Reactions of Dialkylaurate(I) with Electrophiles: Synthesis of Trialkylgold(III) Compounds

By **Akihiro Tamaki** and **Jay K. Kochi**,* Chemistry Department, Indiana University, Bloomington, Indiana 47401, U.S.A.

The formation of new dialkylaurate(I) species from alkylgold(I) complexes and alkyl-lithium is described. Lithium dimethyl(triphenylphosphine)aurate(I) is stable only in ether solutions, but the crystalline bis-pyridine analogue can be isolated. A variety of mixed primary, secondary, and tertiary dialkylaurate(I) analogues can also be prepared *in situ* and reacted directly with alkyl halides in the convenient synthesis of trialkylgold(III) complexes. The stereospecific synthesis of *trans*- or *cis*-alkyldimethyl(triphenylphosphine)gold compounds is possible from the reaction of dimethyl(triphenylphosphine)aurate(I) and alkyl halide or *cis*-dimethyliodo(triphenylphosphine)gold and alkyl-lithium, respectively. Bromination and protonolysis of dialkylaurate(I) proceed readily at 0 °C. The lack of selectivity in the cleavage of mixed alkylmethylaurate(I) with hydrogen chloride suggests that it proceeds by oxidative addition, in contrast with the direct proton transfer to the alkyl ligand as in many other electrophilic cleavages. Unsuccessful attempts to add alkenes and co-ordinated olefinic ligands to dialkylaurate(I) are described.

ALKYLGOLD(I) complexes have been shown to undergo oxidative addition with alkyl halides to form trialkylgold(III) species *via* dialkylgold(III) intermediates,[1] *e.g.*,

$$\mathrm{MeAuPR_3 + MeI \longrightarrow [Me_2AuIPR_3] \xrightarrow{MeAuPR_3} Me_3AuPR_3 + IAuPR_3} \quad (1)$$

However, the synthesis of trialkylgold(III) compounds by this method is somewhat limited by the rather slow step involving oxidative addition and also by their limited stability under the reaction conditions.

Anionic organometallate complexes generally show greater nucleophilic reactivity than their neutral counterparts,[2-4] and we felt that they represented the desired species for effecting oxidative addition to gold(I). A method for the preparation of a variety of dialkylaurate(I) complexes given in equation (2) was recently described.[5] In this report we wish to elaborate

$$\mathrm{RAuPR_3 + R'Li \longrightarrow RR'AuPPR_3Li} \quad (2)$$

on the formation and reactions of dialkylaurate(I) species, particularly with electrophiles (*i.e.*, oxidative

---

[1] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1972, **40**, C81.

[2] W. Tochterman, *Angew. Chem. Internat. Edn.*, 1966, **5**, 351.

[3] G. Wittig, *Quart. Rev.*, 1966, **20**, 191.

[4] J. F. Normant, *Synthesis*, 1972, 63.

[5] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1973, **51**, C39.

addition). The following study is presented in 5 parts: (i) synthesis of dialkylaurate(I) and an examination of their reactions with (ii) alkyl halides, (iii) bromine, (iv) Brönsted acids, and (v) alkenes as well as unsaturated ligands.

RESULTS AND DISCUSSION

Formation of Dialkylaurate(I) *Species*.—A colourless homogeneous solution was obtained when methyl(triphenylphosphine)gold was treated with an equimolar amount of methyl-lithium in ether or dimethoxyethane (DME). The ^{1}H n.m.r. spectrum of this solution showed a single methyl resonance at δ $-0{\cdot}19$ p.p.m., relative to external Me_4Si. Since the integrated intensity corresponded to six protons compared to 15 for the phenyl resonance, we deduced that the product contained two equivalent methyl groups for each triphenylphosphine.[5] The methyl singlet broadened as the solution was cooled to −70 °C, but did not split. The n.m.r. spectrum in the presence of an excess of methyl-lithium consisted of the superposition of the individual spectra of lithium dimethylaurate(I) and methyl-lithium as shown in Table 1. The observations of separate resonances for MeAu(I) and MeLi together with the small chemical shifts in the examples above suggest that further association of methyl-lithium with dimethylaurate(I) is small. The rate of such an exchange (if any) is undetermined at this point.

TABLE 1

^{1}H N.m.r. spectra of mixtures of methyl(triphenylphosphine)gold and methyl-lithium in ether

CH_3AuPPh_3 (mmol)	CH_3Li (mmol)	Mol ratio (Au : Li)	Chemical shift δ p.p.m. [a] CH_3Au	CH_3Li	Intensity ratio [b] $CH_3Li : CH_3Au$
	0·239	0·00		−1·94	
0·060	0·239	0·25	−0·23	−1·89	(1·50)
0·120	0·239	0·50	−0·20	−1·84	0·44(0·50)
0·179	0·239	0·75	−0·19	−1·80	0·19(0·17)
0·239	0·239	1·00	−0·18		

[a] Relative to external Me_4Si, ±0·05 p.p.m. [b] Calculated value in parentheses.

