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Short communication

N-heterocyclic carbene-stabilized homoatomic lithium(0) complexes with a lithium–lithium covalent bond: A theoretical design and characterization

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ABSTRACT

Density functional theory calculations (B3LYP and B2PLYP-D2) have been utilized to design and characterize novel homoatomic lithium(0) organometallic complexes of the NHC → Li–Li ← NHC type (NHC = N-heterocyclic carbenes). The computed Li–Li bond length and energy are consistent with those experimentally observed for Li_2(g). These and other structural and energetic data suggest that such organolithium compounds should be viable targets for synthesis. These compounds would represent a new class of molecular "allotropes" and could have novel reactivities.

A significant recent development in main-group organometallic chemistry has been the utilization of strong σ-donor ligands, typically N-heterocyclic carbenes (NHC), in stabilizing low-valent and zerovalent main-group complexes containing homoatomic element–element bonds [1]. The zerovalent complexes have been described as molecular "allotropes" of elements. The study of these low-valent and zerovalent NHC complexes also dovetails with the field of main-group multiple bonding chemistry [2], thereby leading to the extraordinary synthesis of molecules with boron–boron double and triple bonds, as shown in Fig. 1 [3,4]. It should be noted that computational studies and predictions of relevant boron systems contributed to these experimental achievements [5–9]. A recent computational study suggests that beryllium(0) complexes of the NHC → Be = Be ← NHC type could also occur as stable molecules [10]. Could this chemistry be extended to the Group 1 element lithium, with an aim at homoatomic lithium(0) complexes of the NHC → Li–Li ← NHC type with a 2c–2e lithium–lithium covalent bond? It is well known that lithium has a greater tendency to exhibit covalent bonding than any other Group 1 metal [11]. To our knowledge, lithium(0) complexes have not been known experimentally or theoretically. Dilithium (Li_2), a molecule with two lithium(0) atoms, has been observed in the gas phase with a Li–Li bond distance of 2.673 Å [12] and a bond energy in the range of 22.7–26.4 kcal/mol [13–17]. A number of lithium(I) complexes with NHC ligands have been synthesized and characterized, in which the lithium(I) centers coordinate to the NHC carbenic carbon atoms [18–24].

In this Communication, we report a computational study on NHC → Li–Li ← NHC complexes at the B3LYP and the higher B2PLYP-D2 levels of density functional theory (DFT) [25,26], B3LYP being the common hybrid functional [27] and B2PLYP-D2 being a dispersion-corrected double hybrid functional that combines exact Hartree–Fock exchange with an MP2-like correlation [28].

A general method for attaining low-coordinate complexes is to employ bulky ligands, and as such, the synthesis of NHC → Li–Li ← NHC would require a large NHC to achieve the low coordination number (two) for lithium and to protect the dilithium core. Thus, we used the bulky IDip (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) ligand set to simulate the experimental situation, and studied the geometries of IDipLiLiIDip at the B3LYP/6–31 + G (d) level of theory. We successfully located two conformational isomers of IDipLiLiIDip (**1a** and **1b**) as energy minima (Fig. 2). The DFT wavefunctions of **1a** and **1b** both were checked to be stable. Thermodynamically, **1a** is more stable than **1b** by 0.5 kcal/mol in Gibbs free energy.

Both **1a** and **1b** exhibit an essentially linear arrangement of the C–Li–Li–C axis. The two NHC rings in **1a** are slightly deviated from coplanar (dihedral angle = 8.4°), and those in **1b** are perpendicular to each other. The Li–C bond distances are 2.156 and 2.161 Å in **1a** and **1b**, respectively, which are consistent with the sum of the covalent radii of lithium and carbon (2.07 Å) [29,30]. More importantly, the Li–C bond distances are similar to the experimentally determined bond lengths (2.056–2.169 Å) for the Li–C bonds to the terminal carbenic carbon atoms in several Li(I)–NHC complexes that have been crystallographically characterized [18,19,21–24]. This comparison gives convincing support for the Li–C coordinate covalent bonds in **1a** and **1b**. The Li–Li bond distances are 2.894 and 2.906 Å in **1a** and **1b**, respectively, which are slightly longer than that in Li_2 (2.673 Å) [12]. This is

