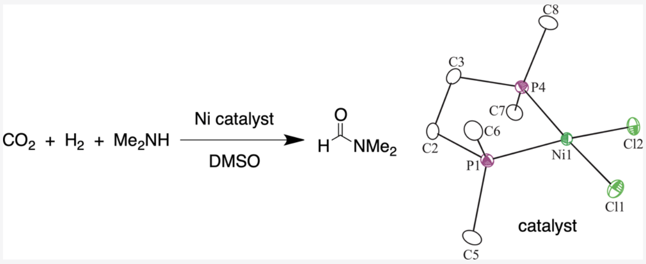
ABSTRACT: Preparation of formamides by CO_2 hydrogenation requires an efficient catalyst and temperatures around 100 °C or higher, but most catalysts reported so far incorporate rare and toxic precious metals. Five cobalt(II) or nickel(II) complexes with dmpe or PNN (dmpe = 1,2-bis(dimethylphosphino)ethane; PNN = [(2-(di-*tert*-butylphosphinomethyl)-6-diethylaminomethyl)pyridine) have been evaluated as precatalysts for the hydrogenation of CO_2 to prepare formamides from the corresponding secondary amines. The most active catalyst for these reactions was found to be [$NiCl_2$(dmpe)] in DMSO, producing dimethylformamide (DMF) from CO_2, H_2, and dimethylamine in up to 6300 TON, the highest activity reported for this reaction with an abundant metal-phosphine complex.



■ INTRODUCTION

Carbon dioxide is appealing as a chemical feedstock or reagent because it is sustainable, inexpensive, and much less toxic than other carbonyl-introducing agents such as phosgene and carbon monoxide.[1] However, a catalyst is required for most reactions of CO_2, other than simple acid−base reactions, to overcome the kinetic stability.[2]

Hydrogenation of CO_2 to formic acid or formamides has been extensively studied: from the initial report by Farlow and Adkins[3] of the production of formamides by reaction of CO_2 with H_2 and an amine over Raney nickel catalyst giving 2 turnovers. Early examples of homogeneous catalysts for CO_2 hydrogenation included the work by Inoue et al.[4] and Trzebiatowska et al.[5] in the 1970s. In general, homogeneous catalysts have been used for many transformations of CO_2,[6−8] but almost always platinum group metals were used, which is unfortunate due to their cost and toxicity.[9−11]

Abundant metal catalysts, although they have been historically under-represented in the homogeneous catalysis literature, are certainly capable of being excellent hydrogenation catalysts.[12] Since 2003, there have been quite a few reports of abundant-metal catalysts for CO_2 hydrogenation, but few of them have reported very high activities; typically the best activity is 5000 TON or often much lower. Many years ago, we showed using combinatorial screening that catalysts active for CO_2 hydrogenation to formic acid could be formed from many abundant metals, including Co, Cr, Fe, In, Mo, Nb, Ni, and W. For example, $NiCl_2$(dcpe) produced formic acid in 4400 TON (dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[13]

Because the hydrogenation of CO_2 to formamides proceeds via catalytic hydrogenation to formic acid followed by a thermal amidation of that acid with primary or secondary amine, it may seem that catalysts for formamide production would be the same as those for formic acid production. This is not, however, always the case. That thermal amidation step requires elevated temperatures of typically 100 °C, significantly higher than that typically used for CO_2 hydrogenation to formic acid. For that reason, catalysts for producing formamides are often not the same as those for producing formic acid.

Among the literature examples of abundant metal homogeneous catalyst precursors for CO_2 reduction to formamides are the $(Ph_3P)_3CuCl$ complex, by Haynes et al.,[14] and the $Fe(BF_4)_2{\cdot}6H_2O/P(CH_2CH_2PPh_2)_3$ and $Co(BF_4)_2{\cdot}6H_2O/P(CH_2CH_2PPh_2)_3$ combinations, by Federsel et al.,[15,16] which were shown to convert CO_2 and dimethylamine to *N*,*N*-dimethylformamide (DMF) in 900, 727, and 1254 TON, respectively: still lower than the activities reported for precious metal catalysts. In 2012, $[Fe(P_3P)F]BF_4$, [P_3P = $(C_6H_4PPh_2)_3P$] was shown by Ziebart et al.[17] to produce DMF in 5100 TON. We showed that the *in situ* combination of $Ni(acac)_2$ and dmpe allowed morpholine to be converted into the corresponding formamide in 18000 TON (dmpe = 1,2-bis(dimethylphosphino)ethane).[18]

