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Communication

A Stable Naked Dithiolene Radical Anion and Synergic THF Ring-Opening

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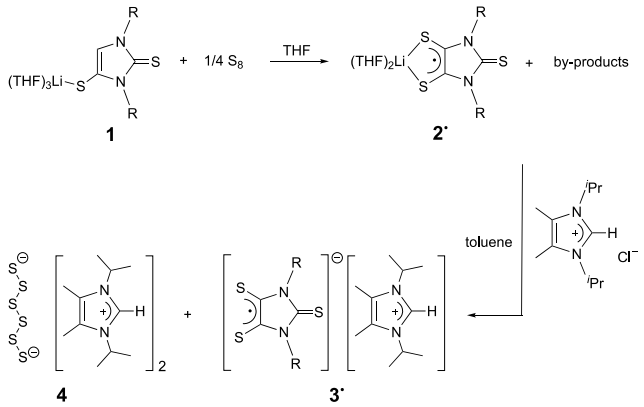
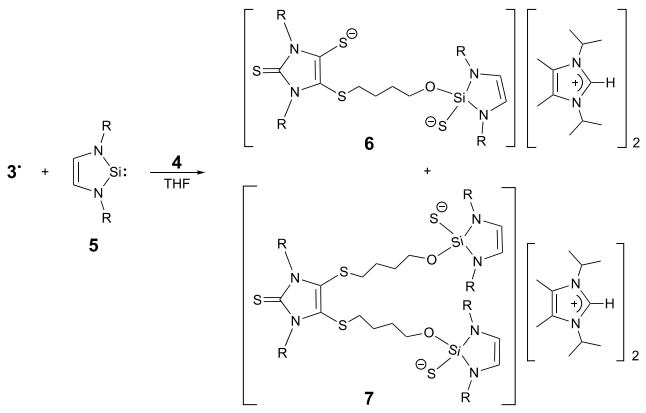
ABSTRACT: Reaction of the lithium dithiolene radical **2**• with the imidazolium salt $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+[Cl]^-$ (in a 1:1 molar ratio) gives the first stable naked anionic dithiolene radical **3**•, which, when coupled with hexasulfide, $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+_2[S_6]^{2-}$ (**4**), and N-heterocyclic silylene **5**, unexpectedly results in synergic THF ring-opening via a radical mechanism.

The presence of anionic dithiolene-based radicals in transition-metal complexes was first proposed nearly six decades ago.[1,2] Subsequently, the radical character of the monoanionic dithiolene moieties in transition-metal complexes has been extensively studied.[3−13] In the absence of transition-metal coordination, highly reactive anionic dithiolene radical species have been probed both computationally and by electron paramagnetic resonance.[14−17] The prototype anionic dithiolene radical ($C_2H_2S_2^{\bullet-}$) was studied in a low-temperature matrix.[18] Notably, the first structurally characterized s-block element (i.e., lithium)-based dithiolene radical (**2**•; Scheme 1) was recently reported by this laboratory.[19,20] Radical **2**• presents a convenient platform for the synthesis of elusive main-group element-based dithiolene radicals. To this end, by reaction of **2**• with the corresponding borane agents, we recently synthesized boron-based dithiolene radicals $[(L^{\bullet})B(R_1)_2$, $R_1 = C_6H_{11}$ or Br; $L^{\bullet} = R_2timdt^{\bullet}$, R = 2,6-$iPr_2C_6H_3]$.[21] In contrast to these metal (or semimetal) dithiolene radical species, a naked dithiolene radical anion is intriguing due to its unique electronic and structural character (i.e., bearing both anionic radical character and two available coordination sites). Consequently, unusual utility would be expected from such a unique radical species. Herein, we report the synthesis,[22] structure,[22] and computations[22] of **3**• (Scheme 1), the first stable naked anionic dithiolene radical. Furthermore, we report that reaction of **3**• with N-heterocyclic silylene (NHSi) (**5**), unexpectedly, affords synergetic ring-opening reactions of THF in the presence of hexasulfide $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+_2[S_6]^{2-}$ (**4**), giving compounds **6** and **7** (Scheme 2).[22] Notably, low-oxidation-state main-group chemistry studies involving dithiolenes have only begun to emerge: This laboratory recently prepared the first dianionic silicon tris(dithiolene) complex via reaction of **2**• with carbene-stabilized disilicon(0).[23]