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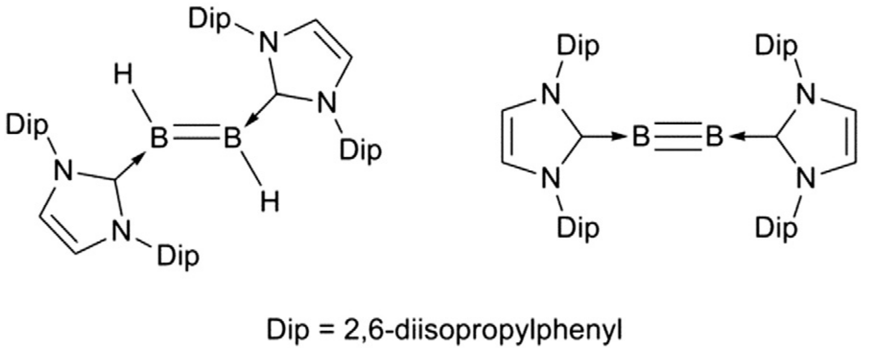


Fig. 1. NHC-stabilized complexes containing B = B and B ≡ B bonds.

understandable by considering that each lithium atom in **1a** and **1b** is two-coordinate as opposed to the mono-bonded lithium atoms in Li_2. Nevertheless, the Li–Li bond distances in **1a** and **1b** are shorter than the closest Li–Li bond distance in the metallic crystal of lithium (3.04 Å) [31], and are much less than two times the Van der Waals radius of lithium (3.64 Å) [32]. Thus, a Li–Li covalent bond occurs in **1a** and **1b**, which is corroborated by the calculated Wiberg bond indices for the lithium–lithium bonds (0.89 in **1a** and 0.90 in **1b**).

To further characterize and validate NHCLiLiNHC complexes, we used 1,3-dimethylimidazol-2-ylidene (IMe), namely the methyl-substituted NHC, as a model to compute the structures and energetics of IMeLiLiIMe at higher levels of theory. We studied the geometries of IMeLiLiIMe using both B3LYP and B2PLYP-D2 combined with the more complete basis set 6–311++G(d,p). The two methods gave consistent geometric and energetic results, as shown in Table 1.

The conformers **2a** and **2b** of IMeLiLiIMe are analogous to **1a** and **1b** of IDipLiLiIDip. The bond lengths and angles of **2a** and **2b** indicate that each lithium(0) atom is *sp*-hybridized, forming a covalent bond with the other lithium(0) atom and a coordinate covalent bond with a carbenic carbon atom. To further characterize the bonding in **2a** and **2b**, we have performed an MO analysis using the method known as the Adaptive Natural Density Partitioning (AdNDP) [33]. The AdNDP-generated localized MOs indicate three pairs of electrons involved in lithium-containing bonds, including a Li–Li covalent bond and two Li–C coordinate covalent bonds (Fig. 3). The Li–C bonds are of the coordinate nature because the electrons derive entirely from the carbenic carbon atoms in the partitioning process. The full set of AdNDP MOs is given in the Supplementary data (Figures S1 and S2).

Thermodynamically, the conformers **1a** and **2a**, where the two NHC rings are approximately coplanar, are somewhat more stable than the corresponding perpendicular isomers **1b** and **2b**. An insight into this difference is to consider two opposing forces—steric repulsion and dispersion attraction—that can operate between the two substituted-NHC ligands. The large separation (by three bonds) of the NHC ligands minimizes steric repulsion, and the nearly coplanar orientation in **1a**/**2a** positions the NHC ligands, particularly the hydrocarbon substituents, somewhat closer to each other than in **1b**/**2b**, thereby inducing stronger attractive dispersion forces. This analysis is illustrated in Fig. 4 using **2a** and **2b**.