Examination of the phosphorus n.m.r. spectrum of an ether solution prepared from equimolar amounts of methyl(triphenylphosphine)gold and methyl-lithium consisted of a single sharp resonance at 5·8 p.p.m. upfield from phosphoric acid (external standard). The chemical shift and lineshape were unchanged in the presence of an equimolar excess of either methyl-lithium or triphenylphosphine. Indeed, the phosphorus resonance coincided with that of free triphenylphosphone (δ $-5{\cdot}8$ p.p.m.) under the same conditions. Since it is highly unlikely that free triphenylphosphine and that co-ordinated to dimethylaurate(I) have identical chemical shifts, we conclude that lithium dimethyl(triphenylphosphine)aurate(I) is extensively dissociated in ether solution.*

Indeed, triphenylphosphine can be separated by crystallization from an ether solution (*ca.* 2M) of lithium dimethyl(triphenylphosphine)aurate(I) on cooling to −78 °C. The n.m.r. spectrum of the resulting colourless solution still shows the single methyl resonance with the same chemical shift as that of the solution of the precursor. A solution of lithium dimethylaurate(I) prepared in this manner is relatively stable at room temperature. Attempts to isolate lithium dimethylaurate(I) as a stable crystalline solid have been unsuccessful as yet, and this probably indicates that it exists in solution as a complex with co-ordinated ether.

Further evidence for this structure was obtained by isolating and characterizing the bis-pyridine derivative. Pyridine (2 equivalents) was added to an ether solution of lithium dimethyl(triphenylphosphine)aurate(I) which was allowed to stand for an hour when it slowly afforded very pale yellow crystals of lithium dimethylbis(pyridine)aurate(I), which although stable at 0 °C was sensitive to air and moisture. The n.m.r. spectrum consisted of a single methyl resonance in pyridine. The methyl singlet (δ $-0{\cdot}30$ p.p.m.) in ether solution remained unshifted down to −90 °C, and its integrated intensity showed the presence of one CH_3 group for each pyridine ligand.

The α,α'-bipyridine adduct crystallized as a colourless solid when one equivalent of bipyridine was added to an ether solution of dialkyl(triphenylphosphine)aurate(I).

Mixed dialkylaurate(I) complexes (R = Me, Et, Pr^i, Bu^t, Ph, or neopentyl) could be prepared from other alkylgold(I) complexes and alkyl-lithium reagents.

Synthesis of Trialkylgold(III) *Compounds*.—Dialkylaurate(I) complexes were found to give trialkylgold(III) compounds on oxidative addition of alkyl or aryl halides according to reaction (3) (see Experimental section).

$$R^1R^2AuPR^3{}_3Li + R^4X \longrightarrow R^1R^2R^4AuPR^3{}_3 + LiX \quad (3)$$

$$(R^1 = R^2 = Me;\ R^3 = Ph \text{ or } Me;\ R^4 = Me, CD_3, Et, Pr^i, Pr^n, Bu^i, Bu^n, \text{ or } Ph;\ X = Br \text{ or } I)$$

n-Propyl, n-butyl, and isobutyl iodides reacted to afford the corresponding *trans*-alkyldimethyl(triphenylphosphine)gold in a relatively high state of stereochemical purity. This could be readily determined from the n.m.r. spectra, since *cis*-CH_3 groups in square planar trialkyl(triphenylphosphine)gold compounds show doublet splittings in the range δ $-0{\cdot}1$ to $0{\cdot}3$ p.p.m. (*J ca.* 7 Hz) and *trans*-CH_3 groups are doublets further downfield (δ 1·0—1·3 p.p.m., *J ca.* 9 Hz) with a 6 : 3 intensity ratio relative to 15 for phenyl in ether or DME.

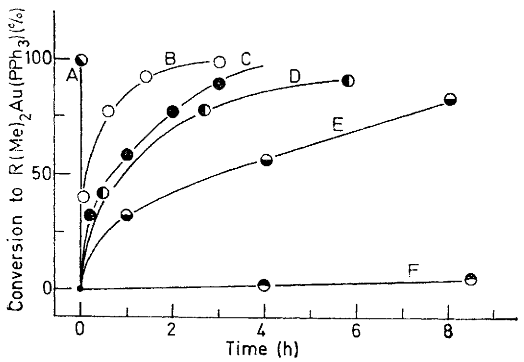
Iodobenzene was unique in that it reacted to afford

---

* The compound prepared *in situ* from methyl(triphenylphosphine)gold and methyl-lithium will be referred to as lithium dimethyl(triphenylphosphine)aurate(I) despite the extensive dissociation of triphenylphosphine in ether solution. Dr. S. Tobias also found, from Raman studies that this dissociation is extensive (personal communication).

almost exclusively *cis*-phenyldimethyl(triphenylphosphine)gold, together with large amounts of trimethyl- and some methyl-(triphenylphosphine)gold. The presence of the latter compounds indicated that alkyl exchange was a factor.[1,6] Dimethylaurate(I) reacted with t-butyl chloride to deposit a purple solid on the walls of the flask, which was not investigated further.

