CHEMISTRY LETTERS, pp. 63-66, 1988.

Selective Displacement of a Triphenylphosphine Ligand in Triorgano-(triphenylphosphine)gold(III) with Alkyl Lithiums Affording Tetraalkylaurates(III)

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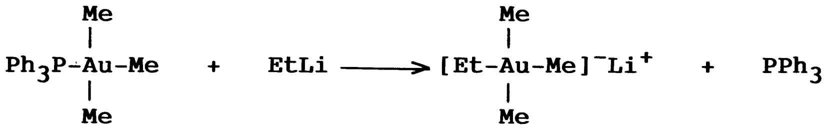
Reactions of cis- and trans-dimethylethyl(triphenylphosphine)gold(III) with ethyl lithium selectively afford anionic square planar cis- and trans-dimethyldiethylaurates(III), respectively. On hydrolysis, the former gives cis-methyldiethyl(triphenylphosphine)gold(III), whereas the latter trans-dimethylethyl(triphenylphosphine)gold(III).

Although anionic organotransition metal ate complexes are frequently utilized in various organic syntheses and are sometimes proposed as active intermediates in the transition metal promoted organic reactions, the chemistry of such ate complexes has been less explored by comparison with that of neutral complexes, except for organocuprates,[1] -(carbonyl)ferrates,[2] and -palladates.[3] In general, combinations of neutral transition metal alkyl complexes with alkylating reagents such as alkyl lithiums and magnesium compounds are known to give such ate complexes in solution.[4] We and Tobias previously reported the formation and some reactions of a simple tetramethylaurate(III).[5] In this paper, we wish to describe the regioselective formation of series of tetraalkylaurates(III) and their hydrolyses resulting in selective formation of novel trialkylgold(III) complexes having a triphenylphosphine ligand.

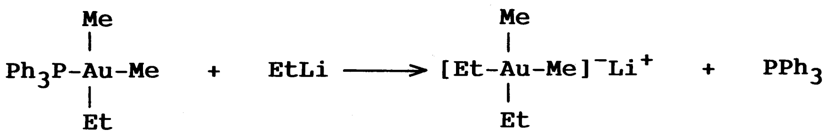
On addition of an equimolar amount of ethyl lithium into a benzene solution of a square planar trimethyl(triphenylphosphine)gold(III), **1** at room temperature, a homogeneous clear solution was obtained and the original two sets of doublets due to methyl-gold in ^{1}H NMR slowly transformed to two singlets in 1:2 ratio at 0.09 and 0.18 ppm. New signals assignable to ethyl-gold are also detected. The spectral change suggests the conversion of trimethyl(triphenylphosphine)gold(III) into a lithium trimethylethylaurate(III), $[\mathrm{AuMe_3Et}]^-\mathrm{Li}^+$, similar to the reaction of **1** with methyl lithium giving lithium tetramethylaurate(III).



$$\mathrm{Ph_3P{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Me} + \mathrm{EtLi} \longrightarrow [\mathrm{Et{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Me}]^-\mathrm{Li}^+ + \mathrm{PPh_3} \qquad (1)$$

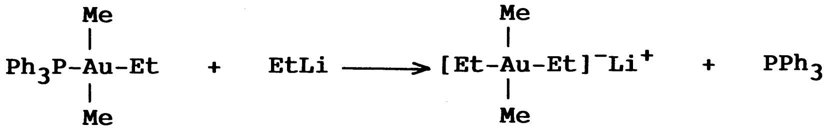
1

The same compounds were also obtained by the reactions of cis- and trans-dimethylethyl(triphenylphosphine)gold(III),[6] **2** and **3** with methyl lithium. Absence of couplings between the methyl or ethyl group with phosphorus nucleus suggests the loss of a triphenylphosphine ligand in solution. Analogous liberation of a tertiary phosphine ligand in the formation of ate complexes has been previously reported in the case of organoaurate(III) -aurate(I) and -palladate(II) complexes.[3,5] The ^{1}H NMR data for a series of tetraalkylaurates(III) described in this report are summarized in Table 1. Thus, the similar reactions of **2** and **3** with equimolar amounts of ethyl lithium in benzene afforded square planar dimethyldiethylaurates(III). The aurates obtained here are considered to be cis and trans isomer, respectively. A methyl signal in trans isomer resonates at slightly lower field than in cis isomer, reflecting their trans influence.



$$\mathrm{Ph_3P{-}}\underset{\mathrm{Et}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Me} + \mathrm{EtLi} \longrightarrow [\mathrm{Et{-}}\underset{\mathrm{Et}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Me}]^-\mathrm{Li}^+ + \mathrm{PPh_3} \qquad (2)$$

2



$$\mathrm{Ph_3P{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Et} + \mathrm{EtLi} \longrightarrow [\mathrm{Et{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Et}]^-\mathrm{Li}^+ + \mathrm{PPh_3} \qquad (3)$$

3

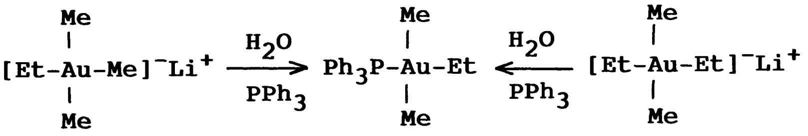
As previously reported, hydrolysis of tetramethylaurates(III) in the presence of triphenylphosphine ligand gives a square planar trimethyl(triphenylphosphine)gold(III).[5] Thus the hydrolyses of these tetraalkylaurates(III) were per-

