

C5-Metalation of Imidazole-Based Monothiolates en Route to Selenothiolates

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ABSTRACT: Lithiation of an imidazole-based monothiolate, **2**, by excess *n*-butyllithium gives a white powder containing both a lithiated product and an *n*BuLi contaminant (in ca. 1:1 molar ratio). This white powder not only reacts with TMEDA in toluene to give **4**, a C5-lithiated-imidazole-based monothiolate dimer, but also cleaves THF to give a pair of enantiomers of **5** (as a result of ‘capturing’ LiOCH=CH₂ fragment by a C5-lithiated-imidazole-based monothiolate monomer). Further reaction of the lithiated product of **2** with selenium results in the first dimeric (**7**) and monomeric (**8**) selenothiolates. The nature of the bonding in **7** and **8** was further probed by DFT computations.

Since Arduengo’s seminal 1991 synthesis,¹ N-heterocyclic carbenes (NHCs; **I**, Figure 1) have demonstrated remarkable utility in both transition metal and main group chemistry.²⁻⁷ Although somewhat less stable, *abnormal* NHCs (*a*NHCs; **II**, Figure 1) generally possess stronger electron-donating capabilities than **I**.^{8,9} The first stable metal-free *a*NHC ligand, reported by Bertrand,¹⁰ involved aryl-functionalization of the C2 and C5 carbon atoms. Ghadwal recently reported a stable C5-protonated *a*NHC.¹¹ In addition, ditopic carbanionic NHCs, including anionic C2/C4 N-heterocyclic dicarbenes (NHDCs; **III**, Figure 1)¹²⁻¹⁴ and anionic C4/C5 dicarbenes (**IV**; Figure 1),¹⁵ have been synthesized *via* metalation of the corresponding carbene precursors **I** and **II**, respectively.

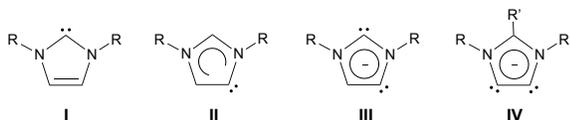
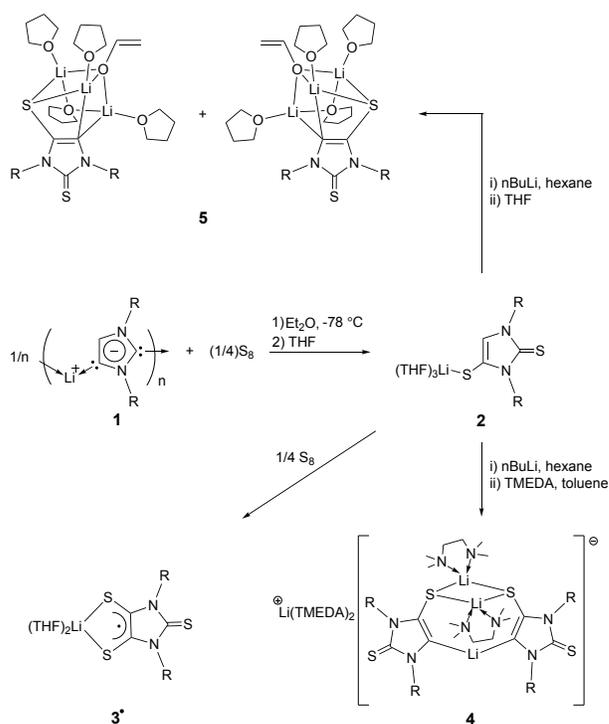


Figure 1. Imidazole-based carbenes: (**I**) normal N-heterocyclic carbenes (NHCs); (**II**) abnormal N-heterocyclic carbenes (*a*NHCs); (**III**) anionic C2/C4 N-heterocyclic dicarbenes (NHDCs); (**IV**) anionic C4/C5 N-heterocyclic dicarbenes.

