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Diaminogermylene and Diaminostannylene Derivatives of Gold(I): Novel AuM and AuM₂ (M = Ge, Sn) Complexes

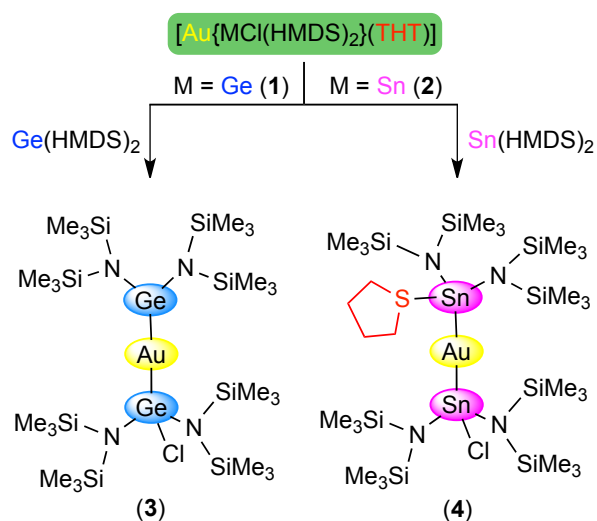
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Abstract

The reactions of $[\text{AuCl}(\text{THT})]$ (THT = tetrahydrothiophene) with 1 equiv. of the group-14 diaminometalenes $\text{M}(\text{HMDS})_2$ [$\text{M} = \text{Ge}, \text{Sn}$; $\text{HMDS} = \text{N}(\text{SiMe}_3)_2$] lead to $[\text{Au}\{\text{MCl}(\text{HMDS})_2\}(\text{THT})]$ ($\text{M} = \text{Ge}$ (**1**), Sn (**2**)), which contain a metalate(II) ligand that arises from the insertion of the corresponding $\text{M}(\text{HMDS})_2$ reagent into the $\text{Au}-\text{Cl}$ bond of the gold(I) reagent. While compound **1** reacts with more $\text{Ge}(\text{HMDS})_2$ to give the germanate-germylene derivative $[\text{Au}\{\text{GeCl}(\text{HMDS})_2\}\{\text{Ge}(\text{HMDS})_2\}]$ (**3**), which results from the substitution of $\text{Ge}(\text{HMDS})_2$ for the THT ligand of **1**, an analogous treatment of compound **2** with $\text{Sn}(\text{HMDS})_2$ gives the stannate-stannylene derivative $[\text{Au}\{\text{SnCl}(\text{HMDS})_2\}\{\text{Sn}(\text{HMDS})_2(\text{THT})\}]$ (**4**), which has a THT ligand attached to the stannylene tin atom and that, in solution at room temperature, participates in a dynamic process that makes equivalent (in the NMR time scale) its two $\text{Sn}(\text{HMDS})_2$ fragments. A similar dynamic process has not been observed for the AuGe_2 compound **3** or for the AuSn_2 derivatives $[\text{Au}\{\text{SnR}(\text{HMDS})_2\}\{\text{Sn}(\text{HMDS})_2(\text{THT})\}]$ ($\text{R} = \text{Bu}$ (**5**), HMDS (**6**)), which have been prepared by treating complex **4** with LiR . The structures of compounds **1** and **3–6** have been determined by X-ray diffraction.



Introduction

The investigation of the transition-metal chemistry of the heavier analogues of diaminocarbenes, that is, group-14 diaminometalenes [M = Si, Ge, Sn, or Pb],^{1,2} started some decades ago following the seminal discovery by Lappert in 1974 of the first specimens of this family, M(HMDS)₂ [M = Ge, Sn, Pb; HMDS = N(SiMe₃)₂].³ These acyclic compounds were soon complemented with some cyclic relatives (N-heterocyclic metalenes), the first stable N-heterocyclic silylenes,⁴ germylenes,⁵ stannylenes,⁶ and plumbylenes⁷ being reported in 1994, 1989, 1974, and 1982, respectively. However, despite their early discovery, the transition-metal chemistry of group-14 diaminometalenes^{1,2} is currently underdeveloped in comparison with that of diaminocarbenes,⁸ whose first stable specimen was isolated much later (1991)⁹ than the first diaminometalenes.

Among the synthetic and reactivity studies on group-14 diaminometalene derivatives of transition metals that can be found in the chemical literature, the works regarding group-11 metals are very scarce. Those dealing with diaminoplumbylenes are nonexistent and only one involves a diaminosilylene (compound **A** in Figure 1).¹⁰ Disubstituted diaminogermylenes are only represented in copper chemistry (compounds **B** and **C** in Figure 1),¹¹ but trisubstituted diaminogermylenes have been attached to the three group-11 metals (compounds **D**,¹² **E**,¹³ and **F**¹⁴ in Figure 1). No copper, silver, or gold derivatives of disubstituted diaminostannylenes have ever been reported although some examples of trisubstituted diaminostannylene derivatives of copper and silver are known (compounds **F** in Figure 1).¹⁴ It should be noted that all complexes shown in Figure 1 have been prepared using the corresponding diaminometalenes as reagents.

