Unique Digoldgermanes: Structural Characteristics, Dynamic Behaviour and Distinctive Reactions

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Abstract

Digoldgermanes with a gold coordinated by a dialkylgermylene ligand, $R'_2\text{Ge}(\text{AuPR}_3)(\text{AuGeR}'_2)$ (**3a**; $R = \text{Me}$, **3b**; $R = \text{Et}$), were synthesized as green solids through the reactions of stable dialkylgermylene **1** with $R_3\text{PAuCl}$ followed by the reduction with KC_8 at ambient temperatures. The structural characteristics of **3a** and **3b** were elucidated using NMR spectroscopy, X-ray crystallography, and DFT calculations. An intense absorption maximum was observed at 590 nm in the UV-vis spectrum of **3a** in hexane. A pendular motion of AuPR_3 group between Ge(IV) and Ge(II) of **3a** and **3b** occurring in the NMR time scale was found by the dynamic ^1H NMR analysis, suggesting that the Ge(II) ligand has an enhanced electrophilicity to be attacked by the nucleophilic gold atom which closes to -1 oxidation state. DFT calculations of **3a** revealed the existence of high-lying $\sigma(\text{Ge-Au})$ type HOMO and low-lying LUMO with germylene π nature. We show the bond formation and activation alternatively at Au or Ge atom, a methylation of digoldgermane **3a** with MeOTf affords methylgermane **5**. Moreover, the digoldgermane **3a** reacts with Cl^- ion of Ph_4PCl and $\text{CH}_3\text{C(O)Cl}$ smoothly to form the corresponding chloride-addition product **7** and chlorogoldgermane **9**, respectively. Cyclic trimerization reactions of aromatic isocyanates were high-efficiently catalyzed by **3a** giving the corresponding 1,3,5-triaryl isocyanurates.

Full Text

With the advent of new interests in catalysis, microelectronics, materials, and pharmacology, gold and its complexes have become the focus of intense research both in theoretical and experimental chemistry for decades.¹⁻¹⁵ Among transition metal elements, gold is unique with the large electronegativity ($\chi = 2.54$)¹⁶ and high electron affinity (2.30 eV) owing to the large relativistic effects.¹ Auride ion Au^- serving as a halogen-like anion with the electronic configuration of $5d^{10}6s^2$ has been known since the discovery of caesium auride by Sommer in 1943.¹⁷ Related gold compounds bonded to main group metal and metalloidal atoms have long attracted much attention since then.

The chemistry of gold compounds bonded to main group elements has been developed extensively.^{7,18-21} Very recently, a nucleophilic gold complex **I** released by Goicoechea, Aldridge and colleagues (Chart 1), was employed firstly in the activation of CO_2 and carbodiimide unfolding an unprecedented nucleophilicity of auride complex.²⁰ The umpolung reactivity of gold was ascribed to its high polarization of Au-Al bond. The halogen-like behaviour of gold has been applied to furnish these species containing B-Au bond due to the electronegativity values of boron are also lower than that of gold. Two borylgold complexes of $\text{Ph}_3\text{PAu}(\text{boryl})$ **II** and **III** (Fig. 1) were reported by Nozaki, and Kinjo, respectively, utilizing boryl anions as strong σ -donating ligands in combination with Ph_3PAuCl .^{18,19}

In a previous paper, we have found that reducing a stannylgold by KC_8 at a low temperature followed by the addition of an excess PEt_3 gives diphosphine-coordinated digoldstannane **IV** as shown in Fig. 1,²² and intermediacy of **V** was suggested during the reactions. Compounds with a gold-germanium bond

may be particularly interesting because the bond is polarized due to the difference of electronegativity between germanium ($\chi = 2.01$) and gold.^{1,16} Although a variety of compounds with gold-germanium bonds have been studied, since the first report of Glockling and Hooton in 1962,²³ knowledge of the chemistry including the bonding characteristics and reactivities is still limited in gold-monosubstituted germanes²⁴⁻³¹ and germynes gold complexes.³²⁻⁴¹ To the best of our knowledge, the isolable digoldgermane is still unknown to date, where two gold atoms are ascribed as halogen-like atom with an oxidation state of -1 .

Digoldgermanes **3** were synthesized by the reduction of **2** obtained by the insertion of stable dialkylgermylene **1**⁴²⁻⁴⁵ into Cl-Au bond of R_3PAuCl (Scheme 1). Compounds **3** are unique with the two gold atoms heterolytically coordinated by dialkylgermylene **1** and a trialkylphosphine. Characteristics of the two different types of Au-Ge bonding, fluctuation of the $AuPR_3$ group between 1Ge and 2Ge atoms of **3** in solution, and their distinctive reactions are also discussed in this paper.

Digoldgermanes **3a** ($R = Me$) and **3b** ($R = Et$) are synthesized by applying a reaction route shown in Scheme 1; see the Supplementary Information for the experimental details. The reactions of an isolable dialkylgermylene **1** with R_3PAuCl ($R = Me$ and Et) in tetrahydrofuran (THF) at ambient temperature give **2a** ($R = Me$) and **2b** ($R = Et$), respectively, as a white solid in almost quantitative yields; many similar insertion reactions of terylenes into Au-X bonds have been reported until now.^{26,40} When **2a** and **2b** are treated with potassium graphite (KC_8) in THF at room temperature, the corresponding digoldgermanes **3a** and **3b** are obtained as a dark-green solid in 49 and 54% yields, respectively. Compounds **3** are isolated as pure materials by recrystallization from a cooled hexane solution, stable in the solid state under argon and stored at ambient temperatures for a few months.

