Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Accepted Article

Title: CO2-based N-formylation of Amines Catalyzed by Fluoride and Hydroxide Anions

Authors: Martin Hulla, Felix Daniel Bobbink, Shoubhik Das, and Paul J. Dyson

To be cited as: *ChemCatChem* 10.1002/cctc.201601027

Link to VoR: http://dx.doi.org/10.1002/cctc.201601027

A Journal of
ChemPubSoc Europe

WILEY-VCH www.chemcatchem.org

10.1002/cctc.201601027

CO_2-based N-formylation of Amines Catalyzed by Fluoride and Hydroxide Anions

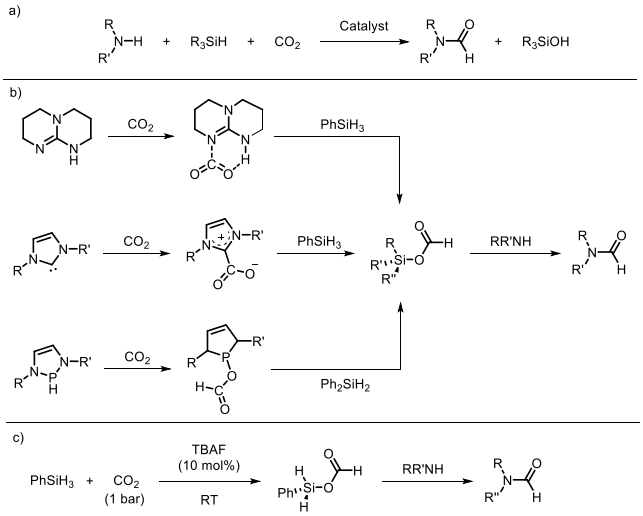
Martin Hulla, Felix D. Bobbink, Shoubhik Das and Paul J. Dyson*

Abstract: We describe a simple approach for N-formylation with CO_2 and hydrosilane reducing agents. Fluoride and hydroxide salts efficiently catalyze the reaction, principally via the activation of the hydrosilanes, leading to hydrosilane reactivities comparable to $NaBH_4$/$LiAlH_4$. Consequently, N-formylation of amines with CO_2 may be achieved at room temperature and atmospheric pressure. The mechanism of these anionic catalysts contrasts with that of the currently reported systems, where activation of CO_2 is the key mechanistic step. Using TBAF as a simple ammonium salt catalyst, N-formylated products of both aliphatic and aromatic amines could be obtained in excellent yields and with high selectivity.

Carbon dioxide is cheap, non-toxic and renewable (C1) building block for chemical synthesis. However, CO_2 is thermodynamically and kinetically stable, posing a challenge to its efficient use in the production of commodity chemicals.[1] The non-catalytic reduction of CO_2 and its subsequent functionalization can be achieved with stoichiometric amounts of strong reducing agents such as $NaBH_4$ and $LiAlH_4$.[2] However, the high cost and low selectivity of these reagents make them unsuitable for industrial scale chemical synthesis. Consequently, the development of CO_2 activation catalysts for novel C-C, C-O and C-N bond formation reactions in combination with milder reducing agents has attracted attention in recent years.[3]

Among these catalyzed reactions the N-formylation of amines with CO_2 is of particular interest as the resulting formamides are commonly employed solvents as well as versatile building blocks in the synthesis of pharmaceuticals and agrochemicals.[3a,4] On an industrial scale formamides are prepared from carbon monoxide,[5] which could be replaced with CO_2 in combination with a reducing agent. In drug-related pharmacokinetic studies employing positron emission topography, the rapid preparation of ^{11}C labelled drug molecules is required. Since ^{11}C is generated in a cyclotron in the form of thermodynamically stable $^{11}CH_4$ or $^{11}CO_2$, and the direct incorporation of CO_2 into drug molecules is difficult, its transformation into $^{11}CH_3I$ or ^{11}CO is frequently required.[6] It would be advantageous, however, to directly incorporate CO_2 into drug and drug-like molecules.

