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Communication

Activation of Ammonia by a Carbene-Stabilized Dithiolene Zwitterion

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ABSTRACT: A carbene-stabilized dithiolene zwitterion (**3**) activates ammonia, affording **4**• and **5**, through both single-electron transfer (SET) and hydrogen atom transfer (HAT). Reaction products were characterized spectroscopically and by single-crystal X-ray diffraction. The mechanism of the formation of **4**• and **5** was probed by experimental and computational methods. This discovery is the first example of metal-free ammonia activation via HAT.

The utilization of ammonia in homogeneous catalysis, and as a carbon-free fuel, is intriguing due to its high energy density, low cost, and substantial global production[1] (presently exceeding 150 million tonnes annually).[2−4] Although transition metal complexes have demonstrated the capability to activate a number of E−H bonds (E = H, B, Si, and C), their utility in ammonia activation remains limited. This is largely due to the pronounced tendency of ammonia to form stable Werner-ammine coordination complexes with transition metals coupled with the considerable N−H bond dissociation energy[5] (107 kcal mol^{-1}) of ammonia.[2] Nonetheless, transition metal-mediated activation of ammonia may involve oxidative addition,[6−15] deprotonation,[16] and hydrogen atom transfer[17−19] (HAT) reactions.[6−33]

Considering their lower toxicity and greater natural abundance, mimicking the reactivity of transition metals with main group elements represents a promising research field.[34] Bertrand previously reported cyclic (alkyl)(amino)carbene (CAAC)-mediated ammonia activation through oxidative addition.[35] A series of heavier group 14 analogues of carbenes,[36−42] *m*-terphenyl-anchored Ga(I) species,[43] P(III)-pincer complexes,[44−47] and Si = E (E = Si[48] and O[49]) bonds were subsequently employed to activate ammonia.[50−53] Interestingly, both an N-heterocyclic carbene and a cationic P(III)-pincer complex have been reported to accomplish reversible NH_3 activation.[54,55] Frustrated Lewis pairs (FLPs) have also been reported to activate ammonia via deprotonation.[56−59] Notably, metal-free ammonia activation via hydrogen atom transfer has not been achieved.

The non-innocence of dithiolene ligands (Figure 1) has played a pivotal role in the abundant redox chemistry of transition metal dithiolene complexes.[60] In contrast to ene-1,2-dithiolates (L^{2-}), the neutral dithiolenes (L^0) are electron-deficient and may serve as an electron acceptor.[61] In addition to the well-documented 1,2-dithiones and 1,2-dithietes,[61−64] neutral dithiolenes (L^0) may also exist as a zwitterion (Figure 1) through Lewis base coordination. Indeed, this laboratory recently reported carbene-complexed dithiolene (L^0) zwitterions [such as **3** (Scheme 1), in which carbene is ^{Me}CAAC[65−68]

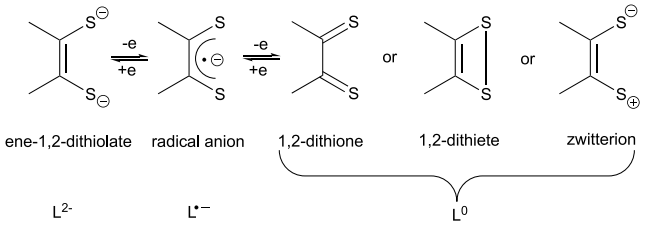
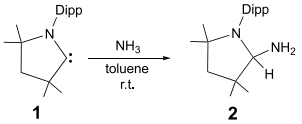


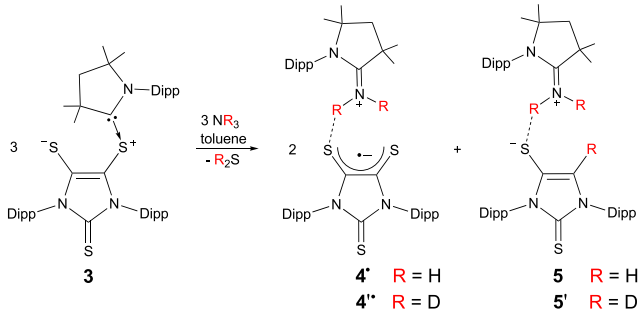
Figure 1. Redox states of dithiolene ligands.

