

# Aromaticity as Stabilizing Element in the Bidentate Activation for the Catalytic Reduction of Carbon Dioxide

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Supporting Information Placeholder

**ABSTRACT:** A new transition metal free mode for the catalytic reduction of carbon dioxide via bidentate interaction has been developed. In the presence of  $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$  **9**  $\text{CO}_2$  can be selectively transformed to either methane or methanol depending on the reducing agent. The bidentate nature of binding is supported by X-ray analysis of an intermediate analog, which experiences special stabilization due to aromatic character in the bidentate interaction. Kinetic studies revealed a first order reaction rate. The transformation can be conducted without any solvent.

Catalysis has been – and still is – the basis for the success of efficient and sustainable chemical transformations.<sup>1</sup> Although there have been tremendous developments in the past centuries the need for new concepts for catalysis is as high as ever. Most catalytic processes are based on a monodentate interaction between catalyst and substrate. Nature, however, shows that multidentate interactions offer much higher specificity and selectivity.<sup>2</sup> Recently, we could show that bidentate Lewis acids are highly selective and effective catalysts for the inverse electron demand Diels-Alder (IEDDA) reaction of 1,2-diazene.<sup>3</sup> The usual complication of bidentate catalysis, product inhibition, was circumvented as the coordinating functionality in the substrate (-N=N-) was eliminated during the transformation. Carbon dioxide ( $\text{CO}_2$ ) with its two Lewis basic oxygen atoms should also be an ideal target substrate for bidentate activation (Fig. 1).  $\text{CO}_2$  is highly attractive as cheap and readily available C1 building block.<sup>4</sup>

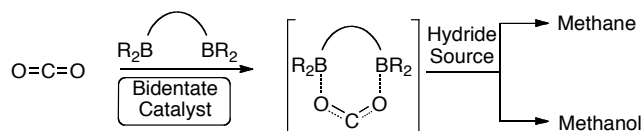


Figure 1. Activation of carbon dioxide by a bidentate catalyst for the conversion to methane or methanol.

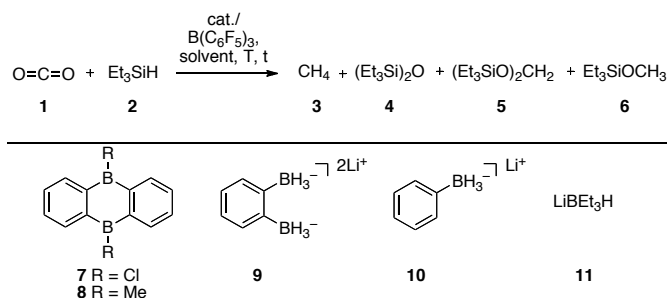
The strong bidentate interaction will fixate the  $\text{CO}_2$  molecule and enhance the electrophilicity of the carbon atom. The drastic change in structure due to the nucleophilic attack, e.g. by a

hydride, should change the character of the bidentate interaction and allow re-generation of the catalyst. Stephan and co-workers showed the effective interaction of a bidentate Lewis acid in a frustrated Lewis pair (FLP) with  $\text{CO}_2$ .<sup>5</sup> However, it was not possible to transform the complex further in a catalytic fashion to products such as methanol or methane due to its high stability. Besides transition-metal catalyzed processes for the reduction of  $\text{CO}_2$ ,<sup>6-9</sup> only a few non-transition metal-based catalysts have been recently presented.<sup>10</sup> These approaches are mainly based on the afore mentioned FLP concept,<sup>11-12</sup> strong Lewis acids,<sup>13</sup> Lewis bases such as amines<sup>14</sup> or N-heterocyclic carbenes.<sup>15</sup> Besides the different modes of interaction, all methods allow only the conversion of carbon dioxide to only one type of product, either methane or methanol. In this report we show, that based on a new activation mode a bidentate borohydride catalyst is highly effective for both transformation either for the reaction to methane or to methanol.

