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## Phosphazenes: efficient organocatalysts for the catalytic hydrosilylation of carbon dioxide†

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Phosphazene superbases are efficient organocatalysts for the metal-free catalytic hydrosilylation of carbon dioxide. They react with CO<sub>2</sub> to form the respective phosphine oxides, but in the presence of hydrosilanes, CO<sub>2</sub> can be selectively reduced to silvl formates, which can in turn be reduced to methoxysilanes by addition of an extra loading of silanes. Activities reach a TOF of 32 h<sup>-1</sup> with a TON of 759. It is also shown that unexpectedly, *N*,*N*-dimethylformamide can reduce CO<sub>2</sub> to a mixture of silvl formates, acetals and methoxides in the absence of any catalyst.

The alarming rate at which the concentration of carbon dioxide is increasing in the atmosphere is pushing the scientific community to find solutions in order to limit these emissions and remove this greenhouse gas from the atmosphere.<sup>1</sup> While many advances have been made in the capture and storage of  $CO_{2}$ , the use of carbon dioxide as a feedstock for the synthesis of valuable products could provide an important incentive for CO<sub>2</sub> recycling.<sup>2</sup> Of notorious importance is the large scale production of energy vectors such as methanol from CO<sub>2</sub>, which would be one very efficient way to sequester considerable amounts of carbon dioxide. This concept is promoted by Nobel laureate George A. Olah as the methanol economy.<sup>3</sup> While some heterogeneous systems have been reported for the CO2 reduction to methanol, the use of transition metal catalyzed homogeneous systems have also been reported for the hydroboration,<sup>4</sup> the hydrosilylation<sup>5</sup> and to a lesser extent the hydrogenation<sup>6</sup> of carbon dioxide. However, the search for new environmentally friendly and efficient systems remains a very active field of study.

During the past few years, metal-free catalysis has been shown to be a viable alternative to the transition-metal catalyzed reduction of  $CO_2$ . In fact, in some cases organocatalysts have even been shown to exhibit catalytic activities surpassing that of transition-metal based systems.<sup>7</sup> The advent of frustrated Lewis

pairs (FLP) chemistry,<sup>8</sup> notably for CO<sub>2</sub> capture,<sup>9</sup> has led to the development of efficient organocatalytic systems for the hydroboration of carbon dioxide to methoxide derivatives that can be readily hydrolysed to methanol.<sup>10,11</sup> It was later shown that phosphines,<sup>12</sup> strong nitrogen bases,<sup>13</sup> and even BH<sub>4</sub><sup>-</sup> could act as catalysts for the hydroboration of CO<sub>2</sub>.<sup>14</sup> In a seminal report, Ying and co-workers have reported that N-heterocyclic carbenes (NHCs) could act as catalysts for the hydrosilylation of carbon dioxide to methoxysilanes with TOF and TON reaching 25.5 h<sup>-1</sup> and 1840, respectively.<sup>15</sup> Since then, a number of systems have emerged for the reduction of CO<sub>2</sub> using hydrosilanes to generate value added products such as formamides,<sup>16a</sup> formamidines,<sup>16b</sup> methylamines,<sup>17</sup> acetals<sup>5c</sup> and methane.<sup>9b</sup> While base-activation of hydrosilanes has been used for the hydrosilylation of aldehydes, ketones and esters,<sup>18</sup> to the best of our knowledge, Ying's report of NHC-catalyzed system remains the only metal-free system for the hydrosilylation of CO2 to methanol or formic acid derivatives. Phosphazene derivatives of the general structure (R2N)3P=N-R have been developed by Schwesinger as very strong organic bases.<sup>19</sup> They are well established as an alternative to NHC organocatalysts for the ring opening polymerization of cyclic esters.<sup>20</sup> Surprisingly, the use of those bases as catalysts for CO2 reduction was never reported. In an effort to broaden the scope of organocatalyzed reduction of CO<sub>2</sub>, we herein report that commercially available phosphazene superbases can catalyze the reductive hydrosilylation of  $CO_2$ .

