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Diaminogermylene and Diaminostannylene Derivatives of Gold(I): Novel AuM and AuM_2 (M = Ge, Sn) Complexes

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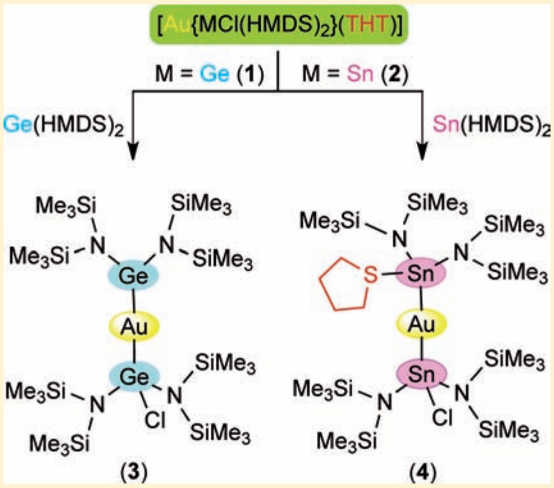
Supporting Information

ABSTRACT: The reactions of [AuCl(THT)] (THT = tetrahydrothiophene) with 1 equiv of the group 14 diaminometalenes $M(HMDS)_2$ [M = Ge, Sn; HMDS = $N(SiMe_3)_2$] lead to $[Au\{MCl(HMDS)_2\}(THT)]$ [M = Ge (**1**), Sn (**2**)], which contain a metalate(II) ligand that arises from insertion of the corresponding $M(HMDS)_2$ reagent into the Au−Cl bond of the gold(I) reagent. While compound **1** reacts with more $Ge(HMDS)_2$ to give the germanate−germylene derivative $[Au\{GeCl(HMDS)_2\}\{Ge(HMDS)_2\}]$ (**3**), which results from substitution of $Ge(HMDS)_2$ for the THT ligand of **1**, an analogous treatment of compound **2** with $Sn(HMDS)_2$ gives the stannate−stannylene derivative $[Au\{SnCl(HMDS)_2\}\{Sn(HMDS)_2(THT)\}]$ (**4**), which has a THT ligand attached to the stannylene tin atom and which, in solution at room temperature, participates in a dynamic process that makes its two $Sn(HMDS)_2$ fragments equivalent (on the NMR time scale). A similar dynamic process has not been observed for the $AuGe_2$ compound **3** or for the $AuSn_2$ derivatives $[Au\{SnR(HMDS)_2\}\{Sn(HMDS)_2(THT)\}]$ [R = 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, 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 = $N(SiMe_3)_2$].[3] These acyclic compounds were soon complemented with some cyclic relatives (N-heterocyclic metalenes), with the first stable N-heterocyclic silylenes,[4] germylenes,[5] stannylenes,[6] and plumbylenes[7] 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 (compound **F** in Figure 1).[14]

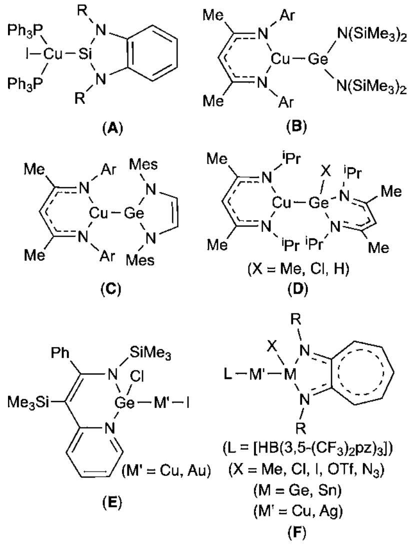


Figure 1. Examples of silicon, germanium, and tin diaminometalene derivatives of group 11 metals.

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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 (compound **G** in Figure 2)[15] or displacing one (compound **H** in Figure 2)[16−18] or two (compounds **I**[18] and **J**[19] in Figure 2) anionic ligands 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]

