Spontaneous Isomerization of t-Butylgold(III)

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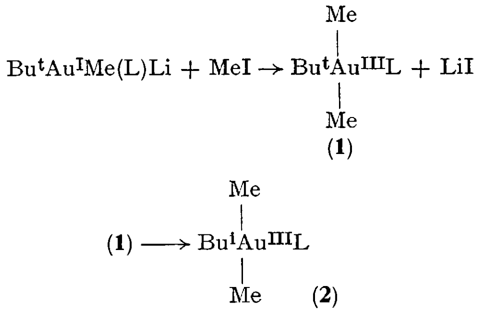
Summary The rearrangement of a t-butylgold(III) complex to the isobutylgold(III) isomer occurs readily by an intramolecular mechanism.

WE have observed an unusually facile rearrangement of a t-butyl group into the isobutyl isomer when it is σ-bonded to gold(III). Thus, *trans*-t-butyldimethyl(triphenylphosphine)gold(III) (**1**) is readily formed from lithium t-butylmethyl(triphenylphosphine)gold(I) and methyl iodide in diethyl ether solution at −78 °C by a reaction previously described[1] [$L = PPh_3$]. The presence of (**1**) is readily indicated by ^1H n.m.r. Attempts to purify (**1**) led to its spontaneous conversion into the isomeric *trans*-isobutyldimethylgold(III) (**2**) (Scheme).



$$Bu^tAu^IMe(L)Li + MeI \rightarrow Bu^tAu^{III}(Me)_2L + LiI \quad (\mathbf{1})$$

$$(\mathbf{1}) \longrightarrow Bu^iAu^{III}(Me)_2L \quad (\mathbf{2})$$

SCHEME

Authentic (**2**) was independently synthesized from Bu^iAu-$Me(PPh_3)Li$ and methyl iodide and identified by elemental analysis and by its ^1H n.m.r. spectrum.

The isomerization of (**1**) was examined at room temperature in diethyl ether solution by ^1H n.m.r., using the well resolved *cis*-Me_2 resonances. As the rearrangement progressed, the doublet at δ 0·27 increased monotonically and that at δ 0·03 decreased concomitantly. Integration showed that the sum of the intensities of the two signals always remained constant (and equal to 6 relative to the 15 aromatic protons), from which we conclude that the isomerization proceeds quantitatively. Finally, removal of the solvent afforded, after recrystallization, pure (**2**) in high yield.

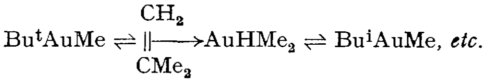
The kinetics of isomerization in dimethoxyethane (DME) solution were first order in (**1**) with $k_1 = 1{\cdot}1 \times 10^{-5}\ s^{-1}$ at 25 °C, $\Delta H^{\ddagger} = 29$ kcal mol^{-1} and $\Delta S^{\ddagger} = 16$ e.u. The rearrangement was not materially affected by the presence of a 3-fold excess of propylene or a 25-fold excess of but-1-ene. The observed first-order rate constant, however, decreased with increasing amounts of added triphenylphosphine. This cannot be due to an associative process such as equation (1)

$$Bu^tAuMePPh_3 + PPh_3 \rightleftharpoons Bu^tAuMe(PPh_3)_2 \qquad (1)$$

since phosphorus n.m.r studies[†] show no indication of the presence of any phosphine adducts in sufficient concentrations to cause the magnitude of rate decrease which occurs.

The following proposed mechanism is based on the observed kinetic parameters and the trapping experiments, which suggest that the rearrangement is dissociative and intramolecular.

$$Bu^tAuMe_2L \rightleftharpoons Bu^tAuMe_2 + L \qquad (2)[‡]$$



$$Bu^tAuMe \rightleftharpoons \overset{CH_2}{\underset{CMe_2}{\|}} \longrightarrow AuHMe_2 \rightleftharpoons Bu^iAuMe,\ etc.$$

The isopropylgold(III) analogue does not rearrange under the same conditions and the use of higher temperatures causes reductive elimination.[1] Furthermore, t-butyl(triphenylphosphine)gold(I) shows no indication of undergoing isomerization. There are other examples of the rearrangement of t-butyl groups attached to the main group elements, boron and aluminium; but these occur only at elevated temperatures [190 and 120 °C (30%), respectively.][2] Among the few known examples of t-alkyl derivatives of transition metals, there are no reports of rearrangement,[3] although there is recent evidence which indirectly suggests the isomerization of sec-alkyliridium(III) and nickel(II) complexes.[4]

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[†] Successive additions of Ph_3P do not alter the phosphorus n.m.r. spectrum of isobutyldimethylgold(III)L under the conditions of the isomerization.

[‡] The dissociation constant for reactions of the type shown in equation (2) is small since a solution of isobutyldimethylgold(III)L in DME shows only one sharp phosphorus resonance at 26·4 p.p.m. (relative to external H_3PO_4).

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