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VIP CO_2 Recycling

A Diagonal Approach to Chemical Recycling of Carbon Dioxide: Organocatalytic Transformation for the Reductive Functionalization of CO_2**

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CO_2 recycling is a priority to reduce our dependence on petrochemicals to produce chemical commodities and, in a broader context, to develop new fuels.[1] With 6.8 Gt of recyclable CO_2 produced each year at point sources,[2] carbon dioxide is a very attractive, nontoxic and abundant C1 building block.[1,3] Yet, only a handful processes utilizing CO_2 have been industrialized to date.[3] Urea synthesis is the main process utilizing carbon dioxide[1,3] and more recently, reaction of CO_2 and epoxides in the presence of a catalyst was developed to commercialize new polycarbonates and cyclic carbonates.[4] Importantly, in these processes new C–O and C–N bonds are formed but there is no formal reduction of the carbon center and therefore no significant energy storage. In parallel to this "horizontal approach" to CO_2 utilization (Figure 1), extensive research efforts have been devoted to CO_2 reduction to formic acid, formaldehyde, and methanol using electrochemical, photo-electrochemical, and chemical methods ("vertical approach", Figure 1).[5] For example, CO_2 could be reduced to formic acid derivatives with H_2 using a homogenous catalytic system and highly efficient catalysts have been proposed recently for this reaction.[6–7] Though it is expected that formic acid and methanol will play a growing role in future nonfossil fuel economies, these chemicals do not cover the whole feedstock necessary for fine chemicals synthesis or high-energy fuels production.[1] In contrast, petrochemicals (hydrocarbons) are extensively used as fuels and basic reagents to access other chemicals, because they are energetic and easy to derivatize. Novel methods for CO_2 recycling that aim to compete with petrochemistry require new processes that combine both reduction of CO_2 and formation of C–C, C–N, and C–O bonds (Figure 1), to enlarge the spectrum of compounds directly available from CO_2. Ideally, these "diagonal transformations" are catalytic and proceed in a single step to ensure energy economy and a positive carbon balance; yet, viable examples remain scarce and lack generality because the functionalization is induced by the reductant itself.[8] In this context, we have investigated three-component systems where CO_2 is reacted, in a single step, with a functionalization reagent and a reducing reagent which can be modified *independently*. Herein we report novel diagonal transformations for CO_2 recycling, including an unprecedented organocatalytic synthesis of formamides from CO_2.

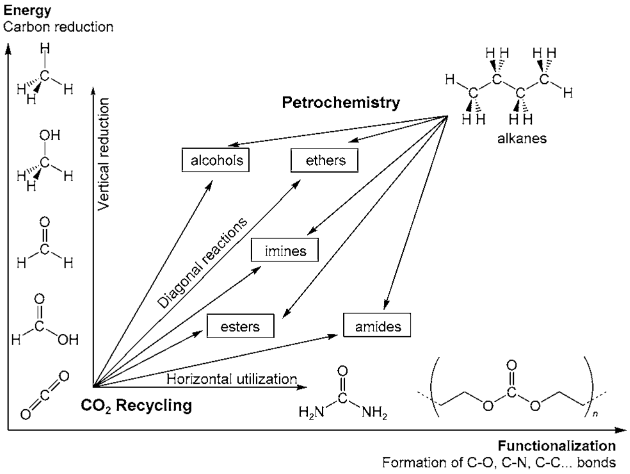

Figure 1. Approaches to recycling transformations of CO_2 as alternatives to petrochemical methods.

Amines and alcohols react with CO_2 in the presence of a base to afford carbamate and carbonate salts, respectively, and were thus chosen as functionalization reagents.[9] On the other hand, organosilanes are attractive reducing agents because they are cheap and nontoxic. In addition, they have a mild reducing potential and are thus an attractive energy source to reduce CO_2-derived systems without wasting energy.[10] Our entry point into developing new reductive functionalization of CO_2 was therefore to explore the reaction chemistry of the CO_2/alcohol/silane and CO_2/amine/silane three-component systems.