Scheme 1. Synthesis of Naked Anionic Dithiolene Radical 3• (R = 2,6-Diisopropylphenyl)



Scheme 2. Synergic THF Ring-Opening by 3• and $NHSi^{Dipp}$ (5) in the Presence of the Hexasulfide (4) (R = 2,6-Diisopropylphenyl)



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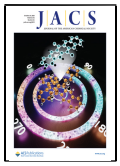

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The reaction of crystalline imidazole-based monothiolate **1** with elemental sulfur (in THF) gave raw **2**$^{\bullet}$ as a fine purple powder (Scheme 1).[19] Without further purification, this material was combined with $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+[Cl]^-$ salt (1:1 molar ratio) in toluene and subsequently sonicated, giving radical **3**$^{\bullet}$ and $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+_2[S_6]^{2-}$ (**4**) (Scheme 1). Refluxing of the mixture of **3**$^{\bullet}$ and **4** in THF, followed by room-temperature recrystallization results in the separation of **3**$^{\bullet}$ as dark purple X-ray quality single crystals (in 53.4% yield, based on the quantity of **1**) from minor byproduct **4** (orange-red crystals).[22] While reaction of pure **2**$^{\bullet}$ (crystals) with the same imidazolium salt only gives **3**$^{\bullet}$, formation of **4** (as shown in Scheme 1) may suggest the presence of a certain uncharacterized sulfide byproduct in the raw material of **2**$^{\bullet}$. Polysulfide dianions and radical monoanions have attracted considerable attention due to their utility in organic syntheses, oxygen-poor biological systems, and sulfur-based batteries.[24,25] Pyrrolidinium hexasulfide analogues of **4** have been synthesized by reacting pyrrolidinium TMS-S salts (TMS = trimethylsilyl) with S_8.[26]

The paramagnetic properties of radical **3**$^{\bullet}$ are characterized by room-temperature EPR spectroscopy. The EPR spectrum of **3**$^{\bullet}$ in THF (Figure 1a) displays an $S = 1/2$ quintet ($g_{av} = 2.017$) due

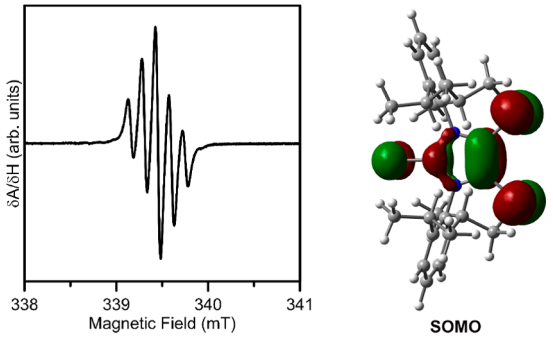
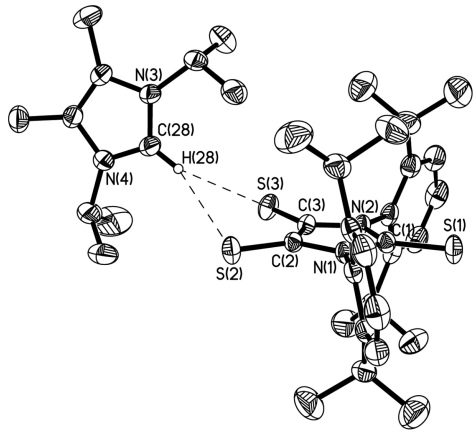


Figure 1. (a) Room-temperature X-band EPR spectrum of **3**$^{\bullet}$ in THF, recorded at 9.584 GHz with a modulation amplitude of 0.02 mT and a microwave power of 1 mW. (b) SOMO of $[\mathbf{3}^{\bullet}]^-$.

