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Diverse catalytic reactivity of a dearomatized PN^{3}P*-nickel hydride pincer complex towards CO_2 reduction

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A dearomatized PN^{3}P*-nickel hydride complex has been prepared by oxidative addition process. The first nickel-catalyzed hydrosilylation of CO_2 to methanol has been achieved, with unprecedented turnover numbers. Selectvie methylation and formylation of amines with CO_2 were demonstrated by such PN^{3}P*-nickel hydride complex, highlighting its versatile functions in CO_2 reduction.

CO_2 is a renewable, nontoxic and abundant feedstock, and thus it is an attractive C1 building block for the synthesis of organic molecules.[1] However, the transformation and activation of CO_2 is highly challenging due to its inherent thermodynamic and kinetic stability.[1f] Considerable efforts have been devoted to developing efficient catalysts or catalytic systems to overcome these challenges for the CO_2 utilization to produce various value-added chemicals.[2] In particular, the reduction of CO_2 to methanol under mild conditions is a challenging goal.[3] While some homogeneous catalytic systems have been reported for the hydrogenation[4] and the hydroboration of CO_2 to methanol,[5] examples of hydrosilylation of CO_2 to methanol are still rare. Ir(CN)(CO)dppe (dppe = 1,2-bis(diphenylphosphino)ethane) was the first reported catalyst for the hydrosilylation of CO_2 to silylated methanol from which methanol could be generated upon hydrolysis in 1989 by Eisenberg and Eisenschmid,[6] but the catalytic efficiency was very low as the transformation required weeks to complete. In 2009, Zhang and Ying group reported the reduction of CO_2 to silylated methanol with silanes catalyzed by N-heterocyclic carbenes with the highest turnover number (TON) of 1840.[7] These reports remain the only two homogeneously catalyzed systems to directly reduce CO_2 to silylated methanol in one-step. More recently, the groups of Fontaine,[8] Oestreich[9] and Abu-Omar[10] developed the hydrosilylation of CO_2 to silylated formate or silylated formal compounds, rather than silylated methanol. These products could in turn be reduced to silylated methanol by addition of an additional reductant, at elevated reaction temperatures or over a longer reaction time. The selective one-step reduction to silylated methanol for the hydrosilylation of CO_2 to methanol remains challenging.

On the other hand, efficient hydrosilylation of CO_2 to valuable formamides, methylamines or aminals in the presence of amines has emerged as a promising methodology recently.[11] These novel catalytic strategies for CO_2 utilization feature the formation of the new carbon-nitrogen bond. Cantat and co-workers first described the catalytic reductive formylation of amines using CO_2 and silanes in 2012.[12] The catalytic reduction of CO_2 with hydrosilanes and amines to methylamines was unveiled independently by Cantat and co-workers and Beller and co-workers in 2013.[13] After these initial reports, rapid progress in this area has led to the discovery of several amine formylation or methylation catalysts for the hydrosilylation of CO_2.[11] However, among these systems, only a few cases have been reported where not only methylamines but also formamides could be selectively produced using the same catalyst.[14, 15] These catalysts suffer from either the low reactivity or the poor selectivity, especially for the methylation reaction. Interestingly, both of formylation and methylation reactions could be achieved by using and inorganic salt (e.g. Cs_2CO_3)[14b] or an organic inner salt (Betaine)[15] as catalysts, but they only showed moderate reactivity towards the methylation reaction of primary amines along with the formation of mixtures of the monomethylated and dimethylated products. Clearly, the development of a general and highly active catalytic system for the selective formation of methylamines and formamides derived from CO_2 and amines is still highly desirable.