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

Ammonia activation via oxidative addition:



Ammonia activation via SET and HAT:



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(**1**)] by reactions of carbenes with an imidazole-based dithione dimer.[69] Herein, we report the unusual capability of **3**, as a metal-free molecular system, to activate ammonia via both single-electron transfer (SET) and hydrogen atom transfer (HAT).

As previously observed by Bertrand,[35] oxidative addition (Scheme 1) occurs when **1** is combined with ammonia in toluene, quantitatively giving **2** as colorless crystals (Figure S1).[70] The ^{1}H NMR spectrum of **2** (in C_6D_6) exhibits a doublet resonance at 0.93 ppm for the NH_2 unit and a triplet at 4.40 ppm for the proton at the carbene carbon atom. In contrast, room-temperature reaction of **3** with NH_3 results in a mixture containing both **4**$^\bullet$ and **5** (Scheme 1), which can be separated by multiple recrystallizations. Radical **4**$^\bullet$ (dark purple crystals) and compound **5** (colorless crystals) were isolated in 85.2% and 70.4% yield, respectively. The formation of H_2S as a byproduct (Scheme 1) was confirmed by the lead acetate paper analysis technique[71] (Figure S4).[70]

The paramagnetic nature of **4**$^\bullet$ was probed by EPR spectroscopy. The EPR spectrum of **4**$^\bullet$ in tetrahydrofuran (THF) at 298 K (Figure 2a) exhibits an $S = 1/2$ quintet (g_{av} = 2.014) due to hyperfine coupling with two equivalent ^{14}N (I = 1) nuclei, $A_{av}(^{14}N)$ = 4.3 MHz. It compares well to those of compounds containing the same "naked" dithiolene radical unit [g_{av} = 2.017, $A_{av}(^{14}N)$ = 4.1 MHz for **6**$^\bullet$ (with an imidazolium countercation);[72] g_{av} = 2.014, $A_{av}(^{14}N)$ = 4.4 MHz for **9**$^\bullet$ (with a $Cp^*_2Co^+$ countercation)[70]]. The density functional theory (DFT) computations of **4**$^\bullet$ at the B3LYP/6-311G** level reveal that the singly occupied molecular orbital (SOMO) (Figure 2b) involves both C−C π-bonding and C−S π-antibonding character. Notably, the unpaired electron is predominately localized on the C_2S_2 unit in **4**$^\bullet$ (the spin density of the C_2S_2 unit = 0.82).

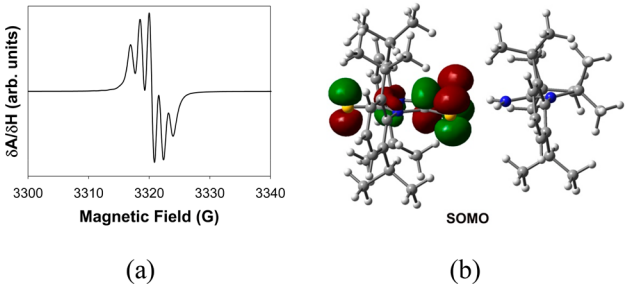

Figure 2. (a) Room-temperature X-band EPR spectrum of **4**$^\bullet$ in THF. The spectrum was recorded at 9.358 GHz with a modulation amplitude of 0.2 G and a microwave power of 1.0 mW. (b) SOMO of **4**$^\bullet$.

