

Synthesis, Characterization, and Reaction of Digermynes

Shuai-Cong Huo^{+, [a]}, Yao Li^{+, [a]}, De-Xiang Zhang,^[a] Qi Zhou,^[a] Ying Yang,^{*, [a]} and Herbert W. Roesky^{*, [b]}

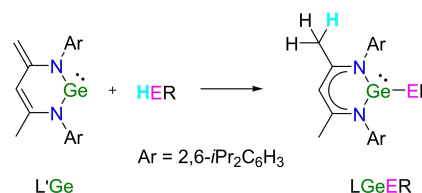
Dedicated to Professor Matthias Dri  on the occasion of his birthday

Abstract: A series of digermynes R(EGeL)₂ (L = CH[C(Me)N(Ar)]₂, Ar = 2,6-*i*Pr₂C₆H₃; E = O, R = 1,3-C₆H₄ (1), 1,4-C₆H₄ (2), Me₂C(CH₂)₂ (3); E = NH, R = 1,4-C₆H₄ (4), 1,4-C₆H₁₀ (5); E = C(O)O, R = 1,3-C₆H₄ (6)) were synthesized by the reactions of L'Ge (L' = HC[C(CH₂)N(Ar)]C(Me)N(Ar), Ar = 2,6-*i*Pr₂C₆H₃) with selected diphenols, diol, diamines, and *o*-/*m*-phthalic acids, respectively. Treatment of digermylene 1,3-C₆H₄(OGel)₂ (1)

with sulfur, selenium and CuX (X = Cl, Br, I) led to the formation of 1,3-C₆H₄[OGe(S)L]₂ (8), 1,3-C₆H₄[OGe(Se)L]₂ (9), and (CuX)₂[1,3-C₆H₄(OGel)₂]₂ (X = Cl (10), Br (11), I (12)), respectively. The obtained products were characterized by melting point, elemental analysis, FT-IR, ¹H and ¹³C NMR spectroscopy, and single-crystal X-ray diffraction.

Introduction

In past decades, the stabilization and isolation of heavier analogues of carbenes have attracted widespread attention for their great importance in fundamental and applied chemistry.^[1] Parallel to the significant studies on the ditetrelenes (R₂M=M'R₂)^[2] and ditetrylenes,^[3] particularly digermynes featured with the multiple- or single-bonded Ge(I)-Ge(I) structure,^[4] the research on the digermynes with more distant Ge(II)⋯Ge(II) separation has been extensively explored. One representative example is the digermylene oxide with the oxygen atom connecting the two Ge(II) centers.^[5] Greater spacing distances between two Ge(II) sites have been achieved by using *p*-benzenediamido,^[6] *p*-phenylene, *p*-biphenylene,^[7] *p*-terphenylene,^[8] cyclohexylene,^[9] or flexible alkyl chains^[10] linkers in specially designed ligands. Intriguingly, the elimination of HCl from the β-diketiminato ligand supported germylene chloride LGeCl (L = CH[C(Me)NAr]₂, Ar = 2,6-*i*Pr₂C₆H₃)^[11] gave a heterofulvene-like germylene L'Ge (L' = HC[(C-CH₂)CMe](NAr)₂) (Scheme 1),^[12] which unexpectedly produced digermynes by reactions with dibromoethane,^[12] HN(SiMe₃)₂,^[13] PhC(NtBu)₂GeCl,^[14] or (HO)₂BPh.^[15] Furthermore, L'Ge has been found to show abundant reactivity with HER (E = N, O, P),



Scheme 1. The reaction of L'Ge with HER (E = N,^[16] O,^[17] and P^[18]).

forming LGeER through bond cleavage and nucleophilic addition of H-N,^[16] H-O,^[17] and H-P^[18] (Scheme 1). This strategy appears more convenient and attractive for the synthesis of digermynes when considering the use of (HE)₂R which contains two functional groups for the reaction with L'Ge. In a recent practice, we used (HO)₂BR (R = 2,4,6-Me₃C₆H₂, 1-Naph) as the organoboryl source to treat L'Ge in a 1:2 ratio, precisely leading to the formation of digermylene RB(OGel)₂ as expected,^[19] while another parallel reaction with (HO)₂BR (R = 2,4-Me₂C₆H₃) only afforded RB(OH)OGel, rather than a binuclear product. These findings suggest that the above approach is useful in the synthesis of digermynes and also deserves more exploration when the effect of substituents is taken into account.

Herein, we report the synthesis of the digermynes via the direct reaction of L'Ge with diphenols, diol, diamines, and *o*-/*m*-phthalic acids. The reactivity concerning the functional groups, spacer size, and substituent position are investigated. Furthermore, as known, germynes show efficient Ge—Cu donation^[5c,10f, 20] and have oxidative addition reactivity with elemental chalcogen,^[21] allowing stabilization of new derivatives. Based on our synthetic work on germynes^[22] and diacylthioureas,^[23] the reactivity studies on the obtained representative digermylene with sulfur, selenium, and CuX (X = Cl, Br, I, C₆F₅) are carried out. The resultant products were characterized by melting point, elemental analysis, FT-IR, ¹H and ¹³C NMR spectroscopy, and single-crystal X-ray diffraction.

[a] S.-C. Huo,⁺ Y. Li,⁺ D.-X. Zhang, Q. Zhou, Prof. Dr. Y. Yang
School of Chemistry and Chemical Engineering
Central South University
Lushannan Road 932, 410083 Changsha (P. R. China)
E-mail: yangy@csu.edu.cn

[b] Prof. Dr. H. W. Roesky
Institut für Anorganische Chemie
Georg-August-Universität
Tammannstraße 4, 37077 Göttingen (Germany)
E-mail: hroesky@gwdg.de

[†] These authors contributed equally to this work.

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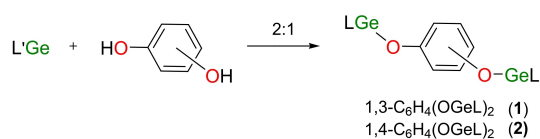
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Results and Discussion

The reaction of L'Ge with diphenols

Previously, we have proved that the addition reaction of L'Ge with PhOH enabled the synthesis of the mononuclear germylene LGeOPh.^[17] To ascertain the applicability of the reaction of diphenol with L'Ge for the preparation of digermylene, the toluene solution of L'Ge was treated with *o*-, *m*-, and *p*-diphenols in ether, respectively, in a 2:1 ratio (Scheme 2). After slowly mixing the reactant solutions at -78°C and then stirring the reaction mixtures overnight at room temperature, volatiles were removed *in vacuo*, and ^1H NMR spectra of C_6D_6 solutions of the residues were recorded. It was indicated that the reaction of L'Ge with *o*-diphenol gave a complex mixture of products, involving the large presence of free ligand LH, which may be formed by the ligand exchange between L' and *o*-diphenol. This reaction, which did not follow the pre-design, was mainly initialized by the bidentate nature of *o*-diphenol. In contrast, the digermylene $1,3\text{-C}_6\text{H}_4(\text{OGeL})_2$ (**1**) was readily formed by the reaction of L'Ge with *m*-diphenol, as yellowish solid powders in high yield (90%).

