Registry No. $ZnPS_3$, 56172-70-4; $FePS_3$, 12140-43-1.

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Synthesis of Tetramethylaurate(III). Studies on the Structures of Li[$(CH_3)_2Au$] and Li[$(CH_3)_4Au$] in Solution

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Reaction of CH_3Li with $(CH_3)_3AuP(C_6H_5)_3$ in diethyl ether solution gives essentially a quantitative conversion to $Li[(CH_3)_4Au]$. Both the Raman and proton magnetic resonance spectra are consistent with a structure in solution involving solvated Li^+ ions and essentially square planar $(CH_3)_4Au^-$ anions, i.e., solvent-separated ion pairs. The d^8 anion is coordinatively saturated, for $P(C_6H_5)_3$ does not interact with it. This system provides a good example of the declining significance of $d\pi$–$d\pi$ back bonding as an explanation of the stabilization of electron rich systems. The analogous gold(I) species, $Li[(CH_3)_2Au]$, produced by the known reaction between CH_3Li and $CH_3AuP(C_6H_5)_3$ also occurs as a solvent-separated ion pair with a coordinatively saturated d^{10} anion. This has a linear skeletal structure, and the Raman active vibrations correlate smoothly with those of $(CH_3)_2Hg$, $(CH_3)_2Tl^+$, and $(CH_3)_2Pb^{2+}$. The strengths of the metal–carbon bonds decrease from Au to Pb in a reversal of the usual variation with nuclear charge. Ether solutions of CH_3Li give weak Raman scattering, and the spectrum is compared with that of t-C_4H_9Li and discussed in terms of the nature of the lithium alkyls in solution.

Introduction

Although the existence of simple dialkylaurate(I) species was suggested by Coates and Parkin[1] in 1962 and a compound characterized as $[Et_4N^+][((C_6H_5)_3Ge)_2Au^-]$ was isolated by Glockling and Wooten[2] in the same year, only recently have studies on the simple dimethylaurate(I) and its higher homologs been reported.[3,4] This is in marked contrast to the analogous copper compounds, the "homocuprates", which have been considered since 1952.[5] Their chemistry and applications in organic synthesis have been reviewed recently.[6]

Lithium dimethylaurate(I) has been reported by Tamaki and Kochi to be formed as a clear, colorless solution in diethyl ether or dimethoxyethane according to reaction 1. Proton

$$CH_3AuPR_3 + CH_3Li \rightarrow (CH_3)_2AuPR_3Li \qquad (1)$$

NMR showed the methyl groups in the product to be equivalent, yielding a single resonance unsplit at −70°. It was concluded[4] that the phosphine was not coordinated to gold based on (i) the absence of ^{31}P coupling to the methyl–gold protons, (ii) the chemical shift of the ^{31}P resonance of the phosphine, (iii) the separation, on cooling, of the triphenylphosphine from a sample prepared from CH_3AuPPh_3, and (iv) Raman spectra obtained by us on a sample of $(CH_3)_2AuPPh_3Li$ provided by Professor Kochi.

In this paper we report the synthesis of the first peralkylgold(III) complex, lithium tetramethylaurate(III). In spite of the fact that alkyl derivatives of gold(III) along with platinum(IV) were the first stable metal alkyls isolated,[7] the aurate(III) species have not been observed previously. As discussed by Wilkinson,[8] one way in which an alkyl can be stabilized against decomposition is by coordinative saturation of the metal. This appears to be the case for both the aurate(I) and aurate(III) species. Extensive studies using laser Raman and ^1H NMR spectroscopy have been carried out on both the dimethylaurate(I) and tetramethylaurate(III) species in solution, and conclusions concerning their structures have been drawn.

Experimental Section

Synthesis. Diethyl ether used for solutions was distilled from $LiAlH_4$ under dry nitrogen immediately before use. Sample preparation was carried out under an atmosphere of prepurified nitrogen or argon which had been passed through a drying column. A solution of halide-free methyllithium in diethyl ether was prepared from $(CH_3)_2Hg$ and lithium sand; excess lithium and lithium amalgam were removed by filtration. Methyllithium-d_3 was prepared by reaction of methyl iodide-d_3 with lithium wire. Elemental analyses were carried out in the Departmental Microanalytical Laboratory.

