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# Germanium(II) Dithiolene Complexes

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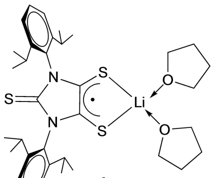
*This work is dedicated to the following professors for their contributions to main group chemistry: Hansjörg Grützmacher, Dietrich Gudat, Evamarie Hey-Hawkins, Manfred Scheer, Rainer Streubel, and Werner Uhl.*

The 1:2 reaction of the imidazole-based dithiolate (**2**) with $GeCl_2$•dioxane in THF/TMEDA gives **3**, a TMEDA-complexed dithiolene-based germylene. Compound **3** is converted to monothiolate-complexed (**5**) and N-heterocyclic carbene-complexed (**7**) germanium(II) dithiolene complexes via Lewis base ligand exchange. A bis-dithiolene-based germylene (**8**), involving a 3c–4e S-Ge-S bond, has also been synthesized through controlled hydrolysis of **7**. The bonding nature of **3**, **5**, and **8** was investigated by both experimental and theoretical methods.

## Introduction

Low oxidation-state main group chemistry emerged as an important research field during the past decades. Numerous complexes containing highly reactive low-oxidation state main group cores have been synthesized. Sterically demanding ligands (such as *m*-terphenyls,[1] carbenes,[2] and NacNacs[3]) have proven critical in the stabilization of various low-oxidation state main group species. Dithiolenes are well documented as redox non-innocent ligands[4] in transition metal-dithiolene complexes. The chemistry of the corresponding main group element-based dithiolene species has received considerably less attention.

The chemistry of germylenes, the heavier analogues of carbenes, have evolved from reaction intermediates[5] to stable[6] versatile ligands for transition metal coordination and catalysis.[7] The utility of germylenes in catalysis[8] and small molecule activation is intriguing.[8b,9] While N-heterocyclic germylenes have been extensively explored,[6e,8b,10] the corresponding S-heterocyclic germylenes have not been studied to a comparable extent.[11] Indeed, the literature reveals only one report regarding dithiolene-based germylenes.[12] This laboratory recently synthesized a sterically demanding lithium-based dithiolene radical (**1**) (Figure 1).[13] Radical **1** has been utilized in the syntheses of group 14 element (Si and Ge)-based tris(dithiolene)dianions,[14] with the silicon and germanium atoms residing in the +4 oxidation state. Herein, we report the first structurally characterized TMEDA (tetramethylethylenediamine)-complexed dithiolene-based germylene (**3**). Compound **3** may be converted to monothiolate or NHC (i.e., N-heterocyclic carbene)-complexed dithiolene-based germylenes (**5** and **7**) via ligand exchange reactions. A bis-dithiolene-based germylene dianion (**8**), containing a 3c–4e S-Ge-S bond, was also synthesized via controlled hydrolysis of **7**.



**1**

**Figure 1.** Stable lithium-based dithiolene radical (**1**).

## Results and Discussion

The monoanionic dithiolene radical **1** may be readily converted to the corresponding dithiolate **2** via potassium graphite ($KC_8$)-mediated one-electron reduction.[15] Reaction of the in-situ prepared **2** with $GeCl_2$•dioxane (in a molar ratio of 1:1.2) in THF/TMEDA mixed solvent gives **3** as colourless crystalline solid (in 48% yield) (Scheme 1). X-ray quality single crystals of **3** can be obtained by recrystallization in toluene/hexane mixed solvent. The subsequent Lewis base ligand exchange study showed that while being inert toward $P(NMe_2)_3$, **3** may react with the imidazole-based monothiolate[13] (**4**) and NHC$^{iPr}$ (**6**),[16] rendering **5** (72% yield) and **7** (61%), respectively (Scheme 1). The $^1H$ NMR olefin resonance[17] of **5** (6.90 ppm in THF-$d_8$) is lower field shifted than that of **4** (6.14 ppm in THF-$d_8$).[13] While X-ray quality colourless crystals of **5** can be obtained via