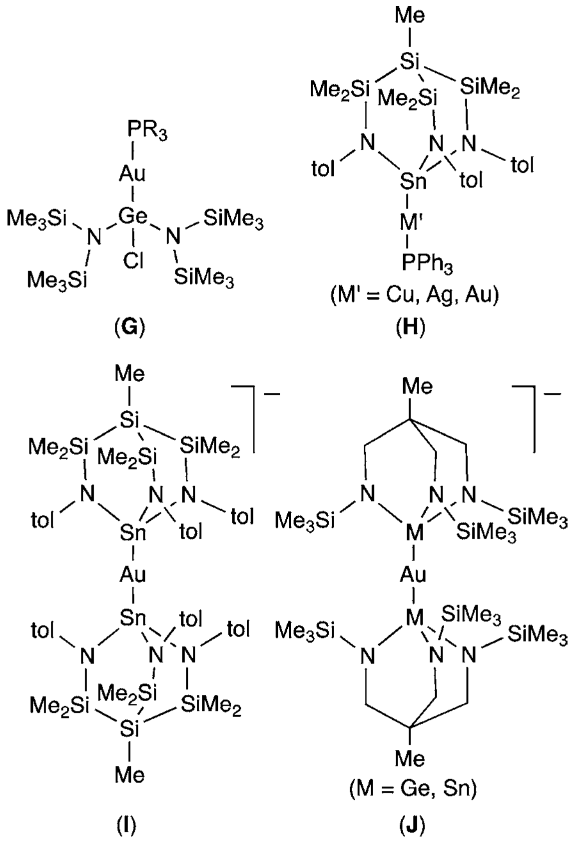


Figure 2. Examples of germanium and tin di- and triaminometalate derivatives of group 11 metals.

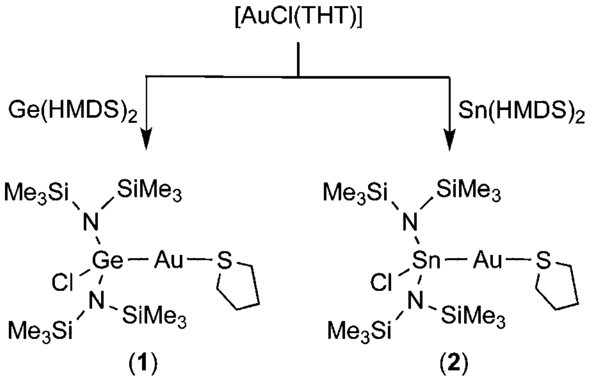
All of the above-mentioned data prompted us to attempt the synthesis of simple germanium and tin diaminometalene derivatives of gold(I), of which no examples had been previously reported. We also had in mind that diaminocarbene complexes of gold(I) had recently been identified as very efficient catalyst precursors for many catalytic reactions that are important in organic chemistry,[20] and we wondered whether group 14 diaminometalene derivatives of gold(I) would also be useful in catalysis. We chose [AuCl(THT)] (THT = tetrahydrothiophene) as a gold(I) precursor because its THT ligand can be readily displaced by other ligands.[21] Lappert's compounds $M(HMDS)_2$ (M = Ge, Sn) were chosen as diaminometalene reagents because their syntheses can easily be 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 $^{13}C\{^1H\}$ NMR spectra of both compounds indicated that they contain THT and HMDS in a 1:2 ratio, denoting that these reactions do not lead to 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)] because 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 and Table 1). Related reaction processes that afford $[Au\{GeCl(HMDS)_2\}(PR_3)]$ (R = Et, Cy, Ph) derivatives (**G** in Figure 2) have been reported to occur between $[AuCl(PR_3)]$ and $Ge(HMDS)_2$.[15]

The treatment of [AuCl(THT)] with 2 equiv of $M(HMDS)_2$ (M = Ge, Sn) quantitatively afforded the air- and moisture-sensitive $AuGe_2$ and $AuSn_2$ 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**.

The molecular structures of compounds **3** (Figure 4 and Table 2) and **4** (Figure 5 and 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 metal atoms. Thus, while both Au−Ge distances of compound **3** are very similar [2.4120(5) and 2.4038(5) Å], the Au−Sn distances