Firstly, as other strong Lewis bases such as NHCs (N-heterocyclic carbenes) are known to bind carbon dioxide, the reaction between various commercially available phosphazene bases (Scheme 1, 1–3) and carbon dioxide was investigated in order to verify if the isolation of a  $CO_2$  adduct was possible. When 0.03 mmol of 1 was dissolved in benzene- $d_6$  and was exposed to 1 atm of  $CO_2$ , a small amount of a new signal resonating at 21.3 ppm was observed by <sup>31</sup>P{<sup>1</sup>H} spectroscopy. Complete conversion to the new species was achieved after 8 hours with only one notable change in the <sup>1</sup>H NMR spectra. Indeed, the resonance attributed to the *t*-Bu groups was shifted from 1.5 ppm to 0.9 ppm, with the loss of the <sup>4</sup>J<sub>P-H</sub> coupling (1.2 Hz). Upon evacuation of the volatiles *in vacuo* 

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 $\label{eq:scheme1} \begin{array}{l} \mbox{Rearrangement of phosphazenes in the presence of $CO_2$ with proposed intermediate.} \end{array}$ 

and re-dissolution in benzene- $d_6$ , the <sup>31</sup>P{<sup>1</sup>H} NMR spectra remained unchanged showing a singlet at 21.3 ppm while the signal attributed to the *t*-Bu protons was no longer present in the <sup>1</sup>H NMR spectrum.

Based on these experimental evidences, it was hypothesized that the 21.3 ppm species was not a simple adduct between 1 and CO<sub>2</sub>, but was the product of a transformation of the phosphazene with the elimination of the t-Bu group. Comparison of the <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR signals for the new *t*-Bu containing species and that of a commercial sample confirmed that the solution contained t-Bu isocyanate. Repeating the experiment at a larger scale (see ESI<sup>+</sup>) allowed the isolation of the phosphine oxide 4 in quantitative yield. As noted in Scheme 1, a plausible mechanism would first involve the formation of an adduct between 1 and CO<sub>2</sub>, leading to the formation of a Lewis acidic phosphonium center that can interact with the oxygen atom of the activated CO<sub>2</sub> molecule. tBuNCO and 4 are then formed in a concerted fashion, through a 2+2 rearrangement, reminiscent of the Wittig reaction mechanism.<sup>21</sup> A similar rearrangement has been observed previously in a titanium complex leading to the generation of carbodiimides.<sup>22</sup> The less bulky phosphazene 2 undergoes the same rearrangement in the presence of carbon dioxide within 15 minutes, while the more bulky 3 also undergoes a similar rearrangement, releasing ethylisocyanate after 12 hours under 1 atm of  $CO_2$  at 60 °C. It is interesting to note that in the case of 3, one phosphinimine moiety remains intact.

Since the rearrangement with phosphazenes 1 and 3 is slow, we were curious to see if they could be active catalysts in the hydrosilylation of carbon dioxide. In an initial experiment, 1 was dissolved in benzene- $d_6$  in the presence of 5 equiv. of Ph<sub>2</sub>SiH<sub>2</sub>. The sealed J-Young NMR tube was then exposed to *ca.* 3 atm of CO<sub>2</sub> and heated at 80 °C for 4 hours. Interestingly, <sup>1</sup>H NMR spectroscopy revealed that the hydrosilane was completely consumed, giving rise to set of resonances in the  $\delta \sim 3.8$ ,  $\sim 5.8$ , and  $\sim 8.6$  regions, indicative of CO<sub>2</sub> reduction to methoxy-, acetaland formylsilanes. In order to ascertain that the reduction products did originate from CO<sub>2</sub> reduction, the reaction was carried out using <sup>13</sup>CO<sub>2</sub> in *N*,*N*-dimethylformamide since polar and coordinating solvents have been shown to accelerate the reduction process.<sup>15</sup> In a typical experiment, *ca.* 3 atm. of <sup>13</sup>CO<sub>2</sub> was condensed in a J-Young NMR tube containing a 19.0 mM solution of **1** in presence of Ph<sub>2</sub>SiH<sub>2</sub> (2.5 mol% based on Si–H) in DMF-*d*<sub>7</sub>. After 30 minutes of reaction at room temperature, the signals belonging to silyl formates ( $\delta = 8.6$ , <sup>1</sup>*J*<sub>C-H</sub> = 231.8 Hz), silyl acetals ( $\delta = 5.8$ , <sup>1</sup>*J*<sub>C-H</sub> = 171.8 Hz) and silyl methoxides ( $\delta = 3.8$ , <sup>1</sup>*J*<sub>C-H</sub> = 144.2 Hz) could be identified using <sup>1</sup>H NMR.<sup>23</sup> The C–H correlations were confirmed using HSQC experiments. Upon reaction completion, the sample was degassed by three subsequent freeze pump thaw cycles to ensure complete removal of <sup>13</sup>CO<sub>2</sub> from the reaction medium after which a second loading of Ph<sub>2</sub>SiH<sub>2</sub> (2.5 mol% based on Si–H) was added. After 36 hours, the silyl formates had completely converted to methoxysilane derivatives with <sup>1</sup>H chemical shifts ranging between 3.0–3.8 ppm.

