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Bridging Amines with CO_2: Organocatalyzed Reduction of CO_2 to Aminals

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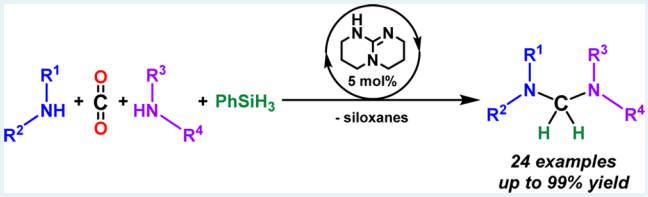
Supporting Information

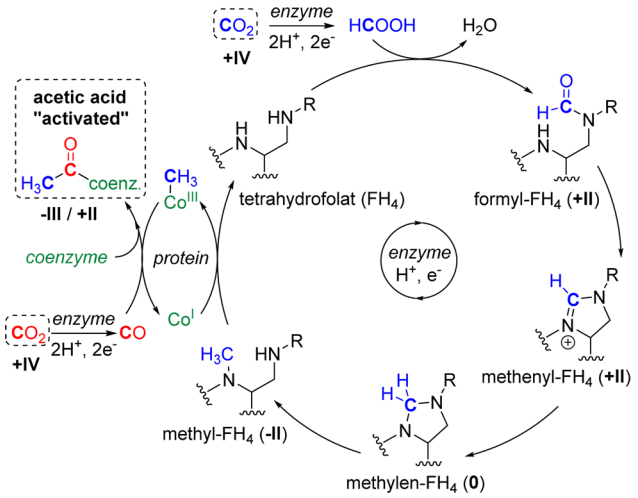
ABSTRACT: The four-electron reduction of CO_2 in the presence of secondary aromatic amines is described for the first time to access aminals. Under metal-free hydrosilylation conditions, the four C−O bonds of CO_2 are cleaved, and the organocatalysts are able to balance the reactivity of CO_2 to promote 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_2, organocatalysis, amines, hydrosilylation, reduction, aminal*

Because CO_2 is a renewable, cost-efficient, and nontoxic resource, it is a desirable carbon feedstock for the production of value-added chemicals, and many groups have focused their attention on designing new transformations involving CO_2 over the past few years.[1] In particular, the reductive functionalization of CO_2 with nitrogen reagents has known tremendous developments using various types of reductants such as hydrosilanes, hydroboranes, and dihydrogen.[2] These reactions have enabled the conversion of CO_2 into formamides,[2b,3] formamidines,[4] and methylamines.[5] Notably, the carbon oxidation state in these products is either +2 or −2, and the formation of C^0 organic functional groups from CO_2 remains a challenge. This trend reflects the higher electrophilicity of C^0 groups compared to C^{+II} functions in carbonyl derivatives. It is indeed well established that upon hydrogenation of CO_2, formate derivatives can be accumulated, whereas formaldehyde is an elusive species because its reduction to methanol is more rapid than the hydrogenation of formic acid.[1a] As a consequence of this limitation, only a few reports have tackled the formation of C^0 species from CO_2. Under hydrosilylation conditions, the selective reduction of CO_2 into a bis(silyl)acetal species with triethylsilane has been revealed.[6] Using a hydroborane reductant, Bontemps, Sabo-Etienne et al. successfully trapped transient formaldehyde, obtained from CO_2, with 2,6-diisopropylaniline, yielding the corresponding imine.[7] To unlock new four-electron reduction transformations of CO_2, one should focus on the use of well-balanced catalysts that are able to finely control the kinetics of CO_2 reduction. In nature, acetogenic bacteria are able to produce over 10^9 tons of acetic acid annually, following the Wood−Ljungdahl pathway (Scheme 1).[8] In this biochemical cycle, CO_2 is anchored to a diamine moiety and undergoes successive two-electron reduction steps to yield a methylamine (C^{-II}) after formation of the corresponding formamide (C^{+II}), formamidine (C^{+II}), and aminal (C^0) intermediates. Although CO_2 conversion to formamides, formaminides, and methylamines has been described, the synthesis of aminals[9] directly from CO_2 remains unknown and was only suggested as a possible intermediate in the Ru-based methylation of amines.[5b] To open up the variety of products accessible from CO_2, we describe herein the first catalytic synthesis of aminals by intermolecular coupling of two amines using CO_2 as a C1-bridge.

