

Preliminary Communication

Synthesis and applications of $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$, a versatile labile intermediate for gold(I) chemistry

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Abstract

$[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ may be synthesised in high yields by heating a mixture of gold powder and NOBF_4 in PhCN under reflux for several hours. It represents a labile form of solvated gold(I), which may be used as a convenient intermediate for the synthesis of a wide range of gold(I) compounds.

Key words: Gold; Benzonitrile; Solvated gold(I); Synthone for gold(I) compounds

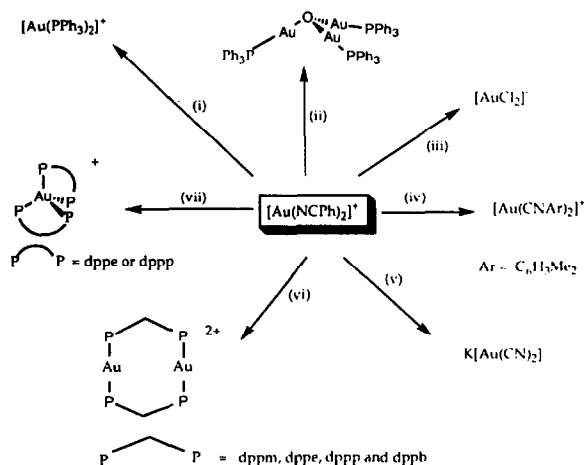
Nitrile compounds of the transition metals have proved to be extraordinarily useful intermediates, because of their substitutional lability [1]. The relevant nitrile compounds of gold have by comparison received little attention. This can be attributed to the absence of convenient routes to these compounds and their sensitivity to moisture. For example, the acetonitrile solvate of gold(I), $[\text{Au}(\text{NCCH}_3)_2]^+$, has been obtained by the direct oxidation of gold metal by NOClO_4 , but the extreme moisture sensitivity of the compound and the juxtaposition of a thermally labile CH_3CN compound and ClO_4^- make it an unattractive intermediate [2]. Geier et al. [3] in 1993 reported an alternative electrochemical synthesis of $[\text{Au}(\text{NCCH}_3)_2]^+$, but it requires somewhat specialized equipment and long synthesis times to build up appreciable quantities of the solvated gold compound. We describe below a convenient route to a benzonitrile compound of gold(I) and illustrate the use of this compound as an intermediate in gold(I) chemistry.

The salt $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ may be obtained in yields of greater than 90% by heating under reflux a mixture

of gold powder and NOBF_4 [4] in anhydrous acetonitrile/benzonitrile (1:2) for 4 h. The compound is obtained as a colourless crystalline solid by adding toluene to the solution. It is much more stable than $[\text{Au}(\text{NCMe})_2][\text{BF}_4]$, which has been obtained by the same route. It is slightly moisture sensitive, but may nonetheless be weighed out in the open laboratory and is thermally stable (decomp. temp. 167–169°C). It is only slightly light sensitive and may be stored under nitrogen in a sealed tube at -25°C for months without decomposition. The photosensitivity leads to the development of a pinkish colouration in the solid, presumably resulting from gold particle formation. The salt $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ shows a weak band at 2295 cm^{-1} in the infrared spectrum that may be attributed to the antisymmetric $\nu(\text{CN})$ stretching mode. It is very soluble in CH_3CN and PhCN, but decomposes on dissolution in other organic solvents such as acetone and ethanol.

The great versatility of $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ as an intermediate may be gauged from the reactions summarized in Scheme 1. The reactions were all performed in acetonitrile solutions and the products were obtained in high yields. The benzonitrile ligands are readily displaced by neutral ligands to give the mononuclear cationic phosphine complexes $[\text{Au}(\text{PPh}_3)_2]^+$ [5] $[\text{Au}(\text{dppe})_2]^+$ and $[\text{Au}(\text{dppp})_2]^+$ [6]. The binuclear complexes $[\text{Au}_2(\text{dppm})_2]^{2+}$, $[\text{Au}_2(\text{dppe})_2]^{2+}$, $[\text{Au}_2(\text{dppp})_2]^{2+}$ and $[\text{Au}_2(\text{dppb})_2]^{2+}$ were obtained [7] when the mole ratio of phosphine to gold compound was reduced to 1:1. All of these compounds have been characterized by elemental analysis and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The oxonium cation $[\text{Au}_3\text{O}(\text{PPh}_3)_3]^+$, which has proved so useful for the synthesis of homo- and hetero-metallic gold cluster compounds and Schmidbaur's interesting interstitial compounds [8], may be formed directly from the solvated benzonitrile complex by adding 1 molar equivalent of PPh_3 in CH_3CN and then diluting the solution with propanol. Dropwise addition of the correct molar ratio of KOH in methanol leads to the formation of the oxonium salt in good yields. This route is much simpler than the conventional synthetic route [9]. Although it was not isolated as a solid compound, $^{31}\text{P}\{^1\text{H}\}$ NMR studies have confirmed the formation of $[\text{Au}(\text{PPh}_3)(\text{NCCH}_3)]^+$ in situ when 1 molar equivalent of PPh_3 is added to $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ in CH_3CN . This cation has been widely used in capping reactions in cluster chemistry

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Scheme 1. The reagents used for the transformations which were undertaken in CH_3CN are: (i) PPh_3 , (ii) PPh_3 and KOH/MeOH , (iii) $\text{N}^n\text{Bu}_4\text{Cl}$, (iv) CNAr , (v) $\text{KCN}/\text{H}_2\text{O}$, (vi) dppm , dppe , dppp or dppb in (1:1 ratio), and (vii) dppp or dppe in (2:1 ratio).

and is more usually formed by the addition of silver or thallium salts to $[\text{AuCl}(\text{PPh}_3)]$ [10].

The cationic isonitrile complex $[\text{Au}(\text{CNC}_6\text{H}_3(\text{CH}_3)_2)_2]^+$ has been obtained in virtually quantitative yields from the benzonitrile intermediate, and shows $\nu(\text{CN})$ at 2225 cm^{-1} .

More surprisingly $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ may also be used for the synthesis of salts of anionic gold(I) complexes such as $[\text{AuCl}_2]^-$ and $[\text{Au}(\text{CN})_2]^-$. The former salt is made by adding NBu_4Cl directly to a solution of $[\text{Au}(\text{NCPH})_2][\text{BF}_4]$ in CH_3CN and precipitating out the

salt with an $\text{Et}_2\text{O}/\text{EtOH}$ mixture, and the latter by adding a CH_3CN solution of the gold benzonitrile complex to an aqueous solution of KCN . The conventional route to these anionic halide complexes is quite tedious, and involves the initial formation of gold(III) compounds followed by their reduction [11].

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