Monitoring the same catalytic reaction using  ${}^{31}P{}^{1}H$  NMR spectroscopy revealed that after 30 minutes, the signal of  $1 (\delta = -2.1)$ completely disappeared to form one new species resonating at 22.9 as well as 4 in a 6:1 ratio. It is important to note that both signals remain unchanged throughout the entire catalytic process. Interestingly, the signal at 22.9 ppm slowly reverted back to the signal of 1 at -2.1 ppm upon additional loading of silane in the absence of  ${}^{13}CO_2$ . When the transformation of the silyl formates to methoxysilanes was complete, the signal at 22.9 ppm also completely reverted back to the signal of 1 at -2.1 ppm. Based on the aforementioned spectroscopic observations, it seems that the signal at 22.9 ppm arises from an interaction between 1 and silvl formates. The absence of coupling with the <sup>13</sup>C nucleus, points to an N-Si interaction rather than an N-C interaction. In a blank experiment, heating 1 at 80 °C for 1 hour in the presence of an equimolar amount of Ph<sub>2</sub>SiH<sub>2</sub> in benzene- $d_6$  yielded no change in the NMR spectra. Similarly, exposing 4 to *ca.* 3 atm of  $CO_2$  in the presence of  $Ph_2SiH_2$  in benzene- $d_6$  did not yield any reaction, even in the presence of t-Bu-isocyanate, suggesting that neither 4 nor the isocyanate has a role in the reduction of  $CO_2$ .

With a better understanding of the reaction, the reduction of 3 atm of  $CO_2$  with a 13 mM solution of 1 in DMF using 40 equiv. of  $Ph_2SiH_2$  as a reductant was monitored using <sup>1</sup>H NMR spectroscopy. After only 60 minutes, 60% of the silane was consumed (TOF = 41 h<sup>-1</sup>, TON = 48) while 90% was converted after 5 hours (TOF = 14.4 h<sup>-1</sup>, TON = 72). Interestingly, it was observed that under these conditions, silyl formates were the predominant reduction products, contrasting with the reported reactivity of NHC catalysts which formed a majority of methoxysilanes (see Fig. S6A, ESI<sup>†</sup>).<sup>15</sup>

The preferential formation of silylformates over methoxy species suggests that the first reduction of  $CO_2$  to generate formates occurs faster than the subsequent reduction steps which will generate acetal and methoxysilane derivatives. Performing the catalytic reduction (1.25 mol% 1, Ph<sub>2</sub>SiH<sub>2</sub>) under 5 atm of  $CO_2$  led almost exclusively to the formation of silylformates in a 97% ratio when compared to silylacetals (2%) and methoxysilanes (1%) after only two hours (see ESI†). The remaining  $CO_2$  was then removed *in vacuo* and an additional loading of Ph<sub>2</sub>SiH<sub>2</sub> was added, leading to complete conversion of the silyl formates into methoxysilane derivatives



Scheme 2 Product ratio after the catalytic reduction under 5 atm of  $CO_2$  and after addition of an extra loading of silane in the absence of  $CO_2$ . Yield based on Si–H.

after 36 h (Scheme 2). Such selectivity in the formation of either silylformates or silylmethoxydes is of notable interest.

