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Isolation of Stable Tetraalkylammonium Tetraalkylaurate(III) Complexes

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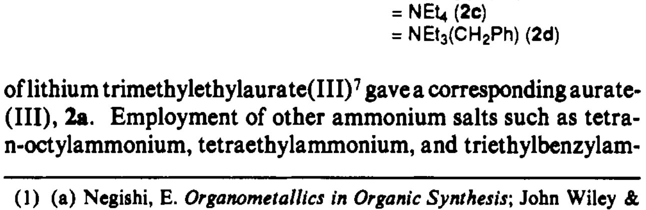
Polymethylmetalates of late transition metals have attracted much attention in relation to organic syntheses and catalyses.[1] However, the chemistry of such metalate complexes has been relatively less explored in comparison with the neutral transition metal alkyl complexes, since their highly anionic character frequently prevents the isolation in a pure form. Lithium polymethylaurates(I or III) are not the exceptions and have been reported to be very unstable both in solution and in the solid state, when exposed to moisture or air.[2-5] However, they are thermally very stable in ether solution and can be isolated as colorless insoluble solids when the lithium cation is ligated with donors such as *N,N,N′,N″,N″*-pentamethyldiethylenetriamine,[3] although they are still extremely sensitive toward moisture. Nevertheless, fluorinated aryl derivatives of aurates are known to be stable.[6] We now report the isolation of stable tetraalkylaurates(III) which are fairly resistant toward hydrolysis and soluble in benzene, by replacing the lithium by a tetraalkylammonium cation.

Treatment of a solution of lithium tetramethylaurate(III), which was prepared by the reaction of trimethyl(triphenylphosphine)gold(III) with an equimolar amount of methyl lithium in ether,[3] with tetra-*n*-butylammonium bromide at room temperature gave stable colorless crystals of tetra-*n*-butylammonium tetramethylaurate(III) (**1**) in 43% yield (eq 1). A similar reaction of lithium trimethylethylaurate(III)[7] gave a corresponding aurate(III), **2a**. Employment of other ammonium salts such as tetra-n-octylammonium, tetraethylammonium, and triethylbenzylammonium also afforded analogous complexes, **2b–d**, whereas the isolation of the aurate with the tetramethylammonium cation failed.



$$[\mathrm{Me{-}}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}R}]^-\mathrm{Li}^+ + (\mathrm{R'})_4\mathrm{NBr} \longrightarrow [\mathrm{Me{-}}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Au}}}\mathrm{{-}R}]^-(\mathrm{R'})_4\mathrm{N}^+ + \mathrm{LiBr} \qquad (1)$$

R = Me; $N(R')_4$ = $N(n\text{-}Bu)_4$ (**1**)
R = Et; $N(R')_4$ = $N(n\text{-}Bu)_4$ (**2a**)
= $N(octyl)_4$ (**2b**)
= NEt_4 (**2c**)
= $NEt_3(CH_2Ph)$ (**2d**)

These complexes were characterized mainly by IR and ^1H NMR spectroscopy and elemental analysis as well as by chemical reactions. Unfortunately, X-ray structural determination of the aurates was not feasible, since the crystals were decomposed by X-ray irradiation. IR spectra of **1** and **2a–d** show no bands which can be assigned to triphenylphosphine ligand, but a ν(Au–C) band at 490 cm^{-1} is seen. Absence of the triphenylphosphine ligand in these aurates(III) is also confirmed by the ^1H NMR spectra which show no signals of triphenylphosphine. Au–Me signals in **1** (0.63 ppm) and **2a–d** (0.5–0.8 ppm) resonate at considerably lower magnetic field than that of the lithium tetramethylaurate(III) (0.24 ppm). Observation of two Au–Me singlets in 1:2 ratio for **2a–d** suggests a square planar structure for the anion.

