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

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S *Supporting Information*

ABSTRACT: A new transition-metal-free mode for the catalytic reduction of carbon dioxide via bidentate interaction has been developed. In the presence of $Li_2[1,2\text{-}C_6H_4(BH_3)_2]$, 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 analogue, 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.[1] Although there have been tremendous developments over 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.[2] Recently, we showed that bidentate Lewis acids are highly selective and effective catalysts for the inverse electron demand Diels−Alder (IEDDA) reaction of 1,2-diazene.[3] The usual complication in bidentate catalysis, product inhibition, was circumvented, as the coordinating functionality in the substrate (-N═N-) was eliminated during the transformation. Carbon dioxide (CO_2), with its two Lewis basic oxygen atoms, should also be an ideal target substrate for bidentate activation (Figure 1). CO_2 is highly attractive as a cheap and readily available C1 building block.[4]
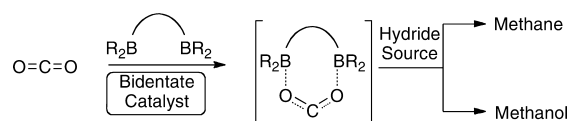

Figure 1. Activation of carbon dioxide by a bidentate catalyst for the conversion to methane or methanol.

The strong bidentate interaction will fixate the 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 regeneration of the catalyst. Stephan and co-workers showed the effective interaction of a bidentate Lewis acid in a frustrated Lewis pair (FLP) with CO_2.[5] 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 CO_2,[6−9] only a few non-transition-metal-based catalysts have been recently presented.[10] These approaches are mainly based on the aforementioned FLP concept,[11,12] strong Lewis acids,[13] Lewis bases such as amines,[14] or N-heterocyclic carbenes.[15] Besides the different modes of interaction, all methods allow only the conversion of CO_2 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 transformations of the reaction to methane or to methanol.

To investigate the above-outlined rationale, 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 CO_2 (Table 1). Triethylsilane (**2**, Et_3SiH) was employed as reducing agent with $B(C_6F_5)_3$ as activator.[16] However, none of the compounds showed catalytic activity. After a thorough screening, lithium *o*-phenylbisborate (**9**, $Li_2[1,2\text{-}C_6H_4(BH_3)_2]$)[17] was shown to be an effective candidate. When 10 mol% of **9** (relative to silane **2**) was reacted under an atmosphere of CO_2 (1 bar) in the presence of **2**, all the silane was consumed (Table 1, entry 1). $(Et_3Si)_2O$ (**4**) was the main product, along with $(Et_3SiO)_2CH_2$ (**5**) and Et_3SiOMe (**6**). The presence of **3** was indicated by a singlet at 0.14 ppm by ^{1}H NMR spectroscopy.[18] Without **9** or $B(C_6F_5)_3$, no conversion of silane **2** was observed, proving the need for both catalysts. The solubility of **9** in C_6D_5Br is poor; therefore, the reaction was carried out in THF-d_8 in order to increase the solubility. No transformation of silane **2** occurred under these conditions (Table 1, entry 2). Complexation of $B(C_6F_5)_3$ with THF might decrease the Lewis acidity of $B(C_6F_5)_3$, which is critical for the activation of **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**/$B(C_6F_5)_3$ led to a dramatic decrease of the catalytic efficiency (Table 1, entry 6). However, if the amount of $B(C_6F_5)_3$ was increased to 3 mol% and the reaction temperature elevated to 80 °C, the initial activity could be re-installed (Table 1, entry

Table 1. Optimization of the Catalytic Reduction of CO_2[a]

$$O=C=O \;+\; Et_3SiH \xrightarrow[\text{solvent, T, t}]{\substack{\text{cat./}\\ B(C_6F_5)_3,}} CH_4 \;+\; (Et_3Si)_2O \;+\; (Et_3SiO)_2CH_2 \;+\; Et_3SiOCH_3$$

