Synthetic Methods

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Effective Formylation of Amines with Carbon Dioxide and Diphenylsilane Catalyzed by Chelating bis(*tz*NHC) Rhodium Complexes**

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Abstract: *The reductive formylation of amines using CO_2 and hydrosilanes is an attractive method for incorporating CO_2 into valuable organic compounds. However, previous systems required either high catalyst loadings or high temperatures to achieve high efficiency, and the substrate scope was mostly limited to simple amines. To address these problems, a series of alkyl bridged chelating bis(NHC) rhodium complexes (NHC = N-heterocyclic carbene) have been synthesized and applied to the reductive formylation of amines using CO_2 and Ph_2SiH_2. A rhodium-based bis(tzNHC) complex (tz = 1,2,3-triazol-5-ylidene) was identified to be highly effective at a low catalyst loading and ambient temperature, and a wide substrate scope, including amines with reducible functional groups, were compatible.*

The incorporation of CO_2 into organic compounds is highly desirable since CO_2 is a low-cost, abundant, and nontoxic raw material. However, CO_2 represents the highest oxidation state of carbon and this limits its synthetic utility to the formation of low-energy synthetic targets by CO_2 insertion reactions or to multielectron chemical reductive processes to generate energy-rich small molecules such as formic acid, carbon monoxide, methanol, and methane.[1,2] With respect to catalytic reduction of CO_2, hydrogen gas is the cleanest and most atom-economical reductant, but harsh reaction conditions, such as a high pressure of a mixture of gases and high reaction temperature, prevents broad application of this reducing agent. In contrast, the use of boranes[3] and hydrosilanes[4] as reductants facilitates the catalytic reduction of CO_2 under much milder reaction conditions. In a related process, the reduction of CO_2 in the presence of amines ultimately affords formamides or methylamines, which are value-added bulk and fine chemicals.[5,6] Since the initial report by Cantat and co-workers on the catalytic reductive formylation of amines with CO_2 and silanes,[6a] rapid development in this field has led to the disclosure of various organocatalyts[6a,b] and organometallic complexes (copper,[6c,d] iron[6e]) as active catalysts. However, in all cases, a high catalyst loading and/or high temperature were necessary for this reductive coupling process. Furthermore, the substrate scope for this transformation is mostly limited to simple amines. Therefore, the development of new types of catalysts, which can facilitate the reductive formylation reaction both at a low catalyst loading and ambient temperature, is of great interest.

To achieve this goal, we turned our attention to the application of N-heterocyclic carbene (NHC)/metal complexes as potential catalysts. Based on the fact that the common intermediate in metal-catalyzed hydrosilylation reactions is the metal hydride complex,[7] we rationalized that the strong electron-donating ability of NHC ligands may increase the nucleophilicity of the metal hydride species and facilitate the reduction of the weakly electrophilic CO_2. Moreover, the ability of NHCs to form strong bonds with various transition metals would lead to more robust catalysts and would permit lower catalyst loadings without causing catalyst decomposition.[8] Although the use of electron-rich NHC/metal complexes to facilitate nucleophilic additions to CO_2, to afford carboxylic acids or esters, is well known,[1] there are few examples of its use for catalytic hydrosilylation reactions of CO_2.[6i,9] To the best of our knowledge, a selective NHC/metal-catalyzed formylation of amines with CO_2 has not been reported.

Recently, bis(NHC) complexes of rhodium were found to be effective catalysts for the hydrosilylation of ketones at ambient temperature.[10] These bis(carbene) ligands not only improved the stability of the rhodium complexes against decomposition, but also enabled better control of the steric and electronic properties around the metal center.[10a] We hypothesized that these types of metal complexes could be promising catalysts for hydrosilylation reactions of CO_2. Furthermore, since the high electron density of NHC/metal complexes may be crucial for the favorable interaction between CO_2 and the key metal hydride intermediate, we envisioned that modifying the ligands from normal to abnormal NHCs should generate better catalysts because of the superior electron-donating ability of the latter.[11] Such an effect was previously observed for the copper-catalyzed carboxylation reaction of benzoxazoles and benzothiazoles with CO_2,[12] and the iridium-catalyzed transfer hydrogenation of CO_2 with 2-propanol.[13] Among various types of abnormal NHCs, *tz*NHCs (*tz* = 1,2,3-triazol-5-ylidene) stand out as excellent candidates because they are easily accessed and diversified by the [3+2] cycloaddition of azides and alkynes.[14] Herein, we report the modular synthesis of alkyl-bridged bis(*tz*NHC) rhodium complexes and their application

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as effective catalysts for the reductive formylation of amines with CO_2 and Ph_2SiH_2.

