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# Bridging Amines with CO<sub>2</sub>: Organocatalyzed Reduction of CO<sub>2</sub> to Aminals

Xavier Frogneux,<sup>‡</sup> Enguerrand Blondiaux,<sup>‡</sup> Pierre Thuéry and Thibault Cantat\*

CEA, IRAMIS, NIMBE, CNRS UMR 3685 91191 Gif-Sur-Yvette Cedex, France

Fax: (+33) 1.6908.6640 E-mail: [thibault.cantat@cea.fr](mailto:thibault.cantat@cea.fr) Homepage: <http://iramis.cea.fr/Pisp/thibault.cantat/index.html>

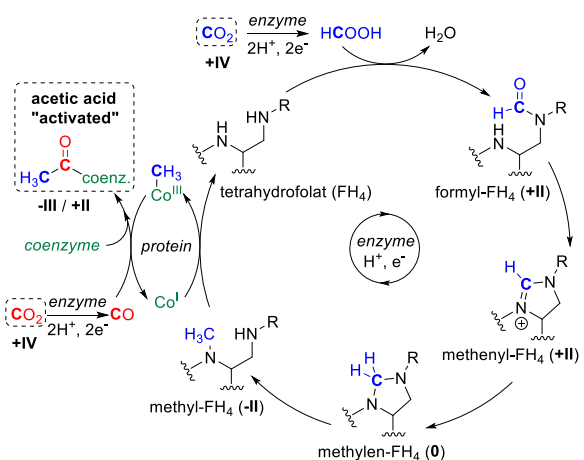
Supporting Information Placeholder

**ABSTRACT:** The 4-electron reduction of CO<sub>2</sub> in the presence of secondary aromatic amines is described for the first time to access aminals. Under metal-free hydrosilylation conditions, the four C–O bonds of CO<sub>2</sub> are cleaved and the organocatalysts are able to balance the reactivity of CO<sub>2</sub> to promote the selective formation of two C–N and two C–H bonds. The methodology enables the formation of various symmetrical and unsymmetrical aminals.

**KEYWORDS:** CO<sub>2</sub> – organocatalysis – amines – hydrosilylation – reduction – aminal

Because CO<sub>2</sub> is a renewable, cost-efficient and non-toxic resource, it is a desirable carbon feedstock for the production of value-added chemicals and a lot of groups have focused their attention on designing new transformations involving CO<sub>2</sub> over the last few years.<sup>1</sup> In particular, the reductive functionalization of CO<sub>2</sub> with nitrogen reagents has known tremendous developments using various types of reductants such as hydrosilanes, hydroboranes and dihydrogen.<sup>2</sup> These reactions have enabled the conversion of CO<sub>2</sub> into formamides,<sup>2b, 3</sup> formamidines<sup>4</sup> and methylamines.<sup>5</sup> Notably, the carbon oxidation state in these products is either +2 or –2 and the formation of C<sup>0</sup> organic functional groups from CO<sub>2</sub> remains a challenge. This trend reflects the higher electrophilicity of C<sup>0</sup> groups compared to C<sup>+II</sup> functions in carbonyl derivatives. It is indeed well established that upon hydrogenation of CO<sub>2</sub>, formate derivatives can be accumulated while formaldehyde is an elusive species because its reduction to methanol is more rapid than the hydrogenation of formic acid.<sup>1a</sup> As a consequence of this limitation, only a few reports have tackled the formation of C<sup>0</sup> species from CO<sub>2</sub>. Under hydrosilylation conditions, the selective reduction of CO<sub>2</sub> into a bis(silyl)acetal species with triethylsilane has been revealed.<sup>6</sup> Using a hydroborane reductant, Bontemps, Sabo-Etienne *et al.* successfully trapped transient formaldehyde, obtained from CO<sub>2</sub>, with 2,6-diisopropylaniline, yielding the corresponding imine.<sup>7</sup> To unlock new 4-electron reduction transformations of CO<sub>2</sub>, one should focus on the use of well-balanced catalysts, able to finely control the kinetics of CO<sub>2</sub> reduction. In nature, acetogenic bacteria are able to produce over 10<sup>9</sup> tons of acetic acid annually, following the Wood-Ljungdahl pathway (Scheme 1).<sup>8</sup> In this biochemical cycle, CO<sub>2</sub> is anchored to a diamine moiety and undergoes successive 2-electron reduction steps to yield a methylamine (C<sup>-II</sup>) after formation of the corresponding formamide (C<sup>+II</sup>), formamidine (C<sup>+II</sup>) and aminal