The scope and efficiency of various silanes, solvents and phosphazene catalysts were probed using a variety of conditions (Table 1). As can be observed in entry 3, changing the silane from Ph<sub>2</sub>SiH<sub>2</sub> to the less bulky PhSiH<sub>3</sub> resulted in the reaction sustaining 41 turnovers over 4 h. On the other hand, no catalytic activity was observed using the bulkier Et<sub>3</sub>SiH, even after 24 hours under 3 atm of CO<sub>2</sub> (entry 4). The alkoxysilane (EtO)<sub>3</sub>SiH did show modest activity, completing 41 turnovers after 24 h under 3 atm of CO<sub>2</sub> (entry 5), while PMHS (polymethylhydrosiloxane) decomposed readily in the presence of 1 in DMF to generate a gas which was assigned to be MeSiH<sub>3</sub> as well as an insoluble white solid indicative of the formation of polysiloxanes. Indeed, base catalyzed decomposition of PMHS is well documented.<sup>24</sup> Changing the solvent to another polar, coordinating solvent such as acetonitrile gave activities comparable to those obtained in DMF, as can be seen in entry 6 with TOF of 16  $h^{-1}$ . On the other hand, the use of non-coordinating solvents such as toluene or DCM resulted in a dramatic decrease in reactivity (entries 7-8).

Although 2 was shown to rapidly rearrange to 5 in the presence of carbon dioxide, it was found to exhibit catalytic activity in the presence of  $Ph_2SiH_2$ , reaching 31 turnovers after 4 hours of reaction under 3 atm of  $CO_2$  (entry 9). The bulkier phosphazene 3 did not surpass the activity of 1 but still managed 93 TON in 4 h for a TOF of 23 h<sup>-1</sup> (entry 10). Since a phosphinimine moiety remains intact in the transformation

of **3** to **6**, the activity of **6** was also investigated, but no significant reaction was observed (entry 11).

In order to mimic the activity presented in the reduction of CO<sub>2</sub> with NHC catalysts, the use of very low catalytic loading was carried out. With a catalytic loading of 0.01 mol%, complete conversion of the silanes was achieved after 48 hours. These results would represent a TOF of 206  $h^{-1}$  and a TON of 9900, which is quite unexpected since one would not expect such an increase in turn-over frequency upon dilution (entry 13). To our surprise, repeating the experiment with the same parameters while omitting the catalyst showed that 21% of the silane was consumed after 4 h and as much as 82% was consumed after 24 h (entries 14-15). It is important to note that no silane was consumed when the experiment was repeated without CO<sub>2</sub>, confirming that the products do not originate from DMF reduction. While it was previously observed that the choice of solvent was an important factor in silane mediated CO<sub>2</sub> reductions,<sup>15,25</sup> it is surprising that such an important reduction of CO<sub>2</sub> by the solvent alone was not reported.<sup>26</sup> When comparing the conversion with and without catalyst (entries 1 and 14), it can be shown that the phosphazenes are nevertheless efficient catalysts for the hydrosilylation of CO2. In acetonitrile or THF, the presence of a catalyst was required to induce the reduction of CO2. In acetonitrile, the reduction catalyzed by 1 reached a TON of 759 after 24 h, representing a TOF of 32 h<sup>-1</sup>. The latter result shows that phosphazene remains robust catalyst over a long period of time. A large scale reaction was carried out using 4.0 g of Ph<sub>2</sub>SiH<sub>2</sub> in the presence of 1 (1.25 mol%) in CH<sub>3</sub>CN and from which methanol was generated with 69% yield upon hydrolysis.

The reduction mechanism for this system is most likely similar to the NHC catalyzed CO<sub>2</sub> hydrosilylation mechanism which was studied computationally and was proposed to occur *via* activation of the hydrosilane rather than through activation of CO<sub>2</sub>.<sup>27</sup> While an experimental/theoretical report by Ying contested the study,<sup>28</sup> the important solvent effects were not studied in detail in any of the two reports. Another plausible