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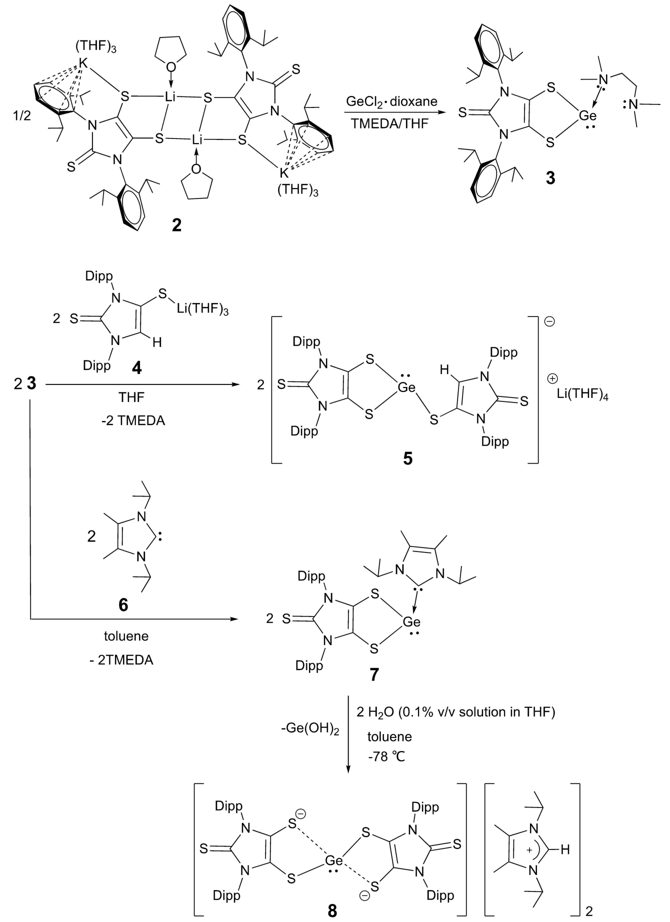
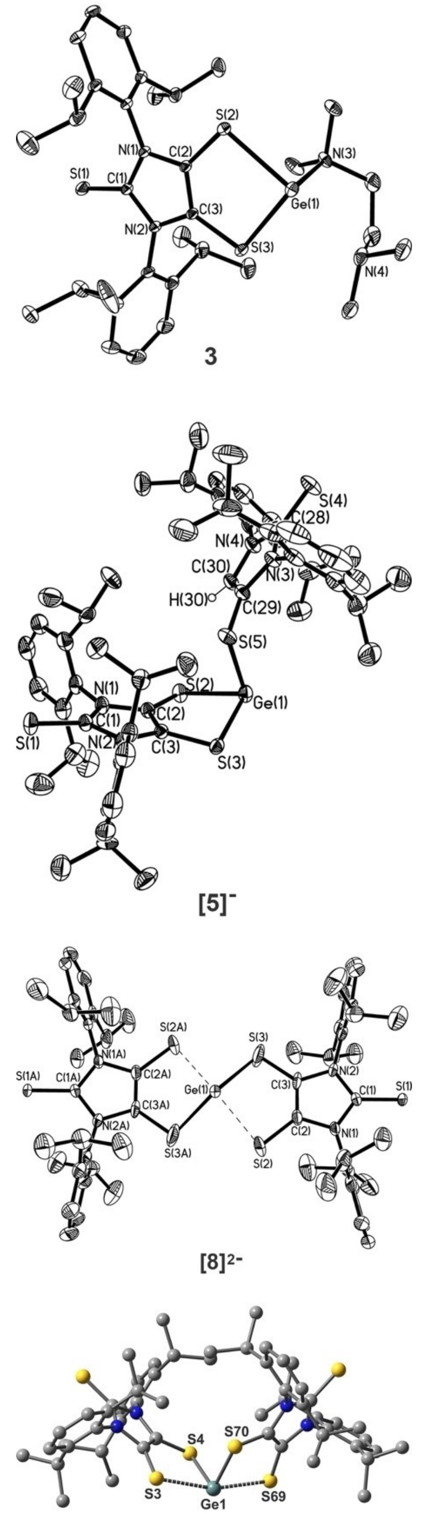


**Scheme 1.** Synthesis of **3**, **5**, **7** and **8** (Dipp = 2,6-diisopropylphenyl).

recrystallization in THF/hexane, our efforts toward obtaining X-ray single crystals of **7** were repeatedly unsuccessful. The methine $^1$H NMR resonance[17] of the NHC$^{iPr}$ moiety in **7** (5.97 ppm in THF-$d_8$), while being shifted downfield relative to that of the free NHC$^{iPr}$ ligand (**6**) (3.95 ppm in $C_6D_6$),[16] compares to that of the NHC$^{iPr}$-coordinated germanium(IV) bis(dithiolene) complex (6.26 ppm in $C_6D_5F$).[14b] Inspired by our previous discovery that the germanium(IV) tris(dithiolene)dianion may be prepared via NHC-mediated partial hydrolysis,[14b] the 1 : 1 combination of **7** with water (as 0.1% v/v solution in THF) at low-temperature in toluene afforded **8** as yellow crystalline solid (in 54% yield) (Scheme 1). The singlet $^1$H NMR resonance[17] (8.43 ppm in $CD_3CN$) of **8** supports the presence of the imidazolium moiety in this compound. Notably, **8** is extremely air- and moisture-sensitive. Even in the glovebox under argon atmosphere, yellow crystals of **8** readily decompose (as evidenced by the colour changing into purple).