The melting range of **1** ($271.3\text{--}273.8^{\circ}\text{C}$) is much higher than that of LGeOPh (203°C).^[17] The ^1H NMR spectrum of **1** exhibits a characteristic singlet at δ 4.68 ppm, corresponding to the $\gamma\text{-CH}$ protons on the framework of β -diketiminato ligands, while two septets at δ 3.10 and 3.48 ppm in a ratio of 1:1 are assignable to the methine protons of the isopropyl groups on the Ar groups. The sharp singlet at δ 1.60 ppm for the protons of methyl groups connected to the $\beta\text{-C}$ indicated the successful cleavage and nucleophilic addition of H–O moieties. It was suggested the two [LGe] moieties are equivalent in solution due to the conformational averaging by free rotation of σ bonds. Besides the presence of all the expected protons, the correct integral ratio confirmed the 2:1 reaction. Compound **1** has good solubility in toluene and tetrahydrofuran but is less soluble in *n*-hexane. Pale yellow bulk crystals of **1** with a quality suitable for single-crystal X-ray diffraction characterization were obtained from the mixed solvent of toluene and hexane at -20°C for one week. Compound **1** crystallizes in the triclinic *P*-1 space group. As shown in Figure 1a, in the solid-state the two [LGe] moieties adopted asymmetric arrangement. One C_3N_2 quasi-plane is nearly perpendicular to the bridging phenyl plane, while the other is almost parallel to the latter. The $\text{C}_3\text{N}_2\text{Ge}$ six-membered rings both adopt the twisted boat conformation, where Ge atoms are located in the bow position and $\gamma\text{-C}$ atoms in the stern position. From the perspective of the O atoms, the Ge(1) boat is placed in a normal face-up position and the other Ge(2) boat is placed upside down,



Scheme 2. The reactions of L'Ge with *m*-diphenol and *p*-diphenol.

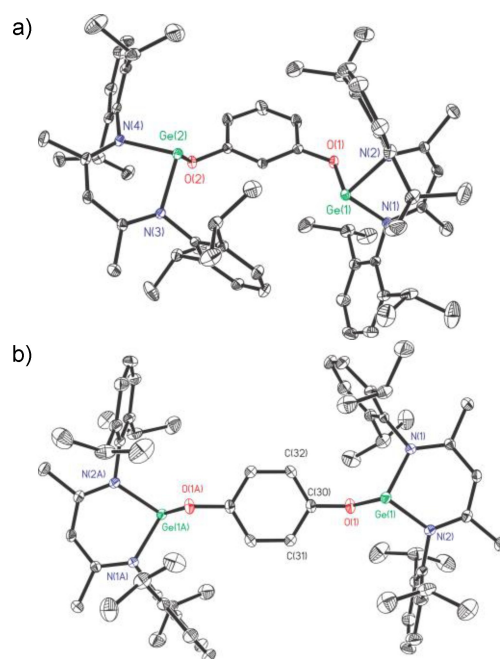


Figure 1. The molecular structures of **1** (a) and **2** (b) with the anisotropic displacement parameters are depicted at the 30% probability level. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): a) for **1**, Ge(1)–O(1) 1.884(2), Ge(2)–O(2) 1.849(2); Ge(1)–O(1)–C(60) 125.4(2), Ge(2)–O(2)–C(64) 117.11(19); b) for **2**, Ge(1)–O(1) 1.8494(17); Ge(1)–O(1)–C(30) 116.09(14).

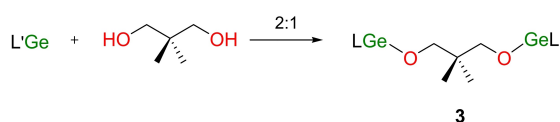
suggesting the flexibility of the β -diketiminato ligand by complying with the crystallization. The Ge–O bond lengths (1.884(2) Å and 1.849(2) Å) are within the reasonable range.^[24] The two Ge atoms are located on the same side of the molecule, with distances of 0.389 Å and 1.452 Å from the bridging phenyl plane, respectively (Figure S1). Besides, the Ge...Ge separation of **1** (5.668 Å) is much longer than those in $\text{Mes}_2\text{B}(\text{OGeL})_2$ (Mes = 2,4,6-Me₃C₆H₂) (3.682 Å)^[19] and digermylene oxides (3.1–3.2 Å),^[5c] while shorter than those in $[\text{LGe}(\text{OBPh})_2]_2\text{O}$ (9.555 Å) or $[(\text{LGeOBO})_2\text{O}]_2\text{OBMes}$ (6.962 Å).^[15] Based on our experience with diacylthioureas,^[23] this donor...donor distance in **1** is suitable as a chelating ligand to coordinate CuX (X = Cl, Br, I, C₆F₅). The distance would undergo adaptive changes in the coordination reaction, especially considering the change of ligand conformation due to the free α -bond rotation in the solution.

The 2:1 reaction of L'Ge with *p*-diphenol smoothly afforded $1,4\text{-C}_6\text{H}_4(\text{OGeL})_2$ (**2**, Scheme 2). The melting point of **2** ($276.3\text{--}278.8^{\circ}\text{C}$) is even slightly higher than that of its meta isomer **1**. The ^1H NMR of **2** presented a whole set of characteristic resonances for the β -diketiminato ligands, as well as a singlet at δ 6.04 ppm denoting the protons on the phenyl bridge with the correct integration. Compound **2** crystallizes in the monoclinic *P*2₁/*c* space group. The two [LGe] moieties are centrosymmetric with respect to the central phenyl ring (Figure 1b). The two Ge atoms in **2** are arranged in the most opposite positions, seemingly giving the farthest Ge...Ge distance (7.937 Å, Figure S1) in such [LGe] systems fused by $\text{--OC}_6\text{H}_4\text{O--}$ bridge.

The reaction of L'Ge with a diol

The diphenol type bridge is basically a short and rigid linker. In order to expand the scope of the study, we will consider the introduction of longer or more flexible linkers. For this reason, neopentyl glycol was used as the bridging precursor to react with L'Ge in a ratio of 1:2 in toluene solution (Scheme 3) to afford digermylene $\text{Me}_2\text{C}(\text{CH}_2\text{OGeL})_2$ (**3**).

The melting point of **3** was found to be dramatically as low as 154.6–156.8 °C, possibly in response to the use of a flexible carbon chain linker.^[25] The ¹H NMR spectrum of **3** features with two singlets at δ 2.90 and δ 0.14 ppm, representing the proton resonances of methylene $(-\text{OCH}_2)_2\text{C}$ and methyl $-\text{CMe}_2$ groups, respectively, on the bridging chain. Compound **3** crystallizes in the triclinic space group *P*-1. In the molecular structure of **3** (Figure 2), the Ge–O bond lengths (1.818(3), 1.839(3) Å) are shorter than those of **1** (1.884(2), 1.849(2) Å) and **2** (1.8494(17) Å), while comparable to that in LGeOtBu (1.827(2) Å).^[26] When comparing with **1** that connects two [LGe] moieties also using $-\text{OC}_3\text{O}-$ fragment with the same amount of atoms, the Ge...Ge distance (6.770 Å, Figure S1) of **3** is much longer, benefiting from a more stretchable saturated carbon chain. Another interesting observation is that the Ge(2)-tipped C_2OGe triangular pyramid points towards the outer sphere of the molecule, in sharp contrast to the situations in **1** and **2**, where the C_2OGe pyramid pairs point to the inner sphere of the molecule and even roughly point to each other (Figure S3). This outer direction of the Ge donor vector may be useful for the intermolecular assembly in complexation, just like the sulfur ligands did.^[23]



Scheme 3. The reaction of L'Ge with neopentyl glycol.