To investigate the above outlined rational different bidentate Lewis acid catalysts, e.g. **7** and **8**, which have been highly effective in the IEDDA of 1,2-diazenes, have been tested for the activation of  $\text{CO}_2$  (Table 1). Triethylsilane (**2**) was employed as reducing agent with  $\text{B}(\text{C}_6\text{F}_5)_3$  as activator.<sup>16</sup> However, none of the compounds showed catalytic activity. After a thorough screening lithium-*ortho*-phenylbisborate **9** ( $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$ )<sup>17</sup> was shown as an effective candidate. When 10 mol% of **9** (relative to silane **2**) was reacted under an atmosphere of  $\text{CO}_2$  (1 bar) in the presence of  $\text{Et}_3\text{SiH}$  (**2**) all the silane was consumed (Table 1, entry 1).  $(\text{Et}_3\text{Si})_2\text{O}$  (**4**) was the main product, along with  $(\text{Et}_3\text{SiO})_2\text{CH}_2$  (**5**) and  $\text{Et}_3\text{SiOMe}$  (**6**). The presence of  $\text{CH}_4$  (**3**) was observed as a singlet at 0.14 ppm by  $^1\text{H-NMR}$  spectroscopy.<sup>18</sup> Without **9** or  $\text{B}(\text{C}_6\text{F}_5)_3$  no conversion of silane **2** was observed, proving the necessity of both catalysts. The solubility of **9** in  $\text{C}_6\text{D}_5\text{Br}$  is poor; therefore the reaction was carried out in  $\text{THF-d}_8$  in order to increase the solubility. No transformation of silane **2** occurred under these conditions (Table 1, entry 2). Complexation of  $\text{B}(\text{C}_6\text{F}_5)_3$  with THF might decrease the Lewis acidity of  $\text{B}(\text{C}_6\text{F}_5)_3$  which is critical for the activation of  $\text{Et}_3\text{SiH}$  (**2**). A reduction of the catalyst loading reduced the silane consumption (Table 1, entry 4). This effect could be attributed to the insufficient mixing of the solution and the gas phase as all optimization reactions were carried out in a NMR tube. Consequently, a larger surface area

(running the reaction in a round bottom Schlenk flask) improved significantly the efficiency of the reaction (Table 1, entry 5). Reducing the loading of catalyst further to 1 mol% of **9** / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> led to a dramatic decrease of the catalytic efficiency (Table 1, entry 6). However, if the amount of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was increased to 3 mol% and the reaction temperature elevated to 80 °C the initial activity could be re-installed (Table 1, entry 7). In contrast to **9**, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is highly moisture and air sensitive. Therefore, if the amount of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is too low, degradation might further reduce the amount and impede catalysis. The catalytic reduction of CO<sub>2</sub> to CH<sub>4</sub> using **9** / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as catalyst can also be done in a solvent-free manner (Table 1, entry 8). All the silane **2** was consumed within 5 days at 80 °C (analyzed by NMR Spectroscopy).

**Table 1. Optimization of the catalytic reduction of CO<sub>2</sub>.**<sup>a</sup>



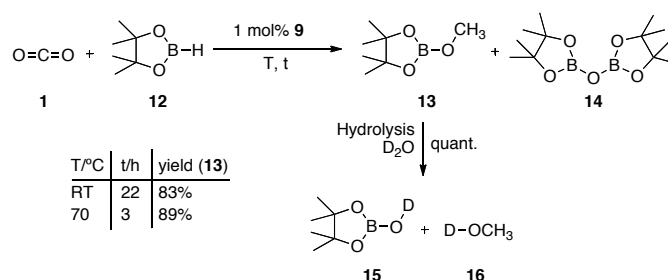
entry	cat	cat/mol% ratio (cat/B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> )	solvent	T/°C	t/h	product <sup>b</sup> /%		
						4	5	6
1	<b>9</b>	10, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	RT	60	69	31	–
2	<b>9</b>	10, (1:1)	THF-d <sub>8</sub>	RT	24	–	–	–
3	<b>9</b>	10, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	50	18	73	27	–
4	<b>9</b>	5, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	50	40	41	43	1
5 <sup>c</sup>	<b>9</b>	5, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	50	21	81	19	–
6 <sup>c</sup>	<b>9</b>	1, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	50	65	–	45	–
7 <sup>c</sup>	<b>9</b>	1, (1:3)	C <sub>6</sub> D <sub>6</sub> Br	80	56	78	22	–
8 <sup>d</sup>	<b>9</b>	2, (1:1)	–	80	5d	58	42	–
9	<b>10</b>	10, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	50	41	18	54	3
10	<b>11</b>	10, (1:1)	C <sub>6</sub> D <sub>6</sub> Br	50	24	4	91	–

<sup>a</sup> Reaction conditions: The reaction was performed with CO<sub>2</sub> (1 bar) in a Young-NMR tube. <sup>b</sup> Based on the consumption of **2**; determined by <sup>1</sup>H NMR with toluene as an internal standard. <sup>c</sup> The reaction was performed in a 25 mL Schlenk flask. <sup>d</sup> The yield was determined by GC-MS.