Single-crystal X-ray diffraction analyses and DFT computations (wB97xd[18]/6-311G** level) are employed to probe the nature of **3**, **5**, and **8**.[17] In the solid state (Figure 2), the five-membered dithiolene-germanium ring in **3** is slightly bent. The bend angle ($\eta = 8.6°$) between the $C_2S_2$ plane and $GeS_2$ plane in **3** compares well to the calculated value of **3** ($\eta = 9.8°$). The three-coordinate germanium atom in **3**, adopting a distorted


**3**

**[5]$^-$**

**[8]$^{2-}$**

**[8]$^{2-}$ model**

**Figure 2.** Molecular structures of **3**, the anionic unit of **5**, the anionic unit of **8**, and **[8]$^{2-}$-model**. Thermal ellipsoids represent 30% probability (for **3**, **[5]**$^-$, and **[8]**$^{2-}$): hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): For **3**, C(2)-C(3) 1.354(2), C(2)-S(2) 1.7271(17), Ge(1)-S(2) 2.4300(5), Ge(1)-N(3) 2.220(5); C(2)-C(3)-S(3) 126.10(13), C(2)-S(2)-Ge(1) 96.93(5), S(2)-Ge(1)-N(3) 91.11(14). For **[5]**$^-$, C(2)-C(3) 1.351(4), C(2)-S(2) 1.731(3), Ge(1)-S(2) 2.3719(8), Ge(1)-S(5) 2.3451(9); C(2)-C(3)-S(3) 125.8(2), C(2)-S(2)-Ge(1) 93.81(9), S(2)-Ge(1)-S(5) 96.86(3). For **[8]**$^{2-}$**-model**, C8-C9 1.359, C8-S3 1.732, Ge1-S4 2.430, Ge1-S3 2.757; S4-Ge1-S70 99.0, S3-Ge1-S69 165.0.

trigonal pyramidal geometry, bonds to two sulphur atoms of the dithiolene ligand and one nitrogen atom of the TMEDA solvent molecule. Both the experimental (2.390 Å, av) and theoretical (2.351 Å, av) Ge–S bond distances of **3** are comparable with those of the anionic chlorogermanium(IV)-bis(dithiolene) complex [2.3290(8)–2.3561(8) Å].[13] The TMEDA moiety in **3** is disordered. The experimental Ge–N bond distance in **3** (2.204 Å, av) is ca. 0.17 Å shorter than the corresponding theoretical value (2.379 Å). However, both of values reside within the range [from 2.157(5) Å to 2.458(5) Å] of the dative Ge–N bond distances in the TMEDA-chelated Ge(II)$Cl_2$ complex.[19]

X-ray structural analysis shows that **5** exists as an ionic pair.[17] The lithium cation in **5** is coordinated by four THF molecules. The anionic moiety of **5** (Figure 2) involves a dithiolene-based germanide species, wherein the three-coordinate germanium atom, in a distorted trigonal pyramidal geometry, is embraced by two sulphur atoms from the dithiolene ligand and one sulphur atom from the anionic monothiolate ligand. The Ge-S bond distances in **5** [2.3451(9)–2.3749(8) Å] are similar to those in **3** (2.390 Å, av) and in [$(Me_3Si)_3CS]_3GeLi(THF)$ (2.405–2.420 Å).[20] The $C_2S_2Ge$ ring in **5** [$\eta = 29.3°$ (experimental); 31.4° (theoretical)] is obviously more puckered than that in **3** [$\eta = 8.6°$ (experimental); 9.8° (theoretical)]. Considering the steric crowding of the dithiolene ligand and the imidazole-based monothiolate ligand in **5**, LDF (London dispersion force) may have a remarkable effect on the conformation of the $C_2S_2Ge$ ring in **5**.[21] The structural parameters of the $C_2S_2$ units of both **3** [$d_{C=C} = 1.354(2)$ Å; $d_{C-S} = 1.731$ Å, av] and **5** [$d_{C=C} = 1.351(4)$ Å; $d_{C-S} = 1.734$ Å, av] are comparable with those in reported dithiolates.[4a] The germanium atoms in **3** and **5** reside in the oxidation state of +2. Natural bond orbital (NBO) analysis shows that the germanium atom in **3** bears a positive charge of +0.68, while that in **5** has a positive charge of +0.44. The Ge-S bonds in both **3** and **5** have dominant 4p character at the germanium atom.