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was chosen as a base to promote the insertion of CO_2 to O–H and N–H bonds. Indeed, we have recently isolated the first CO_2 adduct of a nitrogen base, using TBD [**1**, Eq. (1)], enabling the

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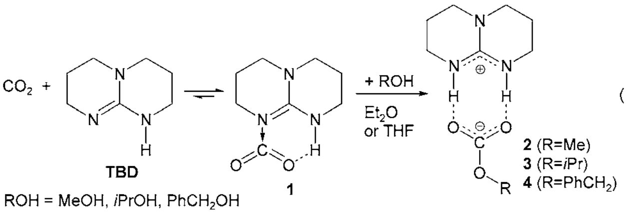
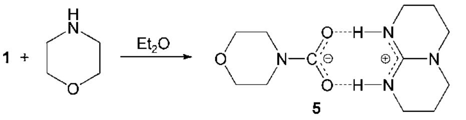
possibility to investigate the reaction chemistry of CO_2-base adducts.[11] As shown in Equation (1), addition of MeOH to **1** affords [TBDH][O_2COMe] (**2**) in quantitative yield. Critically, the $TBDH^+$ cation has the ideal topology to stabilize the methyl-carbonate anion by H-bonds (see the Supporting Information). Carbonates **3** and **4** were also prepared from the more acidic benzyl alcohol and the bulkier isopropanol, respectively [Eq. (1)]. Both **3** and **4** decarboxylate readily under reduced pressure and were characterized by their solution ^1H and ^{13}C NMR spectra. Similarly to the formation of carbonates **2**–**4**, carbamate **5** was obtained in quantitative yield by reacting **1** with morpholine [Eq. (2)]. Interestingly, the carbamate salt $[O(C_2H_4)_2NCO_2^-][O(C_2H_4)_2NH_2^+]$ obtained from CO_2 and neat morpholine is converted to **5** by subsequent addition of two equivalents of **1**. This route is especially attractive for the synthesis of the dimethylcarbamate **6** [Eq. (3)], because $[Me_2NCO_2^-][Me_2NH_2^+]$ is commercially available and easier to handle than dimethylamine gas.



(1)



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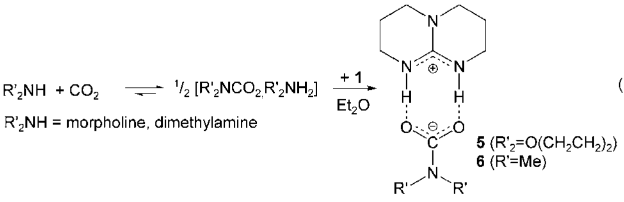
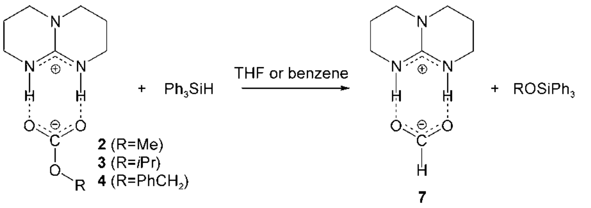


(3)

Having a series of functionalized carbonate and carbamate anions at hand, their reduction chemistry was explored using silanes R_3SiH. Silanes are indeed efficient reductants for CO_2 in its conversion to methane and its reduction to methanol.[10] The choice of silanes was also motivated by their mild reduction potentials which are well-positioned to reduce carbonates and carbamates to alkyl formates and formamides, respectively, with an only slightly negative free-energy balance of -9.1 and -10.2 kcal mol^{-1}, respectively.[12]

Reduction of **2** with Ph_3SiH in THF was achieved after 20 min at 25 °C, but the formate salt **7** was isolated as the product instead of the expected methylformate MeOC(O)H [Eq. (4)]. Though this reaction demonstrates that silanes are well-suited for the reduction of carbonates, the reduction step also results in the release of the alcohol function as a silylether derivative ($MeOSiPh_3$) and therefore in the loss of the functionalization group in our strategy. Reduction of **3** and **4** led to the same result showing that the carbonate has no influence on the fate of the reaction [Eq. (4)]. All three silylether derivatives $ROSiPh_3$ (R = Me, *i*Pr, and $PhCH_2$) were independently prepared and characterized. To better understand the factors responsible for the formation of unwanted silylethers, the mechanism for the reduction of carbonates mediated by silanes has been investigated using DFT calculations (for the reduction of **2** with the parent silane SiH_4, Scheme 1). The complete potential energy surface is given in the Supporting Information.