In order to gain insights into the stability of the designed NHCLiLiNHC complexes and the strength of the Li–Li bonds thereof, we have selected **2a** as a representative and performed energy analysis on its decomposition. We considered two different reaction routes (Eqs (1) and (2)) and calculate the associated thermodynamic changes in the

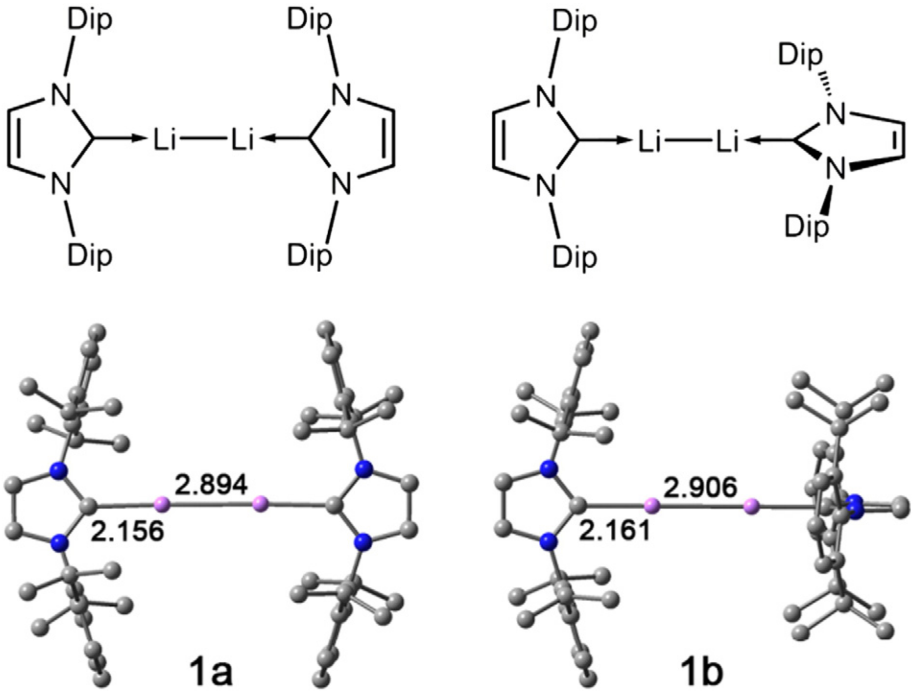
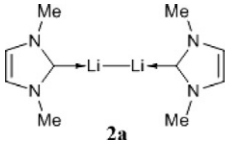
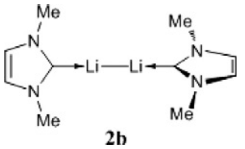


Fig. 2. Geometries of the rotamers **1a** and **1b** of IDipLiLiIDip optimized with B3LYP/6–31 + G (d). Hydrogen atoms are omitted for clarity. Selected bond distances are given in units of Å.

Table 1
Geometry and energy data for IMeLiLiIMe.[a]

	 **2a**		 **2b**	
	B3LYP	B2PLYP-D2	B3LYP	B2PLYP-D2
r(Li–Li)	2.857	2.832	2.855	2.831
r(Li–C)	2.138	2.151	2.137	2.150
θ(C–Li–Li)	180.0	180.0	180.0	180.0
θ(N–C–C–N)	0.2	0.2	90.0	90.0
Δ*G*	0.0	0.0	1.5	1.6

[a] Basis set 6–311++G(d,p). *r* indicates bond distances in units of Å, *θ* bond or dihedral angles in degrees, and Δ*G* Gibbs free energies relative to **2a** in kcal/mol.