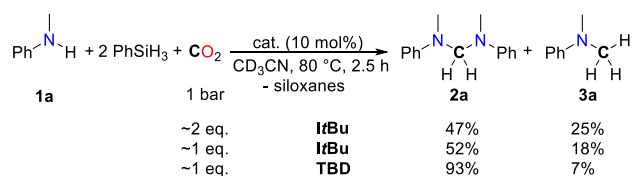
(C<sup>0</sup>) intermediates. While CO<sub>2</sub> conversion to formamides, formamidines and methylamines has been described, the synthesis of aminals<sup>9</sup> directly from CO<sub>2</sub> remains unknown and was only suggested as a possible intermediate in the Ru-based methylation of amines.<sup>5b</sup> To open up the variety of products accessible from CO<sub>2</sub>, we describe herein the first catalytic synthesis of aminals by intermolecular coupling of two amines using CO<sub>2</sub> as a C1-bridge.



**Scheme 1. Simplified mechanism of the Wood-Ljungdahl pathway for acetogenesis with CO<sub>2</sub>**

Hydrosilanes are mild reductants, cheap, non-toxic with a redox potential well poised for CO<sub>2</sub> reduction. Additionally, their slightly polar Si–H bond can be activated with metal-free catalysts, using either Lewis bases or Lewis acids.<sup>10</sup> Using phenylsilane as reductant, the reactivity between *N*-methylaniline (**1a**) and CO<sub>2</sub> has been explored using a variety

of organocatalysts able to form adducts with CO<sub>2</sub><sup>11</sup> or promote its reduction, such as guanidines, amidines, *N*-heterocyclic carbenes (NHCs) and phosphorus-bases.<sup>3a, 3b, 5f, 5g, 12</sup> Using 10 mol% of the NHC **lBu**, CO<sub>2</sub> undergoes hydrosilylation in the presence of *N*-methylaniline (**1a**) in CH<sub>3</sub>CN, and after 2.5 h at 80 °C, 76% of **1a** was converted to the expected aminal **2a** in 47% yield (Scheme 2). Nonetheless, methylamine **3a** is also produced at a similar rate reaching 25% yield. Interestingly, after prolonged reaction time (24 h) methylamine **3a** is formed as the main nitrogen product (>95%), indicating that the aminal is an intermediate in the formation of **3a** and that the catalyst is unable to prevent over-reduction of the C<sup>0</sup> carbon center in **2a**. Reducing the quantity of CO<sub>2</sub> in the reaction vessel to *circa* 1 equiv. per amine somewhat improves the **2a/3a** ratio of the reaction from 1.9 to 2.9 (Scheme 2).



