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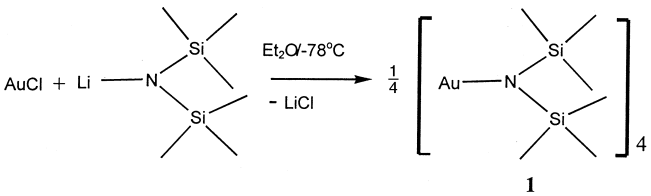
[{Au[μ-N(SiMe$_3$)$_2$]}$_4$]: The First Base-Free Gold Amide**

Scott D. Bunge, Oliver Just, and William S. Rees, Jr.*

Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

Throughout the Periodic Table, the use of the bis(trimethylsilyl)amido ligand $N(SiMe_3)_2^-$ has played a central role in the synthesis and characterization of metal and metalloid complexes with low coordination numbers.[1] Despite the extensive use, only a few examples of noble- or heavier coinage-metal derivatives have been reported. This deficiency may be attributed to the instability of these compounds, which arises from the combination of a soft metal with a hard amide ligand.[2] Herein, the first synthesis and X-ray structural characterization of a base-free homoleptic gold(I) di(silyl)amide, [{Au(μ-N(SiMe$_3$)$_2$)}$_4$] (**1**), is reported.

The gold(I) amide **1** was prepared in 19% yield by the metathesis reaction of lithium bis(trimethylsilyl)amide with gold(I) chloride in diethyl ether (Scheme 1). ^{1}H NMR and ^{13}C NMR spectroscopic analyses of **1** in $CDCl_3$ revealed the presence of singlets at $\delta = 0.34$ and 6.707, respectively. The EI and CI mass spectra revealed a tetranuclear parent ion, with the expected fragment ions.



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Scheme 1. Synthetic route leading to the formation of **1**.

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Several other gold tetramers have been reported previously; $[\{Au[SSi(OtBu)_3]\}_4]$,[3a] $[\{Au[TeC(SiMe_3)_3]\}_4]$,[3b] $[\{Au[SC(SiMe_3)_3]\}_4]$,[3b] $[\{Au(PhNNNPh)\}_4]$,[4a] and $[\{Au(PhNCHNPh)\}_4]$.[4b]

The development of gold(I) chemistry is dominated by the viewpoint that gold is a prototypical soft Lewis acid, which forms its most stable complexes with soft Lewis bases. Accordingly, the synthesis of gold(I) complexes with a hard Lewis base, such as nitrogen, has been limited to a select number of complexes.[5] Schmidbaur et al., have reported the following base-stabilized gold–nitrogen derivatives; $[AuN(SiMe_3)_2(PMe_3)]$ and $[Au_2N(SiMe_3)_2(PEt_3)_2]BF_4$ (**2**).[6a,b] It is notable that these complexes employ phosphane donors to stabilize the valency configuration of gold.

Compound **1** was shown by single-crystal X-ray diffraction to be tetrameric and solvent-free in the solid state (Figure 1).

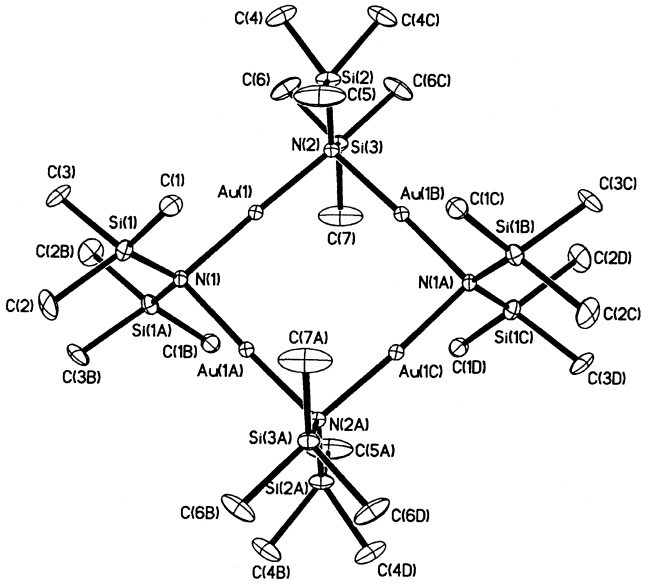
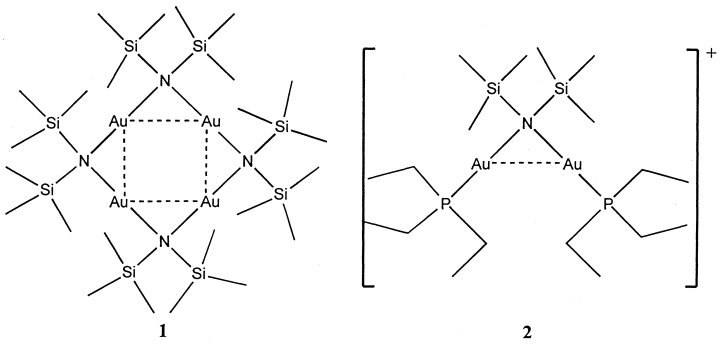