Concerning anionic group-14 di- or triaminometalate ligands in group-11 metal complexes, a few examples are known for the three transition metals. They all have been prepared by either inserting a diaminometalene into an Au–Cl bond (compounds **G** in Figure 2)¹⁵ or by displacing one (compounds **H** in Figure 2)^{16–18} or two anionic ligands (compounds **I**¹⁸ and **J**¹⁹ in Figure 2) from the appropriate transition-metal precursor with a group-14 triaminometalate reagent. Similar substitution reactions have also allowed the preparation of some gold(II) and gold(III) complexes, not depicted in Figure 2, that contain the triaminostannate ligand of **H** and **I**.¹⁸

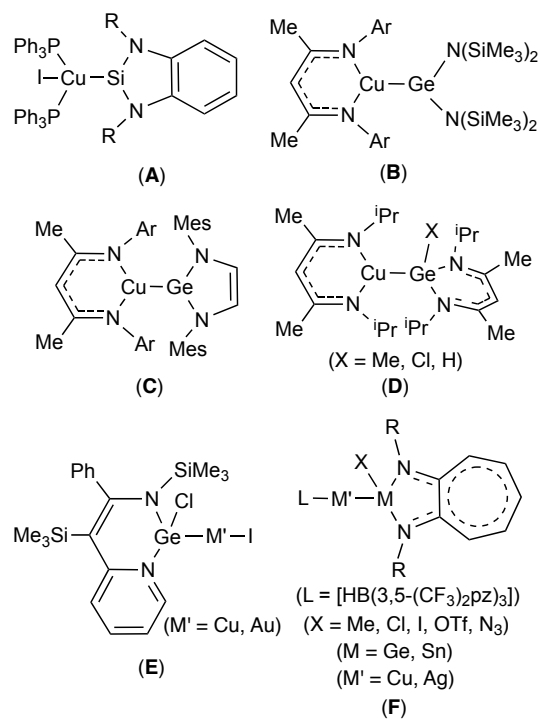


Figure 1. Examples of Si, Ge, and Sn diaminometalene derivatives of group-11 metals.

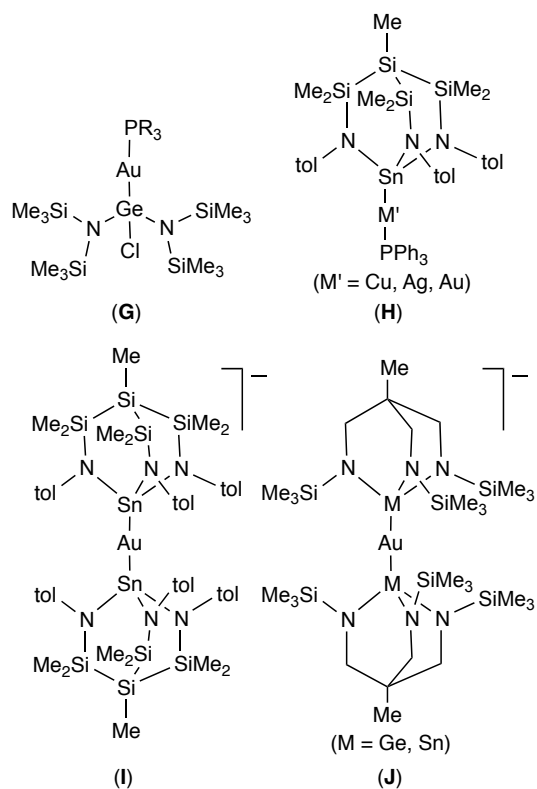


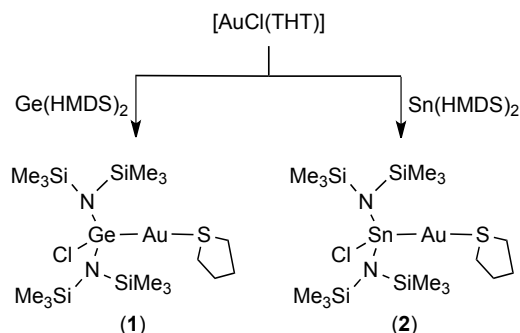
Figure 2. Examples of Ge and Sn di- and triaminometalate derivatives of group-11 metals.

All the above-commented data prompted us to attempt the synthesis of simple germanium and tin diaminometalene derivatives of gold(I), of which no examples had been previously reported. We also had in mind that diaminocarbene complexes of gold(I) had recently been identified as very efficient catalyst precursors for many catalytic reactions that are important in organic chemistry²⁰ and we wondered whether group-14 diaminometalene derivatives of gold(I) would also be useful in catalysis. We chose [AuCl(THT)] (THT = tetrahydrothiophene) as gold(I) precursor because its THT ligand can be readily displaced by other ligands.²¹ The Lappert's compounds M(HMDS)₂ (M = Ge, Sn) were chosen as diaminometalene reagents because their syntheses can be easily accomplished.³

We now report that appropriate combinations of these reagents have led to novel complexes containing Au–M and M–Au–M (M = Ge, Sn) metallic cores in which the germanium or tin atoms belong to neutral metalene and/or anionic metalate ligands. Unfortunately, the high sensitivity of these complexes to oxygen and moisture discourages their use in homogeneous catalysis.

Results and Discussion

The treatment of [AuCl(THT)] with equimolar amounts of M(HMDS)₂ (M = Ge or Sn) in toluene at room temperature led to the quantitative formation of the air- and moisture-sensitive products [Au{MCl(HMDS)₂}(THT)] (M = Ge (**1**), Sn (**2**)) (Scheme 1).