The rates of reduction of alkyl halides with dimethylaurate(I) were measured in ether solution by periodic examination of the n.m.r. spectra The reactivities of various organic halides illustrated in the Figure indicate the sequence: Me > Et > Bu^n and I > Br ≫ Cl. Isopropyl bromide and iodide showed no significant reaction with dimethylaurate(I) under these conditions.



Rates of oxidative addition of various alkyl halides (0·239 mmol) to an equimolar amount of lithium dimethyl(triphenylphosphine)aurate(I) in diethyl ether solution at room temperature; A, MeI; B, EtI; C, Bu^nI; D, PhI; E, Bu^nBr; F, Bu^nCl

At this point, it is interesting to compare the reactivity of methyl(triphenylphosphine)gold and dimethyl(triphenylphosphine)aurate(I) to oxidative addition of methyl iodide. The formation of trimethyl- from methyl-(triphenylphosphine)gold requires a week at 0 °C, despite the use of methyl iodide as solvent.[1] The reaction is severely retarded by dilution. Under the same conditions, dimethylaurate(I) reacts completely on mixing a stoicheiometric amount of methyl iodide in ether solution.

Reaction of Alkyl(or Aryl)methylaurate(I) *with Methyl Iodide*.—The alkyl(or aryl)methylaurate(I), $RMeAu^I$ (R = Et, Bu^t, neopentyl, or phenyl) were prepared from the alkyl(or aryl)(triphenylphopshine)gold(I) compounds and methyl-lithium in ether solution. Methyl iodide (1 mol equivalent) was added and the alkyl(or aryl)dimethylgold(III) product was isolated in the usual way. All the solutions showed, in the n.m.r. spectra, the presence of two methyl groups *cis* to phosphorus.

The t-butyl compound spontaneously rearranged to give isobutyldimethyl(triphenylphosphine)gold(III) as has been reported.[7]

Reaction of cis-*Dimethyliodo*(*triphenylphosphine*)*gold with Alkyl-lithium*.—A report by Tobias *et al*.[8] indicated that *cis*-dimethyliodo(triphenylphosphine)gold and cyclopentadienylsodium underwent exchange with retention of configuration.

$$cis\text{-}Me_2Au(PPh_3)I + RLi \longrightarrow cis\text{-}Me_2Au(PPh_3)R + LiI \quad (4)$$

We find that an analogous reaction can be carried out with alkyl-lithium, which allows a variety of *cis*-alkyldimethyl(triphenylphosphine)gold compounds to be synthesized, which are isomeric with the *trans*-compounds prepared above from dimethylaurate(I) and alkyl iodides. The n.m.r. spectra of all of these compounds in benzene solution showed two pairs of doublet resonances for Me *cis* to P (δ 0·1—0·2 p.p.m., *J ca.* 7 Hz) and Me *trans* to P (δ 1·3—1·4 p.p.m., *J ca.* 9 Hz) in a 3 : 3 intensity ratio relative to 15 for phenyl.

Reaction of Dialkyl(*triphenylphosphine*)*aurate*(I) *with Bromine*.—Lithium dimethyl(triphenylphosphine)aurate(I) reacted rapidly with an equimolar amount of bromine in ether solution. The resulting colourless crystals consisted of a mixture of predominantly trimethyl-, some methyl- and small amounts of dimethylbromo- and bromo-(triphenylphosphine)gold.

Since the expected product, $Me_2AuBr(PPh_3)$, was not obtained in high yield, oxidative addition of bromine (equation 5) may have been followed by a fast subsequent alkyl exchange (equation 6). Methyl transfer from the neutral $MeAu(PPh_3)$ to $Me_2AuBr(PPh_3)$ has been shown previously.[1] When an excess of bromine was employed the resulting solid contained triphenylphosphine but no methyl groups (n.m.r. analysis).

$$Me_2Au(PPh_3)Li + Br_2 \longrightarrow Me_2AuBr(PPh_3) + LiBr \quad (5)$$

$$Me_2AuBr(PPh_3) + Me_2Au(PPh_3)Li \xrightarrow{\text{fast}} Me_3Au(PPh_3) + MeAu(PPh_3) + LiBr \quad (6)$$

Protonolysis of Dialkylaurate(I) *Complexes*.—Ethylmethyl(triphenylphosphine)aurate(I) was prepared from a suspension of ethyl(triphenylphosphine)gold and an equimolar amount of methyl-lithium at room temperature. After the mixture became homogeneous, a dilute solution of hydrogen chloride in ether was slowly and carefully added at 0 °C. Lithium chloride precipitated immediately and a gaseous mixture of methane

$$EtMeAu(PPh_3)Li + HCl \begin{cases} \longrightarrow CH_4 + EtAu(PPh_3) + LiCl \\ \longrightarrow C_2H_6 + MeAu(PPh_3) + LiCl \end{cases} \quad (7)$$

---

[6] A. Tamaki and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 6487.