Scheme 1. Simplified Mechanism of the Wood−Ljungdahl Pathway for Acetogenesis with CO_2



Hydrosilanes are mild reductants, cheap, and nontoxic with a redox potential well poised for CO_2 reduction. Additionally, their slightly polar Si−H bond can be activated with metal-free catalysts, using either Lewis bases or Lewis acids.[10] Using phenylsilane as reductant, the reactivity between *N*-methylani-

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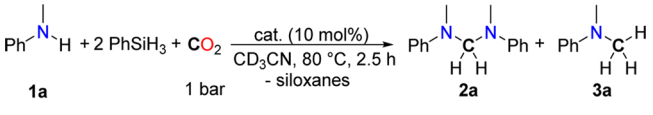
line (**1a**) and CO_2 has been explored using a variety of organocatalysts able to form adducts with CO_2[11] or promote its reduction, such as guanidines, amidines, *N*-heterocyclic carbenes (NHCs), and phosphorus bases.[3a,b,5f,g,12] Using 10 mol% of the NHC **I*t*Bu**, CO_2 undergoes hydrosilylation in the presence of *N*-methylaniline (**1a**) in CH_3CN, 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

Scheme 2. Formation of Aminal 2a via CO_2 Hydrosilylation



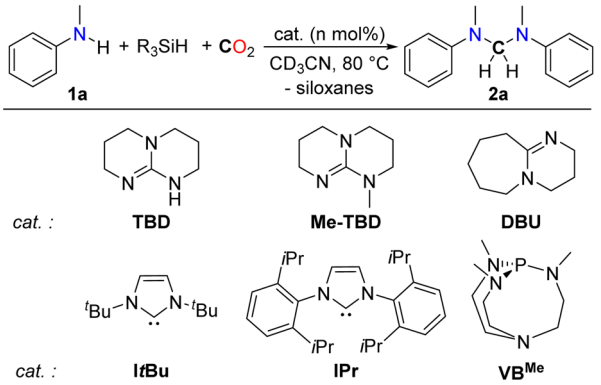
1a	1 bar		2a	3a
	~2 eq.	**I*t*Bu**	47%	25%
	~1 eq.	**I*t*Bu**	52%	18%
	~1 eq.	**TBD**	93%	7%

also produced at a similar rate and reaches 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^0 carbon center in **2a**. Reducing the quantity of CO_2 in the reaction vessel to ca. 1 equiv per amine somewhat improves the **2a**/**3a** ratio of the reaction from 1.9 to 2.9 (Scheme 2).

Although encouraging, these results stress the need for a catalyst having a balanced reactivity in CO_2 hydrosilylation, to avoid the methylation of the amine. While **IPr**, Verkade's base **VB^{Me}** or guanidine **Me-TBD** enables 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_2 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_2SiH_2 exhibits a reactivity close to that of $PhSiH_3$ (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).

Having in hand a selective and efficient catalytic system for this novel reaction, the coupling of various amines to aminals was attempted with CO_2 (Scheme 3). When electron-donating groups (EDGs) or electron-withdrawing groups (EWGs) were introduced on the aromatic ring of *N*-methylaniline, the corresponding aminals **2b−2k** were obtained in good yields (55−98%), after 4 h at 80 °C in CH_3CN, in the presence of 2 equiv of $PhSiH_3$ and 5 mol% **TBD**; negligible over-reduction was observed within 18 h. Importantly, the reduction of CO_2 to aminals 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**

Table 1. Catalyst Screening for the Coupling of 1a to 2a[a]



entry	catalyst (mol%)	reductant	time (h)	yield **2a** (%)	yield **3a** (%)
1	**I*t*Bu** (10)	$PhSiH_3$	2.5	52	18
2	**IPr** (10)	$PhSiH_3$	4.5	79	3
3	**VB^{Me}** (10)	$PhSiH_3$	2.5	71	0
4	**Me-TBD** (10)	$PhSiH_3$	4.5	78	0
5	**DBU** (10)	$PhSiH_3$	2.5	93	4
6	**TBD** (10)	$PhSiH_3$	2.5	93	7
7	**TBD** (5)	$PhSiH_3$	3.0	91	6
8	**TBD** (1)	$PhSiH_3$	7.0	92	6
9	**TBD** (5)	PMHS	96	5	0
10	**TBD** (5)	TMDS	96	0	0
11[b]	**TBD** (5)	$PhSiH_3$	48	5	0
12[c]	**TBD** (5)	$PhSiH_3$	48	7	0
13[d]	**TBD** (5)	$PhSiH_3$	19	26	0

[a]Reaction conditions: NMR tube (2.5 mL), catalyst, amine (0.10 mmol), hydrosilane (6 eq. "Si−H"), solvent (0.30 mL), CO_2 (1 bar). Yields determined by ^{1}H NMR with Ph_2CH_2 as internal standard. [b]In toluene-d_8. [c]In THF-d_8. [d]At RT.

