

Mesoionic Dithiolates (MIDTs) Derived from 1,3-Imidazole-Based Anionic Dicarbenes (ADCs)

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Dedicated to Professor Cameron Jones on the occasion of his 60th birthday

Abstract: Mesoionic dithiolates [(MIDt^{Ar})Li(LiBr)₂(THF)₃] (MIDt^{Ar} = {SC(NDipp)}₂CAr; Dipp = 2,6-*i*-Pr₂C₆H₃; Ar = Ph **3 a**, 3-MeC₆H₄ (3-Tol) **3 b**, 4-Me₂NC₆H₄ (DMP) **3 c**) and [(MIDt^{Ph})Li(THF)₂] (**4**) are readily accessible (in ≥ 90% yields) as crystalline solids on treatments of anionic dicarbenes Li(ADC^{Ar}) (**2 a-c**) (ADC^{Ar} = {C(NDipp)}₂CAr) with elemental sulfur. **3 a-c** and **4** are monoanionic ditopic ligands with both the sulfur atoms formally negatively charged, while the 1,3-imidazole unit bears a formal positive charge. Treatment of **4** with (L)GeCl₂

(L = 1,4-dioxane) affords the germylene (MIDt^{Ph})GeCl (**5**) featuring a three-coordinated Ge atom. **5** reacts with (L)GeCl₂ to give the Ge–Ge catenation product (MIDt^{Ph})GeGeCl₃ (**6**). K₂C₈ reduction of **5** yields the homoleptic germylene (MIDt^{Ph})₂Ge (**7**). Compounds **3 a-c** and **4–7** have been characterized by spectroscopic studies and single-crystal X-ray diffraction. The electronic structures of **4–7** have been analyzed by DFT calculations.

Dithiolenes (DTs) (Figure 1a) are an important class of ligands that have eased spectacular advances in fundamental transition metal (TM) chemistry.^[1] DT-TM complexes had been known since the pioneering works by Schrauzer,^[2] Gray,^[3] Davidson and Holm^[4] in the early 1960s. DTs are usually regarded as the first non-innocent chelating ligands as they can exist in three different oxidation state (DT²⁻, DT⁻, and DT⁰) (Figure 1a).^[5] The term “dithiolene” was originally introduced by McCleverty to avoid the necessity of specifying distinct oxidation states.^[6] The interest in DT-TM complexes continues to grow because of their applications in optoelectronics,^[7] energy harvesting,^[8] catalysis, and beyond.^[9] Moreover, DTs are also known as key structural motifs in many metal-containing natural enzymes.^[10]

N-Heterocyclic carbenes (NHCs), the classical C2-carbenes like IPr (**I**) (Figure 1b), are very versatile carbon-donor neutral ligands in synthesis, catalysis, and materials science.^[11] NHCs are also appealing building blocks for the development of new sets of ligands.^[12] In 2010, Robinson et al. isolated the anionic

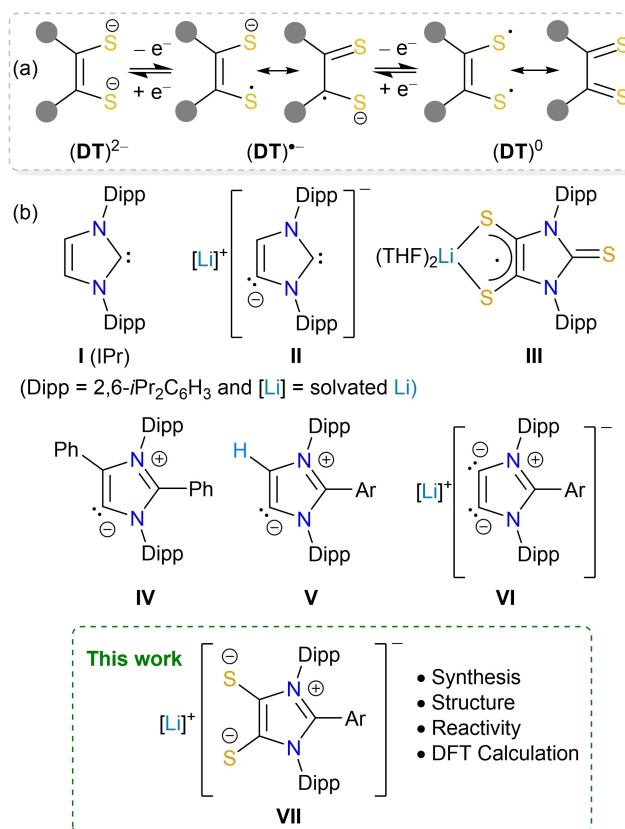
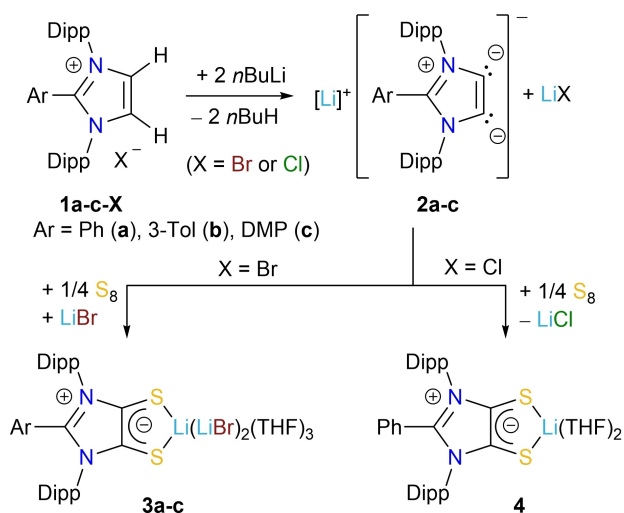


