ChemPubSoc Europe

DOI: 10.1002/chem.201304870

CHEMISTRY
A European Journal
Communication

Carbenes

Carbene-9-BBN Ring Expansions as a Route to Intramolecular Frustrated Lewis Pairs for CO_2 Reduction**

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Abstract: Reactions of phosphine-derived carbenes with 9-borabicyclo[3.3.1]nonane (9-BBN) result in ring-expansion reactions to generate novel intramolecular frustrated Lewis pairs (FLPs). These FLPs effect the catalytic reduction of CO_2 in the presence of boranes to give BOB and methoxy-borate species.

The first isolation of a stable carbene by Bertrand in 1989[1] and the subsequent generation of N-heterocyclic carbenes (NHCs) by Arduengo and co-workers[2] in 1991 are important milestones in modern chemistry. Since then, NHCs have been widely utilized in various fields including transition-metal chemistry,[3–5] catalysis[6–9] and main group chemistry[10–14] because of their robust two-electron σ-donor ability and their easy modification. NHCs were generally considered to be robust ligands until the Bertrand group uncovered reactions of NHCs with pinacolborane (HBpin) resulted in the C–N bond cleavage.[15] Subsequently the Hill group discovered related C–N bond activation and ring opening of an NHC on $(NHC)BeH_2$ compound under mild conditions.[16] More recently, Radius and co-workers reported elegant work on the C–N bond cleavage and ring expansion of NHCs using hydrosilanes on heating to 100 °C for a few days.[17] Rivard has also reported C–N bond cleavage and ring expansion of NHCs with borane hydrides in the reactions of IPr (IPr = *N*,*N*′-bis-[2,6-(diisopropyl)phenyl]imidazol-2-ylidene) with $BH_2NHDipp$ (Dipp = 2,6-(diisopropyl)-phenyl) at 100 °C.[18]

Recently, our group has reported the isolation of the simple NHC adducts of 9-borabicyclo[3.3.1]nonane (9-BBN) en route to the borenium salt $[(IiPr_2)(BC_8H_{14})][B(C_6F_5)_4]$.[19] This species, in the presence of $PtBu_3$, behaves as a frustrated Lewis pair (FLP) to activate hydrogen gas and catalyze the hydrogenation of imines and enamines. Following this work, we were interested to utilize carbenes of the form $C_3H_2(NPR_2)_2$ to generate an intramolecular borenium-phosphine FLP. However, herein we report that the reaction of such NHC derivatives with 9-BBN proceeds through C–N bond cleavage and insertion into the B–C bond of 9-BBN under mild conditions. Nonetheless, these ring-expanded products behave as intramolecular FLPs, combining strongly basic sites with a weakly Lewis acidic borane center, to effect the catalytic, metal-free reduction of CO_2 in the presence of borane hydrides under mild conditions.

Only recently have the N-phosphorylated NHCs of the form $C_3H_2(NPR_2)_2$ been synthesized.[20–22] Following literature procedures, we prepared the sterically demanding and electron donating analogues $C_3H_2(NPR_2)_2$ (R = *t*Bu **1**, N*i*Pr$_2$ **2**) in straightforward treatment of imidazolate-phosphine $C_3H_3N(NPR_2)$ with sodium triflate and the secondary phosphorus chloride, R_2PCl. Deprotonation of these triflate salts with potassium hexamethyldisilazane afforded the corresponding carbenes. Compound **1** gives rise to a ^{31}P signal at 98.1 ppm. During the course of our work an analogous preparation and crystallographic study of **1** has appeared.[23]

The reaction between 9-BBN and **1** in [D$_5$]bromobenzene at room temperature was monitored by $^{31}P\{^1H\}$ NMR spectroscopy revealing the formation of a new product as evidenced by the two resonances at $\delta = 76.7$ and 71.2 ppm. This product also gave rise to a $^{11}B\{^1H\}$ NMR resonance at $\delta = 50.34$ ppm. Subsequent workup and extraction into hexane and subsequent cooling afforded the colorless, crystalline solid **3** in 30 % yield. The ^1H NMR spectrum of **3** is consistent with inequivalent carbene backbone C–H groups as two distinct resonances at $\delta =$ 5.67 ($^3J_{H\text{-}H} = 6.3$ Hz and $^3J_{H\text{-}P} = 2.0$ Hz) and $\delta = 6.01$ ($^3J_{H\text{-}H} = 6$ Hz and $^3J_{H\text{-}P} = 1$ Hz) were observed. An X-ray crystallographic study revealed **3** as the product is the result of an unusual C–N bond cleavage and ring expansion of NHC (Figure 1 a). This results in a six-member ring in which the carbene carbon has inserted in to the B–C bond of 9-BBN affording a $BCNC_2N$ ring. In a similar fashion, the reaction of 9-BBN with **2** afforded the analogous insertion product **4** in 43 % yield. The spectral data of **4** were analogous to those of **3** and this species was also characterized by X-ray crystallography (Figure 1 b).

