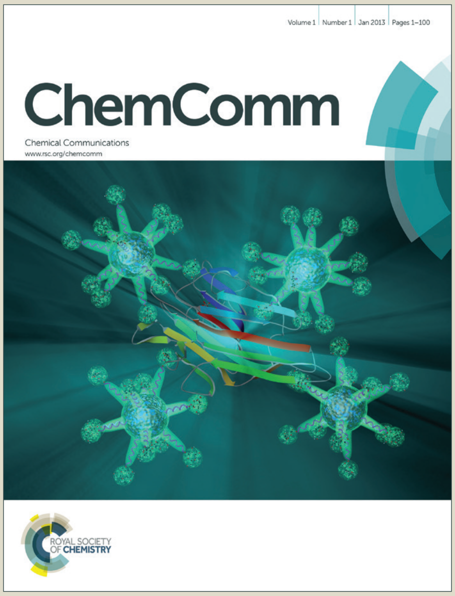
ChemComm

Accepted Manuscript



Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Lewis Base Activation of Borane-Dimethylsulfide into Strongly Reducing Ion Pairs for the Transformation of Carbon Dioxide to Methoxyboranes

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Marc-André Légaré,[a] Marc-André Courtemanche[a] and Frédéric-Georges Fontaine*[a]

The hydroboration of carbon dioxide into methoxyboranes by borane-dimethylsulfide using different base catalysts is described. Non-nucleophilic proton sponge is found to be the most active catalyst, with TOF reaching 64 h^{-1} at 80 °C, and is acting *via* the activation of $BH_3{\bullet}SMe_2$ into a boronium-borohydride ion pair.

Due to its availability and its role in climate change, carbon dioxide has attracted considerable interest in recent years. Although several sequestration technologies are known,[1] chemical storage of CO_2 in the form of valuable hydrogen containing molecules, such as methanol, is highly desirable since these chemicals could be a green alternative to fossil fuels, both as a source of organic building blocks and as energy media.[1,2]

Although they are costly and not economically viable for large scale processes, hydroboranes are amongst the most efficient reagents for the catalytic reduction of carbon dioxide to methanol.[3,4] Although the hydroboration of C=O bonds is a well-studied reaction for a large variety of substrates,[5] carbon dioxide remains resistant to uncatalyzed hydroboration by neutral hydroboranes, even when using the most reactive BH_3 adducts. It has been shown that sodium or lithium borohydride can reduce CO_2 with low selectivity to a mixture of formate and methoxy products without the use of a catalyst, illustrating the superior reducing power of these anionic boron hydrides.[6] In order to facilitate the reaction of neutral hydroboranes with CO_2, transition metal catalysts have been used to activate the B-H bonds and reduce CO_2 via an hydrometallation reaction.[3,7] The most notable example of this type of catalysis is a nickel pincer complex developed by Guan *et al.* that catalyzes the hydroboration of CO_2 to methoxyboranes with a TOF of 495 h^{-1} using HBcat.[7b] Recently, Cantat has shown that one of the most reactive boranes, 9-borabicyclo[3.3.1]nonane (9-BBN), can be used as a reductant in the presence of some nitrogen bases to generate methoxyboranes from CO_2.[4f] It was proposed that the role of the catalysts was to activate the borane, either in a Frustrated Lewis Pair (FLP) fashion or by the formation of ion pairs. A similar reaction with 9-BBN was also reported using phosphines as catalysts to reduce carbon dioxide into methoxyboranes.[4g] However, the most active metal-free organocatalyst to date is a phosphine-borane complex reported by our group that activates borane-dimethylsulfide ($BH_3{\bullet}SMe_2$) and CO_2 to yield methoxyboranes ($(MeOBO)_n$) with a TOF exceeding 900 h^{-1} at 70 °C.[4b] The transformation was proposed to occur through simultaneous nucleophilic activation of the borane and electrophilic fixation of carbon dioxide.[8] In such a mechanism, the reductant is made more nucleophilic by receiving electron density from the phosphine moiety. It is important to note that it is one of the only two CO_2 reduction systems reported to use $BH_3{\bullet}SMe_2$ as a hydrogen source, the other being a more recent report by Stephan of an ambiphilic catalyst for the hydroboration of CO_2.[4h] BH_3 adducts are by far the most interesting boranes to use, since they have the highest hydrogen content of any hydroboranes in addition of being less expensive than most of them. Their reactivity, however, tends to be limited by its strong tendency to form stable borane adducts with Lewis bases.

