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Synthesis, structure and a nucleophilic coordination reaction of Germanetellurones†

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β-Diketiminato cyclopentadienyl and ferrocenylethynyl germylenes LGeR (L = HC[C(Me)N-2,6-iPr$_2$C$_6$H$_3$]$_2$, R = Cp (**1**) and C≡CFc (**2**)) were prepared and utilized to synthesize the Ge═Te bond species. Reactions of **1**, **2**, and LGeC≡CPh (**3**) with an excess of Te powder proceeded in toluene under reflux successfully yielded germanetellurone L(R)GeTe (R = Cp (**4**), C≡CFc (**5**), and C≡CPh (**6**)). Further reaction of **4** with GeCl$_2$·dioxane at −78 °C resulted in L(Cp)GeTe(GeCl$_2$) (**7**), the first example of a germylene germanetellurone adduct. Both compounds **4** and **7** contain two isomers that are generated by the simultaneous 1,2-H- and 1,3-H-shifts over the Cp ring at the Ge atom. The reactions of L(Me)GeE with AuC$_6$F$_5$·SC$_4$H$_8$ at room temperature led to pentafluorophenyl gold(I) germanethione and germaneselone compounds L(Me)GeE(AuC$_6$F$_5$) (E = S (**8**) and Se (**9**)). The formation of compounds **7–9** exhibits a rare nucleophilic coordination reaction pathway by the Ge═E (E = S, Se, Te) bond towards the metal-containing Lewis acidic species. The structures of compounds **1**, **2**, and **4–9** are studied by the NMR and/or IR spectroscopy and X-ray crystallography.

Introduction

The chemistry of the heavier group 14 analogues of aldehydes and ketones and their heavier congeners has been intensively studied in the last two decades, which reveals a general strategy for synthesizing these compounds by taking advantage of the sterically demanding group protection and/or additional donor stabilization due to the high reactivity of the M═E bond (M = Si, Ge, Sn, Pb; E = O, S, Se, Te).[1,2] Recently, the Ge═O species L′Ge(D)═O (L′ = HC[C(Me)N-2,6-iPr$_2$C$_6$H$_3$][C(CH$_2$)-N-2,6-iPr$_2$C$_6$H$_3$], D = *N*-heterocyclic carbene[3] or 4-dimetylaminopyridine (DMAP)[4]) and (Eind)$_2$Ge═O (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl)[5] have been successfully prepared by means of this strategy. Meanwhile, the reactivity of these compounds has also been examined by the reaction of L′Ge(DMAP)═O with AlMe$_3$ to L′Ge(Me)OAlMe$_2$(DMAP)[4] and the reactions of (Eind)$_2$Ge═O with LiAlH$_4$, MeLi, H$_2$O, Me$_2$CO, PhSiH$_3$ and CO$_2$ to the corresponding novel addition products,[5] consistent with that for the charge-separated species. The heavier congeners have been previously synthesized and the charge-separated character of the Ge═E bond (E = S, Se, Te) has also been studied.[2b,6,7] In comparison, the reactivity of these compounds has been investigated in a lesser extent, which is probably suppressed by the steric protection of the group(s) at the Ge atom.[1g] Strikingly, the Ge═Te complexes appear fewer in number than those with the Ge═S or Ge═Se bonds.[2b] Synthesis of the Ge═Te complexes often requires more complex conditions, for example the presence of trialkylphosphine as the catalyst,[7a] or a longer reaction time in the absence of light[7b] or upon heat treatment,[7c] compared to those of their Ge═S and Ge═Se congeners. The bulky β-diketiminato ligand stabilized L(Cl)GeE (L = HC[C(Me)N-2,6-iPr$_2$C$_6$H$_3$]$_2$, E = S or Se) and the derivatives have been synthesized by Roesky and coworkers.[6a–d] However, the related tellurium compound has not yet been prepared although the reaction of LGeCl with Te has been attempted.[8]

We recently reported on the use of LGeR (R = Me, C≡CPh, C(SiMe$_3$)N$_2$) for the donor–acceptor reaction with organocoinage metal(I) species, in which the GeM (M = Cu, Ag, Au) complexes were formed yielding varied aggregates when the R group was altered.[9] This shows the influence of the R group on the donor reactivity by the lone pair of electrons at the Ge center. We then became interested in tuning the R group to promote the reducing reactivity of this pair to approach the L(R)GeTe species. In this regard the cyclopentadienyl and ferrocenylethynyl germylene compounds LGeR (R = Cp (**1**) and

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† Electronic supplementary information (ESI) available: tables of crystal data collection and structure refinements details, molecular structures of **4a**, **4b**, **7a** and **7b** and CIF data of compounds **1**, **2** and **4–9**. CCDC 982310–982317. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00937a

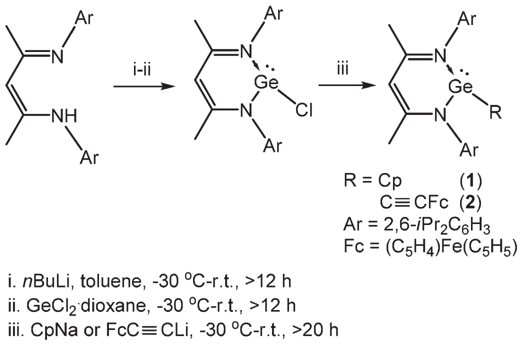
C≡CFc (**2**)) were prepared. The reactions of **1**, **2**, and LGeC≡CPh (**3**)[9b,10] with Te were carried out and germanetellurones L(R)GeTe (R = Cp (**4**), C≡CFc (**5**), and C≡CPh (**6**)) were successfully formed. The Cp and alkynyl groups are electron-rich, which probably facilitate the reactions of **1–3** by the Ge(II) lone pair with Te. Compounds **4–6** exhibit a new type of heavier ketones containing the cyclopentadienyl or alkynyl group at Ge. We further investigated the reaction of **4** with $GeCl_2$·dioxane[11] and obtained compound L(Cp)GeTe($GeCl_2$) (**7**), the first example of a germylene germanetellurone adduct. The formation of **7** exhibits a rare example of the nucleophilic coordination reaction pathway. Furthermore, reactions of L(Me)GeE[6a] with $AuC_6F_5·SC_4H_8$ [12] were explored, producing pentafluorophenyl gold(I) germanethione and germaneselone compounds L(Me)GeE(AuC_6F_5) (E = S (**8**), Se (**9**)).

Results and discussion

Synthesis of LGeR (R = Cp (1) and C≡CFc (2)) and reactions of 1, 2, and LGeC≡CPh (3) with Te powder

β-Diketiminato cyclopentadienyl and ferrocenylethynyl germylene compounds LGeR (R = Cp (**1**) and C≡CFc (**2**)) were prepared by the reaction of the *in situ* generated LGeCl with the respective CpNa and FcC≡CLi in a consecutive route (Scheme 1). This pathway proves efficient by its high yield production of **1** (87%) and **2** (81%) when compared to other pathways for the preparation of similar compounds using separated LGeCl as the precursor.[6a–d] Compound **1** is orange colored while **2** is deep red. They were characterized by NMR and/or IR spectroscopy and elemental analysis.