[7] A. Tamaki and J. K. Kochi, *J.C.S. Chem. Comm.*, 1973, 423.

[8] S. W. Krauhs, G. C. Stocco, and R. S. Tobias, *Inorg. Chem.*, 1971, **10**, 1365.

and ethane was evolved simultaneously. N.m.r. analysis of the residue indicated the presence of ethyl- and methyl-(triphenylphosphine)gold in 32 and 37% yields, respectively. Analyses of the hydrocarbon mixture obtained from reaction carried out at various temperatures are listed in Table 2.

t-Butylmethylaurate(I) prepared from t-butyl(triphenylphosphine)gold and methyl-lithium was similarly treated with a solution of hydrogen chloride in ether at 0 °C. The gaseous mixture of hydrocarbons consisted of 48% methane and 50% isobutane. N.m.r. analysis of the residue indicated the presence of t-butyl- and methyl-(triphenylphosphine)gold in 41 and 43%, respectively.

This striking lack of selectivity in the protonolysis of dialkylaurate(I) complexes is unusual. A variety of mechanisms have been proposed in the electrophilic cleavages of alkyl–metal bonds,[9] but all of them proceeding by proton transfer favour methyl cleavage over ethyl cleavage. The specificity increases with steric hindrance imposed by α-branching, and usually alkylmetals containing methyl and secondary or tertiary alkyl groups can be highly selectively cleaved.

$$\mathrm{Me_3CAuMe(PPh_3)Li + HCl}\left\{\begin{array}{l}\longrightarrow \mathrm{Me_3CH + MeAu(PPh_3) + LiCl} \\ \longrightarrow \mathrm{CH_4 + Me_3CAu(PPh_3) + LiCl}\end{array}\right. \qquad (8)$$

TABLE 2

Protonolysis of ethylmethylaurate(I) with hydrogen chloride

	Yield (mol %)		
Products	0 °C	−15 °C	−78 °C
Methane	43	38	30
Ethane	54	45	50
$\mathrm{EtAu(PPh_3)}$		32	
$\mathrm{MeAu(PPh_3)}$		37	

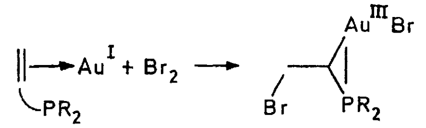
We suggest that protonolysis of dialkylaurate(I) proceeds *via* oxidative addition to form an hydridogold(III) intermediate,* from which alkane could be

$$\mathrm{RMeAu(PPh_3)Li + HCl \longrightarrow RMeAu(H)(PPh_3) + LiCl} \qquad (9)$$

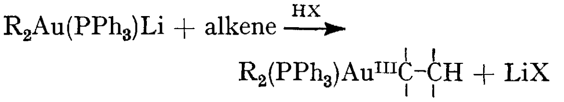
formed by subsequent reductive elimination from the *cis* or *trans* adduct. The rapid rate of reaction suggests that the addition of a proton to the aurate(I) complex is exothermic and may occur without a high degree of stereoselectivity. We are unable at this point to delineate the stereoselectivity in the reductive elimination. However, if we were to take analogy with the reductive elimination of two alkyl groups from trialkylgold(III) complexes,[6] we would describe it as *cis*-elimination. Preliminary n.m.r. studies at low temperatures did not detect the presence of such a hydridogold(III) species, but further studies are planned.

The protonolysis of alkylmetals by a mechanism involving oxidative addition is not without precedent. Thus, Belluco *et al.*[10] suggested on the basis of kinetic evidence that the protonolysis of square planar *trans*-methylhalogeno(triphenylphosphine)$_2$platinum(II) proceeds *via* a six-co-ordinate hydridoplatinum(IV) adduct, followed by *cis*-elimination of methane.

Reaction of Dialkylaurate(I) *with Alkenes and Unsaturated Ligands.*—Gold(I) complexes are known to form π-olefin complexes.[11] A bromine-induced oxidative addition of an olefinic phosphine co-ordinated to gold(I) schematically represented in equation (10) was recently reported.[12] We wished to examine the possibility of effecting a similar transformation to dialkylaurate(I) complexes in order to afford trialkylgold(III) compounds, *e.g.*,



(10)



$$\mathrm{R_2Au(PPh_3)Li + alkene \xrightarrow{HX} R_2(PPh_3)Au^{III}C{-}CH + LiX} \qquad (11)$$

Alkene addition to lithium dimethyl(triphenylphosphine)aurate(I) was examined in a concentrated ether solution diluted with a large excess of but-1-ene at −78 °C. Hydrogen chloride, as well as the hindered bases, 2,6-lutidinium chloride and 2,6-di-t-butyl-*p*-cresol reacted rapidly with this solution, but afforded mainly methyl(triphenylphosphine)gold. The n.m.r. spectrum of the solution indicated the presence of only small amounts of MeAu^{III} species (*vide supra*). Similar reactions with buta-1,3-diene were also unsuccessful.

