Inorg. Chem. **1996,** *35,* 3713−3715 **3713**

Triamidogerma- and Triamidostannaaurates(I): First Structural Characterization of a Ge−Au−Ge Unit

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Received December 13, 1995

Introduction

In contrast to the extensive investigations into the chemistry of organogold(I) complexes,[1] there are comparatively few compounds containing direct metal−metal bonds between gold and the heavier group 14 elements.[2] Recently, there have been several structural investigations of gold−silicon species;[3] however, the area of molecular Au−Ge and Au−Sn chemistry is still virtually unexplored.[4−7] An underlying motivation for studying these materials is their potential photoactivity, either as emissive species finding application as photosensitizers or, upon photolytic fragmentation, as radical chain initiators.[8]

We have recently synthesized several thermally stable triamidometalates of the group 14 elements[9] which readily bond to late transition metal complex fragments.[10] In view of their excellent behavior as metal building blocks and capability to stabilize otherwise labile molecular units, we set out to systematically deploy them to give simple heterobimetallic systems involving monovalent gold. There has only recently been a report of a structural characterization of two Au−Ge complexes[6] and of several compounds containing Au−Sn units.[7] In order to exclude the influence of other ligands upon Au−M (M = Ge, Sn) bond formation, digerma- and distannaaurate salts were chosen as target compounds for this study in the expectation that they would feature unsupported Au−M bonds.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze−pump−thaw" cycles and dried over 4-Å molecular sieves.

The ^{1}H-, ^{29}Si-, ^{31}P-, ^{119}Sn-, and ^{7}Li-NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 39.76, 81.03, 74.63, and 77.78 MHz, respectively) with tetramethylsilane, LiI (1 M, external), $SnMe_4$, and H_3PO_4 (85%, external) as references. Elemental analyses were carried out in the microanalytical laboratory of the Chemistry Department at Würzburg. $[H_3CC\{CH_2N(Li)Si(CH_3)_3\}_3]_2$ (**1**) was prepared as reported previously by us.[11] All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of Compounds. General Procedure for the Preparation of $H_3CC(CH_2NSiMe_3)_3MLi(THF)_2$ (M = Ge, Sn). To a stirred solution of 527 mg (0.75 mmol) of $H_3CC[CH_2N(Li)SiMe_3]_3(THF)_3$ in 30 mL of THF which was cooled at −30 °C was added 143 mg (0.75 mmol) of $SnCl_2$ (for compound **1**) or 174 mg of $GeCl_2$(dioxane) (for compound **2**). After warming to room temperature the solution was allowed to react for another 6 h. The THF was removed by vacuum distillation, the oily residue was dissolved in 30 mL of pentane and filtered through Celite (removal of LiCl), and the solvent was removed again by distillation *in vacuo*. The products were obtained analytically pure as pale yellow oils and dried in high vacuum for 6h.

$H_3CC(CH_2NSiMe_3)_3SnLi(THF)_2$ (1). Yield: 92%. ^{1}H-NMR (200.13 MHz, toluene-d_8, 273 K): δ 0.29, 0.45 (s, 27H, $Si(CH_3)_3$), 0.68 (s, 3H, H_3CC), 1.38 (m, 8H, CH_2CH_2O), 2.94 [d, 2H, CH_2N, $^{2}J_{HH}$ = 11.5 Hz], 3.28 (d, 2H, CH_2N), 3.37 (s, 2H, CH_2N), 3.55 (m, 8H, CH_2CH_2O). {^{1}H}^{13}C-NMR (50.32 MHz, toluene-d_8, 245 K): δ 1.1, 1.4 [$Si(CH_3)_3$], 25.34 (CH_2CH_2O), 27.8 (H_3CC), 41.0 (H_3CC), 57.2, 59.3 (CH_2N), 68.5 (CH_2CH_2O). {^{1}H}^{119}Sn-NMR (74.63 MHz, toluene-d_8, 273 K): δ −398.8. Anal. Calcd for $C_{22}H_{52}LiN_3O_2Si_3Sn$: C, 44.00; H, 8.73; N, 7.00. Found: C, 43.87; H, 8.71; N, 6.93.