While the N-formylation of amines with CO_2 may be achieved using hydrogen as the reducing agent,[7] harsh reaction conditions and poor functional group tolerance led to the employment of other reducing agents such as hydrosilanes (Scheme 1a).[3e,4] N-formylation of amines with hydrosilanes has been achieved with transition metal-based catalysts (copper[8,9] and iron[10]) and a number of organocatalysts.[11-14]



Scheme 1. N-Formylation of amines with CO_2 and silane reducing agents. a) General reaction scheme. b) Known CO_2 activation modes for the synthesis of formoxysilane intermediates on route to N-formylated products. c) New direct method to the formoxysilane intermediates catalyzed by TBAF and subsequent N-formylation of amines

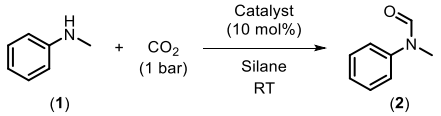
Activation of CO_2 has been achieved with nitrogen superbases[11] via Lewis base-Lewis acid (LB-LA) interactions between the lone pair on the nitrogen and the electropositive CO_2 carbon. In the case of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) the interaction is further stabilized by H-bonding between the auxiliary amine functionality of the base and an oxygen atom on the CO_2. Formation of LB-LA adducts with CO_2 and subsequent N-functionalization of amines was also reported with N-heterocyclic carbene (NHC) and thiazolium carbene catalysts.[12] Further improvements were made with 1,3,2-diazaphospholenes,[13] in which insertion of CO_2 into the phosphorus-hydrogen bond of the catalyst activates the CO_2 for further functionalization (Scheme 1b). Despite these advances, limitations to the current catalysts exist, e.g. long reaction times (frequently beyond 24 hours) are required with the carbene catalysts and over reduction to the N-methylated products is frequently observed with the 1,3,2-diazaphospholene systems. Furthermore, increasingly air and moisture sensitive catalysts are used to achieve more efficient CO_2 activation, hindering their widespread use.

[a] M. Hulla, F. D. Bobbink, Prof. Dr. P. J. Dyson Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne (Switzerland)
E-mail: paul.dyson@epfl.ch
[b] Dr. S. Das
Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Göttingen, Germany

Supporting information for this article is given via a link at the end of the document

We report an alternative approach to the N-formylation reaction with CO_2, based principally on the activation of the hydrosilane reducing agent, which overcomes the above mentioned limitations. Using simple fluoride or hydroxide salts the hydrosilane reducing agent is activated leading to reactivities comparable to $NaBH_4$/$LiAlH_4$. As such, N-formylation of amines with CO_2 may be rapidly achieved at RT and atmospheric pressure with cheap, commercially available catalysts.

Table 1. Optimization of N-formylation reaction conditions using N-methylaniline as a model substrate.

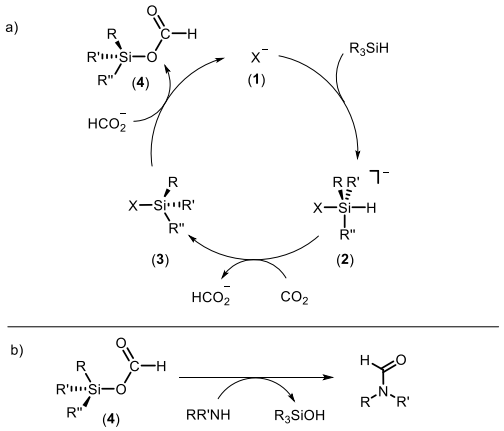


Entry	Catalyst	Silane	Solvent	T [h]	Yield [%]
1	[BMIm]Cl	$PhSiH_3$	-	20	6
2	[BdMIm]Cl	$PhSiH_3$	-	20	38
3	[BMP]Cl	$PhSiH_3$	-	20	47
4	TBAI	$PhSiH_3$	-	20	2
5	TBAB	$PhSiH_3$	-	20	6
6	TBAC	$PhSiH_3$	-	20	65
7	TBAF.3H_2O	$PhSiH_3$	-	2	66
8	TBAOH.30H_2O	$PhSiH_3$	-	2	73
9	TBAF.3H_2O	$PhSiH_3$	-	6	99
10	TBAF.3H_2O	Ph_2SiH_2	-	6	25
11	TBAF.3H_2O	PMHS	-	6	0
12	TBAF.3H_2O	$PhSiH_3$	Pentane	2	13
13	TBAF.3H_2O	$PhSiH_3$	THF	2	67
14	TBAF.3H_2O	$PhSiH_3$	MeCN	2	69
15	TBAF.3H_2O	$PhSiH_3$	DMF	2	91
16	-	$PhSiH_3$	DMF	20	55