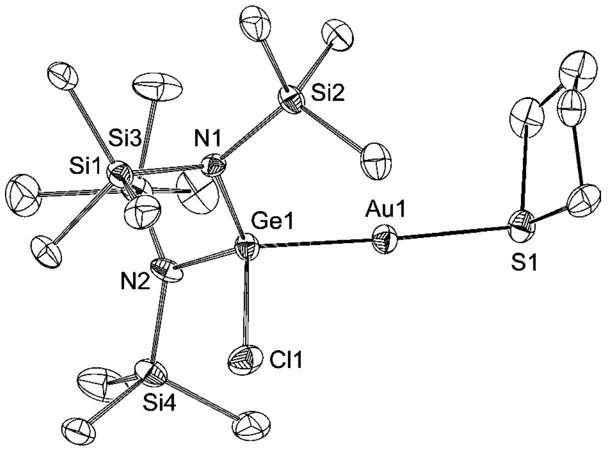


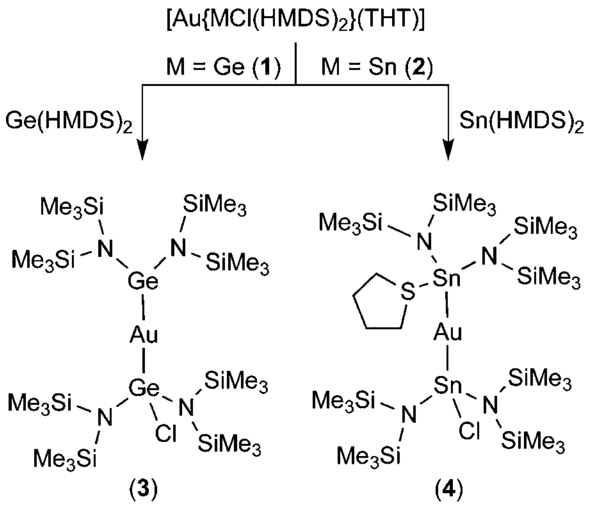
Figure 3. Molecular structure of compound **1** (thermal ellipsoids set at 30% probability). Hydrogen atoms have been omitted for clarity. The Au(THT) fragment is disordered over two positions in a 83:17 ratio. Only the fragment with 83% occupancy is represented.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in Compound 1[a]

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)

[a] Only data corresponding to the Au(THT) fragment with 83% occupancy are given.

Scheme 2



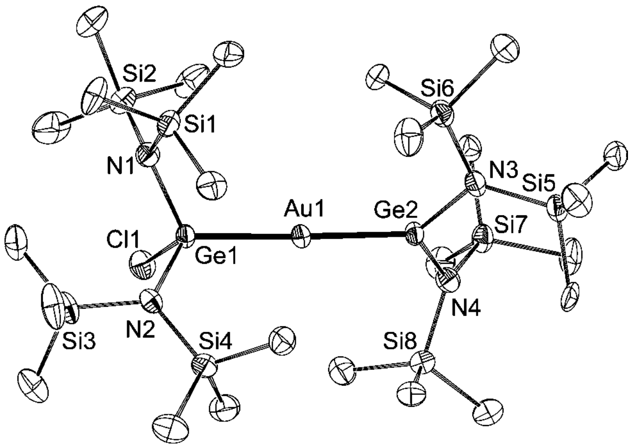


Figure 4. Molecular structure of compound **3** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) 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)

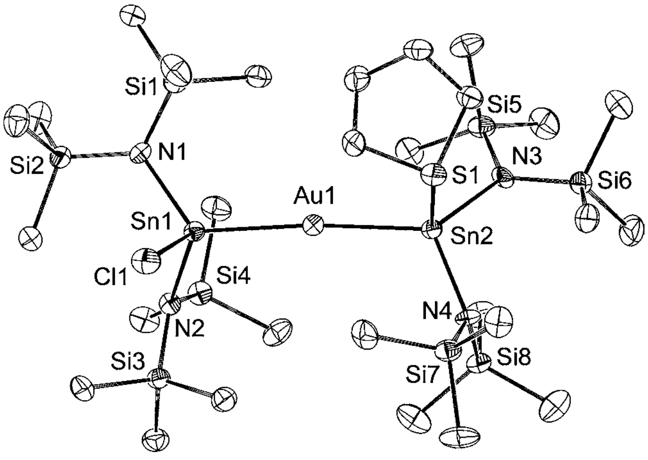


Figure 5. Molecular structure of compound **4** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

of compound **4** [2.5711(5) and 2.5845(5) Å] differ by 0.013 Å, with the longest one being associated with the most crowded tin atom, Sn2, which is the one 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)° in compound **3** (M = Ge) but only 107.7(3)° in

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in Compounds 4−6

	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)

compound **4** (M = Sn). In contrast, the coordination environment of the germylene Ge2 atom in complex **3** is perfectly planar.

The higher tendency of Sn(HMDS)$_2$ ligands, in comparison with that of Ge(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 germylene derivatives.[24] We are not aware of any transition-metal diaminometalene complex having the group 14 metal atom attached to a sulfur-donor ligand.