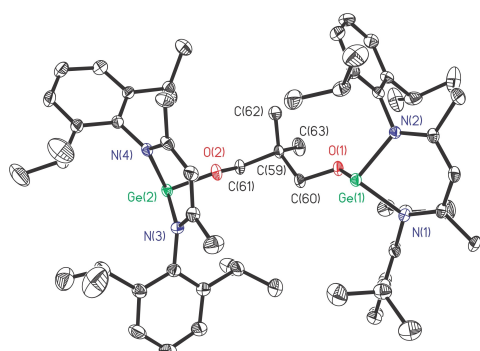
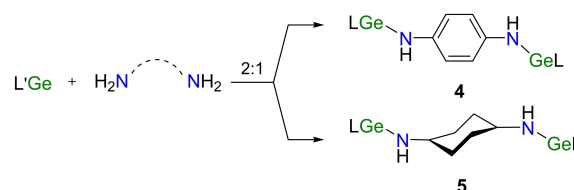


Figure 2. The molecular structure of **3** with the anisotropic displacement parameters is depicted at the 30% probability level. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–O(1) 1.818(3), Ge(2)–O(2) 1.839(3); Ge(1)–O(1)–C(60) 116.3(2), Ge(2)–O(2)–C(60) 124.8(2).

The reaction of L'Ge with diamines

By widening the reaction of N–H breakage and nucleophilic addition to L'Ge for the synthesis of mononuclear germylene,^[16] diamines were employed in the hope of the preparation of new digermylenes. The reaction of L'Ge with *o*-phenylenediamine also gave free ligand LH, due to the bidentate feature of the latter, just like *o*-diphenol mentioned above. Treatment of *p*-phenylenediamine with L'Ge in a 1:2 ratio in toluene formed the reddish-brown solids of 1,4- $\text{C}_6\text{H}_4[\text{N}(\text{H})\text{GeL}]_2$ (**4**) in a moderate yield (48%) (Scheme 4).

In the ¹H NMR spectrum of **4**, the singlet at δ 4.34 ppm is responsible for the protons of bridging amino groups. The melting range of **4** (290.3–293.6 °C) is almost 15 °C higher than that of its O-bridged analogue **2**. The saturated solution of **4** in toluene was stored at –20 °C for 5 days to crop red block crystals. Compound **4** crystallizes in the triclinic *P*-1 space group with an inversion center. As shown in Figure 3, when compared with **2**, the C_3N_2 quasi planes of β -diketiminato ligands in **4** are almost vertical to the bridging phenyl plane (84.26°, Figure S1). The Ge...Ge separation of **4** (8.481 Å) is slightly longer than that of **2** (7.937 Å), due to the longer N(3)–C and N(3)–Ge bond



Scheme 4. The reactions of L'Ge with *p*-phenylenediamine and *trans*-*p*-cyclohexanediamine.

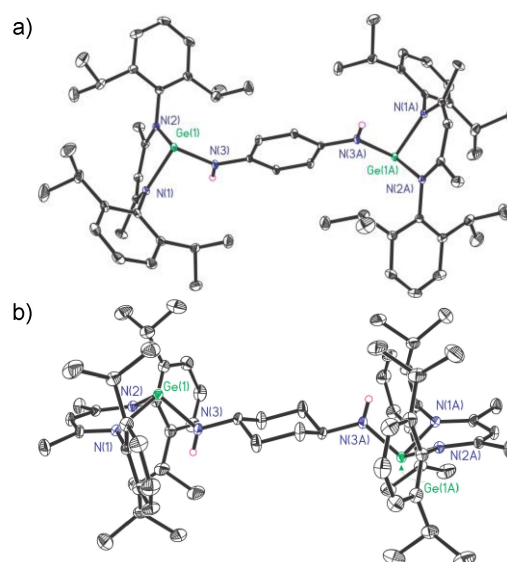


Figure 3. The molecular structures of **4** (a) and **5** (b) with the anisotropic displacement parameters are depicted at the 30% probability level. The H atoms except for NH groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): a) for **4**, Ge(1)–N(3) 1.8823(15); Ge(1)–N(3)–C(30) 127.22(12); b) for **5**, Ge(1)–N(3) 1.839(3); Ge(1)–N(3)–C(30) 121.7(3).

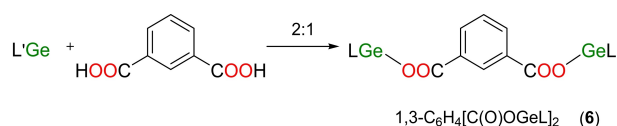
lengths as well as wider Ge–N–C angle. Both Ge-tipped pyramids point to the outer sphere of the molecule.

For comparison, the *trans-p*-cyclohexanediamine with a more flexible framework was used for the synthesis of digermylene 1,4-C₆H₁₀[N(H)GeL]₂ (5) (Scheme 4). The melting range of 5 (285.6–287.1 °C) is slightly lower than that of 4. In the ¹H NMR spectrum of 5, the resonances appearing at δ 0.64–1.54 ppm are assignable to the methine and methylene protons of the bridging cyclohexyl group. The saturated *n*-hexane solution of 5 at room temperature for 4 days produced red-brown bulk crystals suitable for X-ray diffraction analysis. Compound 5 crystallizes in the monoclinic space group *P*2₁/*c* (Figure 3), bearing an inversion center. The C₃N₂ quasi-planes of the β-diketiminato ligands almost overlap with the calculated cyclohexyl plane. Typically, the cyclohexyl ring adopts a chair conformation. As expected, the Ge...Ge distance (8.714 Å, Figure S1) is even longer than that of 4 (8.481 Å).

The reaction of L'Ge with *o*-/*m*-phthalic acids

In view of the smooth reaction, L'Ge with PhC(O)OH to generate mononuclear germylene PhC(O)OGeL,^[17] the 2:1 reactions of L'Ge with *m*-/*p*-phthalic acids were carried out for the formation of extended digermylene derivatives (Scheme 5).

Treatment of L'Ge with *m*-phthalic acid smoothly afforded pale yellow powders of 1,3-C₆H₄[C(O)OGeL]₂ (6, Scheme 5) in moderate yield (68%). The melting range of 6 (254.4–256.9 °C) is much higher than that of PhC(O)OGeL (167 °C),^[17] but it is almost 17 °C lower than that of 1,3-C₆H₄(OGeL)₂ (1). The ¹H NMR spectrum of 6 exhibits a similar resonance pattern to 1, while the ¹³C NMR spectrum of 6 confirms the presence of C=O resonance at δ 169.31 ppm. The molecular structure of 6 is depicted in Figure 4.



Scheme 5. The reaction of L'Ge with *m*-phthalic acid.

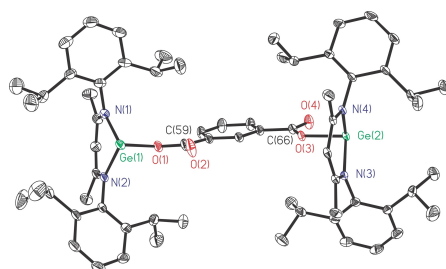


Figure 4. The molecular structure of 6 with the anisotropic displacement parameters is depicted at the 30% probability level. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–O(1) 1.925(4), Ge(2)–O(3) 1.942(3); Ge(1)–O(1)–C(59) 122.0 (4), Ge(2)–O(3)–C(66) 115.8(3).

