Polynuclear Gold Complexes of the Carbodiimide Unit $[N{=}C{=}N]^{2-}$

W. Schneider, K. Angermaier, H. Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstrasse 4, D-85747 Garching, Germany

Dedicated to Professor Marianne Baudler on the occasion of her 75th birthday

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The reaction of N,N'-bis(trimethylsilyl)carbodiimide with equimolar quantities of tris[(triphenylphosphine)gold]oxonium tetrafluoroborate in dichloromethane at -40°C gives high yields of a trinuclear complex $\{[(Ph_3P)Au]_2NCN[Au(PPh_3)]\}^+ BF_4^-$ (**1**). According to variable temperature NMR data the cation is fluxional in solution with a rapid site exchange of the $[(Ph_3P)Au]$ units, but has an unsymmetrical (N,N,N') low temperature ground state configuration. A single crystal X-ray diffraction study has shown that in the crystal lattice these cations are associated further into cyclic, hexanuclear dimers through two short head-to-tail Au–Au contacts (auriophilicity). Treatment of complex **1** with one equivalent of $[(Ph_3P)Au]^+ BF_4^-$ in tetrahydrofuran affords a tetranuclear complex $\{[(Ph_3P)Au]_2NCN[Au(PPh_3)]_2\}^{2+} 2BF_4^-$ (**2**). The ambient temperature NMR spectra of **2** suggest a fluxional, pseudo-symmetrical structure, but at low temperature a set of three ^{31}P signals (1:2:3 intensity) indicates an aggregation into higher nuclearity species with non-equivalent $[Au(PPh_3)]$ units.

Introduction

In a series of recent studies it has been demonstrated that ammonia [1 - 7], primary [8 - 20] and secondary amines [21 - 27] can serve as aggregation centers for high-nuclearity gold(I) clusters. As many as five (and possibly six) [4] gold atoms can be accommodated at the nitrogen nucleation centers. While nitrogen is in the classical valence configuration in the cases with lower coordination numbers (C.N. 2, 3 and 4), the non-classical, hypercoordinate species (C.N. 5, 6) require a more sophisticated theoretical treatment for the description of their structure and bonding. It appears that both electron-deficient radial N-Au bonding and peripheral Au–Au interactions are responsible for the unexpected stability of the clusters [28 - 31].

Clusters built around the nitrogen atom of ammonia or amines $E\text{-}NH_2$ with stepwise substitution of hydrogen atoms by (phosphine)gold(I) moieties have thus been investigated quite extensively, but analogous studies with imines $E{=}NH$ have been initiated only recently. Following our work on monofunctional phosphine imines $R_3P{=}NH$ [32], we subsequently turned to carbodiimines $HN{=}C{=}NH$ as difunctional substrates. Although carbodiimines have been employed as donors for a number of other metals [33 - 41], they have not yet been considered as units with two nitrogen nucleation sites for gold.

Results

A number of aurating agents is available for the introduction of $[LAu]^+$ units at a given substrate, including (phosphine)gold fluoroborates, triflates and perchlorates, but also tris[(phosphine)gold]oxonium salts and (phosphine)gold acetylacetonates. For the present purpose we have chosen *the oxonium route*, because the high affinity of the oxide function for silyl groups (to form inert disiloxanes) was considered a useful driving force for the synthetic reactions. And, in fact, all preparative attempts with these reagents were immediately successful. If the reaction is carried out with equimolar quantities of the components at -40°C in a mixture of dichloromethane and tetrahydrofuran, the products are hexamethyldisiloxane and a trinuclear compound of formula **1** (eq. (1)).

$$\begin{aligned}&(Me_3Si)_2N_2C + \{[(Ph_3P)Au]_3O\}^+BF_4^- \\ &\quad\rightarrow (Me_3Si)_2O + \underset{\mathbf{1}}{\{[(Ph_3P)Au]_3N_2C\}^+BF_4^-} \qquad (1)\end{aligned}$$

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[*] Reprint requests to Prof. Dr. H. Schmidbaur.

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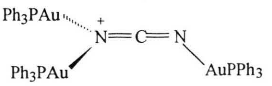
Table I. Crystallographic Data for Tris[(triphenylphosphin)gold(I)] carbodiimide(+1) tetrafluoroborate(-1)(**1**).