The structures of **2** and **3** were determined by multi-nuclear NMR spectroscopy and single crystal X-ray diffraction analysis; see also the Supplementary Information (SI) for the details. The solid-state structures of **3a** and **3b** (Fig. 2) show that their skeletal structures are like each other. The $^1Au-^1Ge$ and $^2Au-^1Ge$ bond distances are 2.4475(4) and 2.4460(5) Å for **3a** and 2.4371(7) and 2.4307(8) Å for **3b**. On the other hand, the distance between a divalent germanium (2Ge) and 1Au [2.4146(4) and 2.4089(8) Å for **3a** and **3b**, respectively] is slightly shorter than those of $^1Au-^1Ge$ and $^2Au-^1Ge$ bonds, suggesting significant difference in the bonding nature between $Ge(IV)-Au$ and $Ge(II)-Au$ bonds. The latter bond would be strengthened by the significant back-bonding interaction between a gold lone-pair orbital with a vacant germylene pp orbital. The bond angles $^1Ge-^1Au-^2Ge$ and $^1Ge-^2Au-P$ of **3a** are 168.042(5) and 175.25(3) ° and those of **3b** are 171.73(3) and 174.02(7) °, indicating they are almost linear and these five atoms are almost in the same plane, being in accord with the VSEPR theory. The dihedral angle between the averaged planes of the two germacyclopentane rings is 78.915 ° for **3a** and 84.588 ° for **3b**, suggesting these two planes are intrinsically perpendicular to each other. The $^1Au-^1Ge-^2Au$ angle of **3a** (and **3b**) is 106.909(16) ° [and 107.61(3) °], indicating the tetrahedral geometry around 1Ge . Trigonal planar geometry around 2Ge is evidenced by the sum of the bond angles around 2Ge atom of **3a** (and **3b**),

which is 359.999 ° (and 359.994 °). The unique bonding feature of **3** is discussed later based on the theoretical calculations.

The ^1H , ^{13}C , ^{29}Si and ^{31}P NMR spectra of **3a** and **3b** at ambient temperatures are consistent with the structures determined by X-ray crystallography, though the spectra are a little confused by the fluxionality of the molecules, whose dynamic behaviour was analyzed using DNMR; see the SI for their detailed NMR data and spectra. In the ^1H NMR at room temperature in THF- d_8 , the signals of ring and trimethylsilyl (TMS) protons of $^1\text{GeC}_4$ and $^2\text{GeC}_4$ rings of **3a** (and **3b**) appear at 2.28 and 0.29 ppm as broad singlets (Fig. S1). However, at -30 °C in THF- d_8 , three sharp singlets are observed at 0.35, 0.28, and 0.26 ppm for the TMS protons of **3b** with the ratio of 2:1:1, being in accordance with the asymmetric structure with respect to the $^1\text{GeC}_4$ ring (Fig. S22). A similar but a little more broadened spectral pattern is observed in the ^1H NMR spectrum of **3a** at -30 °C (Fig. S17).

Broadening of the signals of TMS and ring methylene protons shown in the ^1H NMR spectra of **3a** and **3b** suggests the fluxionality of the molecules occurring in the NMR time scale. Because the methyl proton signals of PMe_3 and methyl and methylene proton signals of **3b** remains sharp even at room temperature, the dynamic process is suggested to be the pendular motion of the AuPR_3 group or the isomerization between the two equivalent structures shown in Scheme 2. The variable temperature ^1H NMR spectra of **3b** in the TMS proton resonance region are shown in Fig. S1. The TMS proton signals on ^1Ge and ^2Ge atoms coalesce at around -10 °C. The isomerization rate k_c at the coalescence temperature ($T_c = 263\text{ K}$) is estimated as ca. 90 s^{-1} using the equation of , where n_1 is the resonance frequency of TMS protons on ^2Ge (0.35 ppm, 175 Hz) and n_2 as the average of two TMS resonances on ^2Ge (0.27 ppm, 135 Hz). The activation free energy ($\Delta G_c^\ddagger$) at the T_c is evaluated as $13.0\text{ kcal mol}^{-1}$. While the transition state of the interconversion remains open, a plausible transition state is suggested to be **3a**^T due to the aurophilicity⁴⁶⁻⁴⁸ as shown in Scheme 2.

The mechanism for the formation of **3** remains open but may be proposed to proceed as shown in Scheme 3. The initial reduction of **2** with KC_8 affords **A** as an intermediate whose nucleophilic attack to another molecule of **2** gives **3** undergoing a substitution reaction. While no experimental evidence for the intermediacy of **A** has been obtained, the DFT calculations (at B3PW91-GD3 level in the gas phase with the basis sets of SDD level for Au) suggest that **A** would be better described as a trigonal pyramidal germynyl anion as shown in Fig. S54. The NBO analysis shows that the lone pair electrons are largely localized on 4s orbital of Ge with hybridization of $\text{sp}^{0.25}$ but developed to the 6p and other vacant orbitals of Au; the natural charges on Au and Ge are -0.330 and 0.502, respectively. The Au center of **A** would be allowed to nucleophilic attack the germanium atom of **2**.