The mechanism of these insertions and ring expansions is thought to proceed by initial coordination of the NHC to the boron center of 9-BBN. This view is supported by the inhibition of the reaction by the addition of excess pyridine to the reaction mixture of **1** and 9-BBN. Migration of the H atom from boron to the electron-deficient carbene carbon atom prompts coordination of one of the adjacent nitrogen atoms to B, thus breaking the C–N bond. The electrophilic carbon center in the resulting zwitterion prompts subsequent migration of a B–C bond to yield the new C–C bond containing the products **3** and **4** (Scheme 1). Recent computational studies have been shown to support such a mechanism.[24,25] It is noteworthy that

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[**] *9-BBN = 9-borabicyclo[3.3.1]nonane*

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304870.

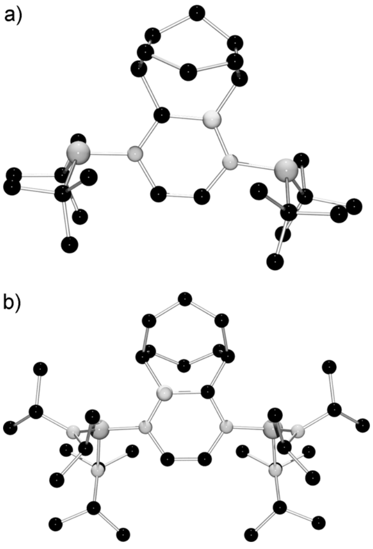
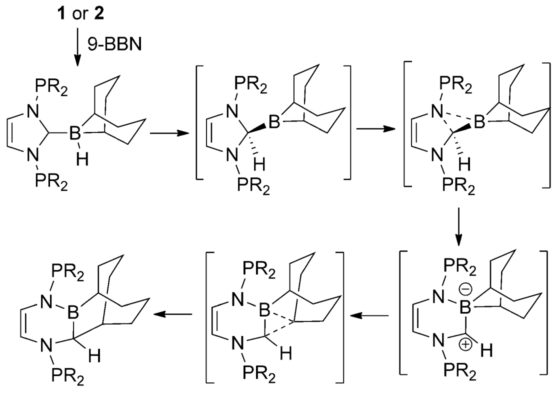


Figure 1. POV-ray drawing of: a) **3** and b) **4**. All hydrogen atoms are omitted for clarity.



R = *t*Bu **3**, N(*i*Pr)$_2$ **4**

Scheme 1. Proposed mechanism for the formation of **3** and **4**.

Table 1. Catalytic reduction of CO_2.[a]

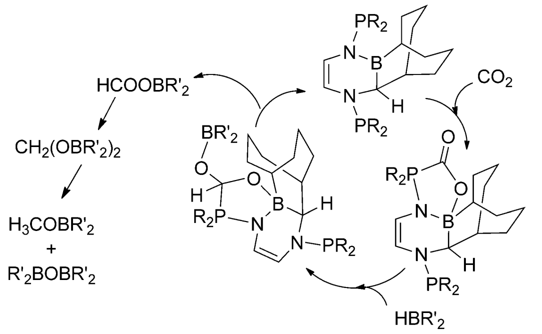
Entry	Borane	Cat. ([mol%])	*t* [h]	Yield [%]	TON	Product ratio **5/6/7**			**8**
1	HBpin	–	114	0	0	0	0	0	–
2	HBpin	**3**(5)	114	95	19	1	0.06	0.01	–
3	HBpin[b]	**3**(1)	66	89	89	1	0.08	2.6	–
4	HBpin	**4**(5)	21	100	20	1	0.02	0.1	–
5	HBpin[b]	**4**(1)	66	100	100	1	0.30	0.3	–
6	HBcat[b,c]	**3**(1)	21	99	99	0	0	1	–
7	HBcat[b]	**3**(1)	4.5	100	100	0	0	1	–
8	HBcat[b,c]	**4**(1)	1.0	100	100	0	0	1	–
9	HBcat[b]	**4**(1)	0.25	100	100	0	0	1	–
10	$BH_3(SMe_2)$[b]	**3**(1)	11	80	240	–	–	–	1
11	$BH_3(SMe_2)$[b]	**4**(1)	11	80	240	–	–	–	1

[a] Reactions conducted in J-Young tubes; monitored by NMR spectroscopy; C_6D_5Br (0.8 mL); $P(^{13}CO_2)$: CO_2 (5 atm), 60 °C, borane (20 equiv); [b] borane (100 equiv); no reaction was observed in the absence of FLP catalyst;[27] [c] 25 °C.

the ring expansion observed in the formation of **3** and **4** is reminiscent of the work of Soderquist's group who exploited the insertion into the B–C bonds of 9-BBN to generate oxazaborolidines and chiral 9-BBD derivatives.[26]