Better progress has been made in the search for abundant metal-catalysts for the synthesis of formic acid or formate

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anion, although as mentioned above, there is no guarantee that such catalysts would necessarily be suitable for formamide production. An *in situ* combination of a Fe PNP complex with a Lewis acid cocatalyst was found by Zhang et al.[19] to hydrogenate CO_2 to formate in 59000 TON. Klankermayer's group[20] reported a Ni(II) *in situ* complex with the tris(2-(diphenylphosphino)ethyl)amine tetradentate ligand showing for the first time that a base-metal catalyst could have sufficient stability to give a TON of over 1 million. This milestone was particularly important as stability rather than rate has been the most significant concern with base metal hydrogenation catalysts.

Beside abundant metal-phosphine complexes, abundant-metal pincer complexes as precatalysts have also recently drawn attention for the synthesis of formic acid or formate anion.[21,22] The synthesis and characterization of a pyridine-based iron(II)-pincer complex were reported by the Milstein group.[21] They utilized the isolated iron complex for the hydrogenation of CO_2 to formate in the presence of a base at low-temperature with a TON of up to 788.

In 2016, the Bertini group reported two iron(II) pincer complexes bearing the 2,6-diaminopyridine scaffold [Fe(PNP^{H}-^{i}Pr)(H)(CO)(Br)] and [Fe(PNP^{Me}-^{i}Pr)(H)(CO)(Br)], respectively. Both complexes showed high catalytic activity as homogeneous catalysts for the hydrogenation of CO_2 to formate in a protic solvent at room temperature.[22]

The cobalt(I) complex $[(^{i}PrPNP)Co(CO)_2]^+$ with lithium triflate (LiOTf) as cocatalyst was employed for the hydrogenation of CO_2 to formate.[23] Among the cobalt(I) catalysts, the paired Co(I)/LiOTf system improved the catalytic activities, obtaining a TON of up to 30000, although this TON value is less than that of the [(*i*PrPNP)Fe] catalyst. Also, solvent effects were also screened under the reaction conditions, and acetonitrile solvent afforded a maximum TON of 14,000.

Recently, Bernskoetter et al.[24] developed a few Fe- and Co-pincer catalysts bearing alkali metal salts for the selective CO_2 hydrogenation to formate, showing that the Lewis acid stabilizes and increases the activity of the primary catalyst.

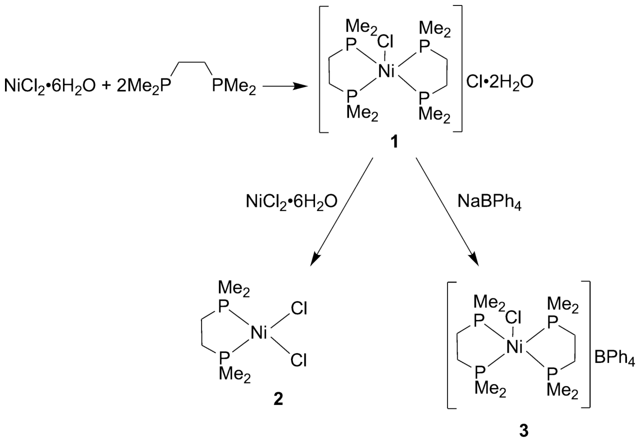
A low valent molybdenum-pincer complex [(κ^4-PN^{Me}P)-Mo(C_2H_4)(κ-O_2CH)] and an alkali metal salt were developed by Zhang et al.[25] for CO_2 hydrogenation to formic acid, although the TON of 35 was quite modest compared to the results of Bernskoetter.