The room-temperature ^{1}H and ^{13}C{^{1}H} NMR spectra of the AuGe$_2$ compound **3** are in complete agreement with the solid-state molecular structure of this compound because they contain two singlet resonances assignable to the chemically inequivalent methyl groups of its germanate and germylene ligands. However, the room-temperature ^{1}H and ^{13}C{^{1}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 of the SiMe$_3$ groups, indicating the occurrence of a dynamic process that makes the environments of the two tin atoms equivalent (on the NMR time scale). A variable-temperature ^{1}H 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.

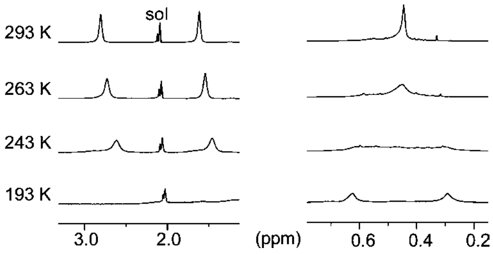
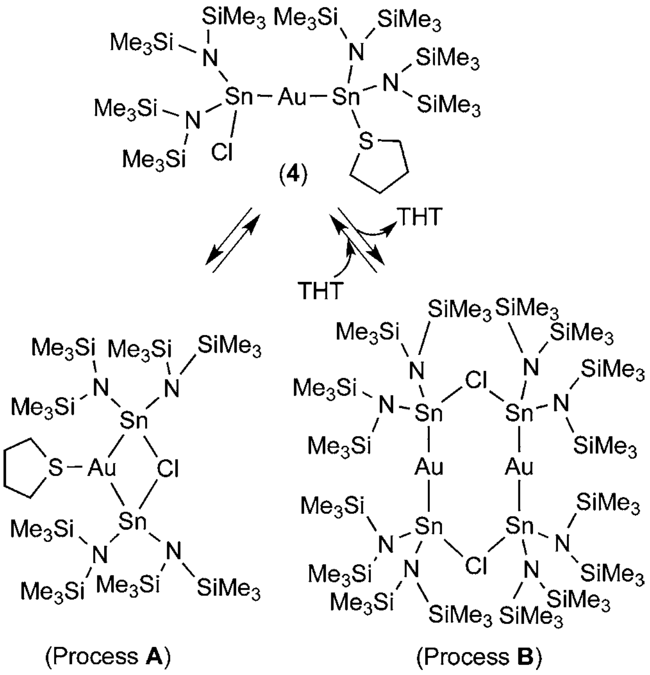


Figure 6. THT (left) and HMDS (right) regions of ^{1}H NMR spectra of compound **4** in toluene-d_8 at different temperatures (sol = toluene + residual protons of toluene-d_8; small sharp peaks are due to impurities).

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 unusual[27] tricoordinated gold atom, process **B** involves the release of THT from **4** and dimerization of the resulting unsaturated species to form a symmetric Au$_2$Sn$_4$ intermediate. Interestingly, a variable-temperature ^{1}H 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 SiMe$_3$ 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.

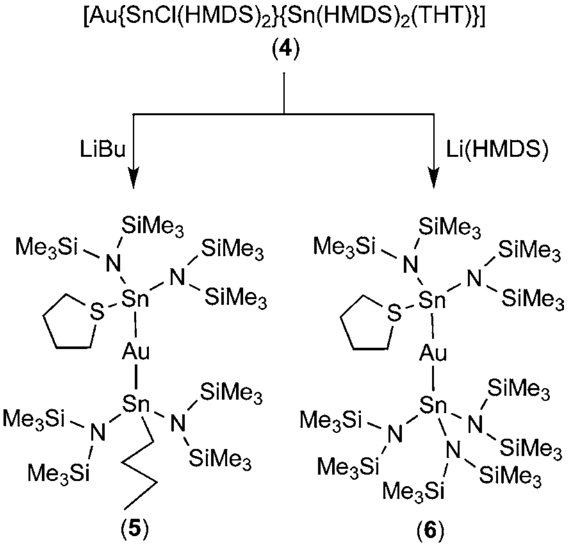
Scheme 3



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 the formation of chloride-bridged Au_2Ge_4 dimeric species less favorable, 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 $AuGe_2$ complex **3** is not involved in a dynamic process analogous to that observed in solution for the $AuSn_2$ 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, respectively. 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, especially 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**.