$H_3CC(CH_2NSiMe_3)_3GeLi(THF)_2$ (2). Yield: 94%. ^{1}H-NMR (200.13 MHz, toluene-d_8, 245 K): δ 0.35 (s, 18H, $Si(CH_3)_3$), 0.54 (s, 9H, $Si(CH_3)_3$), 0.73 (s, 3H, H_3CC), 1.27 (m, 8H, CH_2CH_2O), 2.77 [d, 2H, CH_2N, ^{2}J(HH) 10.8 Hz], 3.10 (d, 2H, CH_2N), 3.25 (s, 2H CH_2N), 3.56 (m, 8H, CH_2CH_2O). {^{1}H}^{13}C-NMR (50.32 MHz, toluene-d_8, 245 K): δ 0.7, 1.1 [$Si(CH_3)_3$] 25.1 (CH_2CH_2O), 26.2 (H_3CC), 35.4 (H_3CC), 55.9, 57.5 (CH_2N), 68.3 (CH_2CH_2O). Anal. Calcd for $C_{22}H_{52}GeLiN_3O_2Si_3$: C, 47.66; H, 9.45; N, 7.58. Found: C, 47.52; H, 9.39; N, 7.51.

General Procedure for the Preparation of [Q][$\{H_3CC(CH_2NSiMe_3)_3M\}_2Au$] (M = Ge, Sn; Q = $BzPPh_3$, PPh_4). To a stirred solution of 300 mg (0.50 mmol) of $H_3CC(CH_2NSiMe_3)_3SnLi(THF)_2$ (for compound **3**) or 277 mg (0.50 mmol) of $H_3CC(CH_2NSiMe_3)_3GeLi(THF)_2$ (for compound **4**) in THF which was cooled at −50 °C was added 155 mg (0.25 mmol) of $[Ph_3PBz][AuCl_2]$ or, respectively, 174 mg (0.25 mmol) of $[Ph_4P][AuBr_2]$, and the reaction mixture was slowly warmed to ambient temperature. After the mixture was stirred for another 6 h, the solvent was removed *in vacou*, and the residue was extracted with 15 mL of toluene. After filtration through Celite, the solution was concentrated to 5 mL and stored at −35 °C. Over a period of several days **3** and **4** are obtained as highly crystalline colorless solids.

$[BzPPh_3][\{H_3CC(CH_2NSiMe_3)_3Sn\}_2Au]$ (3). Yield: 38%. ^{1}H-NMR (200.13 MHz, C_6D_6, 295 K): δ 0.35 [s, 54H, $Si(CH_3)_3$], 0.77 (s, 6H, CH_3), 3.67 (s, 12H, CH_2−N), 3.83 (d, 2H, CH_2−P, ^{2}J(PH) 12.4 Hz), 6.91−7.51 (m, 20H, C_6H_5). {^{1}H}^{29}Si-NMR (39.76 MHz, C_6D_6,

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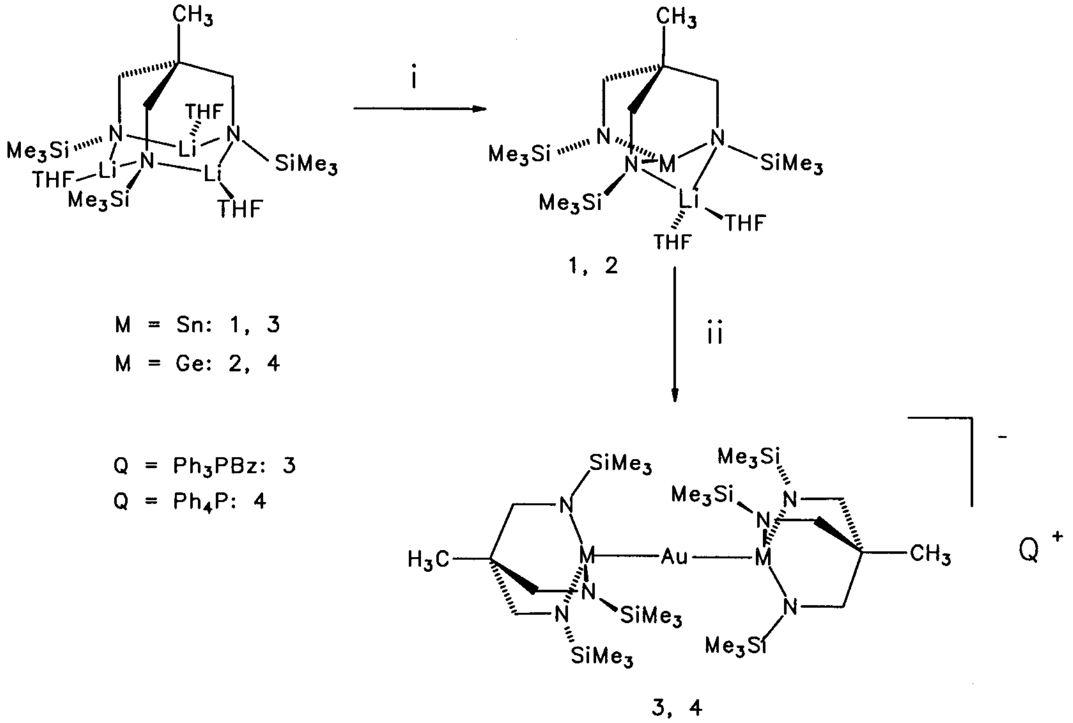
S0020-1669(95)01582-5 CCC: $12.00