The preparation of the first C2/C4 NHDC (**1**, Scheme 1), *via* lithiation of the corresponding N-heterocyclic carbene, was reported by this laboratory a decade ago.¹² NHDCs have subsequently demonstrated diverse utility in the synthesis of *a*NHC complexes, C4-functionalized and poly-NHCs, and NHDC-based binuclear complexes.^{6,16-19} Indeed, we recently reported that **1** undergoes both *disulfurization* (giving an imidazole-based monothiolate (**2**)) and *trisulfurization* (giving a stable lithium dithiolene radical (**3***)) (Scheme 1).²⁰ While employing **3*** as an effective platform for accessing various novel *s*- and *p*-block dithiolene species,²¹⁻²³ we are also interested in the metalation of **2**, which may lead to novel applications in heterocyclic and coordination chemistry. Herein, we report the syntheses²⁴ and structures²⁴ of C5-lithiated-imidazole-based monothiolates

4 and **5** (Scheme 1). Lithiation of **2** provides a unique synthetic route to the dilithium dithiolate dimer (**6**) and selenothiolates (**7** and **8**) (Scheme 2). Although dithiolenes and diselenolenes have been extensively studied,²⁵⁻³¹ compounds **7** and **8** represent the first report of selenothiolates. The nature of the bonding in **7** and **8** was probed by DFT computations.²⁴

Scheme 1. Synthesis of 4 and 5 (R = 2,6-diisopropylphenyl).



Lithiation of crystalline **2** with an excess of *n*BuLi in hexane gives the lithiated product as a white powder, which further reacts with TMEDA in toluene to give **4** (49.6% yield, Scheme

1).²⁴ Attempts to obtain X-ray quality crystals of the white powder (without TMEDA coordination) in toluene were unsuccessful, repeatedly yielding only a viscous solution. Notably, the white powder was shown to cleave THF, rendering a pair of enantiomers of **5** (72.3% yield; Scheme 1) in a 1:1 ratio (as observed in the crystal lattice).²⁴ After being rinsed with hexane, the white powder still contained both the lithiated ligand and the nBuLi contaminant (in a molar ratio of ca. 1:1 in terms of the ¹H NMR spectrum of the white powder in THF-d₈). The presence of the lithium enolate of acetaldehyde (LiOCH=CH₂) moiety in **5** may be due to fragmentation of THF by nBuLi.³² Notably, **4** does not react with THF. The ¹H NMR resonances of the enolate of acetaldehyde fragment of **5** are observed at 3.37 (broad d, 1H, ³J_{cis} = 4.7 Hz, HC=), 3.68 (d, 1H, ³J_{trans} = 13.6 Hz, HC=), and 6.92 (dd, 1H, ³J_{cis} = 5.3 Hz and ³J_{trans} = 13.6 Hz, =CHO) ppm, which compares well to those (3.41, 3.96, and 6.51 ppm) for the LiOCH=CH₂ units in (THF)₆Li₁₂{2-(MeO)C₆H₄N}₆P₃N₃(CH₂=CHO)₆.³³