Figure 1. (a) Various oxidation states of dithiolene (DT) ligands. (b) Selected examples of singlet carbenes (**I**, **IV**, **V**), dicarbenes (**II**, **VI**), and dithiolene derivatives (**III** and **VII**).

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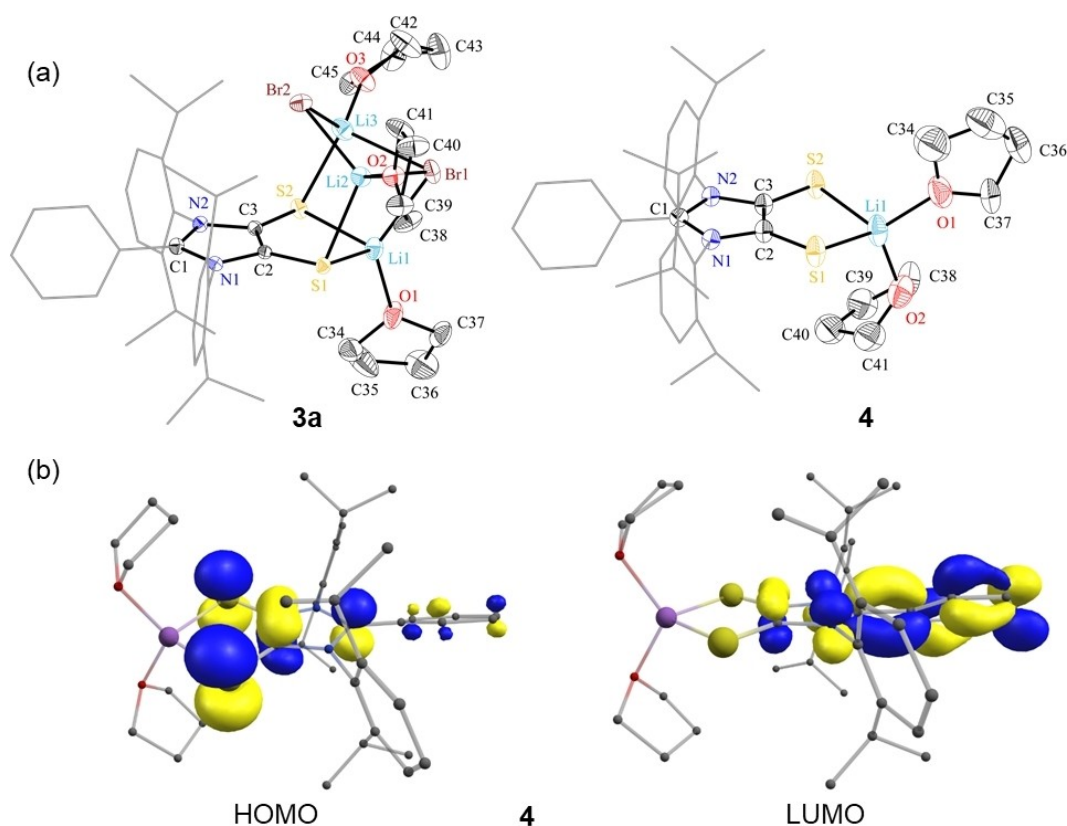
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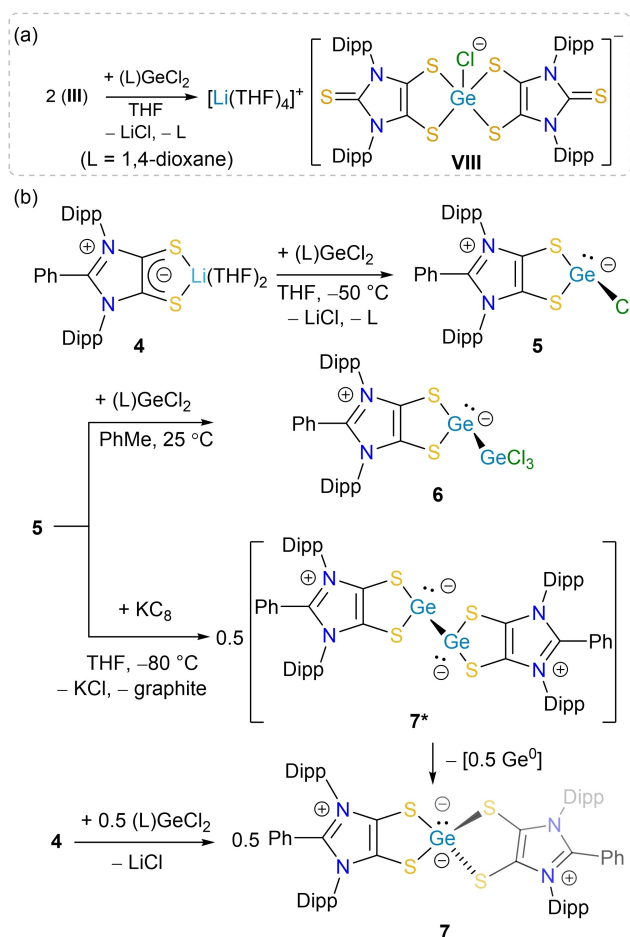
Scheme 1. Synthesis of **3 a–c** and **4**.