Scheme 1. Synthesis of the Tripodal Triamidometalates **1** and **2** and Their Coupling with $[AuX_2]^-$ To Yield **3** and **4**[a]



[a] Key: (i) $SnCl_2$ or $GeCl_2$(dioxane) in THF; (ii) [Q][AuX_2] (X = Cl, Br) in THF.

295 K): δ −0.7. $^{31}P\{^1H\}$ NMR (81.03 MHz, C_6D_6, 295 K): δ 24.3. $\{^1H\}^{119}$Sn-NMR (74.63 MHz, C_6D_6, 295 K): δ 480.1. Anal. Calcd for $C_{53}H_{94}AuN_6PSi_6Sn_2$: C, 43.93; H, 6.54; N, 5.80. Found: C, 43.84; H, 6.47; N, 5.74.

$[PPh_4][\{H_3CC(CH_2NSiMe_3)_3Ge\}_2Au]$ (4). Yield: 46%. ^{1}H-NMR (200.13 MHz, C_6D_6, 295 K): δ 0.21 [s, 54H, $Si(CH_3)_3$], 0.64 (s, 6H, CH_3), 3.13 (s, 12H, CH_2-N), 7.58 - 7.95 (m, 20H, C_6H_5). $\{^1H\}^{31}$P-NMR (81.03 MHz, C_6D_6, 295 K): δ 24.3. Anal. Calcd for $C_{52}H_{92}AuGe_2N_6PSi_6$: C, 46.51; H, 6.90; N, 6.26. Found: C, 46.39; H, 6.84; N, 6.20.

X-ray Crystallographic Study of 4. A pale yellow crystal of **4** with dimensions 0.34 × 0.30 × 0.18 mm was sealed under argon in a Lindemann tube for data collection. A total of 3167 unique data (R_{int} = 0.0834) were collected on a Philips PW1100 four-circle diffractometer in the θ range 3−23°. The positions of the gold and germanium atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent Fourier and difference-Fourier syntheses.[11]

Crystal data: $C_{52}H_{92}N_6Ge_2PAu$, $M = 1342.97$, monoclinic, $C2/c$, $a = 24.129(4)$, $b = 11.617(2)$, $c = 24.918(4)$ Å, $\beta = 108.42(3)°$, $V = 6627(2)$ Å^3, $Z = 4$, $F(000) = 2752$ $D_c = 1.346$ g cm^{-1}, μ(Mo Kα) = 32.78 cm^{-1}.

After refinement with isotropic thermal parameters for all non-hydrogen atoms, an empirical absorption correction[13] (transmission factors: maximum 0.788, minimum 0.297) was applied. In the final cycles of full-matrix least-squares refinement on F^2, anisotropic thermal parameters were assigned to all the ordered non-hydrogen atoms of the complex. Final R_1 and wR_2 values for 309 parameters were 0.0733 and 0.1518 for data with $I > 2\sigma(I)$.