Compound 6 crystallizes in the monoclinic *P*2₁/*n* space group. The two [LGeOOC] moieties are *trans*-arranged in a way just like that in 1,4-C₆H₄[N(H)GeL]₂ (4). The Ge...Ge separation of 6 is further increased to 9.785 Å (Figure S1), much longer than those of 1–5. Another feature of the solid structure of 6 is that the C₃N₂Ge rings are largely flat, where the distances of bow Ge atoms deviating from the C₂N₂ quasi-planes are only 0.286 and 0.351 Å (Figure S2).

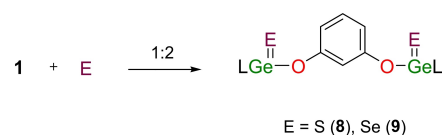
The product of L'Ge and *p*-phthalic acid was less soluble in common organic solvents, as precluded further characterization. In contrast, the reaction of L'Ge with *p*-tert-butylbenzoic acid proceeded smoothly to give the mononuclear product *p*-tBu-C₆H₄C(O)OGeL (7, Figure S4). One counterintuitive observation in 1–6 is that the γ-C and Ge atoms are roughly located on the same plane (Figure S3), regardless of the variation of linker groups.

Oxidative addition of 1,3-C₆H₄(OGeL)₂ (1) with sulfur and selenium

The reactivity of the representative digermylene 1,3-C₆H₄(OGeL)₂ (1) with sulfur and selenium was examined (Scheme 6). The oxidative additions proceeded straightforwardly to produce the products 1,3-C₆H₄[OGe(S)L]₂ (8) and 1,3-C₆H₄[OGe(Se)L]₂ (9), with the ¹H NMR patterns similar to that of 1,3-C₆H₄(OGeL)₂ (1).

The melting points of the obtained Ge(IV) products are nearly 20 °C (8) and 50 °C (9) higher than that of the parent digermylene 1. The toluene solutions of 8 and 9, respectively, were stored at –20 °C for 2 days to result in each being a crop of colorless block crystals. Compound 8 crystallizes in the monoclinic *C*2/*c* space group with unit cell parameters *a* = 20.3204(17) Å, *b* = 16.3836(13) Å, *c* = 48.118(4) Å; β = 97.378(5)°; *V* = 15886.9 Å³. However, its crystal data was not complete due to the pulverization during several measurements. In contrast, crystals of compound 9 are robust and crystallize in the triclinic *P*-1 space group. As shown in Figure 5, each Ge(IV) atom is bonded by two nitrogen, one oxygen, and one selenium atom.

The two [LGe(Se)O] moieties are located in a *cis* arrangement. The Ge–Se bond lengths (2.1779(3), 2.1802(3) Å) are slightly shorter than that of mononuclear LGe(Se)Me (2.199(1) Å).^[27] The Ge–O bond lengths (1.7960(14), 1.7903(14) Å) become shorter than those in parent 1 (1.884(2), 1.849(2) Å), as a result of the increase in oxidation state. In addition, Ge–O–C bond angles in 9 (133.60(13), 133.39(13)°) are much wider than those in 1, helping to increase the Ge...Ge distance (8.064 Å, Figure S5) of 9, which is noticeably longer than that of 1 (5.668 Å).



Scheme 6. The reactions of 1,3-C₆H₄(OGeL)₂ (1) with sulfur and selenium.

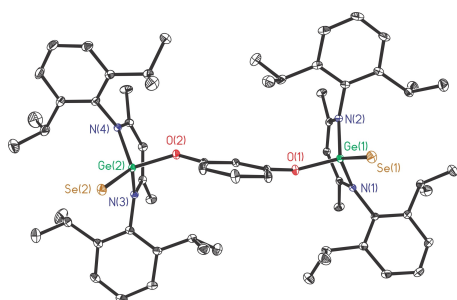


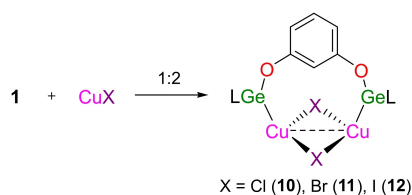
Figure 5. The molecular structure of **9** with the anisotropic displacement parameters is depicted at the 30% probability level. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–Se(1) 2.1779(3), Ge(2)–Se(2) 2.1802(3), Ge(1)–O(1) 1.7960(14), Ge(2)–O(2) 1.7903(14); Ge(1)–O(1)–C(60) 133.60(13), Ge(2)–O(2)–C(64) 133.39(13).

Complexation of 1,3-C₆H₄(OGel)₂ (**1**) with CuX

Treatment of 1,3-C₆H₄(OGel)₂ (**1**) with CuX (X = Cl, Br, I) in a 1:2 ratio generated the corresponding donor-acceptor complexes (CuX)₂[1,3-C₆H₄(OGel)₂] (X = Cl (**10**), Br (**11**), I (**12**)) (Scheme 7).

The molecular structures of **10–12** are shown in Figure 6. They are fundamentally isostructural and share a highly similar structural skeleton (Figure S6), where the halogen atoms are arranged in bridging positions. The common feature of them is that the digermylene **1** therein exhibits chelating properties with two Ge(II) donors to embrace the (CuX)₂ core, in which each Cu atom is bonded to one Ge and two bridging halogen atoms. The (CuX)₂ fragments in the molecules of **10–12** are significantly twisted as a down-folded quadrangle, with dihedral angles between Cu₂X planes 42.35° (**10**), 38.90° (**11**), and 36.98° (**12**), respectively (Figure S7). This observation is totally different from the rhombic plane conformation in (μ²-Cu₂)₂[LGeOtBu]₂ completed by two discrete mononuclear germynes.^[20b] A comparable example to our work is the germylene oxide supported (CuI-pyridine)₂ bearing the tetracoordinate Cu centers,^[5c] with a smaller dihedral angle between Cu₂I planes (25.61°). From **10** to **12**, both Ge–Cu and Ge–X bond lengths increased with the increase of the atomic number of X, accompanied by a progressive decrease of the Cu–X–Cu angles (Table S1).

One surprising observation is that among **10–12** the shortest Cu–Cu bond length (2.5852(8) Å) and Ge...Ge distances (5.846 Å) appear in the bromide derivative (**11**), probably due to its Ge–X bond length and Cu–X–Cu bond angle both happen to be relatively small. Nevertheless, all three Cu–Cu bond lengths (2.6196(6), 2.5852(8), 2.5916(17) Å) are shorter when



Scheme 7. The reaction of 1,3-C₆H₄(OGel)₂ (**1**) with CuX (X = Cl, Br, I).

