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Gold Clustering at Hydroxylamine

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The last two decades have seen a rapid development in the chemistry of gold clusters with interstitial main group elements.[1] For *nitrogen* as the heteroatom, the pioneering synthesis of tetra(gold)ammonium salts with a standard tetrahedral structure of the $[(LAu)_4N]^+$ cation (L = tertiary phosphine donor ligand) by Nesmeyanov and his school[2] was followed by the discovery[3] of hypercoordinate species with pentacoordinate nitrogen atoms in the center of a trigonal bipyramid of gold atoms.[3−5] In extensive analytical, spectroscopic, structural, and theoretical work, it was possible to put these results into the general context of the heterocluster frameworks.[6−15]

Gold clustering phenomena were observed not only for ammonia (above) but also for primary and secondary amines,[13−21] amides, imines,[22,23] imides, etc. and very recently and most notably for *hydrazine*: The hexa(gold)hydrazinium dication $[(LAu)_6N_2]^{2+}$ features a dinitrogen unit encapsulated by six gold atoms.[24] The stability of this species is remarkable because hydrazine—and *hydroxylamine*—are strongly reducing agents which are expected to reduce any gold(I) salt to metallic gold. To date, no gold(I) compound of hydroxylamine has been described in the literature.

We now report the synthesis and the analytical, spectroscopic, and structural characterization of a series of salts containing a triply aurated *O*-(trimethylsilyl)hydroxylammonium cation. *N*,*O*-Bis(trimethylsilyl)hydroxylamine[25] reacts with tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate[2] and triethylamine in the molar ratio 2:1:2 in dichloromethane at −70 °C to give a 94% yield of a pale yellow, crystalline material which analyzes as $\{[(Ph_3P)Au]_3N{-}OSiMe_3\}^+BF_4^-$ (**1**). Although this does not show up in the mass balance (eq 1), the additions of the triethylamine

$$Me_3SiNH{-}OSiMe_3 + \{[(Ph_3P)Au]_3O\}^+X^- \rightarrow Me_3SiOH + \underset{\mathbf{1-4}}{\{[(Ph_3P)Au]_3N{-}OSiMe_3\}^+X^-} \quad (1)$$

base and of a 2-fold excess of the oxonium salt were found to be essential ingredients for obtaining high yields.

Compound **1** is soluble in $CDCl_3$, and the solutions show singlet resonances in the $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra (at δ 29.5 and 2.28 ppm, respectively). The FAB mass spectrum features the mass of the cation at $m/z = 1479.8$ as the parent peak. Since crystals of compound **1** grown from various solvents and mixed solvents proved unsuitable for X-ray crystal structure studies, three salts with different anions X^- (**2**, PF_6; **3**, SbF_6; **4**, OSO_2CF_3) were also prepared from the corresponding oxonium salts. The products of these reactions gave correct analytical data and almost identical NMR and mass spectra.[26] Compound **4** finally gave somewhat more satisfactory single crystals, although of very small size.

The analogous reaction with the oxonium tetrafluoroborate containing tri(*o-tolyl*)phosphine instead of tri*phenyl*phosphine leads to a cleavage of the $[(o\text{-}Tol)_3PAu]$ units from the oxygen and nitrogen centers to give decomposition products including mainly $[(o\text{-}Tol)_3P{-}AuNEt_3]^+\ BF_4^-$.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with 4 formula units in the unit cell.[27] The lattice contains isolated tris[(triphenylphosphine)gold](trimethylsilyl)hydroxylammonium cations which have no crystallographically imposed symmetry and no sub-van der Waals contacts with neighboring ions (Figure 1). The heavy-atom skeleton of this cation (disre-

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(26) Preparation and transformation of compound **1**: The oxonium tetrafluoroborate[2] (150 mg, 0.101 mmol) was dissolved in CH_2Cl_2 (15 mL) at −70 °C and treated with $Me_3SiONHSiMe_3$ (37.4 mg, 0.210 mmol)[25] and NEt_3 (21.3 mg, 0.210 mmol). The mixture was allowed to warm to room temperature. After 150 min, the volume of the solution was reduced to 5 mL in a vacuum and layered with diethyl ether (10 mL) to crystallize the product (48 h; pale yellow, fibrous crystals; 150 mg, 94.4% yield; mp 155−158 °C dec). Anal. Calcd for $C_{57}H_{54}NOAu_3BF_4P_3Si$ (M_r = 1567.77): C, 43.67; H, 3.47; N, 0.89; Au, 37.69. Found: C, 43.24; H, 3.47; N, 0.80; Au, 36.30. Compounds **2**−**4** were prepared in a similar way from the analogous oxonium hexafluorophosphate, hexafluoroantimonate, or trifluoromethanesulfonate, respectively: **2**, 96.2% yield, mp 162−165 °C dec; **3**, 90% yield, mp 160−162 °C dec; **4**, 90.0% yield, mp 152−153 °C dec. The products gave correct elemental analyses. (For details see the Supporting Information.)

