DOI: 10.1002/anie.201107815

Lewis Base Stabilized Dicarbon: Predictions from Theory**

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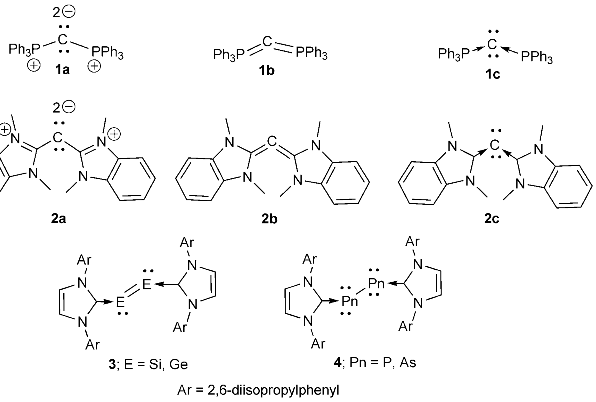
The synthesis and theoretical assessment of Lewis base-stabilized E^0 "allotropes" of p-block elements continues to provide exciting developments, with new molecules having recently been synthesized for elements in Groups 14 and 15, including "C_1",[1] "Si_2",[2] "Ge_2",[3] "P_2",[4] and "As_2".[5] In the majority of cases the stabilizing base is an N-heterocyclic carbene (NHC) ligand. For "C_1" phosphine ligands have also been used; these are the long-known carbodiphosphorane class of compounds (**1**), described as either a di-ylide (**1a**), or $R_3P{=}C{=}PR_3$ species (**1b**).[6,7] Modern theoretical studies point towards a $R_3P{\rightarrow}C{\leftarrow}PR_3$ framework, with the central C^0 atom carrying two lone pairs of electrons (**1c**).[8] This concept also extends to the carbodicarbene class of molecules (**2a–c**).[9,10] In each case, both lone pairs of electrons on carbon were predicted and confirmed to be chemically accessible.[11–13] Phosphine-stabilized "C_3" has also been reported, but not structurally verified.[14]

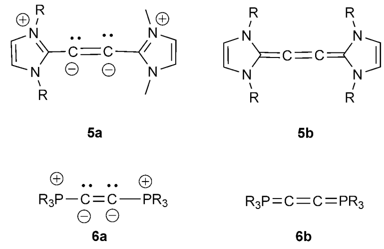


NHC-stabilized "allotropes" of "E_2" have been reported for Si/Ge from Group 14, and P/As from Group 15. For the Group 14 species, *trans*-bent NHC-E=E-NHC motifs are observed.[2,3] In the latter case E–E single bonds are observed, with two lone pairs of electrons about each Group 15 center.[4,5] Either a *trans*-bent or *gauche* configuration was observed in the crystal structures depending on the steric demands of the NHC used. Calculations indicate that the *gauche* arrangement is the energetic minimum for both P and As.

Dicarbon (C_2), the lighter homologue of Si_2 and Ge_2, is a fundamentally interesting and much studied molecule. It can be transiently synthesized and observed by a variety of high-energy methods.[15,16] The ground state for free C_2 has been described as having two π bonds between the C atoms, with each C atom also bearing a lone pair of electrons and an absence of σ bonding.[17] A recent reexamination has suggested a C–C triply bonded species as being the major contributer.[18] Numerous excited states of C_2 have also been detected and described.[16]

Free dicarbon cannot be readily isolated, however the C_2 fragment has been stabilized in the coordination spheres of metals[19,20] and also in the push–pull molecule $R_3P{-}CC{-}BR_3$, which is proposed to have a C_2 core with a C–C triple bond.[21] Bisphosphine-stabilized C_2 has also been invoked as a reactive intermediate by Stang and co-workers, but they did not isolate or directly observe the C_2 molecule.[22]

Herein, we report the first evaluation of bis(Lewis base)-stabilized C_2 analogous to **3**. We have carried out a detailed theoretical investigation of the L–CC–L system, where L = NHC (**5**) and R_3P (**6**), in order to predict whether these molecules are stable, and if so, to investigate their electronic structure and molecular properties. Several canonical representations could be envisioned for these compounds, the extremes being a diylide/zwitterion (**5a**, **6a**), or cumulene-type structures (**5b**, **6b**). One purpose of this study is to determine which of these is the best description for this class of compounds, in order to anticipate their properties.