**Scheme 2.** Formation of aminal **2a** via CO<sub>2</sub> hydrosilylation

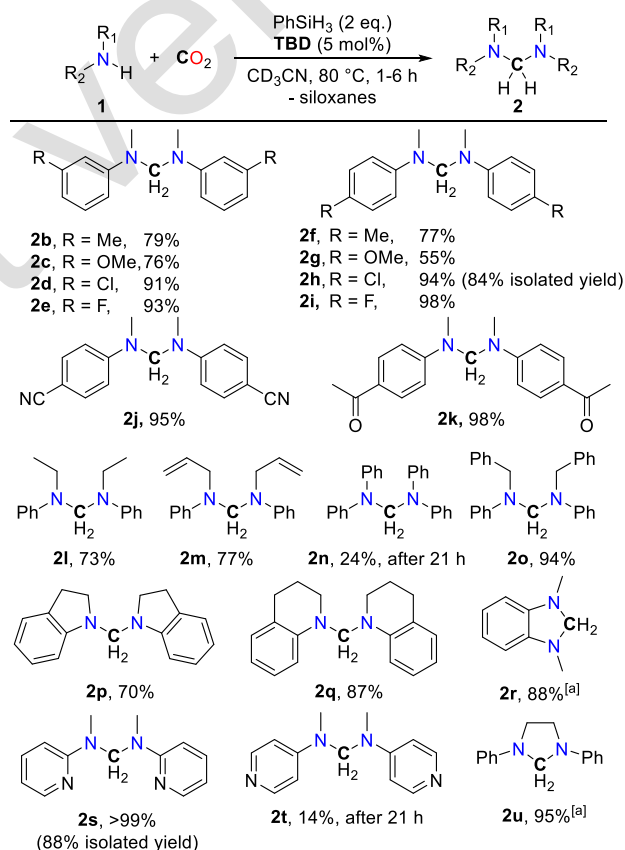
**Table 1.** Catalyst screening for the coupling of **1a** to **2a**

Entry	Catalyst (mol%)	Reductant	Time (h)	Yield <b>2a</b> (%)	Yield <b>3a</b> (%)
1	<b>lBu</b> (10)	PhSiH <sub>3</sub>	2.5	52	18
2	<b>IPr</b> (10)	PhSiH <sub>3</sub>	4.5	79	3
3	<b>VB<sup>Me</sup></b> (10)	PhSiH <sub>3</sub>	2.5	71	0
4	<b>Me-TBD</b>	PhSiH <sub>3</sub>	4.5	78	0
5	<b>DBU</b> (10)	PhSiH <sub>3</sub>	2.5	93	4
6	<b>TBD</b> (10)	PhSiH <sub>3</sub>	2.5	93	7
7	<b>TBD</b> (5)	PhSiH <sub>3</sub>	3.0	91	6
8	<b>TBD</b> (1)	PhSiH <sub>3</sub>	7.0	92	6
9	<b>TBD</b> (5)	PMHS	96	5	0
10	<b>TBD</b> (5)	TMDS	96	0	0
11 <sup>[a]</sup>	<b>TBD</b> (5)	PhSiH <sub>3</sub>	48	5	0
12 <sup>[b]</sup>	<b>TBD</b> (5)	PhSiH <sub>3</sub>	48	7	0
13 <sup>[c]</sup>	<b>TBD</b> (5)	PhSiH <sub>3</sub>	19	26	0

Reaction conditions: NMR tube (2.5 mL), catalyst, amine (0.10 mmol), hydrosilane (6 eq. “Si–H”), solvent (0.30 mL), CO<sub>2</sub> (1 bar). Yields determined by <sup>1</sup>H NMR with Ph<sub>2</sub>CH<sub>2</sub> as internal standard. <sup>[a]</sup> in toluene-*d*<sub>8</sub> <sup>[b]</sup> in THF-*d*<sub>8</sub>, <sup>[c]</sup> at RT.

Although encouraging, these results stress the need for a catalyst having a balanced reactivity in CO<sub>2</sub> hydrosilylation, to