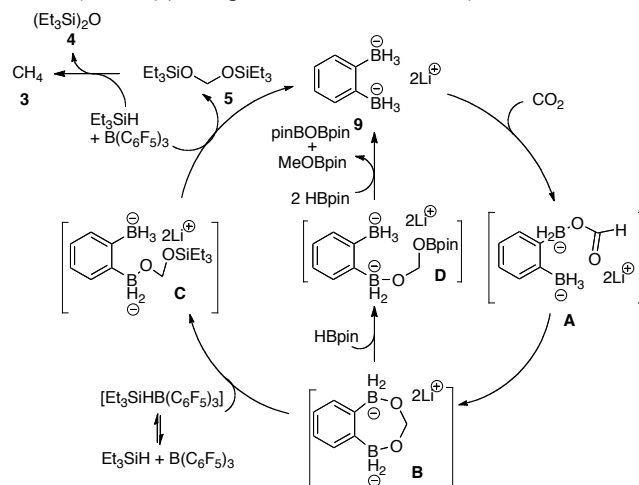
The bidentate nature of the catalyst is essential for the high activity. When the mono-borate **10** (LiPhBH<sub>3</sub>) was employed,<sup>16</sup> which is the monodentate analogue to **9**, significantly less conversion was observed (Table 1, entry 9). Especially, the amount of (Et<sub>3</sub>Si)<sub>2</sub>O (**4**) was greatly reduced compared to the bidentate catalyst **9**. Interestingly, when the reaction with **10** was conducted at RT, after a rather long induction period only one turn

over was observed (see Supporting Information for details). Also, super hydride LiBHET<sub>3</sub> **11** was tested as catalyst (Table 1, entry 10). Although it is known that simple borohydrides can activate CO<sub>2</sub><sup>19-20</sup> only (Et<sub>3</sub>SiO)<sub>2</sub>CH<sub>2</sub> (**5**) was detected as the main product and not methane.

**Scheme 1. Reduction of CO<sub>2</sub> to methanol using the bidentate catalyst **9**.**



To prove the versatility of our catalyst, an alternative reducing agent, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**12**, HBpin) was tested, which has been applied in the reduction of CO<sub>2</sub> to methanol with transition metal catalysts.<sup>10</sup> With HBpin **12** there is no need to add B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as co-catalyst. Thus, a mixture of **9** (10 mol%) and HBpin **12** in THF-d<sub>8</sub> was subjected to CO<sub>2</sub> (1 bar) at RT. After 2 h, MeOBpin **13** was the only CO<sub>2</sub>-reduction product detectable. Hydrolysis with D<sub>2</sub>O generates methanol, which was unambiguously confirmed by GC. Employment of only 1 mol% of **9** was also effective in the CO<sub>2</sub> reduction, and gave 83% of MeOBpin after 22 h at RT (Scheme 1). Since a higher reaction temperature might increase the efficiency of the catalytic system the reaction was carried out with 1 mol% catalyst loading at 70 °C. Indeed, 51% conversion of MeOBpin was observed after only 30 min, and a total conversion was achieved after 3 h. Simple borohydrides such as LiPhBH<sub>3</sub>, LiEt<sub>3</sub>BH or NaBH<sub>4</sub> were less effective (see Supporting Information for details).