X-ray structural analysis (Figure 3) shows that **4**$^\bullet$ exists as a (^{Me}CAAC-based iminium cation/dithiolene radical anion) adduct in the solid state.[70] The hydrogen atoms on the N(4) atom were located from the difference Fourier map. While consistent with the corresponding theoretical values [$d_{C=N}$ = 1.303 Å, d_{C-C} = 1.431 Å, $d_{C-S(av)}$ = 1.697 Å],[70] the structural parameters of the iminium fragment [$d_{C(28)=N(4)}$ = 1.304(3) Å] and the C_2S_2 unit of the anionic dithiolene moiety [d_{C-C} = 1.421(3) Å, $d_{C-S(av)}$ = 1.674(2) Å] in **4**$^\bullet$ are comparable with those for ([^{Me}CAAC = NH_2]N_3)$_2$·H_2O (**7**)[73] [$d_{C=N}$ = 1.3037(19) Å] and for **6**$^\bullet$[72] [d_{C-C} = 1.420(2) Å, $d_{C-S\ (av)}$ = 1.667(2) Å], respectively. The Wiberg bond indices (WBIs) of C−S bonds in the C_2S_2 unit of **4**$^\bullet$ (1.36, av) indicate their partial double-bond character. Each of the two sulfur atoms in the C_2S_2 unit of **4**$^\bullet$ bears a negative charge of ca. −0.26. Besides the predominant electrostatic forces, there also exists the N(4)−H(4B)···S(3) hydrogen bonding interaction [$d_{H(4B)\cdots S(3)}$ = 2.301(17) Å, $d_{N(4)\cdots S(3)}$ = 3.175(2) Å, $\theta_{N(4)-H(4B)\cdots S(3)}$ = 169.0(2)°] between the anionic dithiolene moiety and the iminium cation in **4**$^\bullet$.[74,75] Compound **5** may be regarded as a derivative of **4**$^\bullet$ by *formally* replacing one neutral sulfur atom from the C_2S_2 unit in **4**$^\bullet$ with one hydrogen atom (i.e., H$^\bullet$). The hydrogen atoms on the C(3) and N(4) atoms in **5** were located from the difference Fourier map (Figure 3). The anionic moiety of **5** is the same as that of the reported lithium monothiolate (**8**).[76] Both **5** and **8** exhibit similar bonding parameters [for **5**, $d_{C=C}$ = 1.352(4) Å, $d_{C(2)-S(2)}$ = 1.713(3) Å; for **8**, $d_{C=C}$ = 1.355(5) Å, $d_{C(3)-S(2)}$ = 1.716(4) Å]. By comparison with those [WBI_{C-S} = 1.36, av; charge on each sulfur atom ≈ −0.26] for the C_2S_2 unit of **4**$^\bullet$, compound **5** has a decreased WBI value (1.17) of the C(2)−S(2) bond and increased negative charge of −0.50 on the S(2) atom. Similar to **4**$^\bullet$, there exists a N(4)−H(4A)···S(2) hydrogen bond between the iminium cation and the thiolate unit in **5** [$d_{H(4A)\cdots S(2)}$ = 2.37(2) Å, $d_{N(4)\cdots S(2)}$ = 3.230(3) Å, $\theta_{N(4)-H(4A)\cdots S(2)}$ = 167.0(3)°].[74,75]