Table 1	Catalytic activity of phosphazene bases for the hydrosilylation of $CO_2^a$										
Entry	Catalyst ([ ] µmol L <sup>-1</sup> )	Silane <sup><math>c</math></sup> ([ ] mmol L <sup><math>-1</math></sup> ; equiv.)	Solvent	Pressure (atm)	Time (h)	Conversion (% Si-H)	HCO <sub>2</sub> <sup>b</sup> (%)	$OCH_2O^b$ (%)	$CH_3O^b$ (%)	${\mathop{\rm TOF}^c}{\left( {{{{\rm{h}}^{ - 1}}}}  ight)}$	TON <sup>c</sup>
1	1 (12.5)	$Ph_2SiH_2$ (1; 80)	DMF	1	4	96	84	13	3	19	77
2	1 (12.5)	$Ph_2SiH_2$ (1; 80)	DMF	5	2	95	97	2	1	38	76
3	1 (12.5)	$PhSiH_{3}(1; 80)$	DMF	1	4	42	85	15	0	8	33
4	1 (25)	$Et_{3}SiH(1; 40)$	DMF	3	24	0	0	0	0	0	0
5	1 (25)	(EtO) <sub>3</sub> SiH (1; 40)	DMF	3	24	41	100	0	0	1	16
6	1 (12.5)	$Ph_2SiH_2$ (1; 80)	CH <sub>3</sub> CN	1	4	79	66	24	10	16	63
7	1 (12.5)	$Ph_2SiH_2(1; 80)$	Toluene	1	4	14	33	50	17	3	11
8	1 (12.5)	$Ph_2SiH_2$ (1; 80)	DCM	1	4	1	Trace	Trace	Trace	0	0
9	2 (12.5)	$Ph_2SiH_2$ (1; 80)	DMF	3	4	39	81	19	0	8	31
10	3 (12.5)	$Ph_2SiH_2(1; 80)$	DMF	3	4	93	84	12	4	19	74
11	6 (12.5)	$Ph_2SiH_2(1; 80)$	DMF	1	1	1	Trace	Trace	Trace	0	0
$12^d$	1 (0.5)	$Ph_2SiH_2$ (1; 2000)	DMF	1	24	93	72	23	5	N/A	N/A
$13^d$	1 (0.1)	$Ph_2SiH_2$ (1; 10000)	DMF	1	48	98	66	24	9	N/A	N/A
14		$Ph_2SiH_2(1; -)$	DMF	1	4	21	62	38	0	N/A	N/A
15	_	$Ph_2SiH_2(1; -)$	DMF	1	24	82	68	29	3	N/A	N/A
16	1 (0.1)	$Ph_2SiH_2$ (1; 1000)	CH <sub>3</sub> CN	1	24	76	62	29	10	32	759

 $^{a}$  The reactions were carried out at ambient temperature and the yields were determined using <sup>1</sup>H NMR integration with cyclohexane as an internal standard.  $^{b}$  Distribution of products observed.  $^{c}$  Based on the number of Si–H transferred.  $^{d}$  Under these conditions, the DMF will be responsible for the reduction.

pathway would involve the formation of a 6-coordinate hypervalent silicon center bearing a strongly nucleophilic hydride. In fact, C—O bond reduction by hypervalent silicon species is well documented.<sup>29</sup> It was even shown by Kobayashi that the use of DMF could promote the formation of hypervalent silicon species.<sup>30</sup> Further investigation of the reaction mechanism is currently ongoing in our research group.

In summary, it was shown that although phosphazene superbases can rearrange to their respective oxide in an unusual way, they represent an efficient new class of organocatalysts for the reduction of carbon dioxide. One can easily control selectivity to methoxysilanes or silyl formates by controlling the reaction conditions. Using a very simple protocol TOF reaching 32 h<sup>-1</sup> and TON reaching 759 were observed. Furthermore, it was shown that the role of DMF in such a reduction process is of critical importance and its role as a catalyst should be considered when evaluating the catalytic efficiency of organocatalysts for CO<sub>2</sub> reduction. Current studies focus on the use of phosphazene bases for other transformations involving the formation of value added products from carbon dioxide reductions and will be reported in due course.