Following the report on 1-butyl-3-methylimidazolium chloride ([BMIm]Cl)[14] as a catalyst for the N-formylation reaction of amines with CO_2, we decided to investigate the reactivity of a number of related imidazolium-based salts. It quickly became apparent to us that the imidazolium cation does not participate in the reaction. Although the in-situ formation of NHC carbenes by self-deprotonation is possible with imidazolium salts,[15] methylation of the acidic C2 position would inhibit the reaction if carbene formation is necessary for the reaction. We found that methylation of [BMIm]Cl at the C2 position to afford 1-butyl-2,3-dimethylimidazolium chloride ([BdMIm]Cl), leads to a six times higher reaction rate (Table 1, entries 1 and 2). In addition, replacement of [BMIm]Cl with 1-butyl-1-methyl-pyrrolidinium chloride ([BMP]Cl) or tetrabutylammonium chloride (TBAC) further improves the catalytic activity (Table 1, entries 3 and 6).

For organic chloride salts the reactivity follows the order [BMIm]Cl < [BdMIm]Cl < [BMP]Cl < TBAC. The highest activity demonstrated by TBAC, with a benign tetrabutylammonium cation, indicates that the reaction is driven by the anion with the cation acting as a non-interacting counter ion. Subsequent screening of TBA salts revealed a strong anion dependency on the reaction rate, with $I^- < Br^- < Cl^- << F^- \sim OH^-$ (Table 1, entries 4-8). Harder, more nucleophilic anions with high affinity for silicon such as F^- and OH^- catalyze the reaction much more efficiently than soft, less nucleophilic anions.

The overall catalytic activity of the salt is based on a combination of the nucleophilicity of the anion and the extent of the cation-anion interactions in solution. Strong ionic interactions promote the formation of less nucleophilic ion pairs, which result in lower catalytic activities. In contrast, large, sterically hindered cations such as TBA minimize cation-anion pairing and promote the formation of 'free', highly nucleophilic anions. Note, in a solvent free system 66% conversion of N-methylaniline is achieved with TBAF and phenylsilane in 2 hours at RT (Table 1, entry 7) while no conversion is observed with CsF under equivalent conditions. This finding is consistent with earlier reports on CsF with dimethylphenylsilane that required 39 hours at elevated temperature for the reaction to proceed.[16]



Scheme 2. Proposed reaction mechanism for the N-Formylation reaction. a) Formation of formoxysilane intermediate. b) Reaction of the formoxysilane with amines.

TBAF and other fluoride salts are known to interact with silanes and are frequently employed as catalysts in the hydrosilane reduction of carbonyls.[17] The reaction proceeds via nucleophilic attack on the silane and the formation of a hypervalent silicon intermediate.[17f] Presumably the silicon hydride in the hypervalent silicon intermediate is able to directly reduce CO_2 via insertion into the polarized $Si^{\delta+}$-$H^{\delta-}$ bond. CO_2 insertion into polarized $[E]^{\delta+}$-$H^{\delta-}$ bonds is known for many group 13 and 14 hydrides with examples reported for B,[2a-b,18] Al,[2c,19] Ga,[20] Ge,[21] Sn[22] and even proposed for silicon.[23] To confirm this hypothesis we recorded ^1H and ^{19}F NMR spectra of phenylsilane with 10 mol% TBAF (SI). After addition of the salt, a centered at -0.24 ppm, not present in neat phenylsilane, was observed. This finding is consistent with the formation of a 5-coordinate trigonal bipyramidal silicon center with a hydride in an axial position coupling to two equatorial hydrogen nuclei J_{H-H} = 4.1Hz. The related doublet was identified by COSY NMR spectroscopy at 3.64 ppm at slightly lower frequency (0.32 ppm) to the original phenylsilane singlet (see SI). No coupling to the anion was observed presumably due to rapid anion exchange in solution at RT.[17f] A number of different CO_2 reduction mechanisms are possible by the silicon hydride. However, while direct CO_2 insertion into the polarized $Si^{\delta+}$-$H^{\delta-}$ bond was previously suggested,[23] and partly supported by the detection of the hypervalent silicon intermediate, a recent DFT study of related systems indicates that in the presence of CO_2 a

