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A Viable Anionic N-Heterocyclic Dicarbene

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Abstract: The first anionic N-heterocyclic dicarbene, polymeric $[\mathrm{:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi(THF)\}}]_n$ **1**, containing both normal (C2) and abnormal carbene (C4) centers in the same five-membered imidazole ring (**III**), has been prepared by lithiation of the imidazole monocarbene, $\mathrm{:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2}$. The dicarbene nature of **1** was unambiguously demonstrated by the formation of the group 13 Lewis acid adducts $\mathrm{(THF)_2Li{:}C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHC(LA)\}}$, where LA = $\mathrm{AlMe_3}$ [**2·(THF)₂**] and $\mathrm{BEt_3}$ [**3·(THF)₂**].

The quest for persistent carbenes[1,2] rather than just transient divalent carbon intermediates[3] was achieved by Bertrand's (phosphino)(silyl)carbene[4,5] and Arduengo's imidazol-2-ylidene[6] (**I** in Figure 1). The subsequent rapid development of N-heterocyclic carbene (NHC) chemistry has not only afforded extensive applications in organic and transition-metal homogeneous catalysis,[7] but also resulted in novel advances involving main-group elements.[1,8−12] In particular, a number of highly reactive molecules, including HB═BH,[13,14] a $\mathrm{Ga_6}$ octahedron,[15] group 14 and 15 diatomic $\mathrm{E_2}$ species (E = Si,[16] Ge,[17] P,[18,19] As[20]), $\mathrm{R_2Si{=}O}$,[21] $\mathrm{SiX_2}$ (X = Br,[22] Cl[23]), $\mathrm{P_{12}}$,[24] $\mathrm{P_2^{2+}}$,[25] and PH,[26] have all recently been stabilized using NHC ligands.

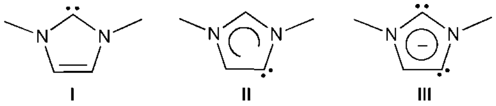
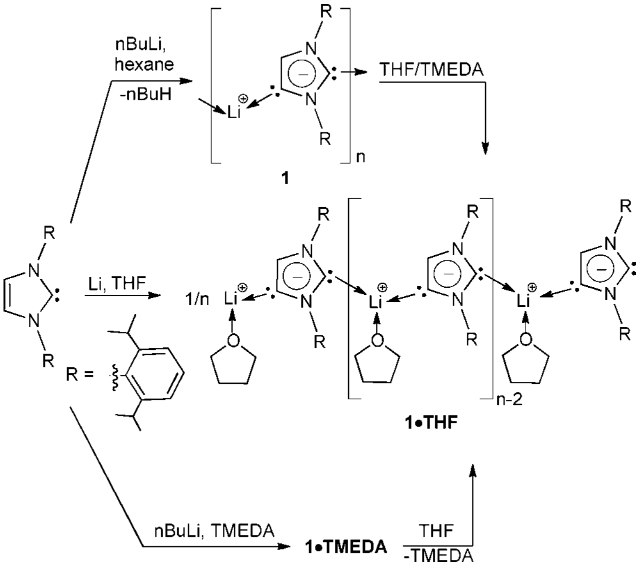


Figure 1. Types of imidazole-based carbenes: (**I**) normal carbenes (NHCs); (**II**) abnormal carbenes (*a*NHCs); (**III**) anionic dicarbenes (NHDCs).

Crabtree's discovery of the first metal complexes involving "abnormal" carbenes[27] (*a*NHCs; **II** in Figure 1) initiated the study of these interesting species.[28−30] Abnormal carbenes are kinetically and energetically (by 19 kcal/mol for the parent $\mathrm{C_3H_4N_2}$ species[31]) less stable than their normal NHC isomers and exhibit stronger electron-donating capabilities.[32,33] Notably, Bertrand recently succeeded in crystallizing both a viable metal-free *a*NHC[34] and free mesoionic carbenes (MICs).[35]