Acidolysis of **1** with concentrated sulfuric acid liberated methane and ethane in 189 and 99 %/mol of **1**, respectively, and colloidal gold. Successive protonolysis of **1** gave two moles of methane and dimethylgold(III) sulfate, which is spontaneously decomposed by reductive elimination to give ethane.[8] A similar acidolysis of **2a** liberated a mixture of gases containing methane (161%), ethane (54%), propane (44%), and *n*-butane (22%). Although an analogous reaction path may be conceivable, formation of *n*-butane is puzzling in this case. An additional intermolecular process involving coupling of two ethyls during the acidolysis may be involved.[9]

Hydrolysis of **1** with a large excess of water slowly proceeded in the presence of triphenylphosphine in THF. After 1 day at room temperature, trimethyl(triphenylphosphine)gold(III) was formed with concomitant evolution of an equimolar amount of methane (eq 2). The result suggests that the initial stage in the acidolysis involves the formation of a neutral trialkylgold(III) species. It is surprising that the hydrolysis of **1** at 0 °C for 6 h resulted in only 4% conversion, since lithium tetramethylaurate(III) is known to be hydrolyzed by water instantaneously under the same conditions.[5] This unexpected decrease in the nucleophilicity of the tetraalkylaurate(III) by replacing the cation from lithium to tetraalkylammonium is noteworthy.[10] A similar hydrolysis of **2a** in the presence of PPh_3 also proceeded slowly at 0 °C, and further reaction at room temperature for 1 day liberated a mixture of methane and ethane in 77 and 12% yields, respectively (eq 3). Resultant gold(III) products were mainly *trans*-$AuMe_2Et(PPh_3)$ (90%) in addition to a small amount of $AuMe_3(PPh_3)$ (ca. 10%).[11] The alkyl group trans to ethyl is more susceptible to the attack of the proton than that trans to Me. The present high regio- and stereoselectivities in the hydrolysis reflect the large trans effect of the ethyl group. Such

$$\underset{\mathbf{1}}{[\mathrm{AuMe_4}]^-(\mathrm{n\text{-}Bu})_4\mathrm{N}^+} + \mathrm{H_2O} \underset{+\mathrm{PPh_3}}{\longrightarrow} \mathrm{AuMe_3(PPh_3)} + \mathrm{CH_4} \qquad (2)$$

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(10) (a) Such decrease in nucleophilicity of the anion by replacing Li with a nonpolarlyzing countercation is also known in borohydride chemistry in which the nucleophilicity of MBH_4 decreases in the order of M = Li^+ > Na^+ > NR_4^+ (House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin, Inc.: Los Angeles, CA, 1972; p 45. Sullivan, E. A.; Hinckley, A. A. *J. Org. Chem.* **1962**, *27*, 3731). (b) Stable tetrabutylammonium salts of tetramethylruthenates are known (Shapley, P. A.; Kim, H.; Wilson, S. R. *Organometallics* **1988**, *7*, 928).

(11) The amount of a possible gold(III) product, *cis*-$AuMe_2Et(PPh_3)$, is considered to be less than 5%, since the signals assignable to the cis isomer were not detected clearly in ^1H NMR spectra.

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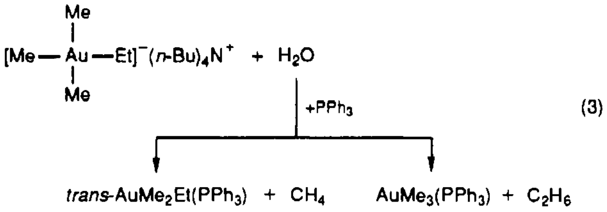

$$[\mathrm{Me{-}AuMe_2{-}Et}]^-(n\text{-}Bu)_4N^+ + H_2O \xrightarrow{+PPh_3} trans\text{-}AuMe_2Et(PPh_3) + CH_4 \quad AuMe_3(PPh_3) + C_2H_6 \qquad (3)$$

a trend has been also observed in the hydrolysis of lithium tetraalkylaurates(III) in the presence of triphenylphosphine ligand.[7]

Unfortunately, the tetraalkylaurates(III) have low chemical reactivities, although most other anionic organometallic metalate complexes, such as organocuprates, are versatile nucleophilic reagents in organic synthesis.[1c] For example, **1** did not react with methyl vinyl ketone in THF at room temperature for 5 days.

Thermolysis of **1** was performed in the solid state at 140 °C. Gases evolved after 2 h consisted of a mixture of methane (16%), ethane (74%), and 1-butene (21%). Further heating at 160 °C for 2 h completed the thermolysis. In the case of **2a** under the same conditions, a mixture of methane, ethane, propane, 1-butene, and *n*-butane was formed. The tetraalkylaurates(III) isolated here are considerably more thermally stable than the corresponding square planar trialkylgold(III) complexes stabilized by the triphenylphosphine ligand, which decompose immediately under these reaction conditions. The reason for the high thermal stability of these aurates has previously been noted.[5] Poorer leaving group properties of the alkyl group compared to the triphenylphosphine ligand prevents the formation of a very unstable T-shaped trialkylgold(III) intermediate. Although ethane from **1** and ethane, propane, and *n*-butane from **2a** may be formed by reductive elimination, the origin for the formation of methane and 1-butene is not well understood. One possible pathway is abstraction of a hydrogen from a butyl group in the cation by the methyl radical giving methane and 1-butene.