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).

In order to widen the scope of aminal 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 aminal 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 byproducts. 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 aminal **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 aminal product could be detected by ^{1}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 aminals.

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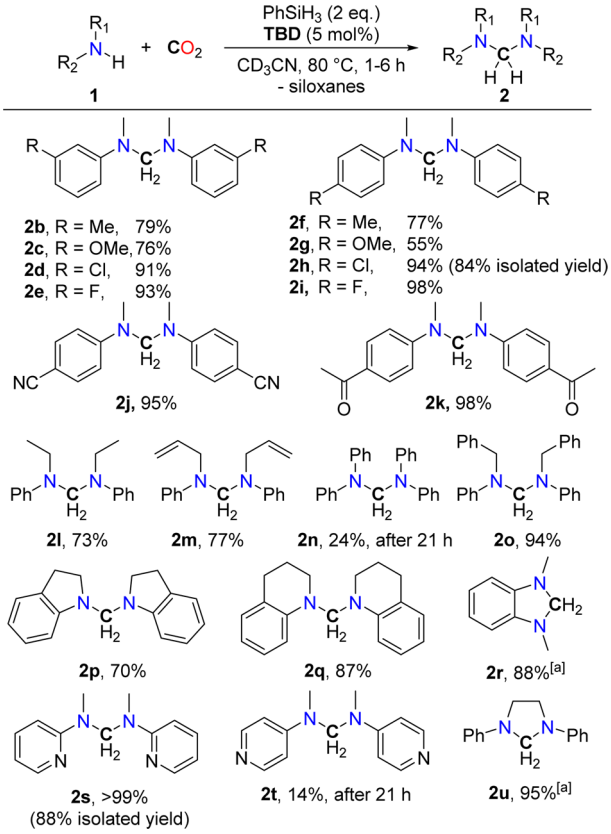
Scheme 3. Synthesis of Aminals Starting from Secondary Aromatic Amines[#]



[#]Reaction conditions: NMR tube (2.5 mL), TBD (0.0050 mmol), amine (0.10 mmol), $PhSiH_3$ (0.20 mmol), CD_3CN (0.30 mL), CO_2 (1 bar). Yields determined by ^1H NMR with Ph_2CH_2 as internal standard. [a]Amine (0.050 mmol).

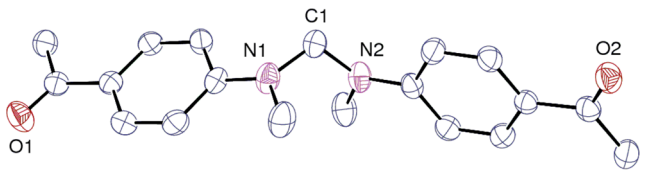
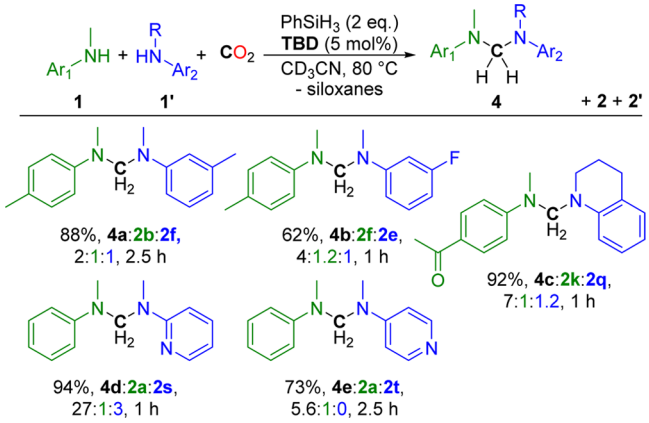


Figure 1. Molecular structure of **2k** with displacement ellipsoids drawn at the 50% probability level.

The coupling of two different amines was identified as the next challenge facing this four-component reaction, to access unsymmetrical aminals (Scheme 4). Reacting two amines with similar electronic properties (**1b** and **1f**) with CO_2, $PhSiH_3$, and 5 mol% **TBD** led to a statistical distribution of all possible aminals **4a**, **2b**, and **2f** (44/44/44%). Nonetheless, when two amines of different nucleophilic character are used, the selectivity to the unsymmetrical aminals increases. For example, aminals **4b**, **4c**, **4d**, and **4e** were obtained as the major products in 40, 82, 69, and 61% yield, respectively, with the symmetrical aminals being formed as side products.