dicarbene (ADC) **II** by the C4-deprotonation of **I**.^[13] Later, they prepared a lithium dithiolene radical **III** by reacting **II** with S_8 .^[14] The widespread applications of NHCs is largely attributed to their auspicious stereoelectronic features, in particular the σ -donor strength.^[15] Mesoionic carbenes (iMICs), the so-called abnormal NHCs, are C4-(or C5) carbenes and are superior σ -donors than C2-carbenes.^[16] Unlike NHCs, stable iMICs are

however rather scarce. The first free iMIC **IV** was reported by Bertrand et al. in 2009.^[17] Very recently, we reported on C5-protonated iMICs **V**,^[18] which can be further deprotonated to give C4,C5-dicarbene **VI**. We have also shown the suitability of these vicinal dicarbene **VI** in accessing a variety of main-group heterocycles,^[19] including diradicals.^[20] Herein, we report on the high-yielding synthetic access to a new class of dithiolene ligands, namely the mesoionic dithiolate (MIDTs) **VII**, derived from **VI**.

The desired precursors $\text{Li}(\text{ADC}^{\text{Ar}})$ ($\text{ADC}^{\text{Ar}} = \{\text{CN}(\text{Dipp})\}_2\text{CAr}$; Dipp = 2,6-*i*Pr₂C₆H₃; Ar = Ph **2 a**, 3-MeC₆H₄ (3-Tol) **2 b**, 4-Me₂NC₆H₄ (DMP) **2 c**) were prepared in situ (Scheme 1)^[19,20] by the direct double deprotonation of the C2-arylated 1,3-imidazolium bromides ($\text{IPr}^{\text{Ar}}\text{Br}$) ($\text{IPr}^{\text{Ar}} = \{\text{HCN}(\text{Dipp})\}_2\text{CAr}$; Ph **1 a-Br**, 3-Tol **1 b-Br**, DMP **1 c-Br**)^[21] with $n\text{BuLi}$. Treatment of a freshly prepared THF solution of **2 a–c** with LiBr ^[22] and S_8 afforded compounds **3 a–c**. Solid-state molecular structures of **3 a** (Figure 2a), **3 b** (Figure S25 in Supporting Information), and **3 c** (Figure S26) reveal the presence of a cluster like $\text{S}_2\text{Li}_3\text{Br}_2$ unit.^[23] Each four-fold coordinated lithium bears a THF molecule, while both the bromides serve as bridging ligands. The ¹H and ¹³C NMR spectra of **3 a–c** exhibit expected signals for the ADC^{Ar} and THF moieties. The corresponding derivative **4** free from LiBr was prepared using **1 a-Cl** instead of **1 a-Br** to generate **2 a**. This may be due higher lattice energy of LiCl than LiBr . **3 a–c** and **4** are orange or yellow solids, accessible in $\geq 90\%$ yields, and indefinitely stable under an inert gas (N_2 or Ar) atmosphere.

Figure 2. (a) Molecular structures of **3 a** and **4**. (b) HOMO and LUMO of **4**.

Scheme 2. (a) Reaction of III with (L)GeCl₂ to VIII. (b) Synthesis of 5, 6, and 7.

In **4**, the four-coordinated lithium atom bears two THF molecules and binds to the sulfur atoms of the MIDt^{Ph} to form a five-membered C₂S₂Li ring. The lithium atom in **4** is protruded out of the C₂S₂-plane and has a fold angle of 13.0(1)° between the LiS₂ and S₂C₂ planes, which is slightly smaller than Robinson's radical anion III (14.2°).^[14c] Notably, **4** has an additional electron than III. The C2–C3 bond length of **4** (1.383(2) Å) is intermediate of that of **1a-Br** (1.353(2) Å) and III (1.417(3) Å). The C–S bond lengths of **4** (1.717(1), 1.729(2) Å) are middle of those of Me₂S (1.79863(13) Å)^[9] and (IPr)=S (1.670(1) Å).^[24] and compare well with those of thiophene (1.7126(5) Å)^[10] and metal-dithiolates.^[2] These features suggest the presence of a delocalized π-electron system over the C₂S₂Li ring.