Experimental Section

All manipulations were performed under deoxygenated nitrogen or argon using standard Schlenk techniques. Solvents such as ether, THF, benzene, and hexane were dried over benzophenone ketyl and distilled and stored under nitrogen before use. Trialkyl(triphenylphosphine)gold(III) complexes were prepared by the literature methods.[12] Tetraalkylammonium chlorides commercially available were used after drying under vacuum for a few days. Alkyllithiums were prepared from lithium and corresponding alkyl halides in ether or pentane. IR spectra were recorded on JASCO FT-5M and A-302 spectrometers. NMR spectra were taken using JEOL FX-200 and PMX-60 spectrometers.

Tetra-*n*-butylammonium Tetramethylaurate(III) (1). To a solution (5 mL) of lithium tetramethylaurate(III) prepared from $AuMe_3(PPh_3)$ (123.4 mg, 0.245 mmol) and methyllithium (0.245 mmol) was added a THF solution (5 mL) of tetra-*n*-butylammonium bromide (85.0 mg, 0.246 mmol) at 0 °C. After 6 h of stirring at room temperature, all the volatiles were removed in vacuo to give a white solid, which was then extracted with benzene. Benzene was evaporated in vacuo to give again a colorless solid, which was washed with hexane a few times. The colorless solid was recrystallized from THF/ether to give colorless needles. Yield: 52.2 mg (43%). Mp: 97–100 °C. Anal. Found: C, 47.72; H, 9.05; N, 2.95. Calcd for $C_{20}H_{48}NAu$: C, 48.08; H. 9.69; N, 2.80. IR: 495 cm^{-1}. ^1H NMR (ppm from TMS in C_6D_6): 0.63 (s, 12 H, AuMe), 0.96 (t, 12 H, J = 6.6 Hz, $CH_2(CH_2)_2\mathit{CH_3}$), 1.2–1.4 (m, 16 H, $CH_2(\mathit{CH_2})_2CH_3$), 3.0–3.2 (m, 8 H, NCH_2).

Tetra-*n*-butylammonium Trimethylethylaurate(III) (2a). A similar reaction of tetra-*n*-butylammonium bromide (214.3 mg, 0.665 mmol) with trimethylethylaurate(III) prepared from $AuMe_3(PPh_3)$ (299.6 mg, 0.594 mmol) and ethyllithium (0.637 mmol) gave a colorless solution. Workup similar to that for tetramethylaurate(III) gave colorless crystals. Yield: 196.2 mg (64%). Mp: 83–85 °C. Anal. Found: C, 49.18; H, 9.83; N, 2.83. Calcd for $C_{21}H_{50}NAu$: C, 49.11; H, 9.81; N, 2.73. IR: 495 cm^{-1}. ^1H NMR (ppm in C_6D_6): 0.55 (s, 3 H, AuMe trans to Et), 0.63 (s, 6 H, AuMe cis to Et), 0.92 (t, 12 H, J = 7.3 Hz, $CH_2(CH_2)_2\mathit{CH_3}$), 1.1–1.3 (m, 16 H, $CH_2(\mathit{CH_2})_2CH_3$), 1.37 (q, 2 H, J = 7.8 Hz, $Au\mathit{CH_2}CH_3$), 1.94 (t, 3 H, J = 7.8 Hz, $AuCH_2\mathit{CH_3}$), 2.7–2.9 (m, 8 H, NCH_2).

Other tetraalkylaurates(III) were also prepared analogously. However, no pure crystals were obtained, and only spectroscopic data are described below.

Tetra-*n*-octylammonium Trimethylethylaurate(III) (2b). IR: 490 cm^{-1}. ^1H NMR (ppm in C_6D_6): 0.54 (s, 3 H, AuMe trans to Et), 0.60 (s, 6 H, AuMe cis to Et), 0.98 (t, 12 H, J = 7.6 Hz, $CH_2(CH_2)_4\mathit{CH_3}$), 1.2–1.6 (m, 48 H, $CH_2(\mathit{CH_2})_4CH_3$ and $Au\mathit{CH_2}CH_3$), 1.91 (t, 3 H, J = 7.8 Hz, $AuCH_2\mathit{CH_3}$), 3.1 (br, 8 H, NCH_2).

