Solvated Gold(I) in Acetonitrile with Inert Counterions: a Versatile Starting Material for Gold(I) Chemistry

Reinhard Kissner, Petr Latal and Gerhard Geier

Laboratorium für Anorganische Chemie, ETH Zürich, 8092 Zurich, Switzerland

Solvated Au^+ in acetonitrile with a variety of non-coordinating anions, an advantageous starting material for syntheses of gold(I) compounds, is conveniently prepared by halide-catalysed electrolysis.

Most procedures for the preparation of gold(I) compounds use commercially available starting materials containing $AuCl_4^-$. Normally the Au^{III} is reduced by an excess of a potential ligand. In many cases the oxidation products and Cl^- have to be removed, the latter by precipitation with Ag^+ or Tl^+. Remaining traces of these metals may cause problems in subsequent applications.

Alternatively, Au solvates in acetonitrile (MeCN) have been prepared by oxidation of gold metal by $NOClO_4$[1] and electrolysis.[2–4] However, nitrosyl salts are very hazardous chemicals, and electrolysis may yield products contaminated by tetraalkylammonium salts. It is also limited to perchlorate electrolytes which yield potentially explosive compounds.

We have now generalised the electrolytic method, in a smooth and safe process, to prepare solutions and solid salts of solvated Au^+ with anions other than perchlorate and free from tetraalkylammonium electrolytes.

Experiments were carried out in a two-compartment cell with an electrolyte bridge (Fig. 1). Bridge and compartments were separated by Teflon membranes covered by an anion-exchanging resin (*e.g.* Serva Permion 4035), which allows only anionic and neutral particles to pass. The cathodic reaction was the reduction of 0.1 mol dm^{-3} Ag^+ in MeCN with the appropriate anion. The corresponding 0.1 mol dm^{-3} tetraethylammonium salt was also added to prevent a conductivity drop due to the consumption of Ag^+. The bridge contained 0.1 mol dm^{-3} tetraethylammonium electrolyte. The anodic compartment was filled either with 0.1 mol dm^{-3} supporting electrolyte or pure MeCN. The MeCN was commercial analytical grade and used without purification. A coiled silver wire served as cathode while a coiled wire of highly pure gold was mounted as a sacrificial anode. The gold coil was heated gently in an oxidising gas flame to remove surface impurities. The potential difference between anode and cathode was set to 2 V. Under these conditions gold is oxidised to the solvated Au^+ ion while MeCN is not attacked.

When we tried to carry out the anodic dissolution of Au in MeCN solutions of tetraethylammonium salts of $CF_3SO_3^-$, BF_4^- and PF_6^-, the current quickly dropped to zero after an initial rise, while the gold anode became covered by a brownish layer. An explanation is provided by a study[5] on the influence of traces of water on gold oxidation in MeCN

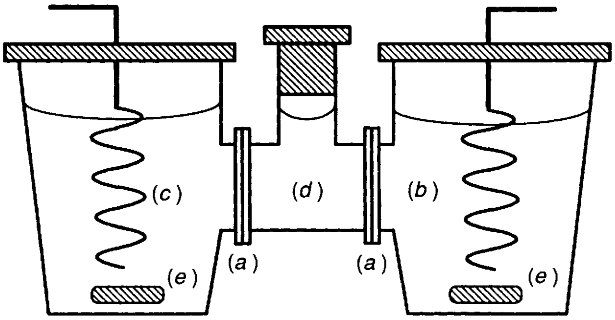

Fig. 1 Electrochemical two-compartment cell with electrolyte bridge: (*a*) anion exchanging membranes clamped between planar glass junctions, (*b*) cathodic compartment with coiled Ag wire electrode, 0.1 mol dm^{-3} Ag^+ and 0.1 mol dm^{-3} Et_4N^+ together with 0.2 mol dm^{-3} selected anion in MeCN, (*c*) anodic compartment with coiled Au wire electrode (50 cm, ϕ 1 mm) and 10^{-6} mol dm^{-3} Et_4NI catalyst in MeCN, (*d*) bridge with 0.1 mol dm^{-3} Et_4N^+ and 0.1 mol dm^{-3} selected anion in MeCN, (*e*) magnetic stirrer bars. Compartment volume: 50–200 cm^3

solution containing $Bu^n_4NPF_6$ as electrolyte; the water normally accompanying MeCN causes the formation of an insulating oxide layer on an anodically polarised gold electrode. Au^+ is formed only in very dry MeCN. This condition is difficult to maintain during a prolonged electrolysis and thus not very practicable. Therefore, we investigated the cause of the easy oxidation in the presence of perchlorate in moist MeCN.