In an effort to broaden the scope of $BH_3{\bullet}SMe_2$ as a reducing agent for the functionalization of CO_2, the effect of various commercially available bases on the catalytic activity was studied. We thus decided to monitor by ^1H NMR spectroscopy the reaction between the bases and 25 equiv of $BH_3{\bullet}SMe_2$ under one atm of CO_2 at 80 °C in a *J Young* NMR tube. The yields were calculated using the integration of the $(MeOBO)_n$ generated in comparison to the internal standard (hexamethylbenzene) present in the solution, as shown in Figure S1 (Supporting Information). Contrary to the reactivity observed using 9-BBN as a reductant,[4g] phosphines (PPh_3, P*t*Bu_3 and PCy_3) proved ineffective for the CO_2 reduction, as they are known to generate stable $BH_3{\bullet}PR_3$ adducts.[9] Inorganic bases such as CsF, KCN and $CsCO_3$ also did not have any effect on the reduction of CO_2. However, sodium alkoxides (MeONa, EtONa, and *t*BuONa) proved to convert some of the CO_2 to $(MeOBO)_n$, notably getting up to 3 turn-overs in the first hour of reaction with *t*BuONa (Table 1, entries 1-3). It is known that the addition of alkoxides to BH_3 leads to the generation of alkoxyborohydrides.[10] These species possess increased nucleophilicity when compared to neutral BH_3 adducts and can disproportionate to give sodium borohydride.[11] The low activity of sodium alkoxides can either be attributed to their low solubility or to the low rate of the disproportion reaction in benzene-*d*$_6$. On the other hand, anionic amides (lithium diisopropylamide and lithium dimethylamide) were found to be inactive in the reduction of CO_2.

Several nitrogen Lewis bases also proved to be inefficient under the conditions tested, including triethylamine, diisopropylethylamine, 2,2,6,6-tetramethylpiperidine, pyridine, 4-dimethylaminopyridine, 2,6-lutidine, 4-pyrrolopyridine and 2,6-di*tert*butylpyridine. However, as shown in Table 1, some species proved to exhibit significant activity in the generation of methoxyboranes.

Table 1. Catalytic activity of different bases for the hydroboration of CO_2 by $BH_3{\bullet}SMe_2$.

$$CO_2 + BH_3.SMe_2 \xrightarrow{\text{Base (cat.)}} [MeOBO]_3$$

Entry	Base (mol. %)	t(h)	T (°C)	Yield (%) (TON)	TOF
1	MeONa (4)	1	80	1.3 (1)	1
2	EtONa (4)	1	80	2.6 (2)	2
3	^{t}BuONa (4)	1	80	4.0 (3)	3
4	DBU (4)	1	80	23 (17)	**17**
5	TBD (4)	1	80	25 (19)	**19**
6	Terpyridine (4)	1	80	47 (35)	**35**
7	**1** (4)	1	80	68 (51)	**51**
8[a]	**1** (4)	1	25	4.0 (3)	3
9[a]	**1** (4)	24	25	39 (29)	1
10[a]	**1** (4)	1	80	85 (64)	**64**
11[a]	**1** (4)	21	80	**>99** (75)	4
12[a]	**1** (1)	24	80	7.6 (23)	1
13	**2-BH$_4$** (4)	0.16	25[b]	24 (18)	**108**
14[a]	**2-BH$_4$** (1)	3	25[b]	21 (62)	62
15[a]	**2-BH$_4$** (1)	24	25	28 (84)	4
16[a]	**2-BH$_4$** (1)	1	80	21 (64)	64
17[a]	**2-BH$_4$** (1)	24	80	25 (75)	3

Conditions: 0.01 mmol of base catalyst in benzene-*d$_6$* (0.4 mL), the number of equivalents of $BH_3{\bullet}SMe_2$ was calculated to obtain the desired catalytic loading, 1 atm CO_2. The yield was measured by NMR spectroscopy using hexamethylbenzene as an internal standard. TONs and TOFs are given in regard to the number of hydrides transferred. [a] Solvent = Dichloromethane-*d$_2$*. [b] Although the tube was kept at room temperature, the exothermic reaction caused internal heating of the system.