^{1}H NMR spectra show the characteristic septet and doublet resonances for the C*H*Me$_2$ and CH*Me*$_2$ of the L ligand contained in both **1** and **2**. A singlet at δ 5.68 ppm in the ^{1}H NMR spectrum and the resonance at δ 113.64 ppm in the ^{13}C NMR spectrum of **1** correspond to the Cp proton and carbon atoms. These NMR resonances suggest that the Cp ring in **1** is fluxional.[13] The most similar resonance pattern is found in [N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)]GeCp (δ_{1H} 6.07 and δ_{13C} 113.54 ppm).[14] In the ^{1}H NMR spectrum of **2**, two multiplets (δ 3.95 and 4.39 ppm) are assigned to the C_5H_4 and one singlet (δ 4.15 ppm) to the C_5H_5, which are both from the ferrocenyl (Fc) part. In the ^{13}C spectrum of **2**, the C_5H_4 carbon atoms resonate at δ 68.10, 68.64 and 71.31 ppm while the C_5H_5 carbon atoms resonate at δ 70.06 ppm. These resonance data are characteristic for Fc-containing compounds.[15] The ferrocenylethynyl C≡C functionality in **2** is revealed from the ^{13}C NMR (δ 100.28 and 108.26 ppm) and IR ($\tilde{\nu}$ 2124 cm^{-1}) spectra.



Scheme 1 Synthesis of compounds **1** and **2**.

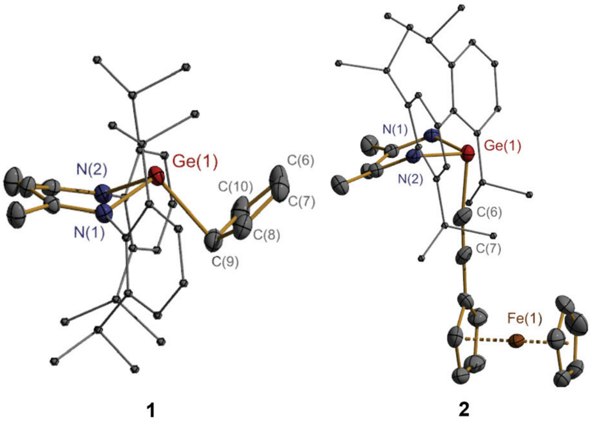
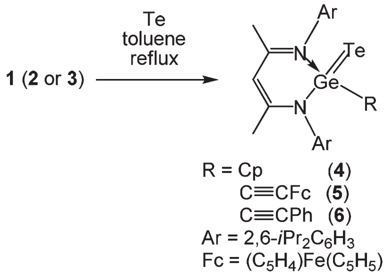


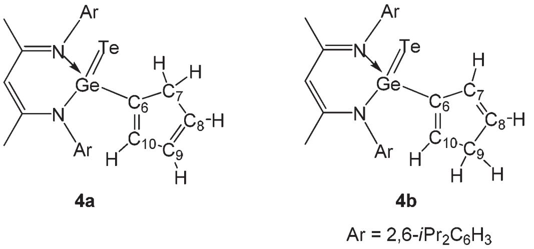
Fig. 1 Crystal structures of **1** and **2** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Ge(1)–N(1) 2.046(1), Ge(1)–N(2) 2.047(1), Ge(1)–C(9) 2.167(2), Ge(1)···C(10) 2.659, Ge(1)···C(8) 2.663, Ge(1)···C(6) 3.160, Ge(1)···C(7) 3.164, Ge(1)···C$_{\text{Cp(centroid)}}$ 2.520, C(6)–C(7) 1.411(3), C(7)–C(8) 1.365(3), C(8)–C(9) 1.438(3), C(9)–C(10) 1.441(3), C(10)–C(6) 1.355(3); N(1)–Ge(1)–N(2) 86.26(5). For **2** (the data in the square bracket is for another independent molecule): Ge(1)–N(1) 2.000(2) [2.007(5)], Ge(1)–N(2) 1.999(1) [2.009(3)], Ge(1)–C(6) 2.008(3) [1.997(3)], C(6)–C(7) 1.203(4) [1.201(3)]; N(2)–Ge(1)–N(1) 90.38(8) [90.54(8)], N(2)–Ge(1)–C(6) 91.46(9) [92.21(9)], N(1)–Ge(1)–C(6) 92.41(9) [93.42(9)], Ge(1)–C(7)–C(6) 173.7(2) [176.7(2)].

X-ray single-crystal diffraction studies further confirmed the structures of **1** and **2**, in agreement with those analyzed by the NMR and/or IR spectroscopy. The crystal structures of **1** and **2** are shown in Fig. 1, which reveal a linkage of the L ligand and Cp in **1** and that of the L and C≡CFc in **2** both at the Ge atom. The Ge–Cp bonding in **1** can be better ascribed in an η^1-mode rather than the η^5 one. The Ge(1)–C(9) bond length is found to be 2.167(2) Å, which is significantly shorter than those of the other Ge(1)···C$_{\text{Cp}}$ bonds (2.520 to 3.164 Å). The Ge···C$_{\text{Cp(centroid)}}$ distance is 2.520 Å. The Ge(1)–C(9) bond length in **1** is shorter but the related Ge···C$_{\text{Cp(centroid)}}$ distance is longer when compared with those in the η^5-bonding complex (η^5-Cp*)$_2$Ge (Ge–C$_{\text{Cp*}}$, 2.403(4)–2.646(4); Ge···C$_{\text{Cp*(centroid)}}$, 2.209 and 2.231 Å).[16] The sum of the peripheral angle around the Ge atom is 285.36°, which is a little wider than that observed in **2** (274.25°) for the three-coordinate Ge center in a triangular pyramidal geometry. This indicates the presence of a lone pair of electrons at the Ge center, which greatly influences the geometric array of the Cp ring.

DFT calculations were performed to pin point the location of the lone pair at the molecular orbitals (MO) of the Ge atom, which were run by using the Gaussian 09 program with geometry optimization for **1** and simplified for **2**, LGeC≡CH on B3LYP/6-31+G(d). The natural bond orbital (NBO) analysis



Scheme 2 Reactions of **1–3** with Te to form germanetellurones **4–6**.



Scheme 3 Two possible structures caused by the distinguishable 1,2-H- and 1,3-H-shifts over the Cp ring.

indicates that the Ge atom carries the positive charge of 1.047 for **1** and 0.983 for LGeC$\equiv$CH, respectively, with 1.967 and 1.943 electrons occupied mainly in the *s* orbital of each Ge center (for the HOMO picture see Fig. 7s in the ESI†). UV-vis spectra recorded in toluene exhibit a weak peak at λ 366 nm for **1** while a moderate peak at λ 344 nm for **2** (see the ESI†). This may imply that an electronic interaction occurred between the Ge(II) lone pair and the adjacent Cp or C$\equiv$CFc group. The latter interaction appears stronger.