X-ray structural analysis confirms that the bis(dithiolene)germanium unit in **8** is dianionic (Figure 2), with two imidazolium counter-cations. Like the imidazole proton [i.e., H(30)] of the monothiolate ligand in **5** (Figure 2), the protons of the imidazolium units in **8** were located from the difference Fourier map. Both the Ge(1) and S(3) atoms in **8** are crystallographically disordered.[17] Thus, only the computed structural values of the **[8]**$^{2-}$ model (Figure 2) will be discussed. The $GeS_4$ core in the **[8]**$^{2-}$ model adopts a distorted seesaw geometry ($S_4$-$Ge_1$-$S_{70}$ bond angle = 99.0°; $S_3$-$Ge_1$-$S_{69}$ bond angle = 165.0°). The Ge-$S_{ax}$ (i.e., $S_3$ and $S_{69}$) distances (2.758 Å, av) are considerably longer than the Ge-$S_{eq}$ (i.e., $S_4$ and $S_{70}$) bonds (2.430 Å, av) in the **[8]**$^{2-}$ model and the sum of the covalent radii of the germanium and sulphur atoms (2.25 Å).[22] Similar bonding parameters have been reported for the bis(anisobidentate dithiophosphinate)germanium(II) complex ($d_{Ge-S(ax)} = 2.722$ Å, av; $d_{Ge-S(eq)} = 2.415$ Å, av).[23] In addition, in the **[8]**$^{2-}$ model, the C-$S_{ax}$ bonds (1.732 Å) are shorter than the C-$S_{eq}$ bonds (1.745 Å), which, coupled with the Wiberg bond index (WBI) of the C-$S_{ax}$ bonds (1.15), suggests modest double bond character of the C-$S_{ax}$ bonds. In contrast to the germanium atom, bearing a positive charge of +0.54, the $S_{ax}$ atoms in the **[8]**$^{2-}$ model have a negative charge of −0.35. While being covalently bonded to two $S_{eq}$ atoms, the germanium atom in the **[8]**$^{2-}$ model accepts the electron donation from the two anionic thiolate groups (i.e., $S_3$ and $S_{69}$) to form a 3c–4e S-Ge-S bond. Thus, the Ge atom in **[8]**$^{2-}$ model is in +2 oxidation state.

Molecular orbital studies (Figure 3) show that the HOMOs of **3**, **[5]**$^{-}$, and **[8]**$^{2-}$ models are mainly dithiolene ligand-based, involving both C–C π-bonding and C–S π-antibonding character. The HOMO-2 of **3**, HOMO-3 of **[5]**$^{-}$, and HOMO-2 of **[8]**$^{2-}$ contain the lone pair character of the germanium atom. In addition, the HOMO-2 and HOMO-10 of the **[8]**$^{2-}$ model (Figure 3) involve the nonbonding and bonding orbitals of the 3c–4e S-Ge-S bond, respectively.

## Conclusions

The imidazole-based dithiolate **2** serves as an effective platform for accessing a series of Lewis base-complexed dithiolene-based