Diallyl ether or allyl methyl ether (employed as the medium) showed no reaction with dimethylaurate(I) even after 4 days at room temperature. Addition of hydrogen chloride or di-t-butylcresol at −78 °C was followed by a rapid reaction, but only methyl(triphenylphosphine)gold could be identified. Methylgold(III) species were present in higher concentrations than with simple olefins; but the yields were still so low that no effort was made to isolate them.

---

* Owing to its lability the presence or absence of triphenylphosphine in the hydridogold intermediate has not yet been established.

[9] For a review see M. H. Abraham, ' Comprehensive Chemical Kinetics,' eds., C. Bamford and L. Tipper, vol. XII, Elsever, 1973.

[10] U. Belluco, M. Giustiniani, and M. Graziani, *J. Amer. Chem. Soc.*, 1967, **89**, 6494.

[11] R. Hüttel and H. Reinheimer, *Chem. Ber.*, 1966, **99**, 2778.

[12] M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 1971, **93**, 4591.

Pent-4-enyl(triphenylphosphine)gold was treated with an equimolar amount of methyl-lithium to generate the *mixed* aurate(I) species, $CH_2{:}CH{\cdot}[CH_2]{\cdot}AuMe(PPh_3)Li$. Reaction with either hydrogen chloride or di-t-butylcresol did not afford a $MeAu^{III}$ species.

Pent-4-enyldiphenylphosphine and but-3-enyldiphenylphosphine were used to prepare the corresponding chlorogold(I) phosphine complex. Treatment of either complex with two equivalents of methyl-lithium afforded the corresponding $Me_2(RPPh_2)Au^{I}$ species [R = pent-4-enyl or but-3-enyl]. However, there was no evidence for the formation of $MeAu^{III}$ species on further reaction with either hydrogen chloride or di-t-butylcresol.

We conclude from these studies that oxidative addition of dialkylaurate(I) cannot be achieved with the C=C function by protonation. We suspect that the difficulty may lie in the inability of dialkylaurate(I) to form olefinic π-complexes in sufficient concentrations to compete with the direct protonolysis described in the previous section.

EXPERIMENTAL

Materials.—Diethyl ether and DME were dried with sodium benzophenone ketyl. After refluxing, the ethers were distilled under nitrogen.

Methyl-lithium (Foote Chemical Co.) was recrystallized three times from ether. A DME solution of methyl-lithium was prepared by drying the recrystallized material *in vacuo* and redissolving it in the solvent. The concentrations of methyl-lithium were determined by acidimetric titration with standard hydrochloric acid solution. Ethyl-lithium in benzene and t-butyl-lithium in n-pentane were from Foote Chemical Co. and used as such.

Alkyl halides were commercial samples (Eastman white label or Aldrich Chemical Co.) and dried over phosphorus pentoxide and transferred *in vacuo*.

Methyl(triphenylphosphine)gold and phenyl(triphenylphosphine)gold were prepared from chloro(triphenylphosphine)gold and the corresponding organolithium reagent according to a procedure described by Coates and Parkin.[13] Ethyl- and neopentyl-(triphenylphosphine)gold were prepared from chloro(triphenylphosphine)gold and the corresponding Grignard reagent by the procedure described by Gregory and Ingold [14] for methyl(triphenylphosphine)gold. Isopropyl- and t-butyl-(triphenylphosphine)gold were described previously.[15]

Lithium Dimethylbispyridineaurate(I).—In a typical preparation $MeAu(PPh_3)$ (218 mg, 0·450 mmol) was suspended in ether (2 ml), then methyl-lithium (0·450 mmol) was added at room temperature. The mixture was stirred under nitrogen until a colourless homogeneous solution was obtained. Pyridine (0·920 mmol) in ether (0·33 ml) was then added and the solution separated into two pale yellow layers. Crystals grew in both layers on standing for 2 h. The combined crystals were washed three times with ether and dried *in vacuo* below 0 °C.

The analysis for gold was carried out by heating a weighted sample in sulphuric acid (0·5 ml). The gold metal was washed successively with sulphuric acid, water, and acetone on a tared glass frit, which was finally dried with a gas flame and weighed.[16] The analysis was also repeated with a sample twice as large.

Lithium was analysed by addition of water to the sample, and filtering the resulting metallic gold. The mixture was dried *in vacuo* and the residue redissolved in water and titrated with standard hydrochloric acid (Found: Au, 49·5, 50·6; Li, 1·8, 2·0. Calc. for $C_{12}H_{16}AuLiN_2$: Au, 50·25; Li 1·8%).

The n.m.r. spectrum of a crystallized sample of lithium dimethylbispyridineaurate(I) examined in DME solution showed a sharp singlet at δ −0·30 p.p.m. (relative to external Me_4Si). Multiplet resonances at δ 7·2—7·6, 7·6—8·0, and 8·8—9·2 p.p.m. were assigned to the 3,5, 4, and 2,6 protons of pyridine and the integrated intensities 4H, 2H, and 4H, respectively, taking the methyl absorption as 6H. Proton resonances due to triphenylphosphine were absent.