Results and Discussion

The starting materials for the Au−M complexes was the tripodal lithium amide $H_3CC(CH_2N(Li)SiMe_3)_3(THF)_3$,[11] which upon reaction with $SnCl_2$ and $GeCl_2$(dioxane) in THF gave the triamidometalates $H_3CC(CH_2NSiMe_3)_3MLi(THF)_2$ (M = Sn (**1**), Ge (**2**)) (Scheme 1). Compound **1** is closely related to $H_3CC(CH_2NSiMe_3)_3SnLi(Et_2O)$ which has been previously reported by us;[9] its Ge analogue **2** has essentially identical spectroscopic properties at low temperature (^{1}H-, ^{13}C-NMR spectra recorded at 245 K) and is therefore assigned a similar structure with an overall molecular C_s symmetry. When the temperature is raised, exchange broadening of the ^{1}H-NMR resonances is observed, coalescence occurs at 293 K, and the high temperature limit is reached above 320 K reflecting an effective 3-fold symmetry of the molecule. This may be interpreted as due to rapid exchange of the $(THF)_2Li^+$ fragment between the three equivalent bridging positions in **2** at high temperatures, the free activation enthalpy of the process being $\Delta G^\ddagger = 59.8$ kJ mol^{-1}. A similar behavior is observed in the high temperature range for compound **1** ($\Delta G^\ddagger = 74.5$ kJ mol^{-1}).

Upon reaction of 2 molar equiv of **1** and **2** with [Q][AuX_2] (Q = Ph_3PBz, Ph_4P; X = Cl, Br), the respective distanna- and digermaaurates $[Ph_3PBz][\{H_3CC(CH_2NSiMe_3)_3Sn\}_2Au]$ (**3**) and $[Ph_4P][\{H_3CC(CH_2NSiMe_3)_3Ge\}_2Au]$ (**4**) are formed as shown in Scheme 1. The analytical and spectroscopic data are consistent with linearly configurated gold complex anions. A remarkable spectroscopic feature of **3** is the considerable coordination shift of *ca.* 880 ppm observed in the ^{119}Sn NMR spectrum upon coordination of the stannate **1** [$\delta(^{119}Sn)$ −398.8] to the Au(I) center in the formation of **3** [$\delta(^{119}Sn)$ 480.1].[14]

In order to establish their molecular structure and provide the first structural evidence for a Ge−Au−Ge unit, a single-crystal X-ray structure analysis of **4** was carried out. The molecular structure of **4** is shown in Figure 1 along with the principal bond lengths and interbond angles; the fractional atomic coordinates of **4** are listed in Table 1.

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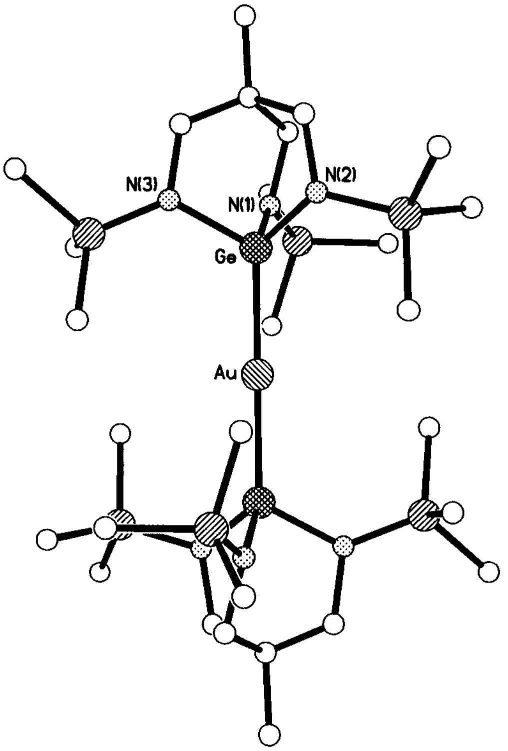

Figure 1. Structure of the $[\{H_3CC(CH_2NSiMe_3)_3Ge\}_2Au]^-$ anion in **4**. Principal bond lengths and interbond angles are as follows: Au−Ge 2.423(2), Ge−N(1) 1.885(13), Ge−N(2) 1.858(14), Ge−N(3) 1.89(2) Å; Ge−Au−Ge 180.0, N(1)−Ge−N(2) 99.4(7), N(1)−Ge−N(3) 97.8(6), N(2)−Ge−N(3) 97.6(6), N(1)−Ge−Au 118.7(5), N(2)−Ge−Au 121.1(5), N(3)−Ge−Au 117.6(5)°.