Several model systems of **5** and **6** were considered, with R substituents of hydrogen, methyl and phenyl. Within each class (**5** or **6**), similar optimized geometries are predicted.

Geometry optimization (B3LYP/TZVP) of **5R** (R = H, Me, Ph) yields an essentially linear C-C-C-C framework (Figure 1; C2-C4-C3 bond angles are 178.8°, 172.4°, and 173.7°

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[**] We thank La Trobe University for funding of this work. The authors acknowledge support from the National Computational Infrastructure National Facility (NCI-NF), Victorian Partnership for Advanced Computing (VPAC), Victorian Life Science Computing Initiative (VLSCI), and the high-performance computing facility of La Trobe University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107815.

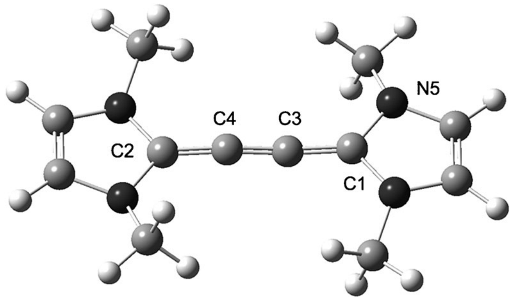


Figure 1. B3LYP/TZVP-optimized geometry of **5 Me**. Selected bond lengths [Å] and angles [°]: C3–C4 1.263, C1–C3 1.336, C1–N5 1.412; C2–C3–C4 172.4, C1-C3-C4-C2 180.0.

for R = H, Me, Ph, respectively). The central C3−C4 bond is quite short, being 1.25–1.26 Å, while the C1−C3 bonds are 1.33–1.34 Å. The endocyclic C1−N5 bonds were elongated from the free NHC at 1.41–1.42 Å, similar to that calculated (and found experimentally) for **2**.

The calculated geometries for **6** (R = Me, Ph) are substantially different to that for **5**. No minimum was located for the **6H** species but rather it readily dissociates to a PH_3−C_2 species. For **6Me** a *trans*-bent arrangement of the two PMe_3 ligands about a C=C core is predicted, similar to that observed in **3** (Figure 2). The central C3−C4 bond lengths are 1.34 Å (**6Me**), and 1.32 Å (**6Ph**), consistent with double-bond character. The P−C bonds are 1.77–1.78 Å, consistent with single-bond character. The P-C-C angles indicate non-linearity (**6Me** 116°; **6Ph** 125°), and the P-C-C-P dihedral angle is 179–180°, giving the *trans*-bent geometry.

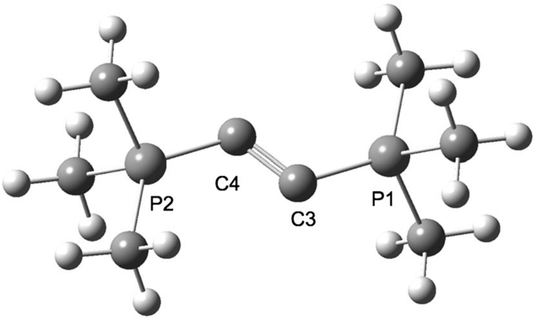


Figure 2. B3LYP/TZVP-optimized geometry of **6 Me**. Selected bond lengths [Å] and angles [°]: C3–C4 1.349, P1–C3 1.780; P2-C4-C3 116.2, P1-C3-C4-P2 180.0.

Natural bond orbital (NBO) analysis (B3LYP/TZVP) of **5Me** reveals strong π interactions between the central C_2 carbon atoms, as well as the C−C linkages from the NHCs to the C_2 core, in line with the linear cumulene geometry (see Supporting Information).[23] This results in the lone pairs on the endocyclic nitrogen atoms of the NHC ring becoming largely localized. There are no NBO lone-pair orbitals on the central carbon atoms. The calculated molecular orbitals (MO) are largely in agreement with the NBO analysis, showing strong π interactions between the central C atoms in the HOMO and HOMO−1 (Figure 3). The HOMO also contains contributions from the C−C π bond in the NHC backbone, as well as the lone pairs of electrons on the nitrogen atoms. However, some delocalization of the N electron pairs is evident in the HOMO−1.