As part of our ongoing interest in the PN^3-pincer complexes for their unique kinetic and thermodynamic properties,[16] we report

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† Electronic Supplementary Information (ESI) available: Experimental details, NMR spectra of products. CCDC 1505721, 1530059 and 1571043. For crystallographic data in CIF or other electronic format see DOI:

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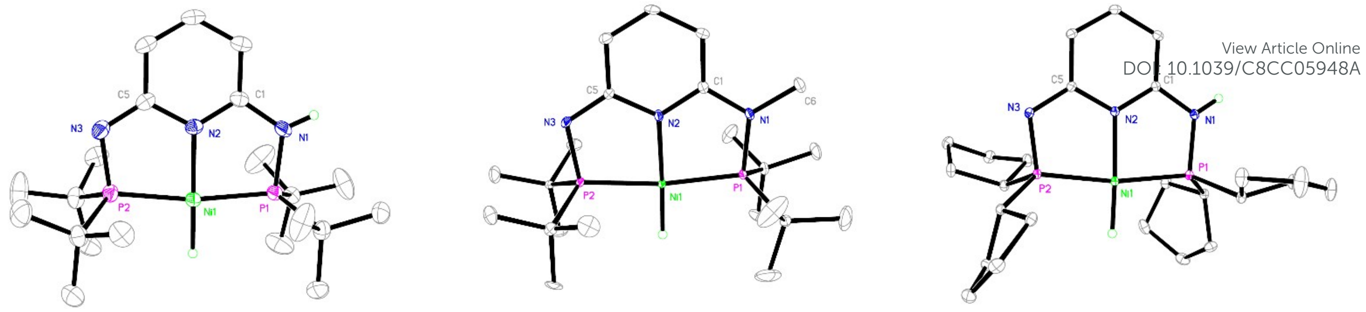
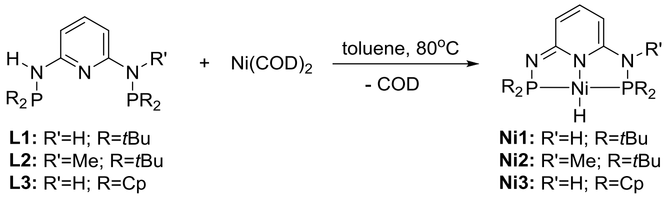


Fig. 1 ORTEP diagram of PN^{3}P*-Ni hydride complexes **Ni1**, **Ni2** and **Ni3** at 30% ellipsoid probability. Hydrogen atoms (except for pincer arms and Ni-H) are omitted for clarity.



Scheme 1 Synthesis of the dearomatized Ni-H pincer complexes via oxidative addition.

herein the preparation of well-defined dearomatized PN^{3}P*-nickel hydride complexes and their applications on hydrosilylation of CO_2. To the best of our knowledge, this catalytic system represents the first nickel-catalyzed hydrosilylation of CO_2 to methanol, with the highest TON reported to date. To further extend the diverse range of products accessible from CO_2 and silanes, this dearomatized PN^{3}P*-nickel hydride catalytic system is employed to the reductive functionalization of CO_2 with amines as well to offer a methodology for the selective formation of formamides and methylamines.

The dearomatized PN^{3}P*-nickel hydride complexes **Ni1**, **Ni2**, and **Ni3** were synthesized by oxidative addition of the corresponding pincer ligands (**L1**-**L3**) to bis(1,5-cyclooctadiene)nickel(0) in toluene in one step (Scheme 1).[17] In ^1H NMR spectra, the characteristic Ni-H resonance appears at -15.87, -15.62, and -16.44 ppm for complexes **Ni1**, **Ni2**, and **Ni3**, respectively. The ^{31}P NMR spectra show two doublets, corresponding to the two magnetically different phosphorus atoms of the dearomatized pincer ligands. All **Ni1**, **Ni2** and **Ni3** were characterized by single crystal X-ray diffraction, exhibiting a similar coplanar geometry with shorter C-N bond distance for the imine arm of the dearomatized pyridine ring (Fig. 1).