The structural center piece of the molecular anion is the linear Ge−Au−Ge unit [Au(1)−Ge(1) = 2.423(2) Å] which is effectively shielded by the peripheral $SiMe_3$ groups. The Au−Ge distance of 2.423(2) Å lies between the values determined by Schmidbaur and co-workers for $(Ph_3P)AuGeCl_3$ and $(Ph_3P)_3AuGeCl_3$ [*d*(Au−Ge) = 2.406(1) Å and 2.536(1) Å, respectively].[6]

The Au atom resides upon a crystallographic center of symmetry which relates the two triamidogermanate units of the complex and imposes exact linearity on the Ge−Au−Ge linkage. The tripodal amido ligands adopt a mutually staggered conformation with their respective $SiMe_3$ groups interlocking to offset steric repulsion arising from the convergence of the triamidogermanate units to the Au(I) center.

Table 1. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2 \times 10^3$] for **4**

	x	*y*	*z*
Au	2500	2500	5000
Ge	1946(1)	2990(2)	5627(1)
C(5)	917(8)	3739(17)	6757(8)
C(4)	1292(7)	3488(15)	6373(8)
C(1A)	885(14)	3716(32)	5716(15)
C(1B)	872(25)	3061(58)	5836(26)
N(1)	1126(6)	3102(12)	5324(6)
Si(1)	693(2)	3143(5)	4639(3)
C(11)	1009(8)	2329(21)	4184(8)
C(12)	−34(8)	2604(22)	4575(9)
C(13)	577(12)	4611(20)	4333(12)
C(2)	1724(12)	4421(17)	6420(10)
N(2)	2097(7)	4334(12)	6053(7)
S1(2)	2355(2)	5630(4)	5888(3)
C(21)	1800(10)	6513(18)	5374(10)
C(22)	2651(10)	6528(16)	6551(9)
C(23)	2957(8)	5372(16)	5601(8)
C(3A)	1487(15)	2310(27)	6450(16)
C(3B)	1797(21)	2557(44)	6709(21)
N(3)	1977(7)	1958(11)	6222(6)
Si(3)	2077(3)	526(5)	6206(3)
C(31)	2143(13)	−128(19)	6920(9)
C(32)	1440(10)	−161(18)	5654(10)
C(33)	2762(8)	217(15)	6042(9)
P(1)	0	−250(6)	7500
C(41)	−200(9)	681(16)	6891(9)
C(42)	−49(10)	356(19)	6424(12)
C(43)	−231(11)	1049(25)	5942(12)
C(44)	−576(10)	1991(23)	5941(12)
C(45)	−734(11)	2290(23)	6396(13)
C(46)	−533(9)	1635(17)	6892(10)
C(51)	615(10)	−1143(18)	7545(9)
C(53)	1610(9)	−1746(22)	7912(12)
C(52)	1166(8)	−988(18)	7886(9)
C(54)	1512(12)	−2624(20)	7564(12)
C(55)	961(11)	−2831(19)	7176(10)
C(56)	516(9)	−2066(21)	7175(10)

Acknowledgment. We grateful to the Deutsche Forschungsgemeinschaft (L.H.G.), the Fonds der Chemischen Industrie (L.H.G.), the EPSRC (M.McP.), the DAAD and British Council (ARC grant to M.McP. and L.H.G.) and the European Science Foundation (M.C.) for financial support and Wacker Chemie AG for a generous gift of basic chemicals. Thanks are also due to Frank Fecher for assistance with the experimental work and Professor H. Werner (Würzburg) for his continued interest and support.

Supporting Information Available: Text detailing the structure determination, a figure showing the numbering scheme, and tables positional and thermal parameters, and interatomic distances and angles for compound **4** (6 pages). Ordering information is given on any current masthead page.

IC9515822