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.

Utilizing ammonia as a carbon-free alternative fuel and in homogeneous catalysis is intriguing due to its high energy density, low cost, and substantial global production[1] (presently exceeding 150 million tons annually).[2-4] Although transition metal complexes have demonstrated the capability to activate a number of E–H bonds (such as E = H, B, Si, and C), their utility in ammonia activation is still 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] Transition metal-mediated N–H bond cleavage of ammonia may involve oxidative addition,[6-15] deprotonation,[16] and hydrogen atom transfer[17-19] (HAT) reactions.[6-33] Considering the lower toxicity, higher natural abundance of main group species, mimicking the reactivity of transition metals with main group elements represents a remarkable 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] and P(III) pincer complexes[44-47] were subsequently employed to activate ammonia.[48-51] An iminodisilene was shown to activate ammonia either via an anti-addition pathway (giving the hydroamination product) or through the Si=Si bond cleavage (giving the oxidative addition product of the silylene unit).[52] Interestingly, both an N-heterocyclic carbene and a cationic P(III)-pincer complex have been reported to conduct reversible NH_3 activation.[53,54] In addition, frustrated Lewis pairs (FLPs) have been reported to activate ammonia via deprotonation.[55-58] Notably, metal-free ammonia activation via hydrogen atom transfer has not been achieved.

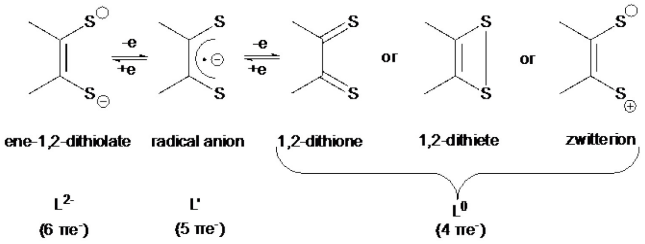
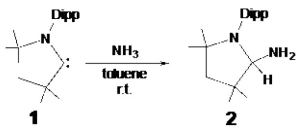


Figure 1. Redox states of dithiolene ligands.

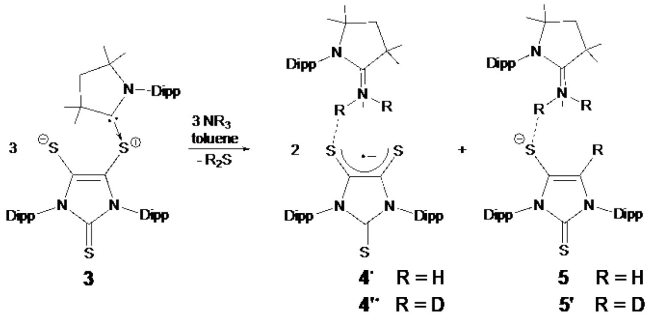
The non-innocence of dithiolene ligands (Figure 1) has played a pivotal role in the abundant redox chemistry of transition metal dithiolene complexes.[59] In contrast to ene-1,2-dithiolates (L^{2-}, containing 6π-electrons), the 4πe-containing neutral dithiolenes (L^0) are electron-deficient and may serve as an electron-acceptor.[60] In addition to the well documented 1,2-dithiones and 1,2-dithietes,[60-63] 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[64] (**1**)] by reactions of carbenes with an imidazole-based dithione dimer.[65] 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).

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

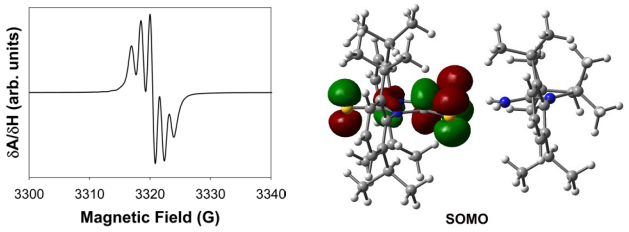
Ammonia activation via oxidative addition:



Ammonia activation via SET and HAT:



As Bertrand's discovery,[35] the oxidative-addition (Scheme 1) occurs when **1** is combined with ammonia in toluene, quantitatively giving **2** as colorless crystals[35] (Figure S1).[66] 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, the room-temperature reaction of **3** with NH_3 results in a mixture containing both **4•** and **5** (Scheme 1), which can be separated by multiple-step recrystallization. Radical **4•** (dark purple crystals) and compound **5** (colorless crystals) were isolated in 85.2% yield and in 70.4% yield, respectively. The formation of H_2S as a by-product (Scheme 1) was confirmed by the lead acetate paper analysis technique.[67] (Figure S4).[66]



(a) (b)

Figure 2. (a) Room-temperature X-band EPR spectrum of **4•** 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•**.

The paramagnetic nature of **4•** was probed by EPR spectroscopy. The EPR spectrum of **4•** in THF at 298 K (Figure 2a) exhibits a S = ½ 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•** (with an imidazolium counter-cation)[68]; g_{av} = 2.014, $A_{av}(^{14}N)$ = 4.4 MHz for **9•** (with a $Cp^*_2Co^+$ counter-cation)[66]]. The DFT computations of **4•** at the B3LYP/6-311G** level reveals that the SOMO (Figure 2b) involves both C–C π-bonding and S–C π-antibonding character. The unpaired electron is mainly localized on the C_2S_2 unit in **4•** (the spin density of the C_2S_2 unit = 0.82).

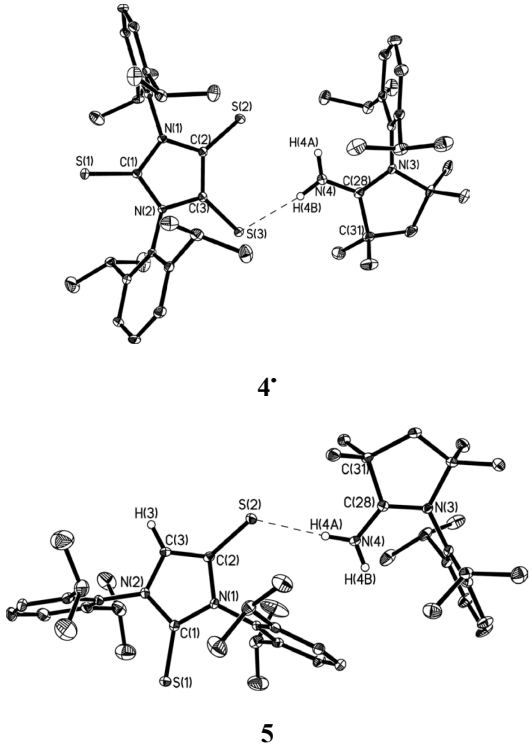


Figure 3. Molecular structures of **4•**, and **5**. Thermal ellipsoids represent 30% probability. Hydrogen atoms on carbon atoms [except for C(3) in **5**] have been omitted for clarity. Selected bond distances (Å) and angles (deg): For **4•**, S(1)–C(1), 1.659(2); C(2)–C(3), 1.421(3); C(2)–S(2), 1.671(2); 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**, S(1)–C(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).

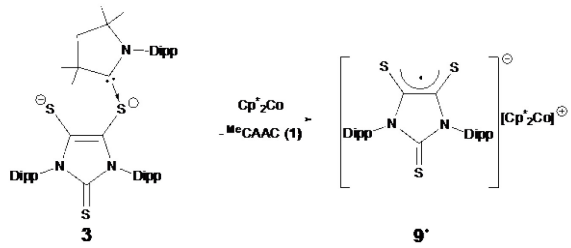
X-ray structural analysis (Figure 3) shows that **4•** exists as a (^{Me}CAAC-based iminium cation/dithiolene radical anion) adduct in the solid state.[66] The hydrogen atoms on the N(4) atom were located from difference Fourier map. While being consistent with the corresponding theoretical values [$d_{C=N}$ = 1.303 Å, d_{C-C} = 1.431 Å, $d_{C-S\ (av)}$ = 1.697 Å],[66] 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•** are comparable with those for ([^{Me}CAAC=NH_2]N_3)$_2$·H_2O (**7**)[69] [$d_{C=N}$ = 1.3037(19) Å] and for **6•**[68] [d_{C-C} = 1.420(2) Å, $d_{C-S\ (av)}$ = 1.667(2) Å], respectively. The Wiberg bond indices (WBIs) of S–C bonds in the C_2S_2 unit of **4•** (1.36, av) indicate their partial double bond character. Each of the two sulfur atoms in the C_2S_2 unit of **4•** 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 dithi-