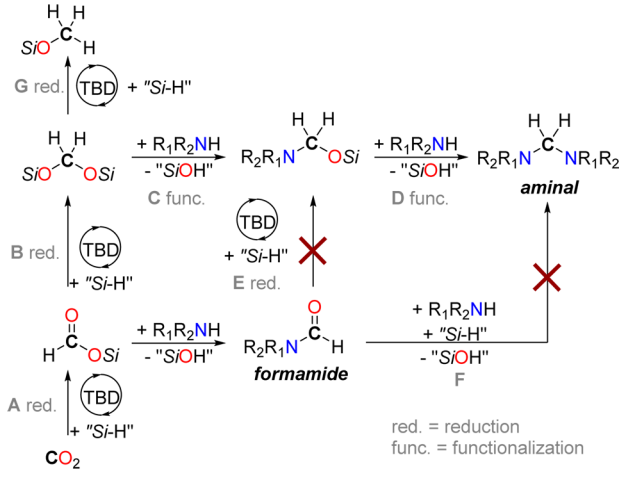
The conversion of CO_2 to aminals is a rare example of a catalytic reaction leading to the complete deoxygenation of CO_2.[4,13] Overall, it involves the cleavage of four C−O bonds and the formation of two C−H bonds (reduction) and two C−N bonds (functionalization). The nature of the organic intermediates involved in this reaction was investigated so as

Scheme 4. Synthesis of Unsymmetrical Aminals[a]



[a]Reaction conditions: NMR tube (2.5 mL), TBD (0.0050 mmol), amine **1** (0.050 mmol), amine **1′** (0.050 mmol), $PhSiH_3$ (0.20 mmol), CD_3CN (0.30 mL), CO_2 (1 bar). Average conversion of amines determined by ^1H NMR with Ph_2CH_2 as internal standard (see SI).

Scheme 5. Proposed Pathway to Access Aminals



to explain the observed reactivities and facilitate future catalysts design. Possible pathways are depicted in Scheme 5.[14] The reductive functionalization of CO_2 to formamides is well established, **TBD** being a known catalyst for this transformation.[3a] Nonetheless, no reaction is observed when *N*-methylformanilide **5a** is reacted with $PhSiH_3$ and 5 mol% **TBD**, at 80 °C, in the presence (step **F**) or absence (step **E**, under Ar or CO_2) of *N*-methylaniline. Formamides thus appear as competition products in CO_2 conversion to aminals. Classically, aminals can be prepared by condensation of amines onto paraformaldehyde, and an alternative pathway for the formation of aminals from CO_2 could thus rely on catalytic hydrosilylation of CO_2 to a C^0 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_2, prior to the formation of silylmethoxides end-products.[12b] These considerations suggest that the conversion of CO_2 to aminals proceeds via reduction of CO_2 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

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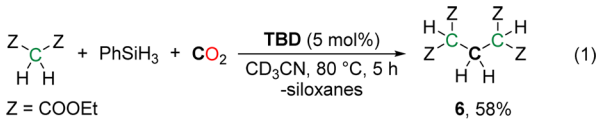
bis(silyl)acetal is a stronger electrophile, the most nucleophilic amine should be rapidly consumed in step **C**, so that unsymmetrical aminals can be selectively formed. According to this mechanism, the reduction and functionalization steps are consecutive but their relative rates are important to ensure CO_2 conversion to the desired aminal while avoiding formamide and silylmethoxide competition products. Experimentally, highly nucleophilic amines (e.g., morpholine) indeed prevent the formation of aminals because they are readily converted to their corresponding formamides (vide supra) and catalysts able to promote the rapid conversion of CO_2 to silylacetals will be necessary to access aminals 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 were indeed observed as the major product in the conversion of diphenylamine with CO_2, $PhSiH_3$, 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_2.[15] In fact, addition of 2 equiv of $PhSiH_3$ to diethylmalonate, under an atmosphere of CO_2, 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



(1)

of two malonate moieties with CO_2, and to the best of our knowledge, it represents the first example of a homogeneous catalytic reaction leading to the formation of two C−C bonds at the CO_2 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_2 to aminal derivatives via a four-component reaction. The organocatalysts are able to balance the reactivity of CO_2 reduction and selectively stabilize carbon(0) products for the formation of both symmetric and unsymmetric aminals.

■ 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. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00734.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Goeppert, 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.

(2) (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.

(3) (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.

(4) (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.

(5) (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.

(6) (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, Proteins Proteomics* **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.

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ACS Catal. 2015, 5, 3983−3987

(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 aminals (see SI). This pathway is omitted in Scheme 5 for the sake of clarity.

(15) Li, Y.; Yan, T.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 10476−10480.

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