Empirical formula	$C_{55}H_{45}Au_3BF_4N_2P_3{*}0.5\ CH_2Cl_2$
Formula weight	1547.01
Crystal system	triclinic
Space group (No.)	$P\bar{1}$ (No.2)
a [Å]	13.994 (2)
b [Å]	14.079 (2)
c [Å]	27.651 (3)
α [°]	104.32 (1)
β [°]	95.81 (1)
γ [°]	99.64 (1)
V [Å^3]	5145.7
ρ_{calc} [gcm^{-3}]	1.997
Z	4
F(000) [e]	2932
μ (Mo-K$_\alpha$) [cm^{-1}]	87.3
T [°C]	–62
Diffractometer	Enraf Nonius CAD4
Scan	ω
hkl range	± 16/ ± 16/ +32
Measured reflections	17912
Unique reflections	15828
Observed reflections	12581
R_{int}	0.000
$F_o \geq$	$4\sigma(F_o)$
refined parameters	647
H-atoms (found/calcd)	– / 46
Absorption corr.:	empirical
$T_{\mathrm{min}}/T_{\mathrm{max}}$	0.4327 / 0.9997
R^*	0.0423
$R_w{}^{**}$	0.0357
Weighting scheme***	$l = 1.0000$ / $k = 0.000116$
ρ_{fin}(max/min) [eÅ^{-3}]	+ 1.62 / - 1.59

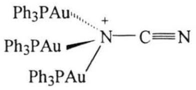
$^{*}R = \sum(||F_o|-|F_c||)/\sum|F_o|$;
$^{**}R_w = [\sum(w(|F_o|-|F_c|)^2)/\sum w(F_o^2)]^{1/2}$;
$^{***}w = 1/[\sigma^2(F_o) + k\,F_o^2]$.

The complex salt **1** is formed in about 70% yield as a colourless stable material (m.p. 217°C), which shows satisfactory elemental analysis data. The FAB and FD mass spectra have the mass of the complete cation as the parent ion in high abundance, accompanied by fragment ions generated in the loss of Ph_3PAu and/or $(Ph_3P)_2Au$ units.

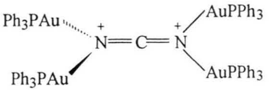
^{31}P NMR spectra of the compound in dichloromethane show a broad singlet resonance at 20°C, which is broadened further and finally split into two resonances of the integral ratio 2:1 as the temperature is lowered progressively to -60°C. This observation suggests a fluxionality process involving rapid positional exchange of the Ph_3PAu groups between the two nitrogen coordination sites (**A**). It should be noted that a N,N,N structure (**B**) must be considered as a likely alternative, which would feature a common trigoldammonium unit attached to a nitrile group. The latter is ruled out also on the grounds of the IR spectrum, however, which has no nitrile absorption band.



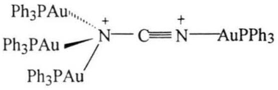
A



B



C



D

Colourless single crystals of compound **1** are obtained by layering dichloromethane solutions with toluene and cooling to -25°C. The crystals are triclinic, space group $P\bar{1}$, with four formula units in

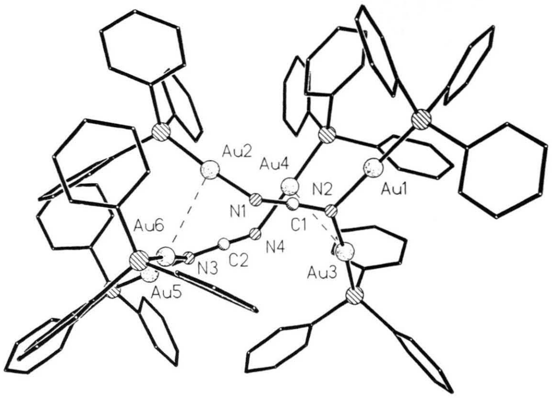


Fig. 1. Structure of a cation-dimer in the crystal of **1** with atomic labeling. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au2 - Au6 3.098(1), Au3 - Au4 3.316(1), Au1 - Au3 3.663(1), Au5 - Au6 3.473(1), Au1 - N2 2.054(9), Au3 - N2 2.05(1), Au2 - N1 2.015(8), Au5 -N3 2.029(8), Au6 - N3 2.03(1), Au4 - N4 2.006(9), N1 - C1 1.19(1), C1 - N2 1.25 (1), N3 - C2 1.28(2), C2 - N4 1.18(2), Au1 - N2 - Au3 126.4(5), Au1 - N2 - C1 116.7(8), Au3 - N2 - C1 115.0(7), N1 - C1 - N2 176(1), Au2 - N1 - C1 136.3(8), Au5 - N3 - Au6 117.6(5), Au5 - N3 - C2 118.6(7), Au6 - N3 - C2 123.2(7), N3 - C2 - N4 177(1), C2 - N4 - Au4 143.8(9).