To access the desired bis(*tz*NHC)-ligated rhodium complexes, the standard method of utilizing silver NHCs as carbene transmetallation agents, a method reported for the synthesis of the bis(*im*NHC) rhodium complexes **1** and **2** (*im* = imidazole-2-ylidene), was applied (Figure 1).[15] In addition to KPF_6, different anion sources were examined to generate a series of rhodium complexes (**3a–f**).[16]

The catalytic activity of the newly synthesized metal complexes was investigated for the formylation of dibenzylamine (**4a**) with CO_2 as a C1 source and Ph_2SiH_2 as the reductant (Table 1). Rhodium complexes containing the *im*NHC backbone (**1** and **2**) were initially examined as catalysts, but the desired formamide **5a** was not observed (entries 1 and 2). In contrast, the complex **3a**, bearing a *tz*NHC backbone, showed high activity, even at lower catalyst loadings (entries 3 and 4). Encouraged by these results, we began to screen various bis(tzNHC) rhodium complexes (**3b–f**) bearing a trimethylene linker (entries 5–9). By varying the catalyst structure, we found that the counteranions influenced the activity of these catalysts. Although no clear trend was uncovered, we found that the rhodium complexes possessing either ^-OTf, $^-NTf_2$, or $^-BPh_4$ counteranions enjoyed the highest catalytic activity (entries 6–8). Moreover, since NHCs are known as effective organocatalysts for this type of reaction,[6b] we also examined the use of the *tz*NHC precursor as a catalyst (entry 10). In this case, **5a** was not observed, thus indicating that the real catalyst species in our system was not the dissociated free carbene. Based on these results, **3c** was chosen as the best catalyst for the reductive formylation reaction of dibenzylamine (**4a**) with CO_2 and Ph_2SiH_2.

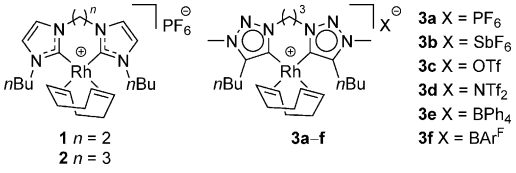
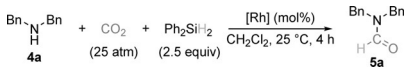


Figure 1. Chelating bis(NHC) rhodium complexes used in this work. Tf = trifuoromethanesulfonyl.

Table 1: Optimization of the reductive formylation of dibenzylamine (**4a**) with CO_2 and Ph_2SiH_2.[a]

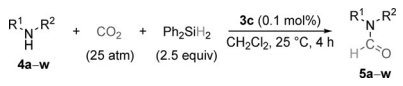


Entry	[Rh] (mol%)	Yield [%][b]	Entry	[Rh] (mol%)	Yield [%][b]
1	**1** (0.5)	n.d.	6	**3c** (0.1)	>95
2	**2** (0.5)	n.d.	7	**3d** (0.1)	>95
3	**3a** (0.5)	>95	8	**3e** (0.1)	>95
4	**3a** (0.1)	80	9	**3f** (0.5)	85
5	**3b** (0.1)	83	10	–[c]	n.d.

[a] Reaction conditions: **4a** (0.25 mmol), Ph_2SiH_2 (0.625 mmol), and [Rh] (0.25–1.25 μmol) in CH_2Cl_2 (1 mL) under 25 atm of CO_2. [b] Yields were determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c] Bis(triazolium) salt (5 mol%) and KO*t*Bu (10 mol%) was used as the catalyst. n.d. = not detected.