The UV-vis spectrum of **3a** in THF shows the maximum absorption wavelength at 590 nm with the absorptivity $\epsilon/(\text{M}^{-1}\text{ cm}^{-1})$ of 3,560 (see Fig. S5). It is worth mentioning, the band is broad but more red-shifted than the $\text{n} \rightarrow 4\text{p}$ band of germylene **1** ($\lambda_{\text{max}} = 450\text{ nm}$, $\epsilon/\text{M}^{-1}\text{ cm}^{-1} = 320$).⁴²

To gain more insight into the structural characteristics of **3a** and related compounds, the DFT calculations were performed at B3PW91-GD3 level (see the SI for calculation details). As shown in Table S2, the structural parameters of $R'_2Ge(AuP)(AuGe)$ skeleton of **3a** determined by X-ray analysis are well reproduced by the calculations. Frontier molecular orbitals (FMOs) of **3a** are shown in Fig. 3. HOMO and HOMO-1 are assigned as the symmetric and antisymmetric combinations of two ^1Ge-Au s orbitals, respectively, and LUMO has the nature of originally vacant 2Ge pp orbital. The HOMO and LUMO energy levels of **3a** are -4.46 and -2.31 eV, respectively, and they are significantly higher and lower than those of germylene **1** (-5.55 and -1.77 eV, respectively at the same calculation level), suggesting higher reactivity of **3a** than **1**. The narrower HOMO-LUMO gap of **3a** (2.15 eV) than that of **1** (3.70 eV) is also in good agreement with the absorption maximum of **3a** (λ_{max} = 590 nm) observed at longer wavelength than that of **1** (λ_{max} = 450 nm).

Natural Bond Orbital (NBO) analysis of the theoretical structure of **3a** shows that it is comprised of three molecular units of R'_2GeAu_2 , PMe_3 , and GeR'_2 , where the latter two ligands coordinate to each of the two Au atoms. The $^1Ge-^1Au$ [and $^1Ge-^2Au$] bonds are both covalent formed by the overlap between a $4sp^{3.13}$ hybrid orbital of 1Ge and a 6s orbitals of 1Au and 2Au ; their Wiberg bond index is 0.6251 and 0.7122 with the occupancy of 1.8740 and 1.8909, respectively. The occupancies of the lone-pair and a vacant orbital on 2Ge are 1.6123 and 0.2173, showing the existence of significant dative bond between 1Au and 2Ge and small back bonding from 1Au to 2Ge . The second-order perturbation theory analysis shows the strong dative bonds from phosphine and germylene to 2Au and 1Au , respectively; the largest perturbation energy between the phosphine lone-pair orbital and $^2Au-^1Ge$ antibonding orbital amounts 127.5 kcal mol $^{-1}$ and that between the germylene lone-pair orbital and $^1Au-^1Ge$ antibonding orbital is 249.8 kcal mol $^{-1}$. To study the charge distribution in the Ge-Au bond of complexes **3**, the effective atomic charges of all atoms in **3a** were calculated using AIM.⁴⁹ The effective charges of the gold atoms in **3a** are -0.516 and -0.549, while that of germanium atoms are +1.088 and +0.699 respectively (Fig. 3). The balancing negative charge in **3a** is mostly localized at two gold atoms with the -1 oxidation state, in which gold atom demonstrates firstly the halogen-like behaviour featuring two conspicuously polarized $Au^{\delta-}-Ge^{\delta+}$ bonds.

Upon the DFT results, **3** could be regarded as amphoteric molecules, which involves a nucleophilic gold atom with the -1 oxidation state and a dialkylgermylene ligand having an enhanced electrophilicity. We may expect their distinctive types of reactions. The treatment of **3a** with two moles of PMe_3 at room temperature (Eq. 1) gives the corresponding digoldgermane coordinated by two phosphines, **4**, which is isolated and characterized by X-ray (Fig. S5) and NMR analysis (Fig. S27-30). HOMO of **4** holds almost the same shape and the energy level with that of **3a**; the HOMO of **4** features the anti-symmetric combination of the two Ge-Au s orbitals with the energy of -4.52 eV. On the other hand, the LUMO has mainly the nature of the vacant Au 6p orbitals and its energy level (-0.54 eV) is much higher than that of **3a** (Fig. S53). No reaction occurs when excess stannylene is added in the solution of **3a**. Neither *N*-Heterocyclic carbene (NHC) nor carbon monoxide (CO) does react with **3a**.

Because the negative charge in **3** is mostly localized equally at two gold atoms, they should react with electrophiles via addition or substitution reactions. The treatment of **3a** with a powerful electrophilic methylation agent, methyl triflate (MeOTf), was performed subsequently at ambient temperature (Eq. 2). Unexpectedly, the methylation occurs on germanium atom instead of gold atom accompanying the elimination of Me_3PAu^+ moiety.

The corresponding product **5** was identified by NMR spectroscopy and single crystal X-ray diffraction analysis (Fig. 4). Three Ge1-Au1 distance [2.4330(7) Å] of **5** is similar to those of Ge-Au covalent bonds found for **2** and **3** but a little longer than the Au1-Ge2 distance [2.3997(6) Å] of **5**. The Ge1-Au1-C17 and Ge1-Au1-Ge2 bond angles of **5** are 105.02(18) ° and 168.47(2) °, respectively. The dihedral angle between the two five-membered rings is 68.98 °, which is slightly acute than that (78.91 °) of **3a**.

We initially expected that the MeOTf as an electrophile is attacked by an Au atom in **3a**, but in reality, Me^+ formed a bond with the Ge atom in **3a**. To elucidate the pathways of the reaction of **3a** with MeOTf giving **5**, DFT calculations were performed at the B3PW91/def2-SVP level in the gas phase. While two intermediates **Int1** and **Int2** were located by the calculations, **Int1** is 19.5 kcal/mol higher in energy than **Int2** and **3a**, indicating **Int1** will not be an intermediate of the reaction, as shown in Fig. 6. Instead, the reaction would proceed directly via **Int2**, which is slightly more stable than the starting materials $\Delta G = 1.0 \text{ kcal}\cdot\text{mol}^{-1}$. The formation of Me_3PAuOTf was determined by ^{31}P NMR ($\delta = 13.13 \text{ ppm}$); see the Supplementary Information for the details.