The room-temperature ^1H and $^{13}C\{^1H\}$ 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**.

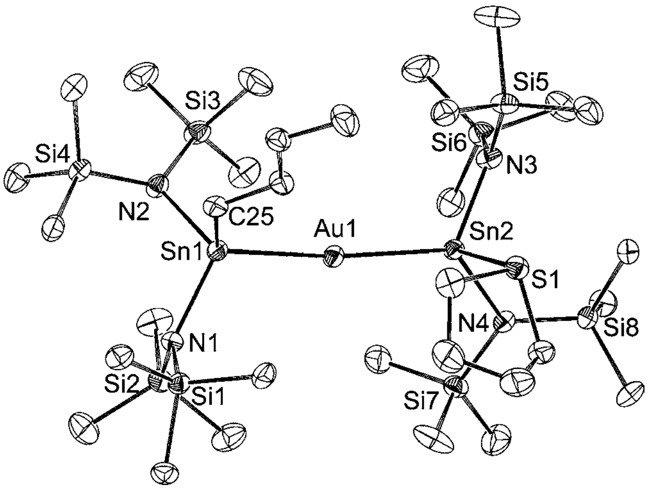


Figure 7. Molecular structure of compound **5** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

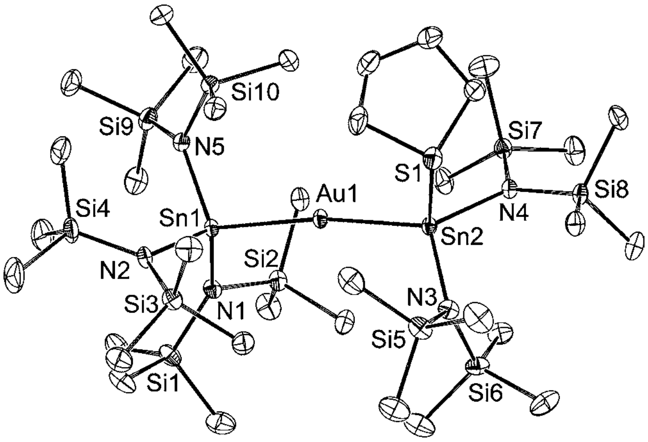


Figure 8. Molecular structure of compound **6** (thermal ellipsoids set at 40% probability). Hydrogen atoms have been omitted for clarity.

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 reactions of $M(HMDS)_2$ (M = Ge, Sn) with [AuCl(THT)] do not result in displacement of the THT ligand but in insertion of the diaminometalene reagent into the Au–Cl bond to give the germanate and stannate derivatives $[Au\{MCl(HMDS)_2\}(THT)]$ [M = Ge (**1**), Sn (**2**)], the addition of a supplementary equivalent of $M(HMDS)_2$ results in the subsequent displacement of THT from the gold coordination shell to give **3** and **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 the environments of its two tin atoms equivalent on 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.

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

	1	**3**·$0.5C_7H_8$	**4**·C_7H_8	**5**	**6**
formula	$C_{16}H_{44}AuClGeN_2Si_4$	$C_{24}H_{72}AuClGe_2N_4Si_8\cdot 0.5C_7H_8$	$C_{28}H_{80}AuClN_4SSi_8Sn_2\cdot C_7H_8$	$C_{32}H_{89}AuN_4SSi_8Sn_2$	$C_{34}H_{98}AuN_5SSi_{10}Sn_2$
fw	713.96	1065.24	1291.67	1221.20	1324.48
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*21/*n*	*C*2/*c*	*P*21/*n*	*P*21/*n*	*P*21/*c*
a, Å	8.8810(4)	20.4748(4)	19.8189(3)	11.3691(2)	22.3141(4)
b, Å	30.358(1)	14.6467(2)	11.8064(2)	31.7882(5)	13.6340(2)
c, 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
V, Å^3	2872.1(7)	9823.7(3)	5703.4(2)	5466.2(1)	5971.2(2)
Z	4	8	4	4	4
F(000)	1416	4326	2600	2464	2688
D_{calcd}, g cm^{-3}	1.651	1.441	1.504	1.484	1.473
μ(Cu Kα), mm^{-1}	13.926	9.487	14.235	14.376	13.582
cryst size, mm	0.04 × 0.03 × 0.02	0.08 × 0.06 × 0.03	0.15 × 0.11 × 0.09	0.08 × 0.05 × 0.04	0.15 × 0.11 × 0.04
T, K	123(2)	123(2)	123(2)	123(2)	123(2)
θ range, deg	2.91−62.50	3.72−72.49	2.86−74.29	3.24−72.49	3.95−72.50
min/max *h*, *k*, *l*	−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. of colld reflns	4569	18831	27663	20904	22846
no. of unique reflns	4569	9565	11302	10629	11586
no. of reflns with $I > 2\sigma(I)$	3541	8209	8644	9034	10797
no. of param/restraints	276/7	445/6	494/0	458/0	508/0
GOF (on F^2)	1.053	1.053	1.022	1.117	1.048
R1 [on *F*, $I > 2\sigma(I)$]	0.075	0.031	0.050	0.038	0.026
wR2 (on F^2, all data)	0.208	0.088	0.143	0.118	0.068
min/max of $\Delta\rho$, e Å^{-3}	−3.931/3.314	−1.309/0.744	−1.716/2.371	−1.965/1.156	−1.283/1.233