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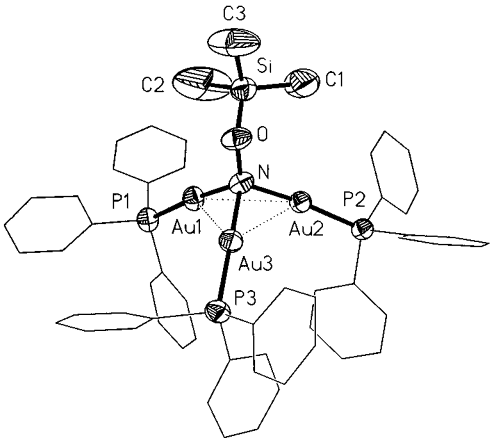

Figure 1. Molecular structure of the cation $\{[(Ph_3P)Au]_3NOSiMe_3\}^+$ in the trifluoromethanesulfonate salt **4** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity).

garding the phenyl rings) closely obeys mirror symmetry, with the atoms Si−O−N−Au3 on the mirror plane. The conformation can thus be described as staggered. The *O*-(trimethylsilyl)-hydroxylamino group has N−O and Si−O bond lengths of 1.467(10) and 1.656(7) Å, respectively, very similar to data of simple hydroxylamine reference molecules.[28] The Si−O−N angle [121.8(5)°] is larger than in (silyl)hydroxylamines, where these angles are compressed owing to β-coordination.[29] This effect is absent for silylhydroxylammonium cations.

The $N(AuL)_3$ cluster unit in the cation of compound **4** closely resembles the corresponding framework of $[R-N(AuL)_3]^+ X^-$ salts[1] with R = alkyl, aryl, AuL, $N(AuL)_3$, etc.: Owing to narrow angles Au−N−Au [Au1−N−Au3 96.0(4)°, Au2−N−Au3 97.2(3)°, Au1−N−Au2 106.1(3)°] there are three short intramolecular Au--Au contacts [Au1−Au2 3.2714(8), Au1−Au3 3.0637(7), Au2−Au3 3.0505(7) Å] suggesting significant metal−metal interactions. The coordination geometry at all three gold atoms is nevertheless close to linear [N−Au1−P1 174.9(2)°, N−Au2−P2 174.4(2)°, N−Au3−P3 174.7(2)°]. The tight bonding within the NAu_3 unit with its small Au−N−Au angles, on one hand, and the wide Si−O−N angle, on the other, probably reduces bond pair/lone pair repulsion otherwise typical for hydroxylamines. This is confirmed by the N−O distance and the surprisingly high stability of the triply aurated species.

There is severe disorder of the triflate anion in the lattice of compound **4**, and the position of its atoms had to be treated with considerable restraints. However, this is not expected to affect the essence of the discussion of the structure of the cation.

The present results have provided a new example of the (isolobal) analogy between $[LAu]^+$ units and the proton:[1] With the trimethylsilyl group as another substituent of "protic" quality, the cation of compounds **1**−**4** resembles the hydroxylammonium cation $[H_3N-OH]^+$. The positioning of the hydroxylamine above the triangle of gold atoms is probably also a model of the anchoring of amines on the gold metal surface typical for self-assembly monolayers (SAMs).[30]

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Supporting Information Available: Tables giving crystal data, structure refinement details, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen positional parameters for **4** and text presenting experimental, analytical, and spectroscopic details for **2**−**4** (8 pages). Ordering information is given on any current masthead page.

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(27) Data collection and structure solution and refinement for compound **4**: Preliminary examination and data collection were carried out on a CCD system (KappaCCD; Nonius) equipped with a rotating anode (Nonius FR591; 50 kV; 60 mA) and graphite-monochromated Mo Kα radiation (λ = 71.073 pm). Data collection was performed at 293 K within the θ range of 9.05 °< 2θ < 52.75 °with an exposure time of 20 s per image (rotation scan modus from $\phi = 0.0$ to 214° with $\Delta\phi = 1°$). A total number of 21 649 reflections were collected. Data were corrected for Lorentz and polarization effects. The unit cell parameters were obtained by full-matrix least-squares refinements of 21 649 reflections with the program DENZO-SMN.[31] Crystal data: monoclinc, space group $P2_1/c$, a = 18.0574(3) Å, b = 17.9319(3) Å, c = 18.2050(2) Å, β = 90.7161(11)°. A total of 8489 reflections ($I > 0$) were used for refinement against F^2 (SHELXL-93).[32] Non-H atoms of the cation were refined with anisotropic atomic displacement parameters, whereas the triflate anion was located and included in the refinements with fixed isotropic contributions. Hydrogen atoms were calculated in idealized geometry, and their isotropic thermal parameters were associated with those of the adjacent carbon atoms by a factor of 1.5. A total of 595 refined parameters were obtained; $wR_2 = 0.1431$, $R_1 = 0.0512$ [$I > 2\sigma(I)$]. The function minimized was $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0922$, $b = 16.76$, $\rho_{fin} = +3.390/-2.013$ e Å^{-3} [located at the triflate anion].

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