the unit cell (Table I). The molecules are arranged as crystallographically equivalent dimers, with no crystallographically imposed internal symmetry.

The association follows a head-to tail pattern (Fig. 1), with each mononuclear terminal unit $=N\text{-}AuPPh_3$ of one monomer approaching one of the gold atoms of the bifurcated, dinuclear end $=N(AuPPh_3)_2$ of a second monomer to form intermolecular "auriophilic" contacts. These contacts are in the typical range for this type of aggregation [Au3-Au4 3.316(1), Au2-Au6 3.098(1) Å]. Note that Au1 and Au5 remain without any intra- or intermolecular gold contacts. The dimers are thus macrocyclic systems.

Regarding the NMR results, it is conceivable that in solution the roles of free and engaged $AuPPh_3$ units are changing rapidly for each dimer on the NMR time scale, either in a dimer/monomer dissociation equilibrium, in a ring opening at only one end at a time, and/or through internal rearrangements of the contacts of the dimer without ring opening. No experiments have been carried out to clarify the mechanism, which may be a combination of all modes, with very similar energy characteristics for the individual process.

The configuration of the two tri-coordinate nitrogen atoms (N2, N3) is virtually trigonal planar, with sums of the angles for N2 at 358.1° and for N3 at 359.4°. The angles at the two two-coordinate nitrogen atoms are 136.3(8)° (for N1) and 143.8(9)° (for N4), and thus far from the 120° or 180° standards, indicating a mixed hybridization and a flat energy profile for bending.

The two crystallographically independent carbodiimide units N=C=N are quasi-linear, with the angles N1-C1-N2 at 176(1)°, and N3-C2-N4 at 177(1)°. The planes C1-N1-Au2 and C1-Au1-Au3 (C2-N4-Au4 and C2-Au5-Au6) are roughly perpendicular, in agreement with the fundamental structural motif of allenes (and carbodiimides), which is based on D_{2d} (C_2) symmetry.

Treatment of complex **1** with one equivalent of $(Ph_3P)Au^+BF_4^-$ (obtained in situ from the chloride and $AgBF_4^-$ in thf) gives high yields of the tetranuclear complex $\{[(Ph_3P)Au]_4CN_2\}^{2+}\ 2BF_4^-$ (**2**) (eq. (2)).

$$\mathbf{1} + [(Ph_3P)Au]^+BF_4^- \rightarrow \underset{\mathbf{2}}{\{[(Ph_3P)Au]_4N_2C\}^{2+}\ 2BF_4^-} \qquad (2)$$

It can be isolated from the reaction mixture by precipitation with diethyl ether as a colourless solid (decomposition temperature 212°C), but no single crystals could be generated. The elemental analysis data confirm the proposed composition, and in FD mass spectra the dication is observed as the parent peak, while FAB mass spectra show only the cation of compound **1**. Dichloromethane solutions of compound **2** at room temperature show a sharp singlet resonance in the ^{31}P NMR spectrum, which broadens at -30°C and is finally split into a set of three signals of the intensity ratio 1:2:3. The chemical shifts of these signals are different from those of compound **1** in the same solvent and at the same temperature. The process is fully reversible.

Unfortunately there is no straightforward explanation for this set of resonances, and only tentative structures can be advanced. It should be noted that two isomers can be envisaged for the dication of the tetranuclear complex. One is a symmetrical, allene-type N,N,N',N'-structure (skeletal core point group D_{2d}, **C**), and the other is a N,N,N,N'-structure (point group C_{3v}, **D**). None of these can account alone for the pattern of the low temperature ^{31}P NMR spectra, but a 2:1 mixture or adduct is in full agreement: $[\{[(Ph_3P)Au]_3NCN[Au(PPh_3)]\}_2\{[(Ph_3P)Au]_2NCN[Au(PPh_3)]_2\}]^{6+}$. In the absence of other evidence, we are reluctant to accept this formula, and a definite answer will have to await the results of future studies.