to hyperfine coupling with two equivalent ^{14}N ($I = 1$) nuclei, A_{av} (^{14}N) = 4.1 MHz. These values are comparable to those obtained for **2**$^{\bullet}$ ($g_{av} = 2.016$ and A_{av} (^{14}N) = 3.9 MHz).[19] While the spin densities of the C_2S_2 units in both [**2-Ph**]$^{\bullet}$ (0.88)[19] and $[\mathbf{3}^{\bullet}]^-$ (0.87) are slightly larger than those (0.71, R_1 = Br; 0.77, R_1 = C_6H_{11}) for boron dithiolene radicals, $[(L^{\bullet})B(R_1)_2$, $R_1 = C_6H_{11}$ or Br; $L^{\bullet} = R_2timdt^{\bullet}$, R = 2,6-i$Pr_2C_6H_3$],[21] the spin density of the terminal S(1) atom increases in sequence: $[\mathbf{3}^{\bullet}]^-$ (0.12) < [**2-Ph**]$^{\bullet}$ (0.18) < boron dithiolene radicals (0.27, R_1 = Br; 0.23, R_1 = C_6H_{11}).

While the UV−vis absorption spectrum of **2**$^{\bullet}$ (purple) in toluene shows two absorptions at 554 and 579 nm,[19,20] that of **3**$^{\bullet}$ (violet) in THF demonstrates two absorptions at 526 and 616 nm. Regarding the solid-state structure of **3**$^{\bullet}$ (Figure 2), the three sulfur atoms are coplanar with the five-membered imidazole ring.[22] The S(1)−C(1) bond distance [1.6591(18) Å] is only marginally shorter than that of the S(2)−C(2) bond [1.6637(18) Å] and the S(3)−C(3) bond [1.6698(18) Å]. All of them compare well to those for **2**$^{\bullet}$ (1.654−1.680 Å)[19] and for the $[\mathbf{3}^{\bullet}]^-$ model (1.683−1.686 Å).[22] The corresponding Wiberg bond index (WBI) values of S−C bonds in the $[\mathbf{3}^{\bullet}]^-$ model



3$^{\bullet}$

Figure 2. Molecular structure of **3**$^{\bullet}$. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): S(1)−C(1), 1.6591(18); C(2)−C(3), 1.420(2); C(2)−S(2), 1.6637(18); C(3)−S(3), 1.6698(18); C(2)−C(3)−S(3), 129.87(14). Nonbonding distances (Å): S(2)···H(28), 3.004; S(3)···H(28), 2.902.

[1.446 for the S(1)−C(1) bond; 1.426 for the S(2)−C(2) and S(3)−C(3) bonds] suggest the modest double-bond character of all three sulfur−carbon bonds in **3**$^{\bullet}$. While the imidazole ring of the $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+$ cation in **3**$^{\bullet}$ is almost perpendicular to the dithiolene (i.e., C_2S_2) plane, the proton [H(28)] residing at the carbene carbon [C(28)] (Figure 2) points to the middle of the C_2S_2 unit of the dithiolene ligand. However, the 3.004 Å S(2)···H(28) and 2.902 Å S(3)···H(28) distances, much longer than the sum of covalent radii of sulfur and hydrogen (1.36 Å),[27] rule out the presence of covalent bonding interactions between the H(28) atom of the imidazolium cation and the sulfur atoms [i.e., S(2) and S(3)] of the anionic dithiolene fragment in **3**$^{\bullet}$. Consequently, this interaction between them is largely dominated by electrostatic forces. Thus, **3**$^{\bullet}$ represents the first stable naked dithiolene radical. In contrast to those of the dithiolate $(NMe_4)_2(C_3S_5)$[28] [d_{C-C} = 1.371(8) Å, d_{S-C} = 1.724(6) Å], the elongated C−C [1.420(2) Å] and concomitant shortened S−C bonds [1.667 Å, av] in the C_2S_2 unit of **3**$^{\bullet}$ may be attributed to the SOMO of $[\mathbf{3}^{\bullet}]^-$, possessing both C−C π-bonding and S−C π-antibonding character (Figure 1b). Similar to pyrrolidinium hexasulfides,[26] the byproduct **4** (see Figure S1)[22] exhibits a disordered chain-like sulfur cluster, in which the negative charges are mainly localized at the two terminal sulfur atoms.[29]