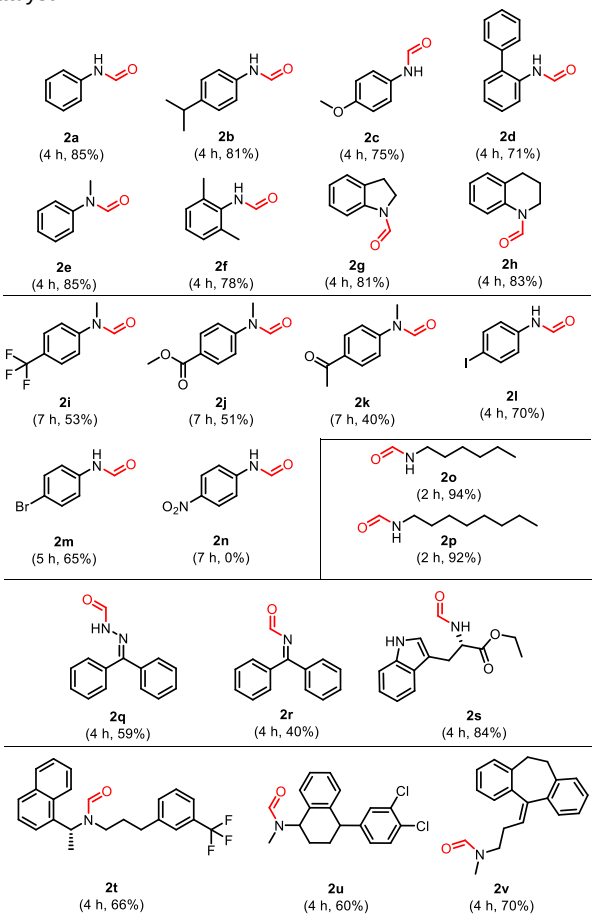
concerted hydride transfer via an S_n2-type mechanism with a structurally equivalent 5-coordinate silicon transition state, followed by reinsertion of a formate anion, is energetically favoured.[24]

Based on our experimental data and previous studies,[14,16,23] an alternative reaction mechanism for the N-formylation of amines with CO_2 and hydrosilanes may be proposed (Scheme 2), which conforms with a recently published theoretical study.[24] In the first step the hydrosilane is activated via nucleophilic interactions with the anion to form a hypervalent silicon center (**2**).[17a-d,f] Hydride transfer from **2** to CO_2 generates the formate anion and a neutral R_3SiX (**3**) species.[48] Reinsertion of the formate anion into **3** eliminates the formoxysilane intermediate (**4**)[16] and regenerates the catalytically active anion (**1**). Finally, the formoxysilane **4** reacts with the amine to afford the desired N-formylated product.

We then investigated the influence of different hydrosilanes on the reaction rate. More sterically congested hydrosilanes such as Ph_2SiH_2 were less effective under the solvent free conditions employed. With PMHS an N-formylation product was not observed and, instead, cross-linking of the polymer occurred. The decrease in the reaction rate observed with Ph_2SiH_2 is consistent with the proposed S_n2-type mechanism for the reaction of hydrosilanes with hydroxide anions[25] and the calculated S_n2-type mechanism of CO_2 reduction with silicon hydride[24] as well as the formation of an axial silicon hydride bond. The steric congestion induced by an additional phenyl ring hinders nucleophilic attack by the anion on the silicon centre and prevents its activation.

Although the reaction operates under solvent-free conditions with liquid amines, a solvent is required to solubilize solid substrates. In THF and MeCN the reaction proceeds at an equivalent rate to the solvent free system (Table 1, entries 13 and 14). A positive solvent effect is observed in DMF and the reaction rate is greatly enhanced (Table 1, entry 15). DMF has been demonstrated to activate hydrosilanes[26] and more recently proposed to activate CO_2 by interacting with the electrophilic carbon center.[27] However, while these mechanisms could partially account for the higher activity, in the presence of far superior nucleophiles, i.e. F^- or OH^- anions, such mechanisms seems less likely to significantly improve the reaction rate. Moreover, the effect cannot be attributed to the enhanced homogenization of the system as TBAF completely dissolves in all of the aforementioned solvents. Since DMF and DMSO were recently reported to catalyze the reaction,[28] albeit at a much lower rate than the anions (Table 1, entries 15 and 16), and amine activation by the solvent has been proposed, it is not unreasonable to conclude that a synergistic effect on the activation of phenylsilane with F^- or OH^- anions and amine activation with DMF are responsible for the reaction rate enhancements observed in DMF. A weak autocatalytic activity was observed with N-formanilides, presumably due to the delocalisation of the nitrogen lone pair onto the benzene ring (see SI).