Trimethyl(triphenylphosphine)gold.—Methyl iodide was added to dimethylaurate(I) prepared from methyl(triphenylphosphine)gold (1·08 mmol) and of methyl-lithium (1·2 mmol). After an exothermic reaction occurred, the resulting colourless solution was evaporated *in vacuo* and the residue extracted with pentane. Trimethyl(triphenylphosphine)gold was obtained in 75% yield on cooling the solution; m.p. 115° (decomp.), lit.,[14,17] 119; 120°. N.m.r. ($DCCl_3$): CH_3 *cis* to P (6H), δ 0·55 p.p.m., *J* 7·0 Hz, CH_3 *trans* to P (3H), δ 1·64 p.p.m., *J* 9·2 Hz. In dioxane solution: CH_3 *cis* to P: δ 0·15 p.p.m., *J* 7·0 Hz; CH_3 *trans* to P: δ 1·27 p.p.m., *J* 9·1 Hz.

Reaction of Dimethylaurate(I) *with* [$^2H_3$] *Methyl Iodide.*—Methyl(triphenylphosphine)gold (86·8 mg. 0·182 mmol) was dissolved in DME (0·156 ml) containing methyl-lithium (0·183 mmol). An equimolar amount of [$^2H_3$]-methyl iodide was added at 0 °C. The n.m.r. spectrum of the resulting solution showed a doublet due to *cis*-Me groups at δ 0·14 p.p.m. (*J* 7·0 Hz, intensity = 4·8 H taking the phenyl signal as 15·0H) and another doublet due to *trans*-Me groups at δ 1·18 p.p.m. (*J* 8·9 Hz intensity = 0·4 H). We estimate the yields of *trans*- and *cis*-$CD_3Me_2Au(PPh_3)$ as 73 and 13%, respectively. Methyl(triphenylphosphine)-gold was also formed in 13% yield.

Trimethyl(trimethylphosphine)gold.— Dimethyl(trimethylphosphine)aurate(I) prepared from $(PMe)_3AuCl$ (1·65 mmol) and methyl-lithium (3·7 mmol) was treated with an excess of methyl iodide. The resulting solution was quenched with water (20 ml), and the mixture extracted with pentane. The pentane solution was dried and concentrated *in vacuo*. The residual trimethyl(trimethylphosphine)gold [18] (45%) remained as a colourless oil, which was transferred bulb to bulb *in vacuo*. N.m.r. (dioxane): CH_3 *cis* to P (6H), δ 0·62 p.p.m., *J* 7·8 Hz; CH_3 *trans* to P (3H), δ 1·34 p.p.m., *J* 9·7 Hz; CH_3–P (9H), δ 1·13 p.p.m., *J* 9·9 Hz.

trans-*Ethyldimethyl(triphenylphosphine)gold.*—A solution of dimethylaurate(I) prepared from 474 mg (1·00 mmol) of methyl(triphenylphosphine)gold (474 mg, 1 mmol) and methyl-lithium (1 mmol) in ether (1·86 ml) was treated with

---

[13] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3220.

[14] B. J. Gregory and C. K. Ingold, *J. Chem. Soc.* (*B*), 1969, 276.

[15] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, in press.

[16] C. L. Wilson and D. W. Wilson, ' Comprehensive Analytical Chemistry,' Elsevier, Amsterdam, vol IC, 1961, p. 390.

[17] C. Calvin, G. E. Coates, and P. S. Dixon, *Chem. and Ind.*, 1959, 1628.

[18] A. Shiotani, H.-F. Klein, and H. Schmidbaur, *J. Amer. Chem. Soc.*, 1971, **93**, 1555.

ethyl iodide (1·25 mmol) at room temperature for 20 h. The solvent was removed *in vacuo* and the residue extracted with pentane (100 ml). The pentane extract was concentrated to 20 ml and chilled to −20 °C, whereupon a 56% yield of ethyldimethyl(triphenylphosphine)gold was obtained as colourless crystals (Found: C, 50·6; H, 4·95; Au, 37·5. Calc. for $C_{22}H_{26}AuP$: C, 51·0; H, 5·05; Au, 38·0%). In the n.m.r. spectrum (dioxane solution), the two methyl groups appeared as a doublet (δ 0·29 p.p.m., *J* 7·0 Hz) and the ethyl and phenyl groups as multiplets between δ 0·9—2·4 and 7·4—8·1 p.p.m., respectively, with the correct intensity ratios. Molecular weight in n-heptane (v.p.o.) 528 (calc. 518).

trans-*n-Butyldimethyl(triphenylphosphine)gold* was prepared in 48% yield by a similar procedure from n-butyl iodide (Found: Au, 35·6. Calc. for $C_{24}H_{30}AuP$: Au, 36·0%). N.m.r. (dioxane): Me_2Au: δ 0·25 p.p.m., *J* 6·5 Hz; Bu^n: δ 1·0—2·3 p.p.m. multiplet.