avoid the methylation of the amine. While **IPr**, Verkade’s base **VB<sup>Me</sup>** or guanidine **Me-TBD** enable the formation of **2a** in up to 79% yield, the best activities and selectivities were obtained with 1,8-diazabicyclo[5.4.0]undec-7-ene (**DBU**) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (**TBD**) as catalysts for which the reaction was complete after 2.5 h, yielding 93% of the desired aminal **2a** and **3a** as side-product (7%) (Entries 2–6, Table 1). As expected, no reaction occurred after 24 h in the absence of CO<sub>2</sub> or catalyst. Importantly, with a low catalyst loading of 1 mol% **TBD**, aminal **2a** was still obtained in 92% yield after 7 h at 80 °C (Entry 8, Table 1). Whereas polymethylhydrosiloxane (PMHS) or tetramethyldisiloxane (TMDS) are unreactive in the formation of **2a**, Ph<sub>2</sub>SiH<sub>2</sub> exhibits a reactivity close to that of PhSiH<sub>3</sub> (Entries 9–10, Table 1 and SI). The polarity of the solvent also has a positive influence on the transformation. Although **2a** is formed in <10% yield from **1a** in toluene or THF (ε<7.5), the corresponding yield increases to 91% in MeCN (ε=37.5) under analogous conditions (Entries 7, 11–12, Table 1). Finally, the conversion of **1a** can proceed at RT, yet only 26% of the desired aminal could be obtained under these conditions and 49% of *N*-methylformanilide was also formed (Entry 13, Table 1).

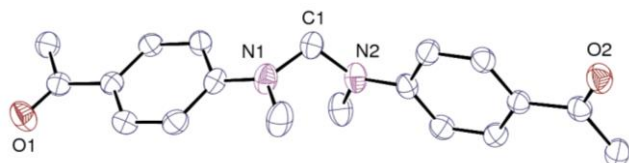


Reaction conditions: NMR tube (2.5 mL), TBD (0.0050 mmol), amine (0.10 mmol), PhSiH<sub>3</sub> (0.20 mmol), CD<sub>3</sub>CN (0.30 mL), CO<sub>2</sub> (1 bar). Yields determined by <sup>1</sup>H NMR with Ph<sub>2</sub>CH<sub>2</sub> as internal standard. <sup>[a]</sup> amine (0.050 mmol).

**Scheme 3.** Synthesis of aminals starting from secondary aromatic amines

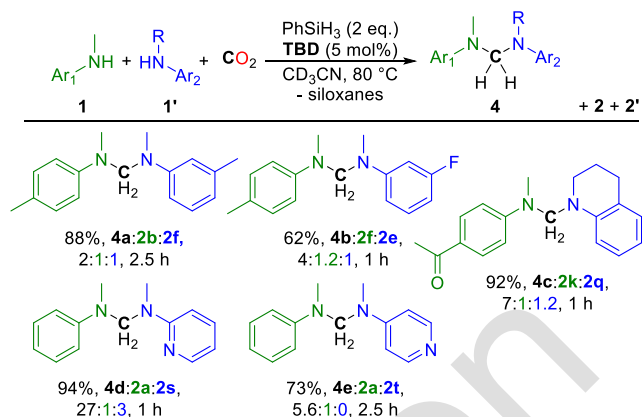
Having in hand a selective and efficient catalytic system for this novel reaction, the coupling of various amines to aminals was attempted with CO<sub>2</sub> (Schemes 3). Introducing electron-

donating groups (EDGs) or electron-withdrawing groups (EWGs) on the aromatic ring of *N*-methylaniline, the corresponding amins **2b–2k** were obtained in good yields (55–98%), after 4 h at 80 °C in CH<sub>3</sub>CN, in the presence of 2 equiv. PhSiH<sub>3</sub> and 5 mol% **TBD**; and negligible over-reduction was observed within 18 h. Importantly, the reduction of CO<sub>2</sub> to amins is also chemoselective and oxidizing groups such as a nitrile or ketone are tolerated, as exemplified in the formation of **2j** (95% yield) and **2k** (98% yield). Indeed, crystals of **2k** grown from the crude mixture confirmed the presence of the untouched carbonyl group and, hence, the ability of the catalyst to avoid over-reduction (Figure 1).



