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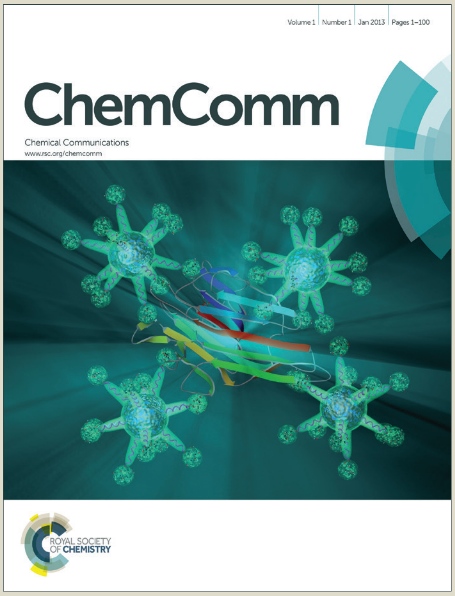

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COMMUNICATION

Formation of a Zwitterionic Boronium Species from the Reaction of a Stable Carbenoid with Borane: CO2 Reduction

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The treatment of $Li_2C(PPh_2NMes)_2$ (1, Mes = 2,4,6-$Me_3C_6H_2$) with hexachloroethane yielded the corresponding carbenoid 2 in good yields. The reactivity of 2 was studied with $BH_3.SMe_2$ to give a zwitterionic boronium species 4, also a stable carbenoid. Both carbenoid species were found to be excellent catalysts for the CO_2 reduction by $BH_3.SMe_2$.

In recent years there have been important developments in the search for stable Li-Cl carbenoid species.[1,2] We have proposed a novel reaction pathway to these compounds in 2007: mild oxidation of stable geminal dianions.[1c] Their stabilities appear to depend on the efficient Li-Cl separation in the molecule (Chart 1). This is achieved when at least one P(V) substituent is present at the C position. These carbenoids, like carbenes, possess ambivalent character (nucleophilic and electrophilic), with however pronounced electrophilic character due to the presence of strongly accepting P(V) moiety at the C center. They are in particular able to insert BH bonds of BH_3.[1d,2c] The first step of this insertion is coordination of BH_3 via the lone pair of electrons at C. It was therefore postulated that the presence of more nucleophilic iminophosphorane, instead of thiophosphinoyl, would strongly influence the outcome of the reaction with BH_3.

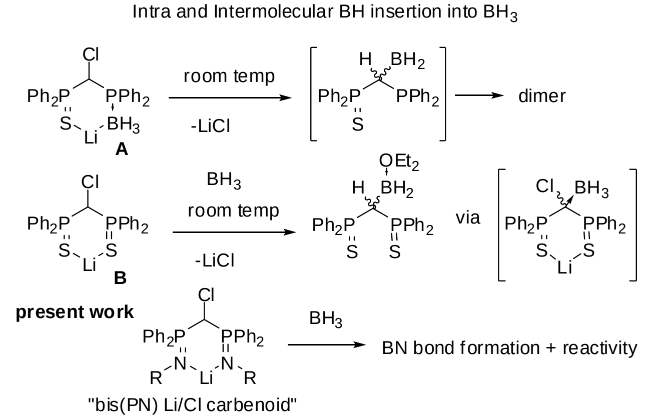
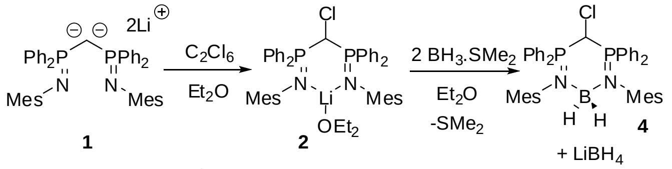


Chart 1. Synthesis of carbenoid compounds and reactivity toward BH_3.

From another standpoint, activation of boranes (CatBH[3], PinBH[4], 9BBN[3c,4,5], or BH_3[6]) by Lewis bases has been shown recently to be a crucial step in the catalyzed reduction of CO_2. We report here the synthesis of a stable "bis(PN) Li/Cl carbenoid" (Chart 1), and its reactivity toward BH_3. This species is able to promote the disproportionation of BH_3 into BH_2^+ and BH_4^- moieties, key to reduction of CO_2.