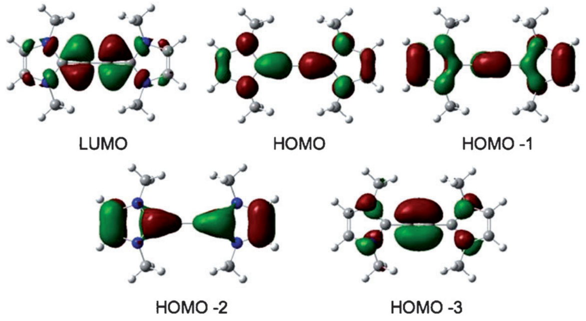


Figure 3. Frontier molecular orbitals for **5 Me**.

For **5Me**, the B3LYP/TZVP-calculated Wiberg bond indices (WBI) for C3−C4 and C1−C3 are 2.12 and 1.53, respectively. The WBI for C1−N5 is 1.05, and for the ring C=C is 1.73. This suggests that C3−C4, C1−C3 and C2−C4 are best described as double bonds, but that C3−C4 has greater double-bond character than C1−C3 and C2−C4. For **5H** the WBI are 2.11 (C3−C4), 1.57 (C1−C3), and 1.05 (C1−N5), which is almost identical to that of **5Me**.

Natural resonance theory (NRT) results from HF/TZVP calculations indicate that the cumulene structure (**5b**) is the dominant Lewis structure for **5H** and **5Me** (calculation failed for **5Ph** due to too many resonance structures). Significant delocalization may be expected since **5a**-type structures, as well as hybrid **5a**/**5b** structures, make near equivalent contributions to those of **5b**.[23] This is consistent with the calculated WBI, optimized geometry and NBO results: the central C3−C4 bond is best described as C=C (WBI 2.1–2.2), and the C1−C3 bond has single- and double-bond character (WBI 1.5–1.6). We suggest that the most appropriate representation of **5** is as a cumulene (**5b**). However, the relative importance of **5a**-type structures hints towards greater reactivity than may be expected for a cumulene due to accessible lone pair(s) of electrons on the linking carbons.

NBO analysis of **6Me** indicates a very different electronic structure. Each carbon of the C_2 fragment bears a σ-symmetric lone-pair orbital, which are also evident in the HOMO of the MO representation (Figure 4). The NBO

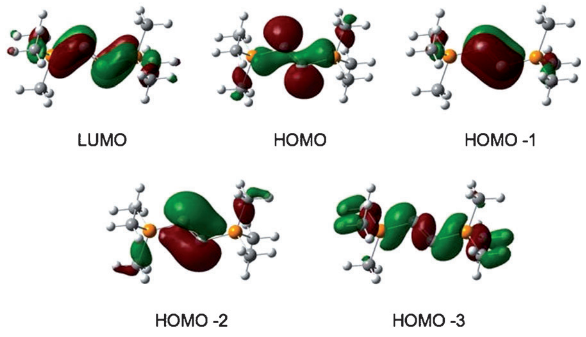


Figure 4. Frontier molecular orbitals for **6 Me**.

orbitals show π and σ C3–C4 bonding orbitals indicative of a C=C bond, but only a σ orbital between the phosphorus and C_2 carbon atoms (see Supporting Information). The WBIs for **6Me** are 2.00 (C–C) and 1.14 (P–C). NRT analysis indicates that the **6a** Lewis structure dominates the electronic description (weight of 69%). The orbital and NRT analysis, and the distinctly bent geometry about the C atoms, consistently suggests that the most accurate representation for **6** is a double ylide (**6a**). A dative model could also be invoked, giving a bis-phosphine stabilized C_2, analogous to **1c** and **2c**.

The MP2/TZVP//B3LYP/TZVP-calculated free energy (ΔG) of the reaction **6Me** + $Me_2NHC \rightarrow$ **5Me** + Me_3P is -274 kJ mol^{-1}, indicating that **5Me** is a significantly more stable species. The carbodicarbene $(Me_2NHC)_2C$ is more stable than **5Me** based on the reaction **5Me** + $2\,Me_2NHC \rightarrow 2\,(Me_2NHC)_2C$ ($\Delta G = -144$ kJ mol^{-1}). Surprisingly, **6Me** is calculated to be more thermodynamically stable than the hypothetical carbodiphorphorane $(Me_3P)_2C$, with ΔG for the reaction **6Me** + $2\,Me_3P \rightarrow 2\,(Me_3P)_2C = +24.1$ kJ mol^{-1}.