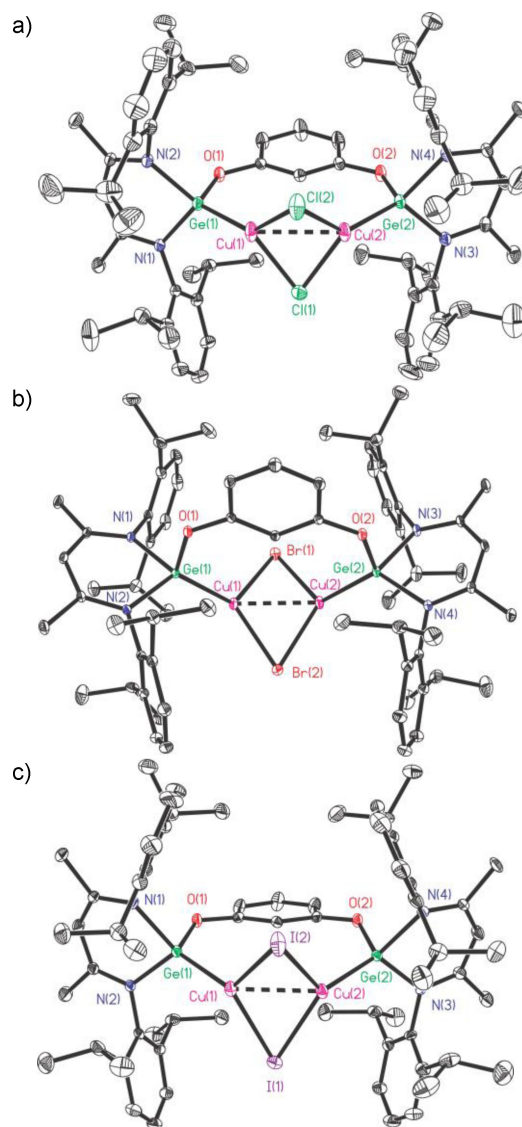


Figure 6. The molecular structures of **10** (a), **11** (b) and **12** (c) with the anisotropic displacement parameters are depicted at the 30% probability level. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): a) for **10**, Ge(1)–Cu(1) 2.2567(6), Ge(2)–Cu(2) 2.2550(6), Cu(1)–Cu(2) 2.6196(6); Cu(1)–Cl(1)–Cu(2) 68.18(4), Cu(1)–Cl(2)–Cu(2) 71.09(4); b) for **11**, Ge(1)–Cu(1) 2.2677(7), Ge(2)–Cu(2) 2.2643(7), Cu(1)–Cu(2) 2.5852(8); Cu(1)–Br(1)–Cu(2) 63.79(2), Cu(1)–Br(2)–Cu(2) 65.78(2); c) for **12**, Ge(1)–Cu(1) 2.2969(17), Ge(2)–Cu(2) 2.2827(16), Cu(1)–Cu(2) 2.5916(17); Cu(1)–I(1)–Cu(2) 60.66(4), Cu(1)–I(2)–Cu(2) 60.50(4).

compared with that in [(*i*Bu)₂ATIge]₂O(Cu₂I₂)(C₅H₅N)₂ (2.836 Å).^[5c]

Furthermore, 1,3-C₆H₄(OGel)₂ (**1**) was treated with one equivalent of (CuC₆F₅)₄, producing a partially hydrolyzed product [(F₅C₆Cu)₂OCu₂][1,3-C₆H₄(OGel)₂] (**13**, Figure S8), due to the high moisture sensitivity of this reaction.

Further exploration of trigermylene

We have shown the feasibility of synthesizing digermynes using L'Ge with species containing double OH, NH, or C(O)OH

functionalities. Along these lines, germlylenes with trinuclear or more should also be relatively easy to obtain. Here, we report the preparation of trigermylene using L'Ge with phloroglucinol in a 3:1 ratio. As expected, trigermylene 1,3,5-C₆H₃(OGeL)₃ (**14**) was readily obtained and structurally characterized (Figures S9, S10). The reactivity studies of **14** and the preparation of exciting multinuclear germlylenes are in progress.

Moreover, although the digermylene products in this paper are relatively predictable (almost exclusively 1,4-adducts), at a broader level the study of the reaction pathways of L'Ge with protic and hydric E–H bonds of HER would still be an issue worthy of further investigation.

Conclusion

In conclusion, we have demonstrated the feasibility of utilizing L'Ge with diphenols, diol, diamines, and dicarboxylic acids (HE)₂R (E=O, N, C(OO)) to synthesize the β-diketimate ligand supported digermlylenes R(EGeL)₂ (L=CH[C(Me)NAr]₂, Ar=2,6-*i*Pr₂C₆H₃) (**1–6**) by H–E bond cleavage and nucleophilic addition reaction. X-ray single-crystal structure analysis revealed that the Ge–Ge separations in digermlylenes **1–6** were affected by the rigidity/flexibility and size of the linker R. The representative digermylene 1,3-C₆H₄(OGeL)₂ (**1**) exhibited good reactivity with sulfur and selenium, as well as CuX (X=Cl, Br, I, C₆F₅) to form donor-acceptor complexes, where the two Ge donors cooperate to chelate the (CuX)₂ core. This strategy is also useful in synthesizing multinuclear germlylenes and promoting the advance in the assembly and application of Ge→M complexes.

Experimental Section

General procedures

All manipulations were carried out in a standard Schlenk technology in a dry argon atmosphere or in the glovebox with oxygen content less than 0.1 ppm. Solvents needed for synthesis in the laboratory were pre-dried with the molecular sieve 4 Å for 3 days, then added with appropriate Na/K alloy and benzophenone, heated, and refluxed to make the solvents dark blue or purple. After evaporation, the solvents were stored in anhydrous and oxygen-free solvent bottles in the argon atmosphere for reserve. Compound L'Ge was prepared based on the literature procedure.^[17] Other reagents involved in this article were purchased from Aladdin without special instructions.

The melting point of obtained compounds was measured on a digital display micro melting point meter (X-4B⁺). Infrared spectra were recorded by using KBr pellets with a NEXUS670 (Thermo Fisher Scientific) FT-IR spectrometer. The ¹H and ¹³C NMR spectra were measured on a Bruker Advance II 400 MHz NMR instrument at ambient temperature. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Thermo Quest Italia SPA EA1110 instrument.

Digermlylenes

1,3-C₆H₄(OGeL)₂ (1). A solution of *m*-diphenol (0.111 g, 1 mmol) in ether (10 mL) was added to the stirred solution of L'Ge (0.978 g,

2 mmol) in toluene (40 mL) at –78 °C. The solution slowly turns orange. After rising to room temperature, the reaction continued at room temperature for 12 hours, and the volatile substances were dried to obtain yellowish solids. Yield: 0.980 g (0.9 mmol, 90%). M.p.: 271.3–273.8 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 6.96 (m, 12H, Ar-H), 6.54 (s, 1H, Ph-H), 5.76 (s, 2H, Ph-H), 5.40 (s, H, Ph-H), 4.68 (s, 2H, γ-CH), 3.48 (sept, *J*=13.4, 6.6 Hz, 4H, CHMe₂), 3.10 (sept, *J*=13.6, 6.8 Hz, 4H, CHMe₂), 1.39 (s, 12H, CMe), 1.13 (d, *J*=6.7 Hz, 12H, CHMe₂), 0.99 (d, *J*=6.8 Hz, 12H, CHMe₂), 0.93 (d, *J*=6.8 Hz, 24H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm): δ 162.57, 161.48, 145.53, 142.61, 139.02 (Ar-C), 128.03 (Ph-C), 123.89, 123.05 (Ar-C), 110.52, 109.85 (Ph-C), 96.53 (γ-C), 30.76, 19.34, 27.95, 27.33 (CHMe₂), 24.68 (CHMe₂), 24.33, 23.66, 23.55 (CHMe₂), 22.00 (CMe). FT-IR (cm⁻¹): ν 3448.34 (w), 3054.84 (w), 2966.13 (s), 2921.77 (m), 2869.71 (w), 1618.63 (vw), 1560.21 (s), 1475.35 (w), 1380.85 (w), 1319.36 (m), 1174.49 (m), 1137.35 (w), 1103.14 (w), 1018.28 (w), 971.99 (m), 856.28 (vw), 790.49 (s), 755.99 (w), 694.28 (vw), 619.07 (w), 586.28 (w), 526.49 (vw). Anal. Calcd. for C₆₄H₈₆Ge₂N₄O₂ (1088.68): C, 70.61; H, 7.96; N, 5.15%; found C, 70.37; H, 7.83; N, 4.96%. A pale-yellow crystal suitable for single-crystal X-ray diffraction was obtained by dissolving the solid compound **1** in toluene solution and concentrating it to 3 mL, then dropping 2 mL of *n*-hexane solution and storing the mixture solution in a refrigerator at –20 °C for 4 days.