The dianion **1** was synthesized as per the literature.[7] The carbenoid **2** was synthesized by the addition of a diethyl ether solution of dianion **1** and 1 equivalent of hexachloroethane as mild oxidizing agent (Scheme 1)[‡]. $^{31}P\{^1H\}$ NMR spectrum of the crude mixture showed a single signal at 27.2 ppm, downfield shifted from **1** by 10.3 ppm. The compound was readily isolated by crystallization upon cooling. The ^1H NMR spectrum showed only the phenyl and mesityl groups as well as one molecule of diethyl ether coordinated to the Li cation. ^7Li NMR spectrum showed a singlet at 1.7 ppm. Although highly sensitive to air and moisture (which gives the expected hydrolyzed product **3** at 31.0 ppm, see ESI, in the $^{31}P\{^1H\}$ NMR spectrum) the carbenoid is stable at room temperature both in the solid state and in a solution. Single crystals were grown from a concentrated solution of diethyl ether at room temperature (Figure 1). The carbenoid is monomeric and has a 6 member ring of CPNLiNP structure which is almost planar, as is the carbenoid carbon (sum of the angles = 353.7°, see ESI for a side view of compound **2**). This planar geometry is in marked contrast with a related PN carbenoid species reported by Gessner et al while this work was in progress.[2e] A most important feature of compound **2** is the Li^+ and Cl^- separation, which is the reason for its stability at such a high temperature, like the related bis PS system (**B**, Chart 1). The Cl atom is bound to the C center, whereas the Li cation is bound to both N atoms.



Scheme 1. Synthesis of carbenoid compounds **2** and **4**.

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With this carbenoid in hand, the reactivity toward BH_3 was studied, which readily reacted at room temperature. However, unlike what we had observed with other carbenoid species **A** and **B** (Chart 1), two equivalents of $BH_3.SMe_2$ were needed to obtain full conversion. In this case, a single new P containing species was observed at 37.1 ppm. In the ^{11}B NMR spectrum of the crude mixture, the quintet at -39.9 ppm confirmed the formation of $LiBH_4$ together with a broad signal at -4.6 ppm. The ^1H NMR spectrum featured a broad signal at 4.29 ppm integrating for two H for a "BH_2" moiety. This data suggested the disproportionation reaction of two molecules of BH_3 into BH_4^-/BH_2^+ fragments rather than insertion of the carbenoid into the BH bond of BH_3. Single crystals were obtained from a concentrated Et_2O solution at room temperature, confirming the formation of a zwitterionic species featuring a boronium fragment and a P(V) stabilized anion. As obvious from the structure (Figure 1), the central core features a CPNBNP ring with a half chair conformation. The central carbon remains almost planar (sum of the angles = 355.64°). The compound is a novel example of a stable carbenoid "R_2CClM", and the first example of such a species where M is a BH_2 cationic fragment. We believe that the stability of this carbenoid resides in the efficient separation of the Cl^- and BH_2^+ moieties, because of the strong stabilization of BH_2^+ by the two PN moieties. The structure of the novel carbenoid compound confirmed that a disproportionation reaction had occurred from BH_3.

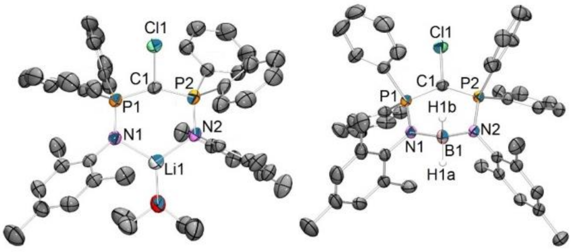
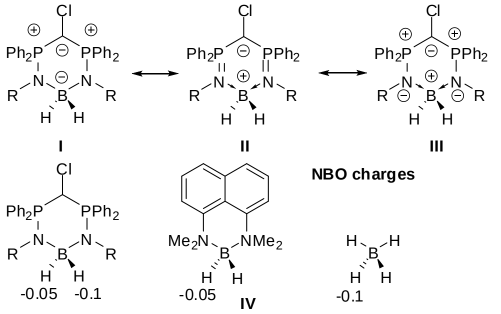