Scheme 1

The ¹H and ¹³C{¹H} NMR spectra of both compounds indicated that they contain THT and HMDS in 1:2 ratio, denoting that these reactions do not lead to the substitution of the THT ligand but to the addition of the corresponding M(HMDS)₂ reagent to

[AuCl(THT)]. Therefore, these reactions differ from those reported for [AuCl(THT)] and diaminocarbenes, in which substitution of the carbene for the THT ligand occurs.²²

An X-ray diffraction analysis showed that compound **1** formally results from the insertion of Ge(HMDS)₂ into the Au–Cl bond of [AuCl(THT)], since the gold atom is linearly attached to the germanium atom of a chloro(diamino)germanate(II) ligand and to the sulfur atom of a THT ligand (Figure 3, Table 1). Related reaction processes that afford [Au{GeCl(HMDS)₂}(PR₃)] (R = Et, Cy, Ph) derivatives (**G** in Figure 2) have been reported to occur between [AuCl(PR₃)] and Ge(HMDS)₂.¹⁵

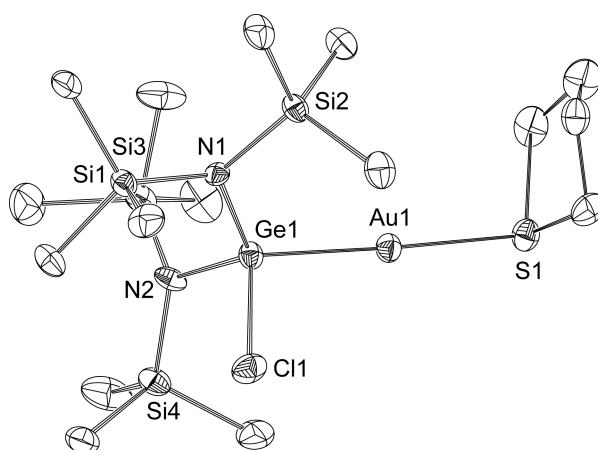
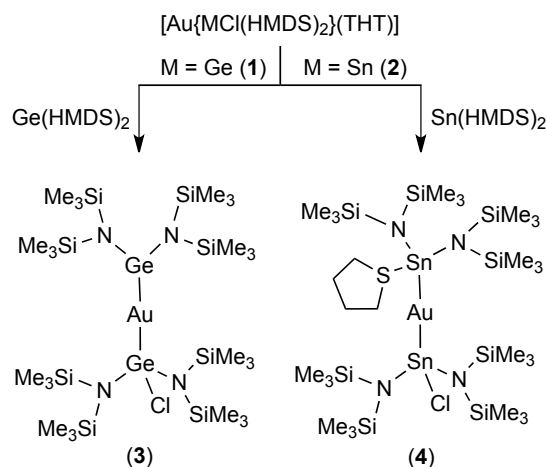


Figure 3. Molecular structure of compound **1** (thermal ellipsoids set at 30% probability). Hydrogen atoms have been omitted for clarity. The Au-THT fragment is disorder over two positions in a 83:17 ratio. Only the fragment with 83% occupancy is represented.

The treatment of [AuCl(THT)] with two equivalents of M(HMDS)₂ (M = Ge, Sn) quantitatively afforded the air- and moisture-sensitive AuGe₂ and AuSn₂ derivatives [Au{GeCl(HMDS)₂}{Ge(HMDS)₂}] (**3**) and [Au{SnCl(HMDS)₂}{Sn(HMDS)₂(THT)}] (**4**), respectively (Scheme 2). These reactions demonstrate that the THT ligand of compounds **1** and **2** can be displaced from the gold atom by a group-14 diaminometalene reagent. However, while the germylene derivative **3** arises from the simple substitution of Ge(HMDS)₂ for the THT ligand of **1**, the stannylene derivative **4** contains a THT ligand attached to the stannylene tin atom, thus it can be considered as resulting from the formal insertion of Sn(HMDS)₂ into the Au–S bond of compound **2**.



Scheme 2

The molecular structures of compounds **3** (Figure 4, Table 2) and **4** (Figure 5, Table 3) have been determined by X-ray diffraction. Both complexes contain an almost linear M–Au–M arrangement in which the Au–M distances reflect the atomic volume and the steric congestion of the M atoms. Thus, while both Au–Ge distances of compound **3** are very similar, (2.4120(5) Å and 2.4038(5) Å, the Au–Sn distances of compound **4**, 2.5711(5) Å and 2.5845(5) Å, differ by 0.013 Å, the longest one being associated to the most crowded tin atom, Sn2, which is that attached to the THT ligand. The presence of the THT ligand in complex **4** results in pyramidalization of the coordination sphere of the Sn2 atom and reduces the metalene N3–M2–N4 angle, which is 112.6(2)^o in compound **3** (M = Ge) but only 107.7(3)^o in compound **4** (M = Sn). In contrast, the coordination environment of the germylene Ge2 atom in complex **3** is perfectly planar.

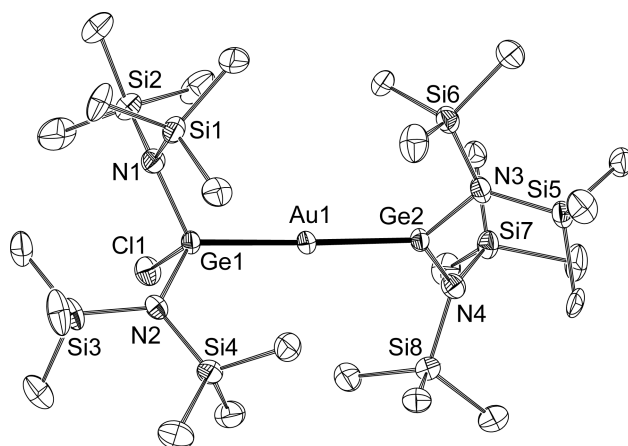


Figure 4. Molecular structure of compound **3** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

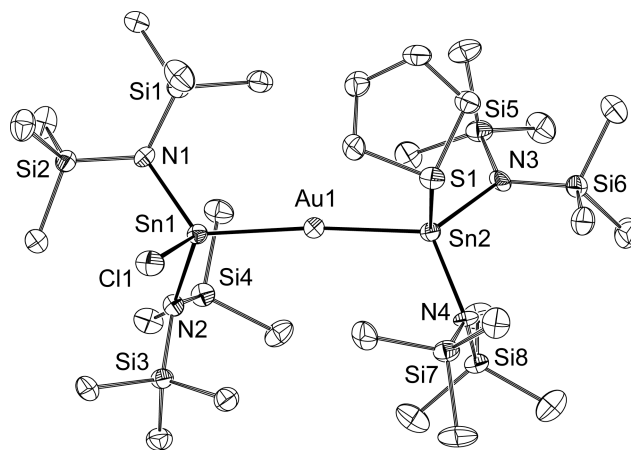


Figure 5. Molecular structure of compound **4** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