Since tetraalkylammonium perchlorates are likely to contain substantial traces of chloride, we examined the possibility that this contaminant was responsible for the observed reaction. Indeed we found that chloride is more abundant in Et_4NClO_4 than in tetraethylammonium salts with other anions. Several samples of Et_4NClO_4 were shown by high pressure ion chromatography to contain 1–7 × 10^{-4} mol of Cl^- per mol of ClO_4^-. The crucial role of chloride became evident when we observed that the addition of corresponding amounts to tetraethylammonium salts of $CF_3SO_3^-$, BF_4^- or PF_6^- in the anodic compartment facilitated the oxidation of gold. Moreover, it was found that bromide and iodide have the same effect at one tenth the concentration. Iodide is partially precipitated as AuI, indicating it is active at even lower concentrations than bromide. The catalytic mechanism is still under investigation, but there are indications that the halides are active in a surface reaction. They prevent the formation of the brown oxide layer, since the anode remains bright during the whole electrolysis. When the potential is applied before the halide is added, the brown oxide layer forms and cannot be removed by subsequent halide addition.

The solutions obtained this way, though containing up to 0.1 mol dm^{-3} solvated Au^+, are not very attractive for preparative applications, because it is difficult to remove the supporting electrolyte. Fortunately, it turned out that the production of Au^I is also possible without an inert electrolyte in the anodic compartment. Small initial concentrations of halide catalyst between 10^{-6} and 10^{-5} mol dm^{-3} provide enough background conductivity together with catalytic activity to start the electrolysis. Hence the concentration of ions and the corresponding conductivity increase. This leads to a higher electrochemical reaction rate. Anions are supplied through the membranes between the compartments whereas tetraethylammonium and Ag^+ cannot enter the anodic compartment. The process becomes self-propagating in this way. Final Au^+ concentrations up to 0.1 mol dm^{-3} can be obtained while the halide concentration remains at the initial value or becomes even lower in the case of iodide because it is partially precipitated.

An approximately 0.1 mol dm^{-3} Au^+ solution is produced within 24–36 h using 10^{-6} mol dm^{-3} iodide catalyst. The resulting solutions have a great potential for the synthesis of Au^I complexes and introduction of Au^I into clusters. The contamination by the catalyst is very low (1 in 10^5 with respect to Au^+) and well defined in contrast to the residues left from the conventional precipitations with Ag^+ or Tl^+.

From the electrolyte-free solutions, we crystallised $[Au(MeCN)_2]CF_3SO_3$ and $[Au(MeCN)_2]PF_6$. Both solids are decomposed by moisture and by loss of MeCN, the $CF_3SO_3^-$ salt being much more sensitive. It is interesting that the coordination number in these solids is two as in $[Au(MeCN)_2]ClO_4$[1]. However, in solution $[Au(MeCN)_4]^+$ exists.[6]

Finally, we have so far synthesised $[Au(mpt)_2]CF_3SO_3$, $[Au(mpt)_2]BF_4$ (mpt = *N*-methylpyridine-2-thione) and $[Au\{(NH_2)_2CS\}_2]PF_6$, which are stable in dry air, simply by mixing the gold salt and the ligand in MeCN followed by evaporation of the solvent.

We thank H. Seiler of the University of Basel for support and advice in the high pressure ion chromatography experiments and L. M. Venanzi of the ETH Zürich for helpful discussions.

Received, 2nd October 1992; Com. 2/05313F

References

1 G. Bergerhoff, *Z. Anorg. Allg. Chem.*, 1964, **327**, 139.
2 A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, 1968, **40**, 1978.
3 R. Roulet and R. Favez, *Chimia*, 1975, **29**, 346.
4 P. N. Dickson, A. Wehrli and G. Geier, *Inorg. Chem.*, 1988, **27**, 2921.
5 D. Wagner and H. Gerischer, *J. Electroanal. Chem.*, 1989, **258**, 127.
6 S. Ahrland, K. Nilsson, I. Persson, A. Yuchi and J. E. Penner-Hahn, *Inorg. Chem.*, 1989, **28**, 1833.