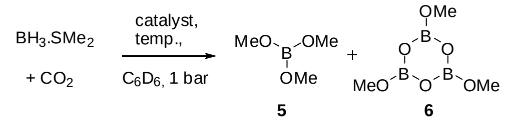
Figure 1. Molecular structure of compounds **2** (left) and **4** (right). Thermal ellipsoids are drawn at the 50% probability level. H atoms (except the 2 H of B1 in **4**), disordered atoms and solvent molecule for **2** are omitted for clarity. Selected bond lengths [Å] and angles [°]. **2:** Cl1-C1 1.792(3), C1-P1 1.740(3), C1-P2 1.724(3), P1-N1 1.596(3), P1-C2 1.812(3), N(1)-Li(1) 1.953(6), P2-N2 1.593(2), N(2)-Li(1) 1.939(6), Li(1)-O(1) 1.887(10), P2-C1-P1 130.92(17), Cl1-C1-P1 112.14(16), Cl1-C1-P2 109.60(16), N2-Li1-N1 114.1(3). **4**: Cl1-C1 1.776(2), C1-P1 1.720(2), C1-P2 1.715(2), P1-N1 1.629(2), P2-N2 1.626(2), N1-B1 1.585(3), N2-B1 1.596(3), B1-H1a 1.12(5), B1-H1B 1.13(2); P2-C1-P1 126.75(11), P2-C1-Cl1 115.24(11), P1-C1-Cl1 113.65(10), N1-B1-N2 110.59(15).

It is interesting to compare the metric parameters of the two novel carbenoid species **2** and **4**. The C-Cl bonds are identical and normal at 1.792(3) and 1.776(2) Å respectively, as in the other stable carbenoid compounds. The PN bond distances in **4** are slightly elongated (1.629(2) and 1.626(2) Å) compared to the ones in **2** (1.596(3) and 1.593(2) Å). This is linked to a stronger donation to B than Li. As a consequence the lone pair at N in compound **2**, now involved in the NB bond in **4**, is less stabilized by hyperconjugation into the σ* PC orbitals. Several Lewis structures can be drawn for compound **4** (Scheme 2). Form **I** corresponds to a diamino borohydride with a formal negative charge at the B atom, whereas forms **II** and **III**, being donor stabilized BH_2 fragment (boronium) possess a formal positive charge at B. Computations were carried out to further characterize the new carbenoid species **2** and **4**. NBO charges for compound **2** confirmed negative charges at C and N (q_C = -1.18 and q_N = -1.21), highly positive charge at P (q_P = +1.93) as well as a lower than +1 positive charge at Li (q_{Li} = +0.74) due to coordination to Et_2O. Wiberg bond indexes pointed single bonds between P-C and P-N (WBI 1.00 av. and 1.01 resp.) as well as a purely electrostatic N-Li interaction (WBI 0.06). The same analysis with compound **4** revealed similar charges at P and C (q_P =+1.95 and q_C = -1.20) where the charge at N was significantly reduced (q_N = -1.02). The charges at the "BH_2" fragment were computed and compared with the ones of BH_4^- and the "proton sponge BH_2^+" adduct, **IV**.[6a] The charge at B is similar in compound **4** and **IV** (q_B = +0.30 and +0.31), and quite higher than in BH_4^- (q_B = -0.6), because of the two bonds with highly electronegative N atoms. The two H atoms in compound **4** possess different environment in the crystal, and as a consequence different charges (q_H = -0.10 and q_B = -0.05). As a comparison, the charge is q_H = -0.10 in BH_4^- and q_H = -0.05 in compound **IV**. The PN WBIs decreased from **2** to **4** (1.01 to 0.90), in line with an increase of bond length, whereas the PC WBIs remained constant at 1.0. The BN WBIs in **4** were computed at 0.66 and 0.67, slightly higher than in **IV** (0.61). Overall, a strong electron transfer from the two N atoms to the BH_2 fragment in the boronium carbenoid **4** pointed a hydridic character as strong as in borohydride.