trans-*n-Propyldimethyl(triphenylphosphine)gold* was obtained in 42% yield from dimethylaurate and n-propyl iodide. N.m.r. (dioxane): Me_2Au: δ 0·22 p.p.m., *J* 7·1 Hz, Pr^n: δ 1·0—2·4 p.p.m. multiplet. Molecular weight in n-heptane (v.p.o.) 538 (calc. 532).

trans-*Isobutyldimethyl(triphenylphosphine)gold* was obtained from either dimethylaurate and isobutyl bromide (after 9 days at room temperature) or isobutyl iodide (3 days). It was isolated as a colourless crystalline solid in 42% yield from pentane. N.m.r. (dioxane): Me_2Au: δ 0·27 p.p.m., *J* 7·4 Hz; $(CH_3)_2C$: δ 1·27 p.p.m., *J* 6·6 Hz.

trans-*Isopropyldimethyl(triphenylphosphine)gold* was prepared from $LiMePr^iAu(PPh_3)$ and methyl iodide in 33% yield. N.m.r. (dioxane): Me_2Au: δ 0·14 p.p.m., *J* 6·9 Hz; $(CH_3)_2CH$: δ 1·56 p.p.m. doublet (*J* 12·4 Hz) of doublets (*J* 6·4 Hz). In benzdne: Me_2Au: δ 0·37 p.p.m.; *J* 7·0 Hz; $(CH_3)_2CH$: δ 1·50 p.p.m., *J* 7·0 Hz; doublet (*J* 12·7 Hz) of doublets (*J* 6·9 Hz).

trans-*Phenyldimethyl(triphenylphosphine)gold* was obtained in 30% yield, together with 35% $Me_3(PPh_3)Au$ and 17% $Me(PPh_3)Au$ when dimethylaurate(I) was treated with iodobenzene at room temperature for one day. N.m.r. (CH_2Cl_2): CH_3 *cis* to P, δ 0·76 p.p.m., *J* 7·4 Hz. CH_3 *trans* to P: δ 1·77 p.p.m., δ 9·0 Hz.

Reaction of (Alkyl or Aryl)methylaurate(I) *with Methyl Iodide*.—*Phenyl(triphenylphosphine)gold* (128·3 mg, 0·239 mmol) was dissolved in ether and methyl-lithium (0·239 mmol) added at 0 °C. Addition of methyl iodide caused an exothermic reaction to take place, the solution was then evaporated and the residue extracted with dioxane. The n.m.r. spectrum in dioxane indicated a 4 : 1 mixture of *cis*-phenyldimethyl(triphenylphosphine)gold (CH_3 *cis* to P, 0·34 p.p.m., *J* 7·3 Hz; CH_3 *trans* to P: δ 1·33 p.p.m. *J* 9·0 Hz) and trimethyl(triphenylphosphine)gold (CH_3 *cis* to P: δ 0·16 p.p.m., *J* 7·0 Hz; CH_3 *trans* to P: δ 1·24 p.p.m., *J* 9·0 Hz).

Ethylmethylaurate(I) was prepared in ether solution from equimolar amounts of $EtAu(PPh_3)$ and MeLi. The n.m.r. spectrum showed the presence of a methyl (δ −0·18 p.p.m., singlet) and an ethyl ligand (CH_2: δ 0·6—1·1 p.p.m. multiplet; CH_3, δ 1·58 triplet). On addition of an equimolar amount of methyl iodide, the original signal disappeared immediately and was replaced by three pairs of doublets due to $Me_3Au(PPh_3)$, *cis*- and *trans*-$EtMe_2Au(PPh_3)$. The latter (70%) was the same as that derived from dimethylaurate(I) and ethyl iodide (*vide supra*).

neo-Pentamethylaurate(I) prepared from neopentyl(triphenylphosphine)gold (0·237 mmol) and methyl-lithium (0·237 mmol) completely reacted in 8 min with an equimolar amount of methyl iodide at 0° C to afford *trans*-neopentyldimethyl(triphenylphosphine)gold as the principal adduct. N.m.r. spectrum (dioxane solution): two methyl groups *cis* to phosphorus, δ 0·05 p.p.m., *J* 6·9 Hz; neopentyl group, δ 1·09 p.p.m. (singlet) Me_3, δ 2·18 p.p.m. doublet *J* 8·0 Hz) CH_2.

t-Butylmethylaurate(I) also formed one principal isomer, t-butyldimethyl(triphenylphosphine)gold, on reaction with methyl iodide at −78 °C. The mixture was warmed to room temperature and the ether removed *in vacuo*. The crude mixture was extracted with pentane and afforded *trans*-t-butyldimethyl(triphenylphosphine)gold, which spontaneously rearranged to the isobutyl isomer on standing.[7]

Reactions of Mixed Alkylmethylaurate(I) *with Methyl Iodide (Alkyl = Isopropyl, t-Butyl, or Neopentyl)*.—All aurate(I) species were prepared from alkyl(triphenylphosphine)gold and methyl-lithium in ether solutions. An equimolar amount of methyl iodide was added and the trialkylgold(III) product isolated in the usual manner. All the solutions showed the presence of Me_2 *cis* to phosphorus which integrated to 6H in the n.m.r. spectra. For example, in dioxane solution the methyl groups in the neopentyl moiety showed a singlet resonance at δ 1·09 and the methylene group a doublet (δ 2·18 p.p.m., *J* 8·0 Hz), which showed the correct intensity ratios relative to *cis*-Me_2 (δ 0·05 p.p.m., *J* 6·9 Hz).