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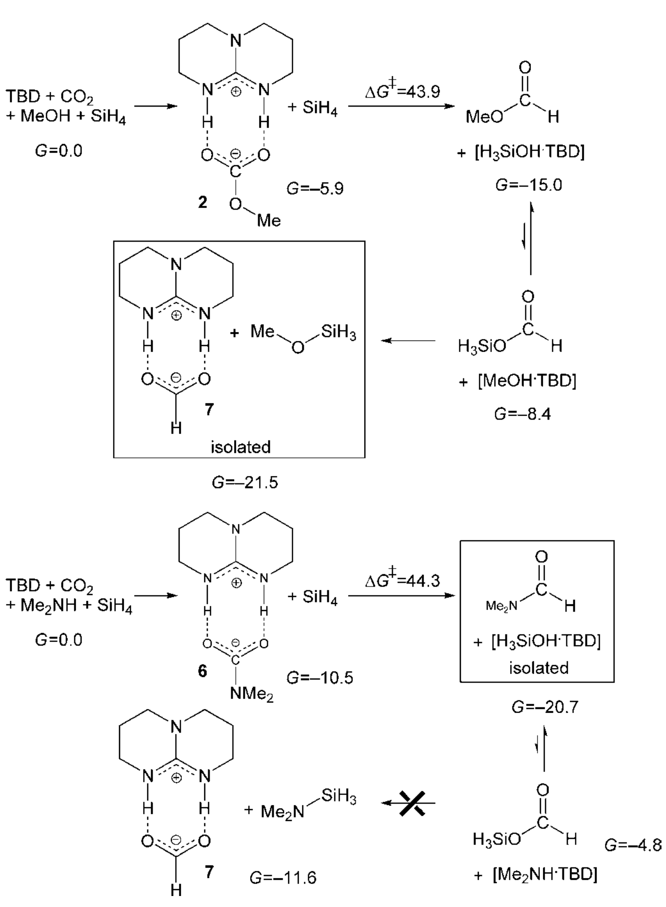
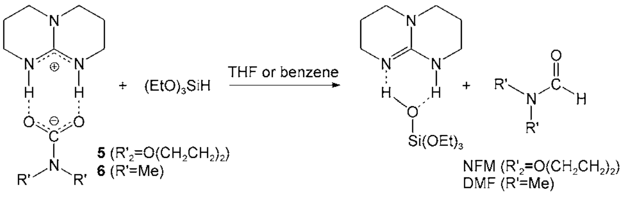


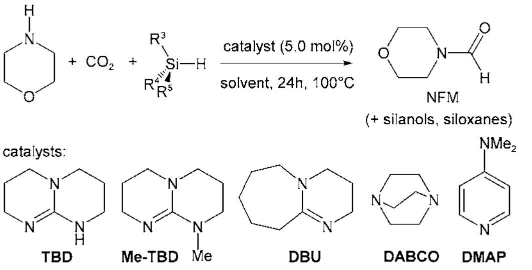
Scheme 1. Computed pathways for the reduction of **2** and **6** by silane, at the M05-2X/6-311++G** level of theory (free energies *G* are given in kcal mol^{-1}).

