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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 = 1,2,3triazol-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 CO₂ is a low-cost, abundant, and nontoxic raw material. However, CO₂ represents the highest oxidation state of carbon and this limits its synthetic utility to the formation of low-energy synthetic targets by CO₂ 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 CO₂, 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 CO₂ 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 CO₂ and silanes,^[6a] rapid development in this field has led to the disclosure of various organocatalyts^[6a,b] and organometallic complexes (copper,^[6c,d]

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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 CO₂. 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 CO₂, to afford carboxylic acids or esters, is well known,^[1] there are few examples of its use for catalytic hydrosilylation reactions of CO₂.^[6i,9] To the best of our knowledge, a selective NHC/metal-catalyzed formylation of amines with CO₂ 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 CO₂. 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 CO₂,^[12] and the iridium-catalyzed transfer hydrogenation of CO2 with 2-propanol.^[13] Among various types of abnormal NHCs, tzNHCs (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 alkylbridged bis(tzNHC) 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 KPF₆, 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 imNHC 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 tzNHC 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, ⁻NTf₂, or ⁻BPh₄ 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 CO2 and Ph2SiH2.



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

Table 1: Optimization of the reductive formylation of dibenzylamine (4a) with CO₂ and Ph_2SiH_2 .^[a]

	Bn _N , Bn H 4a	+ CO ₂ + Ph ₂ Si⊢ ₂ (25 atm) (2.5 equiv)	[Rh] (m CH ₂ Cl ₂ , 25	Bn N ² Bn 5 °C, 4 h H ² C ⊂ 5a	
Entry	[Rh] (mol%)	Yield [%] ^[b]	Entry	[Rh] (mol%)	Yield [%] ^[b]
1	1 (0.5)	n.d.	6	3 c (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	3 a (0.1)	80	9	3 f (0.5)	85
5	3b (0.1)	83	10	_[c]	n.d.

[a] Reaction conditions: **4a** (0.25 mmol), Ph₂SiH₂ (0.625 mmol), and [Rh] (0.25–1.25 μ mol) in CH₂Cl₂ (1 mL) under 25 atm of CO₂. [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 KOtBu (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 CO₂ and Ph₂SiH₂.^[a]

 $\begin{array}{c} R_{1}^{1} N_{R}^{2} + CO_{2} + Ph_{2}SiH_{2} \\ H \\ \textbf{4a-w} \end{array} \begin{array}{c} 3c \ (0.1 \ mol\%) \\ CI_{2}CI_{2}, 25 \ ^{\circ}C, 4 \ h \\ H^{-C}C_{0} \end{array} \begin{array}{c} R_{1}^{1} N_{R}^{-R^{2}} \\ H^{-C}C_{0} \end{array}$

			54 H	
Entry		Substrate	Product	Yield [%] ^[b]
1 2 3	Bn _{`N} ∕R H	4a R=Bn 4b R=Me 4c R=Et	^{Bn} ∼N ^{,R} cHO 5a-c	95 (quant.) ^[c] quant. 92
4	nOct_N_nOct	4d	nOct∼ _N ∕nOct CHO 5d	88
5	NH	4e	N ^{CHO} 5e	99
6 7 8 ^[d]	X NH	$4 f X = CH_2$ 4 g X = O 4 h X = NPh	X 5f-h	99 89 97
9 10 11 ^[d]	R Ph NH ₂	4i $R = H$ 4j $R = Me^{[e]}$ 4k $R = Ph$	R Ph ↓ N CHO N Si−k	96 quant. ^[f] quant.
12 13 14 ^[d] 15 ^[d]	R-NH ₂	4 I R= <i>n</i> Hex 4 m R= <i>c</i> Hex 4 n R=TBSO(CH ₂) ₃ 4 o R= <i>t</i> Bu	", NНСНО NНСНО 5р	quant. 85 82 60
16 ^[d,g]	NH2 NH2	4p (<i>rac</i>)	NHCHO 5p	75
$17^{[d]}$ $18^{[d]}$ $19^{[d]}$ $20^{[d,h]}$ $21^{[d]}$ $22^{[d]}$ $23^{[d]}$	RH2 R	4 q R = 4-Me 4 r R = 4-tBu 4 s R = 4-OMe 4 t R = 4-Br 4 u R = 3-Me 4 v R = 2-Me 4 w R = 2,6-Me ₂	HN ^{-CHO}	89 quant. 95 40 80 30 n.d.