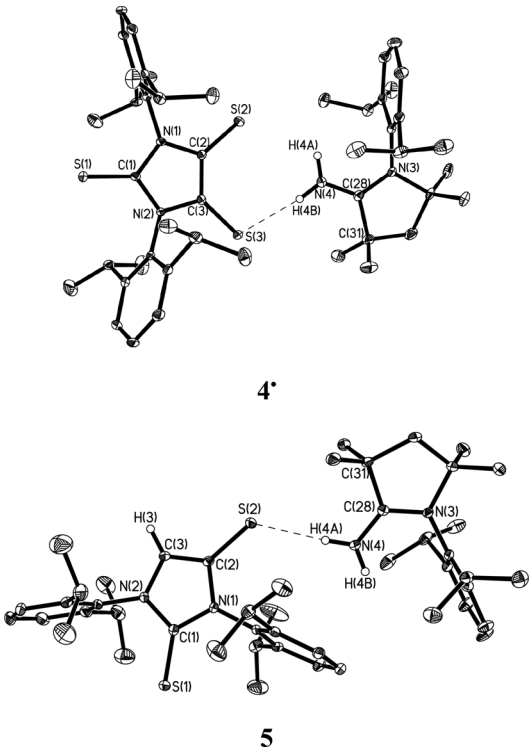

Figure 3. Molecular structures of **4**$^\bullet$ and **5**. Thermal ellipsoids represent 30% probability. Hydrogen atoms on carbon atoms [except for C(3) in **5**] have been omitted for clarity. Selected bond distances (Å) and angles (deg): for **4**$^\bullet$, C(1)−S(1), 1.659(2); C(2)−C(3), 1.421(3); C(2)−S(2), 1.671(2); C(28)−N(3), 1.314(3); C(28)−C(31), 1.506(3); C(28)−N(4), 1.304(3); S(2)−C(2)−C(3), 130.61(15); C(31)−C(28)−N(3), 112.67(17); C(31)−C(28)−N(4), 124.2(2); N(3)−C(28)−N(4), 123.1(2); for **5**, C(1)−S(1), 1.678(3); C(2)−C(3), 1.352(4); C(2)−S(2), 1.713(3); C(28)−N(3), 1.315(3); C(28)−C(31), 1.496(4); C(28)−N(4), 1.313(3); S(2)−C(2)−C(3), 131.1(2); C(31)−C(28)−N(3), 112.5(2); C(31)−C(28)−N(4), 123.2(2); N(3)−C(28)−N(4), 124.2(3).

The room-temperature ^{1}H NMR spectrum (in THF-d_8) of **5** exhibits a singlet imidazole resonance at 6.09 ppm, which is similar to that (6.14 ppm) of **8**.[76] However, the iminium

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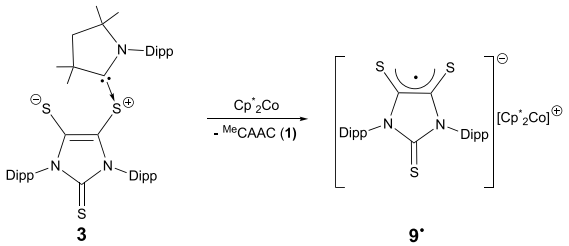
proton resonance of **5** can only be observed at decreased temperatures according to variable-temperature ^{1}H NMR spectroscopic study of **5** (Figure S11).[70] The ^{1}H NMR spectrum of **5** (in THF-d_8, at −40 °C, Figure S10)[70] exhibits two broad singlet resonances (7.79 and 12.75 ppm) for the two iminium protons. The same ^{Me}CAAC-based iminium salt (with an azide counteranion) (**7**) exhibits a broad iminium (and H_2O) ^{1}H NMR resonance at 6.2 ppm (in $CDCl_3$).[73] The significant downfield shift of the iminium proton resonance (12.75 ppm) of **5** should be ascribed to the N−H···S$^-$ hydrogen bond in **5** (Figure 3).[77] The infrared (IR) spectra[70] of both **4**$^\bullet$ and **5** exhibit a H−N−H scissoring (mixed with C═N stretching) absorption at 1655 cm^{-1}, indicating the existence of a C═NH_2 fragment in **4**$^\bullet$ and **5**.[78] Considering the significant red-shift effect of the N−H···S$^-$ hydrogen bond on the N−H stretch,[79] for both **4**$^\bullet$ and **5**, only the absorption at 3379 cm^{-1} was assigned to the N−H stretch.