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## Notes and references

- 1 R. Monastersky, Nature, 2013, 497, 13-14.
- 2 D. M. D'Alessandro, B. Smit and J. R. Long, Angew. Chem., Int. Ed., 2010, 49, 6058–6082.
- 3 G. A. Olah, A. Goeppert and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim, 2006.
- 4 (a) R. Shintani and K. Nozaki, Organometallics, 2013, 32, 2459–2462;
  (b) S. Chakraborty, J. Zhang, J. A. Krause and H. J. Guan, J. Am. Chem. Soc., 2010, 132, 8872–8873;
  (c) S. Bontemps, L. Vendier and S. Sabo-Etienne, Angew. Chem., Int. Ed., 2012, 51, 1671–1674;
  (d) L. Zhang, J. Cheng and Z. Hou, Chem. Commun., 2013, 49, 4782–4784;
  (e) S. Bontemps, L. Vendier and S. Sabo-Etienne, J. Am. Chem. Soc., 2014, 136, 4419–4425.
- (a) S. Park, D. Bézier and M. Brookhart, J. Am. Chem. Soc., 2012, 134, 11404-11407; (b) S. J. Mitton and L. Turculet, Chem. - Eur. J., 2012, 48, 15258-15262; (c) A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, Chem. Sci., 2013, 4, 2152-2162; (d) F. A. LeBlanc, W. E. Piers and M. Parvez, Angew. Chem., Int. Ed., 2014, 126, 808-811; (e) M. Khandelwal and R. J. Wehmschulte, Angew. Chem., Int. Ed., 2012, 51, 7323-7326; (f) K. Motokura, N. Takahashi, D. Kashiwame, S. Yamaguchi, A. Miyaji and T. Baba, Catal. Sci. Technol., 2013, 3, 2392-2396; (g) R. J. Wehmschulte, M. Saleh and D. R. Powell, Organometallics, 2013, 32, 6812-6819; (h) O. Jacquet, X. Frogneux, C. Das Neves Gomes and T. Cantat, Chem. Sci., 2013, 4, 2127-2131; (i) X. Cui, X. Dai, Y. Zhang, Y. Deng and F. Shi, Chem. Sci., 2014, 5, 649-655; (j) X. Frogneux, O. Jacquet and T. Cantat, Catal. Sci. Technol., 2014, 4, 1529-1533; (k) Y. Li, X. Fang, K. Junge and M. Beller, Angew. Chem., Int. Ed., 2013, 52, 9568-9571; (l) T. Matsuo and H. Kawaguchi, J. Am. Chem. Soc., 2006, 128, 12362-12363.
- 6 (a) C. A. Huff and M. S. Sanford, J. Am. Chem. Soc., 2011, 133, 18122–18125; (b) M. S. Jeletic, M. T. Mock, A. M. Appel and J. C. Linehan, J. Am. Chem. Soc., 2013, 135, 11533–11536; (c) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, Angew. Chem., Int. Ed., 2010, 49, 9777–9780; (d) S. Wesselbaum, T. von Stein, J. Klankermayer and W. Leitner, Angew. Chem., Int. Ed., 2012, 51, 7499–7502; (e) K. Beydoun, T. vom Stein, J. Klankermayer and W. Leitner, Angew. Chem., Int. Ed., 2013, 52, 9554–9557; (f) N. M. Rezayee, C. A. Huff and M. S. Sanford, J. Am. Chem. Soc., 2015, 137, 1028–1031.