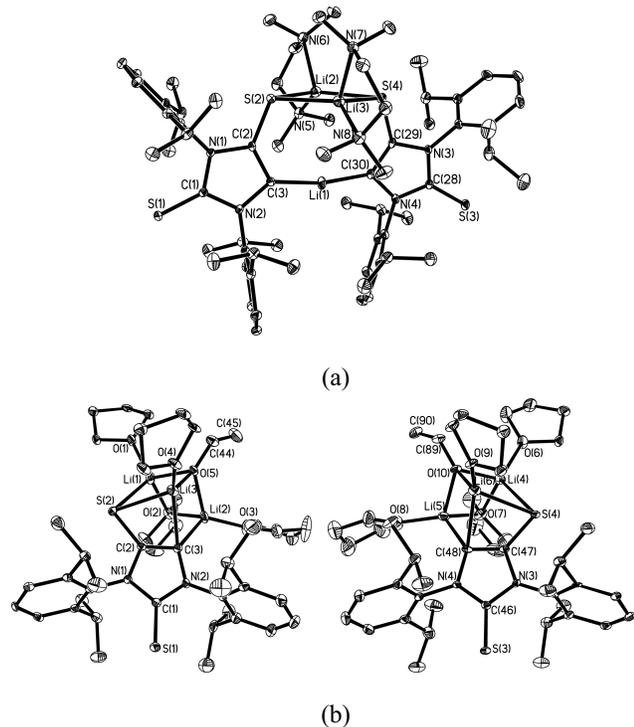


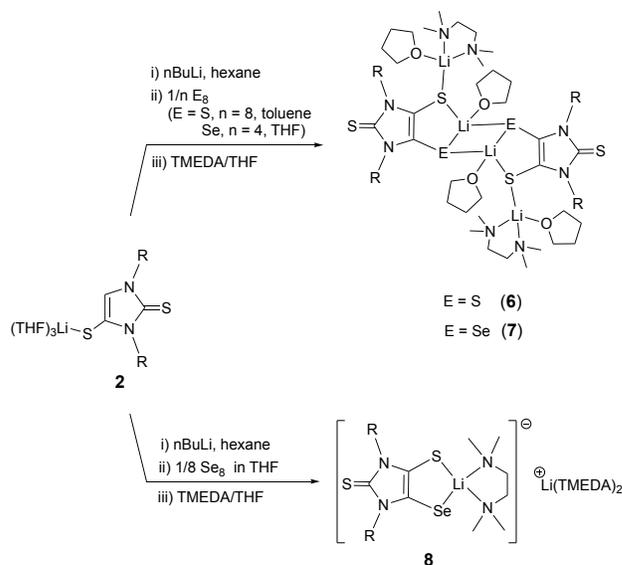
Figure 2. Molecular structures of [4]⁻ (a) and enantiomers of **5** (b). Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity. Selected bond distances (Å) and angles (deg): For [4]⁻, C(2)–C(3) 1.368(4), C(2)–S(2) 1.758(3), C(3)–Li(1) 2.007(6), S(2)–Li(2) 2.467(5), S(2)–Li(3) 2.451(5); C(2)–C(3)–Li(1) 119.4(3), C(3)–Li(1)–C(30) 169.4(3), C(3)–C(2)–S(2) 129.9(2), S(2)–Li(2)–S(4) 108.22(19), Li(2)–S(2)–Li(3) 72.22(17). For **5**, C(2)–C(3) 1.358(6), C(2)–S(2) 1.757(4), C(3)–Li(2) 2.154(9), C(3)–Li(3) 2.230(10), S(2)–Li(1) 2.418(9), Li(1)–O(5) 1.918(9), O(5)–C(44) 1.329(6), C(44)–C(45) 1.290(8); C(2)–C(3)–Li(2) 121.8(4), C(2)–C(3)–Li(3) 81.2(4), C(3)–C(2)–S(2) 128.7(4), C(2)–S(2)–Li(1) 100.7(2), C(2)–S(2)–Li(3) 65.8(3), O(5)–C(44)–C(45) 127.6(6).

X-ray structural analysis²⁴ reveals that the anionic moiety of **4** (Figure 2a) contains two C5-lithiated-imidazole-based monothiolate ligands, bridged by three lithium cations. While one two-coordinate lithium atom is bound to the two C5 carbons of neighboring imidazole rings, the other two TMEDA-chelated lithium atoms are four-coordinate, forming an almost planar

ring with two sulfur atoms (dihedral angle between two SLi₂ planes = 176.1°) (Figure 2a). The presence of two-coordinate lithium in **4** is presumably due to the steric shielding of the bulky thiolate ligands and two TMEDA molecules. The two-coordinate lithium atom in **4** has a somewhat bent geometry [C(3)–Li(1)–C(30) bond angle = 169.4(3)°]. The C–Li bond distances in **4** [2.007(6) and 2.024(6) Å] are shorter than those in **1** [2.125(6) and 2.175(6) Å].¹² Both C4–S bond distances (1.760 Å, av) and S–Li bond distances (2.469 Å, av) in **4** are longer than those in **2** (d_{C4-S}=1.716 Å, d_{S-Li}=2.369 Å), respectively.²⁰