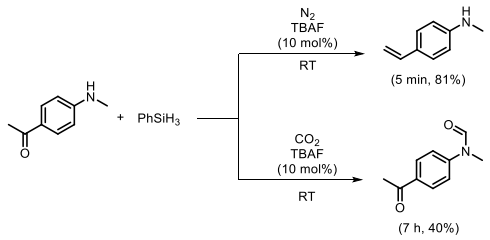
TBAF was used to evaluate the scope of the N-formylation reaction with various amines as the reaction between phenylsilane and TBAOH can be very exothermic and requires careful control. The reference substrate, N-methylaniline (**2e**), was fully converted within 4 hours at RT and the product isolated in 85% yield. Electron donating substituents on the aniline ring (**2b-2d**) accelerate the reaction rate whereas electron withdrawing groups (**2i-2m**) retard it. Competing N-methylation was observed for **2i-2m**, whereas p-nitroaniline (**2n**) was unreactive under the reaction conditions. Primary aliphatic amines (**2o-2p**) afford the corresponding N-formylamines as the only reaction product within 2 hours. Polyformylation, observed with NHC carbenes[12a] or [BMIm]Cl at elevated pressures,[14] was not observed with the TBAF catalyst.



Scheme 3. Substrate scope for the N-formylation reaction with TBAF.$3H_2O$ catalyst, $PhSiH_3$ and CO_2. Reaction conditions: Amine (1 mmol), phenylsilane (1.2 mmol), CO_2 (1 atm), TBAF (10 mol%), 2-7 h at RT. Isolated yields.

Although fluoride activated hydrosilanes are potent reducing agents of carbonyl, imine and nitrile bonds,[17] methylacetate and acetyl substituted anilines (**2j,2k**), benzophenone imine (**2r**) and benzophenone hydrazone (**2q**) were converted to their corresponding N-formylamines without the reduction of the unsaturated bond. An unprecedented selectivity for the reduction of CO_2 is observed. Note, 4-acetyl-N-methylaniline is rapidly reduced to the corresponding alkene under the same reaction conditions in the absence of CO_2 (Scheme 4). The observed selectivity indicates that the reduction of CO_2 and the formation of the formoxysilane intermediate is extremely fast. The rate limiting step probably corresponds to the amine formylation step rather than the reduction of the otherwise unreactive CO_2. This suggestion is consistent with the proposed reaction mechanism, in which the formylation reaction is essentially uncatalyzed, and because anilines with electron withdrawing groups are less reactive than those with electron donating groups. Finally, to demonstrate that our methodology can be used for the direct preparation of

^{11}C labeled drug molecules we formylated cinacalcet (**2t**), setraline (**2u**) and nortriptyline (**2v**) as well as the amino acid ethyl formyl-L-tryptophanate (**2s**). The N-formylated products were isolated in good yields (66-84%).



Scheme 4. Reduction of 4-acetyl-N-methylaniline with $PhSiH_3$ under CO_2 or N_2.

In conclusion, we have demonstrated that simple nucleophilic anions with a high affinity for silicon act as hydrosilylation catalysts for the reduction of CO_2 and the subsequent N-formylation of amines under ambient conditions. A mechanism for the catalysts is described based on the activation of the silane reducing agent followed by the direct reduction of CO_2 with silicon hydride. The system has an unprecedented selectivity for the reduction of CO_2 over the otherwise more reactive carbonyls, imines and hydrazones. The novel approach described here should lead to the development of more active catalysts for the reductive functionalization of CO_2 in the future.

ACKNOWLEDGMENT

We thank Bastien L. Roulier for his technical assistance and the Fondation Claude et Juliana (M.H.) and the Swiss Competence Centre for Energy Research (F.D.B.) for financial support.

[1] Aresta, M. *Carbon Dioxide as Chemical Feedstock*; Wiley-VCH Verlag GmBh, Weinheim; **2010**.