Experimental Part

General

All experiments were routinely carried out under dry and pure nitrogen. Solvents and glassware was dried and saturated/filled with nitrogen. Conventional equipment was used throughout. $(Me_3Si)_2N_2C$ was purchased, $(Ph_3P)AuCl$ and $[(Ph_3P)Au]_3O^+\ BF_4^-$ were prepared following literature methods [42, 43].

Tris[(triphenylphosphine)gold(I)]carbodiimide(+1) tetrafluoroborate(-1) (**1**)

Bis(trimethylsilyl)carbodiimide (35 μl, 0.15 mmol) is added at -40°C to a solution of tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate (0.215 g, 0.15 mmol) in a dichloromethane /tetrahydrofuran mixed solvent (30 ml, 1:1 [vol]). The clear solution is allowed to warm to 0°C in the course of 2 h. The solvents are removed in a vacuum, the residue is taken up twice in dichloromethane and precipitated by addition of diethyl ether; yield 0.148 g (68%), m.p. 217°C. - ^{1}H NMR ($CDCl_3$): δ = 7.35-7.45 ppm [m, Ph]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 127.2 ppm [d, ^1J(CP) = 62.5 Hz, $\underline{C}P$]; 128.4 [d, ^3J(CP) = 18.2, C(*meta*)]; 131.3 [d, ^4J(CP) = 2.0, C(*para*)]; 133.0 [d, ^2J(CP) = 21.2, C(*ortho*)]; $\underline{C}N_2$ was not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 20°C: δ = 30.6 [br. s]; 0°C: 30.5 and 30.3 [two br. s]; -30°C: 30.1 and 29.8 [two br. s]; -60°C: 29.6 [br. s, 1P] and 29.3 [br. s, 2P]. - MS (FAB): *m/z* = 1417.4 [43.0%, M^+]; 959.2 [7.5, M^+-$AuPPh_3$], 721.0 [35.5, $(Ph_3P)_2Au^+$], 459.2 [100, Ph_3PAu^+]. FD: 1418.5 [25.6, M^++H], 721.7 [100, $(Ph_3P)_2Au^+$].

Analysis for $C_{55}H_{45}Au_3BF_4N_2P_3$ **1** (1504.6)
Calcd C 43.90 H 2.99 N 1.86 F 5.05%,
Found C 43.45 H 3.07 N 1.95 F 5.06%.

Tetrakis[(triphenylphosphine)gold(I)]carbodiimide(+2) bis[tetrafluoroborate(-1)] (**2**)

A solution of chloro(triphenylphosphine)gold(I) (0.079 g, 0,16 mmol) in thf (20ml) is cooled to -40°C and treated with $AgBF_4$(0.031 g, 0.16 mmol). After 30 min of stirring the AgCl precipitate is removed by filtration and a solution of **1** (0.240 g, 0.16 mmol) in 20 ml of CH_2Cl_2 is added. After stirring the mixture for 2 h the solution is allowed to warm to 0°C, and the solvents are removed in a vacuum. The colourless residue is purified by precipitation from dichloromethane/diethyl ether (0.266 g, 81% yield). - ^{1}H NMR ($CDCl_3$): δ = 7.30-7.60 [m, Ph]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 20°C: δ = 29.5 [br. s]; -30°C: 28.8 [br. s]; -60°C: 29.5 [br. s, 1P], 29.2 [br. s, 2P], 28.0 [br. s, 3P]. - MS (FD): *m/e* = 936.7 [100%, M^{2+}].

Analysis for $C_{73}H_{60}Au_4B_2F_8N_2P_4$ **2** (2050.7)
Calcd C 42.76 H 2.95 N 1.37 Au 38.41 F 7.41%,
Found C 41.81 H 3.06 N 1.34 Au 35.7 F 7.25%.

Crystal structure determination

Details of the X-ray structure determination of compound **1** are summarized in Table I. Further information on the structure determinations may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D–76344 Eggenstein-Leopoldshafen, Germany, on quoting the names of the authors, the journal citation and the CSD number 59219.

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