Thus, the catalytic activity of abundant metal catalysts has been well demonstrated for the hydrogenation of CO_2 to formic acid but not nearly as well for the formylation of amines to formamides. There is still much scope for the further development of highly selective and cost-effective catalysts for the hydrogenation of CO_2 to formamides. Here, we report the synthesis and characterization of Ni(II)-dmpe and Co(II)/Ni(II)-PNN pincer complexes and their catalytic activities toward the hydrogenation of CO_2 to formamides. The preformed [$NiCl_2$(dmpe)] precatalyst showed the best catalytic activity for the synthesis of DMF with the highest TON value of 6300 among base metal catalysts.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Ni(II)-dmpe Complexes. The reaction of $NiCl_2 \cdot 6H_2O$ and a slight excess of $Me_2PCH_2CH_2PMe_2$ (dmpe) in ethyl alcohol at reflux temperature produced a five-coordinate nickel(II) species, $[NiCl(dmpe)_2]Cl \cdot 2H_2O$ **1** (see Scheme 1 and Figure S1). The compound **1** was characterized by ^1H, $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum of **1** showed the characteristic resonance of the CH_2 group protons as a singlet at 2.14 ppm while the methyl groups appeared at 1.69 ppm. The $^{31}P\{^1H\}$ NMR spectrum showed one singlet at 43.9 ppm due to the two similar Me_2P groups of the dmpe ligand. Crystallography revealed the structure of $\mathbf{1} \cdot 2H_2O$ (see Supporting Information) which was, apart from the extra water molecule, similar to the previously published structure of $\mathbf{1} \cdot H_2O$.[26]

Scheme 1. Syntheses of Nickel(II) Complexes 1-3



Complex **2**, *cis*-[$NiCl_2$(dmpe)] has also been previously prepared by the reaction of $[Ni(dmpe)_2Cl]Cl$ with $NiCl_2 \cdot 6H_2O$ in a 2:1 ratio in ethyl alcohol under a nitrogen atmosphere, but unfortunately, the compound was only characterized by elemental analysis and UV−visible spectroscopy.[27] The $^{31}P\{^1H\}$ NMR spectrum had only a single peak at 50.0 ppm; this indicated that Ni(II) has a square-planar geometry in solution. Then, we attempted to repeat the synthesis of **2** according to Handley et al.[26] by the treatment of **1** with $NaBPh_4$ in 1:1.5 ratio in MeOH and obtained the related nickel complex, $[Ni(dmpe)_2Cl]BPh_4$ **3**, instead.[28] Complex **3** was obtained in fair to good yield and was found to be soluble in chloroform and methanol.

Structure of 2. The slow vapor diffusion of ether produced crystals in a saturated solution of **2** in MeOH. The solid-state molecular structure of [$NiCl_2$(dmpe)] **2** is shown in Figure 1 (see Tables S1−S4 for details). In the solid state, this is a *cis*

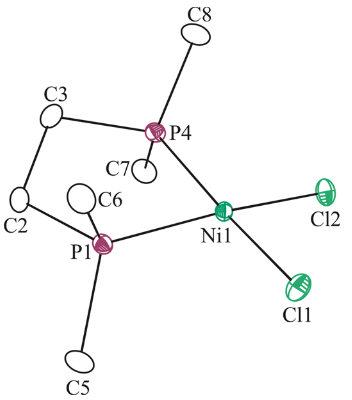
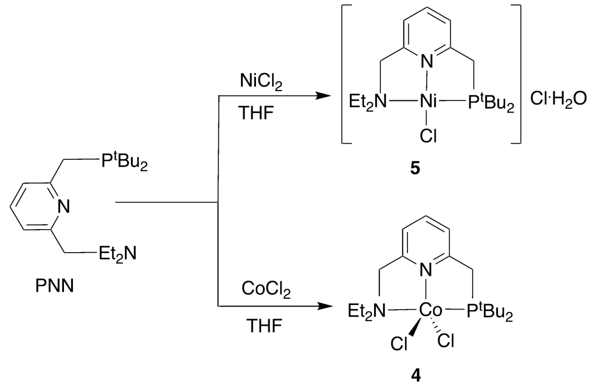


Figure 1. Molecular structure of [$NiCl_2$(dmpe)] (**2**) with the thermal ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity.

square planar nickel(II) diphosphine complex, despite the fact that in the literature, the same crystallographically determined structure is described as a *trans* tetrahedral complex.[26] Complex **2** is slightly distorted from a perfect square-planar geometry; the P(4)−Ni(1)−Cl(1) 168.588(17)° and the P(1)−Ni(1)−Cl(2) 168.013(16)° angles are similar to other nickel complexes containing dppe/dmpe in a five-membered chelate ring.[29,30] The bite angle P(4)−Ni(1)−P(1) is 86.614(15)° which is slightly lower than the ideal 90.00° but similar to related complexes having a diphosphine five-membered chelate ring.[31] The Ni−Cl bond distances [(2.2182(4) and 2.2325(4)Å)] are within the typical range for such bonds in Ni-diphosphine complexes.[32] The two Ni−P bond lengths 2.1322(4)Å and 2.1394(2)Å are very close due to the chemical equivalence of the two phosphorus atoms but slightly shorter than that observed in nickel bidentate phosphine complex, [Ni(dmpe)$_2$](PF$_6$)$_2$].[30] The solution phase ^{31}P{^{1}H} NMR spectrum of **2** is also consistent with a square planar geometry. If **2** had been tetrahedral in solution, its resulting paramagnetism would have at least broadened the NMR spectrum.