Because **3a** has a low-lying LUMO that is even lower than that of germylene **1**, **3a** should be highly electrophilic at the ^2Ge center. Facile isomerization between **3** and **3'** as shown in Scheme 3 suggests the high electrophilicity at the ^2Ge to be attacked by an intramolecular gold nucleophile. Expectedly, **3a** readily reacts with external nucleophiles at the ^2Ge center of **3a**. It reacts with stoichiometric amounts of tetraphenylphosphonium chloride **6** ($\text{Ph}_4\text{P}^+\text{Cl}^-$) at ambient temperature giving the corresponding

chlorogermane **7** featuring a Ge-Cl bond (Fig. 7a). The structure of **7** was determined by NMR spectroscopy and single crystal X-ray diffraction analysis (Fig. 7b). In ^1H NMR spectra, trimethylsilyl proton resonances of **7** appear as four sharp singlets at 0.31, 0.25, 0.24 and 0.20 ppm, respectively, with 1:1:1:1 intensity ratio (Fig. S34), showing that the solid-state structure is maintained in solution. A doublet ^1H NMR signal appeared at 1.34 ppm is assigned to the methyl protons of a PMe_3 group. Two signals in the ^{31}P NMR appearing at 26.51 and 21.20 ppm are assignable to a PMe_3 ligand and a Ph_4P^+ cation in **7**, respectively (Fig. S37). Three Ge-Au distances of **7** [2.4325(5), 2.4284(5), and 2.4458(5) Å] are similar to those of Ge-Au covalent bonds found for **2** and **3** but a little longer than the $^1\text{Au}-^2\text{Ge}$ distance of **3a**. The $^1\text{Ge}-^2\text{Au}-\text{P}$ and $^1\text{Ge}-^1\text{Au}-^2\text{Ge}$ bond angles of **7** are $173.81(4)^\circ$ and $163.649(17)^\circ$, respectively. The dihedral angle between the two five-membered rings is 78.915° , which is similar with that found in **3a**.

Acyl chlorides were also used as a chloride source to react with germylene and stannylenes, in which the corresponding acylgermanes and acylstannanes have been obtained undergoing an insertion of acyl-Cl bond.⁵⁰⁻⁵² While the reaction of **3a** with acetyl chloride **8** was carried out at ambient temperature giving the chlorogoldgermane **9** in 67% together with acetyl(triethylphosphine)gold (Fig. 7a). The formation of **9** may occur concertedly from an acetylchloride-**3a** complex, from which the cleavage of the C-Cl bond and the recombination of Ge-Cl bond afford an acetyl derivate of **7** as the intermediate. Subsequently, acetyl cation possessing a stronger Lewis acidity than that of tetraphenylphosphonium (Ph_4P^+) would considerably promote the dissociation of Ge-Au bond through the electrostatic and steric effect giving the final product **9** (Scheme S2). The structure of **9** was determined by NMR spectroscopy and single crystal X-ray diffraction analysis (Fig. 7c). The Au1-Ge1-Cl1 and Ge1-Au1-Ge2 bond angles of **9** are $97.614(65)^\circ$ and $167.659(34)^\circ$, respectively. It is worth noting that the dihedral angle between the two five-membered rings is 166.99° , two planes almost parallel with each other, which is quite different with those of **3**, **5**, and **7**.

Digoldgermane **3a** has been found to exhibit effective catalytic ability for the cyclic trimerization of aryl isocyanates (Eq. 3). In the presence of 0.01 mol% of **3a**, the trimerization of various phenyl isocyanates **10a-e** takes place smoothly giving triaryl isocyanurates **11a-e** in 78-98% isolated yields (Scheme S3). The high electrophilicity of the ^2Ge atom in **3a** may be essential to the catalytic activity. Related goldgermanes without germylene coordination like **2a** or **4a** showed no catalytic activity for the trimerization of aryl isocyanates. There have been many catalysts discovered and diverse mechanisms

have been proposed for the trimerization.⁵³⁻⁵⁵ Though no evidence has been obtained, the Lewis acidity of **3** may be essential for the present catalytic mechanism; see Fig. S3 for a proposed catalytic cycle.

In conclusion, unprecedented digoldgermanes having a germylene ligand, **3a** and **3b**, are synthesized through the reaction of stable dialkylgermylene **1** with (R₃P)AuCl followed by the KC₈ reduction. The DFT calculations of **3a** show that the HOMO has the nature of Ge-Au σ bonding orbital, the LUMO has largely germylene vacant 4p_{np} nature with significantly lower energy level than that of **1**. These support that the heterolytically coordinated digoldgermanes **3** feature amphipathic behaviour in theory involving nucleophilic gold atoms with the -1 oxidation state and stronger electrophilicity than the germylene itself. In accord with these characteristics, **3** shows (1) the pendular motion of AuPR₃ ligand between two germanium atoms of **3** occurring in an NMR time scale; (2) a methylation of **3a** with MeOTf exhibiting the nucleophilic behaviour of gold atom with the -1 oxidation state; (3) facile reactions with Ph₄P⁺Cl⁻ and acetylchloride to give the corresponding chloride adducts; and (4) catalytic activity towards the cyclic trimerization of aryl isocyanates giving the corresponding triaryl isocyanurates.