olene moiety and the iminium cation in **4**•.[70,71] Compound **5** may be regarded as a derivative of **4**• by *formally* replacing one neutral sulfur atom from the C_2S_2 unit in **4**• with one hydrogen atom (i.e., H•). The hydrogen atoms on the C(3) and N(4) atoms in **5** were located from difference Fourier map (Figure 3). The anionic moiety of **5** is the same as that of the reported lithium monothiolate (**8**).[72] 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 = ca. -0.26] for the C_2S_2 unit of **4**•, 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**•, 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)°].[70,71]

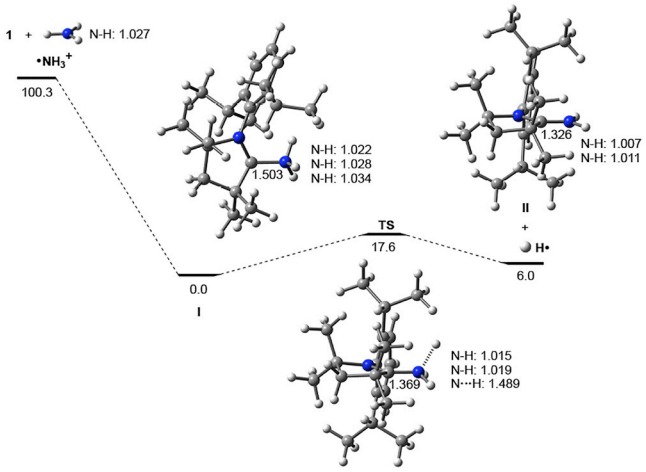
The room-temperature ^{1}H NMR spectrum (in THF-d_8) of **5** exhibits a singlet imidazole resonance at 6.09 ppm, which is similar to that (6.14 ppm) of **8**.[72] However, the iminium proton resonance of **5** can only be observed at decreased temperatures according to variable-temperature (VT) ^{1}H NMR spectroscopic study of **5** (Figure S11).[66] The ^{1}H NMR spectrum of **5** (in THF-d_8, at -40 °C, Figure S10)[66] exhibits two broad singlet resonances (7.79 ppm and 12.75 ppm) for the two iminium protons. The same ^{Me}CAAC-based iminium salt (with an azide counter-anion) (**7**) exhibits a broad iminium (and H_2O) ^{1}H NMR resonance at 6.2 ppm (in $CDCl_3$).[69] 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).[73] The infrared (IR) spectra[66] of both **4**• 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**• and **5**.[74] Considering the significant red-shift effect of the N–H···S$^-$ hydrogen bond on the N–H stretch,[75] for both **4**• and **5**, only the absorption at 3379 cm^{-1} was assigned to the N–H stretch.

The **3**-to-**4**• conversion indicates that the electron-deficient dithiolene core (containing 4πe) may act as an electron reservoir to accept one electron from ammonia *via* single electron transfer (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.[76] As a zwitterion, **3** exhibits a 2.08 eV HOMO-LUMO energy gap.[65] The low-lying LUMO (-2.35 eV) of **3**,[65] 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^*_2Co-mediated single electron reduction of **3**, which gives the anionic "naked" dithiolene radical (**9**•) (Dipp = 2,6-diisopropylphenyl, Scheme 2).[66]

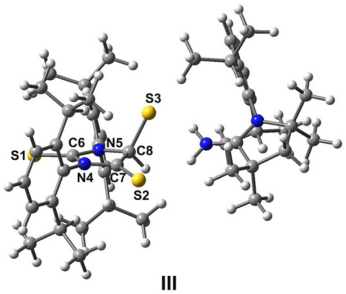
Scheme 2. Synthesis of 9•.