While being best known for their extensive utilities (as σ-donors) in transition-metal coordination and catalysis,[30,31] N-heterocyclic silylenes (NHSis) may also react with radical species[32] (such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl) or muonium,[33] giving a series of a new type of neutral silyl radicals. Inspired by these interesting discoveries, we combined **3**$^{\bullet}$ with $NHSi^{Dipp}$ (Dipp = 2,6-diisopropylphenyl) (**5**),[34,35] in the presence of **4** (in an approximate molar ratio of 1:2:0.25) in THF. This resulted in consecutive THF ring-opening reactions, giving both **6** and **7** as colorless crystals (in 16.0% and 41.4% yields, respectively) (Scheme 2).[22] Compounds **6** and **7** were effectively separated due to their different solubilities in THF/hexane and toluene/hexane systems. While the formation of **6** involves a single THF ring-opening, compound **7** is obtained via dual THF ring-opening. Both **6** and **7** exhibit similar ^{29}Si NMR

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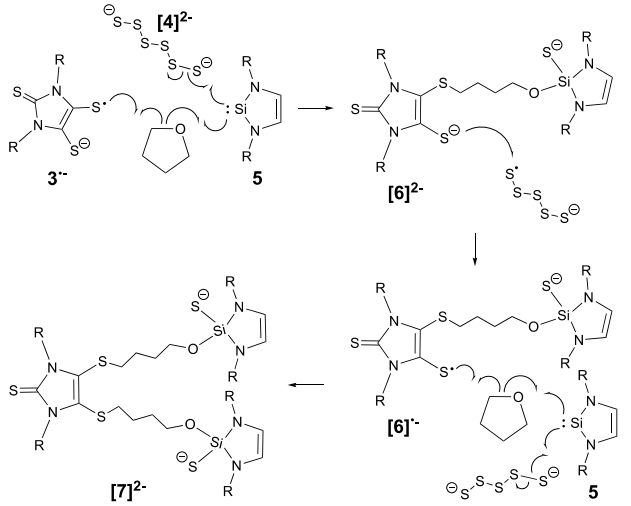
resonances at −24.4 ppm and −24.3 ppm, respectively, which are comparable to that (−38.8 ppm) for dithio-bridged NHSi^{Dipp} dimers.[34]

THF ring-opening reactions usually involve both Lewis acidic metals (or metalloids) and appropriate nucleophiles,[36−47] including frustrated Lewis pair systems.[48] Although the mechanistic details of the formation of **6** and **7** remain unclear, one possible scenario is that the THF ring-openings may proceed through radical processes, involving a three-component (i.e., **3**$^{\bullet}$, **4**, and **5**) synergetic interaction (Scheme 3). Notably,

Scheme 3. Proposed Mechanism of the Synthesis of 6 and 7[a]



[a]The cation moieties of **3**$^{\bullet}$, **4**, **6**, and **7** have been omitted for clarity.