1   2   3   4   5   6

7 R = Cl
8 R = Me   9   10   11   LiBEt$_3$H

entry	cat.	cat. amt/mol%, ratio cat./$B(C_6F_5)_3$	solvent	T/°C	t/h	product[b]/% 4	5	6
1	9	10, 1:1	C_6D_5Br	RT	60	69	31	–
2	9	10, 1:1	THF-d_8	RT	24	–	–	–
3	9	10, 1:1	C_6D_5Br	50	18	73	27	–
4	9	5, 1:1	C_6D_5Br	50	40	41	43	1
5[c]	9	5, 1:1	C_6D_5Br	50	21	81	19	–
6[c]	9	1, 1:1	C_6D_5Br	50	65	–	45	–
7[c]	9	1, 1:3	C_6D_5Br	80	56	78	22	–
8[d]	9	2, 1:1	–	80	5 days	58	42	–
9	10	10, 1:1	C_6D_5Br	50	41	18	54	3
10	11	10, 1:1	C_6D_5Br	50	24	4	91	–

[a]The reaction was performed with CO_2 (1 bar) in a Young NMR tube, unless noted otherwise. [b]Based on the consumption of **2**; determined by ^{1}H NMR with toluene as an internal standard. [c]The reaction was performed in a 25 mL Schlenk flask. [d]The yield was determined by GC-MS.

7). In contrast to **9**, $B(C_6F_5)_3$ is highly moisture and air sensitive. Therefore, if the amount of $B(C_6F_5)_3$ is too low, degradation might further reduce the amount and impede catalysis. The catalytic reduction of CO_2 to CH_4 using **9**/ $B(C_6F_5)_3$ 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).

The bidentate nature of the catalyst is essential for the high activity. When the monoborate **10** (LiPhBH$_3$) was employed,[19] which is the monodentate analogue to **9**, significantly less conversion was observed (Table 1, entry 9). In particular, the amount of $(Et_3Si)_2O$ (**4**) was greatly reduced compared to the reaction with the bidentate catalyst **9**. Interestingly, when the reaction with **10** was conducted at room temperature (RT), after a rather long induction period, only one turnover was observed (see Supporting Information for details). Super-hydride LiBHEt$_3$ (**11**) was also tested as catalyst (Table 1, entry 10). Although it is known that simple borohydrides can activate CO_2,[20] only $(Et_3SiO)_2CH_2$ (**5**) was detected as the main product and not methane.

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_2 to methanol with transition metal catalysts.[7] With **12** there is no need to add $B(C_6F_5)_3$ as co-catalyst. Thus, a mixture of **9** (10 mol%) and **12** in THF-d_8 was subjected to CO_2 (1 bar) at RT. After 2 h, MeOBpin **13** was the only CO_2-reduction product detectable. Hydrolysis with D_2O generates methanol, which was unambiguously confirmed by GC. Employment of only 1 mol% of **9** was also effective in the CO_2 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 yield of 89% was determined after 3 h by NMR. Simple borohydrides such as

Scheme 1. Reduction of CO_2 to Methanol Using the Bidentate Catalyst 9

T/°C	t/h	yield (**13**)
RT	22	83%
70	3	89%
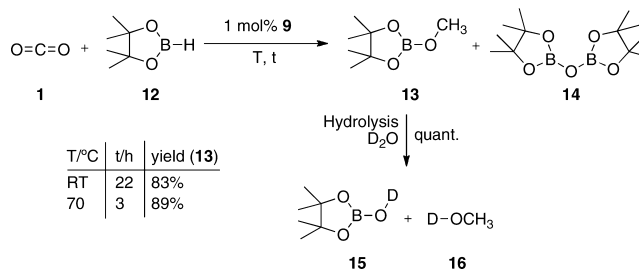
LiPhBH$_3$, LiBEt$_3$H, or NaBH$_4$ were less effective (see Supporting Information for details).