Methods

General synthetic procedure. All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over Na metal or CaH₂ under nitrogen atmosphere. (R₃P)AuCl (R = Me, Et) were synthesized using literature procedures.^{56,57} ¹H, ¹³C, ²⁹Si and ³¹P NMR spectra were obtained with a Bruker AV 400 instrument at 400 MHz (¹H NMR), 101 MHz (¹³C NMR) and 162 MHz (³¹P NMR), as well as Bruker AV 500 instrument at 500 MHz (¹H NMR), 126 MHz (¹³C NMR), 99 MHz (²⁹Si NMR), 202 MHz (³¹P NMR) at 298 K. Unless otherwise noted, the NMR spectra were recorded in benzene-*d*₆ at ambient temperature. The ¹H and ¹³C NMR chemical shifts were referenced to residual ¹H and ¹³C of the solvents. NMR multiplicities are abbreviated as follows: *s* = singlet, *brs* = broad singlet, *d* = doublet, *dt* = doublet of triplets, *t* = triplet, and *m* = multiplet. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at Hangzhou Normal University with a Bruker Daltonics MicroQtof spectrometer. Melting points were measured with a BUCHI Melting Point M-560. Sampling of air-sensitive compounds was carried out using a MBRAUN's MB-10-G glove box. UV-vis spectrum was recorded on a Shimadzu UV-1800 spectrophotometer.

Synthesis of gold(I) complexes 2a and 2b. In a glove box, (R₃P)AuCl (R = Me or Et, 1.0 mmol) was added into a THF (10 mL) solution of germylene **1** (350 mg, 1.02 mmol) and the mixture was stirred at room temperature for 5 min. The solvent was removed under vacuum to afford the residue, which was washed with hexane (5 mL) for 3 times. The residual solvents were evaporated in vacuo affording white gold(I) complex **2a** or **2b**, where both of gold(I) complexes **2** are stable under argon for few months. **2a** (547 mg, 90%): a white powder; mp. 153 °C (dec.); ¹H NMR (400 MHz, C₆D₆) δ 2.46 – 2.38 (m, ring-CH₂, 2H), 2.20 – 2.12 (m, ring-CH₂, 2H), 0.60 (s, SiCH₃, 18H), 0.51 (s, SiCH₃, 18H), 0.46 (d, ²J_{H-P} = 9.20 Hz, PCH₃,

9H); ^{13}C NMR (101 MHz, C_6D_6) δ 35.28 (d, $^4J_{\text{C-P}} = 2.93$ Hz, ring- CH_2), 26.60 (d, $^3J_{\text{C-P}} = 14.04$ Hz, ring- C^q), 14.87 (d, $^1J_{\text{C-P}} = 28.58$ Hz, PCH_3), 5.23 (Si CH_3), 5.13 (Si CH_3); ^{29}Si NMR (99 MHz, C_6D_6) δ 4.17, 2.02; ^{31}P NMR (162 MHz, C_6D_6) δ 26.01; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{49}\text{AuGeClPSi}_4$ (M^+): 725.9677, m/z calcd for $[\text{M}-\text{Cl}]^+$, 691.1538, found: 691.1524. **2b** (580 mg, 92%): a white powder; mp. 172 °C (dec.); ^1H NMR (400 MHz, C_6D_6) δ 2.45 – 2.39 (m, ring- CH_2 , 2H), 2.18 – 2.13 (m, ring- CH_2 , 2H), 0.96 – 0.88 (m, PCH_2 , 6H), 0.71 (dt, PCH_2CH_3 , $^3J_{\text{H-P}} = 17.60$ Hz, $^3J_{\text{H-H}} = 7.60$ Hz, 9H), 0.61 (s, Si CH_3 , 18H), 0.51 (s, Si CH_3 , 18H); ^{13}C NMR (101 MHz, C_6D_6) δ 35.29 (d, $^4J_{\text{C-P}} = 2.52$ Hz, ring- CH_2), 26.56 (d, $^3J_{\text{C-P}} = 13.13$ Hz, ring- C^q), 17.97 (d, $^1J_{\text{C-P}} = 26.06$ Hz, PCH_2), 8.76 (s, PCH_2CH_3), 5.25 (s, Si CH_3), 5.06 (s, Si CH_3); ^{29}Si NMR (99 MHz, C_6D_6) δ 4.10, 2.14; ^{31}P NMR (162 MHz, C_6D_6) δ 60.48. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{55}\text{AuGeClPSi}_4$ (M^+) 768.0474, m/z calcd for $[\text{M}-\text{Cl}]^+$ 733.2023, found: 733.1994.