X-ray structural analysis shows that **5** exists as one pair of enantiomers (Figure 2b) in the asymmetric unit.²⁴ For clarity, only the structural parameters of one enantiomer of **5** is shown in the caption of Figure 2. The formation of **5** may be a result of ‘capturing’ a LiOCH=CH₂ fragment (from nBuLi-mediated THF cleavage) by the C5-lithiated-imidazole-based monothiolate monomer. The LiOCH=CH₂ unit resides either above or below the C=C–S plane through forming two Li–O bonds and one Li–C5 bond, giving one pair of enantiomers of **5**. In compound **5**, three lithium atoms are four-coordinate due to THF solvation. While C4–S bond distances [1.749(5) and 1.757(4) Å] and S–Li bond distances (2.480 Å, av) of **5** are similar to those in **4** [d_{C4-S}=1.760 Å (av), d_{S-Li}=2.469 Å (av)], the C5–Li bond distances [2.147(9)–2.239(10) Å] in **5** are longer than those in **4** [2.007(6) and 2.024(6) Å].²⁴ The carbon-carbon double bond distances of the lithium enolate of acetaldehyde units in **5** (1.295 Å, av) compare with that in a yttrium porphyrinogen complex [1.339(4) Å].³⁴

Scheme 2. Synthesis of **6**, **7**, and **8** (R = 2,6-diisopropylphenyl).



C5-lithiation of **2** provides a convenient synthetic route to heteronuclear dichalcogenolates. Reaction of **2** with excess nBuLi in hexane gives a white powder. This white powder, when combined with elemental selenium in THF (1:2 molar ratio of **2**:Se) and subsequently with excess TMEDA in THF, gives the dimeric selenothiolate **7** (85.9% yield) (Scheme 2).²⁴ Notably, when the molar ratio of **2**:Se is 1:1, the product of the parallel synthesis is the monomeric selenothiolate **8** (74.4% yield; Scheme 2).²⁴ The corresponding 1:1 reaction of **2** with elemental sulfur in toluene, however, affords the dilithium

dithiolate dimer **6** (77.9% yield; Scheme 2).²⁴ Notably, analogues of **6**, containing mixed cations, have been previously reported by this laboratory (*via* KC_8 or cobaltocene-mediated one-electron reduction of the lithium dithiolene radical **3'**).³⁵ In THF- d_8 , the 2,6-diisopropylphenyl-substituted imidazole moieties in both **7** and **8** demonstrate very similar 1H and ^{13}C NMR resonances.

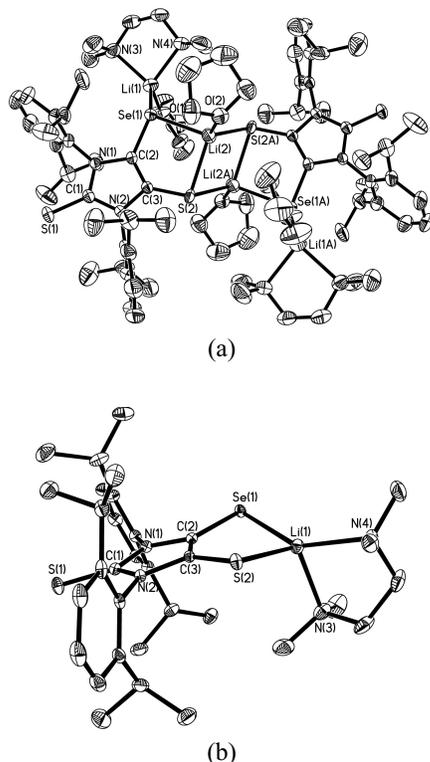


Figure 3. Molecular structures of **7** (a) and enantiomeric **[8]⁻** (b). Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon and disordered atoms [*i.e.*, Se(1'), S(2')] are omitted for clarity.