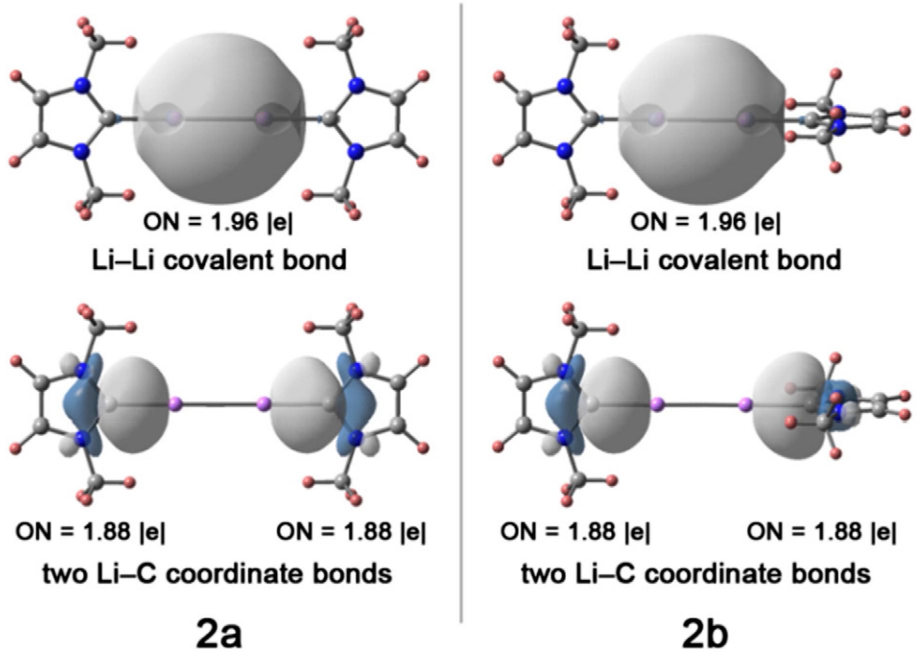


Fig. 3. AdNDP-generated localized MOs concerning Li–C and Li–Li bonds in **2a** and **2b**. ON denotes electronic occupation number.

gas phase at the B2PLYP-D2/6–311++G(d,p) level. The ΔG_1 for the decomposition of **2a** into Li_2 and the free NHC ligand has a large positive value (Eq. (1)). This indicates that **2a** would be stable towards

$$\begin{aligned}&\mathrm{IMeLiLiIMe}(2\mathbf{a})\rightarrow \mathrm{Li}_2+2\mathrm{IMe}\\&\Delta G_1=24.7\ \mathrm{kcal/mol}\end{aligned}\quad(1)$$

decomposition into its molecular components. In other words, the reverse reaction, trapping of the Li_2 molecule in an NHC complex, would be energetically favorable although it might not the best synthetic approach.

To evaluate the Li–Li bond energy of **2a**, we calculated the Δ*E*(0 K) for the dissociation of the Li–Li bond (Eq. (2)), using the zero-point energy-corrected electronic energies (E_{ZPE}). The Δ*E*(0 K) value agrees well with the spectroscopically determined bond energy of Li_2 (22.7–26.4 kcal/mol) [13–17]. Also noteworthy is the fact that the lithium(0) radical complex LiIMe is located as an energy minimum. This offers insight into a potential

$$\begin{aligned}&\mathrm{IMeLiLiIMe}(2\mathbf{a})\rightarrow 2\mathrm{LiIMe}\\&\Delta \mathrm{E}(0\ \mathrm{K})=2E_{\mathrm{ZPE}}(\mathrm{LiIMe})-E_{\mathrm{ZPE}}(2\mathbf{a})=24.1\ \mathrm{kcal/mol}\\&\Delta G_2=16.2\ \mathrm{kcal/mol}\end{aligned}\quad(2)$$

synthetic route; that is, reduction of appropriate Li(I)–NHC complexes could produce a Li(0)–NHC radical intermediate, which could subsequently dimerize to form the target lithium(0) complex

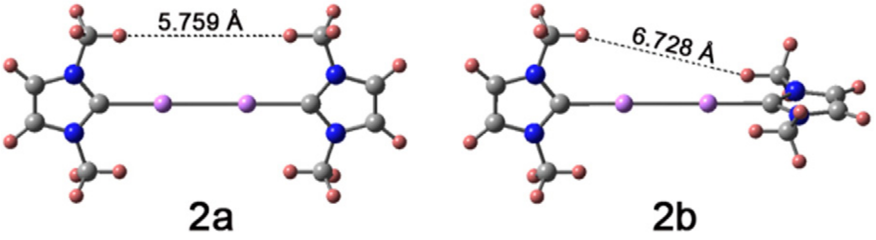


Fig. 4. Attractive dispersion interactions between NHC ligands at the closest distances in **2a** and **2b**.

NHCLiLiNHC. Furthermore, the dimerization, which is the reverse reaction of Eq. (2), would have a favorable driving force (−16.2 kcal/mol).

In conclusion, we have demonstrated computationally that NHC-stabilized homoatomic lithium(0) complexes with a Li–Li covalent bond should be chemically viable and therefore provide synthetic targets for experimentalists. Such zerovalent dilithium complexes would represent a new class of molecular "allotropes" and could have novel reactivities. The study of such compounds would help advance the field of main-group organometallic chemistry.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.11.025.

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