

# Isonitrile gold(I) nitrates as precursors for iron oxide-supported gold catalysts for CO oxidation

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The synthesis and X-ray crystal structure of [Au(NO<sub>3</sub>)(CNBu<sup>t</sup>)] are reported, a first for a C- and O-bonded gold(I) species; it is an effective precursor for chemical deposition of gold on iron oxide to give catalysts which efficiently oxidise CO in air at low temperatures.

Haruta *et al.* have shown that finely-divided metallic gold on iron oxide catalyses the oxidation of CO to CO<sub>2</sub> in air at ambient pressures and at temperatures as low as -70 °C, a process of technological importance for the removal of CO.<sup>1,2</sup> Originally, preparations involved co-precipitation from solutions of Au<sup>III</sup> and Fe<sup>III</sup> followed by heating to generate gold particles on the iron oxide surface.<sup>1</sup> This process requires careful control of the rates of addition and pH to ensure active catalysts, and thorough washing to remove chloride ions which poison the catalyst. More recently a new approach involving vapour deposition of [AuMe<sub>2</sub>(acac)] onto TiO<sub>2</sub> has given active catalysts for CO oxidation.<sup>3</sup>

We are exploring an alternative method of catalyst preparation, using organometallic gold compounds as substrates for deposition. The ideal precursor should be readily prepared, should be adsorbed efficiently onto the metal oxide/hydroxide surface, and preferably should not contain elements such as Cl, S or P which may act as catalyst poisons. Iwasawa and coworkers<sup>4</sup> have prepared active catalysts by adsorption of [Au(NO<sub>3</sub>)(PPh<sub>3</sub>)] onto iron hydroxide followed by calcination, which suggests that phosphorus can be tolerated. Here, we report our parallel studies on the use of the novel gold(I) complex [Au(NO<sub>3</sub>)(CNBu<sup>t</sup>)] **1**, for this purpose.

Complex **1** is prepared from AgNO<sub>3</sub> and [AuCl(CNBu<sup>t</sup>)] in CH<sub>2</sub>Cl<sub>2</sub>-MeOH at -45 °C.† After removal of AgCl from the mixture, **1** can be isolated in reasonable yield (65%) as colourless crystals. The compound is thermally- and light-sensitive but can be readily handled as a solid at room temperature with suitable precautions, and can be stored indefinitely in the dark at -20 °C. Solutions of **1** in CH<sub>2</sub>Cl<sub>2</sub> show signs of decomposition after *ca.* 15 min at room temperature, while MeOH solutions deteriorate much more rapidly. Characterisation of **1** included a single-crystal X-ray structure analysis,‡ which confirms it as the first example of a gold(I) complex with both Au-O and Au-C bonds, incorporating a normal Bu<sup>t</sup>NC ligand and an η<sup>1</sup>-NO<sub>3</sub> ligand about an essentially linearly coordinated gold atom. The only previous example of a gold(I) nitrate complex to be structurally characterised is [Au(NO<sub>3</sub>)(PPh<sub>3</sub>)];<sup>5</sup> the Au-ONO<sub>2</sub> fragments of the two are very similar.

