Different Pathways of the Reaction of InCl with Ph_3PAuCl: Isolation of the First Mixed-Valent Mixed-Metal Gold/Indium Cluster

François P. Gabbaï, Annette Schier, Jürgen Riede, and Hubert Schmidbaur*

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

Received March 2, 1995

In recent years there has been continued interest in mixed-metal gold clusters.[1] However, while the taxonomy of *homo*-atomic gold clusters has matured to a stage where stoichiometry, structure, and bonding of the existing collection can be put into a satisfactory heuristic scheme,[2] the system of gold clusters *with heteroatoms* is far less developed.[3] This is particularly true for the more electropositive main group and early transition metals, which have rarely been considered as components for gold clusters.[4] Following the synthesis of the first *boron*-centered gold clusters[5] and some work with analogous compounds of *aluminum* and *gallium*, we now present results on the first gold−*indium* cluster.

Insertion of indium(I) halides into polar gold−element bonds appeared to be a promising general pathway for the generation of gold/indium compounds. There is scattered precedent for such InX insertions into complexes of late transition elements (e.g. Pt,[6,7] Hg, Rh[7]), but the nature of the products is not always clear. The complex Ph_3PAuCl has also been mentioned as a suitable substrate for InCl insertion,[7] but no details are available.

In our hands, treatment of Ph_3PAuCl with InCl (molar ratio 1:1) in tetrahydrofuran (thf) yields a colorless, gold-free material[8] as the sole tractable product, which was identified as the tetrakis-thf adduct of dimeric $InCl_2$ by X-ray crystallography (**1**, Figure 1).[9] The reaction pathway leading to the formation of **1** remains unclear but presumably involves formation of a series of transient species as indicated by the different shades of color successively taken on by the reaction mixture.

Contrary to other "indium dihalides", which are known to be mixed-valent salts of the type $In[InX_4]$ for X = Br and I,[10,11] $InCl_2$ and $In[InCl_4]$ have never been fully characterized.[12] The structure of compound **1** suggests that, in any experiment carried out with the alleged mixed-valent $In[InCl_4]$ species in a donor solvent, one is in fact dealing with complexes of isovalent In_2Cl_4. Compound **1** can be readily prepared also from the reaction of In metal and $InCl_3$ in xylene, followed by addition of tetrahydrofuran.[8]

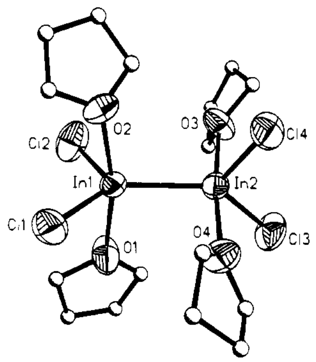

Figure 1. Molecular structure of $In_2Cl_4(thf)_4$, **1**, with the numbering of the heavy atoms (ORTEP; only one orientation of the partly disordered thf molecules shown; arbitrary radii for the thf carbon atoms).

The thf adduct **1** differs from the dioxane complex of Ga_2Cl_4[13] (with tetrahedrally coordinated gallium atoms) in that the In atoms adopt a trigonal-bipyramidal pentacoordination (Figure 1). The In−In stretching frequency[14] was detected in the Raman spectrum of thf solutions of **1** at 180 cm^{-1}, thus indicating that the In−In structure is retained in solution.

The reaction of Ph_3PAuCl with InCl in thf takes a different course if 1,2-bis(diphenylphosphino)ethane (dppe) is added to the solution.[15] The main product is a lemon-yellow cluster compound, mp 105 °C dec, which has been identified as a novel hexanuclear mixed-metal cluster complex (**2**, eq 1). Compound

$$3Ph_3PAuCl + 3InCl + 2dppe + 6thf \rightarrow 3Ph_3P + (dppe)_2Au_3In_3Cl_6(thf)_6\ (\mathbf{2}) \quad (1)$$

2 shows two complex resonances (δ = 41.9 and 59.2 ppm) of equal intensity in the $\{^1H\}^{31}P$ NMR spectrum (CD_2Cl_2 solution at 25 °C, AA′BB′ spin system). The ^{197}Au Mössbauer spectrum (powder, 4 K) has two superimposed quadrupole doublets in the intensity ratio of 1:2 (IS = 2.446 mm s^{-1}, QS = 5.608 mm s^{-1}; IS = 1.000 mm s^{-1}, QS = 6.410 mm s^{-1}), consistent with two different oxidation states and/or coordination environments of the gold atoms. As expected for a gold cluster,[16] compound **2** is photoluminescent with emission maxima at 515 and 580 nm upon UV irradiation at 250 nm.

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(8) $In_2Cl_4(thf)_4$: InCl and Ph_3PAuCl (1 mmol each) are dissolved in thf (10 mL). Dark precipitates are formed, which are filtered out. Cooling of the filtrate affords a 40% yield of colorless, air-sensitive crystals.