The transformation of compound **4** into [Au{SnR(HMDS)$_2$}{Sn(HMDS)$_2$(THT)}] [R = 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 but also demonstrates that the chloride of transition-metal SnCl(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 SnBu(HMDS)$_2$ or Sn(HMDS)$_3$ stannate ligands have been hitherto reported.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under nitrogen, using drybox and/or Schlenk vacuum-line techniques because of 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. [AuCl(THT)],[21b] Ge(HMDS)$_2$,[3] and Sn(HMDS)$_2$[3] were prepared following published procedures. All remaining reagents were purchased from commercial sources. NMR spectra were run on a Bruker DPX-300 or Bruker AV-400 instrument, using as internal standards a residual protic solvent resonance for ^{1}H [δ($C_6D_5CHD_2$) = 2.08; δ(C_6HD_5) = 7.16] and a solvent resonance for ^{13}C [δ($C_6D_5CD_3$) = 20.4; δ(C_6D_6) = 128.1]. Microanalyses were obtained from the University of Oviedo Microanalytical Service.

[Au{GeCl(HMDS)$_2$}(THT)] (1). Ge(HMDS)$_2$ (0.5 mL of a 0.35 M solution in toluene, 0.175 mmol) was added to a suspension of [AuCl(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 the 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. ^{1}H 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}C{^{1}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).

[Au{SnCl(HMDS)$_2$}(THT)] (2). Sn(HMDS)$_2$ (0.5 mL of a 0.37 M solution in toluene, 0.185 mmol) was added to a suspension of [AuCl(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. ^{1}H 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}C{^{1}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**·$0.5C_7H_8$ (123 mg, 69%). Anal. Calcd for $C_{24}H_{72}AuClGe_2N_4Si_8\cdot 0.5C_7H_8$ (1065.25): C, 31.01; H, 7.19; N, 5.26. Found: C, 31.13; H, 7.17; N, 5.32. ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 0.63 (s, 36 H, Me), 0.31 (s, 36 H, Me). ^{13}C{^{1}H} NMR (C_6D_6, 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**·C_7H_8 were obtained by maintaining at −20 °C a concentrated toluene solution (186 mg, 76%). Anal. Calcd for $C_{28}H_{80}AuClN_4SSi_8Sn_2\cdot C_7H_8$ (1291.69): C, 32.55; H, 6.87; N, 4.34. Found: C, 32.59; H, 6.90; N, 4.31. ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 2.74 (s, br, 4 H, CH_2), 1.52 (s, br, 4 H, CH_2), 0.49 (s, 72 H, Me).

^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 37.2 (s, CH_2), 31.1 (s, CH_2), 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 room temperature. The solvent was removed under reduced pressure to give a dark-brown oil, which contained compound **5** as the major hydrogen-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 $C_{32}H_{89}AuN_4SSi_8Sn_2$ (1221.21): C, 31.47; H, 7.35; N, 4.59. Found: C, 31.49; H, 7.38; N, 4.56. ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 2.92 (s, br, 4 H, CH_2 of THT), 1.85 (m, 2 H, CH_2 of Bu), 1.50−1.48 (m, 8 H, 2 CH_2 of THT and 2 CH_2 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). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 37.0 (s, CH_2 of THT), 31.0 (s, CH_2 of THT), 30.9 (s, CH_2 of Bu), 30.8 (s, CH_2 of Bu), 28.2 (s, CH_2 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 room temperature. The solvent was removed under reduced pressure to give a dark-brown oil, which contained compound **6** as the major hydrogen-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 $C_{34}H_{98}AuN_5SSi_{10}Sn_2$ (1324.48): C, 30.83; H, 7.46; N, 5.29. Found: C, 30.86; H, 7.50; N, 5.25. ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ 2.67 (s, br, 4 H, CH_2), 1.41 (s, br, 4 H, CH_2), 0.61 (s, 36 H, Me), 0.30 (s, 54 H, Me). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ 35.7 (s, CH_2), 30.5 (s, CH_2), 8.1 (s, Me), 5.7 (s, Me).