Synthesis and Characterization of Co(II) or Ni(II)-PNN Complexes. Milstein's pincer complex [Co(PNN)Cl$_2$]·C$_4$H$_8$O **4** and the related [Ni(PNN)Cl]Cl·H$_2$O **5** were synthesized by the reaction of anhydrous CoCl$_2$ or NiCl$_2$, respectively, with 1.2 equiv of the PNN ligand in THF (Scheme 2). Complex **4** was dark blue, air/moisture sensitive, and required handling under an inert atmosphere. Complex **4** displayed broad ^{1}H NMR signals, which were thus not very useful for determining the structure in solution. The solid-state structure of complex **4** was confirmed to be the same as that reported by Milstein et al.[33] Complex **5** was a red, air-stable crystalline solid that was soluble in CHCl$_3$ and DMSO but insoluble in common organic nonpolar solvents. The ^{31}P{^{1}H} NMR spectrum of **5** showed a single resonance at 39.9 ppm.

Scheme 2. Synthesis of Complexes 4 and 5 from PNN Ligand



Structure of 5. Single crystals suitable for the X-ray analysis of **5** were obtained by the layering of hexane on a saturated solution of **5** in CHCl$_3$. The solid-state structure of **5** is shown in Figure 2 (see Tables S5 and S6 for details). The Ni(II) center adopt a slightly distorted square-planar geometry in which the Ni(II) ion is coordinated by two N, one P, and one Cl atoms. A second chloride is the counteranion and does not show any close contacts with the nickel center within the crystal packing. The N(8)−Ni(1)−P(14) bond angle ~171.49(6)° and the N(1)−Ni(1)−Cl(1) angle ~178.73(7)° deviate slightly from linearity, and P(14), N(1), N(8), Ni(1) are almost coplanar, consistent with a square planar structure of Ni(II). The two bite angles, N(1)−Ni(1)−P(14) ~86.48(6)° and N(1)−Ni(1)−N(8) ~85.98(8)°, are slightly less than 90°. The Ni−Cl distance of 2.159(7) Å is in the range encountered for a similar square-planar nickel(II) complex [(Me$_2$NNN^Q)NiCl].[34] In complex **5**, the Ni(1)−P(14) bond length of 2.182(6) Å and the average C−C bond lengths of the pyridine ring ~1.374 Å are similar to those previously reported for [Ni(PNP^{i}Pr)Cl)] complexes.[35] The Ni(1)−N(1) (pyridyl) distance of 1.876(2) Å is shorter than the Ni(1)−N(8)(amino) bond length of 2.014 (19)Å; a similar observation is found in complex **4**.

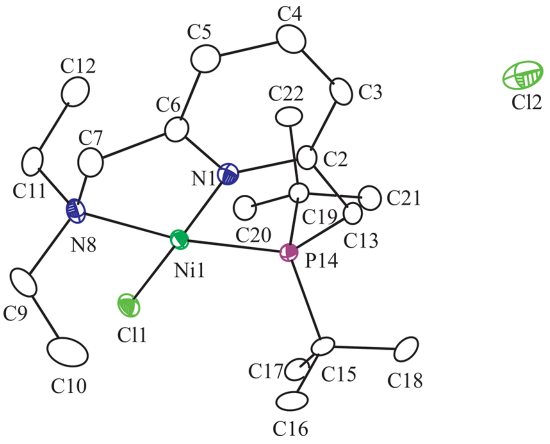
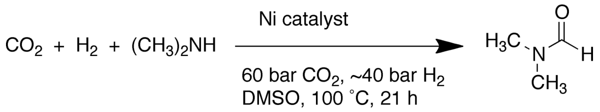


Figure 2. Molecular structure of complex **5** with the thermal ellipsoids at 50% probability level.

Catalytic Activities of Ni(II) Complexes 1−5. The next step was to test whether complexes **1**−**5** work as catalyst precursors for the hydrogenation of CO$_2$ to DMF in anhydrous DMSO as a solvent. The results of these experiments are summarized in Table 1. A blank test confirmed that no activity was observed in the absence of a Ni(II)/dmpe complex. Under the optimized reaction conditions, Ni-complexes **1** and **2** were catalytically active and produced the desired DMF, but complex **3** was surprisingly inactive.