The **3**-to-**4**$^\bullet$ conversion indicates that the electron-deficient dithiolene (L^o) core may act as an electron reservoir to accept one electron from ammonia via SET, giving an ammoniumyl radical cation (i.e., $NH_3^{\bullet+}$) as an elusive intermediate. Notably, the formation of $NH_3^{\bullet+}$ involving an electron transfer (ET) mechanism has been proposed for electrochemical ammonia oxidation.[80] As a zwitterion, **3** exhibits a 2.08 eV HOMO−LUMO energy gap.[69] The low-lying LUMO (−2.35 eV) of **3**,[69] involving mainly C_{CAAC}−N π-antibonding character, may serve as the electrophilic site to initiate the SET reaction of ammonia. Interestingly, our computations show that single electron reduction of **3** results in its dissociation, giving a "naked" anionic dithiolene radical and a free ^{Me}CAAC (**1**) ligand. This is further confirmed by Cp*$_2$Co-mediated single electron reduction of **3**, which gives the anionic "naked" dithiolene radical (**9**$^\bullet$) (Dipp = 2,6-diisopropylphenyl, Scheme 2).[70]

Scheme 2. Synthesis of 9$^\bullet$



Computations[70] (Figure 4a) reveal that the subsequent reaction of the in situ released ^{Me}CAAC (**1**) (as a nucleophile) with the highly reactive $NH_3^{\bullet+}$ species is energetically favored and would give a [carbene-NH_3]$^{\bullet+}$ adduct (i.e., intermediate **I**). Dissociation of intermediate **I**, via a transition state (**TS**) with an energy barrier of 17.6 kcal mol^{-1}, results in the ^{Me}CAAC-based iminium cation (**II**) (which will couple with the already-formed "naked" dithiolene radical anion to give **4**$^\bullet$) and one hydrogen atom. The N−H bond dissociation energy (BDE) for the intermediate **I** (6.0 kcal mol^{-1}) is drastically lower than that for ammonia (107 kcal mol^{-1}).[5]

While hydrogen atoms (H$^\bullet$) could dimerize to evolve H_2 gas, isolation of **5** (in 70.4% yield) and detection of the H_2S byproduct (Scheme 1) suggest that the hydrogen atoms (produced from the dissociation of **I**, Figure 4a) may mainly (ca. 70% hydrogen atoms) participate in multiple HAT