The optimized structure of **4** at the PBE0-D3BJ/def2-TZVPP level of theory (see the Supporting Information) is in good agreement with its solid-state molecular structure (Figure 2a). The Wiberg bond indices (WBIs) of the C2–C3 (1.32 au) and C2–S1/C3–S2 bonds (1.24 au) indicate that they have partial double character. Calculations reveal that the HOMO of **4** is a π-type orbital mainly located at the C₂S₂ unit and has C–C and *trans*-annular S[⋯]S π-bonding character. The LUMO is primarily based on the phenyl group of ADC^{Ph} (Figure 2b). The UV-vis-spectrum of **4** exhibits one main absorption (λ_{max}) at 497 nm,

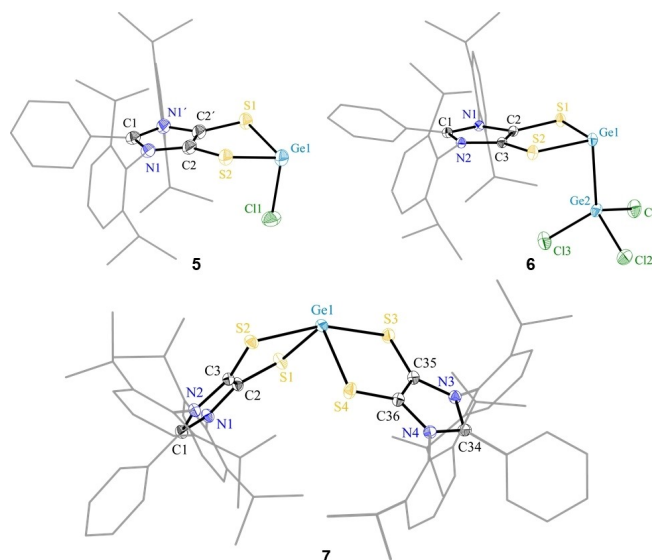


Figure 3. Solid-state molecular structures of **5**, **6**, and **7**. Aryl groups are shown as wireframe models and H atoms are omitted for clarity. Thermal ellipsoids are shown with 50% probability. Selected bond lengths (Å) and angles (°) for **5** (only one of the disordered S₂GeCl unit is shown): Ge1–Cl1 2.295(1), Ge1–S1 2.387(5), Ge1–S2 2.377(5), C2–C2' 1.363(4), C2–S1 1.769(7); S1–Ge1–S2 90.8(1), S1–Ge1–Cl1 95.8(2), C2–S1–Ge1 93.5(2); for **6**: Ge2–Cl 2.202(1)–2.188(1), Ge1–Ge2 2.592(1), Ge1–S1 2.360(1), Ge1–S2 2.363(1), C2–C3 1.366(1), C2–S1 1.7230(1), C3–S2 1.730(1); S1–Ge1–S2 93.3(1), C2–S1–Ge1 96.5(1), S1–Ge1–Ge2 88.5(1), Cl–Ge2–Cl 101.5(1)–102.1(1); for **7**: Ge–S 2.401(1)–2.702(1), C2–C3 1.375(3), C35–C36 1.379(3), C2–S1 1.724(2), C3–S2 1.710(2); S1–Ge1–S2 87.0(1), S1–Ge1–S4 99.4(1), S2–Ge1–S3 162.4(1).

which based on TD-DFT analysis may be assigned to the HOMO→LUMO transition (Table S10).

Robinson et al. isolated a square-planar germanium compound **VIII** by reacting **III** with (L)GeCl₂ (L = 1,4-dioxane) (Scheme 2a). Structural parameters suggest that **VIII** is a Ge(+4) compound. Thus, the ligand is 1e-reduced while germanium is 2e-oxidized in **VIII** with respect to **III** and (L)GeCl₂. This finding prompted us to explore the reactivity of **4** with (L)GeCl₂, given the fact that **4** already has one excess electron than **III**. Interestingly, treatment of **4** with (L)GeCl₂ in THF led to the clean formation of a heteroleptic germylene **5** as an orange solid (Scheme 2b). Further reaction of **5** with (L)GeCl₂ gave a mixed-valent Ge(+1)/Ge(+3) compound **6**. The formation of Ge–Ge catenation product **6** indicates formal insertion of GeCl₂ into the Ge–Cl bond of **5**.

We anticipated the formation of bis-germylene **7*** on KC₈ reduction of **5**. This reaction however led to the formation of a homoleptic germylene **7** instead of **7***, indicating reductive elimination of Ge⁰ from **7***. This may be attributed to the electron-rich nature of MIDt entity. Notably, **7** may also be prepared directly by reacting **4** with (L)GeCl₂ in a 2:1 ratio (Scheme 2b). Compounds **5**, **6** (orange), and **7** (red) are crystalline solids and indefinitely stable under an inert gas atmosphere. The observed ¹H and ¹³C NMR signals for the ADC^{Ph} unit of **5–7** are fully consistent with their solid-state molecular structures (Figure 3).