[a] Reaction conditions: Amines 4a-v (0.50 mmol), Ph₂SiH₂ (1.25 mmol), and 3c (0.50 µmol) in CH₂Cl₂ (2 mL) under 25 atm of CO₂. [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 Ph₂SiH₂. [h] Used 0.5 mol% of 3c. TBS = *tert*-butyldimethylsilyl.

9210 www.angewandte.org

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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 4bromoaniline (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(tzNHC) rhodium complex 3c was found to be an exceptionally effective catalyst for the reduction of CO₂, we then examined the possibility of expanding the substrate scope (Table 3). We hypothesized that under high pressure CO₂, preferential reduction of the large excess of CO₂ 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 **5**x 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 monoformy-

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

3c (0.1 mol%)

 $R^1_N R^2$

	N H 4x–a	+ CO ₂ + Pn ₂ Si⊓ ₂ (25 atm) (2.5 equiv) g	CH ₂ Cl ₂ , 25 °C, 24 h H ^C 5x–ag	
Entry		Substrate	Product	Yield [%] ^[b]
1	Ŷ	- NH 4x	о →N_−сно 5х	90
2 3 4		4y $R = C_6H_5$ 4z $R = 4-BrC_6H_4$ 4aa $R = OtBu$	O R N−CHO 5y−aa	85 quant. 79
5 6 7	Bn`N R	4 ab $R = CH = CH_2$ 4 ac $R = C = CH$ 4 ad $X = CO_2Me$	Bn _N CHO Sab-ad	quant. 63 90
8 ^[c,d]	CO ₂ Me	4ae	CO ₂ Me N-CHO H 5ae	40 ^[e]
9	CO ₂ Me	4 af	CO₂Me Ph N CHO Ph Saf	quant.
10 ^[f,g]	Ph0 MeO ₂ S、	O NH2•HCI OMe 4ag	PhO MeO ₂ S-N H	quant.

[a] Reaction conditions: Amines (4x-ag; 0.50 mmol), Ph_2SiH_2 (1.25 mmol), and **3 c** (0.50 µmol) in CH₂Cl₂ (2 mL) under 25 atm of CO₂. [b] Yields of the isolated products **5 x-ag** were based on **4 x-ag**. [c] Et₃N (0.50 mmol) was added. [d] Enantiopurity of **4 ae** (98.2% *ee*) was determined after formylation with trimethyl orthoformate. [e] 96.1% *ee*. [f] **4 ag** (0.125 mmol), **3 c** (1 mol%). [g] Et₃N (0.25 mmol) was added.

lated 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).

Several possible reaction pathways were considered for the reductive formylation reaction of amines with CO₂ and Ph_2SiH_2 as catalyzed by the rhodium complex **3c**. One possibility is that CO₂ 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 CO2 by Ph2SiH2, 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/CO₂ 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 CO₂ and the amine/CO₂ adduct coexist in equilibrium and the reduction of CO2 should be favored over the adduct because of its higher electrophilicity,^[19] we assumed that CO₂ 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 Ph₂SiH₂ 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–Gadetype mechanism,^[20] and indirect evidence for its formation was obtained by silylene trapping experiments:^[10b] the reaction of Ph₂SiH₂ with *t*BuMe₂SiOH occurred smoothly in the presence of **3c**, while the use of monohydrosilane, such as Ph₂MeSiH, resulted in no reaction.^[16] Consequently, no



Scheme 1. Plausible reaction mechanism.

 $R^1 R^2$

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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 pseudointramolecular 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(tzNHC) bearing a trimethylene linker possesses excellent catalytic activity towards the reductive formylation of amines with CO₂ and Ph₂SiH₂ at ambient temperature with low catalyst loading under an elevated pressure of CO₂. 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 Ph₂SiH₂ (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/CH₂Cl₂ (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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9212 www.angewandte.org

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