The reduction step of **2** by SiH_4 controls the kinetics of the transformation with a free-energy barrier of 43.9 kcal mol^{-1} to yield methyl formate, after elimination of the silanol as the [H_3SiOH·TBD] pair. Formation of methyl formate is slightly favored ($\Delta G = -15.0$ kcal mol^{-1}) over the formation of silylformate $H_3SiOC(O)H$ ($\Delta G = -8.4\,kcal\,mol^{-1}$). However, both formates are engaged in a fast equilibrium and, ultimately, silylformate behaves as a silylating agent towards methanol. This results in the formation of **7** along with silylether $MeOSiH_3$, and therefore loss of the functionalizing group ($\Delta G = -21.5\,kcal\,mol^{-1}$). This mechanism clearly accounts for the absence of kinetic control of the defunctionalization of the alkyl formate observed with the bulkier carbonate **3** or more acidic derivative **4** as the kinetics are controlled by the hydride transfer from silicon to the carbonate carbon. This computational model reveals that the reductive functionalization of CO_2 using silanes requires a functionalizing group exhibiting a lower affinity for silicon and a greater affinity for carbon than alcohols and we therefore attempted the reduction of carbamates using silanes. Addition of three equivalents of $(EtO)_3SiH$ to a THF solution of **5** resulted in the reduction of the C^{IV} carbon center to the corresponding formamide [100 % conversion to *N*-formylmorpholin (NFM) after 15 h at 100 °C, Eq. (5)]. This transformation is the first example of a reduction of a carbamate salt using a silane derivative. In this reaction, silicon both promotes the reduction of the C^{IV} center by supporting the reactive hydride group and acts as the oxygen sink to cleave the C–O bond of CO_2. Ph_2SiH_2 and $PhSiH_3$ exhibit increased kinetics as the reduction of **5** to NFM is complete after 1 h at 100 °C with Ph_2SiH_2 (48 h at 25 °C) and 6 h at 25 °C with $PhSiH_3$. $(EtO)_3SiOH$ is formed as a by-product in Equation (5) (identified by ^1H NMR spectroscopy)[13] and siloxanes are likely oxidation side-products when polysilanes are used, as attested by the formation of the $(PhSiO_{3/2})_8$ silsesquioxane cage from $PhSiH_3$ (see the Supporting Information). Analogously, reduction of **6** with $PhSiH_3$ affords dimethylformamide (DMF) with 100 % yield with respect to **6**, within 6 h at 25 °C [Eq. (5)]. The computed mechanism for the reduction of **6** is similar to the reduction of carbonates with silanes (Scheme 1 and the Supporting Information). First, the hydride transfer from silicon to carbon (reduction step) remains the rate-limiting step which is assisted by the stabilization of the carbamate anion by H bonds with the $TBDH^+$ cation. In fact, no reduction is observed by reacting a THF solution of morpholine and CO_2 with an excess $PhSiH_3$, even after 72 h at 140 °C. Second, the thermodynamics of the reaction are changed so that formation of DMF is favored by 9.1 kcal mol^{-1} over elimination of $[HCO_2^-][TBDH^+]$ and Me_2NSiH_3.



(5)

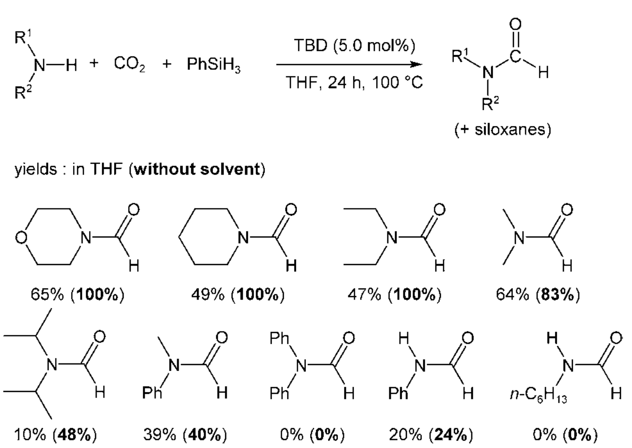
Using a stoichiometric amount of a base shifts the overall energy balance of the reaction to a more negative value ($\Delta G = -20.7\,kcal\,mol^{-1}$) than required for the effective process ($\Delta G = -16.2\,kcal\,mol^{-1}$ in the absence of a base), therefore resulting in energy inefficiency. The formylation reaction of amines using CO_2 and silanes was thus attempted utilizing only a catalytic amount of TBD. Conversion of morpholine to NFM using 2 bar of CO_2, one equivalent $PhSiH_3$ and 5 mol % TBD in a THF solution was complete within 48 h at 100 °C, demonstrating that the catalytic version of this transformation was available. This new organocatalytic reduction of CO_2 was explored to get a better knowledge of its scope (Table 1, Eq. (6), and Scheme 2). Importantly, the reaction proceeds under very mild conditions, at a low CO_2 pressure of 1 to 2 bar at 100 °C. A limited screening of catalysts was performed using the CO_2/morpholine/$PhSiH_3$



(6)

Table 1: Catalytic formylation of morpholine using CO_2 and silanes as shown in Equation (6).