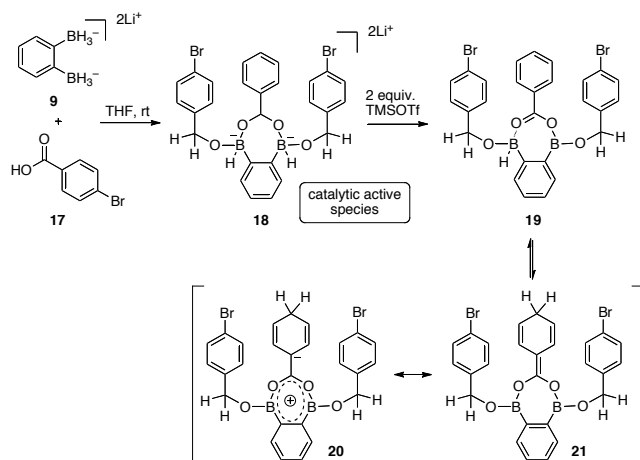


**Figure 2. Proposed mechanism for catalytic reduction of CO<sub>2</sub> to methane and methanol.**

A proposed mechanism for the reduction of CO<sub>2</sub> to methane and methanol is shown in Figure 2. First, catalyst **9** forms an adduct with CO<sub>2</sub>. Intramolecular hydride transfer generates the boron-bound formate adduct **A**, which may be further reduced by another hydride to form the acetal compound **B**. The bidentate nature of the catalyst seems to be important at this stage, in which the intramolecular hydride transfer is promoted as well as the stabilization of the intermediate. In the presence of Et<sub>3</sub>SiH the acetal moiety of intermediate **B** can be cleaved to give the disilyl-acetal **5** which is the main side product. Ultimately, **5** is reduced to CH<sub>4</sub>. In the presence of pinacol borane the cyclic acetal is also opened and delivers **D**. In both cases a catalytically active hydride species is re-generated closing the catalytic cycle.

The mechanistic proposal was supported by the following experiments. Treatment of **9** in THF-CO<sub>2</sub> solution (1 bar) at RT immediately led to the formation of a precipitate, indicating an interaction between CO<sub>2</sub> and **9**. Unfortunately, the poor solubility of the CO<sub>2</sub> adducts even in THF encumbered further characterization by NMR spectroscopy. IR analysis of the CO<sub>2</sub> adduct showed an absorption at 1592 cm<sup>-1</sup> attributable to a C=O stretching vibration resulting from the addition of CO<sub>2</sub> to **9**. The stepwise reaction, first treating catalyst **9** with CO<sub>2</sub> and then adding HBpin showed that three molecules of CO<sub>2</sub> are bound in the catalyst/substrate adduct. During the actual catalysis the excess of reducing agent might already promote the reduction as soon as the CO<sub>2</sub> is activated by the catalyst as shown in Figure 2. To increase solubility and enhance the crystallization ability catalyst **9** was reacted with 1 equiv. of 4-bromobenzoic acid (**17**) as CO<sub>2</sub> surrogate (Scheme 2). Interestingly, the bromine in the bound benzoic acid has been replaced by hydride, probably by a nucleophilic substitution reaction activated by the catalyst.<sup>21</sup> The product of this transformation **18** was subjected as catalyst to CO<sub>2</sub> and Et<sub>3</sub>SiH/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> resulting in full conversion of the silane and methane formation. After liberating LiH via the addition of TMSOTf crystals suitable for X-ray analysis were obtained (Fig. 3).<sup>22</sup>

### Scheme 2. Isolation of a surrogate of a bidentate intermediate.



The structure clearly shows the bidentate activation of one benzoic acid molecule and the binding of two more equivalents,

which have been reduced to the benzyl alcohol. These findings correspond to the experiments described for the CO<sub>2</sub>-complex. Noteworthy is the dioxo-diborepine heterocycle, which has not been described before. The entire ring is planar and is stabilized by aromaticity<sup>23</sup> as can be clearly seen in the X-ray structure. An additional hydride is positioned in the *para* position of the bound benzoic acid in the solid state (Scheme 2, **20** and **21**). NMR-studies, however, support a binding of the hydride at the boron atoms as two broad signals in the B-NMR have been observed. Although the refinement of the X-ray data shows one molecule in the independent unit of the elementary cell, the structure is disordered: 65 % of the molecules are in an upright position while the others are in the opposite position. Because of that only the two central oxygen atoms and bromobenzyl residues are fully occupied and impede an exact location of the hydrogen atoms in the structure.