Proton affinity (PA) has been used to measure the potential for atom centers to act as ligands for related compounds, such as **1** and **2**.[11,13,24] The first (PA1) and second (PA2) proton affinities for **5** and **6** (Table 1) are very high. PA1 ranges from 1163 kJ mol^{-1} for **5Me** to 1256 kJ mol^{-1} for **6Ph**. PA1 for **6** are slightly higher than **5**, likely due to the increased σ character of the lone pairs on the atoms of the C_2 core. These compare to 1231.4 (PA1) and 704.6 kJ mol^{-1} (PA2) calculated for the corresponding Me substituted carbodicarbene and 1164.8 and 653.5 kJ mol^{-1} for the Me-substituted carbodiphosphorane. Based on these results, **5** and **6** could be classified as superbases, with first proton affinities > 1100 kJ mol^{-1}.

Table 1: Calculated (MP2/TZVP//B3LYP/TZVP) first and second proton affinities, and first and second BH_3 dissociation free energies.[a]

$$\text{L-CC(BH)}_3\text{-L} \longrightarrow \text{L-CC-L} + BH_3 \quad (1)$$

$$\text{L-C(BH)}_3\text{C(BH)}_3\text{-L} \longrightarrow \text{L-CC(BH}_3\text{)-L} + BH_3 \quad (2)$$

	Proton affinity		ΔG (BH_3 binding)	
Compound	PA1	PA2	Eq. (1)	Eq. (2)
5H	1235.2	791.0	215.2	235.4
5Me	1163.4	781.5	173.1	222.8
5Ph	1178.4	948.4	141.5	212.1
6Me	1245.1	784.2	215.6	182.7
6Ph	1256.6	901.2	199.0	144.9

[a] Units of kJ mol^{-1}. Thermochemical properties calculated at 298 K (unscaled B3LYP/TZVP vibration frequencies and thermal correction).

The capacity to bind BH_3 has previously been used to evaluate the Lewis basicity of the C_1-centered carbodicarbene and carbodiphosphorane compounds.[11,12] We have considered both mono- and di-BH_3 adducts of compounds **5** and **6**, which shows that these C_2 species are indeed powerful bifunctional Lewis bases. For **6R**, the mono-BH_3 dissociation energy was calculated to be 215.6 and 199.0 kJ mol^{-1} for R = Me and Ph, respectively. This compares to 206.3 kJ mol^{-1} calculated for **2**, which was stated to be "among the strongest donor–acceptor bonds known for the main group".[13] The second BH_3 is less strongly bound to **6R**, with dissociations energies of 182.7 and 144.9 kJ mol^{-1} for R = Me and Ph, respectively. The dissociation energy of a mono-BH_3 adduct of **5R** depends strongly on the R group, with calculated values of 215.2, 173.1, and 141.5 kJ mol^{-1} for R = H, Me, and Ph, respectively.

While addition of BH_3 to **6** induces little change to the geometry (Figure 5), formation of the mono-BH_3 adduct of **5** causes significant changes to the geometry, with the core of the molecule losing its linearity and changing to a *trans*-bent structure. For **5Me·BH$_3$** with BH_3 bound to C3, the calculated WBI are C3–C4 (1.84), C2–C4 (1.03), and C1–C3 (1.42). Binding of BH_3 causes a significant reduction in bond order for C3–C4 and C2–C4, which is reflected in the geometry change. Moreover, the geometry of the NHC ligands becomes closer to that of the free NHC, with the C–N bonds shortening significantly. A σ-symmetric lone pair emerges from the uncomplexed C atom (Figure 6), which can then be used to bind a second BH_3 molecule. As a result, binding of a second BH_3 is significantly stronger than that of the first BH_3, with second BH_3 dissociation energies calculated to be 235.4, 222.8, and 212.1 kJ mol^{-1} for R = H, Me, and Ph. It should be noted that BH_3 addition to **3Si** resulted in cleavage of the Si–Si bond.[25]