Figure 1. An ORTEP plot representation (50% probability) for **1**. Hydrogen atoms have been ommitted for clarity. Selected interatomic distances [Å] and angles [°]: Au(1)-N(1) 2.082(3), Au(1)-N(2) 2.086(3), Au(1)-Au(1A) 3.0100(3), Au(1)-Au(1B) 3.0355(3), Si(1)-N(1) 1.773(3); Au(1)-N(1)-Au(1A) 92.38(19), Au(1)-N(2)-Au(1B) 93.60(19), Si(3)-N(2)-Si(2) 120.9(3).

The molecular structure is tetranuclear, based on a square of two-cooridnate gold atoms. Each Au atom is linked to its neighbor by a singly bridging amido ligand, the nitrogen donor sites thus being four-coordinate and the N-Au-N arrangements being essentially linear. The Au–N interatomic distances observed for compound **1** (2.082, 2.086 Å) are similar to previously reported values. The Au-N-Au angles in **1** are 92.38° and 93.60°, which correspond to Au–Au distances of 3.0100 Å and 3.0355 Å, respectively.

Schmidbaur defines aurophilicity as "the unprecedented affinity between gold atoms even with 'closed-shell' electronic configurations and equivalent electrical charges."[7] The interatomic distance usually observed for these aurophilic interactions is on the order of 3.00 ± 0.25 Å, and the energy associated with these interactions is similar to the energetics of hydrogen bonds. A comparison of Au–Au and Au–N interatomic distances for **1** and **2** (Scheme 2) reveals that the Au–Au interatomic distances in the base-free, air-stable compound **1** are significantly shorter than those in **2**. Therefore, it can be presumed that aurophilic interactions are, in part, stabilizing the tetramer.



Scheme 2. Au–Au and Au–N interatomic distances [Å] in **1** and **2**. Compound **1** (this work): Au-Au 3.0100(3), 3.0355(3); Au-N 2.082(3); compound **2** (reference [6a]): Au-Au 3.071(1); Au-N 2.115(9).

Planar, tetranuclear coinage metal(I) clusters singly bridged by monoanionic amido ligands previously have been reported for copper and silver.[8]

In summary, the first gold(I) amide $[\{Au[\mu\text{-}N(SiMe_3)_2]\}_4]$ has been synthesized without the stabilization of a Lewis base. This result may lead to new directions in the chemistry of gold(I) complexes.

Experimental Section

1: *n*BuLi (1.1 mL of a 2.68 M solution in hexane) was added dropwise to hexamethyldisilazane $HN(SiMe_3)_2$ (0.48 g, 2.97 mmol) in diethyl ether (50 mL) at −78 °C under an argon atmosphere. Subsequently, the reaction mixture was allowed to warm to ambient temperature on its own and was left to stir for 2 h, completing the generation of the lithium amide in situ. The solution was recooled to −78 °C and AuCl (0.69 g, 2.97 mmol) was added through a solid addition tube. After the mixture had been stirred overnight at −78 °C under light exclusion, the solvent was removed and the product was extracted with hexane (10 mL). Following filtration, colorless crystals of **1** were grown from hexane over five days at −40 °C. Yield: 0.20 g (18.9%); Colorless crystals turned purple at 110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.34$ (s, 72 H, 24 CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 6.707$ (s, 24 CH_3); MS (EI, 70 eV, 400 °C): m/z: 1429 [M^++H^+], 1413, 554, 699, 342, 130, 73; elemental analysis calcd (%) for $Au_4N_4Si_8C_{24}H_{72}$: C 20.17, H 5.08, N 3.92; found: C 19.85, H 5.00, N 3.96.

Crystal data: $Au_4N_4Si_8C_{24}H_{72}$, $M_r = 1429.44$ g cm^{-3}, crystal dimensions $0.256 \times 0.160 \times 0.128$ mm, monoclinic, space group $C2/m$, $a = 20.1768(8)$, $b = 13.6852(6)$, $c = 9.2556(4)$ Å, $\beta = 116.1870(10)°$; $V = 2293.37(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.070$ g cm^{-3}, Siemens SMART CCD diffractometer, $1.87 < \theta < 28.28°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), ω scans, $T = 173(2)$ K; of 7267 measured reflections, 2827 were independent and 2572 observed with $I > 2\sigma(I)$, $-25 < h < 26$, $-18 < k < 18$, $-9 < l < 12$; $R_1 = 0.0233$, $wR_2 = 0.0610$, GOF = 1.037 for 149 parameters, $\Delta\rho_{max} = 1.509$ e Å^{-3}. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentzian and polarization corrections and absorption correction SADABS were applied, $\mu = 12.983$ mm^{-1}, min./max. transmission 0.1358/0.2873. For C5 and C7, hydrogen atoms were refined as HFIX from SHELXTL using an appropriate riding model with varied thermal parameters. All other carbon atoms were disordered. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142594. Copies of the data can be obtained free of charge on application to CCDC,