Reactions of compounds **1**, **2**, and LGeC$\equiv$CPh (**3**) with Te powder were treated upon reflux in toluene, readily affording germanetellurone L(R)GeTe (R = Cp (**4**), C$\equiv$CFc (**5**), and C$\equiv$CPh (**6**)) (Scheme 2). Compounds **4–6** were isolated as orange, dark red, and red crystals, respectively, in moderate yields (59% for **4**, 55% for **5**, and 66% for **6**). These compounds are air and moisture sensitive. Melting point measurements indicate that these compounds can tolerate elevated temperature treatments (241 for **4**, 296 for **5**, and 265 °C for **6**). When exceeding these temperatures decomposition of the related compound occurs, as indicated by a change in color. All of these compounds are soluble in solvents like toluene, THF and CH_2Cl_2, but sparingly soluble in *n*-hexane. The ^{1}H NMR spectrum of **5** exhibits two multiplets (δ 3.93 and 4.39 ppm) corresponding to the C_5H_4 (Fc) and one singlet (δ 4.13 ppm) corresponding to the C_5H_5 (Fc). The ^{13}C NMR spectrum of **5** displays three resonances (δ 64.76, 69.05 and 71.75 ppm) and one resonance (δ 70.18 ppm) for the C_5H_4 and C_5H_5, respectively. These data are similar by either the chemical shifts or the resonance pattern to those for **2**. The ferrocenylethynyl C$\equiv$C carbon resonances (δ 124.42 and 124.83 ppm), however, change a lot when compared with those for **2**. This implies the disappearance of the electronic influence of the lone pair electrons at the Ge center on the C$\equiv$C part when the Ge$=$Te bond forms.

The ^{1}H and ^{13}C NMR spectra of **4** are complex and present two sets of the resonance data as typically indicated by the observance of two resonances for either the γ-CH proton (δ 4.90 and 4.92 ppm) or carbon (δ 98.96 and 99.45 ppm) atoms in the L ligand backbone. Also of note are the eight signals at δ 2.63 (2 H), 3.25 (2 H), 6.38 (1 H), 6.48 (1 H), 6.59 (1 H), 7.02 (1 H), 7.22 (1 H) and 7.41 (1 H) ppm in the ^{1}H NMR spectrum of **4**, which are assigned to the Cp ring proton resonances. A similar resonance pattern is only observed for that of the σ-bonded Cp ring in the ^{1}H NMR spectrum of $(NBu_4)[Cp(\eta^4\text{-COD})Os(\mu\text{-H})(\mu\text{-Cl})_2OsCl(\eta^4\text{-COD})]$. The latter is suggested to undergo both the 1,2-H- and 1,3-H-shifts over the Cp ring during the formation of this compound.[17] Thus, we assume that the two structures (**4a** and **4b**) are generated when the Ge$=$Te bond forms during the reaction (Scheme 3). The elevated temperature (25–80 °C) ^{1}H NMR spectral studies were performed to see a possible exchange of these two structures. However, almost no change of such a resonance pattern was observed (see the ESI†). This implies an occurrence of the distinguishable 1,2-H- and 1,3-H-shifts over the Cp ring, which is significantly different from those fluxionally dynamic solution behaviors observed in compounds $[N(SiMe_3)C(Ph)C(SiMe_3)\text{-}(C_5H_4N\text{-}2)]GeCp$[14] and **1**. In the latter two complexes, only one signal is observed for the Cp ring protons by undergoing a series of fast 1,2-H- or 1,3-H-shifts.[13]

To obtain detailed insight into the structures of these germanetellurones, X-ray single crystal diffraction studies of **4–6** were carried out. The structural analysis clearly reveals a formation of the Ge$=$Te bond in these three compounds. The molecular structures of **4–6** are shown in Fig. 2 and 3. The Ge atoms in **4–6** are all four-coordinate adopting a tetrahedral geometry. The Ge–Te bond lengths are 2.424(2) in **4**, 2.416(9) [2.411(7)] in **5** and 2.410(8) Å in **6**, respectively. These distances

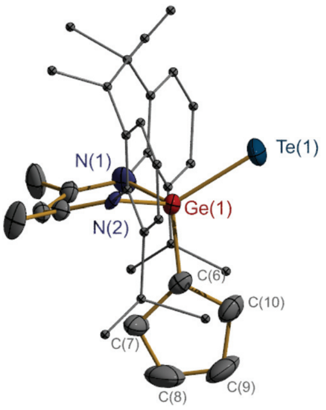
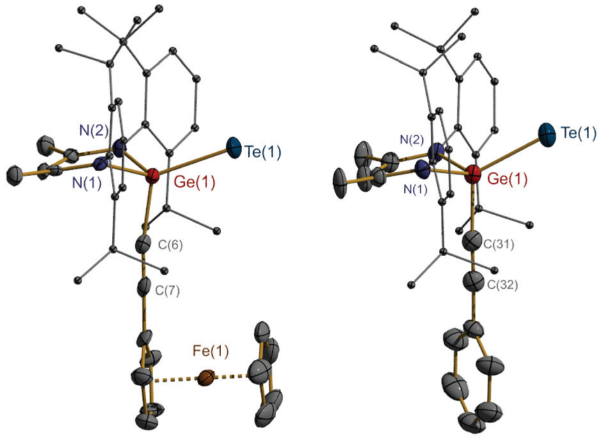


Fig. 2 Crystal structure of **4** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 1.927(7), Ge(1)–N(2) 1.959(7), Ge(1)–Te(1) 2.424(2), Ge(1)–C(6) 1.922(4), C(6)–C(7) 1.482(5), C(7)–C(8) 1.414(6), C(8)–C(9) 1.419(9), C(9)–C(10) 1.485(7), C(10)–C(6) 1.357(5); N(1)–Ge(1)–N(2) 94.59(1), Te(1)–Ge(1)–C(6) 114.46(1).