**Figure 1.** Molecular structure of **2k** with displacement ellipsoids drawn at the 50% probability level

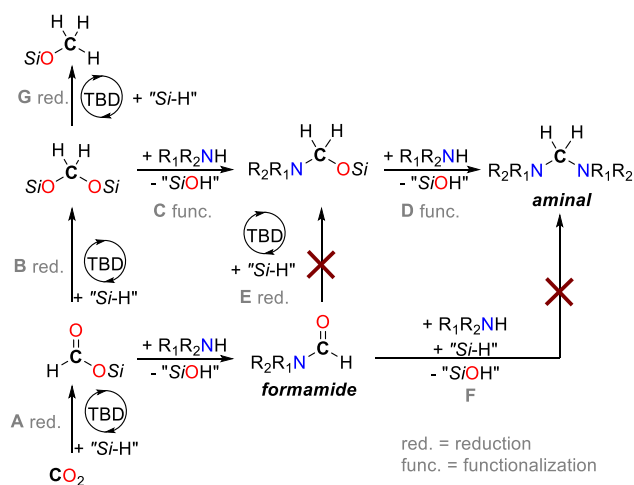
In order to widen the scope of amina compounds available from the present methodology, the influence of the substituent on the nitrogen atom has been investigated. *N*-ethylaniline (**1l**) and *N*-allylaniline (**1m**) were converted in good 73% and 77% yields to **2l** and **2m**, respectively. The bulky *N*-benzylaniline gave the desired product **2o** in 94% after 2 h at 80 °C. *N,N*-diphenylaniline only furnished 24% of **2n** after 21 h, presumably because of its poor nucleophilicity. Cyclic amines such as indoline (**1p**) and 1,2,3,4-tetrahydroquinoline (**1q**) were converted to their amina analogues **2p** and **2q** in good 70% and 87% yields. The reaction is also viable with secondary heteroaromatic amines: the formation of **2s** from 2-methylaminopyridine was accomplished quantitatively and **2s** was isolated in 88% yield after removal of the siloxanes by-products. In contrast, the reaction with 4-methylaminopyridine resulted in the formation of the corresponding formamide as a major product (85%) and only 14% of the amina **2t** were observed. Naturally, the formation of the heterocycle is favored over an intermolecular reaction for diamino substrates, thus providing **2r** and **2u** with excellent 88 and 95% yield, respectively. However, starting from an aliphatic amine such as morpholine, only the corresponding formamide was yielded and no trace of the amina product could be detected by <sup>1</sup>H NMR. This observation may be due to the stronger nucleophilicity of aliphatic amines which facilitates the production of a formamide that is unproductive in the formation of amins.



Reaction conditions: NMR tube (2.5 mL), TBD (0.0050 mmol), amine **1** (0.050 mmol), amine **1'** (0.050 mmol), PhSiH<sub>3</sub> (0.20 mmol), CD<sub>3</sub>CN (0.30 mL), CO<sub>2</sub> (1 bar). Average amines conversion determined by <sup>1</sup>H NMR with Ph<sub>2</sub>CH<sub>2</sub> as internal standard (see SI).

#### Scheme 4. Synthesis of unsymmetrical amins

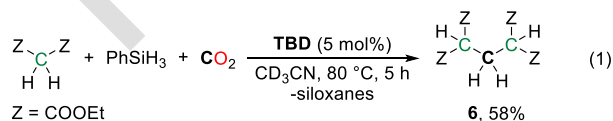
The coupling of two different amines was identified as the next challenge facing this 4-component reaction, to access unsymmetrical amins (Scheme 4). Reacting two amines with similar electronic properties (**1b** and **1f**) with CO<sub>2</sub>, PhSiH<sub>3</sub> and 5 mol% **TBD** led to a statistical distribution of all possible amins **4a**, **2b** and **2f** (44/44/44%). Nonetheless, when two amines of different nucleophilic character are used, the selectivity to the unsymmetrical amins increases. For example, amins **4b**, **4c**, **4d** and **4e** were obtained as the major products in 40, 82, 69 and 61% yield, respectively, with the symmetrical amins being formed as side products.