Table 1. Nickel-Catalyzed Hydrogenation of CO$_2$ to DMF[a]



precursor	Ni/Me$_2$NH	TON[b,c]	Yield[c]
none		0	0
[Ni(dmpe)$_2$Cl]Cl **1**	1:100	60	60
″	1:500	310	70
″	1:10000	2300	23
[Ni(dmpe)Cl$_2$] **2**	1:100	75	75
″	1:1000	800	80
″	1:20000	6300	32
[Ni(dmpe)$_2$Cl]BPh$_4$ **3**	1:100	0	0

[a]Reaction conditions: catalyst (0.67 μmol), and dimethylamine (12.0 mmol, delivered in the form of DIMCARB) in DMSO (0.5 mL), 100 °C, stirring rate of 450 min^{-1}, 21 h reaction time, 60 bar CO$_2$, with enough H$_2$ added to bring the total pressure to 100 bar. [b]Average of the results from two trials. [c]Determined by NMR spectroscopy.

The most active catalyst is complex **2** for the hydrogenation of CO_2 to DMF under our standard reaction conditions, with the highest TON value of 6300. Because complex **2** is a 16e complex, it should be able to quickly react with H_2 to produce a Ni−H intermediate. Subsequent insertion of CO_2 into the Ni−H bond would produce a formato compound. Because complexes **1** and **3** are coordinatively saturated, they may be more stable than **2**, which may be why they are less catalytically active. The TON value of 6300 is the highest observed using a nickel(II) catalyst and comparable to the best base metal catalysts previously reported for this reaction: the Fe(II)/phosphine complex [TON = 5100] and Co(II)/phosphine complex [TON = 1300] reported by Federsel et al.[16] and Beller et al.[17]

It is not clear why $[Ni(dmpe)_2Cl]BPh_4$ **3** fails as a catalyst for the hydrogenation of CO_2 to formic acid or formamide when the structurally similar complex **1** is active. In complex **1**, Cl^- is considered a coordinating counterion, but in complex **3**, BPh_4^- is considered a noncoordinating counterion. We can speculate, therefore, that the second equivalent of chloride in complex **1** plays an important role as a stabilizing ligand for a catalytic intermediate or resting state, while the noncoordinating BPh_4^- anion is incapable of that role. Although the exact reaction mechanism is unknown at this stage, based on the existing literature reports,[17,36] a plausible catalytic cycle for the hydrogenation of CO_2 using nickel(II) complex **2** is shown in Scheme S1. The subsequent thermal amidation step does not require a catalyst.

The isolated Co(II)/Ni(II)-PNN pincer complexes **4** and **5** were tested as precatalysts for the hydrogenation of CO_2 to formamide. Unfortunately, no catalytic activity was observed for the hydrogenation of CO_2 in the presence either of morpholine or dimethylamine as substrates under the applied reaction conditions (Table S7). Attempts to prepare hydrides from complexes **4** and **5** by reaction with H_2 did not give the expected compounds [Co(PNN)(H)Cl] and [Ni(PNN)(H)]-Cl, respectively, and no Co/Ni−H signal were observed by ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR chemical shift was also unchanged from the original compounds, indicating no reaction occurred between **4**/**5** and H_2.

■ CONCLUSIONS

In summary, three Ni(II)/dmpe complexes **1**−**3** were synthesized and characterized. Complexes **1** and **3** have five-coordinate distorted trigonal bipyramidal geometries, while complex **2** displayed a slightly distorted square-planar geometry around the Ni(II) ion. All the synthesized complexes were tested as homogeneous precatalysts for the hydrogenation of CO_2 to formamides. Complex **2** showed the highest catalytic activity with a TON of 6300. Complex **3** did not show any catalytic activity. In the future, mechanistic studies should be carried out to determine the mechanism of catalysis. In contrast, Co(II)/Ni(II)-pincer complexes of the ligand [2-(di*tert*-butylphosphinomethyl)-6-dimethyl aminomethyl)-pyridine] did not show any catalytic activity for the hydrogenation of CO_2 to formamide.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01401.

Experimental methods, possible mechanisms, crystallographic data, and preliminary screening data (PDF)

Accession Codes

CCDC 1538716 and 1538723 contain 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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