- 7 (a) F.-G. Fontaine, M.-A. Courtemanche and M.-A. Légaré, *Chem. Eur. J.*, 2014, 20, 2990–2996; (b) G. Fiorani, W. Guo and A. W. Kleij, *Green Chem.*, 2015, 17, 1375–1389.
- 8 (a) D. W. Stephan and G. Erker, Angew. Chem., Int. Ed., 2010, 49, 46–76;
   (b) D. W. Stephan and G. Erker, Chem. Sci., 2014, 5, 2625–2641.
- 9 (a) C. Mömming, M. Otten, E. G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2009, 48, 6643–6646; (b) A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, 132, 10660–10661; (c) J. Boudreau, M.-A. Courtemanche and F.-G. Fontaine, *Chem. Commun.*, 2011, 47, 11131–11133.
- 10 (a) M.-A. Courtemanche, M.-A. Légaré, L. Maron and F.-G. Fontaine, J. Am. Chem. Soc., 2013, 135, 9326–9329; (b) M.-A. Courtemanche, J. Larouche, M.-A. Légaré, B. Wenhua, L. Maron and F.-G. Fontaine, Organometallics, 2013, 32, 6804–6811; (c) M.-A. Courtemanche, M.-A. Légaré, L. Maron and F.-G. Fontaine, J. Am. Chem. Soc., 2014, 136, 10708–10717; (d) R. Declercq, G. Bouhadir, D. Bourissou, M.-A. Légaré, M.-A. Courtemanche, K. S. Nahi, N. Bouchard, F.-G. Fontaine and L. Maron, ACS Catal., 2015, DOI: 10.1021/acscatal.5b00189.
- (a) T. Wang and D. W. Stephan, *Chem. Eur. J.*, 2014, **20**, 3036–3039;
  (b) G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796–1797.
- 12 T. Wang and D. W. Stephan, Chem. Commun., 2014, 50, 7007-7010.
- (a) M.-A. Légaré, M.-A. Courtemanche and F.-G. Fontaine, *Chem. Commun.*, 2014, **50**, 11362–11365; (b) C. Das Neves Gomes, E. Blondiaux, P. Thuéry and T. Cantat, *Chem. Eur. J.*, 2014, **23**, 7098–7106; (c) E. Blondiaux, J. Pouessel and T. Cantat, *Angew. Chem., Int. Ed.*, 2014, **53**, 12186–12190; (d) S. Y.-F. Ho, C.-W. So, N. Saffon-Merceron and N. Mézailles, *Chem. Commun.*, 2015, **51**(11), 2107–2110.
- 14 K. Fujiwara, S. Yasuda and T. Mizuta, Organometallics, 2014, 33, 6692–6695.
- 15 S. N. Riduan, Y. Zhang and J. Y. Ying, Angew. Chem., Int. Ed., 2009, 48, 3322–3325.
- (a) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, J. Am. Chem. Soc., 2012, 134, 2934–2937; (b) C. Das Neves Gomes,
   O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, Angew. Chem., Int. Ed., 2012, 51, 187–190.
- 17 O. Jacquet, C. Das Neves Gomes, M. Ephritikhine and T. Cantat, ChemCatChem, 2013, 5, 117–120.
- (a) J. A. Fernandez-Salas, S. Manzini and S. P. Nolan, *Chem. Commun.*, 2013, **49**, 9758–9780; (b) M. G. Manas, L. S. Sharninghausen, D. Balcells and R. H. Crabtree, *New J. Chem.*, 2014, **38**, 1694–1700; (c) A. Volkov, F. Tinnis and H. Adolfsson, *Org. Lett.*, 2014, **16**, 680–683; (d) W. L. Xie, M. D. Zhao and C. M. Cui, *Organometallics*, 2013, **32**, 7440–7444; (e) Y. Li, J. A. Molina de La Torre, K. Grabow, U. Bentrup, K. Junge, S. Zhou, A. Brückner and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 11577–11580.
- (a) R. Schwesinger, *Chimia*, 1985, **39**, 269–272; (b) R. Schwesinger and H. Schlemper, *Angew. Chem., Int. Ed.*, 1987, **26**, 1167–1169; (c) R. Schwesinger, J. Willaredt, H. Schlemper, M. Keller, D. Schmitt and H. Fritz, *Chem. Ber.*, 1994, **127**, 2435–2454.
- 20 L. Zhang, F. Nederberg, R. C. Pratt, R. M. Waymouth, J. L. Hedrick and C. G. Wade, *Macromolecules*, 2007, **40**, 4154–4158.
- 21 B. E. Maryanoff, A. B. Reitz, M. S. Mutter, R. R. Whittle and R. A. Olofson, J. Am. Chem. Soc., 1986, 108, 7664–7678.
- 22 U. J. Kilgore, F. Basuli, J. C. Huffman and D. J. Mindiola, *Inorg. Chem.*, 2006, 45, 487-489.
- 23 Another minor set of peaks arising from <sup>13</sup>CO<sub>2</sub> reduction was also identified (see ESI<sup>†</sup> for details).
- 24 K. Revunova and G. I. Nikonov, Chem. Eur. J., 2014, 20, 839-845.
- 25 C. Lescot, D. U. Nielsen, I. S. Makarov, A. T. Lindhardt, K. Daasbjerg and T. Skrydstrup, J. Am. Chem. Soc., 2014, 136, 6142–6147.
- 26 DMF was shown to affect the methylation of amines in the presence of Ph<sub>2</sub>SiH<sub>2</sub> using CO<sub>2</sub> as the carbon source: S. Das, F. D. Bobbink, G. Laurenczy and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2014, 53, 12876-12879.
- 27 F. Huang, G. Lu, L. Zhao, H. Li and Z.-X. Wang, J. Am. Chem. Soc., 2010, 132, 12388–12396.
- 28 S. N. Riduan, J. Y. Ying and Y. Zhang, ChemCatChem, 2013, 5, 1490–1496.
- (a) J. Boyer, R. J. P. Corriu and C. Reye, *Tetrahedron*, 1981, 37, 2165–2171;
   (b) R. J. P. Corriu and C. Reye, *Tetrahedron*, 1983, 39, 999–1009.
- 30 (a) S. Kobayashi and K. Nishio, Tetrahedron Lett., 1993, 34, 3453–3456; (b) S. Kobayashi and K. Nishio, Tetrahedron Lett., 1994, 59, 6620–6628.