Compounds **3** or **4** were exposed to an atmosphere of $^{13}CO_2$ at room temperature. Although compound **3** showed no apparent reaction with CO_2, compound **4** exhibits a ^{31}P resonance at 20.2 ppm and a $^{13}C\{^1H\}$ signal at 166.8 ppm with a P–C coupling constant of 184.5 Hz. This is consistent with the more basic nature of the P centers in **4**. Despite this evidence for a CO_2 adduct of **4** efforts to isolate this species were unsuccessful, suggesting an equilibrium binding. Nonetheless, such equilibria are well suited to catalytic reductions. To this end, catalytic amounts (1–5 mol%) of compounds **3** or **4** were exposed to CO_2 in the presence of one of the reducing boranes HBpin, HBcat, or $BH_3(SMe_2)$ at 60 °C. Using 5 mol% catalyst and 5 atm CO_2 at 60 °C, in the presence of 20 equiv of borane, **3** catalyzed reduction of CO_2 with HBpin resulting in the consumption of 96% of the borane and affording a product mixture of HCO_2Bpin (**5a**), $CH_2(OBpin)_2$ (**6a**), and MeOBpin (**7a**), in a ratio of 1:0.06:0.01 (entry 2, Table 1) together with the byproduct $O(Bpin)_2$. Under comparable conditions compound **4** produces a similar product ratio of **5a**/**6a**/**7a** of 1.0:0.02:0.11 in 21 h (entry 4, Table 1). Increasing the concentration of HBpin to 100 equivalents in the presence of **3** or **4** had very different effects. In the former, the major product becomes the methoxy-borane **7a** (entry 3, Table 1) whereas when using **4** only a small impact on the product distribution is observed (entries 4 and 5, Table 1). In contrast, changing the borane to HBcat and using either **3** or **4** as the catalyst resulted in much faster and complete conversions to the fully reduced product MeOBcat (**7b**), with no evidence of HCO_2Bcat (**5b**), $CH_2(OBcat)_2$ (**6b**). Increasing the temperature from 25 to 60 °C reduced the time to complete reduction of CO_2 from 21 to 4.5 h (entries 6 and 7, Table 1) when **3** was used as the catalyst. On the other hand, when performing the catalysis using **4**, the corresponding reaction times were 1 h and 15 min (entries 8 and 9, Table 1). The higher reactivity of **3** in these latter cases, is thought to be the result of the stronger Lewis basicity of $P(NiPr_2)_2$ over $PtBu_2$, which accelerates CO_2 binding and enhances activation for subsequent reduction. It is interesting that use of $BH_3(SMe_2)$ resulted in similar reactivity of **3** and **4** (entries 10 and 11, Table 1) leading to 80% consumption of the 100 equivalents of borane in 11 h affording exclusively $(MeOBO)_3$ (**8**) as the observed product. These observations confirm a marked dependence of the rate of reduction on both the nature of the FLP catalyst and the reducing agent (borane).

Mechanistically, these reactions are thought to exploit the intramolecular FLP nature of the products **3** and **4**. These compounds are thought to activate CO_2 in a transient fashion allowing reaction with borane to generate the initial boron-formate species **5**. It should be noted that efforts to either observe or isolate these intramolecule FLP–CO_2 complexes were unsuccessful. Nonetheless, subsequent reaction with additional borane is thought to afford the methylene $CH_2(OBR_2)_2$ (**6**) and methoxy-boranes $MeOBR_2$ (**7**) products and R_2BOBR_2. The role of **3** and **4** in the catalysis was further supported by experiments in which the phosphines $PtBu_3$ and $PhP(NiPr_2)_2$ were combined with HBcat and CO_2 at room temperature for 21 h and at 60 °C for 8 h, respectively. In these cases, no MeOBcat was formed. These data suggest that it is the intramolecular binding of CO_2 that initiates these reductions (Scheme 2).



Scheme 2. Proposed mechanism for the reduction of CO_2 by **3** or **4**.

In contrast to other main-group intramolecular FLP systems, **3** and **4** combine strongly donating basic centers with weakly acidic boron centers. The weaker Lewis acidity is thought to offer lability of the reduced CO_2 fragments, prompting catalytic turnover in the reduction cycle. This stands in contrast to FLPs derived from strong Lewis acids in which only stoichiometric reductions are observed.[28–46] This situation is analogous to the recently reported work from Fontaine and co-workers, in which they exploited intramolecular FLPs for similar CO_2 reductions.[27]

In summary, herein we have reported the insertion of C–N bonds of an N-heterocyclic carbene into 9-BBN. The resulting intramolecular phosphine-borane acts as a catalyst for the activation of CO_2 in the presence of several borane reducing agents. Although use of HBpin was shown to provide a product mixture dominated by the boron-formate, use of HBcat and $BH_3(SMe_2)$ resulted in the complete reduction of CO_2 to the corresponding methoxy-borane. These findings point out that the use of weak Lewis acids in the FLP activation and reduction of CO_2 facilitates catalytic turn-over. Efforts to develop related catalytic processes that exploit oxygen atom acceptors such as olefins to generate highly desirable by-products are on-going.

Acknowledgement

D.W.S. gratefully acknowledges the financial support of NSERC of Canada and the award of a Canada Research Chair.

Keywords: borane hydrides · boranes · carbenes · carbon dioxide · frustrated Lewis pairs

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Received: December 13, 2013