Scheme 2. Resonance structures for compound **4**, and NBO charges.

As mentioned in the introduction, recent reports have proved that few Lewis bases can act as catalysts in the reduction of CO_2 by neutral boranes such as catBH, PinBH, 9BBN or BH_3. It was shown by Cantat et al. that an increase in the hydridic character of 9BBN by triazabicyclo derivatives was the key to lower the energetic barrier of the rate determining step in the CO_2 reduction: the first hydride transfer.[3c] Similarly, Fontaine most recently showed that proton sponge allowed the dismutation of BH_3 into BH_4^-/BH_2^+, allowing CO_2 reduction to methanol derivatives.[6a] In fact, it is consistent with the fact that $LiBH_4$ can reduce CO_2 to methanol derivatives in a stoichiometric fashion either as a solid or in solution, without the need of Lewis acidic activation of CO_2.[8] The similar hydridic character in compound **4** and $LiBH_4$ prompted us to study the CO_2 reduction, both from isolated compound **4** and/or *in situ* generated from carbenoid **2**. The results are gathered in Table 1.



Entry	Cat. (mol%)	*T* °C	*t* (h)	Yield **5** (%)	Yield **6** (%)	Total (%)	TON	TOF
1	**4** (10)	80	2	8	91	99	35	17
2	**2** (10)	80	2	9	67	76	28	14
3	**2** (5)	80	2	9	71	80	58	29
4	**2** (5)	25	40	6	77	83	58	1.4
5[a]	**2** (5)	80	4	4	85	89	118	30
6	**2** (1)	80	24	5	78	83	278	12
7[b]	**2** (1)	80	2	6	78	84	286	143
8[b]	**4** (1)	80	2	3	96	99	313	157
9[b,c]	**2** (0.1)	80	4	1	70	71	2213	553
10[b,c]	**4** (0.1)	80	4	2	84	86	2646	661

Table 1. Catalytic activity of **2** and **4** for the reduction of CO_2 by $BH_3.SMe_2$. Conditions: 0.01 mmol of catalyst in C_6D_6 (~0.5 ml), amount of $BH_3.SMe_2$ is calculated then added to obtain the desired catalytic loading, 1 bar CO_2. The yield was obtained by ^1H NMR using the -Mes CH of the ligand as an

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internal standard. TON and TOF are given in reference to the number of hydride transferred. [a] Additional $BH_3.SMe_2$ and CO_2 was added after 2h. [b] Reactions are done in a Schlenk tube to increase the volume of CO_2. [c] Hexamethylbenzene is used as an internal standard. 2 times 1 bar CO_2.

Satisfyingly, **4** alone reacted with CO_2 (1 bar, 80°C) to from methanol derivatives, showing that the BH_2 had indeed the expected hydridic character. Secondly, in the presence of BH_3, **4** was a catalyst for the transformation (entry 1), which showed that the final products are not trapped by the carbenoid fragment. Since the reaction to form **4** from **2** and $BH_3.SMe_2$ is facile at room temperature, carbenoid **2** was subsequently used as pre-catalyst. As shown by entry 2, **2** is slightly less competent than **4** in the catalytic process. Lowering of the catalytic amount to 5% provided similar results (entry 3 *vs* 2). Carrying the reaction at room temperature was possible, yet required 40h instead of 2h at 80°C (entries 3 and 4). Entry 5 showed that after a first catalytic run, addition of $BH_3.SMe_2$ and CO_2 allowed further reduction, proving that little or no decomposition of catalyst occurred. When the catalyst loading was reduced to 1% (NMR tube scale reaction), the reaction became sluggish likely because solid formed during the reaction, which prevented efficient mixing of the reagents. Nevertheless, it reached similar yield (83%) after 24h (entry 6). On the other hand, when the same reaction was carried out in a Schlenk flask with efficient stirring, the reaction was again complete within 2h at 80°C (entry 7). For comparison, starting from **4** (1%, entry 8) provided quantitative yield of methanol derivative, with a better selectivity in compound **6** (96 to 3). The TON reached 313 within 2h. Using the same conditions (Schlenk flask rather than NMR tube) allowed further lowering of the catalyst loading down to 0.1%, with a slightly increased reaction time (entry 9, 4h). Overall, these conditions provide comparable TOF and TON (661 h^{-1} and 2646 respectively) to the best known results for the reduction of CO_2 by $BH_3.SMe_2$.[3a]

