Isolation of Highly Nucleophilic Gold(I) Alkoxides having a Tertiary Phosphine Ligand

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Alkoxogold(I) complexes having a tertiary phosphine ligand, Au(OR)L [R = CH_2CF_3, $CH(CF_3)_2$; L = PPh_3, PCy_3] have been synthesized by the metathetical reactions of chloro(tertiary phosphine)gold(I) and potassium fluorinated alkoxides in tetrahydrofuran at room temperature.

Alkoxides of late transition metals have recently attracted much attention in relation to not only catalysis and synthetic tools but also their possible use as new materials, and considerable efforts for their synthesis have been performed in recent years.[1] Among them gold alkoxides are rare and are unstable unless sterically bulky alkoxides or aryloxides are employed.[2] We recently reported the isolation of trivalent organogold(III) aryloxides and fluoroalkoxides by a simple metathetical reaction.[3] We now report the isolation of stable gold(I) alkoxides containing a tertiary phosphine ligand.

The reaction of chloro(triphenylphosphine)gold(I) with a stoichiometric amount of potassium 2,2,2-trifluoroethoxide in tetrahydrofuran (thf) at −20 °C gave a homogeneous colourless solution. After 2 h stirring, all the volatile materials were evaporated *in vacuo* to give a colourless solid. Dichloromethane extracts were recrystallized from dichloromethane–hexane to afford colourless crystals of (2,2,2-trifluoroethoxo)(triphenylphosphine)gold(I), **1** [eqn. (1)]. A similar reaction with potassium 1,1,1,3,3,3-hexafluoro-2-propoxide also gave a corresponding fluoroalkoxide of gold(I), **2**. Tricyclohexylphosphine (PCy_3) analogues, **3** and **4**, were also prepared. Compounds **1–4** were characterized by elemental analysis, ^1H NMR and IR spectroscopy, as well as by chemical reactions.† They are considerably air and thermally stable.

$$\mathrm{AuClL + KOR \xrightarrow{thf} Au(OR)L + KCl} \qquad (1)$$

1; L = PPh_3, R = OCH_2CF_3
2; L = PPh_3, R = $OCH(CF_3)_2$
3; L = PCy_3, R = OCH_2CF_3
4; L = PCy_3, R = $OCH(CF_3)_2$

Although the ^1H NMR spectrum of the gold(I) alkoxide **2** showed a sharp septet at δ 5.06 due to the methine group in C_6D_6 at room temperature, extensive line broadening of the signals was observed when one equivalent of free 1,1,1,3,3,3-hexafluoropropan-2-ol was added. The result suggests that a fast associative exchange of the alkoxide ligand is taking place under these reaction conditions. When the temperature was lowered to −60 °C, broad signals assignable to OH and CH protons of the hydrogen bonded alcohol appear at δ 8.03 and 4.3 in addition to the CH signal of the alkoxide group (δ 3.8). When the concentration of free alcohol increased, the signal of the hydrogen bonded OH proton collapses with that of free alcohol and shifts to higher field, indicating fast exchange between free and hydrogen bonded alcohols under these conditions [eqn. (2)]. Complex **4** also behaves similarly. The ^1H NMR signals of **1** and **3** are not well resolved probably because of a small contamination of free alcohol causing the extensive line broadening of the signals.

$$\mathrm{Au(OR)L + ROH \rightleftharpoons Au(OR)(ROH)L} \qquad (2)$$

Reactions of the gold(I) alkoxides with an equimolar amount of phenol in benzene gave phenoxo(triphenylphosphine)gold(I)[2c] with liberation of the corresponding alcohol, indicating the high thermodynamic stability of the phenoxide over the alkoxides [eqn. (3)]. Interestingly, the gold(I) alkoxides **1–4** abstracted protons smoothly from malononitrile, methyl cyanoacetate and even acetone to give corresponding C-bonded gold(I) enolates[4] and free alcohol. Acidolysis of **1–4** with dry hydrogen chloride liberated the corresponding fluoroalcohols, supporting the chemical formula of these alkoxides.‡

$$\mathrm{Au(OR)(PPh_3)} \left\langle \begin{array}{l} \mathrm{+\ PhOH \rightarrow Au(OPh)(PPh_3)} \\ \mathrm{+\ RH \rightarrow Au(R)(PPh_3)} \end{array} \right. \qquad (3)$$

$$\mathrm{R = CH(CN)COOEt,\ CH(CN)_2,\ CH_2COMe}$$

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† *Yields, m.p. and selected spectroscopic data of new compounds*: **1**: 71% yield; m.p. 184–187 °C; IR ν/cm^{-1}, 1180, 1280; ^1H NMR(C_6D_6) δ 4.8 (br, CH_2). **2**: 71% yield; m.p. 118–119 °C; IR ν/cm^{-1} 1150, 1280; ^1H NMR(C_6D_6) δ 5.06 (septet, *J* 6.5 Hz, CH). **3**: 48% yield; m.p. 184–185 °C; IR ν/cm^{-1} 1145, 1180, 1280; ^1H NMR(C_6D_6) δ 4.8 (br, CH_2). **4**: 64% yield; m.p. 183–185 °C; IR ν/cm^{-1} 1175, 1205, 1280; ^1H NMR(C_6D_6) δ 5.19 (septet, *J* 6.6 Hz, CH). Satisfactory elemental analytical data for these alkoxides were obtained.

‡ Acidolyses of these gold(I) alkoxides with dry hydrogen chloride were performed in C_6D_6. Corresponding alcohols liberated were quantitatively analysed by ^1H NMR: **1**, 49; **2**, 86; **3**, 70; **4**, 96%.