Like C₂S₂Li ring in **4**, the C₂S₂Ge ring of **5** and **6** is puckered and the germanium atom is protruded out of the plane. The

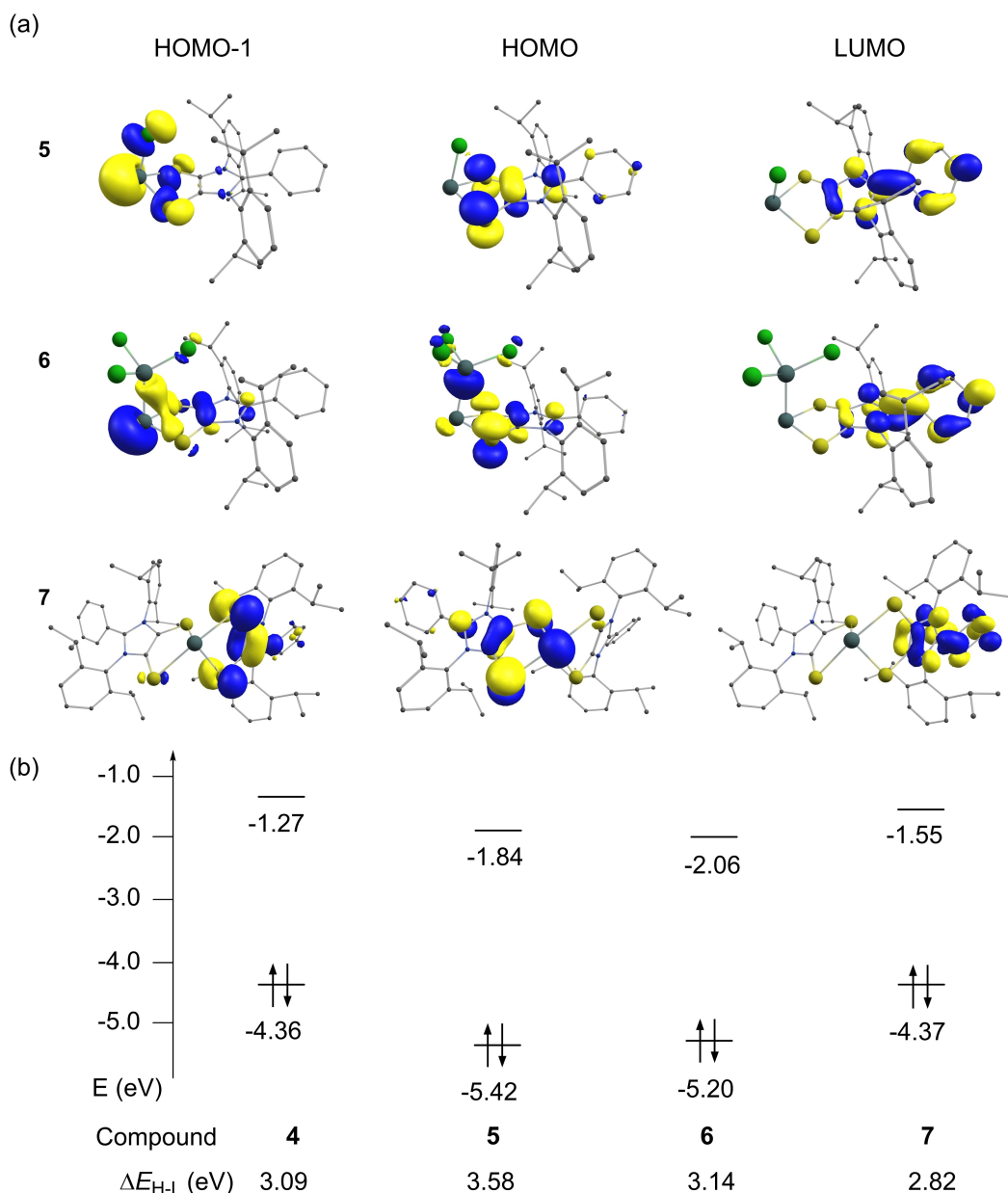


Figure 4. (a) Selected molecular orbitals (HOMO-1, HOMO, and LUMO) of compounds 5, 6, and 7 calculated at the PBE0-D3BJ/def2-TZVPP level of theory. (b) comparison of the HOMO-LUMO energies of 4, 5, 6, and 7.

fold angle between the GeS_2 and S_2C_2 plane of **5** and **6** amounts to $23.0(1)^\circ$ and $5.4(1)^\circ$, respectively. As expected for low-valent germanium compounds, the Ge–S bond lengths of **5** and **6** (av. 2.372 \AA) are slightly larger than those of the Ge(+4) species **VIII** (av. 2.342 \AA). The germanium atom of GeCl_3 moiety in **6** has a trigonal pyramidal geometry with a τ_4 value of 0.85 ($\tau_4=1$ for a perfect tetrahedron and 0.85 for trigonal pyramidal geometry).^[25] The Ge1–Ge2 bond length of **6** ($2.592(1) \text{ \AA}$) is intermediate of those of digermene Ge_2H_6 ($2.403(3) \text{ \AA}$)^[26] and a base-stabilized tetrachlorodigermene $(\text{IPr})\text{GeCl}_2\text{GeCl}_2$ ($2.630(1) \text{ \AA}$).^[27] The $\text{S}_2\text{–Ge1–Ge2}$ bond angle is almost right angled ($88.5(1)^\circ$), indicating the presence of a stereochemically active lone pair of electrons at the germanium atom Ge1.