The higher tendency of $\text{Sn}(\text{HMDS})_2$ ligands, in comparison with that of $\text{Ge}(\text{HMDS})_2$ ligands, to retain THT (Scheme 2) may initially be intriguing. However, it has to be related to the greater metallic character (stronger Lewis acidity) and larger atomic volume (higher capacity to accommodate larger ligands) of tin. In fact, transition-metal stannylene complexes that have the tin atoms additionally attached to neutral ligands^{2e,23} are more represented in the chemical literature than their analogous gemylene derivatives.²⁴ We are not aware of any transition-metal diaminometalene complex having the group-14 metal atom attached to an S-donor ligand.

The room-temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the AuGe_2 compound **3** are in complete agreement with the solid-state molecular structure of this compound, since they contain two singlet resonances assignable to the chemically inequivalent methyl groups of its germanate and gemylene ligands. However, the room-temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the AuSn_2 compound **4** contain two broad singlets for the THT methylene groups and only a broad singlet for all the SiMe_3 groups, indicating the occurrence of a dynamic process that makes equivalent (in the NMR time scale) the environments of the two tin atoms. A variable-temperature ^1H NMR study in toluene- d_8 (Figure 6) showed that the SiMe_3 resonance of the room-temperature spectrum (0.44 ppm) is split into two very broad resonances at 193 K (0.61 and 0.28 ppm) while, at this temperature, the resonances of the THT ligand are almost unobserved. Therefore, the dynamic process is still active at 193 K.

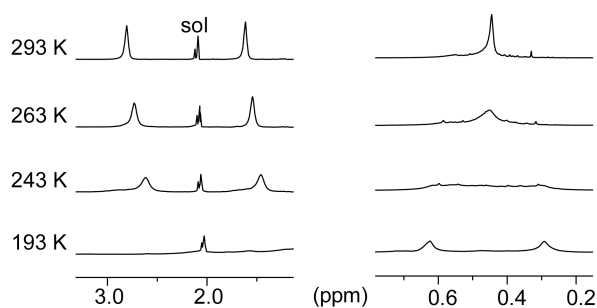
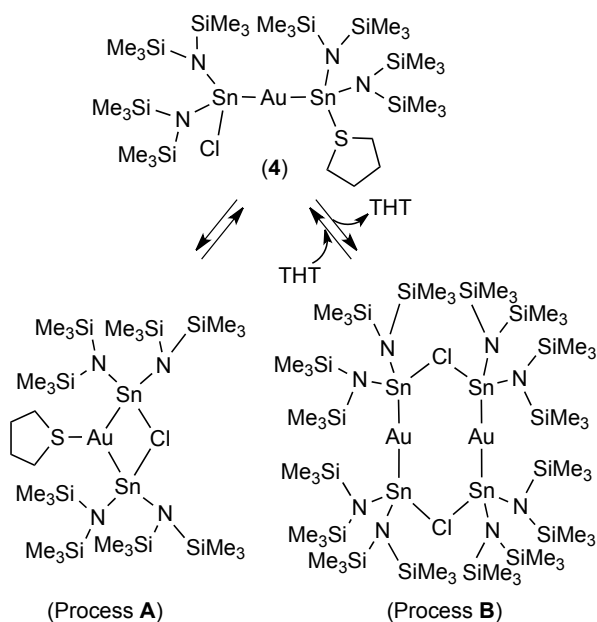


Figure 6. THT (left) and HMDS (right) regions of ^1H NMR spectra of compound **4** in toluene- d_8 at different temperatures (sol = toluene + residual protons of toluene- d_8 ; small sharp peaks are due to impurities).



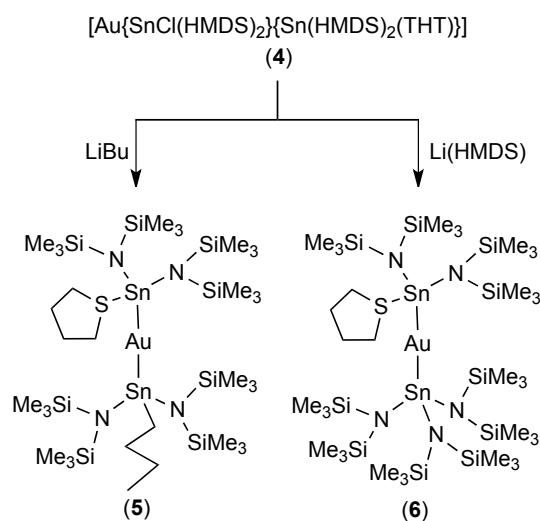
Scheme 3

The spectra shown in Figure 6 are *a priori* compatible with the two dynamic equilibria proposed in Scheme 3, which average the ligand environment of the two tin atoms of **4** by forming symmetric chloride-bridged intermediates. Chloride-bridged diaminostannylene ligands have been previously observed in, for example, rhodium(I)²⁵ and palladium(II)²⁶ complexes. While process **A** is intramolecular and involves a symmetric AuSn_2 intermediate having an unusual²⁷ tri-coordinated gold atom, process **B** involves the release of THT from **4** and the dimerization of the resulting unsaturated species to form a symmetric Au_2Sn_4 intermediate. Interestingly, a variable temperature ^1H NMR study using a 1:3 mixture of compound **4** and THT in toluene- d_8 indicated that the rate of the dynamic process is negatively affected by the presence of free THT in the solution. For example, the

SiMe₃ region of the 193 K spectrum of Figure 3 is comparable to that of a spectrum of the 4/THT mixture run at 233 K. Therefore, these data support the involvement of process **B** and rule out the participation of process **A**, which should not depend on the concentration of free THT.