Table 1. ^{1}H NMR Data for Tetraalkylaurate(III)[a)]

Aurate	Au-CH_3	Au-$C\underline{H}_2CH_3$	Au-$CH_2C\underline{H}_3$
$[AuMe_4]^-Li^+$	0.24s	-	-
$[AuMe_3Et]^-Li^+$	0.09s, 0.18s	0.75q[b)]	1.31t[b)]
cis-$[AuMe_2Et_2]^-Li^+$	0.07s	0.72q[b)]	1.34t[b)]
trans-$[AuMe_2Et_2]^-Li^+$	0.24s	0.68q[b)]	1.32t[b)]

a) In benzene at room temperature. Chemical shifts are referred to internal TMS. b) J=7.8 Hz.

formed in the presence of triphenylphosphine ligand. Addition of excess water into the benzene solution of trimethylethylaurate(III) followed by extraction with ether gave colorless solution. Evaporation of all the volatile matters gave only trans-dimethylethyl(triphenylphosphine)gold(III). Hydrolysis of trans-dimethyldiethylaurate(III) also afforded trans-dimethylethylgold(III) complex.

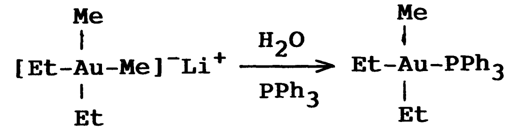


$$[\mathrm{Et{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Me}]^-\mathrm{Li}^+ \xrightarrow[\mathrm{PPh_3}]{\mathrm{H_2O}} \mathrm{Ph_3P{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Et} \xleftarrow[\mathrm{PPh_3}]{\mathrm{H_2O}} [\mathrm{Et{-}}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Et}]^-\mathrm{Li}^+$$

(4)

3(90% selectivity)

On the contrary, cis-methyldiethyl(triphenylphosphine)gold(III), 4 was selectively obtained on hydrolysis of cis-dimethyldiethylaurate(III) which was prepared by the reaction of 2 with ethyl lithium. The complex has been characterized by IR, ^{1}H NMR, and elemental analysis as well as by chemical reactions. Yield 43.6%, d.p.=71 °C. Anal. Found: C, 51.42; H, 5.20%. Calcd for $C_{23}H_{28}PAu$: C, 51.89; H, 5.30%. ^{1}H NMR(in C_6D_6): Au-Me: 0.58ppm (d, J=6.8Hz); Au-$C\underline{H}_2C\underline{H}_3$(cis to P): 1.1-1.3(m); Au-$CH_2C\underline{H}_3$ (trans to P): 1.76 (td, J=13.2, 7.6); Au-$C\underline{H}_2CH_3$(trans to P): 2.44 (qui, J=7.8).

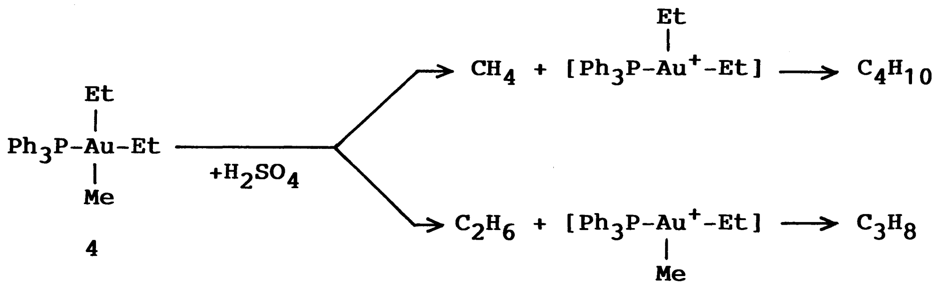


$$[\mathrm{Et{-}}\underset{\mathrm{Et}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}Me}]^-\mathrm{Li}^+ \xrightarrow[\mathrm{PPh_3}]{\mathrm{H_2O}} \mathrm{Et{-}}\underset{\mathrm{Et}}{\overset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}PPh_3}$$

(5)

4(90% selectivity)

Thermolysis of **4** in the solid state at 110 °C liberated mainly propane (22.3%/Au) and n-butane (72.2%). It is interesting to note that no -hydrogen elimination reaction took place and only reductive elimination products were formed in the thermolysis. Acidolysis of **4** with H_2SO_4 gave methane (74.5%) and ethane (16.3%) in addition to propane (21.0%) and n-butane (72.3%). Initial stage of the acidolysis probably gave a mixture of diethylgold(III) and methylethylgold(III) species which further instantaneously decomposed to liberate n-butane and propane, respectively.



(6)

The regioselective hydrolysis of these aurates is best interpreted by the stronger trans effect of ethyl group than methyl in the protonolysis of gold-carbon bond in the tetraalkylaurates(III).

Authors thank for support of the work by Grants in Aid for Scientific Research from the Ministry of Education Science and Culture, Japan (No 62215006).

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(Received October 6, 1987)