5 **6**

Fig. 3 Crystal structures of **5** and **6** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **5** (the data in the square bracket is for another independent molecule): Ge(1)–Te(1) 2.416(9) [2.411(7)], Ge(1)–N(1) 1.915(4) [1.917(4)], Ge(1)–N(2) 1.914(4) [1.912(4)], Ge(1)–C(6) 1.911(6) [1.905(5)], C(6)–C(7) 1.192(7)[1.195(6)]; N(1)–Ge(1)–N(2) 95.21(2) [95.33(18)], C(6)–Ge(1)–Te(1) 118.16(2) [118.40(2)], Ge(1)–C(6)–C(7) 171.2(5) [173.4(5)]. For **6**: Ge(1)–N(1) 1.928(4), Ge(1)–N(2) 1.921(4), Ge(1)–C(31) 1.914(6), Ge(1)–Te(1) 2.415(2), C(31)–C(32) 1.204(8); N(1)–Ge(1)–N(2) 96.22(2), Te(1)–Ge(1)–C(31) 119.59(2), Ge(1)–C(31)–C(32) 173.5(5).

are intermediate between those in three-coordinate Tbt(Dis)GeTe (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dis = bis(trimethylsilyl)methyl, 2.384(2) Å),[7c] five-coordinate Me$_8$taaGeTe (Me$_8$taa = tetramethyldibenzotetra-aza(14)azulene, 2.466(1) Å)[7a] and [(C$_5$H$_4$N)C(SiMe$_3$)$_2$]$_2$GeTe (2.479(1) Å) compounds.[7b]

Clearly, in comparison with the structure of **1**, the Cp ring in **4** adopts a σ-bonding fashion to the Ge (the least-square plane $\Delta_{\text{Ge(1)C(6)C(7)C(8)C(9)C(10)}}$ = 0.0359 Å). The Ge–C$_{\text{Cp}}$ bond length is 1.922(4) Å and is comparable to that observed in the similarly σ-bonded Ge(IV) compound Me$_2$Ge(C$_7$H$_6$)(C$_5$H$_4$)Ti (1.969(2) Å).[18a] However, the formation pathways of the Ge–C$_{\text{Cp}}$ σ-bonding of these two compounds are completely different. The latter is generated *via* the further deprotonation of the C$_5$H$_5$ group commonly observed. The former is a result of the rearrangement of the hydrogen atoms over the C$_5$H$_5$ ring when the Ge=Te bond forms, and represents, to the best of our knowledge, the first example among the cyclopentadienyl germanium compounds and the derivatives.[14,16,18b–h] Within the Cp ring, the C–C bond lengths are 1.357(5) for C(6)–C(10), 1.414(6) for C(7)–C(8), 1.419(9) for C(8)–C(9), 1.482(5) for C(6)–C(7), and 1.485(7) Å for C(9)–C(10), respectively. The C(6)–C(10) is of a double bond character while the C(6)–C(7) and C(9)–C(10) are the single bonds. However, the C(7)–C(8)–C(9) is prone to be in an allylic arrangement. As a consequence, the addition of the two H atoms at C(7) corresponds to structure **4a** *via* the 1,2-H-shift, while structure **4b** is formed by the addition at C(9) *via* a 1,3-H-shift. These two structural features are in good agreement with those analyzed by the NMR spectrum. The final structural refinements gave a perfect convergence by both two hydrogen addition treatments (see the ESI†).

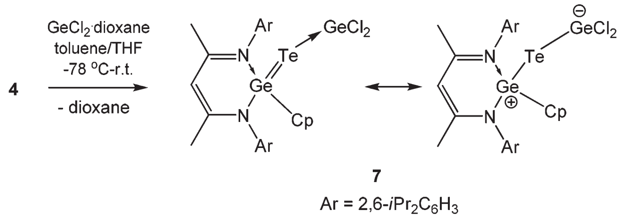
It is also interesting to find that the planarity of the Ge(1)C(6)C(7)C(8)C(9)C(10) can be extended to the Te atom ($\Delta_{\text{Te(1)Ge(1)C(6)C(7)C(8)C(9)C(10)}}$ = 0.0381 Å), which implies a probable electronic conjugation between the Ge=Te bond and the C=C bond of Cp. Then, by means of the DFT calculations for isomers **4a**, **4b**, and a presumed L(η^1-Cp)GeTe (**4c**), the energy difference was found by −2.5 for **4a** and −1.0 for **4b** relative to the 0.0 kcal mol^{-1} for **4c**. Isomers **4a** and **4b** appear more stable than **4c** (see the ESI†). Reasonably, a co-planar rearrangement of the Ge=Te bond and the Cp ring rendered by the electronic conjugation interaction may be responsible for driving the 1,2-H- and 1,3-H-shifts over Cp.

Reactions of 4–6 with GeCl$_2$·dioxane and of L(Me)GeE (E = S and Se) with AuC$_6$F$_5$·SC$_4$H$_8$

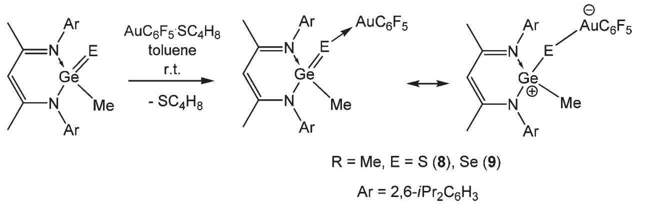
The charge-separated nature of the Ge=E (E = O, S, Se, Te) bond with the electronic resonance structures has been theoretically[19] and experimentally[1k,4,6a–c] discussed. Owing to this property, complexes with the Ge=E bond can be used as a donor molecule. However, the donor reactivity of these complexes is rarely investigated. Driess and coworkers have reported on the reaction of germanone L′Ge(DMAP)=O with AlMe$_3$ to L′Ge(Me)OAlMe$_2$(DMAP)[4] where L′Ge(DMAP)=O(AlMe$_3$) was thought to be an intermediate and the transfer of the Me group to the Ge center easily occurred. Herein we report on the investigation of such donor reactivity by altering the acceptor molecules.

By using compounds **4–6** as the precursors, we screened the reactions of these compounds with several Lewis acidic species, such as AlCl$_3$, GeCl$_2$·dioxane and AuC$_6$F$_5$·SC$_4$H$_8$.[20] However, only the reaction of **4** with GeCl$_2$·dioxane gave compound L(Cp)GeTe(GeCl$_2$) (**7**). The other reactions are complex, as indicated by the ^{1}H NMR analysis. Isolation of the pure compounds was not successful. Compound **7** was prepared by the addition of a THF solution of GeCl$_2$·dioxane to a toluene solution of **4** from −78 °C to room temperature (Scheme 4). In an attempt to explore the donor reactivity of the related sulfur and selenium congeners, we prepared Roesky's compounds L(Me)GeE (E = S, Se),[6a–c] and accomplished the reactions with AuC$_6$F$_5$·SC$_4$H$_8$[12] in toluene at room temperature. Compounds L(Me)GeE(AuC$_6$F$_5$) (E = S (**8**), Se (**9**)) were readily obtained (Scheme 5).

Compound **7** was isolated as an off-white solid in a low yield (29%). It is extremely air and moisture sensitive and



Scheme 4 Reaction of **4** and GeCl$_2$·dioxane to form compound **7**.