Synthesis of gold complexes 3a and 3b. **2a** or **2b** (1.00 mmol) and KC_8 (1.05 mmol, 177 mg) was mixed in THF (10 mL). The mixture was stirred at ambient temperature for 12 h. Then the mixture was concentrated under vacuum. Washing the residue with hexane (4 mL) for 3 times and extracting from the residue with toluene (20 mL) followed by concentration under vacuum gave **3a** or **3b** as a blue-green solid. **3a** (347 mg, 49%): mp. 150 °C (dec.); ^1H NMR (400 MHz, C_6D_6) δ 2.33 (brs, ring- CH_2 , 8H), 0.89 (d, $^2J_{\text{H-P}} = 7.60$ Hz, PCH_3 , 9H), 0.49 (brs, Si CH_3 , 72H); ^1H NMR (600 MHz, $\text{THF-}d_8$, –30 °C) δ 2.47 (brs, ring- CH_2 , 4H), 2.07 (brs, ring- CH_2 , 4H), 1.43 (d, $^2J_{\text{H-P}} = 8.20$ Hz, PCH_3 , 9H), 0.33 (brs, Si CH_3 , 36H), 0.25 (s, Si CH_3 , 18H), 0.22 (s, Si CH_3 , 18H); ^{13}C NMR (101 MHz, C_6D_6) δ 36.99 (ring- CH_2), 30.22 (ring- C^q), 16.20 (d, $^1J_{\text{C-P}} = 21.61$ Hz, PCH_3), 4.36 (brs, Si CH_3); ^{29}Si NMR (99 MHz, C_6D_6) δ 0.14 (brs); ^{31}P NMR (202 MHz, C_6D_6) δ 39.10; HRMS (ESI): m/z calcd for $[\text{C}_{32}\text{H}_{80}\text{AuGe}_2\text{Si}_8]^+$: 1032.2535, found: 1032.2587. **3b** (380 mg, 54%): mp. 162 °C (dec.) ^1H NMR (500 MHz, $\text{THF-}d_8$) δ 2.28 (brs, ring- CH_2 , 8H), 1.81 (m, PCH_2 , 6H), 1.22 (m, PCH_2CH_3 , 9H), 0.29 (brs, Si CH_3 , 72H); ^1H NMR (600 MHz, $\text{THF-}d_8$, –30 °C) δ 2.47 (brs, ring- CH_2 , 4H), 2.07 (brs, ring- CH_2 , 4H), 1.82 (p, $^2J_{\text{H-P}} = 7.7$ Hz, 6H), 1.21 (dt, $^3J_{\text{H-P}} = 16.9$, $^3J_{\text{H-H}} = 7.6$ Hz, 9H), 0.32 (brs, Si CH_3 , 36H), 0.25 (s, Si CH_3 , 18H), 0.23 (s, Si CH_3 , 18H); ^{13}C NMR (126 MHz, $\text{THF-}d_8$) δ 37.20 (s, ring- CH_2), 19.17 (d, $^1J_{\text{C-P}} = 20.50$ Hz, PCH_2), 8.84 (d, $^2J_{\text{C-P}} = 1.52$ Hz, PCH_2CH_3), 4.26 (s, Si CH_3); ^{29}Si NMR (99 MHz, C_6D_6) δ 0.13 (brs); ^{31}P NMR (202 MHz, $\text{THF-}d_8$) δ 55.10; HRMS (ESI): m/z calcd for $[\text{C}_{32}\text{H}_{80}\text{AuGe}_2\text{Si}_8]^+$: 1032.2535, found: 1032.2597.

Synthesis of complex 4. PMe_3 (12 mg, 0.16 mmol) was added into a THF (2 mL) solution of **3a** (100 mg, 0.08 mmol) and the mixture was reacted at room temperature for 20 min. The solution color changed from blue to light green. Washing the residue with cooled hexane (2 mL) for 3 times and extracting from the residue with toluene (2 mL) followed by concentration under vacuum gave **4** as a light green crystal in 92% yield (71 mg): mp. 148 °C (dec.); ^1H NMR (400 MHz, C_6D_6) δ 2.45 (s, ring- CH_2 , 4H), 0.7 (s, Si CH_3 , 36H), 0.68 (d, PCH_3 , $J_{\text{H-P}} = 7.6$ Hz, 18H); ^{13}C NMR (126 MHz, C_6D_6) δ 37.42 (ring- CH_2), 19.74 (t, $^3J_{\text{C-P}} = 6.0$ Hz, ring- C^q), 15.98 (dd, $^1J_{\text{C-P}} = 21.4$ Hz, $^5J_{\text{C-P}} = 3.8$ Hz, PCH_3), 5.86 (Si CH_3); ^{29}Si NMR (99 MHz, C_6D_6) δ

1.93; ^{31}P NMR (162 MHz, C_6D_6) δ 40.95; HRMS (ESI): m/z calcd for $[\text{C}_{22}\text{H}_{58}\text{Au}_2\text{GeP}_2\text{Si}_4]^+$: 964.1624, found: 964.1632.

Synthesis of complex 5. In a glove box, MeOTf (25.1 mg, 0.153 mmol) was added into a THF (10 mL) solution of **3a** (100 mg, 0.0766 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum to afford the residue that was extracted with hexane (20 mL). The residual solvents were evaporated in vacuo and recrystallized in hexane to separate **5** (45.9 mg, 57%): a red solid; mp. 188 °C; ^1H NMR (400 MHz, C_6D_6) δ 2.22 (m, ring- CH_2 , 4H), 2.16 (s, ring- CH_2 , 4H), 1.11 (s, CH_3 , 3H), 0.56 (s, SiCH_3 , 18H), 0.43 (s, SiCH_3 , 18H), 0.23 (s, SiCH_3 , 36H); ^{13}C NMR (101 MHz, C_6D_6) δ 62.09 (ring- C^q), 36.58 (ring- CH_2), 35.92 (ring- CH_2), 18.90 (ring- C^q), 11.31 (CH_3), 5.55 (SiCH_3), 5.21 (SiCH_3), 2.69 (SiCH_3); ^{29}Si NMR (99 MHz, C_6D_6) δ 3.41, 2.43, 1.32. HRMS (ESI): m/z calcd for $[\text{M}+\text{Cl}]^-$: $[\text{C}_{33}\text{H}_{83}\text{AuGe}_2\text{Si}_8\text{Cl}]^-$ 1083.2416, found: 1083.2439.