With the optimized reaction conditions in hand,[16] we began to investigate the substrate scope of this reaction (Table 2). The use of dibenzylamine (**4a**) provided the desired formamide **5a** in 95% yield upon isolation (entry 1). In addition, the reaction could be conveniently scaled up to a gram scale without any loss of activity. Similarly, substitution of a benzyl group with an alkyl group, such as methyl (**4b**) or ethyl (**4c**) did not affect the reactivity (entries 2–3). Dioctylamine (**4d**), possessing two long alkyl chains, was also found to be a suitable substrate for this reaction (entry 4). Various cyclic aliphatic amines (**4e–h**) were tested and excellent yields of the cyclic formamides **5e–h** were obtained (entries 5–8). When the primary aliphatic amines **4i–o** were used, the desired reactions proceeded selectively to provide the monoformylated products **5i–o** (entries 9–15). Notably, the formylation of (*R*)-**4j** proceeded without any racemization. The use of *trans*-1,2-cyclohexanediamine (**4p**) provided

Table 2: Substrate scope for the reductive formylation of amines (**4a–v**) with CO_2 and Ph_2SiH_2.[a]



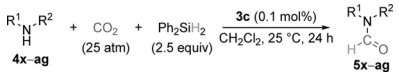
Entry	Substrate	Product	Yield [%][b]
1	**4a** R = Bn	**5a–c**	95 (quant.)[c]
2	**4b** R = Me		quant.
3	**4c** R = Et		92
4	**4d**	**5d**	88
5	**4e**	**5e**	99
6	**4f** X = CH_2	**5f–h**	99
7	**4g** X = O		89
8[d]	**4h** X = NPh		97
9	**4i** R = H	**5i–k**	96
10	**4j** R = Me[e]		quant.[f]
11[d]	**4k** R = Ph		quant.
12	**4l** R = *n*Hex	**5p**	quant.
13	**4m** R = *c*Hex		85
14[d]	**4n** R = TBSO$(CH_2)_3$		82
15[d]	**4o** R = *t*Bu		60
16[d,g]	**4p** (*rac*)	**5p**	75
17[d]	**4q** R = 4-Me	**5q–w**	89
18[d]	**4r** R = 4-*t*Bu		quant.
19[d]	**4s** R = 4-OMe		95
20[d,h]	**4t** R = 4-Br		40
21[d]	**4u** R = 3-Me		80
22[d]	**4v** R = 2-Me		30
23[d]	**4w** R = 2,6-Me_2		n.d.

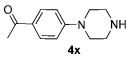
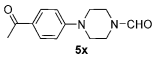
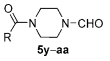
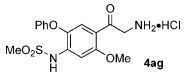
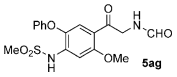
[a] Reaction conditions: Amines **4a–v** (0.50 mmol), Ph_2SiH_2 (1.25 mmol), and **3c** (0.50 μmol) in CH_2Cl_2 (2 mL) under 25 atm of CO_2. [b] Yields of the isolated products **5a–v** were based on **4a–v**. [c] Reaction using 5.03 mmol of **4a.** [d] 24 h. [e] Enantiopurity of **4j** (96.8% *ee*) was determined after formylation with ethyl formate. [f] 98.7% *ee*. [g] Used 0.25 mol% of **3c** and 5 equiv of Ph_2SiH_2. [h] Used 0.5 mol% of **3c**. TBS = *tert*-butyldimethylsilyl.

the diformamide product **5p** in good yield (entry 16). Next, we evaluated aniline derivatives (**4q–w**) as substrates (entries 17–23). Reactions of anilines bearing electron-donating groups on the *para* position (**4q–s**) reacted, albeit with a prolonged reaction time because of the lower nucleophilicity of anilines when compared to aliphatic amines (entries 17–19). The importance of the nucleophilicity of the aniline derivatives was highlighted when we examined 4-bromoaniline (**4t**) as a substrate. In this case, the effectiveness of the formylation reaction was decreased, even under higher catalyst loading (entry 20). In addition, sterically hindered anilines, such as 2-methylaniline (**4v**) and 2,6-dimethylanilines (**4w**), were found to be poor substrates (entries 22–23).