Scheme 5 Reactions of L(Me)GeE (E = S, Se) with $AuC_6F_5{\cdot}SC_4H_8$ to yield compounds **8** and **9**.

thermally unstable (163 °C (dec.)). Even when kept at room temperature in an inert atmosphere (Ar or N_2) compound **7** gradually changed color to grey after 2 d. Compound **8** was isolated as colorless crystals in a yield of 72% while **9** as light-yellow crystals in a yield of 56%. Unlike **7**, these two compounds can bear elevated temperature treatments and decompose at temperatures higher than 238 °C for **8** and 260 °C for **9**. Compounds **8** and **9** are soluble in toluene, THF and CH_2Cl_2. They have been characterized by multinuclear NMR (^{1}H, ^{13}C and ^{19}F) spectroscopy. In contrast, compound **7** is not well soluble in the solvents mentioned above and only the ^{1}H NMR spectral data was obtained in either C_6D_6 or D_8-THF.

The ^{1}H NMR spectrum of **7** in D_8-THF exhibits a resonance mode similar to that of **4**, in which two signals (δ 5.50 and 5.63 ppm) for the γ-C*H* of the L ligand backbone are observed. Eight resonances at δ 2.58 (2 H), 2.98 (2 H), 6.56 (1 H), 6.70 (1 H), 6.78 (1 H), 7.02 (1 H), 7.10 (1 H) and 7.26 (1 H) ppm correspond to the Cp protons, indicative of a retaining of the σ-bonded Cp group at the Ge atom. The ^{1}H NMR spectra of **8** and **9** in C_6D_6 show the respective singlet resonances at δ 0.22 and 0.38 ppm for the Ge*Me*. The ^{19}F spectra display the resonances at δ −162.92 (*m-F*), −161.36 (*p-F*) and −115.12 (*o-F*) for **8** and δ −162.72 (*m-F*), −161.28 (*p-F*) and −114.90 (*o-F*) for **9** with an integral intensity ratio of 2 : 1 : 2, both corresponding to the C_6F_5 group attached to the Au atom.

The structures of **7–9** were determined by the X-ray single crystal diffractions. The structural analysis of **7** confirms a bonding of $GeCl_2$ at the Te atom (Fig. 4). This bonding fashion can be compared to those found for $Si{=}O{\rightarrow}B(C_6F_5)_3$,[21] $Si{=}O{\rightarrow}AlX_3$ (X = Me,[22a] Cl[22b]) and $Al{=}O{\rightarrow}B(C_6F_5)_3$.[23] Compound **7** represents the first example of a germylene germanetellurone adduct. The Ge(1) atom is four-coordinate in a tetrahedral geometry while the Ge(2) is three-coordinate adopting a triangular pyramidal geometry. The Ge(2)–Te(1) bond length (2.750(1) Å) is longer than that of the Ge(1)–Te(1) (2.461(7) Å), and also longer than those in the Ge–Te single bond compounds 4-$CH_3C_6H_4C(O)TeGePh_3$ (2.574(2) Å),[24] $[(Me_3SiN{=}PPh_2)_2C{=}Ge(\mu\text{-}Te)]_2$ (2.585(4) and 2.577(4) Å),[25] and $[((Me_3Si)_2N_2)Ge]_2(\mu\text{-}Te)_2$ (2.595(2), 2.596(2) Å).[26] This implies a probably weak coordinative $L(Cp)Ge{=}Te{\rightarrow}GeCl_2$ bonding. Moreover, the Ge(1)–Te(1) bond length is in between those of the double bond in **4** and the single bond in the above-mentioned complexes.[24–26] All of these probably imply a partial charge transfer from the Ge(1) center to the Ge(2) atom (Scheme 4). The Cp group in **7** remains a σ-bonding mode to the Ge(1) (the least-square plane $\Delta_{Te(1)Ge(1)C(6)C(7)C(8)C(9)C(10)}$ = 0.0473 Å). The C–C bond lengths (1.361(9) for C(6)–C(7), 1.380(1) for C(9)–C(10) and 1.416(1) for C(8)–C(9), and 1.477(1) for C(7)–C(8) and 1.481(1) Å for C(6)–C(10)) over the Cp ring are similar to those in **4**.

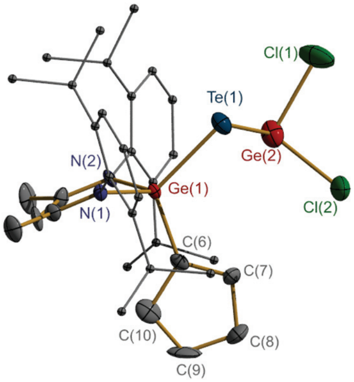


Fig. 4 Crystal structure of **7** with thermal ellipsoids of 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 1.894(6), Ge(1)–N(2) 1.911(6), Ge(1)–Te(1) 2.461(7), Ge(2)–Te(1) 2.750(1), Ge(2)–Cl(1) 2.266(3), Ge(2)–Cl(2) 2.308(3), Ge(1)–C(6) 1.909(8), C(6)–C(7) 1.361(9), C(7)–C(8) 1.477(1), C(8)–C(9) 1.416(1), C(9)–C(10) 1.380(1), C(10)–C(6) 1.481(1); N(1)–Ge(1)–N(2) 97.9(3), Te(1)–Ge(1)–C(6) 116.7(2), Ge(1)–Te(1)–Ge(2) 93.9(2).

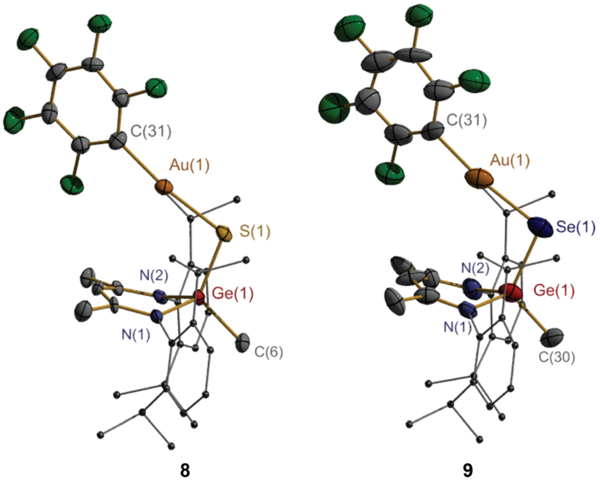


Fig. 5 Crystal structures of **8** and **9** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **8**: Ge(1)–N(1) 1.892(6), Ge(1)–N(2) 1.905(6), Ge(1)–C(6) 1.922(8), Ge(1)–S(1) 2.135(4), Au(1)–S(1) 2.308(2); N(1)–Ge(1)–N(2) 97.3(3), C(6)–Ge(1)–S(1) 115.0(2), Ge(1)–S(1)–Au(1) 105.7(8), S(1)–Au(1)–C(31) 171.7(2). For **9**: Ge(1)–N(1) 1.890(1), Ge(1)–N(2) 1.914(2), Ge(1)–C(30) 1.888(2), Ge(1)–Se(1) 2.272(3), Au(1)–Se(1) 2.414(3); N(1)–Ge(1)–N(2) 96.3(3), C(30)–Ge(1)–Se(1) 113.4(6), Ge(1)–Se(1)–Au(1) 103.20(1), Se(1)–Au(1)–C(31) 172.4(5).