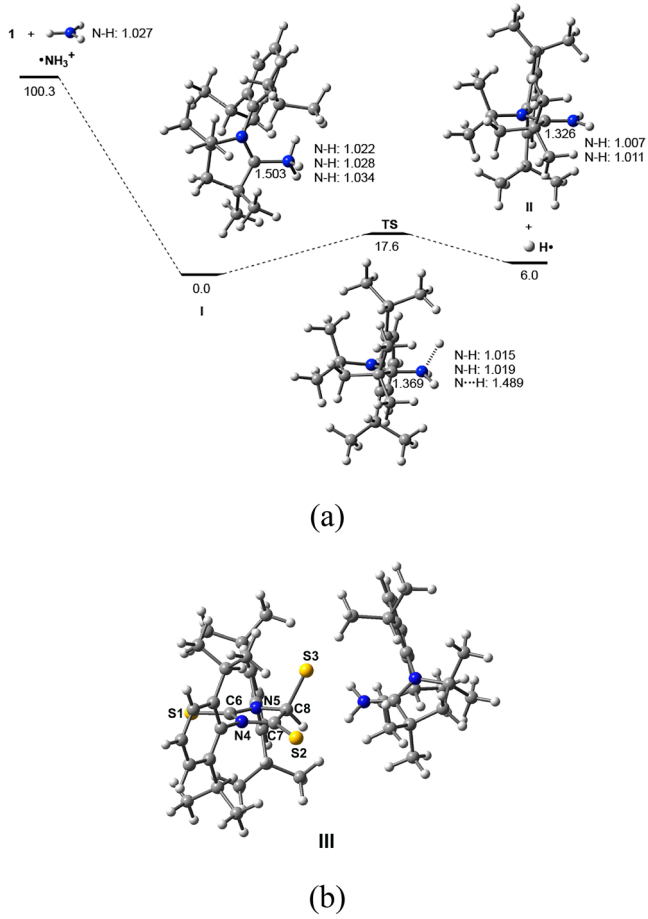


Figure 4. (a) Calculated relative energies (kcal mol^{-1}) for the reaction of ^{Me}CAAC (**1**) with $NH_3^{\bullet+}$ at the B3LYP/6-311G** level and drawings of intermediate **I**, transition state (**TS**), and iminium **II** (the cationic moiety of **4**$^\bullet$) with selected bond distances (Å). (b) The optimized structure of intermediate **III** (at the B3LYP/6-311G** level). Selected bond distances (Å): C(6)−S(1), 1.658; C(7)−C(8), 1.510; C(7)−S(2), 1.669; C(8)−S(3), 1.841.

processes involved in the **4**$^\bullet$-to-**5** conversion (formation of one equivalent of **5** requires three equivalents of hydrogen atoms; see eqs 1 and 2). Although the mechanistic details of the **4**$^\bullet$-to-**5** conversion remain unclear, computations[70] suggest that the energetically favored radical coupling reaction (ΔE = −54.7 kcal mol^{-1}, eq 1) of **4**$^\bullet$ with one equivalent of hydrogen atom (H$^\bullet$) may afford an intermediate **III** (Figure 4b), with the hydrogen atom bonding to one backbone carbon (i.e., C8) of the imidazole ring. Subsequent reaction of **III** with two equivalents of H$^\bullet$, producing one equivalent of **5** and one equivalent of H_2S (eq 2), is also thermodynamically favored (ΔE = −124.6 kcal mol^{-1}).

$$4^\bullet + H^\bullet \rightarrow \textbf{III} \quad \Delta E = -54.7\ \text{kcal mol}^{-1} \tag{1}$$

$$\textbf{III} + 2H^\bullet \rightarrow \textbf{5} + H_2S \quad \Delta E = -124.6\ \text{kcal mol}^{-1} \tag{2}$$

To further experimentally investigate whether the imidazole proton [i.e., H(3)] of **5** is transferred from NH_3, the parallel reaction of **3** with ND_3 (99 atom % D) was investigated, which gave both **4**$^{\bullet\prime\bullet}$ and **5**′ (Scheme 1), the deuterium analogues of **4**$^\bullet$ and **5**, respectively. The obviously weakened intensity of imidazole (at 6.09 ppm) and iminium (at 7.82 and 12.78 ppm) proton resonances of **5**′ (observed in the ^{1}H NMR spectrum at

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−40 °C, Figure S17)[70] supports that the imidazole proton of **5** is acquired from ammonia. In addition, this result also reveals that there exists the H/D exchange[81] between ND_3 and the reaction mixture during the reaction. The IR spectroscopic study[70] reveals the N−D stretches[82] [2504 and 2234 cm^{-1} (involving the N−D···S^- bond)[79]] for **4′•** and the C−D stretch[83] (2203 cm^{-1}) and N−D stretches [2488 and 2153 cm^{-1} (involving the N−D···S^- bond)] for **5′**. Observation of the C−H stretching band (with a decreased band intensity) at 3379 cm^{-1} in the IR spectra (Figures S14 and S15)[70] of **4•′•** and **5′** provides further evidence for the H/D exchange involving ND_3 and the reaction mixture.[81]

While ^{Me}CAAC (**1**) activates ammonia via oxidative addition, the ^{Me}CAAC-stabilized dithiolene (L^0) zwitterion (**3**) exhibits its unique capability of activating ammonia to give both **4•** and **5** via SET and HAT processes. This discovery suggests that carbene (or other Lewis base)-stabilized dithiolene (L^0) zwitterions may be employed as a new type of metal-free bifunctional molecular system: while the neutral dithiolene (L^0) unit serves as an electron reservoir, the in situ released Lewis base species [due to single-electron reduction of the dithiolene (L^0) ligand] may act as a nucleophile. Their unique synergic interaction may result in unusual applications for small-molecule activation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07920.

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

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 2192837−2192842 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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