1,4-C₆H₄(OGeL)₂ (2). The *p*-diphenol (0.111 g, 1 mmol) and L'Ge (0.978 g, 2 mmol) were used for the synthesis of **2**. Yield: 0.936 g (0.86 mmol, 86%). M.p.: 276.3–278.8 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 6.93 (s, 12H, Ar-H), 6.04 (s, 4H, Ph-H), 4.71 (s, 2H, γ-CH), 3.52 (sept, *J*=13.4, 6.6 Hz, 4H, CHMe₂), 3.05 (sept, *J*=13.6, 6.8 Hz, 4H, CHMe₂), 1.36 (s, 12H, CMe), 1.05 (d, *J*=6.7 Hz, 12H, CHMe₂), 0.96 (d, *J*=6.8 Hz, 12H, CHMe₂), 0.86 (d, *J*=6.8 Hz, 12H, CHMe₂), 0.84 (d, *J*=6.8 Hz, 12H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm): δ 163.52, 146.43, 143.53, 140.20, 124.67, 123.76, 119.20 (Ar/Ph-C), 97.92 (γ-C), 57.37, 28.76, 28.00 (CHMe₂), 25.93, 24.94, 24.31 (CHMe₂), 22.95 (CMe). FT-IR (cm⁻¹): ν 3444.41 (w), 2964.23 (w), 2871.63 (w), 1629.63 (w), 1548.64 (w), 1467.64 (w), 1380.85 (w), 1324.92 (w), 1236.21 (w), 1103.14 (w), 1018.28 (w), 969.43 (w), 857.31 (vw), 791.21 (s), 786.85 (w), 759.85 (w), 694.28 (vw), 619.07 (vw), 586.28 (vw), 524.57 (vw). Anal. Calcd. for C₆₄H₈₆Ge₂N₄O₂ (1088.68): C, 70.61; H, 7.96; N, 5.15%; found C, 70.47; H, 7.86; N, 5.06%. A pale-yellow crystal suitable for single-crystal X-ray diffraction was obtained by storing the saturated toluene solution of compound **2** in a refrigerator at –20 °C for 7 days.

Me₂C(CH₂OGeL)₂ (3). The neopentyl glycol (0.104 g, 1 mmol) and L'Ge (0.978 g, 2 mmol) were used for the synthesis of **3**. Yield: 0.866 g (0.8 mmol, 80%). M.p.: 154.6–156.8 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 6.96–7.00 (m, 12H, Ar-H), 4.55 (s, 2H, γ-CH), 3.56 (sept, *J*=13.5, 6.7 Hz, 4H, CHMe₂), 3.09 (sept, *J*=13.5, 6.7 Hz, 4H, CHMe₂), 2.90 (s, 4H, OCH₂), 1.31 (s, 12H, CMe), 1.21 (d, *J*=6.7 Hz, 12H, CHMe₂), 1.08 (d, *J*=6.8 Hz, 12H, CHMe₂), 1.08 (d, *J*=6.8 Hz, 12H, CHMe₂), 0.93 (d, *J*=6.8 Hz, 12H, CHMe₂), 0.14 (s, 6H, CMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm): δ 162.57, 144.32, 143.10, 139.27, 125.93, 123.39, 123.22 (Ar-C), 95.90 (γ-C), 71.65 (OCH₂), 38.49 (CMe₂), 27.59, 27.26 (CHMe₂), 25.25 (CHMe₂), 24.12, 23.71, 23.50, 22.23 (CMe), 21.59, 20.98 (CHMe₂). FT-IR (cm⁻¹): ν 3417.41 (w), 3060.62 (w), 2958.41 (s), 2861.98 (m), 1625.78 (w), 1558.28 (w), 1461.82 (w), 1386.64 (vs), 1317.21 (s), 1259.35 (m), 1078.07 (s), 1020.21 (s), 991.28 (vw), 937.28 (w), 850.50 (w), 794.57 (vw), 754.07 (vw), 673.07 (m), 765.43 (w), 638.35 (vw), 518.78 (vw). Anal. Calcd. for C₆₃H₉₂Ge₂N₄O₂ (1082.72): C, 69.89; H, 8.57; N, 5.17%; found C, 69.78; H, 8.43; N, 5.01%. Compound **3** was placed in concentrated *n*-hexane solvent for 3 days to obtain pale yellow crystals suitable for single-crystal X-ray diffraction analysis.

1,4-C₆H₄(N(H)GeL)₂ (4). The 1,4-C₆H₄(NH)₂ (0.108 g, 1 mmol) and L'Ge (0.978 g, 2 mmol) were used for the synthesis of **4**. Yield:

0.521 g (0.48 mmol, 48%). M.p.: 290.3–293.6 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 6.74–7.13 (m, 12H, Ar-H), 6.09 (s, 4H, Ph-H), 4.64 (s, 2H, γ-CH), 4.34 (br, 2H, NH), 3.31 (sept, *J* = 13.4, 6.6 Hz, 4H, CHMe₂), 3.20 (sept, *J* = 13.6, 6.8 Hz, 4H, CHMe₂), 1.37 (s, 12H, CMe), 1.12 (d, *J* = 6.7 Hz, 12H, CHMe₂), 1.01 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.91 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.87 (d, *J* = 6.8 Hz, 12H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm): δ 163.46, 146.35, 143.30, 141.38, 124.57, 123.73, 116.21 (Ar/Ph-C), 96.18 (γ-C), 28.88, 28.50 (CHMe₂), 26.57, 24.38, 24.03 (CHMe₂), 23.17 (CMe). FT-IR (cm⁻¹): ν 3455.98 (w), 3060.63 (vw), 2960.34 (w), 2927.56 (w), 2871.63 (w), 1621.92 (w), 1550.56 (w), 1496.56 (w), 1459.71 (w), 1442.56 (w), 1390.49 (w), 1317.21 (w), 1263.21 (w), 1170.64 (w), 1103.99 (w), 1027.92 (w), 937.49 (vw), 850.49 (vw), 798.42 (w), 755.99 (w), 746.35 (w), 723.31 (vw), 586.71 (w), 518.78 (vw). Anal. Calcd. for C₆₄H₈₈Ge₂N₆ (1086.71): C, 70.74; H, 8.16; N, 7.73%; found C, 70.87; H, 8.09; N, 7.57%.