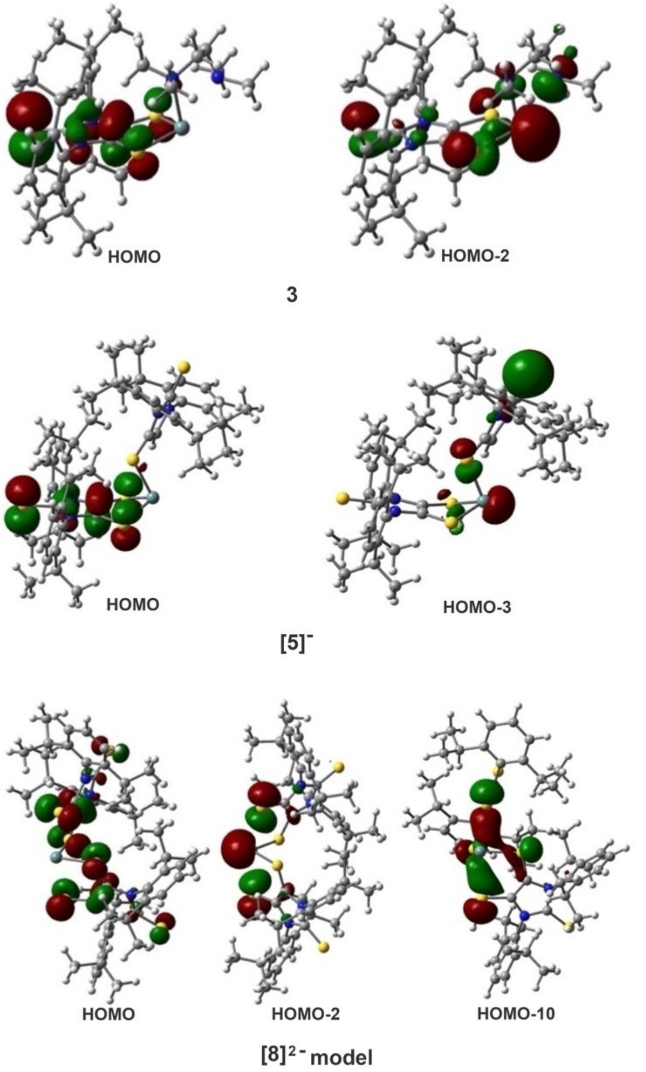


**Figure 3.** Molecular orbitals of **3**, **[5]**$^{-}$, and **[8]**$^{2-}$ models.

germylenes (**3** and **7**) and germanide (**5**). Notably, controlled hydrolysis of the NHC$^{iPr}$-coordinated germanium(II) dithiolene complex, **7**, resulted in a germanium(II) bis-dithiolene dianion **8**. This laboratory continues to develop dithiolene-based low oxidation state main group chemistry.

## Experimental Section

General. The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer. X-ray intensity data for **3·toluene**, **5**, and **8** were collected at 135 K on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (IμS) monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å, sealed tube) using phi and omega-scan technique. Mass spectra (MS) were obtained via direct sample injection using a Shimadzu GCMS-QP2010S with positive mode electron ionization (EI). Infrared spectra were recorded using a Shimadzu IRPrestige-21 FTIR spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ).

Deposition Number(s) 2277646, (**3·toluene**), 2281454 (**5**), 2277648 (**8**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. DFT computations were carried out using the Gaussian16 (Revision C.01) program.[24]

Compound **3**: 50 mL of THF was added to a Schlenk flask containing both radical **1** (0.400 g, 0.631 mmol) and KC$_8$ (0.140 g, 1.036 mmol) at room temperature, which was then stirred for 1 h and resulted in a slurry with white precipitate. Then, 15 mL of TMEDA was added to the reaction mixture. After filtration, the filtrate was combined with GeCl$_2$•dioxane (0.175 g, 0.755 mmol) in 5 mL of THF. The mixture was then stirred at room temperature for an additional 4 h. After the volatile materials were removed in vacuo, the residue was extracted using 35 mL of toluene. The filtrate was concentrated under vacuo to approximately 3 mL. The resulting white crystalized powder of **3** was subsequently isolated and drying in vacuo. Yield: 0.204 g (48%). X-ray quality colourless crystals of **3** were achieved by recrystallization in toluene/hexane mixed solvent. Mp: gradually decomposed (>145.2 °C) and melt at 246 °C. $^1$H NMR (400.22 MHz, THF-d$_8$): δ 1.24 [d, 12H, CH(C$H_3$)$_2$], 1.26 [d, 12H, CH(C$H_3$)$_2$], 2.27 (TMEDA), 2.50 (TMEDA), 2.85 [m, 4H, C$H$(CH$_3$)$_2$], 7.22 [d, 4H, Ar-$H$], 7.34 [t, 2H, Ar-$H$]. $^{13}$C{$^1$H} NMR (100.65 MHz, THF-d$_8$): δ 24.52, 24.63 [CH($C$H$_3$)$_2$], 30.01 [$C$H(CH$_3$)$_2$], 45.15, 57.04 (TMEDA), 124.36 [N$C$CN], 126.15, 130.04, 135.22, 148.12 [Ar-$C$], 168.73 [NC(=S)N]. IR (KBr, cm$^{-1}$): 3063 (w), 3024 (w), 2963 (s), 2916 (m), 2862 (m), 2832 (w), 2785 (w), 1535 (w), 1466 (s), 1366 (s), 1335 (s), 1018 (w), 949 (w), 802 (m), 787 (m), 694 (m). Crystal data for **3·toluene**: $C_{40}H_{58}GeN_4S_3$, fw = 763.67, monoclinic, $P2_1/c$, $a$ = 15.3337(17) Å, $b$ = 15.7045(18) Å, $c$ = 17.2801(19) Å, $\alpha$ = 90°, $\beta$ = 94.489(3)°, $\gamma$ = 90°, $V$ = 4148.4(8) Å$^3$, $Z$ = 4, R1 = 0.0598 for 13769 data ($I > 2\sigma(I)$), $wR_2$ = 0.1461 (all data). Anal. Calcd (found) (%) for $C_{33}H_{50}GeN_4S_3$ (**3**) (671.61): C 59.02 (58.27), H 7.50 (7.30), N 8.34 (8.07).