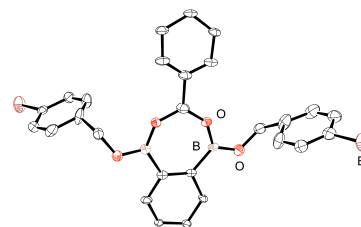
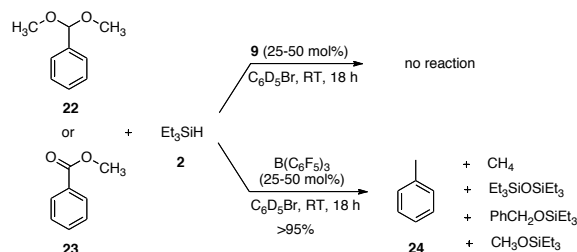


Figure 3. ORTEP plot of **20/21**. Thermal ellipsoids are set at the 50% probability level.

Structure **18** also proves, that the bisborate catalyst **9** is capable of conducting the reduction to the alcoholate state, which is then further reduced by the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/silane system. Nevertheless, benzaldehyde dimethyl acetal (**22**), as well as methylbenzoate (**23**) has been tested as model structures for intermediate **A** and **B** in the catalytic cycle (Figure 2). In both cases the mixture of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and Et<sub>3</sub>SiH induced the formation of toluene, methyl silyl ether and benzylsilyl ether (Scheme 3). In contrast, no reaction took place when **9** was added without the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. This observation indicates that the bidentate borate catalyst **9** activates the CO<sub>2</sub>, while the silane/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is responsible for the final catalytic reduction to methane.

### Scheme 3. Support of the role of the catalytic system **9**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (conversion determined by NMR).



We also investigated the kinetics of the catalytic reaction with **9**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as catalyst by NMR spectroscopy (see Supporting Information). In both cases the consumption of Et<sub>3</sub>SiH, respectively HBpin, showed a first order reaction rate. In the beginning the data revealed an induction period of about 30 min.<sup>23</sup> Interest-

ingly, in the case of silane as reducing agent two different temperature regimes can be observed. At 298 and 323 K a similar rate is observed, however, with a much faster initiation rate. The same is true for 333 and 343 K, although with a faster reaction rate. At 328 K a behavior in between can be seen. Therefore, it seems that in this complex reaction different steps are not equally accelerated with increasing temperature, which also includes physical processes, such as gas absorption in the solvent.

In summary, a new transition metal free mode of activating CO<sub>2</sub> has been presented. The bidentate borohydride Li<sub>2</sub>[1,2-C<sub>6</sub>H<sub>4</sub>(BH<sub>3</sub>)<sub>2</sub>] promotes efficiently the selective reduction to either methane or methanol. The selectivity can be controlled by the reducing agent: In the presence of Et<sub>3</sub>SiH / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> CO<sub>2</sub> will be transformed to methane, while pinacolborane (HBpin) delivers methanol. The reaction can be conducted in a solvent-free manner. The bidentate interaction in the catalysis has been supported by X-ray analysis of a possible intermediate. The novel 1,3-dioxo-4,7-diborepine heterocycle formed during the bidentate activation step is stabilized by aromaticity. The kinetics of both transformations have been studied, showing a first order reaction rate after an initial induction period. For the reduction with Et<sub>3</sub>SiH / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> different rate determining processes depending on the reaction temperature in this highly complex reaction have been observed. Further studies to adopt this highly useful new catalytic metal-free transformation for practical applications are ongoing.

## ASSOCIATED CONTENT

### Supporting Information

Experimental data, crystallographic data of **19**. This material is available free of charge via the Internet at <http://pubs.acs.org>

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### Notes

The authors declare no competing financial interests.