The catalytic studies of the PN^{3}P*-Ni hydride complexes commenced with the reduction of 1 atm of CO_2 in DMF using Ph_2SiH_2 as a reductant under various conditions (Table 1). The hydrosilane was fully consumed in 12 hours as monitored by GC-MS when using complex **Ni1** as the catalyst (Table 1, entry 1). Gratifyingly, after the CO_2-reduction product was subjected to hydrolysis, methanol was obtained in 91% yield. Either in the absence of catalyst or using **L1** alone, only trace amounts of methanol was observed, although Ph_2SiH_2 was completely consumed (Table 1, entries 2 and 3).[8] Relatively lower yields of methanol were observed when complexes **Ni2** and **Ni3** were tested (Table 1, entries 4 and 5; Table S3, entries 2 and 3). Further optimization revealed that DMF was a better solvent. The reaction could also work well in polar solvents such as THF, and CH_3CN, albeit with slower reaction rates. No methanol was formed when the solventwas changed to the nonpolar solvents, such as CH_2Cl_2 and toluene (Table S1). Other hydrosilanes were also investigated when using the same equivalent of Si−H groups. Reactions with $PhSiH_3$ resulted in a good yield of methanol, yet a prolonged reaction time was needed. The bulkier trisubstituted hydrosilanes did not give methanol as the final product (Table S2). The influence of the catalyst loadings was then examined. Catalyst **Ni1** showed high activity even with a catalyst loading as low as 0.02% with the TON up to 4900 (Table 1, entry 10). To the best of our knowledge, this is the highest TON reported for the reduction of CO_2 with silane to methanol.

Table 1 Hydrosilylation of CO_2 with diphenylsilane catalyzed by PN^{3}P*-Ni hydride complexes.[a]

$$CO_2 + Ph_2SiH_2 \xrightarrow[\text{DMF, RT to 60 °C}]{\text{[Ni-H] catalyst}} \xrightarrow[\text{rt, 24 h}]{NaOH/H_2O} CH_3OH$$

Entry	Catalyst	Catalyst loading [% Si-H]	Time [h][b]	Yield [%][c]	TON
1	**Ni1**	1.25	12	91	73
2[d]	—	—	72	Trace	—
3	**L1**	1.25	72	Trace	—
4	**Ni2**	1.25	24	87	70
5	**Ni3**	1.25	17	82	66
6	**Ni1**	5.00	6	91	18
7	**Ni1**	2.50	10	91	36
8	**Ni1**	0.50	14	92	184
9	**Ni1**	0.25	24	90	360
10[e]	**Ni1**	0.02	54	98	4900

[a] CO_2 balloon, catalyst, 1.0 mmol of Ph_2SiH_2, 2.0 mL of DMF. [b] Time required for the full consumption of Ph_2SiH_2 monitored by GC/MS. [c] Yields of CH_3OH determined by GC based on Si-H. [d] Without catalyst. [e] 2.0 mmol of Ph_2SiH_2 was used.

We next further explored the reductive functionalization of CO_2 with amines. The reaction of dibenzylamine **1a** was chosen as a model substrate when employing Ph_2SiH_2 as the reducing agent and CO_2 as a C1 source (Table S4). To our delight, the notable reactivity afforded methylamine **2a** in 85% and formamide **3a** in 11% yield, observed when using 3 mol% **Ni1**, 5 equiv. of Ph_2SiH_2 and 2.7 atm of CO_2 at 100 °C for 24 h (Table S3, entry 1). Only small amounts of **3a** was detected in the absence of thecatalyst (Table S3, entry 2). We found that the higher reaction temperature was favorable for the formation of methylation product (**2a**). Finally, the highest activity towards the formation of **2a** was provided at 120 °C under 2.7 atm of CO_2 (Table S3, entry 3). Interestingly, with the increasing of the CO_2 pressure or decreasing of the reaction temperatures, the improved yields of **3a** were achieved (Table S3, entries 4 and 5).