$CH_3AuP(C_6H_5)_3$ and $CD_3AuP(C_6H_5)_3$. These were prepared by the method of Coates and Parkin.[1] Anal. Calcd for $C_{19}H_{18}PAu$: C, 48.1; H, 3.82. Found: C, 48.0; H, 4.08. Calcd for $C_{19}H_{15}D_3PAu$: C, 47.8; H, 4.43. Found: C, 47.2; H, 4.53.

$(CH_3)_3AuP(C_6H_5)_3$ and $(CD_3)_3AuP(C_6H_5)_3$. These were synthesized by the procedure of Coates and Parkin[9] using $Cl_3Au(py)$ as the starting material. Anal. Calcd for $C_{21}H_{24}PAu$: C, 50.0; H, 4.80. Found: C, 49.9; H, 4.58. Calcd for $C_{21}H_{15}D_9PAu$: C, 49.1; H, 6.47. Found: C, 49.4; H, 6.61.

$Li[(CH_3)_2Au]$ and $Li[(CD_3)_2Au]$. The aurate(I)'s were prepared from the corresponding alkyl(triphenylphosphine)gold(I) complex after the method of Tamaki and Kochi.[3] In a typical experiment, 0.1446 g (0.305 mmol) of $CH_3AuP(C_6H_5)_3$ was placed in a thin-walled NMR tube capped with a serum stopple, an argon atmosphere was provided, and 1.0 ml of 0.5 *M* CH_3Li in ether was syringed into the tube. The ether-insoluble $CH_3AuP(C_6H_5)_3$ readily dissolved with shaking.

$Li[(CH_3)_4Au]$ and $Li[(CD_3)_4Au]$. These were prepared by a procedure analogous to that used for the aurate(I)'s employing $(CH_3)_3AuP(C_6H_5)_3$ and $(CD_3)_3AuP(C_6H_5)_3$, respectively, as starting materials. It also is possible to synthesize the compounds by reaction of $KAuCl_4$ with an excess of CH_3Li using the method employed by Gilman and Woods[10] in the first synthesis of trimethylgold(III) compounds. At room temperature, the solutions are quite stable if air is excluded.

LiI·2py. The bis(pyridine) adduct is formed from a solution of anhydrous LiI in diethyl ether prepared by reacting a saturated solution of I_2 in ether with lithium wire. Excess lithium was removed by filtration from the resulting clear, pale yellow-brown solution. Two equivalents of pyridine dried by distillation from KOH were added for each equivalent of iodide calculated. The precipitate which formed immediately was collected by filtration, washed with ether, and dried under vacuum to yield a white powder which was extremely hygroscopic and liberated pyridine when exposed to air. Anal. Calcd for $C_{10}H_{10}N_2LiI$: C, 41.1; H, 3.45; I, 43.4. Found: C, 41.1; H, 3.58; I, 43.2.

Raman Spectra. Solution spectra were obtained using an instrument which has been described recently.[11] Excitation was with the 514.5 nm line of a Coherent Radiation Model 52 Ar^+ laser, and sample spectra and difference spectra were machine plotted from the digital data using program RAMAN.[11] The ether solutions were contained in 5 mm thin-walled NMR tubes and were irradiated normal to the tube axis. The automatic difference mode[11] of the spectrophotometer could not be used, because of the nature of the sample cells. Consequently the difference spectra had to be obtained from separate scans of the monochromator and are less accurate than our normal difference spectra. Spectra of solids were obtained with a Jarrell-Ash 25-300 spectrophotometer using 632.8 nm He–Ne excitation. The frequencies of sharp bands are believed to be accurate to ±2 cm^{-1}.

Infrared Spectra. A Beckman IR-12 spectrometer was used to obtain the spectra. Calibration was effected with polystyrene film and indene. The frequencies for sharp bands are accurate to ±2 cm^{-1}, while those for broad bands should be accurate within ±5 cm^{-1}. Standard techniques for handling air-sensitive materials[12] were used. The cells employed had polyethylene or KBr windows.

Proton Magnetic Resonance Spectra. Spectra were obtained with Varian A-60A and Perkin-Elmer R-32 (90 MHz) spectrometers with probe temperatures of 40 and 35°, respectively. Solvent peaks, calibrated with TMS, were used for internal references. Chemical shifts are believed to be accurate to ±0.03 ppm.