Since the newly developed bis(*tz*NHC) rhodium complex **3c** was found to be an exceptionally effective catalyst for the reduction of CO_2, we then examined the possibility of expanding the substrate scope (Table 3). We hypothesized that under high pressure CO_2, preferential reduction of the large excess of CO_2 over other functional groups should occur and that our catalytic system could tolerate amines which possess reducible functional groups. In spite of the fact that NHC rhodium complexes are well known to be excellent catalysts for the hydrosilylation of ketones,[7b] the piperazine derivative **4x**, which contains a ketone moiety, was successfully formylated to afford **5x** in high yield (entry 1). Similarly, the piperazine derivatives **4y–aa**, bearing amide functional groups, also reacted smoothly to generate the corresponding formamides **5y–aa** in good to excellent yields (entries 2–4). Furthermore, it was found that amines bearing alkenyl (**4ab**), alkynyl (**4ac**), and ester (**4ad**) moieties were successfully formylated in moderate to excellent yields (entries 5–7). In addition, the amino esters **4ae** and **4af** were found to be viable substrates for this reaction to provide the monoformylated products **5ae–af** (entries 8 and 9). In the case of **4ae**, the reaction occurred with the retention of the original configuration. Finally, the synthetic utility of this methodology was demonstrated by the formylation of the α-aminoketone **4ag** to afford **5ag**, which is a key intermediate in the total synthesis of Iguratimod (an anti-inflammatory drug),[17] in quantitative yield (entry 10).

Table 3: Reductive formylation of amines (**4x–ag**) with reducible functional groups.[a]

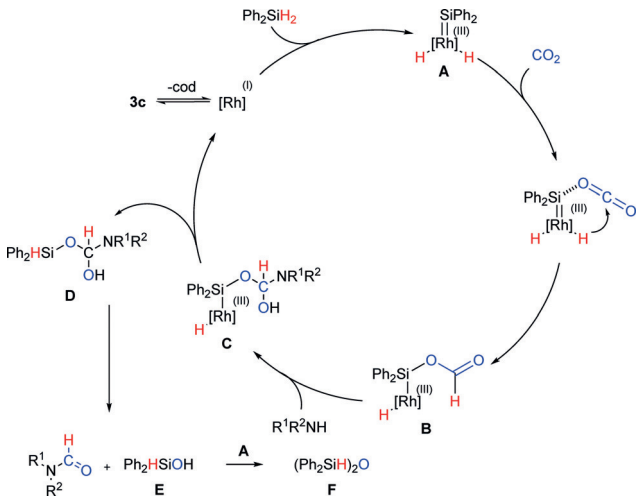


Entry	Substrate	Product	Yield [%][b]
1	 **4x**	 **5x**	90
2	 **4y** R = C_6H_5	 **5y–aa**	85
3	**4z** R = 4-BrC_6H_4		quant.
4	**4aa** R = O*t*Bu		79
5	 **4ab** R = CH=CH_2	 **5ab–ad**	quant.
6	**4ac** R = C≡CH		63
7	**4ad** X = CO_2Me		90
8[c,d]	 **4ae**	 **5ae**	40[e]
9	 **4af**	 **5af**	quant.
10[f,g]	 **4ag**	 **5ag**	quant.

[a] Reaction conditions: Amines (**4x–ag**; 0.50 mmol), Ph_2SiH_2 (1.25 mmol), and **3c** (0.50 μmol) in CH_2Cl_2 (2 mL) under 25 atm of CO_2. [b] Yields of the isolated products **5x–ag** were based on **4x–ag**. [c] Et_3N (0.50 mmol) was added. [d] Enantiopurity of **4ae** (98.2% *ee*) was determined after formylation with trimethyl orthoformate. [e] 96.1% *ee*. [f] **4ag** (0.125 mmol), **3c** (1 mol%). [g] Et_3N (0.25 mmol) was added.