Some reduction products were observed when $BH_3{\bullet}SMe_2$ was added to strong Lewis bases, such as DBU (1,8-diazabicycloundec-7-ene) and TBD (triazabicyclo[4.4.0]dec-5-ene), giving respective TOF of 17 and 19 h^{-1} (Table 1, entries 4 - 5). However, multidentate amines, such as terpyridine and proton sponge (PS; **1**) gave the best activity, with observed TOF of 35 and 51 h^{-1} when the reaction was carried out at 80°C in benzene-*d$_6$* (Table 1, entries 6 - 7). When the reaction was carried out in the presence of **1** as catalyst at ambient temperature a lower activity was observed. The TON and TOF dropped to reach in the best conditions, 29 (Table 1, entry 9) and 3 h^{-1}, respectively (Table 1, entry 8). It is good to note that under these conditions **1** did not present any activity in presence of 9-BBN, as reported by Cantat *et al.*[4f] Running the reaction in dichloromethane-*d$_2$* (Table 1, entry 10) did increase the TON (64) and the TOF of the reaction (64 h^{-1}), presumably by increasing the solubility of the reaction intermediates (*vide infra*). Letting the reaction run for a longer time period allowed for complete conversion of the $BH_3{\bullet}SMe_2$ (Table 1, entry 11).

In order to shed light on the mode of activation of BH_3 by bidentate ligands, the reaction was studied using **1** since it proved to be the most active catalyst. This exceptionally basic amine is thus called because of its almost exclusive affinity for protons, a result of the unique steric environment around its nitrogen atoms which prevents them to coordinate larger electrophiles. The notable exceptions include the fixation of a handful of boron cations,[12] as well as two transition metal complexes and group XIII species.[13] **1** was reported to react rapidly with B_2H_6 or boron trifluoride gas to afford species identified as $[PS(BX_2)]^+[BX_4]^-$ (X = H, F)[12b] or $[PS(BH_2)]^+[B_2H_7]^-$,[12c] but were not structurally characterized. These species are reminiscent of the ‘diammonia of diborane’ that was proposed as a key intermediate in the deshydrogenation of ammonia-borane.[12d-f] Interestingly, Vedejs and coworkers were able to prepare a 9-BBN derived PS stabilized boronium by a more aggressive method.[12g] The cation thus formed was found to be a highly reactive electrophile, contrary to classical boronium cations. This property was proposed to arise from the steric demands of the proton sponge framework. It is important to note that no catalytic activity was ever reported for these species.

The hydroboration of CO_2 using $BH_3{\bullet}SMe_2$ was very slow when catalyzed by **1** at room temperature in benzene-*d$_6$*. However, a solution of $BH_3{\bullet}SMe_2$ and **1** heated to 70 °C for an hour in the absence of CO_2 was found to react rapidly and exothermically upon exposure to CO_2 at room temperature. These observations suggest that a reaction between **1** and $BH_3{\bullet}SMe_2$ is the limiting step in the catalytic transformation. It was possible to isolate single crystals from a reaction mixture between **1**, 50 equiv of $BH_3{\bullet}SMe_2$ and CO_2. Although the limited solubility prevented NMR characterization, the solid state structure consisted of the boronium salt $[PS(BH_2)]_2[B_{12}H_{12}]$ (**2-B$_{12}$H$_{12}$**) (Figure 1). the resolved solid state structure of the boronium cation is similar to a previously reported structure of $[PS(BH_2)][B_{19}H_{22}]$.[12h] Since the $B_{12}H_{12}^{2-}$ dianion is generally isolated as a product of the disproportionation of $[B_3H_8]^-$, which is prepared in oxidative conditions from BH_4^-,[14] it could be suggested that the initial step in the catalytic transformation involves the generation of the ion pair $[PS(BH_2)][BH_4]$ (**2-BH$_4$**).