Entry	Silane ($R^3R^4R^5SiH$)	Catalyst	Solvent	Yield [%]
1	$PhSiH_3$ (1 equiv)	TBD	THF	65
2	$PhSiH_3$ (1 equiv)	DBU	THF	20
3	$PhSiH_3$ (1 equiv)	Me-TBD	THF	15
4	$PhSiH_3$ (1 equiv)	DMAP	THF	17
5	$PhSiH_3$ (1 equiv)	DABCO	THF	<5
6	$PhSiH_3$ (1 equiv)	NEt_3	THF	<5
7	$PhSiH_3$ (1 equiv)	none	THF	0
8	$PhSiH_3$ (1 equiv)	TBD	CH_3CN	93
9	$PhSiH_3$ (1 equiv)	TBD	none	100
10	$PhSiH_3$ (1 equiv)	TBD	DMSO	74
11	$PhSiH_3$ (1 equiv)	TBD	C_6H_6	70
12	Ph_2SiH_2 (1.5 equiv)	TBD	THF	33
13	$(EtO)_3SiH$ (3 equiv)	TBD	THF	46
14	Ph_3SiH (3 equiv)	TBD	THF	0



Scheme 2. Organocatalytic reduction of CO_2 to formamides using amines and $PhSiH_3$.

three-component system as benchmark reaction. The activities of several nitrogen bases were thus compared: TBD, Me-TBD, 1,8-diazabicycloundec-7-ene (DBU), 1,4-diazabicyclo-[2.2.2]octane (DABCO), 4-dimethylaminopyridine (DMAP), and triethylamine (NEt_3; entries 1–6, Table 1). Whereas DABCO and NEt_3 showed no catalytic activity, stronger bases such as Me-TBD, DBU, and DMAP proved to be efficient catalysts for the formylation of morpholine. No conversion of the starting materials was observed in the absence of any catalyst (entry 7).

According to these experiments, TBD performs best and it was thus chosen to explore the scope of amines active in this reaction (Scheme 2). Dialkylamines such as morpholine, piperidine, Et_2NH, Me_2NH (used as its carbonated surrogate) are converted to their formamide derivative in good yields (47–65 %) with a low catalyst charge of 5 mol % (Scheme 2). As expected, the yield is lowered as the steric pressure increases on the nitrogen atom and reaches 10 % when $i\mathrm{Pr}_2NH$ is used. Aromatic amines proved to be active substrates as well, with conversion yields ranging from 20 (for $PhNH_2$) to 39 % (MePhNH). No formamide could be detected by NMR spectroscopy or GC/MS when formylation was attempted with Ph_2NH or a primary aliphatic amine such as hexylamine. Overall, secondary amines proved more reactive than primary amines and aliphatic amines have greater conversions than aromatic amines, indicating that the activity is mainly governed by the basicity of the amine. Change in the silane source confirms that $PhSiH_3$ is a more efficient reductant than Ph_2SiH_2 or $(EtO)_3SiH$ for the formylation of morpholine (entries 1, 11–14, Table 1). For example, formylation of morpholine, using TBD (5 mol %) and $(EtO)_3SiH$ reaches 46 % after 24 h at 100 °C whereas the conversion is 33 % and 65 % using Ph_2SiH_2 and $PhSiH_3$, respectively, under the same conditions. The solvent has a noticeable influence on the conversion and slightly higher yields are observed for polar solvents such as acetonitrile (entries 1 and 8–11 in Table 1). More importantly, in the absence of any solvent, the amine substrate itself as the solvent affords the best conversion as exemplified in Table 1 and Scheme 2: dialkylamines are converted to their formyl derivative in excellent yields (above 83 %) and formation of *N*,*N*-diisopropylformamide is achieved with a reasonable 48 % yield. Under these conditions, both the amine and the formamide formed in situ play the role of a solvent so that utilizing an excess amine is unnecessary.