The smaller atomic volume of germanium in comparison with that of tin and the great steric hindrance exerted by the large HMDS groups should make less favorable the formation of chloride-bridged Au₂Ge₄ dimeric species similar to that depicted in Scheme 3 for M = Sn. In other words, we propose that the smaller volume of germanium is the differential factor that accounts for the fact that the AuGe₂ complex **3** is not involved in a dynamic process analogous to that observed in solution for the AuSn₂ complex **4**.

With the aim of confirming that the ability of the chloride ligand to bridge two metal atoms is an important factor in the dynamic process occurring in solutions of compound **4** and, thus, giving further support to our mechanistic proposal for the dynamic process, we decided to substitute the chloride ligand of compound **4** by other anionic groups with less tendency to bridge metal atoms. That was accomplished by treating compound **4** with LiBu and Li(HMDS). These reactions led to [Au{SnBu(HMDS)₂}{Sn(HMDS)₂(THT)}] (**5**) and [Au{Sn(HMDS)₃}{Sn(HMDS)₂(THT)}] (**6**) (Scheme 4). No previous examples of transition-metal complexes containing SnBu(HMDS)₂ or Sn(HMDS)₃ stannate ligands have been hitherto reported.



Scheme 4

The X-ray diffraction molecular structures of compounds **5** and **6** are shown in Figures 7 and 8. Selected interatomic distances and angles are provided in Table 3. In both structures, the atom connectivity is comparable to that of compound **4**, with the exception that the chloride ligand of the latter has been replaced by an *n*-butyl ligand in **5** or an HMDS ligand in **6**. The larger volume of the *n*-butyl and HMDS ligands, specially the latter, increases the crowding of the ligand shell of the tin atom to which they are attached, Sn1. This effect is clearly manifested by a lengthening of the Au1–Sn bond distances and a decrease of the Sn1–Au1–Sn2 and N1–Sn1–N2 bond angles on going from **4** to **5** and **6**.

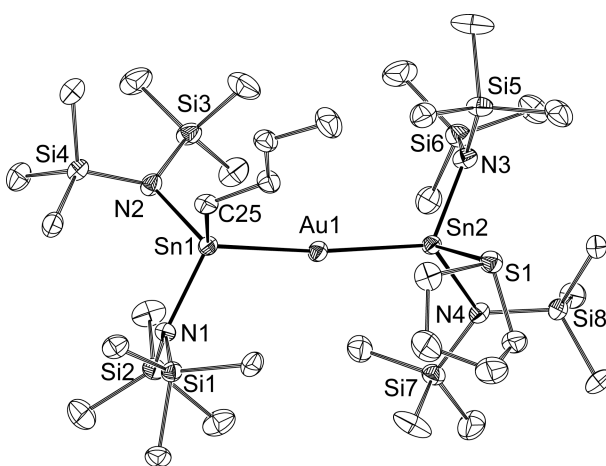


Figure 7. Molecular structure of compound **5** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

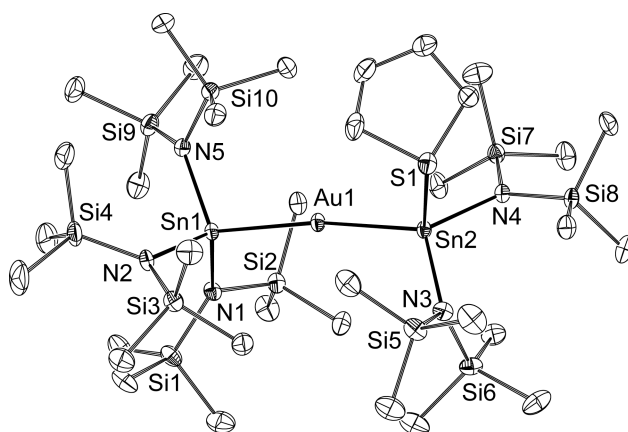


Figure 8. Molecular structure of compound **6** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

The room-temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5** and **6** contain the resonances of two types of HMDS ligands, indicating that those attached to a tin atom are

not equivalent to those attached to the other tin atom. Therefore, in solution at room temperature, these complexes are not involved in a dynamic process similar to that observed for compound **4**. This result supports the proposal that the chloride ligand of compound **4** actively participates in the dynamic process observed in solutions of this complex.

Concluding Remarks

While the reaction of $M(\text{HMDS})_2$ with $[\text{AuCl}(\text{THT})]$ does not result in the displacement of the THT ligand but in the insertion of the diaminometalene reagent into the Au–Cl bond to give the germanate and stannate derivatives $[\text{Au}\{\text{MCl}(\text{HMDS})_2\}(\text{THT})]$ ($M = \text{Ge}$ (**1**), Sn (**2**)), the addition of a supplementary equivalent of $M(\text{HMDS})_2$ results in the subsequent displacement of THT from the gold coordination shell to give $[\text{Au}\{\text{GeCl}(\text{HMDS})_2\}\{\text{Ge}(\text{HMDS})_2\}]$ (**3**) and $[\text{Au}\{\text{SnCl}(\text{HMDS})_2\}\{\text{Sn}(\text{HMDS})_2(\text{THT})\}]$ (**4**). The greater metallic character and the larger atomic volume of tin with respect to those of germanium seem to be responsible for the presence of THT in compound **4** and its absence in compound **3**. Compounds **3** and **4** are the first examples of gold(I) complexes containing group-14 diaminometalenes as ligands.