Compound **7** (Figure 3) is an elusive spiro-cyclic germylene with a four-coordinated germanium atom.^[28] In **5** and **6**, the chelating MIDt ligand binds to the Ge center in an isobidentate manner, thus both Ge–S bond lengths are comparable. The MIDt in **7** exhibits anisobidentate bonding mode and shows larger (axial Ge–S2 $2.691(1)$, Ge–S3 $2.702(1) \text{ \AA}$) and smaller (equatorial Ge–S2 $2.409(1)$, Ge–S4 $2.401(1) \text{ \AA}$) Ge–S bond lengths. This is consistent with the calculated WBIs of 0.65, 0.67, 0.48 and 0.30 for the Ge–S bonds in **7** (Table S4). The four-coordinate germanium atom features a distorted seesaw geometry with a τ_4 value of 0.70 (0.64 for seesaw geometry).^[25] The $\text{S}_2\text{–Ge1–S}_3$ bond angle of $162.4(1)^\circ$ suggests the presence

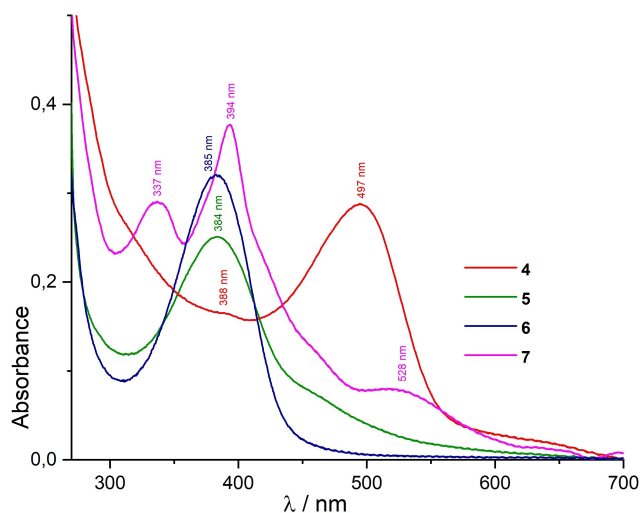


Figure 5. UV-vis spectra of 4–7 (10^{-5} M in THF).

of a stereochemically active lone pair of electrons at the equatorial position.

Further insights into the electronic structures of 5–7 were obtained by computational calculations (see the Supporting Information). The optimized geometries of 5–7 are fully consistent with their X-ray diffraction structures (Figure 3). The HOMO of 5 and 6 is a π -type orbital mainly located at the C_2S_2 framework, while the LUMO is based primarily on the ADC unit (Figure 4a). The HOMO-1 of 5 and 6 is a σ -type lone-pair orbital at the germanium atoms with a considerable contribution from the Ge–S bonds. The HOMO of 7 is based on the C_2S_2Ge framework and has σ -type lone-pair orbital contribution at the germanium atom. The HOMO-1 of 7 is a π -type orbital largely located at the C_2S_2 framework. Very recently, Gessner et al. reported a diylide-stabilized germylene Y_2Ge ($Y = Ph_3PCSO_2ToI$) that has the highest lying HOMO (-5.04 eV), also calculated at the PBE0-D3BJ/def2-TZVPP level of theory, among hitherto known germylenes.^[28a] A comparison of HOMO and LUMO energies of 5–7 with literature known germylenes reveals that the energy of the HOMO of 7 (-4.37 eV) is remarkably high and exceeds that of Y_2Ge (-5.04 eV). Moreover, the LUMO of 7 (-1.55 eV) is lower in energy than that of Y_2Ge (-1.12 eV), resulting a very small HOMO-LUMO energy gap of 2.82 eV for 7.

The UV-vis- spectra of 5 and 6 each exhibits an absorption band (λ_{max}) at 384 and 385 nm (Figure 5), respectively, which based on TD-DFT analyses may be assigned to HOMO→LUMO transitions (Table S11 and S12). The UV-vis spectrum of 7 shows absorption bands at 394 and 528 nm, which according to TD-DFT studies correspond to the HOMO-1→LUMO and HOMO→LUMO+1 transitions, respectively (Table S13).