The structural parameters (Figure S1)²⁴ of the $[C_2S_2Li(THF)]_2$ core in **6** are very similar to those in previously reported dithiolate dimers.³⁵ The $[C_2SSeLi(THF)]_2$ core in **7** (Figure 3a) is isostructural with the $[C_2S_2Li(THF)]_2$ core in **6**. Compound **8** exists as a monomer, in which the lithium atom in the five-membered selenothiolate ring is chelated by a TMEDA molecule (Figure 3b). Consequently, the lithium atom in **8** is four-coordinated and adopts a distorted tetrahedral geometry. In contrast to **6**, however, both dimeric (**7**) and monomeric (**8**) selenothiolates exhibit disorders of Se and S atoms in their solid-state structures (For clarity, disordered Se(1'), S(2') atoms are omitted in molecular structures shown in Figure 3).²⁴ Regarding compound **7**, the occupancies of Se(1) and S(2') are 0.55 and 0.45, respectively, at the position bridging Li(2) and C(2), while the occupancies of Se(1') and S(2) are 0.45 and 0.55, respectively, at the position bridging Li(2) and C(3). For **8**, the occupancies of Se(1) and S(2') are 0.65 and 0.35, respectively, at the position bridging Li(1) and C(2), while the occupancies of Se(1') and S(2) are 0.35 and 0.65, respectively, at the position bridging Li(1) and C(3). Considering the crystallographic disorder present in the selenothiolate cores (*i.e.*, C_2SeS) of **7** and **8**, we thought it prudent to computationally investigate the bonding (*i.e.*, B3LYP/6-311G** DFT computations on the simplified **7-H** and **[8-H]⁻** models).²⁴ Both C–Se and C–S bonds in **7-H** ($d_{C-Se} = 1.904$ Å, $d_{C-S} = 1.755$ Å) and **[8-H]⁻** ($d_{C-Se} = 1.908$

Å, $d_{C-S} = 1.756$ Å) are comparable with the corresponding theoretical values in the reported diselenolates and dithiolates. For example, diselenolates, $[R(Se)C=C(Se)R]^{2-}$, R = Me, CN, CF_3 , and COOMe, exhibit C–Se bond distances in a range from 1.895 to 1.929 Å,³⁶ while the C–S bond distance in the simplified lithium-bridged dithiolate dimer model is 1.754 Å.³⁵ The C_2SeSLi rings in both **7-H** and **[8-H]⁻**,²⁴ are much more planar, unlike than those in the solid state structures of **7** and **8**. This may be due to the steric hindrance of the bulky ligand and packing effects. The HOMOs of **7-H** and **[8-H]⁻** models (Figure 4) are predominantly ligand-based, involving C–C π -bonding, and C–S/Se π -antibonding character.

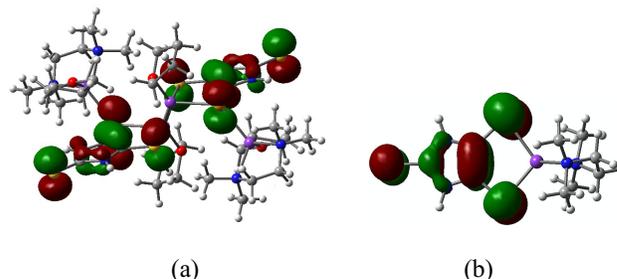


Figure 4. HOMOs of optimized models **7-H** (a) and **[8-H]⁻** (b).

In conclusion, compound **2**, as an intermediate of the synthesis of lithium dithiolene radical **3'**, may also react with excess $nBuLi$ to give a white powder containing both C5-lithiated product and $nBuLi$ contaminant (in ca. 1:1 molar ratio). This white powder not only reacts with TMEDA in toluene to give **4**, but also cleaves THF to give a pair of enantiomers, **5**. Further reaction of the lithiated product of **2** with selenium (in different stoichiometries) results in the first dimeric (**7**) and monomeric (**8**) selenothiolates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Supporting information of syntheses, computations, and X-ray crystallography (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession codes

CCDC 1989492 (**4**), 1989493 (**5**), 1989494 (**6**), 1989495 (**7**) and 1989496 (**8**) 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).

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Notes

The authors declare no competing financial interest.

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