Reaction of Dimethylaurate(I) *with Bromine*.—Dimethylaurate(I) was prepared from $(PPh_3)AuCl$ (0·884 mmol) and methyl-lithium (1·77 mmol) in ether (5 ml). Bromine (0·87 mmol) was added at 0 °C. After 20 min, the solvent was evaporated and the residue dissolved in chloroform. The n.m.r. spectrum showed the presence of $Me_3(PPh_3)Au$ and $Me(PPh_3)Au$, together with small amounts of *cis*-dimethylbromo(triphenylphosphine)gold (n.m.r.: spectrum CH_3 *trans* to P: δ 1·53 p.p.m., *J* 8·8 Hz; CH_3 *cis* to P: δ 1·99 p.p.m., *J* 8·2 Hz) and $(PPh_3)AuBr$.

Reaction of Trimethyl(triphenylphosphine)gold with Iodine.—Trimethyl(triphenylphosphine)gold dissolved in a minimum volume of methylene chloride was treated with one molar equivalent of iodine dissolved in the same solvent.

$$Me_3AuPPh_3 + I_2 \longrightarrow Me_2AuIPPh_3 + MeI$$

The solvent was removed *in vacuo* and the residue recrystallized from acetone afforded *cis*-dimethyliodo(triphenylphosphine)gold in 70% yield, which was identical with that obtained from *bis*-dimethyliodogold(III).[19] The synthesis of *cis*-dimethyliodo(trimethylphosphine)gold was carried out with $Me_3(PMe)_3Au$ using the same procedure.

cis-*Ethyldimethyl(triphenylphosphine)gold* was prepared by mixing equimolar amounts of *cis*-dimethyliodo(triphosphine)gold and ethyl-lithium in ether until the exchange was complete. The mixture was poured into water and extracted several times with ether. The combined ethereal extracts after washing with water and drying over sodium sulphate was evaporated. *cis*-Ethyldimethyl(triphenylphosphine)gold (67%) was recrystallized from pentane. N.m.r. (dioxane): CH_3 *cis* to P: δ 0·15 p.p.m., *J* 6·9 Hz, CH_3 *trans* to P: δ 1·31 p.p.m., *J* 9·0 Hz; *cis*-CH_3–CH_2: δ 1·04 p.p.m., multiplet (Found: C, 50·4; H, 4·95. Calc. for $C_{22}H_{26}AuP$: C, 50·95; H,

---

[19] F. Brain and C. S. Gibson, *J. Chem. Soc.*, 1939, 762.

5·05%). Molecular weight in n-heptane (v.p.o.) 526 (calc. 518).

cis-*n-Propyldimethyl(triphenylphosphine)gold* was prepared by a similar procedure in 62% yield. N.m.r.: CH_3 *cis* to P: δ 0·17 p.p.m., *J* 6·9 Hz; CH_3 *trans* to P: δ 1·32 p.p.m., *J* 8·9 Hz; Pr^n: 0·5—2·0 multiplet. Molecular weight in n-heptane (v.p.o.) 522 (calc. 532).

cis-*Isopropyldimethyl(triphenylphosphine)gold* was prepared by reacting *cis*-iododimethyl(triphenylphosphine)-gold(III) with an equimolar amount of isopropyl-lithium in ether. The mixture was then poured into water and extracted with ether. Removal of the ether afforded *cis*-isopropyldimethyl(triphenylphosphine)gold in 44% yield. N.m.r.: CH_3 *cis* to P: δ 0·13 p.p.m., *J* 7·2 Hz; CH_3 *trans* to P and $(CH_3)_2CH$: 1·0—1·3 multiplets.

Proton n.m.r. spectra were obtained on a Varian HA100 (variable temperature control) spectrometer or routinely on a Varian EM-360 spectrometer. All chemical shifts were measured (±0·05 p.p.m.) relative to external Me_4Si. ^{31}P N.m.r. spectra were taken on a Varian XL-100 Fourier transform spectrometer, using H_3PO_4 as an external reference.

We wish to thank the National Science Foundation for financial support of this work, and Mr. S. Magennis for the synthesis of some of the trialkylgold complexes and Dr. R. S. Tobias for helpful discussions regarding the Raman spectra of dialkylaurate(I).

[3/1090 *Received, 30th May, 1973*]