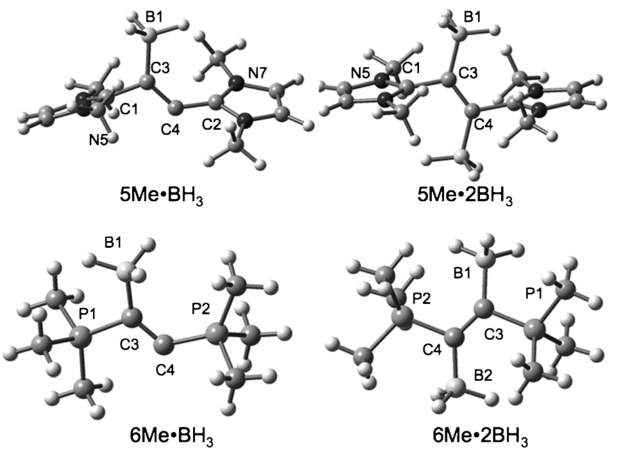


Figure 5. Optimized geometries of **5Me·BH$_3$**, **5Me·2BH$_3$**, **6Me·BH$_3$**, and **6Me·2BH$_3$**. Selected bond lengths [Å] and angles [°]: **5Me·BH$_3$**: C3–B1 1.635, C3–C4 1.340, C1–C3 1.471, C1–N5 1.348, C2–N7 1.379; C2-C3-C4 115.3. **5Me·2BH$_3$**: C3–B1 1.631, C3–C4 1.352, C1–C3 1.465, C1–N5 1.347. **6Me·BH$_3$**: C3–B1 1.635, C3–C4 1.346, P1–C3 1.827, P2–C4 1.763. **6Me·2BH$_3$**: C3–B1 1.628, C3–C4 1.354, P1–C3 1.829.

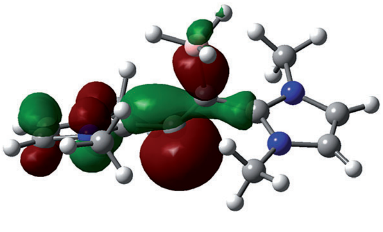


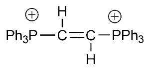
Figure 6. HOMO for **5Me·BH$_3$**.

From these results, **5** could be considered as having a stable cumulene-like resting state (**5a**) that masks the very reactive **5b**-type (or hybrid **5a/5b**) structure with accessible and reactive carbon lone-pair electrons.

It has been suggested[21] that C_2 will not be stabilized by two donor ligand but only in a push–pull molecule, such as $R_3P{-}CC{-}BR_3$. For **5Me** and **6Me** replacement of one of the PMe_3 or MeNHC ligands by BH_3 is calculated to be energetically favored. However, attempts at protonation or addition of a BH_3 adduct to such a push–pull molecule results in dissociation. This is in direct contrast to the situation for **5Me** and **6Me**, which are predicted to be superbases and exhibit donor–acceptor bonds that are competitive with the strongest donor–acceptor bonds yet reported.[13]

Synthetically, the $Ph_3PC{=}CPPh_3$ molecule has been proposed as a highly reactive intermediate from the double deprotonation of dication **7**.[22] The molecule was reported to decompose at temperatures higher than −40 °C, but could be trapped by carbonyl compounds in Wittig-type reactions. However, a systematic attempt to isolate compounds of type **6** did not appear to have been pursued, in modifying R substituents etc. Trapping with metals (i.e. using **6** as a bridging ligand) may also be feasible.

For the synthesis of **5**, a potential starting material has been reported in compound **8**, which may be susceptible to double deprotonation, furnishing **5**.[26]



$\overset{\oplus}{Ph_3P}-\overset{H}{C}=\underset{H}{C}-\overset{\oplus}{P}Ph_3$

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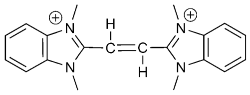

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Given the availability of these possible starting reagents, we are currently targeting the synthetic isolation and applications of **5** and **6** as strong, bifunctional carbon-based ligands.

Received: November 7, 2011

Keywords: dicarbon · N-heterocyclic carbenes · phosphines · super bases · theoretical chemistry

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