(9) **1**: $C_{16}H_{32}Cl_4In_2O_4$ (M_r 659.88), monoclinic, a = 15.323(2) Å, b = 10.524(1) Å, c = 15.601(2) Å, β = 95.69(1)°, space group $P2_1/c$ (No. 14), V = 2503.3 Å^3, Z = 4, D_{calc} = 1.754 g cm^{-3}; T = −59 °C; λ(Mo Kα) = 0.710 69 Å; 5928 reflections measured, 4031 observed [$F_o = 4\sigma(F_o)$]; decay (4%), Lorentz, and polarization corrections, but no absorption correction, applied; 211 parameters, R = 0.0503, R_w = 0.0490; three of the four thf molecules disordered in split positions.

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(15) $(dppe)_2Au_3In_3Cl_6(thf)_3$, **2**: InCl (0.15 g, 1 mmol), Ph_3PAuCl (0.40 g, 0.8 mmol), and dppe (0.32 g, 0.8 mmol) are mixed and cooled to −78 °C, and thf (10 mL) is added. Filtration after 3 h at 20 °C and addition of hexane to the filtrate resulted in the precipitation of an oil which was washed with diethyl ether and toluene before being taken up again in thf (3 mL). The solution was then treated with toluene (6 mL), and the mixture was allowed to stand to give 0.18 g of product **2** (32% yield).

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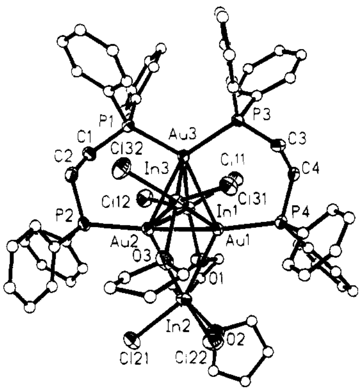

Figure 2. Molecular structure of $(dppe)_2Au_3In_3Cl_6(thf)_3$, **2**, with atomic numbering (ORTEP; arbitrary radii for phenyl and thf carbon atoms; two toluene solvent molecules and all hydrogen atoms omitted for clarity).

The triclinic crystals (from toluene with two solvate molecules, space group $P\bar{1}$, $Z = 2$)[17] contain neutral cluster molecules. The core is composed of an isosceles triangle of gold atoms, with the two long Au−Au edges [Au1−Au3 = 2.939(1) Å, Au2−Au3 = 2.931(1) Å] spanned by dppe ligands and the short Au−Au edge [Au1−Au2 = 2.562(1) Å] bridged by an indium atom (In2). The gold triangle is capped above and below by indium atoms (In1, In3). The symmetry of the hexanuclear core and the phosphorus atoms is thus close to point group C_{2v} (Figure 2).

There is a conspicuous linearity of the axis P2−Au2−Au1−P4, which together with the extremely short bond Au1−Au2 suggests the oxidation state 0 for these two gold atoms and a strong Au−Au bond. Au3 can be assigned oxidation state +1, also by taking into account the Mössbauer data.[18] The face-capping indium atoms (In1, In3) are tentatively assigned oxidation state +2; the edge-bridging atom In2 is assigned oxidation state +1. The reaction of equ 1 would thus formally include a redox process in which two Au^+ units are reduced to Au^0, whereas two In^+ units are oxidized to In^{2+}, while one Au^+ and one In^+ component are left unchanged. A theoretical treatment of the core system using density functional methods (including relativistic effects) has therefore been initiated.[19] In another qualitative description the metal core can be assigned six bonding cluster electrons, which suggests an "oblate" model structure[1,2,20] but offers no prediction as to the geometrical details of this model. Studies reported in the literature on the insertion of $SnCl_2$ units into gold(I) complexes[4,21,22] have led to equally intriguing results in the past. It is hoped that a growing number of new data will help to establish the principles underlying these more sophisticated mixed-metal mixed-valence cluster systems.

Acknowledgment. This work was supported by the Alexander von Humboldt Stiftung (F.P.G.), Deutsche Forschungsgemeinschaft, and Fonds der Chemischen Industrie. Prof. F. E. Wagner is thanked for the Au Mössbauer spectrum.

Supporting Information Available: Fully labeled ORTEP diagrams and listings of crystallographic data and data collection and refinement details, atomic positional parameters, anisotropic thermal parameters, bond distances, and bond angles (32 pages). Ordering information is given on any current masthead page.

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(17) **2**·$2C_6H_5CH_3$: $C_{78}H_{88}Au_3Cl_6In_3P_4O_3$ (M_r 2345.54), triclinic, a = 12.752(1) Å, b = 16.865(2) Å, c = 20.431(2) Å, α = 93.92(1)°, β = 101.39(1), γ = 90.45(1)°, space group $P\bar{1}$ (No. 2), V = 4296.3 Å^3, Z = 2, D_{calc} = 1.813 g cm^{-3}; T = −56 °C; λ(Mo Kα) = 0.710 69 Å; 18 576 reflections measured, 17 366 unique, and 15 172 observed [$F_o \geq 4\sigma(F_o)$]; empirical absorption correction applied (T_{max} = 99.95%, T_{min} = 69.76%); 780 parameters, R = 0.0308 (R_w = 0.0343).

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