1,4-C₆H₁₀[N(H)GeL]₂ (5). The *trans-p*-cyclohexanediamine (0.114 g, 1 mmol) and L'Ge (0.978 g, 2 mmol) were used for the synthesis of 5. Yield: 0.764 g (0.70 mmol, 70%). M.p.: 285.6–287.1 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 7.00–7.07 (m, 12H, Ar-H), 4.64 (s, 2H, γ-CH), 3.55 (sept, *J* = 13.4, 6.6 Hz, 4H, CHMe₂), 3.38 (sept, *J* = 13.6, 6.8 Hz, 4H, CHMe₂), 2.38 (s, 2H, NH), 1.54 (s, 2H, CH), 1.49 (s, 12H, CMe), 1.31 (d, *J* = 6.7 Hz, 12H, CHMe₂), 1.26 (d, *J* = 6.8 Hz, 12H, CHMe₂), 1.13 (d, *J* = 6.8 Hz, 12H, CHMe₂), 1.12 (d, *J* = 6.8 Hz, 12H, CHMe₂), 0.96 (m, 4H, CH₂), 0.64 (m, 4H, CH₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm): δ 163.50, 143.75, 142.91, 139.48, 125.31, 123.48, 122.74 (Ar-C), 94.32 (γ-C), 51.92 (CH), 38.23 (CH₂), 27.54 (CHMe₂), 25.55, 23.92 (CHMe₂), 23.61, 23.44 (CMe), 22.95 (CHMe₂), 22.27 (CHMe₂), 21.91. FT-IR (cm⁻¹): ν 3446.34 (w), 3058.70 (vw), 2960.34 (w), 2925.63 (w), 2861.99 (w), 1569.85 (m), 1523.56 (w), 1465.71 (w), 1442.56 (w), 1384.71 (w), 1315.28 (w), 1253.56 (w), 1170.64 (w), 1106.99 (w), 1054.92 (w), 1022.14 (w), 958.49 (vw), 850.49 (vw), 798.42 (w), 746.35 (w), 723.31 (vw), 628.71 (w), 514.93 (vw). Anal. Calcd. for C₆₄H₉₄Ge₂N₆ (1092.76): C, 70.35; H, 8.67; N, 7.69%; found C, 70.37; H, 8.83; N, 7.51%. Red bulk crystals for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at room temperature after 7 days.

1,3-C₆H₄[C(O)OGeL]₂ (6). The *m*-phthalic acid (0.166 g, 1 mmol) and L'Ge (0.978 g, 2 mmol) were used for the synthesis of 6. Yield: 0.778 g (0.68 mmol, 68%). M.p.: 254.4–256.9 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 9.02 (s, 1H, Ph-H), 8.25 (m, 2H, Ph-H), 7.00 (s, 1H, Ph-H), 6.83–6.98 (m, 12H, Ar-H), 4.92 (s, 2H, γ-CH), 3.45 (sept, *J* = 6.6 Hz, 4H, CHMe₂), 2.96 (sept, *J* = 13.6, 6.8 Hz, 4H, CHMe₂), 1.40 (s, 12H, CMe), 0.95–0.99 (m, 36H, CHMe₂), 0.84 (d, *J* = 6.8 Hz, 12H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm): δ 168.23 (Ar-C), 163.91 (C=O), 145.47, 142.47, 139.40, 135.05, 131.01, 124.04, 122.99 (Ar/Ph-C), 98.90 (γ-C), 30.76, 28.21, 27.15 (CHMe₂), 25.43, 23.53, 23.40, 23.14, 22.95 (CHMe₂), 22.27 (CMe). FT-IR (cm⁻¹): ν 3425.19 (w), 3130.98 (w), 3065.41 (vw), 2967.16 (w), 2859.23 (w), 1716.63 (w), 1646.71 (w), 1527.99 (s), 1465.71 (w), 1442.56 (w), 1376.64 (w), 1319.14 (w), 1257.42 (w), 1173.42 (w), 1096.35 (w), 1015.34 (w), 932.41 (w), 857.28 (w), 796.35 (vw), 757.92 (s), 732.64 (w), 696.14 (w), 645.99 (vw), 587.21 (w), 570.82 (vw), 525.51 (vw). Anal. Calcd. for C₆₆H₈₆Ge₂N₄O₄ (1144.70): C, 69.25; H, 7.57; N, 4.89%; found C, 69.32; H, 7.63; N, 4.96%. The colorless bulk crystals of 6 precipitated on the surface of the bottle during slow volatilization of THF.

Oxidative addition products of 1 with sulfur and selenium

1,3-C₆H₄[OGe(S)I]₂ (8). A solution of 1,3-C₆H₄(OGeL)₂ (0.545 g, 0.5 mmol) and sulfur (0.032 g, 1 mmol) in toluene (40 mL) was stirred at 85 °C for 12 hours. Yield: 0.530 g (0.46 mmol, 91%). M.p.: 290.2–291.9 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ = 7.12 (m, 12H, Ar-H), 6.91 (m, 2H, Ph-H), 6.74 (m, 1H, Ph-H), 6.52 (s, 1H, Ph-H), 4.87 (s, 2H, γ-CH), 3.45–3.53 (m, 4H, CHMe₂), 1.55 (s, 12H, CMe), 1.51 (br, 12H, CHMe₂), 1.15–1.18 (dd, *J* = 6.7 Hz, 24H, CHMe₂), 1.08 (d, *J* =

6.8 Hz, 12H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm) δ 169.65, 158.83, 146.24, 145.21 (Ar-C), 137.65 (Ph-C), 136.92, 128.06, 125.45, 124.83, 124.61 (Ar-C), 113.19, 112.41 (Ph-C), 99.21 (γ-C), 29.15, 28.54, 25.71, 25.45, 24.55, 23.80, 21.20 (CHMe₂, CHMe₂, and CMe). FT-IR (cm⁻¹): ν 3456.34 (w), 3051.84 (w), 2960.13 (s), 2919.71 (m), 2860.72 (w), 1620.23 (vw), 1483.26 (w), 1386.25 (w), 1316.32 (m), 1178.29 (m), 1140.35 (vw), 1104.14 (w), 1018.28 (w), 970.99 (m), 856.28 (vw), 793.49 (s), 752.99 (w), 694.28 (vw), 620.07 (w), 587.28 (w), 552.43 (vw) 526.49 (vw). Anal. Calcd. for C₆₄H₈₆Ge₂N₄O₂S₂ (1152.80): C, 66.68; H, 7.52; N, 4.86%; found C, 66.55; H, 7.75; N, 4.75%.

1,3-C₆H₄[OGe(Se)L]₂ (9). A solution of 1,3-C₆H₄(OGeL)₂ (0.545 g, 0.5 mmol) and selenium (0.078 g, 1 mmol) in toluene (40 mL) was stirred at 85 °C for 12 hours. Yield: 0.561 g (0.45 mmol, 94%). M.p.: 320.4–321.9 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 6.90–7.13 (m, 12H, Ar-H), 6.73 (m, 2H, Ph-H), 6.49 (m, 1H, Ph-H), 6.35 (s, 1H, Ph-H), 4.67 (s, 2H, γ-CH), 3.28–3.34 (m, 4H, CHMe₂), 1.36 (d, *J* = 6.7 Hz, 12H, CHMe₂), 1.31 (s, 12H, CMe), 0.98–1.00 (dd, *J* = 6.8 Hz, 24H, CHMe₂), 0.89 (d, *J* = 6.8 Hz, 12H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm) δ 163.52, 146.43, 143.53, 140.20, 136.34, 124.67, 123.76, 119.20 (Ar/Ph-C), 97.92 (γ-C), 28.76, 28.01, 25.93, 24.94, 24.30, 22.95 (CHMe₂, CHMe₂, and CMe). FT-IR (cm⁻¹): ν 3456.34 (w), 3051.47 (w), 2960.13 (s), 2860.72 (w), 1620.23 (vw), 1542.71 (vw), 1480.46 (w), 1360.52 (w), 1316.32 (m), 1182.29 (m), 1140.35 (w), 1106.15 (w), 1019.28 (w), 970.99 (m), 856.28 (vw), 794.49 (s), 747.99 (w), 694.28 (vw), 620.07 (w), 587.28 (w), 552.43 (vw) 526.49 (vw). Anal. Calcd. for C₆₄H₈₆Ge₂N₄O₂Se₂ (1246.60): C, 61.66; H, 6.95; N, 4.49%; found C, 61.55; H, 6.75; N, 4.35%. The concentrated solution was stored at –20 °C in a freezer for 2 days to get the colorless and transparent massive crystals.