In solution, compound **4** participates in a dynamic process that makes equivalent the environments of its two tin atoms in the NMR time scale. Data are provided that support that a reversible dissociation of THT and the bridging ability of the chloride ligand are essential features of this process.

The transformation of compound **4** into $[\text{Au}\{\text{SnR}(\text{HMDS})_2\}\{\text{Sn}(\text{HMDS})_2(\text{THT})\}]$ ($R = \text{Bu}$ (**5**), HMDS (**6**)) not only supports the proposal that the chloride ligand of compound **4** actively participates in the dynamic process observed in solutions of this complex, it also demonstrates that the chloride of transition-metal $\text{SnCl}(\text{HMDS})_2$ stannate complexes can be successfully replaced by other anionic groups. It is also noteworthy that no previous examples of transition-metal complexes containing $\text{SnBu}(\text{HMDS})_2$ or $\text{Sn}(\text{HMDS})_3$ stannate ligands have been hitherto reported.

Experimental Section

General Procedures. All reactions were carried out under nitrogen, using dry box and/or Schlenk-vacuum line techniques due to the high sensitivity of all reaction products to air and moisture. Toluene and hexane were dried over sodium diphenyl ketyl and distilled under nitrogen before use. $[\text{AuCl}(\text{THT})]$,^{21b} $\text{Ge}(\text{HMDS})_2$,³ and $\text{Sn}(\text{HMDS})_2$ ³ were prepared following published procedures. All remaining reagents were purchased from commercial sources. NMR spectra were run on Bruker DPX-300 or Bruker AV-400 instruments, using as internal standards a residual protic solvent resonance for ^1H [$\delta(\text{C}_6\text{D}_5\text{CHD}_2) = 2.08$; $\delta(\text{C}_6\text{HD}_5) = 7.16$] and a solvent resonance for ^{13}C [$\delta(\text{C}_6\text{D}_5\text{CD}_3) = 20.4$; $\delta(\text{C}_6\text{D}_6) = 128.1$]. Microanalyses were obtained from the University of Oviedo Microanalytical Service.

$[\text{Au}\{\text{GeCl}(\text{HMDS})_2\}(\text{THT})]$ (1): $\text{Ge}(\text{HMDS})_2$ (0.5 mL of a 0.35 M solution in toluene, 0.175 mmol) was added to a suspension of $[\text{AuCl}(\text{THT})]$ (50.9 mg, 0.159 mmol) in toluene (10 mL) and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give a yellow oil that contained compound **1** and some toluene (NMR identification). A few X-ray-quality crystals of **1** were obtained by slow evaporation of a concentrated toluene solution at room temperature. However, all attempts to isolate this compound as a pure solid (by precipitating it from various solvents at room temperature or below) were unsuccessful because they led to partial decomposition. ^1H NMR (C_6D_6 , 300.1 MHz, 293 K): δ 2.36 (s, 4 H, CH_2); 1.23 (s, br, 4 H, CH_2); 0.60 (s, br, 36 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 293 K): δ 38.1 (s, CH_2); 30.6 (s, CH_2); 6.8 (s, Me).

$[\text{Au}\{\text{SnCl}(\text{HMDS})_2\}(\text{THT})]$ (2): $\text{Sn}(\text{HMDS})_2$ (0.5 mL of a 0.37 M solution in toluene, 0.185 mmol) was added to a suspension of $[\text{AuCl}(\text{THT})]$ (53.9 mg, 0.168 mmol) in toluene (10 mL) and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give a dark green oil that contained compound **2** and some toluene (NMR identification). All attempts to isolate this compound as a pure solid (by precipitating it from various solvents at room temperature or below) were unsuccessful because they led to partial decomposition. ^1H NMR (C_6D_6 , 300.1 MHz, 293 K): δ 2.52 (s, br, 4 H, CH_2); 1.36 (s, br, 4 H, CH_2); 0.53 (s, 36 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 293 K): δ 37.9 (s, CH_2); 30.7 (s, CH_2); 6.9 (s, Me).

[Au{GeCl(HMDS)}₂{Ge(HMDS)}₂] (3): Ge(HMDS)₂ (1 mL of a 0.35 M solution in toluene, 0.350 mmol) was added to a suspension of [AuCl(THT)] (53.4 mg, 0.167 mmol) in toluene (10 mL) and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give an orange oil. Slow evaporation at room temperature of a concentrated toluene solution deposited X-ray quality crystals of **3**·(C₇H₈)_{0.5} (123 mg, 69 %). Anal. Calcd. for C₂₄H₇₂AuClGe₂N₄Si₈·(C₇H₈)_{0.5} (1065.25): C, 31.01; H, 7.19; N, 5.26. Found: C, 31.13; H, 7.17; N, 5.32. ¹H NMR (C₆D₆, 300.1 MHz, 293 K): δ 0.63 (s, 36 H, Me); 0.31 (s, 36 H, Me). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ 6.9 (s, Me); 5.5 (s, Me).

[Au{SnCl(HMDS)}₂{Sn(HMDS)}₂(THT)] (4): Sn(HMDS)₂ (1 mL of a 0.37 M solution in toluene, 0.370 mmol) was added to a suspension of [AuCl(THT)] (56.4 mg, 0.176 mmol) in toluene (10 mL) and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give an orange oil. X-ray quality crystals of **4**·C₇H₈ were obtained by maintaining at −20 °C a concentrated toluene solution (186 mg, 76 %). Anal. Calcd. for C₂₈H₈₀AuClN₄SSi₈Sn₂·(C₇H₈) (1291.69): C, 32.55; H, 6.87; N, 4.34. Found: C, 32.59; H, 6.90; N, 4.31. ¹H NMR (C₆D₆, 300.1 MHz, 293 K): δ 2.74 (s, br, 4 H, CH₂); 1.52 (s, br, 4 H, CH₂); 0.49 (s, 72 H, Me). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ 37.2 (s, CH₂); 31.1 (s, CH₂); 6.9 (s, Me).