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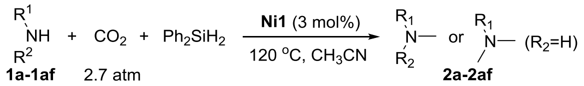
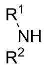
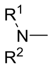
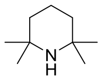
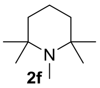
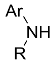
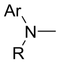
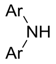
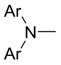
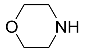
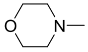
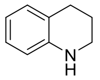
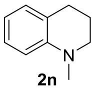
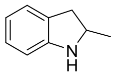
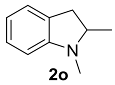
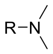
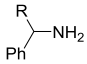
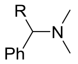
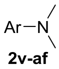
Meanwhile, the decreased amount of the reducing agent and solvent has a positive influence on the selectivity for the formylation reaction (Table S3, entry 6). By increasing the CO_2 pressure to 8.2 atm, the formylation reaction could be performed at room temperature with 96% yield of **3a** (Table S3, entry 7). On the basis of the reaction conditions of entry 3 and 7, the use of the other two PN^{3}P*-Ni hydride complexes **Ni2** and **Ni3** showed lower selectivities or yields in comparison with **Ni1** (Table S3, entries 8-11).

Table 2 Methylation of various amines using CO_2 and Ph_2SiH_2 catalyzed by **Ni1**.[a]

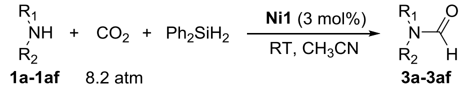


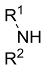
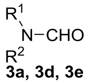
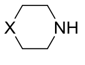
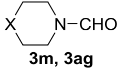
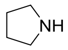
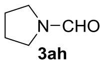
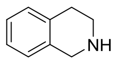
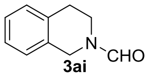
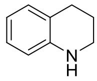
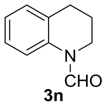
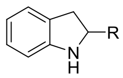
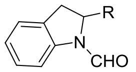
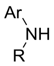
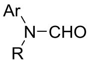
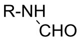
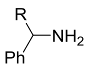
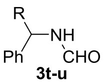
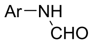
Entry	Substrate		Product	Yield [%]^b
1		**1a** R^1=Bn, R^2=Bn	 **2a-e**	84
2		**1b** R^1=Bn, R^2=Me		91
3		**1c** R^1=Cy, R^2=Cy		82
4		**1d** R^1=R^2=$CH_3(CH_2)_{11}$		88
5^c		**1e** R^1=*t*Bu, R^2=Me		85
6		**1f**	 **2f**	84
7		**1g** Ar=Ph, R=Me	 **2g-k**	86
8		**1h** Ar=Ph, R=Et		88
9		**1i** Ar=4-$CH_3OC_6H_4$, R=Me		90
10		**1j** Ar=4-ClC_6H_4, R=Me		91
11		**1k** Ar=4-BrC_6H_4, R=Me		87
12		**1l** Ar=4-$MeOC_6H_4$	 **2l**	86
13^c		**1m**	 **2m**	92
14		**1n**	 **2n**	86
15		**1o**	 **2o**	84
16	R-NH_2	**1p** R=Bn	 **2p-s**	77
17^c		**1q** R=*t*Bu		90
18		**1r** R=4-$ClC_6H_4CH_2$		81
19		**1s** R=4-$MeOC_6H_4CH_2$		85
20		**1t** R=Me	 **2t-u**	89
21		**1u** R=Ph		84
22	Ar—NH_2	**1v** Ar=4-MeC_6H_4	 **2v-af**	86
23		**1w** Ar=2-MeC_6H_4		83
24		**1x** Ar=4-$MeOC_6H_4$		90
25		**1y** Ar=2-$MeOC_6H_4$		85
26		**1z** Ar=4-BrC_6H_4		87
27		**1aa** Ar=4-FC_6H_4		78
28		**1ab** Ar=3,5-$Me_2C_6H_3$		81
29		**1ac** Ar=2,6-$Me_2C_6H_3$		84
30		**1ad** Ar=2,6-*i*PrC_6H_3		79
31		**1ae** Ar=2,4,6-$Me_3C_6H_2$		78
32		**1af** Ar=4-$EtO_2CC_6H_4$		76

Condition: [a] Complex **Ni1** (0.015 mmol), amine (0.50 mmol), Ph_2SiH_2 (2.5 mmol), CH_3CN (15.0 mL), 2.7 atm of CO_2, 120 °C. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy of the crude reaction mixture using CH_2Br_2 as the internal standard.