[2] a) R. F. Nystrom, W. H. Yanko, W. Brown, *J. Am. Chem. Soc.* **1948**, *70*, 441–441. b) T. Wartik, R. K. Pearson, *J. Am. Chem. Soc.* **1955**, *77*, 1075–1075. c) I. Knopf, C. C. Cummins, *Organometallics* **2015**, *34*, 1601–1603.

[3] a) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem.* **2016**, 128, 7416–7467. b) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem. Int. Ed.* **2016**, DOI 10.1002/anie.201507458. c) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933. d) C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482. e) F. J. Fernández-Alvarez, A. M. Aitani, L. A. Oro, *Catal. Sci. Technol.* **2014**, *4*, 611–624. f) K. Huang, C.-L. Sun, Z.-J. Shi, *Chem. Soc. Rev.* **2011**, *40*, 2435–52. g) M. Liu, T. Qin, Q. Zhang, C. Fang, Y. Fu, B.-L. Lin, *Sci. China: Chem.* **2015**, *58*, 1524–1531.

[4] A. Tlili, E. Blondiaux, X. Frogneux, T. Cantat, *Green Chem.* **2015**, *17*, 157–168.

[5] H. Bipp, Hansjörg; Kieczka, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2000**.

[6] F. Liger, T. Eijsbouts, F. Cadarossanesaib, C. Tourvieille, D. Le Bars, T. Billard, *Eur. J. Org. Chem.* **2015**, *2015*, 6434–6438.

[7] a) L. Zhang, Z. Han, X. Zhao, Z. Wang, K. Ding, *Angew. Chem. Int. Ed.* **2015**, 54, 6186–6189. b) L. Zhang, Z. Han, X. Zhao, Z. Wang, K. Ding, *Angew. Chem.* **2015**, *127*, 6284–6287. c) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* **2012**, *134*, 20701–20704. d) L. Schmid, A. Canonica, A. Baiker, *Appl. Catal., A* **2003**, *255*, 23–33. e) P. Munshi, D. J. Heldebrant, E. P. McKoon, P. A. Kelly, C.-C. Tai, P. G. Jessop, *Tetrahedron Lett.* **2003**, 44, 2725–2727. f) P. G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 344–355.

[8] K. Motokura, N. Takahashi, D. Kashiwame, S. Yamaguchi, A. Miyaji, T. Baba, *Catal. Sci. Technol.* **2013**, *3*, 2392–2396.

[9] S. Zhang, Q. Mei, H. Liu, H. Liu, Z. Zhang, B. Han, *RSC Adv.* **2016**, *6*, 32370–32373.

[10] X. Frogneux, O. Jacquet, T. Cantat, *Catal. Sci. Technol.* **2014**, *4*, 1529–1533.

[11] a) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 187–90 b) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem.* **2012**, 124, 191–194

[12] a) O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.* **2012**, *134*, 2934–7. b) E. Blondiaux, J. Pouessel, T. Cantat, *Angew. Chem. Int. Ed. Engl*. **2014**, 53, 12186–90 c) E. Blondiaux, J. Pouessel, T. Cantat, *Angew. Chem.* **2014**, 126, 12382–12386. d) S. Das, F. D. Bobbink, G. Laurenczy, P. J. Dyson, *Angew. Chem. Int. Ed. Engl.* **2014**, 53, 12876–9. e) S. Das, F. D. Bobbink, G. Laurenczy, P. J. Dyson, *Angew. Chem.* **2014**, 126, 13090–13093. f) S. N. Riduan, J. Y. Ying, Y. Zhang, *J. Catal.* **2015**, DOI 10.1016/j.jcat.2015.09.009. f) S. Das, F. D. Bobbink, S. Bulut, M. Soudani, P. J. Dyson, *Chem. Commun.* **2016**, DOI 10.1039/c5cc08741d.

[13] a) C. C. Chong, R. Kinjo, *Angew. Chem. Int. Ed.* **2015**, 54, 12116–12120. b) C. C. Chong, R. Kinjo, *Angew. Chem.* **2015**, *127*, 12284–12288.

[14] L. Hao, Y. Zhao, B. Yu, Z. Yang, H. Zhang, B. Han, X. Gao, Z. Liu, *ACS Catal.* **2015**, *5*, 4989–4993.