**Scheme 5.** Proposed pathway to access amins. The conversion of CO<sub>2</sub> to amins is a rare example of a catalytic reaction leading to the complete deoxygenation of CO<sub>2</sub>.<sup>4, 13</sup> Overall, it involves the cleavage of four C–O bonds and the formation of two C–H bonds (reduction) and two C–N bonds (functionalization). The nature of the organic intermediates involved in this reaction was investigated so as to explain the observed reactivities and facilitate future catalysts design. Possible pathways are depicted in Scheme 5.<sup>14</sup> The reductive functionalization of CO<sub>2</sub> to formamides is well established, **TBD** being a known catalyst for this transformation.<sup>3a</sup> Nonetheless, no

reaction is observed when *N*-methylformanilide **5a** is reacted with PhSiH<sub>3</sub> and 5 mol% **TBD**, at 80 °C, in the presence (step **F**) or absence (step **E**, under Ar or CO<sub>2</sub>) of *N*-methylaniline. Formamides thus appear as competition products in CO<sub>2</sub> conversion to amins. Classically, amins can be prepared by condensation of amines onto paraformaldehyde and an alternative pathway for the formation of amins from CO<sub>2</sub> could thus rely on catalytic hydrosilylation of CO<sub>2</sub> to a C<sup>0</sup> bis(silyl)acetal species and subsequent nucleophilic addition of the two amine reagents. Using NHCs as catalysts, Zhang and Ying *et al.* have indeed detected successfully bis(silyl)acetal derivatives upon hydrosilylation of CO<sub>2</sub>, prior to the formation of silylmethoxides end-products.<sup>12b</sup> These considerations suggest that the conversion of CO<sub>2</sub> to amins proceeds *via* reduction of CO<sub>2</sub> to a silylacetal species (steps **A** and **B**) which undergoes two successive nucleophilic attacks (steps **C** and **D**). Although steps **C** and **D** are similar processes, they involve different electrophiles, namely a bis(silyl)acetal and an aminosilylacetal derivative. Because the bis(silyl)acetal is a stronger electrophile, the most nucleophilic amine should be rapidly consumed in step **C**, so that unsymmetrical amins can be selectively formed. According to this mechanism, the reduction and functionalization steps are consecutive but their relative rates are important to ensure CO<sub>2</sub> conversion to the desired aminal while avoiding formamide and silylmethoxide competition products. Experimentally, highly nucleophilic amines (*e.g.* morpholine) indeed prevent the formation of amins because they are readily converted to their corresponding formamides (*vide supra*) and catalysts able to promote the rapid conversion of CO<sub>2</sub> to silylacetals will be necessary to access amins from aliphatic amines. Conversely, electron poor amines such as diphenylamine are not nucleophilic enough to trap the bis(silyl)acetal intermediate and the latter is reduced to a silylmethoxide product prior to the formation of C–N bonds (steps, **A**, **B** and **G**). Experimentally, silylmethoxide species (CH<sub>3</sub>OSi(O)Ph) were indeed observed as the major product in the conversion of diphenylamine with CO<sub>2</sub>, PhSiH<sub>3</sub> and 5 mol% **TBD**.

Capitalizing on this mechanism, we envisioned that other nucleophiles, such as malonates, could efficiently replace the amine reagents to promote the challenging formation of C–C bonds from CO<sub>2</sub>.<sup>15</sup> In fact, addition of 2 equiv. PhSiH<sub>3</sub> to diethylmalonate, under an atmosphere of CO<sub>2</sub>, resulted in the formation of 58% **6** after 5 h at 80 °C, in the presence of 5 mol% **TBD** (Eq. 1). **6** formally results from the methylenation of two malonate moieties with CO<sub>2</sub> and, to the best of our knowledge, it represents the first example of a homogeneous catalytic reaction leading to the formation of 2 C–C bonds at the CO<sub>2</sub> carbon atom. This reaction is under further investigation in our laboratories.