With the optimized reaction conditions in hand, we began to examine the substrate scope for each transformation (Table 2 and 3). As shown in Table 2, sterically less sterically hindered aliphatic secondary amines (**1a, 1b,** and **1d**) showed high reactivity to afford the corresponding methylamines. Moreover, the more hindered aliphatic secondary amines, such as *N,N*-dicyclohexylamine **1c**, *N-tert*-butylmethylamine **1e**, and 2,2,6,6,-tetramethylpiperidine **1f** afforded the corresponding methylamines in good yields. Meanwhile, secondary aromatic amines with both electron-donating and electron-withdrawing substituents at the para position (**1g-1k**) reacted smoothly and the corresponding products were obtained in good yields. Notably, the more challenging substrate diaryl secondary amine **1l** was found to be reactive as well.[14b] Several cyclic aliphatic secondary amines (**1m-1o**) were employed and excellent yields of the cyclic methylamines were achieved. In addition, not only aliphatic primary amines (**1p-1u**) but also aromatic primary amines (**1v-1ae**) proceeded selectively to provide the dimethylated products. Remarkably, even the methylation of sterically hindered substrates (**1q**, and **1ac-1ae**) proceeded smoothly to give the corresponding dimethylated products. It is noteworthy that the methylation reaction could be performed in the presence of halides, such as F, Cl, or Br, and reductive dehalogenation was not observed. furthermore, ester-substituted amine **1af** was well tolerated under our reducing conditions, providing the corresponding dimethylated amine **2af** in good yield.

Table 3 Formylation of various amines using CO_2 and Ph_2SiH_2 catalyzed by **Ni1**.[a]



Entry	Substrate		Product	Yield [%]^b
1		**1a** R^1=Bn, R^2=Bn	 **3a, 3d, 3e**	89
2		**1d** R^1=R^2=$CH_3(CH_2)_{11}$		88
3^c		**1e** R^1=*t*Bu, R^2=Me		96
4		**1m** X=O	 **3m, 3ag**	87
5		**1ag** X=NCOPh		78
6^c		**1ah**	 **3ah**	95
7		**1ai**	 **3ai**	89
8		**1n**	 **3n**	90
9		**1o** R=Me	 **3o, 3aj**	75
10		**1aj** R=H		81
11		**1g** Ar=Ph, R=Me	 **3g-j, 3ak**	78
12		**1h** Ar=Ph, R=Et		87
13		**1i** Ar=4-$CH_3OC_6H_4$, R=Me		89
14		**1j** Ar=4-ClC_6H_4, R=Me		92
15		**1ak** Ar=Ph, R=Bn		89
16	R-NH_2	**1p** R=Bn	 **3p-s, 3al-m**	87
17^c		**1q** R=*t*Bu		95
18		**1r** R=4-$ClC_6H_4CH_2$		85
19		**1s** R=4-$MeOC_6H_4CH_2$		91
20		**1al** R=2-$MeOC_6H_4CH_2$		86
21^c		**1am** R=Cy		93
22		**1t** R=Me	 **3t-u**	84
23		**1u** R=Ph		93
24	Ar—NH_2	**1v** Ar=4-MeC_6H_4	 **3v-z, 3ab-ad** **3an, 3af**	88
25		**1w** Ar=2-MeC_6H_4		87
26		**1x** Ar=4-$MeOC_6H_4$		91
27		**1an** Ar=4-*t*BuC_6H_4		85
28		**1y** Ar=2-$MeOC_6H_4$		87
29		**1z** Ar=4-BrC_6H_4		82
30		**1ab** Ar=3,5-$Me_2C_6H_3$		84
31		**1ac** Ar=2,6-$Me_2C_6H_3$		81
32		**1ad** Ar=2,6-*i*PrC_6H_3		85
33		**1af** Ar=4-$EtO_2CC_6H_4$		78

Condition: [a] Complex **Ni1** (0.015 mmol), amine (0.50 mmol), Ph_2SiH_2 (1.25 mmol), CH_3CN (5.0 mL), 8.2 atm of CO_2, room temperature. [b] Yield of isolated product. [c] Determined by ^1H NMR spectroscopy of the crude reaction mixture using CH_2Br_2 as the internal standard.