[15] a) G. Gurau, H. Rodríguez, S. P. Kelley, P. Janiczek, R. S. Kalb, R. D. Rogers, *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 12024–6. b) G. Gurau, H. Rodríguez, S. P. Kelley, P. Janiczek, R. S. Kalb, R. D. Rogers, *Angew. Chem.* **2011**, 123, 12230–12232. c) A. K. L. Yuen, A. F. Masters, T. Maschmeyer, *Catal. Today* **2013**, *200*, 9–16.

[16] K. Motokura, M. Naijo, S. Yamaguchi, A. Miyaji, T. Baba, *Chem. Lett.* **2015**, *44*, 1217–1219.

[17] a) M. Fujita, T. Hiyama, *J. Org. Chem.* **1988**, *53*, 5405–5415. b) M. D. Drew, N. J. Lawrence, W. Watson, S. A. Bowles, *Tetrahedron Lett.* **1997**, *38*, 5857–5860. c) Y. Kobayashi, E. Takahisa, M. Nakano, K. Watatani, *Tetrahedron* **1997**, *53*, 1627–1634. d) M. Drew, N. Lawrence, D. Fontaine, L. Sehkri, S. Bowles, W. Watson, *Synlett* **1997**, *1997*, 989–991. e) K. Revunova, G. I. Nikonov, *Dalton Trans.* **2015**, *44*, 840–66. f) K. Revunova, G. I. Nikonov, *Chem. - Eur. J.* **2014**, *20*, 839–45.

[18] a) K. Fujiwara, S. Yasuda, T. Mizuta, *Organometallics* **2014**, *33*, 6692–6695. b) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660–1.

[19] a) G. Ménard, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 5447–53. b) P.-C. Kuo, I.-C. Chen, J.-C. Chang, M.-T. Lee, C.-H. Hu, C.-H. Hung, H. Lee, J.-H. Huang, *Eur. J. Inorg. Chem.* **2004**, *2004*, 4898–4906.

[20] a) J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed. Engl.* **2015**, 54, 5098–102. b) J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin, S. Aldridge, *Angew. Chem.* **2015**, 127, 5187–5191.

[21] A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab, D. Stalke, *J. Am. Chem. Soc.* **2009**, *131*, 1288–93.

[22] a) A. Jana, H. W. Roesky, C. Schulzke, A. Döring, *Angew. Chem. Int. Ed. Engl*. **2009**, 48, 1106–9. b) A. Jana, H. W. Roesky, C. Schulzke, A. Döring, *Angew. Chem.* **2009**, 121, 1126–1129. c) G. Albertin, S. Antoniutti, J. Castro, S. García-Fontán, G. Zanardo, *Organometallics* **2007**, *26*, 2918–2930.

[23] P. Arya, J. Boyer, R. J. P. Corriu, G. F. Lanneau, M. Perrot, *J. Organomet. Chem.* **1988**, *346*, C11–C14.

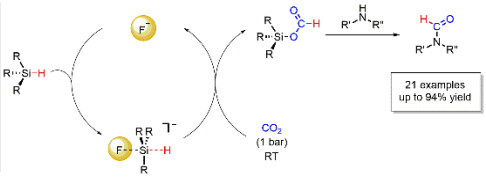
[24] Q. Zhou, Y. Li, *J. Am. Chem. Soc.* **2015**, *137*, 10182–9.

[25] a) L. Kaplan, K. E. Wilzbach, *J. Am. Chem. Soc.* **1955**, *77*, 1297–1302. b) L. H. Sommer, O. F. Bennett, P. G. Campbell, D. R. Weyenberg, *J. Am. Chem. Soc.* **1957**, *79*, 3295–3296. c) J. E. Baines, C. Eaborn, *J. Chem. Soc.* **1955**, 4023.

[26] S. Kobayashi, M. Yasuda, I. Hachiya, *Chem. Lett.* **1996**, 407–408.

[27] L. Wang, L. Lin, G. Zhang, K. Kodama, M. Yasutake, T. Hirose, *Chem. Commun.* **2014**, *50*, 14813–6.
[28] H. Lv, Q. Xing, C. Yue, Z. Lei, F. Li, *Chem. Commun.* **2016**, *52*, 6545–8.

COMMUNICATION



*Martin Hulla, Felix D. Bobbink, Shoubhik Das and Paul J. Dyson**

Page No. – Page No.

CO_2-based N-formylation of Amines Catalyzed by Fluoride and Hydroxide Anions

Keywords: Carbon dioxide, organocatalysis, sustainable chemistry, reduction, silanes