Compound **5**: 10 mL of THF was added to a Schlenk tube containing both **3** (0.200 g, 0.298 mmol) and **4** (0.201 g, 0.298 mmol). The reaction mixture was stirred at room temperature for 6 h. After the volatile materials were removed in vacuo, the residue was recrystallized in THF/hexane mixed solvent, giving **5** as X-ray quality colourless crystals (0.295 g, 72% yield). MP: gradually decomposed (>141 °C) and melt at 178 °C. $^1$H NMR (400.22 MHz, THF-d$_8$): δ 1.12–1.19 [24H, CH(C$H_3$)$_2$], 1.23 [d, 24H, CH(C$H_3$)$_2$], 1.77 (THF), 2.78 [m, 2H, C$H$(CH$_3$)$_2$], 2.86 [m, 2H, C$H$(CH$_3$)$_2$], 2.92 [m, 2H, C$H$(CH$_3$)$_2$], 3.04 [m, 2H, C$H$(CH$_3$)$_2$], 3.62 (THF), 6.90 [s, 1H, NC$H$], 7.08–7.30 [12H, Ar-$H$]. $^{13}$C{$^1$H} NMR (100.65 MHz, THF-d$_8$): δ 24.19, 24.48, 24.50, 24.70, 24.82, 24.87 [CH($C$H$_3$)$_2$], 26.54 (THF) 29.60, 29.82, 29.87 [$C$H(CH$_3$)$_2$], 68.39 (THF), 117.57 [NCH], 123.52, 123.83, 124.14, 124.29, 128.94, 129.33, 129.46, 129.72, 132.79, 134.88, 136.03, 136.19, 147.84, 148.11, 148.40, 148.76 [N$C$CN and Ar-$C$], 166.26, 166.30 [N$C$(=S)N]. IR (KBr, cm$^{-1}$): 3071 (w), 3032 (w), 2963 (s), 2932 (m), 2870 (m), 1535 (w), 1466 (s), 1342 (s), 1234 (w), 1042 (m), 887 (w), 802 (m), 694 (w), 594 (w). Crystal data for **5**: $C_{70}H_{101}GeLiN_4O_4S_5$, fw = 1302.37, triclinic, $P$-1, $a$ = 14.6074(15) Å, $b$ = 15.7727(16) Å, $c$ = 21.213(2) Å, $\alpha$ = 69.326(3)°, $\beta$ = 84.698(3)°, $\gamma$ = 72.060(3)°, $V$ = 4349.6(8) Å$^3$, $Z$ = 2, R1 = 0.0670 for 13666 data ($I > 2\sigma(I)$), $wR_2$ = 0.1990 (all data).

Compound **7**: 2 mL of toluene was added to a Schlenk tube containing both **3** (0.100 g, 0.149 mmol) and **6** (0.027 g, 0.150 mmol). The reaction mixture was stirred at room temperature for 3 h. After filtration and subsequent rinsed with 4 mL of hexane, the residue was dried under vacuum. Finally, compound **7** was isolated as white powder (0.067 g, 61% yield). MP: gradually decomposed (>151 °C) and melt at 219 °C. $^1$H NMR (400.22 MHz, THF-d$_8$): δ 1.24 [d, 6H, CH(C$H_3$)$_2$], 1.28 [d, 12H, CH(C$H_3$)$_2$], 1.34 [d, 6H, CH(C$H_3$)$_2$], 1.53 [d, 12H, CH(C$H_3$)$_2$, NHC], 2.29 [s, 6H, C$H_3$CCC$H_3$), NHC], 2.95 [m, 4H, C$H$(CH$_3$)$_2$], 5.97 [m, 2H, C$H$(CH$_3$)$_2$, NHC], 7.16–7.21 [4H, Ar-$H$], 7.31 [t, 2H, Ar-$H$]. $^{13}$C{$^1$H} NMR (100.65 MHz, THF-d$_8$): δ 10.48 [CH$_3$CC$C$H$_3$, NHC], 22.53, 24.71 [CH($C$H$_3$)$_2$], 30.00 [$C$H(CH$_3$)$_2$, dithiolene], 52.45 [$C$H(CH$_3$)$_2$, NHC], 129.90 [CH$_3$$C$CCH$_3$, NHC], 123.94, 124.51, 126.24, 128.23, 135.59, 147.83, 148.31[N$C$CN and Ar-$C$], 167.48[N$C$(=S)N], 168.31 [N$C$N]. IR (KBr, cm$^{-1}$): 3063 (w), 3024 (w), 2963 (s), 2870 (m), 1628 (w), 1535 (w), 1466 (s), 1366 (s), 1335 (s), 1211 (w), 1180 (w), 1103 (w), 1065 (w), 941 (w), 802 (m), 741(w), 694 (m). MS (EI, positive): 736 (0.5%, M$^+$), 556 (1.0%, [M-NHC]$^+$), 180 (100%, NHC$^+$).