each component itself is inert in THF. Inspired by the fact that monoanionic polysulfide radicals may be formed in solution through disproportionation or partial dissociation of polysulfide dianions[24,25] and N-heterocyclic silylenes may react with radical species,[32] we thus propose that the reaction of hexasulfide dianion **4** with **5** may give a transient sulfurized NHSi^{Dipp}-based silyl radical and a $S_5^{\bullet-}$ byproduct *in situ*. As soon as it was formed, this NHSi^{Dipp}-based silyl radical intermediate, together with **3**$^{\bullet}$, may involve a radical ring-opening reaction of THF, giving **6** (Scheme 3). Subsequently, the $S_5^{\bullet-}$ radical could conduct a one-electron oxidation of the dithiolate unit in **6** (considering the non-innocent character of dithiolenes), giving a dithiolene radical intermediate and dianionic pentasulfide $[S_5]^{2-}$. Eventually, the *in situ* formed dithiolene-based radical species, NHSi^{Dipp} (**5**), and $[S_5]^{2-}$ would follow the radical routes (mentioned above) to give **7** (Scheme 3). Notably, no reaction was observed between **5** and **6** in THF-d_8. However, with the addition of **4** into the mixture of **5** and **6** in THF-d_8, the resonances of compound **7** are observed, accompanying the weakened resonances of **6**. This observation supports the proposed scenario in Scheme 3.

X-ray structural analysis (Figure 3) confirms that crystalline **6** exists as a dianionic salt with two imidazolium counter-cations. As a result of synergetic THF ring-opening, the $-(CH_2)_4O-$ chain bridges the dithiolene and NHSi moieties. While the carbon terminal [i.e., C(28)] is bound to one of the two dithiolene sulfur atoms [i.e., S(2)], its oxygen atom is attached to the silicon atom [i.e., Si(1)] of the NHSi^{Dipp} unit. The C−C [1.356(3) Å] and S−C bonds [1.718 Å, av] in the C_2S_2 unit of **6** compare well to those of $(NMe_4)_2(C_3S_5)$ [d_{C-C} = 1.371(8) Å,

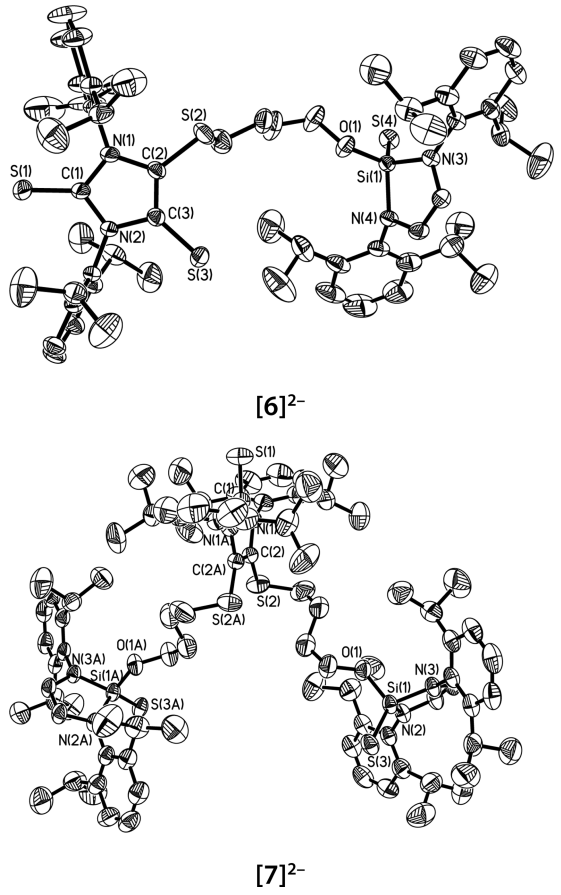


Figure 3. Molecular structures of $[6]^{2-}$ and $[7]^{2-}$. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): For $[6]^{2-}$, S(1)−C(1), 1.677(3); C(2)−C(3), 1.356(3); C(2)−S(2), 1.726(2); C(3)−S(3), 1.710(3); Si(1)−O(1), 1.6534(19); Si(1)−S(4), 2.0135(10); C(2)−C(3)−S(3), 131.6(2); C(3)−C(2)−S(2), 128.7(2); O(1)−Si(1)−S(4), 112.01(8); N(3)−Si(1)−N(4), 90.20(10). For $[7]^{2-}$, S(1)−C(1), 1.661(6); C(2)−C(2A), 1.347(7); C(2)−S(2), 1.734(4); Si(1)−O(1), 1.640(3); Si(1)−S(3), 2.0206(15); C(2A)−C(2)−S(2), 128.82(14); O(1)−Si(1)−S(3), 110.74(12); N(2)−Si(1)−N(3), 90.14(15).