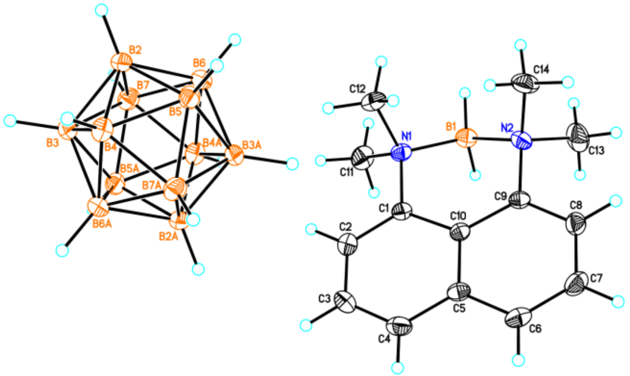
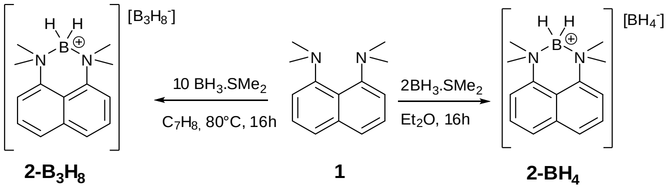


Figure 1: The ORTEP plot of $[PS(BH_2)]_2[B_{12}H_{12}]$ with thermal ellipsoids set at the 40% probability level. Selected bond lengths (Å) and angles (°): N1-B1: 1.601(2), N1-C1: 1.511(2), N2-B1: 1.600(2), N1-B1-N2: 111.62(13), C1-C10-C9: 126.11(15), C1-N1-B1: 111.07(12), C9-N2-B1: 111.07(13).

In order to better understand the reaction between proton sponge and $BH_3{\bullet}SMe_2$, the products formed were characterized using ^{11}B NMR spectroscopy while controlling the stoichiometry of the reagents. Over the course of the reaction, three different boronium salts were observed, depending on the reaction conditions. In all cases, the formation of the dihydroboronium cation is supported by ^1H NMR by a significant downfield shift for the proton sponge resonances to a doublet of doublets at 7.78 ppm (J = 8 Hz) and two doublets at 8.23 and 8.08 ppm (J = 8 Hz) in dichloromethane-*d$_2$*, with a slight variation on the chemical shift depending on the counterion (see Supporting Info). Although the resonances of the $[BH_2]^+$ were not observed by ^1H NMR spectroscopy, the ^{11}B NMR spectra of derivatives of **2** did show a broad resonance at *ca* 1.5 ppm, which is similar to that of previously reported $[PS(BH_2)][B_2H_7]$.[12c] Stirring **1** in diethyl ether with 2 equiv of $BH_3{\bullet}SMe_2$ for 16 hours allowed us to obtain colourless crystals. ^{11}B NMR spectroscopy for this compound showed, in addition to the resonance at 1.57 ppm for the borenium species $[PS(BH_2)]^+$, a sharp quintuplet at -38.4 ppm due to the $[BH_4]^-$ anion. The latter was confirmed by observation of a sharp 4-line ^1H NMR resonance at δ -0.06. These spectroscopic findings strongly suggest the presence of the $[BH_4]^-$ anion and the formation of salt **2-BH$_4$** ($[PS(BH_2)][BH_4]$). However, using 10 equiv of $BH_3{\bullet}SMe_2$ in presence of **1** in toluene afforded $[PS(BH_2)][B_3H_8]$ (**2-B$_3$H$_8$**) as the main product (Scheme 1) after heating. The $[B_3H_8]^-$ anion was characterized by the presence of a nonuplet at -30.0 ppm in the ^{11}B NMR spectrum.[15]



Scheme 1: Reaction of PS with $BH_3{\bullet}SMe_2$ to give boronium salts.

Altough the $[B_{12}H_{12}]^-$ anion could not be observed by NMR spectroscopy, the crystallization of all samples of $[PS(BH_2)][B_3H_8]$ consistently yielded **2-B$_{12}$H$_{12}$**. It is rational to propose that initial activation of $BH_3{\bullet}SMe_2$ by proton sponge affords the ion pair **2-BH$_4$**, which can degrade to **2-B$_3$H$_8$** by reaction with $BH_3{\bullet}SMe_2$ and to **2-B$_{12}$H$_{12}$**. The activity of these compounds was studied by treating them with an atmosphere of carbon dioxide. In this manner, $[PS(BH_2)][B_3H_8]$ was found to be unreactive towards CO_2. Unsurprisingly, a dicholoromethane-*d*^{2} solution of **2-BH$_4$** in absence of additional boranes reacted instantaneously at room temperature with carbon dioxide. Within five minutes, two different signals appeared in the ^1H NMR spectrum at 8.27 and 8.33 ppm, assigned to the formation of formate products, along with the complete disappearance of the BH_4^- resonances. No products of higher reduction level were observed in this manner, suggesting that the catalyst is only active in the reduction of carbon dioxide. Similarly, a solution of **2-BH$_4$** and 25 equiv of $BH_3{\bullet}SMe_2$ reacted within minutes with carbon dioxide to give methoxyboranes at room temperature (Table 1**,** entry 13). The heat produced by the exothermic hydroboration of carbon dioxide likely contributed to the increase in catalytic activity, obtaining a TOF of 108 h^{-1}. However, when looking at its reactivity at 80 °C or for a longer time period, the catalytic activity **2-BH$_4$** was found to be similar to that of **1** (Table 1, entries 14-17).