Compound **8**: 1.2 mL of H$_2$O/THF mixture (0.1% v/v) was added dropwise to a solution of **7** (0.050 g, 0.068 mmol) in 25 mL toluene at −78 °C, which was stirred for 1 h. Next, the low-temperature bath was removed, and the mixture was naturally warmed to room temperature and stirred 3 h at that temperature. After filtration, the residue was dried under vacuo and then combined with 5 mL THF in a Schlenk tube. The slurry was heated under reflux and kept stationary at room temperature over 3 days, giving X-ray quality yellow crystals of **8** (0.026 g, 54% yield based on the $^1$H NMR data). MP: gradually decomposed (>126 °C) and melt at 247 °C. $^1$H NMR (400.22 MHz, CD$_3$CN): δ 1.20 [d, 24H, CH(C$H_3$)$_2$, dithiolene], 1.22 [d, 24H, CH(C$H_3$)$_2$, dithiolene], 1.47 [d, 24H, CH(C$H_3$)$_2$, imidazolium], 1.80 (THF), 2.22 [s, 12H, C$H_3$CCC$H_3$), imidazolium], 2.86 [m, 8H, C$H$(CH$_3$)$_2$, dithiolene], 3.64 (THF), 4.47 [m, 4H, C$H$(CH$_3$)$_2$, imidazolium], 7.18 [d, 8H, Ar-$H$], 7.32 [t, 4H, Ar-$H$], 8.43 [s, 2H, NC($H$)N]. $^{13}$C{$^1$H} NMR (100.65 MHz, CD$_3$CN): δ 9.01 [CH$_3$CC$C$H$_3$, imidazolium], 23.15, 24.61 [CH($C$H$_3$)$_2$], 26.64 (THF), 30.05 [$C$H(CH$_3$)$_2$, dithiolene], 51.63 [$C$H(CH$_3$)$_2$, imidazolium], 68.67 (THF), 124.41 [N$C$CN, dithiolene], 129.70 [CH$_3$$C$CCH$_3$, imidazolium], 130.74 [N$C$(H)N], 128.00, 129.32, 137.23, 148.75 [Ar-$C$], 160.51 [N$C$(=S)N]. IR (KBr, cm$^{-1}$): 3125 (w), 3055 (m), 2963 (s), 2862 (m), 1628 (w), 1551 (m), 1504 (s), 1458 (s), 1373 (s), 1335 (s), 1304 (m), 1265 (w), 1227 (w), 1188 (m), 1142 (w), 1103 (m), 1057 (m), 895 (w), 802 (m), 764 (w), 687 (m), 656 (w), 540 (w). Crystal data for **8**: $C_{76}H_{110}GeN_8S_6$, fw = 1400.66, monoclinic, $P2_1/n$, $a$ = 14.1731(16) Å, $b$ = 16.5369(18) Å, $c$ = 18.446(2) Å, $\alpha$ = 90°, $\beta$ = 92.841(3)°, $\gamma$ = 90°, $V$ = 4318.0(8) Å$^3$, $Z$ = 2, R1 = 0.1009 for 5173 data ($I > 2\sigma(I)$), $wR_2$ = 0.2060 (all data).