Synthesis of complex 7. In a glove box, PPh_4Cl (29.4 mg, 0.078 mmol) was added into a THF (10 mL) solution of **3a** (100 mg, 0.0766 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum to afford the residue that was washed with ether (5 mL) for 3 times. Finally, a light-red solid powder compound **7** was obtained. **7** (125 mg, 97%): mp. 172 °C (dec.); ^1H NMR (400 MHz, $\text{THF}-d_8$) δ 7.97-7.93 (t, Ar- H , J = 7.2 Hz, 4H), 7.79-7.75 (m, Ar- H , 16H), 2.25-2.23 (t, ring- CH_2 , J = 5.60 Hz, 2H), 2.09-2.07 (t, ring- CH_2 , J = 6.4 Hz, 2H), 2.00 (s, ring- CH_2 , 4H), 1.35-1.33 (d, PCH_3 , $^2J_{\text{P-H}}$ = 7.6 Hz, 9H), 0.31 (s, SiCH_3 , 18H), 0.25 (s, SiCH_3 , 18H), 0.23 (s, SiCH_3 , 18H), 0.2 (s, SiCH_3 , 18H); ^{13}C NMR (126 MHz, $\text{THF}-d_8$) δ 136.28 (Ar- C), 135.48 (d, Ar- C , $^3J_{\text{P-C}}$ = 11.0 Hz), 131.20 (d, Ar- C , $^2J_{\text{P-C}}$ = 11.1 Hz), 118.94 (d, $^1J_{\text{P-C}}$ = 89.7 Hz), 37.36 (ring- CH_2), 36.21 (ring- CH_2), 28.82 (ring- C^q), 18.96 (d, PCH_3 , J = 5.4 Hz), 16.82 (d, ring- C^q , J = 18.9 Hz), 5.77 (SiCH_3), 5.46 (SiCH_3); ^{29}Si NMR (99 MHz, $\text{THF}-d_8$) δ 1.81, 1.58, 1.28, -0.04; ^{31}P NMR (162 MHz, $\text{THF}-d_8$) δ 26.47 (PMe_3), 21.21 (PPh_4); HRMS (ESI): m/z calcd for $[\text{C}_{35}\text{H}_{89}\text{Au}_2\text{ClGe}_2\text{PSi}_8]^-$: 1341.2299, found: 1341.2312.

Reaction of dialkylgermylene 1 with Ph_4PCl . In a glove box, PPh_4Cl (29.4 mg, 0.078 mmol) was added into a THF (10 mL) solution of **1** (29.2 mg, 0.070 mmol) and the mixture was stirred at room temperature for 48 h. The solvent was removed under vacuum to afford the residue that was extracted with hexane (5 mL) for 3 times. Finally, a colorless solid powder compound **1·HCl** was obtained (28.9 mg, 91%): mp. 82 °C; ^1H NMR (400 MHz, C_6D_6) δ 6.64 (s, Ge- H , 1H), 1.94 (m, ring- CH_2 , 2H), 1.77 (m, ring- CH_2 , 2H), 0.31 (s, SiCH_3 , 18H), 0.15 (s, SiCH_3 , 18H); ^{13}C NMR (101 MHz, C_6D_6) δ 33.32 (ring- CH_2), 16.41 (ring- C^q), 3.50 (SiCH_3), 2.79 (SiCH_3).

Synthesis of complex 9. In a glove box, CH_3CClO (18.0 mg, 0.23 mmol) was added into a benzene (10 mL) solution of **3a** (150 mg, 0.115 mmol) and the mixture was stirred at room temperature for 10 h. The solvent was removed under vacuum to afford the residue that was extracted with hexane (5 mL) for 3 times. Finally, a rufous solid compound **9** was obtained: (125 mg, 67%): mp. 172 °C (dec.); ^1H NMR (400

MHz, C₆D₆) δ 2.49-2.45 (m, ring-CH₂, 2H), 2.26-2.22 (m, ring-CH₂, 2H), 2.13 (s, ring-CH₂, 4H), 0.56 (s, SiCH₃, 18H), 0.49 (s, SiCH₃, 18H), 0.20 (s, SiCH₃, 36H); ¹³C NMR (126 MHz, C₆D₆) δ 36.44 (ring-CH₂), 35.21 (ring-CH₂), 27.26 (ring-CH₂), 27.19 (ring-CH₂), 4.80 (SiCH₃), 4.78 (SiCH₃), 4.43 (SiCH₃), 4.40 (SiCH₃), 2.66 (SiCH₃), 2.62 (SiCH₃); ²⁹Si NMR (99 MHz, C₆D₆) δ 3.55, 3.45, 0.67, 0.57, -1.02; HRMS (ESI): m/z calcd for [M - C]⁺: [C₃₂H₈₀AuGe₂Si₈]⁺ 1083.2416, found: 1083.2439

General procedure for cyclic trimerization of aryl isocyanates catalyzed by 3a. A THF solution of complex 3a (7.66x10⁻⁴ M in THF, 130 μ L, 0.01 mol%) was introduced in a thick-walled tube which contained the solvent THF (2.0 mL) and the desired aryl isocyanate **10** (1 mmol). The reaction mixture was heated at 80 °C for 14 h. Upon completion, the products were purified by washing with n-hexane. **11a** (125 mg, 97%): ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.45 (m, Ar-H, 6H), 7.43-7.40 (m, Ar-H, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 148.84 (O=C), 133.73 (Ar-C), 129.51 (Ar-C), 128.55 (Ar-C). **11b** (86 mg, 86%): ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.47 (d, *J* = 8.8 Hz, Ar-H, 6H), 7.33-7.31 (d, *J* = 8.8 Hz, Ar-H, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 148.27 (O=C), 135.73 (Ar-C), 131.86 (Ar-C), 129.86 (Ar-C), 129.86 (Ar-C). **11c** (72 mg, 72%): ¹H NMR (400 MHz, C₆D₆) δ 7.81-7.79 (d, *J* = 8.4 Hz, Ar-H, 6H), 7.56-7.54 (d, *J* = 8.4 Hz, Ar-H, 6H); ¹³C NMR (101 MHz, C₆D₆) δ 147.92 (O=C), 136.27 (Ar-C), 132.00 (q, ²*J*_{C-F} = 33.13, Ar-C), 129.23 (Ar-C), 126.83 (q, ³*J*_{C-F} = 3.63, Ar-C), 122.27 (C-F). **11d** (98 mg, 98%): ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 2.4 Hz, Ar-H, 12H), 2.38 (s, CH₃, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 148.98 (O=C), 139.35 (Ar-C), 131.20 (Ar-C), 130.07 (Ar-C), 128.18 (Ar-C), 21.32 (CH₃). **11e** (98 mg, 98%): ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.28 (d, *J* = 8.8 Hz, Ar-H, 6H), 6.99-6.97 (d, *J* = 8.8 Hz, Ar-H, 6H), 3.82 (s, OCH₃, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 159.99 (Ar-C), 149.24 (O=C), 129.52 (Ar-C), 126.39 (Ar-C), 114.69 (Ar-C), 55.59 (OCH₃).