In their five-membered imidazole rings, both NHCs (**I**) and *a*NHCs (**II**) have only one carbene center (C2 and C4, respectively). Is it possible to realize two carbene centers, at the C2 *and* C4 positions, in the same five-membered imidazole ring? Our recent synthesis of L′: P−H (L′: = $\mathrm{:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi(THF)_3\}}$),[26] coupled with Bertrand's discovery of triazole biscarbene silver ionic polymers,[36,37] suggested that metalation of the imidazole backbone may provide a convenient route to an anionic N-heterocyclic dicarbene (NHDC; **III** in Figure 1). Although carbenes **I**, **II**, and **III** are all highly aromatic six-π-electron systems, anionic dicarbene **III** has both normal (C2) and abnormal (C4) carbene centers in the same five-membered imidazole ring. Herein we report the synthesis,[38] molecular structure,[38] and computational analysis[31] of the first anionic N-heterocyclic dicarbene, $[\mathrm{:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi\}}]_n$ (**1**). The "dicarbene" character of **1** is unambiguously evident in the formation of group 13 Lewis acid (LA) adducts $\mathrm{(THF)_2Li{:}C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHC(LA)\}}$, where LA = $\mathrm{AlMe_3}$ [**2·(THF)₂**] and $\mathrm{BEt_3}$ [**3·(THF)₂**]. Notably, **1** differs from anionic NHC ligands having only one carbene (C2) center.[39]

Scheme 1. Syntheses of the Anionic N-Heterocyclic Dicarbene **1**



Dicarbene **1** was prepared in nearly quantitative yield (98%) by reaction of the NHC ligand L: (L: = $\mathrm{:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2}$)[40] with nBuLi in hexane at ambient temperature (Scheme 1). When **1** is dissolved in a tetrahydrofuran/tetramethylethylenediamine (THF/TMEDA) solvent mixture, only a single THF moiety coordinates to each lithium cation to form **1·THF**. The reaction of lithium metal with L: in THF gives **1·THF** directly, albeit in a lower yield. Lithiation of L: by nBuLi in TMEDA gives **1·TMEDA**. Compound **1·TMEDA** is gradually converted into **1·THF** upon dissolution in THF (Scheme 1). Notably, compound **1** is persistent at ambient temperature under an argon atmosphere.

The anionic character of **1** shifts the ^{1}H NMR resonance of the imidazole ring upfield to 6.16 ppm in THF-d_8, relative to 7.19 ppm for its neutral NHC precursor. The X-ray structure[38] shows that **1·THF** exists as a polymeric chain in the solid state (Figure 2b). The asymmetric unit contains two $\mathrm{:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi(THF)\}}$ units (Figure 2a). Each lithium cation is three-

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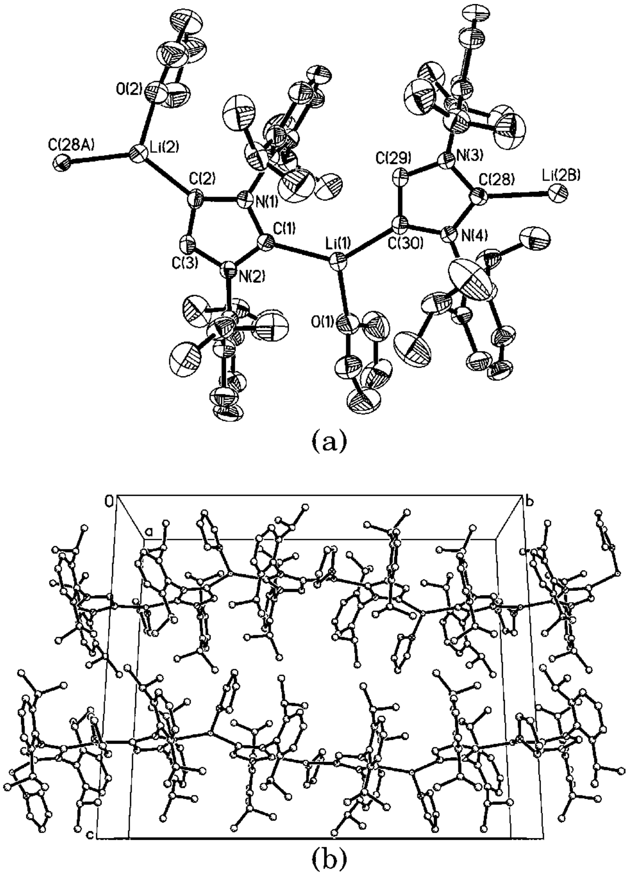