The X-ray structural analysis of **8** and **9** confirms a bonding of AuC_6F_5 at the E atom of L(Me)GeE (E = S, Se) (Fig. 5). The Ge atoms adopt the tetrahedral geometry while the Au atoms are in an almost linear geometry (E(1)–Au(1)–C(31), E = S, 171.7(2); Se, 172.4(5)°). The S–Au bond length (2.308(2) Å) in **8** is slightly shorter than those in $AuC_6F_5{\cdot}SC_4H_8$ (2.317(3) and 2.320(3) Å).[27] The Se–Au bond distance (2.414(3) Å) in **9** is shorter than that in $AuC_6F_5{\cdot}SePPh_2Me$ (2.4353(11) Å).[28] These data suggest a strongly coordinative interaction between L(Me)GeE and AuC_6F_5 by the charge transfer from the Ge center to the Au atom (Scheme 5), which is probably responsible for the higher thermal stability of **8** and **9** than that of **7**. The Ge–S and Ge–Se bond lengths are ranged between those of the non-coordinated double bond[6] and single bond complexes.[6f,h,7b,25]

Conclusion

In summary, by using β-diketiminato cyclopentadienyl and alkynyl germylenes, germanetellurones L(R)GeTe (R = Cp (**4**), $C{\equiv}CFc$ (**5**), and $C{\equiv}CPh$ (**6**)) were successfully prepared. However, when LGeCl was employed as the precursor, no reaction occurred with Te even upon reflux or other treatments,[8] although the reactions of LGeCl with S or Se successfully led to the formation of L(Cl)GeE (E = S, Se).[6a–c] The chloride at the Ge center is more electron-withdrawing than the cyclopentadienyl and ferrocenylethynyl groups, which affects a reduction of the Te element by the lone pair of the electrons at the Ge. The formation of the Ge=Te bond in **4** resulted in a change of the Ge–Cp bond from an η^1-mode in **1** to a σ-bonding one by the simultaneous 1,2-H- and 1,3-H-shifts over the Cp ring, exhibiting a novel Ge–Cp bonding fashion.[14,16,18] The reaction of **4** with $GeCl_2{\cdot}dioxane$ to L(Cp)GeTe($GeCl_2$) (**7**) and reactions of L(Me)GeE with $AuC_6F_5{\cdot}SC_4H_8$ to L(Me)GeE(AuC_6F_5) (E = S (**8**), Se (**9**)) all show a nucleophilic coordination reaction way. It reflects a donor reactivity of the heavier ketones by the charge-separated Ge=E (E = S, Se, Te) bond.

Experimental section

Materials and methods

All manipulations were carried out under dry argon or nitrogen atmosphere by using Schlenk line and glovebox techniques. Solvents toluene, *n*-hexanes and tetrahydrofuran were dried by refluxing with sodium/potassium benzophenone under N_2 prior to use. The NMR (^1H, ^{13}C, and/or ^{19}F) spectra were recorded on a Bruker Avance II 400 or 500 MHz spectrometer. Infrared spectra were obtained on a Nicolet FT-IR 330 spectrometer. Melting points of the compounds were measured in a sealed glass tube using a Büchi-540 instrument. UV-vis spectra were measured on a Shimadzu UV-2550 spectrophotometer with solution samples in toluene (2 mL) at concentrations of 1.0×10^{-5} mol L^{-1} and a slit width (D2 lamp) of 2.0 nm was used with a slow scan speed. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. Compounds $LGeC{\equiv}CPh$ (**3**),[9b] LGeCl,[29] L(Me)Ge=E (E = S, Se),[6a] $GeCl_2{\cdot}dioxane$[11] and $AuC_6F_5{\cdot}SC_4H_8$ [12] were prepared according to the literature.

L(Cp)Ge (1). At −30 °C, *n*BuLi (2 mL 2.5 M solution in *n*-hexane, 5 mmol) was added to a solution of LH (2.091 g, 5 mmol) in toluene (50 mL). The mixture was warmed to room temperature and stirred for 12 h to produce a lithium salt LLi. By cooling again to −30 °C, a precooled (−30 °C) suspension of $GeCl_2{\cdot}dioxane$ (1.160 g, 5 mmol) in toluene (30 mL) was added. The mixture was warmed to room temperature and stirred for 12 h to give LGeCl in an orange-yellow color. Without isolation, LGeCl was cooled to −30 °C and to it CpNa (2.5 mL 2 M THF solution, 5 mmol) was added. The mixture was warmed to room temperature and stirred for 20 h. All volatiles were removed under reduced pressure and the residue was extracted with toluene. The extract was evaporated to dryness under reduced pressure and the residue was washed with cold *n*-hexane (8 mL) to give an orange crystalline solid of **1** (2.06 g). The *n*-hexane washing solution was stored at −20 °C for three days to give X-ray quality single crystals of **1** (0.35 g). Total yield: 2.41 g, 87%. Mp: 205 °C. ^1H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12 H), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 12 H) ($CHMe_2$), 1.52 (s, 6 H, CMe), 3.49 (br, 4 H, $CHMe_2$), 4.68 (s, 1 H, γ-CH), 5.68 (s, 5 H, Cp-H), 7.13–7.19 (m, 6 H, C_6H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 23.03, 24.96, 28.59 (CMe, $CHMe_2$), 95.91 (γ-C), 113.64 (Cp-C), 124.47, 127.01, 141.27, 144.60 (C_6H_3), 164.00 (CN). UV-vis (nm): λ = 320, 366. Anal. Calcd (%) for $C_{34}H_{46}GeN_2$ (M_r = 555.38): C, 73.53; H, 8.35; N, 5.04. Found: C, 73.50; H, 8.09; N, 5.23.

$LGeC{\equiv}CFc$ (2, Fc = $C_5H_4FeC_5H_5$). LGeCl (5 mmol) was prepared in a similar manner to that for synthesizing **1** and used directly for reaction without isolation. $FcC{\equiv}CLi$ was freshly prepared from the reaction of $FcC{\equiv}CH$ (1.05 g, 5 mmol) with *n*BuLi (2 mL 2.5 M *n*-hexane solution, 5 mmol) in toluene (20 mL) from −30 °C to room temperature within 3 h, and added drop by drop to the *in situ* generated LGeCl at −30 °C. The mixture was warmed to room temperature and stirred for 20 h. The insoluble solid was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure to give a deep red crystalline solid of **2**. Yield: 2.82 g, 81%. Mp: 221 °C. ^1H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) ($CHMe_2$), 1.62 (s, 6 H, CMe), 3.44 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 4.12 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) ($CHMe_2$), 3.95 (m, 2 H), 4.39 (m, 2 H) (C_5H_4), 4.15 (s, 5 H, C_5H_5), 5.08 (s, 1 H, γ-CH), 7.11–7.24 (m, 6 H, C_6H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 23.28, 23.91, 24.44, 24.69, 28.06, 28.21, 28.98 (CMe, $CHMe_2$), 68.10, 68.64, 71.31 (C_5H_4), 70.06 (C_5H_5), 99.94 (γ-C), 100.28, 108.26 ($C{\equiv}C$), 123.98, 124.75, 127.25, 141.56, 143.56, 146.65 (C_6H_3), 165.70 (CN). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ = 2124 ($C{\equiv}C$). UV-vis (nm): λ = 284, 377. Anal. Calcd (%) for $C_{41}H_{50}GeFeN_2$ (M_r = 699.33): C, 70.42; H, 7.21; N, 4.01. Found: C, 70.21; H, 7.09; N, 4.19. X-ray quality single crystals of **2** were obtained by recrystallization from *n*-hexane–toluene solvent mixture at −20 °C.