X-ray Diffraction Analyses. Crystals of **1**, **3**·0.5C_7H_8, **4**·C_7H_8, **5**, and **6** were analyzed by X-ray diffraction. A selection of crystal, measurement, and refinement data are given in Table 4. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single-crystal diffractometer. Empirical absorption corrections for **3**·0.5C_7H_8, **4**·C_7H_8, **5**, and **6** were applied using the *SCALE3 ABSPACK* algorithm as implemented in *CrysAlisPro RED*.[28] The *XABS2*[29] empirical absorption correction was applied for **1**. The structures were solved using the program *SIR-97*.[30] Isotropic and full-matrix anisotropic least-squares 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, with restraints on the geometrical parameters of the THT molecules being required. The solvent molecule of **3**·0.5C_7H_8 was disordered about a center of symmetry and required restraints on its geometrical parameters. All non-hydrogen atoms were refined anisotropically, except the carbon atoms of the 17% occupancy THT molecule of **1**, which were kept isotropic because of their tendency to give nonpositive definite ellipsoids. The molecular plots were made with the *PLATON* program package.[32] The *WINGX* program system[33] was used throughout the structure determinations. CCDC deposition numbers: 866820 (**1**), 866819 (**3**·0.5C_7H_8), 866816 (**4**·C_7H_8), 866817 (**5**), and 866818 (**6**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews on acyclic and/or cyclic group 14 diaminometalenes as ligands in transition-metal complexes, see: (a) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (b) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457. (c) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, 5165. (d) Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411. (e) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617*, 209. (f) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704. (g) Lappert., M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267. (h) Petz, W. *Chem. Rev.* **1986**, *86*, 1019. (i) Lappert., M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1985**, 51.

(2) For representative articles that contain an extensive literature coverage on group 14 diaminometalenes as ligands in transition-metal complexes, see: (a) Cabeza, J. A.; García-Álvarez, P.; Polo, D. *Inorg. Chem.* **2012**, *51*, 2569. (b) Cabeza, J. A.; García-Álvarez, P.; Polo, D. *Inorg. Chem.* **2011**, *50*, 5165. (c) Mansell, S. M.; Herber, R. H.; Nowik, I.; Ross, D. H.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2011**, *50*, 2252. (d) Ullah, F.; Kühl, O.; Bajor, G.; Veszpremi, T.; Jones, P. G.; Heinicke, J. *Eur. J. Inorg. Chem.* **2009**, 221. (e) Hahn, F. E.; Zabula, A. V.; Pape, T.; Hepp, A.; Tonner, R.; Haunschild, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 10716. (f) Saur, I.; Rima, G.; Miqueu, K.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2003**, *672*, 77. (g) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162.

(3) (a) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895. (b) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton. Trans.* **1977**, 2004.

(4) Denk, M.; Lennon, R.; Hayashi, R.; West., R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

(5) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245.

(6) Schuefler, C. D.; Zuckerman, C. D. *J. Am. Chem. Soc.* **1974**, *96*, 7160.

(7) Veith, M.; Grosser, M. *Z. Naturforsch.* **1982**, *B37*, 1375.

(8) For excellent reviews on the chemistry of cyclic carbenes and related species, see: (a) Melaimi, M.; Soleihavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(9) Arduengo, A. J. III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(10) Avent, A. G.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewsky, H. *J. Organomet. Chem.* **2003**, *686*, 321.

(11) York, J. T.; Young, V. G.; Tolman, W. B. *Inorg. Chem.* **2006**, *45*, 4191.

(12) Arii, H.; Nakadate, F.; Mochida, K. *Organometallics* **2009**, *28*, 4909.

(13) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. *Organometallics* **2006**, *25*, 2851.