[Au{SnBu(HMDS)}₂{Sn(HMDS)}₂(THT)] (5): LiBu (110 μL of a 1.6 M solution in hexane, 0.176 mmol) was dropwise added to a solution of compound **4** (0.176 mmol) in toluene (10 mL) kept at −78 °C. The mixture was stirred for 1 h while it was allowed to reach the room temperature. The solvent was removed under reduced pressure to give a dark brown oil which contained compound **5** as the major H-containing reaction product (NMR identification). X-ray quality crystals of this compound were obtained by maintaining at −4 °C a concentrated toluene solution (110 mg, 51 %). Anal. Calcd. for C₃₂H₈₉AuN₄SSi₈Sn₂ (1221.21): C, 31.47; H, 7.35; N, 4.59. Found: C, 31.49; H, 7.38; N, 4.56. ¹H NMR (C₆D₆, 300.1 MHz, 293 K): δ 2.92 (s, br, 4 H, CH₂ of THT); 1.85 (m, 2 H, CH₂ of Bu); 1.50–1.48 (m, 8 H, 2 CH₂ of THT and 2 CH₂ of Bu); 1.02 (t, *J* = 7 Hz, 3 H, Me of Bu); 0.48 (s, 36 H, Me of HMDS); 0.32 (s, 36 H, Me of HMDS). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 298 K): δ 37.0 (s, CH₂ of THT); 31.0 (s, CH₂ of THT); 30.9 (s, CH₂ of

Bu); 30.8 (s, CH₂ of Bu); 28.2 (s, CH₂ of Bu); 14.4 (s, Me of Bu); 7.1 (s, Me of HMDS); 6.3 (s, Me of HMDS).

[Au{Sn(HMDS)₃}{Sn(HMDS)₂(THT)}] (6): Li(HMDS)₂ (68 μL of a 1.0 M solution in hexane, 0.068 mmol) was dropwise added to a solution of compound **4** (0.067 mmol) in toluene (2 mL) kept at -78° C. The mixture was stirred for 1 h while it was allowed to reach the room temperature. The solvent was removed under reduced pressure to give a dark brown oil which contained compound **6** as the major H-containing reaction product (NMR identification). X-ray quality crystals of this compound were obtained by maintaining at -4 °C a concentrated toluene solution (39 mg, 44 %). Anal. Calcd. for C₃₄H₉₈AuN₅SSi₁₀Sn₂ (1324.48): C, 30.83; H, 7.46; N, 5.29. Found: C, 30.86; H, 7.50; N, 5.25. ¹H NMR (C₆D₆, 300.1 MHz, 293 K): δ 2.67 (s, br, 4 H, CH₂), 1.41 (s, br, 4 H, CH₂), 0.61 (s, 36 H, Me), 0.30 (s, 54 H, Me). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ 35.7 (s, CH₂), 30.5 (s, CH₂), 8.1 (s, Me); 5.7 (s, Me).

X-Ray Diffraction Analyses. Crystals of **1**, **3**·0.5(C₇H₈), **4**·C₇H₈, **5**, and **6** were analyzed by X-ray diffraction. A selection of crystal, measurement, and refinement data is given in Table 4. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer. Empirical absorption corrections for **3**·0.5(C₇H₈), **4**·C₇H₈, **5** and **6** were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.²⁸ The XABS2²⁹ empirical absorption correction was applied for **1**. The structures were solved using the program SIR-97.³⁰ Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.³¹ The Au-THT fragment of compound **1** was found disordered over two positions in a 83:17 ratio, restraints on the geometrical parameters of the THT molecules being required. The solvent molecule of **3**·0.5(C₇H₈) was disordered about a center of symmetry and required restraints on their geometrical parameters. All non-H atoms were refined anisotropically, except the carbon atoms the 17 % occupancy THT molecule of **1**, which were kept isotropic due to their tendency to give nonpositive definite ellipsoids. The molecular plots were made with the PLATON program package.³² The WINGX program system³³ was used throughout the structure determinations. CCDC deposition numbers: 866820 (**1**), 866819 (**3**·0.5(C₇H₈)), 866816 (**4**·C₇H₈), 866817 (**5**), and 866818 (**6**).

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ASSOCIATED CONTENT

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. Selected Interatomic Distances (Å) and Angles (°) in Compound 1 (Only Data Corresponding to the Au-THT Fragment with 83% Occupancy are Given)

Au1–Ge1	2.362(2)
Au1–S1	2.362(4)
Ge1–N1	1.86(1)
Ge1–N2	1.87(1)
Ge1–Cl1	2.252(4)
Ge1–Au1–S1	177.9(1)
Cl1–Ge1–N1	100.9(3)
Cl1–Ge1–N2	103.5(3)
N1–Ge1–N2	112.5(5)
Cl1–Ge1–Au1	104.62(1)
N1–Ge1–Au1	117.3(3)
N2–Ge1–Au1	104.62(1)

Table 2. Selected Interatomic Distances (Å) and Angles (°) in Compound 3

Au1–Ge1	2.4120(5)
Au1–Ge2	2.4038(5)
Ge1–Cl1	2.244(1)
Ge1–N1	1.882(4)
Ge1–N2	1.877(3)
Ge2–N3	1.819(4)
Ge2–N4	1.829 (4)
Ge1–Au1–Ge2	175.64 (2)
Cl1–Ge1–N1	105.6(1)
Cl1–Ge1–N2	101.5(1)
N1–Ge1–N2	109.6 (2)
Cl1–Ge1–Au1	102.48(3)
N1–Ge1–Au1	116.5(1)
N2–Ge1–Au1	118.8(1)
N3–Ge2–N4	112.6 (2)
N3–Ge2–Au1	123.8(1)
N4–Ge2–Au1	123.5(1)