Coordination products of 1 with CuX

(CuCl)₂[1,3-C₆H₄(OGeL)₂] (10) The 1,3-C₆H₄(OGeL)₂ (0.545 g, 0.5 mmol) and CuCl (0.098 g, 1 mmol) were used for the synthesis of 10. Yield: 0.547 g (0.425 mmol, 85%). M.p.: 337.4–338.9 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm) δ 6.93–7.13 (m, 14H, Ar/Ph-H), 6.53 (m, 2H, Ph-H), 4.91 (s, 2H, γ-CH), 3.46–3.52 (m, 4H, CHMe₂), 3.11–3.14 (m, 4H, CHMe₂), 1.51 (s, 12H, CMe), 1.49 (d, *J* = 6.7 Hz, 12H, CHMe₂), 1.23 (d, *J* = 6.6 Hz, 12H, CHMe₂), 0.94–0.96 (dd, *J* = 20.9, 6.3 Hz, 24H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm) δ 165.91, 160.54, 144.96, 142.29, 137.44, 136.69, 128.13, 127.51, 127.36, 124.49, 123.88, 123.43 (Ar/Ph-C), 110.90 (γ-C), 28.78, 27.05, 26.07, 23.54, 22.57, 20.24 (CHMe₂, CHMe₂, and CMe). FT-IR (cm⁻¹): ν 3447.45 (w), 3033.56 (w), 2966.13 (s), 2921.77 (m), 2868.34 (w), 1617.34 (vw), 1560.21 (s), 1475.35 (w), 1380.85 (w), 1319.36 (m), 1174.49 (m), 1137.35 (w), 1102.78 (w), 1018.28 (w), 971.99 (m), 856.28 (vw), 790.49 (s), 758.34 (w), 692.56 (vw), 618.52 (w), 586.28 (w), 527.35 (vw). Anal. Calcd. for C₆₄H₈₆Ge₂N₄O₂Cu₂Cl₂ (1286.67): C, 59.74; H, 6.74; N, 4.35%; found C, 59.87; H, 6.75; N, 4.25%.

(CuBr)₂[1,3-C₆H₄(OGeL)₂] (11). The 1,3-C₆H₄(OGeL)₂ (0.545 g, 0.5 mmol) and CuBr (0.143 g, 1 mmol) were used for the synthesis of 11. Yield: 0.591 g (0.430 mmol, 86%). M.p.: 340.2–341.6 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm) δ 7.00–7.09 (m, 14H, Ar/Ph-H), 6.56 (d, *J* = 8.0 Hz, 2H, Ph-H), 4.92 (s, 2H, γ-CH), 3.45–3.57 (m, 4H, CHMe₂), 3.09–3.23 (m, 4H, CHMe₂), 1.54 (br, 24H, CMe and CHMe₂), 1.27 (d, *J* = 6.2 Hz, 12H, CHMe₂), 0.93–0.95 (dd, *J* = 25.8, 6.0 Hz, 24H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm) δ 162.57, 161.49, 145.54, 142.61, 139.02, 128.03, 126.44, 123.89, 122.67, 121.37 (Ar/Ph-C), 110.52, 109.85 (Ph-C), 96.53 (γ-C), 29.34, 27.95, 27.33, 24.69, 24.33, 23.55, 20.00 (CHMe₂, CHMe₂, and CMe). FT-IR (cm⁻¹): ν 3447.35 (w), 3054.84 (w), 2989.24 (s), 2873.68 (w), 2869.71 (w), 1618.63 (vw), 1553.85 (s), 1475.35 (w), 1380.85 (w), 1317.38 (m), 1256.49 (m), 1120.57 (w), 1005.14 (w), 1018.28 (w), 971.99 (m), 856.28 (vw), 790.49 (s), 748.78 (w), 694.28 (vw), 628.47 (w), 594.39

(w), 526.49 (vw). Anal. Calcd. for $C_{64}H_{86}Ge_2N_4O_2Cu_2Br_2$ (1375.58): C, 55.88; H, 6.30; N, 4.07%; found C, 55.87; H, 6.17; N, 3.97%.

(CuI)₂[1,3-C₆H₄(OGel)₂] (12). The 1,3-C₆H₄(OGel)₂ (0.545 g, 0.5 mmol) and CuI (0.190 g, 1 mmol) were used for the synthesis of 12. Yield: 0.566 g (0.385 mmol, 77%). M.p.: 345.2–347.8 °C. ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ 6.96 (m, 12H, Ar-H), 6.54 (s, 1H, Ph-H), 5.76 (s, 2H, Ph-H), 5.40 (s, H, Ph-H), 4.68 (s, 2H, γ-CH), 3.48 (sept, J = 13.4, 6.6 Hz, 4H, CHMe₂), 3.10 (sept, J = 13.6, 6.8 Hz, 4H, CHMe₂), 1.39 (s, 12H, CMe), 1.13 (d, J = 6.7 Hz, 12H, CHMe₂), 0.93 (d, J = 6.8 Hz, 12H, CHMe₂), 0.91 (d, J = 6.8 Hz, 12H, CHMe₂), 0.80 (d, J = 6.8 Hz, 12H, CHMe₂). ¹³C NMR (101 MHz, C₆D₆, 298 K, ppm) δ 165.91, 160.53, 144.96, 142.93, 137.44, 136.69, 128.13, 127.52, 127.37, 124.49, 123.88, 123.43 (Ar/Ph-C), 110.90 (γ-C), 28.78, 27.06, 26.07, 23.54, 22.57, 20.24 (CHMe₂, CHMe₂, and CMe). FT-IR (cm⁻¹): ν 3448.34 (w), 3054.84 (w), 2966.13 (s), 2921.77 (m), 2869.71 (w), 1618.63 (vw), 1560.21 (s), 1475.35 (w), 1380.85 (w), 1319.36 (m), 1174.49 (m), 1137.35 (w), 1103.14 (w), 1018.28 (w), 971.99 (m), 856.28 (vw), 790.49 (s), 755.99 (w), 694.28 (vw), 619.07 (w), 586.28 (w), 526.49 (vw). Anal. Calcd. for $C_{64}H_{86}Ge_2N_4O_2Cu_2I_2$ (1469.58): C, 52.31; H, 5.90; N, 3.81%; found C, 52.43; H, 5.88; N, 3.82%.

X-ray crystallographic analysis

The crystallographic data were measured on a Bruker SMART APEX II CCD single crystal diffractometer with MoK α radiation (1–7, 9, 10, and 12–14) and an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with CuK α radiation (11). The data were refined by SHELXL^[28] and all non-proton coordinate values and anisotropic temperature factors were refined by the full-matrix least-squares method. All proton positions in the structure were determined by theoretical calculation

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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.

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