Several possible reaction pathways were considered for the reductive formylation reaction of amines with CO_2 and Ph_2SiH_2 as catalyzed by the rhodium complex **3c**. One possibility is that CO_2 may initially be hydrosilylated to generate a silyl formate, which could be intercepted by a nucleophilic amine to furnish the expected formamide. However, this pathway was ruled out since an attempted reduction of CO_2 by Ph_2SiH_2, in the absence of an amine, failed.[6i,16] An alternative reaction pathway may involve the rapid formation of an ammonium carbamate, derived from the amine and CO_2, followed by the reduction of this salt by hydrosilane and **3c**.[6c,d] This possibility was examined by using a benzylamine/CO_2 adduct[18] as a substrate. Since the formamide **5i** was obtained only under high pressure of CO_2,[16] it is unclear if this adduct could be directly reduced. However, since CO_2 and the amine/CO_2 adduct coexist in equilibrium and the reduction of CO_2 should be favored over the adduct because of its higher electrophilicity,[19] we assumed that CO_2 was reduced by the rhodium hydride intermediate.

Based on these control studies and the previously reports on rhodium-catalyzed hydrosilylation reactions of carbonyl compounds,[7b] a plausible mechanism is shown in Scheme 1. Initially, dissociation of the auxiliary ligand (cod) from **3c**, followed by oxidative addition of Ph_2SiH_2 and subsequent hydride transfer from the silyl ligand to the rhodium center would generate the rhodium silylene intermediate **A**. Such an intermediate was previously proposed in the Hofmann–Gade-type mechanism,[20] and indirect evidence for its formation was obtained by silylene trapping experiments:[10b] the reaction of Ph_2SiH_2 with *t*$BuMe_2SiOH$ occurred smoothly in the presence of **3c**, while the use of monohydrosilane, such as Ph_2MeSiH, resulted in no reaction.[16] Consequently, no



Scheme 1. Plausible reaction mechanism.

catalytic formylation of **4a**, to give **5a**, with CO_2 was observed when different monohydrosilanes, which cannot form the key rhodium silylene intermediate **A**, were used as the reductants. Next, coordination of CO_2 to **A** followed by a pseudo-intramolecular hydride transfer from the rhodium to CO_2 would generate the rhodium silyl formate **B**. The nucleophilic attack of the amine on **B** would afford **C** and subsequent reductive elimination of **C** would furnish the silyl intermediate **D** and close the catalytic cycle. Finally, elimination of the silanol **E** would result in the formation of the desired formamide. Although **E** was not directly observed, indirect evidence for its formation was supported by the detection of the disiloxane **F**, which could be obtained from the reaction between **E** and **A**.

In conclusion, we successfully synthesized a series of chelating bis(NHC) rhodium complexes and found that a rhodium complex derived from a bis(*tz*NHC) bearing a trimethylene linker possesses excellent catalytic activity towards the reductive formylation of amines with CO_2 and Ph_2SiH_2 at ambient temperature with low catalyst loading under an elevated pressure of CO_2. The mild reaction conditions of this catalyst system allowed a broad substrate scope and excellent functional-group tolerance.

Experimental Section

General procedure: **3c** (0.50 μmol, taken as 1 mL from 0.50 mM freshly prepared stock solution in CH_2Cl_2) and a solution of freshly purified amines **4a–g** (0.50 mmol) in 0.5 mL of CH_2Cl_2 were added to a 50 mL stainless steel high pressure reactor. The resulting solution was then stirred (400 rpm) under 25 atm of CO_2 for 15 min. Then, a solution of Ph_2SiH_2 (0.23 g, 1.25 mmol) in CH_2Cl_2 (0.5 mL) was added, and the reaction mixture was stirred under 25 atm of CO_2 for the indicated time. After the reaction, excess CO_2 was vented. The reaction mixture was purified by silica-gel column chromatography eluting with MeOH/CH_2Cl_2 (5:95) or EtOAc/*n*-hexane (3:7) to afford the desired formamides **5a–ag**.

Keywords: amides · carbon dioxide · formylation · N-heterocylic carbenes · rhodium

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[16] Details regarding the synthesis of rhodium complexes (**3a–f**; Part I), optimization of the formylation reaction of **4a** (Part II), and control experiments (Part IV) are described in the Supporting Information.

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