Dialkylgermylene 1 catalyzed cyclic trimerization of 1-isocyanato-4-methylbenzene 10d. A THF-*d*₈ solution of **1** (10 mg, 5 mol%) was introduced in a Young-NMR tube which contained 1-isocyanato-4-methylbenzene **10d** (67 mg, 0.5 mmol). The reaction mixture was heated at 80 °C for 14 h. Upon completion, the product **10d** was detected in 92% yields by ¹H NMR spectrum.

Theoretical calculations. Theoretical calculations were performed for the following compounds **1**, **3a**, **4**, and anion **A**, using the Gaussian 16 program package⁵⁸ at Southern University of Science and Technology. The structures phase were optimized using a dispersion-corrected DFT method at the B3PW91⁵⁹-GD3 level^{60,61} with the basis sets of 6-31+G(d,p) for C, H, Si, P, and Ge atoms + SSD for Au. As shown in Table S2, the structural parameters of R'₂Ge(AuP)(AuGe) moiety of **3a** determined by X-ray analysis are well reproduced by the calculations. The structures related the reaction of **3a** with MeOTf were optimized at the B3PW91/def2-SVP⁶² level in the gas phase. All of the structures obtained herein were verified by examination of their Hessian matrix as minima (all frequencies real). The solvent effects on the relative stability of the compounds were not evaluated. The AIM charges of the atoms were calculated using the basin analysis module of Multiwfn3.8.⁴⁹

Data availability

Metrical data for the solid-state structures of **2b**, **3a**, **3b**, **4**, **5**, **7** and **9** in this paper have been deposited at the Cambridge Crystallographic Data Centre under reference numbers CCDC: 2040233, 2040232, 2040235, 2040234, 2093574, 2040236 and 2093575, respectively. Copies of the data can be obtained free of charges from www.ccdc.cam.ac.uk/structures/. All other data supporting the findings of this study are available within the article and its Supplementary Information.

Declarations

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Author contributions

L.W. performed preliminary experiments on the system. G.Z., Y.L., L.H. and X.C. carried out the synthetic work and analytical characterization. L.W. and M.K. performed DFT calculations. X.C. acquired the XRD data. L.W., X.C., M.K. and Z.L. wrote the paper, all authors discussed and commented on the manuscript. M.K. and Z.L. directed and coordinated the research.

Competing interests

The authors declare no competing financial interest.

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Figures

Figure 1

Literature-known motifs of gold complexes I-V possessing the halogen-like behaviour.

Figure 2

Molecular structures of 3a and 3b. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Trimethylsilyl, ethyl, and methyl groups are depicted in a wireframe model. Selected bond lengths [Å] and angles [°]: 3a: Au1-Ge1 2.4475(4), Au1-Ge2 2.4146(4), Au2-Ge1 2.4460(5), Au2-P1 2.3298(11); Ge2-Au1-Ge1 168.042(15), Au2-Ge1-Au1 106.909(16), P1-Au2-Ge1 175.25(3). 3b: Au1-Ge1 2.4371(7), Au1-Ge2 2.4089(8), Au2-Ge1 2.4307(8), P1-Au2 2.311(2); Ge2-Au1-Ge1 171.73(3), Au2-Ge1-Au1 107.61(3), P1-Au2-Ge1 174.02(7).

Figure 3

FMOs of 3a calculated at B3PW91-GD3 level. Hydrogen atoms are omitted in the wire frame structure of 3a.

Figure 4

Calculated effective atomic charges for the Ge and Au centres in 3a. The effective atomic charges of all atoms in 3a were calculated using the AIM method.

Figure 5

Molecular structures of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Trimethylsilyl, ethyl, and methyl groups are depicted in a wireframe model.

Figure 6

DFT-calculated free-energy profile of a plausible mechanism for the reaction between **3a** and MeOTf in the gas phase, as determined at the B3PW91/def2-SVP level of theory.

Figure 7

(a) Treatment of 3a with tetraphenylphosphonium chloride (Ph_4PCl) 6, and acetyl chloride 8; (b) Molecular structure of 7; (c) Molecular structure of 9; Hydrogen atoms are omitted for clarity. Trimethylsilyl, ethyl, phenyl and methyl groups are depicted in a wireframe model.

Figure 8

Scheme 1. The synthesis of digoldgermanes 3a and 3b.

Figure 9

Scheme 2. Facile isomerization between 3 and its equivalent structure 3'.

Figure 10

Scheme 3. A proposed mechanism for the formation of 3

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