Table 3. Selected Interatomic Distances (Å) and Angles (°) in Compounds 4, 5, and 6

	4	5	6
Au1–Sn1	2.5711(5)	2.5767(4)	2.6087(2)
Au1–Sn2	2.5845(5)	2.5937(4)	2.6141(2)
Sn1–C25		2.183(5)	
Sn1–Cl1	2.412(2)		
Sn1–N1	2.081(6)	2.098(4)	2.101(2)
Sn1–N2	2.080(6)	2.106(5)	2.097(2)
Sn1–N5			2.115(2)
Sn2–N3	2.070(5)	2.080(5)	2.070(2)
Sn2–N4	2.092(6)	2.078(5)	2.080(2)
Sn2–S1	2.682(2)	2.718(2)	2.7154(7)
Sn1–Au1–Sn2	174.25(2)	172.59(2)	171.869(7)
Cl1–Sn1–N1	98.8(2)		
Cl1–Sn1–N2	103.3(2)		
Au1–Sn1–N1	122.2(2)	112.5(1)	110.13(7)
Au1–Sn1–N2	112.2(2)	113.3(1)	114.36(7)
C25–Sn1–N1		109.4(2)	
C25–Sn1–N2		100.9(2)	
Au1–Sn1–Cl1	107.80(6)		
Au1–Sn1–C25		111.3(2)	
N1–Sn1–N2	109.8(2)	108.8(2)	107.85(9)
N1–Sn1–N5			109.6(1)
N2–Sn1–N5			104.98(9)
Au1–Sn1–N5			109.73(6)
N3–Sn2–N4	107.7(3)	110.8(2)	108.72(9)
N3–Sn2–S1	97.5(2)	99.2(1)	97.99(7)
N4–Sn2–S1	101.2(2)	95.1(2)	93.48(7)
Au1–Sn2–N3	128.2(2)	116.9(1)	113.94(7)
Au1–Sn2–N4	115.8(2)	125.5(1)	127.56(7)
Au1–Sn2–S1	100.3(5)	101.65(3)	108.90(2)

Table 4. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-Ray Diffraction

	1	3·0.5(C₇H₈)	4·(C₇H₈)	5	6
formula	C ₁₆ H ₄₄ AuClGeN ₂ Si ₄	C ₂₄ H ₇₂ AuClGe ₂ N ₄ Si ₈ ·0.5(C ₇ H ₈)	C ₂₈ H ₈₀ AuClN ₄ SSi ₈ Sn ₂ ·(C ₇ H ₈)	C ₃₂ H ₈₉ AuN ₄ SSi ₈ Sn ₂	C ₃₄ H ₉₈ AuN ₅ SSi ₁₀ Sn ₂
fw	713.96	1065.24	1291.67	1221.20	1324.48
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 21/ <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 21/ <i>n</i>	<i>P</i> 21/ <i>n</i>	<i>P</i> 21/ <i>c</i>
<i>a</i> , Å	8.8810(4)	20.4748(4)	19.8189(3)	11.3691(2)	22.3141(4)
<i>b</i> , Å	30.358(1)	14.6467(2)	11.8064(2)	31.7882(5)	13.6340(2)
<i>c</i> , Å	11.5384(4)	33.0448(6)	24.3764(3)	15.1248(3)	22.3095(4)
α, β, γ , deg	90, 112.595(5), 90	90, 97.558(2), 90	90, 90.667(1), 90	90, 90.029(1), 90	90, 118.386(2), 90
<i>V</i> , Å ³	2872.1(7)	9823.7(3)	5703.4(2)	5466.2(1)	5971.2(2)
<i>Z</i>	4	8	4	4	4
<i>F</i> (000)	1416	4326	2600	2464	2688
<i>D</i> _{calcd} , g cm ⁻³	1.651	1.441	1.504	1.484	1.473
μ (Cu K α), mm ⁻¹	13.926	9.487	14.235	14.376	13.582
cryst size, mm	0.04 x 0.03 x 0.02	0.08 x 0.06 x 0.03	0.15 x 0.11 x 0.09	0.08 x 0.05 x 0.04	0.15 x 0.11 x 0.04
<i>T</i> , K	123(2)	123(2)	123(2)	123(2)	123(2)
θ range, deg	2.91 to 62.50	3.72 to 72.49	2.86 to 74.29	3.24 to 72.49	3.95 to 72.50
min./max. <i>h, k, l</i>	-10/9, 0/34, 0/13	-19/24, -17/16, -40/40	-24/24, -14/12, -30/29	-13/13, -39/33, -13/18	-20/27, -16/10, -27/24
no. collected reflns	4569	18831	27663	20904	22846
no. unique reflns	4569	9565	11302	10629	11586
no. reflns with <i>I</i> > 2 σ (<i>I</i>)	3541	8209	8644	9034	10797
no. params/restraints	276/7	445/6	494/0	458/0	508/0
GOF (on <i>F</i> ²)	1.053	1.053	1.022	1.117	1.048
<i>R</i> ₁ (on <i>F</i> , <i>I</i> > 2 σ (<i>I</i>))	0.075	0.031	0.050	0.038	0.026
<i>wR</i> ₂ (on <i>F</i> ² , all data)	0.208	0.088	0.143	0.118	0.068
χ^2 (on <i>F</i> ² , all data)	2.021(2) 2.14	1.200(0) 744	1.716(2) 271	1.065(1) 156	1.082(1) 222