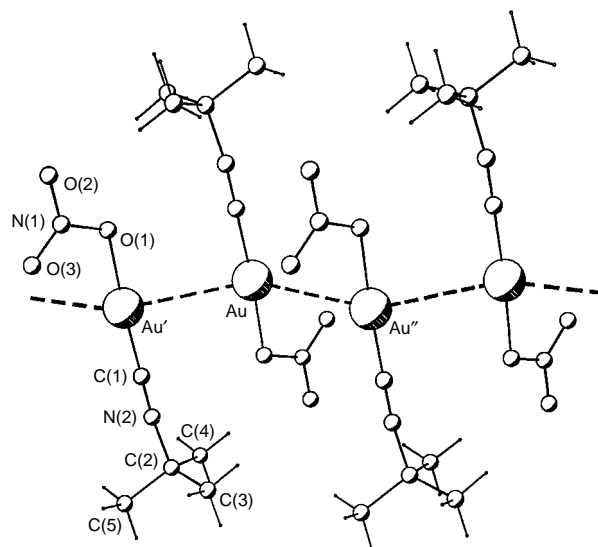
The major structural interest is in the cell packing and intermolecular association which is clearly controlled by secondary Au...Au interactions, as expected from the recent structural and theoretical work on 'auriophilicity' from the groups of Schmidbauer,<sup>6</sup> Pyykkö<sup>7</sup> and others.<sup>8</sup> As shown in Fig. 1, compound **1** adopts a puckered chain arrangement with adjacent parallel monomers packing head-to-tail with alternating Bu<sup>t</sup>NC and NO<sub>3</sub><sup>-</sup> ligands. The alternating Au...Au interactions are 3.296(1) and 3.324(1) Å, which are the shortest yet reported for a chain structure involving Au(CNR)X species, distances less than this having been found mainly for compounds which pack as dimers

or tetramers.<sup>6</sup> For **1** the short distances are presumably encouraged by the small ligands with low electron-donating tendencies. For comparison the Au...Au distances in the chains found for [Au(CN)(CNBu<sup>t</sup>)] are 3.568 Å and those in [AuCl(CNBu<sup>t</sup>)] are 3.695 Å.<sup>9,10</sup>

The corresponding [Au(NO<sub>3</sub>)(CNEt)] complex was isolated similarly, but so far we have only been able to isolate the [Au(CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)<sub>2</sub>]NO<sub>3</sub> compound from analogous reaction mixtures; these structures will be reported separately.

Preparation of a catalyst for CO oxidation from **1** was straightforward.§ A sample of **1** was added to a slurry of freshly precipitated<sup>4</sup> Fe(OH)<sub>3</sub> in acetone to give a *ca.* 3% Au:Fe<sub>2</sub>O<sub>3</sub> ratio by mass in the final product. The gold complex appears to be completely adsorbed onto the solid phase. The suspension was dried by evaporation under vacuum and heated at 400 °C in air for 2 h to convert the adsorbed gold to the metallic state, giving a brown powder. The presence of gold in the sample was confirmed by bulk EDAX analysis, but individual particles of gold were not visible under the scanning electron microscope, suggesting that they were smaller than *ca.* 4 nm, the maximum resolving power available to us. Haruta has shown that highest activity is associated with small gold particle size.<sup>1</sup>

To test the catalytic activity a 10 mg sample was placed in a micro-reactor and a stream of CO (1%) in air was passed through it at 2 ml min<sup>-1</sup>. The effluent stream was monitored by a fuel-cell based detector which showed complete conversion of CO was achieved down to -5 °C, the lowest temperature so far examined. Catalytic activity continued without diminution for many hours.



**Fig. 1** The packing of [Au(NO<sub>3</sub>)(CNBu<sup>t</sup>)] **1** along one chain. Selected bond parameters: Au-C(1) 1.92(1), Au-O(1) 2.062(9), C(1)-N(2) 1.13(2), Au...Au' 3.2955(8) Au...Au'' 3.3243(8) Å; C(1)-Au-O(1) 176.3(4), Au'-Au...Au'' 142.27(3)°. Symmetry operations: Au' -x, 1-y, 1-z; Au'' 1-x, 1-y, 1-z.

It is worth noting that a catalyst prepared in the same way from [AuCl(CNBU<sup>4</sup>)] displayed no catalytic activity towards CO oxidation, even at 100 °C.

In conclusion, we have shown that isonitrile gold nitrates are stable enough for characterisation, that **1** packs with short Au...Au distances, and that chemical deposition of **1** on iron hydroxide provides a simple route to a highly active oxidation catalyst for CO.