Data and Results

Proton Magnetic Resonance Data. The chemical shifts for solutions in diethyl ether of $Li(CH_3)_2Au$ and CH_3Li were reported previously[4] to be τ 10.18–10.23 and 11.80–11.94 ppm, respectively, relative to external TMS with the shift dependent on the amount of excess CH_3Li present. When $(CH_3)_3AuP(C_6H_5)_3$ (I) is reacted with CH_3Li in diethyl-d_{10} ether, changes in the ^1H NMR spectrum analogous to those which occur in the gold(I) case are observed. These are illustrated in Figure 1. The two doublets of I decrease in intensity as CH_3Li is added and are replaced by a single resonance at τ 10.05 ppm which is superimposed on the higher field component of the $(CH_3)_3AuP(C_6H_5)_3$ doublet centered at 9.96 ppm. Simultaneously, the triphenylphosphine resonances characteristic of I are replaced by resonances typical of uncoordinated $P(C_6H_5)_3$. Integration of the final spectrum after reaction was complete shows that there are four equivalent methyl groups bound to gold for each $P(C_6H_5)_3$ present. These data indicate the formation of $Li(CH_3)_4Au$ (II). Under the conditions of these experiments, reaction is not extremely fast as indicated by the data in Figure 1.

The possibility that the single proton resonance arises because of rapid methyl–methyl exchange between I and CH_3Li is ruled out by the simultaneous observation of resonances due both to I and the tetramethylaurate(III) species, II, as illustrated in Figure 1. The chemical shifts in spectra where both I and II are present are the same as those measured for the corresponding resonances in samples containing only a single gold(III) species, indicating that the bands did not arise from time averaging of more than one resonance. Furthermore, when II is prepared directly from $K[AuCl_4]$ and excess CH_3Li, the chemical shift of the methylgold protons is the same as that measured in samples prepared from **I** which contain $P(C_6H_5)_3$, demonstrating that interaction of II with $P(C_6H_5)_3$ is not significant. Finally methyl exchange between II and CH_3Li is not rapid, because signals due to both species are observed in the ^1H NMR spectrum, Figure 1.