(14) (a) Dias, H. V. R.; Wang, X.; Diyabalange, H. *Inorg. Chem.* **2005**, *44*, 7322. (b) Dias, H. V. R.; Ayers, A. E. *Polyhedron* **2002**, *21*, 611. (c) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, 3259. (d) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3890.

(15) Anandhi, U.; Sharp, P. R. *Inorg. Chim. Acta* **2006**, *359*, 3521.

(16) Lutz, M.; Findeis, B.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. *Eur. J. Inorg. Chem.* **2001**, 3155.

(17) Findeis, B.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *Inorg. Chem.* **1997**, *36*, 960.

(18) Findeis, B.; Contel, M.; Gade, L. H.; Laguna, M.; Gimeno, M. C.; Scowen, I. J.; McPartlin, M. *Inorg. Chem.* **1997**, *36*, 2386.

(19) Contel, M.; Hellmann, K. W.; Gade, L. H.; Laguna, M.; Scowen, I. J.; McPartlin, M. *Inorg. Chem.* **1996**, *35*, 3713.

(20) For reviews on the catalytic uses of carbene (mostly diaminocarbene) gold complexes, see: (a) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. *Acc. Chem. Res.* **2012**, *45*, DOI: 10.1021/ar200188f. (b) Nolan, S. P. *Acc. Chem. Res.* **2011**, *44*, 91. (c) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (d) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776.

(21) [AuCl(THT)] was first mentioned in a 1972 paper, but a detailed and easy synthetic procedure was not reported until 1989: (a) Allen, E. A.; Wilkinson, W. *Spectrochim. Acta* **1972**, *A28*, 2257. (b) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.

(22) (a) Chow, A. L.-F.; So, M.-H.; Lu, W.; Zhu, N.-Y.; Che, C.-M. *Chem.—Asian J.* **2011**, *6*, 544. (b) Jahnke, M. C.; Paley, J.; Hupka, F.; Weigand, J. J.; Hahn, F. E. *Z. Naturforsch.* **2009**, *B64*, 1458. (c) Deetlefs, M.; Raubenheimer, H. G.; Esterhuysen, M. W. *Catal. Today* **2002**, *72*, 259.

(23) For example, see: (a) Jambor, R.; Kasna, B.; Koller, S. G.; Strohmann, C.; Schurmann, M.; Jurkschat, K. *Eur. J. Inorg. Chem.* **2010**, 902. (b) Zabula, A. V.; Pape, T.; Hepp, A.; Hahn, E. F. *Dalton. Trans.* **2008**, 5886. (c) Martincova, J.; Dostal, L.; Ruzicka, A.; Taraba, J.; Jambor, R. *Organometallics* **2007**, *26*, 4102. (d) Khrustalev, V. N.; Portnyagin, I. A.; Nechaev, M. S.; Bukalov, S. S.; Leites, L. A. *Dalton Trans.* **2007**, 3489. (e) Jurkschat, K.; Tzschach, A.; Meunier-Piret, J.; van Meerssche, M. *J. Organomet. Chem.* **1998**, *349*, 143. (f) Brice, M. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 4529.

(24) For example, see: (a) Okazaki, M.; Kimura, H.; Komuro, T.; Okada, H.; Tobita, H. *Chem. Lett.* **2007**, *36*, 990. (b) Tobita, H.; Ishiyama, K.; Kawano, Y.; Inomata, S.; Ogino, H. *Organometallics* **1998**, *17*, 789. (c) Knorr, M.; Hallauer, E.; Huch, V.; Veith, M.; Braunstein, P. *Organometallics* **1996**, *15*, 3868.

(25) Veith, M.; Stahl, L.; Huch, V. *Inorg. Chem.* **1989**, *28*, 3278.

(26) Veith, M.; Müller, A.; Stahl, L.; Nötzel, M.; Jarczyk, M.; Huch, V. *Inorg. Chem.* **1996**, *35*, 3848.

(27) Gimeno, M. C.; Laguna, A. *Chem. Rev.* **1997**, *97*, 511.

(28) *CrysAlisPro RED*, version 1.171.34.36; Oxford Diffraction Ltd.: Oxford, U.K., 2010.

(29) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(30) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(31) *SHELXL*: Sheldrick, G. M. ; *Acta Crystallogr.* **2008**, *A64*, 112.

(32) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*, version 1.15; University of Utrecht: Utrecht, The Netherlands, 2008.

(33) *WinGX*, version 1.80.05: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.