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## Notes and References

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† *Synthesis* of [Au(NO<sub>3</sub>)(CNBU<sup>4</sup>)]. An argon-flushed Schlenk flask containing AgNO<sub>3</sub> (0.30 g, 1.8 mmol) in MeOH (30 ml) was covered in foil to exclude light, and cooled to -45 °C. To this stirred solution was added [AuCl(CNBU<sup>4</sup>)] (0.45 g, 1.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) with the temperature maintained at -45 °C. The mixture was stirred for 30 min. The solvent was evaporated under vacuum and the residue extracted with cold CH<sub>2</sub>Cl<sub>2</sub> (5 ml). The filtered extract was treated with light petroleum (60–80 °C fraction) to precipitate [Au(NO<sub>3</sub>)(CNBU<sup>4</sup>)] (0.32 g, 65%) as a colourless, microcrystalline powder after drying under vacuum. Found: C, 17.76; H, 2.47; N, 8.30%. Calc. for C<sub>5</sub>H<sub>9</sub>AuN<sub>2</sub>O<sub>3</sub>: C, 17.55; H 2.65; N, 8.19%. IR (KBr disk, cm<sup>-1</sup>): 2258 [ν(C≡N)], 1512, 1272, 977 (monodentate NO<sub>3</sub><sup>-</sup> ligand<sup>11</sup>). NMR (CDCl<sub>3</sub>): <sup>1</sup>H δ 1.60 (s, BU<sup>4</sup>); <sup>13</sup>C δ 29.7 [s, (CH<sub>3</sub>)<sub>3</sub>CNC], 60.1 [s, (CH<sub>3</sub>)<sub>3</sub>CNC], 122.2 [t, <sup>1</sup>J<sub>C=N</sub> 24 Hz, (CH<sub>3</sub>)<sub>3</sub>CNC]. **WARNING:** The crystals decompose violently without melting at ca. 118 °C. X-Ray quality crystals were obtained by slow diffusion of light petroleum into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex.

‡ *Structure* of [Au(NO<sub>3</sub>)(CNBU<sup>4</sup>)]. C<sub>5</sub>H<sub>9</sub>AuN<sub>2</sub>O<sub>3</sub>, *M* = 342.11, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 6.2642(1), *b* = 13.5595(3), *c* = 10.6118(1) Å, β = 102.18(1)°, *U* = 881.07(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 2.579 g cm<sup>-3</sup>, λ = 0.71073 Å. *T* = 203(2) K, μ(Mo-Kα) = 16.661 mm<sup>-1</sup>, *F*(000) = 624. Data were collected on a Siemens SMART diffractometer using a crystal of dimensions 0.43 × 0.34 × 0.23 mm. A total of 4203 reflections were collected to 2θ = 56°, 1921 unique (*R*<sub>int</sub> = 0.0552), and were corrected for absorption using SADABS (*T*<sub>max, min</sub> 0.102, 0.023). The structure was solved by Patterson methods and refined on *F*<sup>2</sup> to *R*<sub>1</sub> = 0.0574 [1645 data with *F* > 4σ(*F*)], *wR*<sub>2</sub> = 0.1543, *G*o*F* = 1.002 (all data). Largest final features were +4.1, -3.9 e Å<sup>-3</sup>, adjacent to the gold atom. All calculations were with the SHELX-96 suite of programs.<sup>12</sup> CCDC 182/738.

§ *Preparation of the catalyst.* Iron(III) hydroxide was freshly prepared by adding a solution of sodium carbonate to a solution of iron(III) nitrate.<sup>4</sup> The

precipitate was thoroughly washed and then suspended in acetone. Sufficient solid [Au(NO<sub>3</sub>)(CNBU<sup>4</sup>)] was added to give an Au/Fe<sub>2</sub>O<sub>3</sub> ratio of 3% by mass and the slurry was stirred for 10 h. The acetone was pumped away under vacuum and the residue was heated in air for 2 h at 400 °C to convert the adsorbed gold complex to metallic gold particles, and the Fe(OH)<sub>3</sub> to Fe<sub>2</sub>O<sub>3</sub>.

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