Conclusions

In conclusion, we have synthesized a novel example of stable Li/Cl carbenoid compound, **2**, based on the controlled oxidation of bis iminophosphorane geminal dianion. Reaction of this carbenoid species toward $BH_3.SMe_2$ resulted in its disproportionation into BH_4^- and BH_2^+ fragments. The driving force for this reaction is the strong stabilization of the BH_2^+ by the C-chloro bis-iminophosphoranyl methanide moiety. This easily synthesized stable zwitterionic boronium compound **4** was fully characterized. DFT analysis on this compound pointed strongly negative charges at N, positive charge at B and a hydridic character for the H, similar to BH_4^-. As a consequence, using the carbenoid compound **2**, two equivalents of BH_3 are transformed into two borohydride species. Most interestingly, both are capable of reducing CO_2 selectively to form methanol derivatives. Overall, the new carbenoids **2** and **4**, readily generated from a stable bis-iminophosphorane methanediide, are to date among the best catalysts for the CO_2 reduction by $BH_3.SMe_2$.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, solution NMR data, crystallographic information and computational details. CCDC-1034939 (**2**) and CCDC-1034940 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For ESI and crystallographic data, see DOI: 10.1039/c000000x/

‡ Synthesis of compound **2**. To **1** (0.133 g, 0.2 mmol) in ether (10 ml), hexachloroethane (0.0474 g, 0.2 mmol) was added at -78 °C. The reaction was warmed up to room temperature and stirred for 30 mins. The colour changed from bright orange to dark brown. After 30 mins, the mixture was filtered and the filtrate was concentrated to afford crystals of **2** (0.122 g, 73 %). ^1H NMR (C_6D_6, 298 K): δ 0.712 (t, $^3J_{H\text{-}H}$ = 7.11 Hz, 6H, Ether-C*H*$_3$), 2.10 (s, 6H, Mes *p*-C*H*$_3$), 2.24 (s, 12H, Mes *o*-C*H*$_3$), 2.82 (q, $^3J_{H\text{-}H}$ = 7.11 Hz, 4H, Ether-C*H*$_2$), 6.68 (s, 4H, Mes C*H*), 7.12 (m, 12H, *m*,*p*-Ph C*H*), 7.92 (m, 8H, *o*-Ph C*H*). ^7Li NMR (C_6D_6, 298 K): δ 1.7 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 14.5 (s, ether *C*H$_3$), 20.8 (s, Mes *p*-CH$_3$), 21.2 (s, Mes *o*-CH$_3$), 64.9 (s, ether *C*H$_2$), 127.4 (t, $J_{P\text{-}C}$ = 5.69 Hz, Ph *o*-C), 133.4 (t, $J_{P\text{-}C}$ = 4.41 Hz, Mes *ipso*-C), 129.1 (s, Mes *o*-C), 129.3 (t, $J_{P\text{-}C}$ = 2.20 Hz, Ph *p*-C), 129.8 (s, Ph *m*-C), 134.9 (t, $J_{P\text{-}C}$ = 3.32 Hz, Mes *m*-C), 135.3 (d, $J_{P\text{-}C}$ = 96.6 Hz, Ph *ipso*-C), 146.2 (t, $J_{P\text{-}C}$ = 3.72 Hz, Mes *o*-C). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 27.2 (s). Anal. Calc for $C_{47}H_{52}ClLiN_2OP_2$: C, 73.77; H, 6.85; N, 3.66 %. Found: C, 73.77; H, 6.67; N, 3.56 %.

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