In conclusion, we have described herein a novel catalytic transformation to promote the conversion of CO<sub>2</sub> to aminal derivatives *via* a 4-component reaction. The organocatalysts are able to balance the reactivity of CO<sub>2</sub> reduction and selectively stabilize carbon(0) products for the formation of both symmetric and unsymmetric amins.

## ASSOCIATED CONTENT

### Supporting Information

Details of experimental procedures, physical properties of new compounds, tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*thibault.cantat@cea.fr

### Author Contributions

‡These authors contributed equally.

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## REFERENCES

- (a) Goepfert, A.; Czaun, M.; Jones, J.-P.; Surya Prakash, G. K. Olah, G. A., *Chem. Soc. Rev.* **2014**, *43*, 7995-8048. (b) Fernandez-Alvarez, F. J.; Aitani, A. M. Oro, L. A., *Catal. Sci. Technol.* **2014**, *4*, 611-624. (c) Perathoner, S. Centi, G., *ChemSusChem* **2014**, *7*, 1274-1282. (d) Darensbourg, D. J., *Chem. Rev.* **2007**, *107*, 2388-2410. (e) Fiorani, G.; Guo, W. Kleij, A. W., *Green Chem.* **2015**, *17*, 1375-1389.
- (a) Yang, Z.-Z.; He, L.-N.; Gao, J.; Liu, A.-H. Yu, B., *Energy Environ. Sci.* **2012**, *5*, 6602-6639. (b) Tlili, A.; Blondiaux, E.; Frogneux, X. Cantat, T., *Green Chem.* **2015**, *17*, 157-168.
- (a) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuery, P.; Ephritikhine, M. Cantat, T., *Angew. Chem. Int. Ed.* **2012**, *51*, 187-190. (b) Jacquet, O.; Das Neves Gomes, C.; Ephritikhine, M. Cantat, T., *J. Am. Chem. Soc.* **2012**, *134*, 2934-2937. (c) Motokura, K.; Takahashi, N.; Kashiwame, D.; Yamaguchi, S.; Miyaji, A. Baba, T., *Catal. Sci. Technol.* **2013**, *3*, 2392-2396. (d) Shintani, R. Nozaki, K., *Organometallics* **2013**, *32*, 2459-2462.
- (a) Jacquet, O.; Das Neves Gomes, C.; Ephritikhine, M. Cantat, T., *ChemCatChem* **2013**, *5*, 117-120. (b) Yu, B.; Zhang, H.; Zhao, Y.; Chen, S.; Xu, J.; Huang, C. Liu, Z., *Green Chem.* **2013**, *15*, 95-99. (c) Hao, L.; Zhao, Y.; Yu, B.; Zhang, H.; Xu, H. Liu, Z., *Green Chem.* **2014**, *16*, 3039-3044.
- (a) Jacquet, O.; Frogneux, X.; Das Neves Gomes, C. Cantat, T., *Chem. Sci.* **2013**, *4*, 2127-2131. (b) Li, Y.; Fang, X.; Junge, K. Beller, M., *Angew. Chem. Int. Ed.* **2013**, *52*, 9568-9571. (c) Beydoun, K.; vom Stein, T.; Klankermayer, J. Leitner, W., *Angew. Chem. Int. Ed.* **2013**, *52*, 9554-9557. (d) Li, Y.; Sorribes, I.; Yan, T.; Junge, K. Beller, M., *Angew. Chem. Int. Ed.* **2013**, *52*, 12156-12160. (e) Cui, X.; Zhang, Y.; Deng, Y. Shi, F., *Chem. Commun.* **2014**, *50*, 13521-13524. (f) Blondiaux, E.; Pouessel, J. Cantat, T., *Angew. Chem. Int. Ed.* **2014**, *53*, 12186-12190. (g) Das, S.; Bobbink, F. D.; Laurenczy, G. Dyson, P. J., *Angew. Chem. Int. Ed.* **2014**, *53*, 12876-12879. (h) Cui, X.; Dai, X.; Zhang, Y.; Deng, Y. Shi, F., *Chem. Sci.* **2014**, *5*, 649-655.
- (a) Jiang, Y.; Blacque, O.; Fox, T. Berke, H., *J. Am. Chem. Soc.* **2013**, *135*, 7751-7760. (b) LeBlanc, F. A.; Piers, W. E.