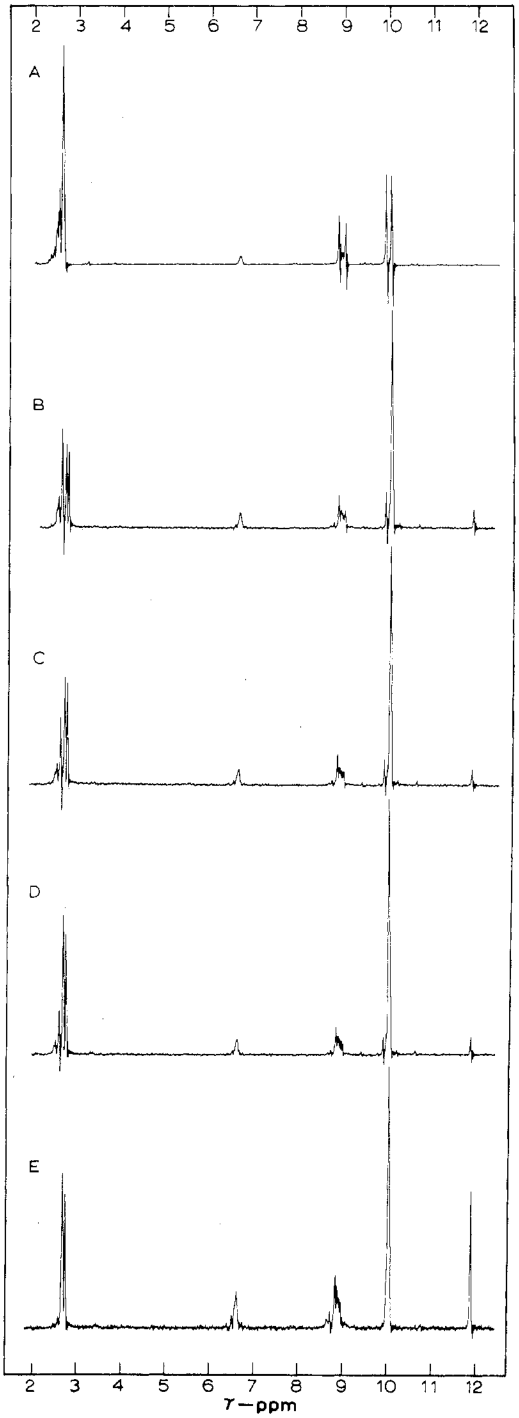


Figure 1. Proton magnetic resonance spectra (60 MHz) of solutions of $(CH_3)_3AuP(C_6H_5)_3$ in diethyl-d_{10} ether with varying mole ratios of CH_3Li: A, $(CH_3)_3AuP(C_6H_5)_3$ alone; B, $(CH_3)_3AuP(C_6H_5)_3$ + CH_3Li, mole ratio 1.41:1, spectrum recorded 2 min after mixing; C, same solution as B, spectrum recorded 5 min after mixing; D, same solution as B, spectrum recorded 8 min after mixing; E, solution containing only $Li[(CH_3)_4Au]$, $P(C_6H_5)_3$, and excess CH_3Li. The signals at τ ca. 8.89 and 6.59 ppm are due to traces of incompletely deuterated diethyl-d_{10} ether.

At first it was considered possible that reaction of I with CH_3Li might have led to reduction to $Li[(CH_3)_2Au]$, since the single resonance at τ 10.05 ppm is only slightly downfield

Table I. NMR Spectral Parameters[a]

Compd	$\tau(CH_3)$, ppm	$^3J(^{31}P\text{-}H)$, Hz	Rel intensity[b]	$\tau[P(C_6H_5)_3]$, ppm	$\tau(CH_3Li)$, ppm
$(CH_3)_3AuP(C_6H_5)_3$	9.96	7	6	2.56, 2.60	
	8.89	9	3		
$Li[(CH_3)_4Au]$	10.05		12	2.68, 2.73[c]	11.88
$CH_3AuP(C_6H_5)_3$	9.47	8	3	2.47, 2.53	
$Li[(CH_3)_2Au]$	10.28		6	2.73, 2.79[c]	11.83
CH_3Li					11.80
$P(C_6H_5)_3$				2.70, 2.77	

[a] All solutions are in diethyl ether except $CH_3AuP(C_6H_5)_3$ which is in $CDCl_3$ solution. [b] Based on a $P(C_6H_5)_3$ intensity of 15. [c] $P(C_6H_5)_3$ quantitatively liberated by the reaction.

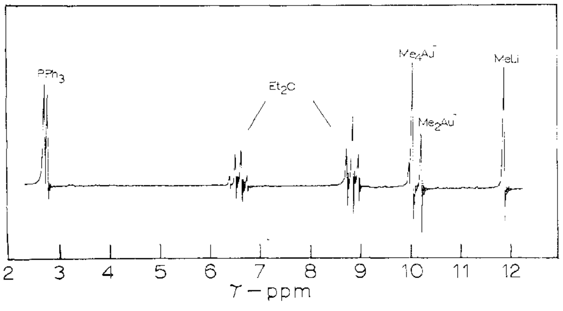


Figure 2. Proton magnetic resonance spectrum (60 MHz) of a solution in diethyl-d_{10} ether containing $CH_3AuP(C_6H_5)_3$, $(CH_3)_3AuP(C_6H_5)_3$, and CH_3Li in a 1:1:6 mole ratio. A small amount of $(C_2H_5)_2O$ is also present.

from the position of the $Li[(CH_3)_2Au]$ resonance which also is somewhat variable. This possibility can be excluded, since reaction of CH_3Li with approximately equimolar amounts of $CH_3AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_6H_5)_3$ gave the ^1H NMR spectrum shown in Figure 2. Resonances due to both dimethylaurate(I) and tetramethylaurate(III) are observed with an intensity ratio of ca. 1:2. The spectrum also shows clearly that only one type of phosphine, uncoordinated, is present. The ^1H NMR data are collected in Table I.

Raman Spectra. Pronounced changes occur in the Raman spectra of $CH_3AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_6H_5)_3$ when they are titrated with CH_3Li in diethyl ether. Figure 3 illustrates the effect of CH_3Li on the spectrum of $CH_3AuP(C_6H_5)_3$. The spectrum of crystalline $CH_3AuP(C_6H_5)_3$ is illustrated, because the compound is only slightly soluble in ether; however, only small changes in band position occur upon dissolution. The spectrum of a saturated solution of $CH_3AuP(C_6H_5)_3$ in ether estimated to be a few millimolar in concentration was obtained. The intense ν(Au–C) and phosphine modes observed with the solid at 544 and 1101 cm^{-1}, respectively, are found at 539 and 1099 cm^{-1} in the solution spectrum. Reaction of $CH_3AuP(C_6H_5)_3$ with CH_3Li causes a decrease in frequency of the (Au–C) stretching vibration and some broadening of the band. The difference spectrum clearly shows moderately intense bands at 526 and 1173 cm^{-1}; in addition, the $P(C_6H_5)_3$ band observed at 1101 cm^{-1} in the monomethyl complex and which is sensitive to coordination of the phosphine shifts to 1093 cm^{-1}, the value observed for $P(C_6H_5)_3$ in diethyl ether solution. All of the phosphine frequencies in ether with or without CH_3Li present are the same showing that there is no interaction between the phosphine and methyllithium. The $\delta(CH_3)$ frequency increases slightly from 1167 (crystal) to 1173 cm^{-1} upon formation of the dimethylaurate(I). The difference spectra also indicate the presence of weak bands in the solution at 1205 and 490 cm^{-1}.