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Umpolung of P–H Bonds**

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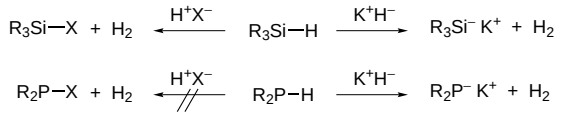
Dedicated to Professor Gerd Becker on the occasion of his 60th birthday

Bonds between p-block elements E and hydrogen are employed as versatile synthons in numerous synthetic transformations.[1] Their reactivity follows a systematic course that is characterized by a change from hydridic (E–H bonds involving elements of Group 13) to protonic (E–H bonds involving elements of Groups 15 – 17) character of the hydrogen atom. Hydrogen compounds of Group 14 elements are a borderline case: whereas the protonic character of the hydrogen atom dominates for C–H bonds, Si–H bonds may react both as the source of a hydride or of a proton (Scheme 1).[1, 2]



Scheme 1. X = halogen, OR.

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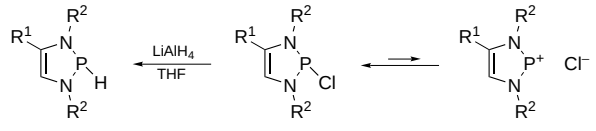
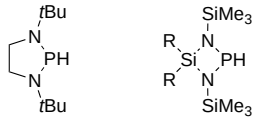
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

The reactivity of P–H bonds in phosphane derivatives is generally determined by the protonic character of the hydrogen atom (Scheme 1), even though in view of the similar electronegativities ($\chi^{AR}(H) = 2.2$, $\chi^{AR}(P) = 2.06$) and resulting low bond polarities it appears conceivable to achieve an umpolung of the reactivity by means of suitable substituent effects.[3] Taking into account our observation that π-delocalization effects which can be described in terms of σ* aromaticity[4] render the P–Cl bonds in *P*-chloro-1,3,2-diazaphospholenes **1** more polar and favor dissociation under formation of the cations **2**,[5] it appeared of interest to establish if the same effects can also be applied to generate hydridic reactivity of the P–H bonds in *P*-hydrido-1,3,2-diazaphospholenes **3** (Scheme 2).



Scheme 2. $R^1 = H$, $R^2 = t$Bu (**1a** – **3a**), 2,4,6-$Me_3C_6H_2$ (Mes) (**1c** – **3c**); $R^1 = Cl$, $R^2 = t$Bu (**1b** – **3b**), Mes (**1d** – **3d**).

The target compounds **3a** – **d** are formed in clean reactions upon treatment of **1a** – **d** with stoichiometric amounts of $LiBEt_3H$ or $LiAlH_4$ in THF and were isolated as light yellow, air- and moisture-sensitive oils or solids after distillative workup (**3a, b**) or crystallization (**3d**). The constitution of all products can be deduced unequivocally from their spectroscopic data. The ^{31}P NMR signals ($\delta^{31}P = 57.1$ (**3a**), 71.6 (**3b**), 64.0 (**3c**), 75.8 (**3d**)) appear at slightly lower field than in the 1,3,2-diazaphospholidine **4** ($\delta^{31}P = 57.9$[6]). The P,H coupling constants display a remarkable substitution dependence: whereas the couplings in the *N*-*tert*-butyl derivatives **3a, b** ($^1J(P,H) = 181$ (**3a**), 219 (**3b**) Hz) are clearly larger than in **4** ($^1J(P,H) = 156$ Hz [6]), those in the *N*-mesityl compounds **3c, d** ($^1J(P,H) = 139$ (**3c**), 147 (**3d**) Hz) come close to the extremely low values of the four-membered heterocycles **5** (R = Me, Ph; $^1J(P,H) = 125 – 127$ Hz[7]). Following common concepts, the decrease of $^1J(P,H)$ can be related with decreasing p-character and lengthening of the P–H bond and should thus indicate a bond-weakening effect. This hypothesis is corroborated by the red shift of the P–H stretching vibration frequencies in **3a** – **d** ($\tilde{\nu}(PH) = 2120 – 2202$ cm^{-1}) as compared to those of known cyclic and acyclic diaminophosphanes($\tilde{\nu}(PH) = 2220 – 2340$ cm^{-1}[6, 8]), and by the result of a single-crystal X-ray diffraction study of **3d**.[9]



4 **5**

The structure of crystalline **3d** is composed of isolated molecules that display no significant intermolecular interactions (Figure 1).[11] The five-membered ring features an "envelope" conformation with the phosphorus atom sticking out of the plane formed by the remaining ring atoms, and the attached hydrogen atom adopting a "flagpole" position. The

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