In conclusions, MIDts 3a–c and 4 have been isolated as crystalline solids and characterized by spectroscopic and X-ray diffraction methods. The use of 4 as a ligand has been shown with germylenes 5, 6, and 7. Electronic structures of 4–7 have been analyzed by DFT calculations. The germylene 7 with a remarkably high-lying HOMO (-4.37 eV) and low-lying LUMO (-1.55 eV) has a promising prospective as ligands. Moreover,

interesting reactivity of 7 based on its small HOMO-LUMO energy gap (2.82 eV) can be envisioned. Further reactivity studies of 4–7 with small molecules as well as ligands for main-group and transition metal compounds are currently underway.

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Conflict of Interest

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 · dithiolene · germanium · lithium · mesoionic

- [1] a) S. Sproules, in *Progress in Inorganic Chemistry Volume 58*, 2014, p. 1–144; b) R. Eisenberg, H. B. Gray, *Inorg. Chem.* **2011**, *50*, 9741–9751; c) S. Sproules, K. Wieghardt, *Coord. Chem. Rev.* **2011**, *255*, 837–860; d) F. J. Hine, A. J. Taylor, C. D. Garner, *Coord. Chem. Rev.* **2010**, *254*, 1570–1579; e) S. Rabaça, M. Almeida, *Coord. Chem. Rev.* **2010**, *254*, 1493–1508; f) B. Garreau-de Bonneval, K. I. Moineau-Chane Ching, F. Alary, T.-T. Bui, L. Valade, *Coord. Chem. Rev.* **2010**, *254*, 1457–1467; g) R. Kato, *Chem. Rev.* **2004**, *104*, 5319–5346; h) A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* **2004**, *104*, 5243–5264; i) E. I. Stiefel, in *Progress in Inorganic Chemistry, Vol. 52*, John Wiley & Sons, Inc., **2003**; j) J. A. McCleverty, in *Progress in Inorganic Chemistry*, **1968**, p. 49–221.
- [2] G. N. Schrauzer, V. Mayweg, *J. Am. Chem. Soc.* **1962**, *84*, 3221–3221.
- [3] R. Eisenberg, J. A. Ibers, R. J. H. Clark, H. B. Gray, *J. Am. Chem. Soc.* **1964**, *86*, 113–115.
- [4] A. L. Balch, I. G. Dance, R. H. Holm, *J. Am. Chem. Soc.* **1968**, *90*, 1139–1145.
- [5] a) W. Kaim, *Inorg. Chem.* **2011**, *50*, 9752–9765; b) K. Ray, T. Petrenko, K. Wieghardt, F. Neese, *Dalton Trans.* **2007**, 1552–1566.
- [6] J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, C. J. Winscom, *J. Am. Chem. Soc.* **1967**, *89*, 6082–6092.
- [7] a) A. Mizuno, H. Benjamin, Y. Shimizu, Y. Shuku, M. M. Matsushita, N. Robertson, K. Awaga, *Adv. Funct. Mater.* **2019**, *29*, 1904181; b) A. Avramopoulos, N. Otero, H. Reis, P. Karamanis, M. G. Papadopoulos, *J. Mater. Chem. C* **2018**, *6*, 91–110; c) S. Dalgleish, J. G. Labram, Z. Li, J. Wang, C. R. McNeill, T. D. Anthopoulos, N. C. Greenham, N. Robertson, *J. Mater. Chem.* **2011**, *21*, 15422–15430.
- [8] C. S. Letko, J. A. Panetier, M. Head-Gordon, T. D. Tilley, *J. Am. Chem. Soc.* **2014**, *136*, 9364–9376.
- [9] a) J. Pitchaimani, S.-F. Ni, L. Dang, *Coord. Chem. Rev.* **2020**, *420*, 213398; b) M. Drosou, F. Kamatsos, C. A. Mitsopoulou, *Inorg. Chem. Front.* **2020**, *7*, 37–71; c) W. R. McNamara, Z. Han, C.-J. Yin, W. W. Brennessel, P. L. Holland, R. Eisenberg, *Proc. Nat. Acad. Sci.* **2012**, *109*, 15594–15599.
- [10] a) S. J. Nieter Burgmayer, in *Dithiolene Chemistry: Synthesis, Properties, and Applications, Vol. 52* (Eds.: K. D. Karlin, E. I. Stiefel), **2003**, p. 491–537; b) J. C. Boyington, V. N. Gladyshev, S. V. Khangulov, T. C. Stadtman, P. D. Sun, *Science* **1997**, *275*, 1305–1308.