From these observations, it is possible to propose a catalytic cycle, as shown in Figure 2. In a first step that is rate-limiting, the bidentate ligand activates borane-dimethylsulfide to generate a highly reactive boronium-borohydride ion pair. Similar boronium species has been synthesized with TBD,[16] but under catalytic conditions, thus explaining the need for higher reaction temperature in order to achieve the catalytic reduction of CO_2 since no activity was observed between DBU and TBD in presence of $BH_3{\bullet}SMe_2$ at 25 °C.[4f] The $[BH_4]^-$ generated can in turn react with carbon dioxide to give formate derivatives. The formate generated can abstract the BH_2^+ fragment generating reduced species such as $HCOOBH_2$. In turn, $BH_3{\bullet}SMe_2$ can very efficiently reduce formatoboranes into $(MeOBO)_n$, thus explaining the highest TOF obtained using $BH_3{\bullet}SMe_2$ instead of other organic hydroboranes.

In summary, the use of $BH_3{\bullet}SMe_2$ as a reducing agent for CO_2 hydroboration is possible in presence of strong Lewis bases. Although limited activity is observed with monodentate species such as DBU and TMP, bidentate amines such as proton sponge proved to be the active catalysts in this reaction. It was possible to isolate single crystals that demonstrated the presence of the boronium species $[PS(BH_2)]^+$. ^{11}B NMR studies demonstrate that the most likely active species for the CO_2 reduction into formates was the borate ion, BH_4^-, whereas the $BH_3{\bullet}SMe_2$ in solution can reduce the formatoborane derivatives into methoxyboranes. Optimization of this system is currently underway.

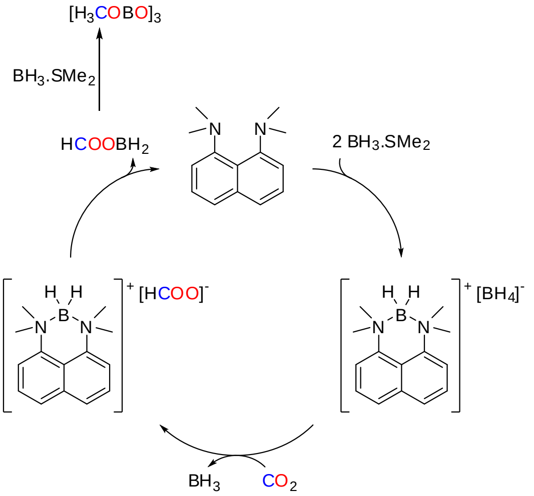


Figure 2: Proposed mechanism for the reduction of CO_2 to methoxyboranes catalyzed by **1**.

The authors would like to acknowledge National Sciences and Engineering Research Council of Canada (NSERC, Canada) and the Centre de Catalyse et Chimie Verte (Quebec) for financial support. M.-A. C. and M.-A. L. would like to thank NSERC and FQRNT for scholarships. We acknowledge W. Bi for the resolution of the crystal structure.