Overall, this new catalytic reaction combines several advantages that make it competitive with the formylation reaction of amines using CO_2 and H_2, developed in the 1980s by L. Vaska and regularly improved since then.[7,14] First, using silanes in place of dihydrogen as a reductant allows the use of an organocatalyst in place of an expensive and/or toxic metal catalyst as usually employed in the formylation of amines with CO_2/H_2. In addition, whereas stoichiometric amounts of bases, a high pressure (typically above 100 bars) and an organic solvent are required in the CO_2/H_2/amine three-component system,[7,14] the reaction depicted in Scheme 2 proceeds without additives, at low pressure (< 3 bar) under solvent-free conditions. Given these mild reaction conditions we were able to promote the formylation of a wide spectrum of amines (Scheme 2), while it is limited to Me_2NH, Et_2NH, and $PhNH_2$ when H_2 is used as a reductant. Further work is underway to extend this diagonal strategy for the recycling of CO_2 to other functionalized and reduced chemicals by tuning independently the functionalizing and reducing agents.

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[1] M. Aresta, *Carbon dioxide as chemical feedstock*, Wiley-VCH, Weinheim, **2010**.

[2] *Tracking industrial energy efficiency and CO_2 emissions, International Energy Agency*, Paris, France, **2007**.

[3] a) K. Huang, C. L. Sun, Z. J. Shi, *Chem. Soc. Rev.* **2011**, *40*, 2435–2452; b) T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387.

[4] a) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388–2410; b) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312–1330.

[5] a) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem. Soc. Rev.* **2009**, *38*, 89–99; b) W. Wang, S. P. Wang, X. B. Ma, J. L. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703–3727.

[6] a) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259–272; b) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168.

[7] C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem.* **2010**, *122*, 9971–9974; *Angew. Chem. Int. Ed.* **2010**, *49*, 9777–9780.

[8] a) I. I. F. Boogaerts, S. P. Nolan, *J. Am. Chem. Soc.* **2010**, *132*, 8858–8860; b) A. Correa, R. Martin, *J. Am. Chem. Soc.* **2009**, *131*, 15974–15975; c) T. Fujihara, T. H. Xu, K. Semba, J. Terao, Y. Tsuji, *Angew. Chem.* **2011**, *123*, 543–547; *Angew. Chem. Int. Ed.* **2011**, *50*, 523–527; d) T. Ohishi, M. Nishiura, Z. M. Hou, *Angew. Chem.* **2010**, *122*, 8852–8855; *Angew. Chem. Int. Ed.* **2008**, *47*, 5792–5795; e) W. Z. Zhang, W. J. Li, X. A. Zhang, H. Zhou, X. B. Lu, *Org. Lett.* **2010**, *12*, 4748–4751.

[9] D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* **2003**, *103*, 3857–3897.

[10] a) S. N. Riduan, Y. G. Zhang, J. Y. Ying, *Angew. Chem.* **2009**, *121*, 3372–3375; *Angew. Chem. Int. Ed.* **2009**, *48*, 3322–3325; b) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660–10661; c) T. Matsuo, H. Kawaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 12362–12363.

[11] C. Villiers, J. P. Dognon, R. Pollet, P. Thuery, M. Ephritikhine, *Angew. Chem.* **2010**, *122*, 3543–3546; *Angew. Chem. Int. Ed.* **2010**, *49*, 3465–3468.

[12] Note: These free energies are computed for the reduction of carbonate **2** to methyl formate and for the reduction of carbamate **6** to DMF.

[13] R. Ishimoto, K. Kamata, N. Mizuno, *Angew. Chem.* **2009**, *121*, 9062–9066; *Angew. Chem. Int. Ed.* **2009**, *48*, 8900–8904.

[14] a) P. G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1994**, *116*, 8851–8852; b) Y. Kayaki, Y. Shimokawatoko, T. Ikariya, *Adv. Synth. Catal.* **2003**, *345*, 175–179; c) F. C. Liu, M. B. Abrams, R. T. Baker, W. Tumas, *Chem. Commun.* **2001**, 433–434; d) P. Munshi, D. J. Heldebrant, E. P. McKoon, P. A. Kelly, C. C. Tai, P. G. Jessop, *Tetrahedron Lett.* **2003**, *44*, 2725–2727; e) L. Schmid, M. Rohr, A. Baiker, *Chem. Commun.* **1999**, 2303–2304; f) S. Schreiner, J. Y. Yu, L. Vaska, *J. Chem. Soc. Chem. Commun.* **1988**, 602–603.