A proposed mechanism for the reduction of CO_2 to methane and methanol is shown in Figure 2. First, catalyst **9** forms an adduct with CO_2. 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_3SiH, the acetal moiety of intermediate **B** can be cleaved to give the disilylacetal **5**, which is the main side product. Ultimately, **5** is reduced to CH_4. In the presence of pinacol borane, the cyclic acetal is also opened and delivers **D**. In both cases a catalytically active hydride species is regenerated, closing the catalytic cycle.

The mechanistic proposal was supported by the following experiments. Treatment of **9** in THF−CO_2 solution (1 bar) at RT immediately led to the formation of a precipitate, indicating an interaction between CO_2 and **9**. Unfortunately, the poor solubility of the CO_2 adducts even in THF encumbered further characterization by NMR spectroscopy. IR analysis of the CO_2 adduct showed an absorption at 1592 cm^{-1} attributable to a
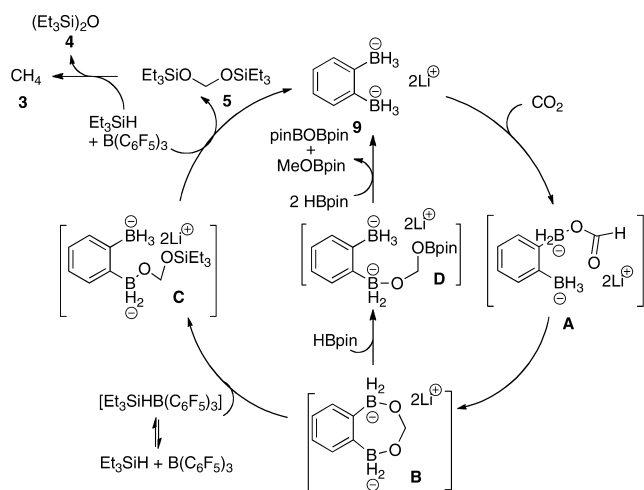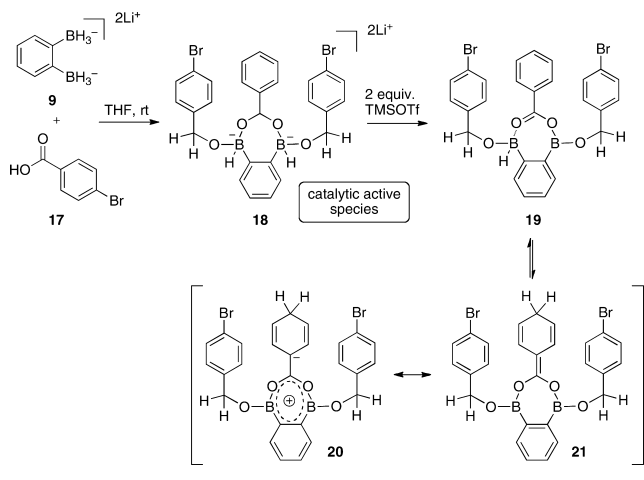
Figure 2. Proposed mechanism for catalytic reduction of CO_2 to methane and methanol.

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

C=O stretching vibration resulting from the addition of CO_2 to **9**. The stepwise reaction, first treating catalyst **9** with CO_2 and then adding HBpin, showed that three molecules of CO_2 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_2 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_2 surrogate (Scheme 2).

Scheme 2. Isolation of a Surrogate of a Bidentate Intermediate

Interestingly, the bromine in the bound benzoic acid has been replaced by hydride, probably by a nucleophilic substitution reaction activated by the catalyst.[21] The product of this transformation, **18**, was used as catalyst to CO_2 and $Et_3SiH/B(C_6F_5)_3$, 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 (Figure 3).[22]

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_2 complex. Noteworthy is the dioxa-diborepine heterocycle, which has not
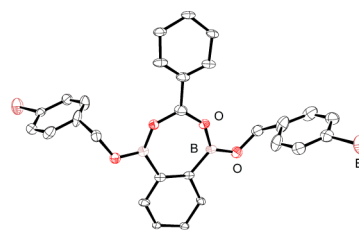
been described before. The entire ring is planar and is stabilized by aromaticity,[23] as can be clearly seen in the X-ray structure. An additional hydride is positioned in the *para* position of the bound benzoic acid in the solid state (Scheme 2, **20** and **21**). NMR studies, however, support a binding of the hydride at the boron atoms, as two broad signals in the B NMR have been observed. 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 bromobenzylic residues are fully occupied and impede an exact location of the hydrogen atoms in the structure.