Tetraethylammonium Trimethylethylaurate(III) (2c). IR: 490 cm^{-1}. ^1H NMR (ppm in C_6D_6): 0.50 (br, 12 H, $NCH_2\mathit{CH_3}$), 0.65 (s, 3 H, AuMe trans to Et), 0.73 (s, 6 H, AuMe cis to Et), 1.42 (q, 2 H, J = 7.8 Hz, $Au\mathit{CH_2}CH_3$), 2.03 (t, 3 H, J = 7.8 Hz, $AuCH_2\mathit{CH_3}$), 2.28 (br, 8 H, NCH_2).

Triethylbenzylammonium Trimethylethylaurate(III) (2d). IR: 490 cm^{-1}. ^1H NMR (ppm in C_6D_6): 0.68 (s, 3 H, AuMe trans to Et), 0.71 (br, 9 H, $NCH_2\mathit{CH_3}$), 0.76 (s, 6 H, AuMe cis to Et), 1.44 (q, 2 H, J = 7.2 Hz, $Au\mathit{CH_2}CH_3$), 1.54 (s, 2 H, $N\mathit{CH_2}Ph$), 2.00 (t, 3 H, J = 7.2 Hz, $AuCH_2\mathit{CH_3}$), 2.44 (q, 8 H, J = 7.3 Hz, $N\mathit{CH_2}$), 6.7–7.2 (m, 5 H, $NCH_2\mathit{Ph}$).

Acidolysis of 1. Complex **1** (9.1 mg, 0.0182 mg) was placed in a Schlenk type flask with a rubber septum and the Schlenk flask was evacuated. Concentrated sulfuric acid (0.5 mL) was added through the septum using a hypodermic syringe at room temperature. Small aliquots of evolved gases were taken with a gastight microsyringe and quantitatively analyzed by GC (Porapack Q) using the standard internal method: CH_4 (189%), C_2H_6 (99%).

Acidolysis of 2a. A similar reaction of **2a** (12.7 mg, 0.0247 mmol) with concentrated sulfuric acid liberated CH_4 (161%), C_2H_6 (54%), n-C_3H_8 (44%), and n-C_4H_{10} (22%).

Hydrolysis of 1 in the Presence of PPh_3. To a THF (2.0 mL) solution of **1** (11.8 mg, 0.0236 mmol) in the presence of PPh_3 (62.4 mg, 0.238 mmol) was added water (1.0 mL) at 0 °C. After 6 h only 4% of methane/mol of **1** was detected. Further reaction at room temperature for 27 h liberated an equimolar amount of methane (0.0225 mmol, 95%). Removal of all the volatile gave a colorless solid, which was extracted with ether. ^1H NMR spectroscopy of the resultant solid revealed the presence of $AuMe_3(PPh_3)$ (95%).

Hydrolysis of 2a in the Presence of PPh_3. A similar hydrolysis of **2a** (15.7 mg, 0.0306 mmol) in the presence of PPh_3 (80.4 mg, 0.307 mmol) as above liberated methane (14%) and ethane (2%) at 0 °C for 6 h. Further reaction for 27 h at room temperature gave a mixture of methane (77%) and ethane (12%). The main gold(III) product was *trans*-$AuMe_2Et(PPh_3)$ (90%). Only a small amount of $AuMe_3(PPh_3)$ (ca. 10%) was also detected in the ^1H NMR spectrum.[11]

Thermolysis of 1. A Schlenk type flask containing **1** (5.5 mg, 0.013 mmol) with a rubber septum was evacuated and heated to 140 °C for 2 h. A mixture containing CH_4 (16%), C_2H_6 (74%), and 1-C_4H_8 (21%) was detected. Further heating at 160 °C for 2 h liberated CH_4 (82%), C_2H_6 (207%), and 1-C_4H_8 (78%).

Thermolysis of 2a. A similar thermolysis of **2a** (9.0 mg, 0.0175 mmol) at 140 °C afforded CH_4 (18%), C_2H_6 (37%), n-C_3H_8 (27%), 1-C_4H_8 (36%), and n-C_4H_{10} (28%). Additional heating at 160 °C for 2 h gave CH_4 (39%), C_2H_6 (122%), n-C_3H_8 (30%), 1-C_4H_8 (66%), and n-C_4H_{10} (28%).

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