d_{S-C} = 1.724(6) Å].[28] The Si(1) atom in **6** is four-coordinate and adopts a distorted tetrahedral geometry. The Si(1)−O(1) bond of **6** [1.6534(19) Å] is in-between those [1.620(2) and 1.639(2) Å] in a dimeric bis(silaselenone)[49] and that (1.6981 Å) in the simplified [**6-Me**]$^{2-}$ model.[22] The Si−S bonds of both **6** [2.0135(10) Å] and [**6-Me**]$^{2-}$ (2.050 Å)[22] are somewhat longer than of the Si═S double bond in the first stable silanethione [1.948(4) Å],[50] but shorter than the typical Si−S single bond (2.11−2.17 Å).[51] This fact, coupled with 1.31 Si−S WBI, suggests that the Si−S bond in **6** may have a modest double-bond character. While the silicon atom in [**6-Me**]$^{2-}$ bears a positive charge of +1.85, the sulfur atom residing on the silicon atom has a negative charge of −0.99. In addition, each of the two terminal sulfur atoms of the dithiolene ligand in [**6-Me**]$^{2-}$ has a negative charge of −0.47, suggesting the delocalization of the negative charge of the imidazole-based dithiolene moiety. Notably, the nonbonding S···H distances in **6** [2.694 Å S(3)···H(69) and 2.712 Å S(4)···H(58)] are somewhat shorter than those in **3**$^{\bullet}$ (2.902 and 3.004 Å).

In the solid-state structure of **7** (Figure 3), the two $-(CH_2)_4O-$ chain-anchored [NHSi^{Dipp}(S)]$^{-}$ moieties reside

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on opposite sides of the imidazole plane due to the steric repulsion between them. Consequently, there is a two-fold axis bisecting the silicon−carbon double bond [S(1)═C(1)]. In contrast to the nearly planar C_2S_2 units in **6** and [**7-Me**]$^{2-}$ model (the S−C−C−S torsion angle = 2.74° for **6** and 3.46° for [**7-Me**]$^{2-}$), the C_2S_2 unit in **7** has a 14.85° S−C−C−S torsion angle, which may largely be attributed to the steric repulsion between the bulky ligands and the packing effects. The bonding parameters involving heteroatoms in **7** [d_{S-C} in the C_2S_2 unit = 1.734(4) Å, d_{Si-O} = 1.640(3) Å, d_{Si-S} = 2.0206(15) Å] are comparable to those in the simplified [**7-Me**]$^{2-}$ model [d_{S-C} in the C_2S_2 unit = 1.756 Å, d_{Si-O} = 1.700 Å, d_{Si-S} = 2.044 Å].[22] Furthermore, each terminal sulfur atom residing on the silicon atoms of [**7-Me**]$^{2-}$ has a negative charge of −0.97, which is similar to that in [**6-Me**]$^{2-}$ (−0.99).

The first stable naked dithiolene radical anion **3**$^{\bullet}$ has been synthesized by reaction of the lithium dithiolene radical anion **2**$^{\bullet}$ with an imidazolium chloride, $[\{(Me)CN(i\text{-}Pr)\}_2CH]^+[Cl]^-$. Radical **3**$^{\bullet}$, together with hexasulfide (**4**) and $NHSi^{Dipp}$ (**5**), affords a three-component-synergic THF ring-opening, rendering compounds **6** and **7**. This three-component system may be employed as a new platform to open other cyclic ether rings.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08495.

Syntheses, computations, and X-ray crystal determination (PDF)

Crystallographic data for compounds **3**$^{\bullet}$, **4**, **6**, and **7**·**toluene** (CIF)

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Notes

The authors declare no competing financial interest.

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