Figure 2. (a) Molecular structure of **1** (thermal ellipsoids represent 30% probability; hydrogen atoms have been omitted for clarity). Selected bond distances (Å) and angles (deg): Li(1)−O(1), 2.036(6); Li(1)−C(1), 2.175(6); Li(1)−C(30), 2.125(6); Li(2)−C(28A), 2.216(6); Li(2)−C(2), 2.122(6); N(1)−C(1), 1.375(3); N(2)−C(1), 1.361(3); C(2)−C(3), 1.356(4); O(1)−Li(1)−C(30), 115.1(3); O(1)−Li(1)−C(1), 112.0(3); C(1)−Li(1)−C(30), 132.7(3); C(1)−N(1)−C(16), 121.9(2); C(1)−N(2)−C(4), 125.2(2). (b) Packing diagram of **1** (hydrogen atoms have been omitted for clarity).

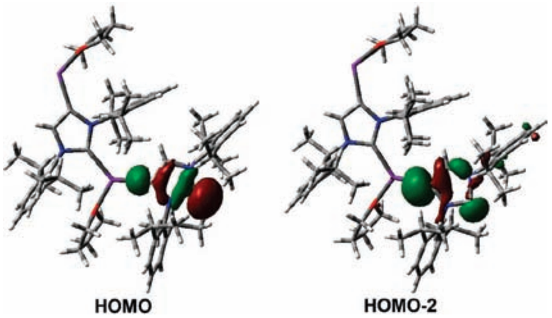
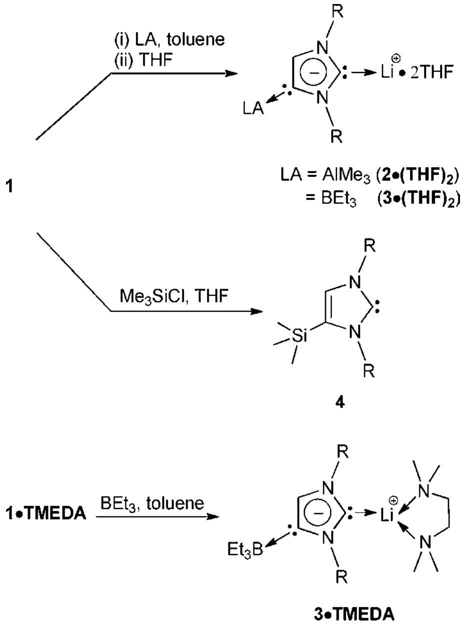


Figure 3. Representation of the carbenoid molecular orbitals of **1·THF**.

Scheme 2. Reactivity Study of Polymeric **1**



coordinate and adopts a trigonal-planar geometry. Besides its THF coordination, the lithium cation also binds ionically to two carbene centers:[41−43] a C2 carbon [i.e., C(1) or C(28)] and a C4 carbon [i.e., C(30) or C(2)] from two neighboring NHDC units. The 2.175(6) Å Li(1)−C(1) and 2.216(6) Å Li(2)−C(28A) bond distances are somewhat longer than the Li(1)−C(30) [2.125(6) Å] and Li(2)−C(2) [2.122(6) Å] distances. These distances all compare well with reported Li−C$_{carbene}$ bond distances, which range from 2.093 to 2.339 Å.[44−47]

The HOMO and HOMO-2[31] of **1·THF** (Figure 3) correspond to the two strongly polarized Li−C bonding orbitals at the C2 and C4 carbon centers. Natural bond orbital (NBO) analysis documents the ionic bonding character of the Li−C bonds in **1·THF**; the Wiberg bond indices of the Li−C bonds are 0.1, and the natural charges of Li$^+$ are +0.84. These data support the anionic character of the NHDC fragment in **1·THF**.

The anionic dicarbene nature of **1** was demonstrated by its reaction with the group 13 Lewis acids AlMe$_3$ and BEt$_3$. Crystallization of the resulting reaction products in THF afforded **2·(THF)$_2$** and **3·(THF)$_2$**, respectively, as colorless crystals (Scheme 2).