L(Cp)GeTe (4). A mixture of **1** (0.278 g, 0.5 mmol) and Te powder (0.128 g, 1.0 mmol) in toluene (20 mL) was refluxed for 12 h. After cooling to room temperature, the unreacted Te powder was filtered off. The filtrate was concentrated (to *ca.* 8 mL) and *n*-hexane (2 mL) layered on the top. After storing at −20 °C for two days, the orange crystals of **4** were formed (0.20 g, 59%). Mp: 241 °C (dec.). The ^{1}H and ^{13}C NMR spectral analyses indicate the presence of two sets of the resonance data corresponding to two isomeric structures, **4a** and **4b**, due to a slight structural difference over the Cp ring (Scheme 3). However, a clear assignment was not possible. The resonances for each same functional group of both **4a** and **4b** are described together. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 0.91 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.01(d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.04 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.08 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.12 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.52 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.64 (d, $^3J_{HH}$ = 6.4 Hz, 6 H), 1.69 (d, $^3J_{HH}$ = 6.4 Hz, 6 H) (CH*Me*$_2$), 1.13 (s, 6 H), 1.53 (s, 6 H) (C*Me*), 2.50 (br, 2 H), 2.67 (br, 2 H), 3.48 (br, 2 H), 3.55 (br, 2 H) (C*H*Me$_2$), 2.63 (br, 2 H), 3.25 (br, 2 H) (Cp-C*H*$_2$), 4.90 (s, 1 H), 4.92 (s, 1 H) (γ-C*H*), 6.38 (br, 1 H), 6.48 (br, 1 H), 6.59 (br, 1 H), 7.02 (overlapped, 1 H), 7.22 (br, 1 H), 7.41 (br, 1 H) (Cp-C*H*), 7.03–7.20 (m, 12 H, C_6H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 24.13, 24.25, 24.33, 24.39, 24.48, 24.54, 25.00, 25.31, 25.40, 26.17, 27.80, 29.49, 29.69 (C*Me*, *C*H*Me*$_2$), 40.41, 45.49 (Cp-*C*H$_2$), 98.96, 99.45 (γ-*C*), 124.43, 124.48, 124.52, 124.64, 128.35, 131.23, 133.73, 134.52, 137.16, 138.26, 138.42, 144.39, 145.89, 146.01, 150.01, 150.13, 150.88 (C_6H$_3$, Cp-*C*H and Cp-*C*), 169.24, 169.49 (*C*N). Anal. Calcd (%) for $C_{34}H_{46}GeN_2Te$ (M_r = 682.98): C, 59.79; H, 6.79; N, 4.10. Found: C, 59.59; H, 6.74; N, 4.23.

L(FcC≡C)GeTe (5). A mixture of **2** (0.675 g, 1.0 mmol) and Te powder (0.256 g, 2.0 mmol) in toluene (30 mL) was refluxed for 12 h. After cooling to room temperature, the unreacted Te powder was filtered off. The filtrate was concentrated to *ca.* 10 mL and *n*-hexane (2 mL) was added to it. The solution was stored at −20 °C for three days to give dark red crystals of **5**. Yield: 0.44 g, 55%. Mp: 296 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.59 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.66 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) (CH*Me*$_2$), 1.55 (s, 6 H, C*Me*), 3.38 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 3.82 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) (C*H*Me$_2$), 3.93 (m, 2 H), 4.39 (m, 2 H) (C_5H_4), 4.13 (s, 5 H, C_5H_5), 4.99 (s, 1 H, γ-C*H*), 6.96–7.35 (m, 6 H, C_6H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 24.02, 24.29, 24.37, 24.86, 27.68, 28.67, 29.64 (C*Me* and *C*H*Me*$_2$), 64.76, 69.05, 71.75 (C_5H$_4$), 70.18 (C_5H$_5$), 100.12 (γ-*C*), 124.42, 124.83 (*C*≡*C*), 128.58, 137.73, 144.54, 145.15 (C_6H$_3$), 169.40 (*C*N). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 2150 (C≡C). Anal. Calcd (%) for $C_{41}H_{50}GeFeN_2Te$ (M_r = 826.93): C, 59.55; H, 6.09; N, 3.39. Found: C, 59.35; H, 5.99; N, 3.57.

L(PhC≡C)GeTe (6). A mixture of **3** (0.591 g, 1.0 mmol) and Te powder (0.256 g, 2.0 mmol) in toluene (30 mL) was refluxed for 12 h. After cooling to room temperature, the unreacted Te powder was filtered off. The filtrate was concentrated to *ca.* 6 mL and *n*-hexane (2 mL) was added to it. The solution was stored at −20 °C for three days to give red crystals of **6**·0.5*n*-hexane. Yield: 0.50 g, 66%. Mp: 263 °C (dec.). ^{1}H NMR (500 MHz, C_6D_6, 298 K, ppm): 1.07 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.21 (d, $^3J_{HH}$ = 7.0 Hz, 6 H), 1.54 (s, 6 H, C*Me*), 1.59 (d, $^3J_{HH}$ = 7.0 Hz, 6 H), 1.60 (d, $^3J_{HH}$ = 7.5 Hz, 6 H) (CH*Me*$_2$), 3.39 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H), 3.80 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H) (C*H*Me$_2$), 5.02 (s, 1 H, γ-C*H*), 6.95–7.46 (m, 11 H, C_6H_3 and C_6H_5). ^{13}C NMR (125 MHz, C_6D_6, 298 K, ppm): 24.27, 24.55, 24.63, 25.08, 27.67, 29.18, 29.43 (C*Me* and *C*H*Me*$_2$), 97.25, 101.45 (*C*≡*C*), 100.35 (γ-*C*), 124.64, 125.12, 128.66, 128.89, 132.15, 138.12, 144.59, 146.87 (C_6H$_3$ and C_6H$_5$), 169.60 (*C*N). IR (KBr plate, cm^{-1}): $\tilde{\nu}$ 2151 (C≡C). Anal. Calcd (%) for $C_{40}H_{53}GeN_2Te$ (**6**·0.5*n*-hexane, M_r = 762.10): C, 63.04; H, 7.01; N, 3.68. Found: C, 62.99; H, 6.84; N, 3.79.