- [11] a) C. A. Smith, M. R. Narouz, P. A. Lummis, I. Singh, A. Nazemi, C.-H. Li, C. M. Crudden, *Chem. Rev.* **2019**, *119*, 4986–5056; b) A. A. Danopoulos, T. Simler, P. Braunstein, *Chem. Rev.* **2019**, *119*, 3730–3961; c) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678–9842; d) A. Vivancos, C. Segarra, M. Albrecht, *Chem. Rev.* **2018**, *118*, 9493–9586; e) R. S. Ghadwal, R. Azhakar, H. W. Roesky, *Acc. Chem. Res.* **2013**, *46*, 444–456; f) L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903–1912; g) S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; h) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.
- [12] a) R. S. Ghadwal, *Acc. Chem. Res.* **2022**, *55*, 457–470; b) A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994–7112; c) T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, *45*, 6327–6344; d) R. S. Ghadwal, *Dalton Trans.* **2016**, *45*, 16081–16095.
- [13] Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2010**, *132*, 14370–14372.
- [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) Y. Wang, Y. Xie, P. Wei, S. A. Blair, D. Cui, M. K. Johnson, H. F. Schaefer III, G. H. Robinson, *J. Am. Chem. Soc.* **2020**, *142*, 17301–17305; c) 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.
- [15] a) A. Gomez-Suarez, D. J. Nelson, S. P. Nolan, *Chem. Commun.* **2017**, *53*, 2650–2660; b) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723–6753.
- [16] a) S. C. Sau, P. K. Hota, S. K. Mandal, M. Soleilhavoup, G. Bertrand, *Chem. Soc. Rev.* **2020**, *49*, 1233–1252; b) R. H. Crabtree, *Coord. Chem. Rev.* **2013**, *257*, 755–766; c) A. Krueger, M. Albrecht, *Aust. J. Chem.* **2011**, *64*, 1113–1117; d) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; e) A. Merschel, T. Glodde, B. Neumann, H.-G. Stammer, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2021**, *60*, 2969–2973; *Angew. Chem.* **2021**, *133*, 3006–3010; f) A. Merschel, D. Rottschäfer, B. Neumann, H.-G. Stammer, R. S. Ghadwal, *Organometallics* **2020**, *39*, 1719–1729.
- [17] E. Aldeco-Perez, A. J. Rosenthal, B. Donnadiou, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556–559.
- [18] a) D. Rottschäfer, T. Glodde, B. Neumann, H. G. Stammer, R. S. Ghadwal, *Chem. Commun.* **2020**, *56*, 2027–2030; b) D. Rottschäfer, F. Ebeler, T. Strothmann, B. Neumann, H.-G. Stammer, A. Mix, R. S. Ghadwal, *Chem. Eur. J.* **2018**, *24*, 3716–3720.
- [19] a) D. Rottschäfer, B. Neumann, H.-G. Stammer, T. Sergeieva, D. M. Andrada, R. S. Ghadwal, *Chem. Eur. J.* **2021**, *27*, 3055–3064; b) D. Rottschäfer, T. Glodde, B. Neumann, H. G. Stammer, D. M. Andrada, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2021**, *60*, 15849–15853; c) M. K. Sharma, T. Glodde, B. Neumann, H.-G. Stammer, R. S. Ghadwal, *Chem. Eur. J.* **2020**, *26*, 11113–11118; d) D. Rottschäfer, S. Blomeyer, B. Neumann, H.-G. Stammer, R. S. Ghadwal, *Chem. Sci.* **2019**, *10*, 11078–11085.
- [20] a) M. K. Sharma, F. Ebeler, T. Glodde, B. Neumann, H.-G. Stammer, R. S. Ghadwal, *J. Am. Chem. Soc.* **2021**, *143*, 121–125; b) M. K. Sharma, D. Rottschäfer, T. Glodde, B. Neumann, H. G. Stammer, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2021**, *60*, 6414–6418.
- [21] N. K. T. Ho, B. Neumann, H.-G. Stammer, V. H. Menezes da Silva, D. G. Watanabe, A. A. C. Braga, R. S. Ghadwal, *Dalton Trans.* **2017**, *46*, 12027–12031.
- [22] Compounds **3a-c** crystallize as LiBr adducts; thus one equivalent of LiBr was added to improve the yields.
- [23] Deposition Numbers 2125903 (for **3a**), 2125904 (for **3b**), 2125905 (for **3c**), 2125906 (for **4**), 2125907 (for **5**), 2125908 (for **6**), 2125909 (for **7**) contains 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.
- [24] D. Rottschäfer, D. E. Fuhs, B. Neumann, H.-G. Stammer, R. S. Ghadwal, *Z. Anorg. Allg. Chem.* **2020**, *646*, 574–579.
- [25] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955–964.
- [26] B. Beagley, J. J. Monaghan, *Trans. Faraday Soc.* **1970**, *66*, 2745–2748.
- [27] S. M. I. Al-Rafia, M. R. Momeni, R. McDonald, M. J. Ferguson, A. Brown, E. Rivard, *Angew. Chem. Int. Ed.* **2013**, *52*, 6390–6395.
- [28] a) C. Mohapatra, L. T. Scharf, T. Scherpf, B. Mallick, K.-S. Feichtner, C. Schwarz, V. H. Gessner, *Angew. Chem. Int. Ed.* **2019**, *58*, 7459–7463; b) S.-H. Zhang, H.-W. Xi, K. H. Lim, C.-W. So, *Organometallics* **2011**, *30*, 3686–3689.

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