X-ray structural analyses[38] (Figure 4) reveal that the AlMe$_3$ and BEt$_3$ Lewis acids cleave the Li−C4 bonds and bind to the *a*NHC centers (i.e., C4 carbons) of **1**. The remaining Li$^+$ is coordinated to the NHDC ligand at the "normal" (C2) carbon as well as to two THF molecules (Figure 4). The formation of **2·(THF)$_2$** and **3·(THF)$_2$** clearly exhibits the "dicarbene" character of **1**. Moreover, the reaction of **1** with excess AlMe$_3$ or BEt$_3$ still gives the same product **2·(THF)$_2$** or **3·(THF)$_2$**, respectively [i.e., insertion of a second Lewis acid into the Li−C$_{carbene}$ (C2) bond does not occur]. This observation suggests that the interaction between the Li$^+$ cation and the anionic carbene is relatively strong. Indeed, the C(1)−Li(1) distances [2.094(6) Å for **2·(THF)$_2$**; 2.096(4) Å for **3·(THF)$_2$**] are among the shortest Li−C$_{carbene}$ bond lengths.[44−47] **3·TMEDA** was prepared by combining **1·TMEDA** with BEt$_3$ in toluene (Scheme 2) and has a structure similar to that of **3·(THF)$_2$**.[38]

Functionalization of the C4 carbon of an NHC, which may allow tuning of the electronic and steric properties of the normal carbene center (C2), is a fascinating concept.[48−50] In addition to its intriguing "dicarbene" applications, compound **1** may also provide a convenient synthetic route to a variety of C4-functionalized NHCs. The fact that the reaction of **1** with Me$_3$SiCl affords $:C\{[N(2,6\text{-}Pr^{i}_{2}C_{6}H_{3})]_{2}CHC(SiMe_{3})\}$ (**4**)[49] in 82% yield (Scheme 2) illustrates this promising utility of **1**.

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Supporting Information Available: Full details of the syntheses, computations, and X-ray crystal structure determinations (including CIF

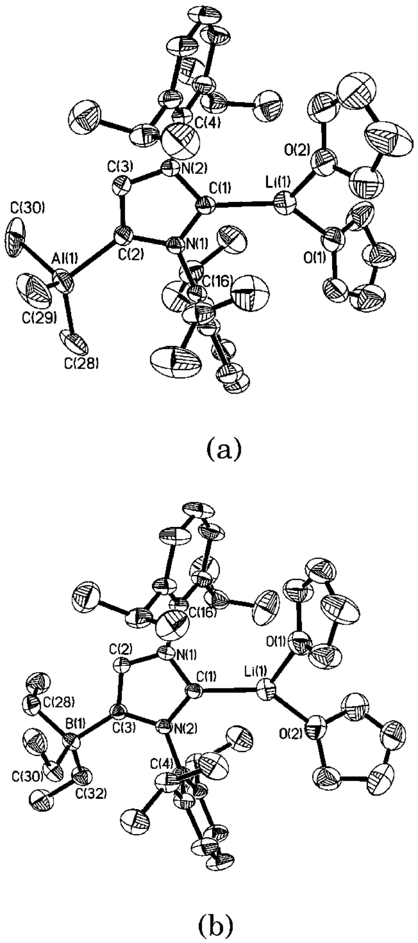

Figure 4. Molecular structures of (a) **2·(THF)$_2$** and (b) **3·(THF)$_2$** (thermal ellipsoids represent 30% probability; hydrogen atoms have been omitted for clarity). Selected bond distances (Å) and angles (deg) in (a): C(2)−Al(1), 2.033(3); C(1)−Li(1), 2.094(6); C(2)−C(3), 1.360(4); C(1)−N(1)−C(16), 121.0(2); C(1)−N(2)−C(4), 123.8(2). In (b): C(1)−Li(1), 2.096(4); C(3)−B(1), 1.656(3); C(2)−C(3), 1.350(2); C(1)−N(1)−C(16), 124.88(15); C(1)−N(2)−C(4), 118.66(15).

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