Notes and references

[a] *Département de Chimie and Centre de Recherche sur la Catalyse et les Interfaces (CERPIC), Université Laval, 1045 Avenue de la Médecine, Québec, Canada.*
E-mail: frederic.fontaine@chm.ulaval.ca; Fax: +1-418-656-7916; Tel: +1-418-656-5140

†Electronic Supplementary Information (ESI) available: Synthetic procedures, solution NMR data and crystallographic information. See DOI: 10.1039/c000000x/

1 D. M. D'Alessandro, B Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058-6082.
2 G. A. Olah, A. Goeppert and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*; Wiley-VCH, Weinheim, 2006.
3 (a) K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435-2452; (b) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365-2387; (c) M. Aresta and A. Dibenedetto *Dalton Trans.*, 2007, 2975-2992.
4 (a) F.-G., Fontaine, M.-A. Courtemanche and M.-A Légaré, *Chem. Eur. J.*, 2014, **20**, 2990-2996; (b) M.-A. Courtemanche, M.-A. Légaré, L. Maron and F.-G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326-9329; (c) M.-A. Courtemanche, J. Larouche, M.-A. Légaré, B. Wenhua, L. Maron, and F.-G. Fontaine, *Organometallics*, 2013, **32**, 6804-6811. (d) S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322-3325; (e) A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660-10661; (f) C. Das Neves Gomes, E. Blondiaux, P. Thuéry, and T. Cantat, *Chem.. Eur. J.* 2014, **23**, 7098-7106; (g) T. Wang and D. W. Stephan, *Chem.*

Commun., 2014, **DOI:** 10.1039/C4CC02103G; (h) T. Wang and D. W. Stephan, D. W. *Chem. Eur. J.*, 2014, **20**, 3036-3039.
5 E. Mincione, *J. Org. Chem.*, 1978, **43**, 1829-1830.
6 (a) T. J. Wartik, and R. K. Pearson *J. Inorg. Nuc. Chem.*, 1958, **7**, 404-411; (b) H. E. Heller, W. G. Brown and J. G. Hurr Jr., *J. Am. Chem. Soc*., 1950, **72**, 2560.
7 (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.
8 M.-A. Courtemanche, M.-A. Légaré, L. Maron and F.-G. Fontaine, *J. Am. Chem. Soc.*, 2014, DOI : 10.1021/ja5047846.
9 H. Schmidbaur, T. Wimmer, G. Reber, and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1071-1074.
10 E. C. Ashby, F. R. Dobbs and H. P. Hopkins Jr. *J. Am. Chem. Soc.*, 1975, **97**, 3158-3162.
11 J. L. Hubbard, Sodium Trimethoxyborohydride. *e-EROS Encyclopedia of Reagents for Organic Synthesis*, 2001.
12 (a) D. D. Axtell, A. C. Campbell, P. C. Keller and J. V. Rund, *J. Coord. Chem.*, 1976, **5**, 129-134; (b) T. Onak, H. Rosendo, G. Siwapinyoyos, R. Kubo and L. Liauw, *Inorg. Chem.*, 1979, **18**, 2943-2945; (c) P. C. Keller and J. V. Rund, *Inorg. Chem*,. 1979, **18**, 3197-3199; (d) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, 1958, **80**, 4-8; (e) M. Bowden, D. J. Heldebrant, A. Karkamkar, T. Proffen, G. K. Schenter and T. Autrey, *Chem. Commun.*, 2010, **46**, 8564-8566; (f) C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279-293; (g) A. Prokofjevs, J. W. Kampf and E. Vedejs, *Angew. Chem. Int. Ed.*, 2011, **50**, 2098-2101; (h) M. G. S. Londesborough, J. Bould, T. Baše, D. Hnyk, M. Bakardjiev, J. Holub, I. Císařová and J. D. Kennedy, *Inorg. Chem.*, 2010, **49**, 4092-4098.
13 (a) J. P. Collman, M. Zhong, C. Zhang and S. Constanzo, *J. Org. Chem.*, 2001, **66**, 7892-7897; (b) T. Yamasaki, N. Ozaki, Y. Saika, K. Ohta, K. Goboh, F. Nakamura, M. Hashimoto and S. Okeya, *Chem. Lett.*, 2004, **33**, 928-929; (c) J. F. Kögel, X. Xie, E. Baal, D. Gesevicius, B. Oelkers, B. Kovacevic and J. Sundermeyer, *Chem. Eur. J.*, 2014, **20**, 7670-7685.
14 V. Geis, K. Guttsche, C. Knapp, H. Scherer and R. Uzun, *Dalton Trans.*, 2009, 2687-2694.
15 J. D. Woollins, *Inorganic Experiments, 3rd Revised Edition*, Wiley-VCH, 2010, Weinheim, 405-408.
16 O. Ciobanu, E. Kaifer, M. Enders and H.-J. Himmel, *Angew. Chem., Int. Ed.*, 2009, **48**, 5538-5541.