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 $B(C_6F_5)_3$/silane system. Nevertheless, benzaldehyde dimethyl acetal (**22**) and methyl benzoate (**23**) have been tested as model structures for intermediates **A** and **B** in the catalytic cycle (Figure 2). In both cases, the mixture of $B(C_6F_5)_3$ and Et_3SiH induced the formation of toluene, methyl silyl ether, and benzyl silyl ether (Scheme 3). In contrast, no reaction took place when **9** was

Scheme 3. Support of the Role of the Catalytic System 9/$B(C_6F_5)_3$ (Conversion Determined by NMR)
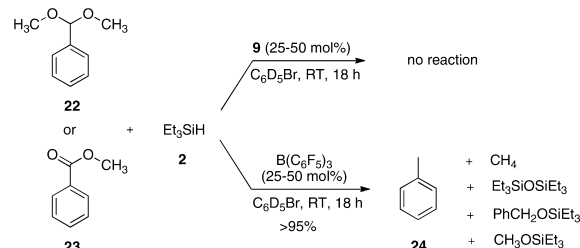
added without the presence of $B(C_6F_5)_3$. This observation indicates that the bidentate borate catalyst **9** activates the CO_2, while the silane/$B(C_6F_5)_3$ is responsible for the final catalytic reduction to methane.

We also investigated the kinetics of the catalytic reaction with 9/$B(C_6F_5)_3$ as catalyst by NMR spectroscopy (see Supporting Information). In both cases, the consumption of Et_3SiH, respectively HBpin, showed a first-order reaction rate. In the beginning the data revealed an induction period of about 30 min.[6d] Interestingly, 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_2 has been presented. The bidentate borohydride $Li_2[1,2-C_6H_4(BH_3)_2]$ efficiently promotes the selective reduction to either methane or methanol. The selectivity can be controlled by the reducing agent: In the presence of $Et_3SiH/B(C_6F_5)_3$, CO_2 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-dioxa-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 $Et_3SiH/B(C_6F_5)_3$, different rate-determining processes have been observed, depending on the reaction temperature in this highly complex reaction. Further studies to adopt this useful new catalytic metal-free transformation for practical applications are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental data; crystallographic data, in CIF format, 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 interest.

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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 of the metal-catalyzed reduction of CO_2 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 of the metal-catalyzed reduction of CO_2 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. Ed.* **2012**, *51*, 7499−7502.

(8) For a selected example of the metal-catalyzed reduction of CO_2 to formaldehyde see: Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2014**, *136*, 4419−4425.

(9) For selected examples of the metal-catalyzed reduction of CO_2 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.; Dobereiner, 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. Ed.* **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, 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. Ed.* **2009**, *48*, 9839−9843. (c) Sgro, M. J.; Stephan, D. W. *Angew. Chem., Int. Ed.* **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. *Angew. Chem., Int. Ed.* **2012**, *51*, 7323−7326. (b) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 2981−2984.

(14) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. *Angew. Chem., Int. Ed.* **2011**, *51*, 187−190.

(15) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **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_4 formed could not been 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 therein.

(21) Egli, R. A. *Helv. Chim. Acta* **1968**, *51*, 2090−2097.

(22) The X-ray data of **20/21** have 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) Martín, N.; Haley, M. M.; Tykwinski, R. R. *Chem. Commun.* **2012**, *48*, 10471.