Our computations[66] (Figure 4a) show 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**•) 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]



(a)



(b)

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, iminium II (the cationic moiety of **4•**) 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.

While the elusive hydrogen atom (H•) may dimerize to evolve H_2 gas, isolation of **5** (in 70.4% yield) and detection of H_2S as the major by-product (Scheme 1) revealed that the hydrogen atoms produced from the dissociation of **I** (Figure 4a) may mainly (ca. 70% hydrogen atoms) participate in multiple hydrogen-atom-transfer (HAT) processes involved in the **4•**-to-**5** conversion (formation of one equivalent of **5** need consume three equivalents of hydrogen atoms, see eq. 1 and 2). Although the mechanistic details of the **4•**-to-**5** conversion remain unclear, our computations[66] suggest that the energetically-favored radical coupling reaction (ΔE = -54.7 kcal mol^{-1}, eq. 1) of **4•** with one equivalent of hydrogen atom (H•) may give an intermediate **III** (Figure 4b), in which the hydrogen atom bonds to one backbone-carbon (i.e., C8) of the imidazole ring. Subsequent reaction of **III** with two equivalents of H•, producing one equivalent of **5** and one equivalent of H_2S (eq. 2), is also thermodynamically favored (ΔE = -124.6 kcal mol^{-1}).

4• + H• ⟶ **III** ΔE = -54.7 kcal mol^{-1} (eq. 1)

III + 2H• ⟶ **5** + H_2S ΔE = -124.6 kcal mol^{-1} (eq. 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••** and **5'** (Scheme 1), the deuterium analogues of **4•** and **5**, respectively. The obviously weakened strength of imidazole (at 6.09 ppm) and iminium proton resonances (at 7.82 and 12.78 ppm) observed in the ^{1}H NMR spectrum of **5'** (in THF, -40 ºC, Figure S17)[66] supports that the imidazole proton of **5** is acquired from ammonia. In addition, this result also reveals that there exists the H/D exchange[77] between ND_3 and the reaction mixture during the reaction. The IR spectroscopic study[66] reveals the N–D stretches[78] [2504 cm^{-1} and 2234 cm^{-1} (involving the N–D···S$^-$ bond)[75]] for **4••** and the C–D stretch[79] (2203 cm^{-1}), N–D stretches [2488 cm^{-1} and 2153 cm^{-1} (involving the N–D···S$^-$ bond)] for **5'**. Observation of the C–H stretching band (with a decreased strength) at 3379 cm^{-1} in the IR spectra (Figure S14 and S15)[66] of **4••** and **5'** provides further evidence for the H/D exchange involving ND_3 and the reaction mixture.[77]

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* single-electron transfer (SET) and hydrogen atom transfer (HAT) processes. This discovery reveals that carbene (or other Lewis bases)-stabilized dithiolene (L^0) zwitterions may be employed as a new type of metal-free bi-functional molecular systems: while the 4πe 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 application for small molecule activation.

ASSOCIATED CONTENT

Supporting Information.
The supporting information is available free of charge on the ACS Publications website at DOI: xxxxxx.

Syntheses, computations, and X-ray crystal determination (PDF)
Crystallographic data for compound **2** (CIF)
Crystallographic data for compound **4•** (CIF)
Crystallographic data for compound **4••** (CIF)
Crystallographic data for compound **5** (CIF)
Crystallographic data for compound **5'** (CIF)
Crystallographic data for compound **9•** (CIF)

Cartesian coordinates for the calculated structures (XYZ)

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Notes
The authors declare no competing financial interest.

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TOC Graphic

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Activation of Ammonia by a Carbene-Stabilized Dithiolene Zwitterion

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