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## REFERENCES

- (1) Kreimeyer, A.; Eckes, P.; Fischer, C.; Lauke, H.; Schuhmacher, P. *Angew. Chem. Int. Ed.* **2015**, *54*, 3178–3195
- (2) Benkovic, S.J.; Hammes-Schiffer, S. *Science*, **2003**, *301*, 1196–1202.
- (3) (a) Kessler, S. N.; Neuburger, M.; Wegner, H. A. *J. Am. Chem. Soc.* **2012**, *134*, 17885–17888. (b) Kessler, S. N.; Wegner, H. A. *Org. Lett.* **2010**, *12*, 4062–4065.
- (4) (a) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 1–15. (b) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365–2387.
- (5) (a) Zhao, X.; Stephan, D. W. *Chem. Commun.* **2011**, *47*, 1833–1835. (b) Sgro, M. J.; Dömer, J.; Stephan, D. W. *Chem. Commun.* **2012**, *48*, 7253–7255.
- (6) For selected examples for the metal-catalyzed reduction of CO<sub>2</sub> to methane see: (a) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362–12363. (b) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 11404–11407. (c) Mitton, S. J.; Turculet, L. *Chem.-Eur. J.* **2012**, *18*, 15258–15262. (d) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *Chem. Sci.* **2013**, *4*, 2152–2162.
- (7) For selected examples for the metal-catalyzed reduction of CO<sub>2</sub> to methanol see: (a) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132*, 8872–8873. (b) Huff, C. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125. (c) Wesselbaum, S.; vom Stein, T.; Klankermayer, J.; Leitner, W. *Angew. Chem. Int. Edit.* **2012**, *51*, 7499–7502.
- (8) For a selected example for the metal-catalyzed reduction of CO<sub>2</sub> to formaldehyde see: Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2014**, *136*, 4419–4425.
- (9) For selected examples for the metal-catalyzed reduction of CO<sub>2</sub> to formic acid see: (a) Munshi, P.; Main, A. D.; Linehan, J. C.; Tai, C.-C.; Jessop, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 7963–7971. (b) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168–14169. (c) Schmeier, T. J.; Dobreiner, G. E.; Crabtree, R. H.; Hazari, N. *J. Am. Chem. Soc.* **2011**, *133*, 9274–9277. (d) Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Edit.* **2011**, *50*, 9948–9952. (e) Shintani, R.; Nozaki, K. *Organometallics* **2013**, *32*, 2459–2462. (f) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, T. *Org. Lett.* **2012**, *14*, 2642–2645.
- (10) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A. *Chem.-Eur. J.* **2014**, *20*, 2990–2996.
- (11) (a) Stephan, D. W.; Erker, G. *Chem. Sci.* **2014**, *5*, 2625–2641. (b) Ashley, A. E.; O'Hare, D. in *Topics in Current Chemistry*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2012**, pp. 191–217.
- (12) (a) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660–10661. (b) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem. Int. Edit.* **2009**, *48*, 9839–9843. (c) Sgro, M. J.; Stephan, D. W. *Angew. Chem. Int. Edit.* **2012**, *51*, 11343–11345. (d) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2013**, *135*, 9326–9329.
- (13) (a) Khandelwal, M.; Wehmschulte, R. *J. Am. Chem. Int. Edit.* **2012**, *51*, 7323–7326. (b) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem. Int. Edit.* **2012**, *51*, 2981–2984.
- (14) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. *Angew. Chem. Int. Edit.* **2011**, *51*, 187–190.
- (15) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Edit.* **2009**, *48*, 3322–3325.
- (16) Fernández-Alvarez, F. J.; Aitani, A. M.; Oro, L. A. *Catal. Sci. Technol.* **2014**, *4*, 611.
- (17) Seven, Ö.; Qu, Z.-W.; Zhu, H.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Chem.-Eur. J.* **2012**, *18*, 11284–11295.
- (18) The exact amount of CH<sub>4</sub> formed could not be determined as it is partially soluble in the reaction mixture as well as released in the gas phase.
- (19) Tsoureas, N.; Bevis, T.; Butts, C. P.; Hamilton, A.; Owen, G. R. *Organometallics* **2009**, *28*, 5222–5232.
- (20) Fujiwara, K.; Yasuda, S.; Mizuta, T. *Organometallics* **2014**, *33*, 6692–6695 (and references herein).
- (21) Egli, R. A. *Helv. Chim. Acta* **1968**, *51*, 2090–2097.
- (22) The X-ray data of **20/21** has been deposited at the CCDC with the number: 1052382.
- (23) (a) Krygowski, T. M.; Szatylowicz, H.; Stasyuk, O. A.; Dominikowska, J.; Palusiak, M. *Chem. Rev.* **2014**, *114*, 6383–6422. (b) Martin, N.; Haley, M. M.; Tykwinski, R. R. *Chem. Commun.*, **2012**, *48*, 10471.

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