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Utilizing optimal formylation reaction conditions at room temperature, various aliphatic and aromatic, secondary and primary amines were successfully converted into the desired formamides with good to excellent yields (Table 3). Both of the acyclic (**1a, 1d, 1e, 1g-1j,** and **1ak**) and cyclic (**1m-1o,** and **1ag-1aj**) secondary amines could be transformed to the corresponding formamides in excellent yields. Importantly, the hydrosilylation of CO_2 to formamides showed the potential chemoselectivity. The carbonyl and ester groups could be tolerated under these conditions, as exemplified by the substrate **1ag** and **1af**. Additionally, primary amines (**1p-1z, 1ab-1ad,** and **1al-1an**) proceeded in a similar fashion to secondary amines, generating monoformylated products. The formylation protocol is also compatible with a variety of halides (**1i, 1j, 1r,** and **1z**). The sterically hindered amines (**1e, 1q, 1ac,** and **1ad**) were also suitable for this transformation, giving the desired formamides in good to excellent yields.

Mechanistic proposals on metal hydride complex catalyzed hydrosilylation of CO_2 usually involve the insertion of CO_2 into a metal-H bond and generate CH_4 as the final product.[18] However, this pathway was ruled out since no reaction was observed between complex **Ni1** with CO_2 at 125 °C. This observation suggests that CO_2 insertion into the Ni-H bond of **Ni1** might not a catalysis related event. Catalyst **Ni2** bearing a NMe arm showed some similar reactivity (Table 1, entry 4; Table S4, entries 8 and 10;), implying that the N-H gorup of **Ni1** was not necessary for the activation of CO_2. Although we have not identified the active catalyst in the aboved CO_2 reduction reactions, we speculate that an alternative pathway for CO_2 activation may involve the nucleophlic attack of CO_2 by the iminic nitrogen of the ligand. The nucleophilicity of the imine arm could be enhanced while a strong σ-donating hydride ligand is introduced. Further mechanistic studies are ongoing.

In summary, we have successfully synthesized and fully characterized several readily accessible dearomatized PN^3P^*-nickel hydride pincer complexes via an oxidative addition process. The first example of nickel catalyzed hydrosilylation of CO_2 to methanol has been achieved, with an unprecedentedly high turnover number of 4900. Moreover, these PN^3P^*-nickel hydride pincer complexes are capable of selectively catalyzing reductive methylation and formylation of amines with CO_2 with a very broad substrate scope.

Conflicts of interest

There are no conflicts to declare.

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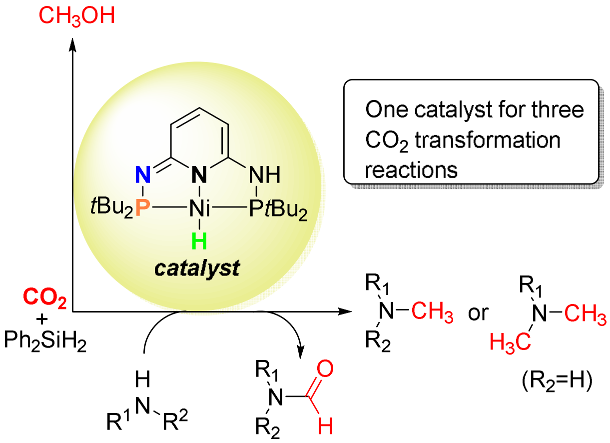

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