- Parvez, M., *Angew. Chem. Int. Ed.* **2014**, *53*, 789-792. (c) Metsänen, T. T. Oestreich, M., *Organometallics* **2015**, *34*, 543-546.
7. Bontemps, S.; Vendier, L. Sabo-Etienne, S., *J. Am. Chem. Soc.* **2014**, *136*, 4419-4425.
8. Ragsdale, S. W. Pierce, E., *Biochim. Biophys. Acta* **2008**, *1784*, 1873-1898.
9. (a) Cheng, X.; Vellalath, S.; Goddard, R. List, B., *J. Am. Chem. Soc.* **2008**, *130*, 15786-15787. (b) Jurčík, V. Wilhelm, R., *Tetrahedron* **2004**, *60*, 3205-3210. (c) Huang, D.; Li, X.; Xu, F.; Li, L. Lin, X., *ACS Catal.* **2013**, *3*, 2244-2247. (d) Neel, A. J.; Hehn, J. P.; Tripet, P. F. Toste, F. D., *J. Am. Chem. Soc.* **2013**, *135*, 14044-14047. (e) Guggenheim, K. G.; Toru, H. Kurth, M. J., *Org. Lett.* **2012**, *14*, 3732-3735. (f) Beifuss, U.; Ledderhose, S. Ondrus, V., *Arkivoc* **2005**, *5*, 147-173. (g) Shaibakova, M. G.; Titova, I. G.; Makhmudiyarov, G. A.; Ibragimov, A. G. Dzhemilev, U. M., *Russ. J. Org. Chem.* **2010**, *46*, 43-48.
10. (a) Oestreich, M.; Hermeke, J. Mohr, J., *Chem. Soc. Rev.* **2015**, *44*, 2202-2220. (b) Berkefeld, A.; Piers, W. E. Parvez, M., *J. Am. Chem. Soc.* **2010**, *132*, 10660-10661. (c) Wang, B. Cao, Z., *RSC Adv.* **2013**, *3*, 14007-14015. (d) Riduan, S. N.; Ying, J. Y. Zhang, Y., *ChemCatChem* **2013**, *5*, 1490-1496.
11. (a) Villiers, C.; Dognon, J. P.; Pollet, R.; Thuery, P. Ephritikhine, M., *Angew. Chem. Int. Ed.* **2010**, *49*, 3465-3468. (b) Duong, H. A.; Tekavec, T. N.; Arif, A. M. Louie, J., *Chem. Commun.* **2004**, 112-113. (c) Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O. Crabtree, R. H., *J. Am. Chem. Soc.* **2007**, *129*, 12834-12846. (d) Pérez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; de Macedo, L. G. M.; Rodrigues-Filho, U. P.; Launay, J.-C. Franco, D. W., *J. Org. Chem.* **2004**, *69*, 8005-8011.
12. (a) Das Neves Gomes, C.; Blondiaux, E.; Thuéry, P. Cantat, T., *Chem. Eur. J.* **2014**, *20*, 7098-7106. (b) Riduan, S. N.; Zhang, Y. Ying, J. Y., *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325.
13. Khandelwal, M. Wehmschulte, R. J., *Angew. Chem. Int. Ed.* **2012**, *51*, 7323-7326.
14. *A reaction pathway involving the formation of transient urea species was ruled out as TBD is unable to promote the hydrosilylation of quaternary ureas to amins (see SI). This pathway is omitted in Scheme 6 for the sake of clarity.*
15. Li, Y.; Yan, T.; Junge, K. Beller, M., *Angew. Chem. Int. Ed.* **2014**, *53*, 10476-10480.