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** carbenes · dithiolenes · germanides · germanium · germylenes

[1] E. Rivard, P. P. Power, *Inorg. Chem.* **2007**, *46*, 10047–10064.
[2] Y. Wang, G. H. Robinson, *J. Am. Chem. Soc.* **2023**, *145*, 5592–5612.
[3] a) M. D. Zhong, S. Sinhababu, H. W. Roesky, *Dalton Trans.* **2020**, *49*, 1351–1364; b) C. Jones, *Nat. Chem. Rev.* **2017**, *1*, 0059.
[4] a) K. Wang in *Progress in Inorganic Chemistry*, Vol. 52 (Eds.: E. I. Stiefel, K. D. Karlin), Hoboken, NJ, **2004**, pp. 267–314; b) R. Eisenberg, H. B. Gray, *Inorg. Chem.* **2011**, *50*, 9741–9751; c) S. Sproules in *Progress in Inorganic Chemistry*, Vol. 58 (Ed.: K. D. Karlin), Hoboken, NJ, **2014**, pp. 1–144.
[5] W. P. Neumann, *Chem. Rev.* **1991**, *91*, 311–334.
[6] a) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479–3511; b) M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.* **1977**, 2004–2009; c) P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1976**, 2268–2274; d) D. H. Harris, M. F. Lappert, *J. Chem. Soc. Chem. Comm.* **1974**, 895–896; e) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396.
[7] a) A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994–7112; b) J. A. Cabeza, P. Garcia-alvarez, *Eur. J. Inorg. Chem.* **2021**, *2021*, 3315–3326; c) W. Petz, *Chem. Rev.* **1986**, *86*, 1019–1047; d) M. F. Lappert, R. S. Rowe, *Coord. Chem. Rev.* **1990**, *100*, 267–292; e) A. Bruck, D. Gallego, W. Y. Wang, E. Irran, M. Driess, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2012**, *51*, 11478–11482; f) J. Hlina, J. Baumgartner, C. Marschner, P. Zark, T. Müller, *Organometallics* **2013**, *32*, 3300–3308; g) D. Gallego, A. Bruck, E. Irran, F. Meier, M. Kaupp, M. Driess, J. F. Hartwig, *J. Am. Chem. Soc.* **2013**, *135*, 15617–15626.
[8] a) N. Sen, S. Khan, *Chem. Asian J.* **2021**, *16*, 705–719; b) R. Dasgupta, S. Khan in *Advances in Organometallic Chemistry*, Vol 74 (Ed.: P. J. Pérez), Cambridge, MA, **2020**, pp 105–152.
[9] a) Y. Peng, J. D. Guo, B. D. Ellis, Z. L. Zhu, J. C. Fettinger, S. Nagase, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 16272–16282; b) A. Jana, I. Objartel, H. W. Roesky, D. Stalke, *Inorg. Chem.* **2009**, *48*, 798–800.
[10] A. V. Zabula, F. E. Hahn, *Eur. J. Inorg. Chem.* **2008**, 5165–5179.
[11] B. Kersting, B. Krebs, *Inorg. Chem.* **1994**, *33*, 3886–3892.
[12] H. Lavayssière, G. Dousse, J. Satgé, *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 440–448.
[13] Y. Wang, H. P. Hickox, Y. Xie, P. Wei, S. A. Blair, M. K. Johnson, H. F. Schaefer III, G. H. Robinson, *J. Am. Chem. Soc.* **2017**, *139*, 6859–6862.
[14] a) Y. Wang, C. A. Tope, Y. Xie, P. Wei, J. L. Urbauer, H. F. Schaefer III, G. H. Robinson, *Angew. Chem. Int. Ed.* **2020**, *59*, 8864–8867; b) P. M. Tran, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III, G. H. Robinson, *Chem. Commun.* **2021**, *57*, 2543–2546.
[15] Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III, G. H. Robinson, *Dalton Trans.* **2019**, *48*, 3543–3546.
[16] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562.
[17] See the Supporting Information for spectroscopic, computational and crystallographic details.
[18] J. D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
[19] F. Cheng, J. M. Dyke, F. Ferrante, A. L. Hector, W. Levason, G. Reid, M. Webster, W. J. Zhang, *Dalton Trans.* **2010**, *39*, 847–856.
[20] T. Kunz, C. Schrenk, A. Schnepf, *Chem. Eur. J.* **2019**, *25*, 7210–7217.
[21] a) D. J. Liptrot, P. P. Power, *Nat. Chem. Rev.* **2017**, *1*, 0004; b) S. Grimme, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2011**, *50*, 12639–12642.
[22] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.
[23] H. H. Karsch, M. Hollstein, G. Müller, *Z. Naturforsch.* **1990**, *45b*, 775–780.
[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2019**.

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