L(Cp)GeTe(GeCl$_2$) (7). GeCl$_2$·dioxane (0.046 g, 0.2 mmol) was dissolved in THF (15 mL) and added to a solution of **4** (0.136 g, 0.2 mmol) in toluene (15 mL) at −78 °C. After the mixture was stirred for *ca.* 0.5 h, an off-white solid of **7** started to form. After warming to room temperature, all of the white solids were collected by filtration and washed with *n*-hexane (3 mL). Yield: 0.048 g (29%). The combined filtrate and *n*-hexane washing solution was stored at −20 °C for three days to give pieces of colorless X-ray quality single-crystals of **7**. Mp: 163 °C (dec). The solubility of **7** is not good in organic solvents, and only the ^{1}H NMR spectral data was recorded. Compound **7** also contains two isomers similar to those of **4a** and **4b** due to the slight structural difference over the Cp ring and two sets of the data were found but not separable. ^{1}H NMR (500 MHz, d_8-THF, 298 K, ppm): δ 0.77 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 0.88 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 0.90 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.05 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.13 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.29 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.43 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.47 (d, $^3J_{HH}$ = 6.5 Hz, 6 H) (CH*Me*$_2$), 1.96 (s, 6 H), 1.97 (s, 6 H) (C*Me*), 2.48 (sept, $^3J_{HH}$ = 6.5 Hz, 2 H), 2.62 (sept, $^3J_{HH}$ = 6.5 Hz, 2 H), 3.34 (sept, $^3J_{HH}$ = 6.5 Hz, 2 H), 3.40 (sept, $^3J_{HH}$ = 6.5 Hz, 2 H) (C*H*Me$_2$), 2.58 (br, 2 H), 2.98 (br, 2 H) (Cp-C*H*$_2$), 5.50 (s, 1 H), 5.63 (s, 1 H) (γ-C*H*), 6.56 (br, 1 H), 6.70 (br, 1 H), 6.78 (br, 1 H), 7.02 (br, 1 H), 7.10 (overlapped, 1 H), 7.26 (br, 1 H) (Cp-C*H*), 7.12–7.25 (m, 12 H, C_6H_3). Anal. Calcd (%) for $C_{34}H_{46}Cl_2Ge_2N_2Te$ (M_r = 826.53): C, 49.41; H, 5.61; N, 3.39. Found: C, 49.61; H, 5.87; N, 3.41.

L(Me)GeS(AuC$_6$F$_5$) (8). $AuC_6F_5\cdot SC_4H_8$ (0.136 g, 0.3 mmol) was dissolved in toluene (10 mL) and added to a solution of L(Me)Ge═S (0.161 g, 0.3 mmol) in toluene (15 mL) at room temperature. An immediate solution color change from orange to light-yellow was observed. After stirring for 4 h, the solution was concentrated to *ca.* 5 mL and *n*-hexane (1 mL) layered on the top. After storing at −20 °C for five days, almost colorless crystals of **8** were formed. Yield: 0.194 g, 72%. Mp: 238 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 0.22 (s, 3 H, Ge*Me*), 0.82 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.57 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) (CH*Me*$_2$), 1.53 (s, 6 H, C*Me*), 2.86 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 4.36 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) (C*H*Me$_2$), 5.22 (s, 1 H, γ-C*H*), 6.88–7.15 (m, 6 H, C_6H_3). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 3.02 (Ge*Me*), 23.24, 23.29, 24.36, 24.72, 27.32, 28.86, 29.12 (C*Me* and *C*H*Me*$_2$), 102.17 (γ-*C*), 123.82, 126.67, 129.23, 135.45, 143.41, 148.44 (C_6H$_3$ and C_6F$_5$), 169.94 (*C*N). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −162.92 (m, 2 F, *m*-*F*), −161.36 (m, 1 F, *p*-*F*), −115.12 (m, 2 F, *o*-*F*). Anal. Calcd (%) for

$C_{36}H_{44}AuF_5GeN_2S$ (M_r = 901.41): C, 47.97; H, 4.92; N, 3.11. Found: C, 47.81; H, 4.97; N, 3.09.

L(Me)GeSe(AuC$_6$F$_5$) (9). $AuC_6F_5\cdot SC_4H_8$ (0.136 g, 0.3 mmol) was dissolved in toluene (10 mL) and added to a solution of L(Me)Ge=Se (0.175 g, 0.3 mmol) in toluene (15 mL) at room temperature. An immediate solution color change from orange to light-yellow was observed. After stirring for 4 h, the solution was concentrated to *ca.* 5 mL and *n*-hexane (1 mL) was added to it. After storing at −20 °C for three days, light-yellow crystals of **9** were formed. Yield: 0.160 g, 56%. Mp: 260 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 0.38 (s, 3 H, Ge*Me*), 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 1.54 (d, $^3J_{HH}$ = 6.8 Hz, 6 H) (CH*Me*$_2$), 1.50 (s, 6 H, C*Me*), 2.87 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 4.26 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H) (C*H*Me$_2$), 5.19 (s, 1 H, γ-C*H*), 6.88–7.14 (m, 6 H, C$_6$*H*$_3$). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ 5.38 (Ge*Me*), 23.39, 23.46, 24.42, 24.70, 28.88, 29.06 (C*Me* and *C*H*Me*$_2$), 102.35 (γ-*C*), 123.96, 126.61, 129.25, 135.48, 143.69 (*C*$_6$H$_3$ and *C*$_6$F$_5$), 169.68 (*C*N). ^{19}F NMR (376 MHz, C_6D_6, 298 K, ppm): δ −162.72 (m, 2 F, *m-F*), −161.28 (m, 1 F, *p-F*), −114.90 (m, 2 F, *o-F*). Anal. Calcd (%) for $C_{36}H_{44}AuF_5GeN_2Se$ (M_r = 948.31): C, 45.60; H, 4.68; N, 2.95. Found: C, 45.45; H, 4.83; N, 2.87.

X-Ray crystallographic analysis

Crystallographic data for compounds **1**, **5**, **7** and **8** were collected on an Oxford Gemini S Ultra system and for **2**, **4**, **6** and **9** on a Rigaku R-Axis Spider IP. During measurements graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) was used. Absorption corrections were applied using the spherical harmonics program (multi-scan type). All structures were solved by direct methods (SHELXS-96)[30] and refined against F2 using SHELXL-97.[31] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. In **2**, two independent molecules were disclosed, in which two C_5H_5, one C_5H_4 and one iPr groups were disordered and treated in a splitting mode by PART method. Carbon atoms C(15A), C(53A), C(54A) and C(54) were isotropically refined. In **5**, two independent molecules were also disclosed, and one C_5H_5 and one iPr groups were disordered and treated in a splitting mode as well. Carbon atoms C(51A) and C(55A) were isotropically refined. In **7**, one carbon atom C(261) was isotropically refined. A summary of cell parameters, data collection, and structure solution and refinements is given in Tables 1s and 2s in the ESI.†

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