The infrared spectra of the $Li[(CH_3)_2Au]$ solutions yield little information. The ether modes combined with the intense absorptions of $P(C_6H_5)_3$ obscure all of the expected aurate(I) fundamentals. Spectra were obtained with dimethylaurate(I) prepared by reaction of CH_3Li with $CH_3AuP(CH_3)_3$, and this solution showed broad bands at 500 and 750 cm^{-1} which were characteristic neither of CH_3Li nor of $P(CH_3)_3$. The former band is only ca. 10 cm^{-1} higher in frequency than one characteristic of the CH_3Li solution.

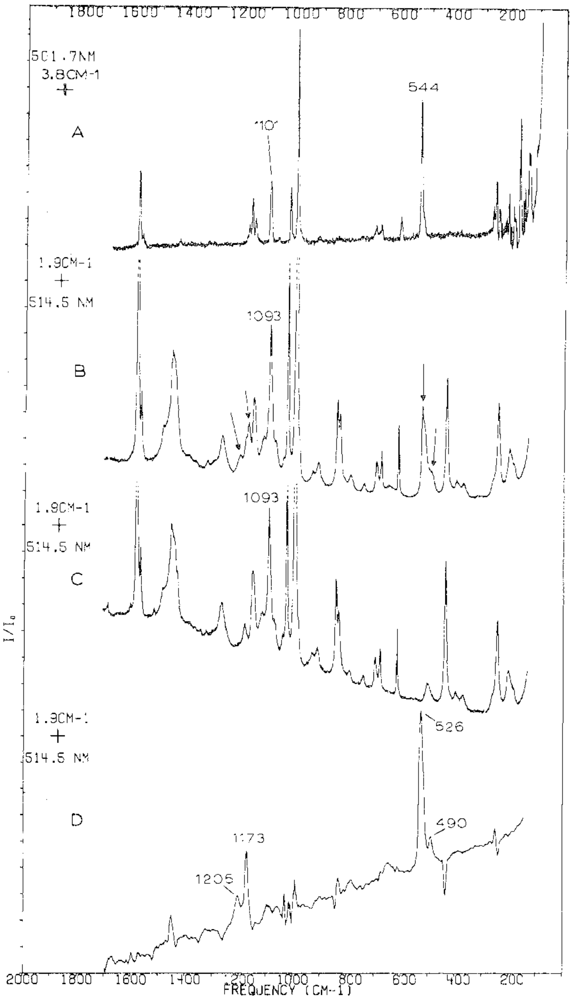


Figure 3. Raman spectra of $Li(CH_3)_2Au$ and related species: A, crystalline $CH_3AuP(C_6H_5)_3$; B, $Li(CH_3)_2AuP(C_6H_5)_3$ in diethyl ether; C, $P(C_6H_5)_3$; D, Raman difference spectrum (B – C).

Halide-free solutions of CH_3Li in diethyl ether show moderately strong Raman active cluster modes at 486, 299, 209, and 171 (shoulder) plus scattering at ca. 1133 cm^{-1} which lies under a complex envelope of $(C_2H_5)_2O$ bands. The typical low frequency ν(C–H) mode appears at 2766 cm^{-1}. Spectra of ether solutions of CH_3Li and diethyl ether are illustrated in Figure 4. The band at 299 cm^{-1}, particularly, is useful for monitoring the concentration of CH_3Li present. It, perhaps, should be noted that methyllithium solutions in diethyl ether prepared by reaction of lithium metal and methyl iodide show none of these cluster modes. Halide ions appear to destroy the $[CH_3Li]_4$ clusters. Even with a 1:3 LiI:CH_3Li solution at 25°, the cluster modes have disappeared. Consequently the spectrum reported here is quite different from that given by

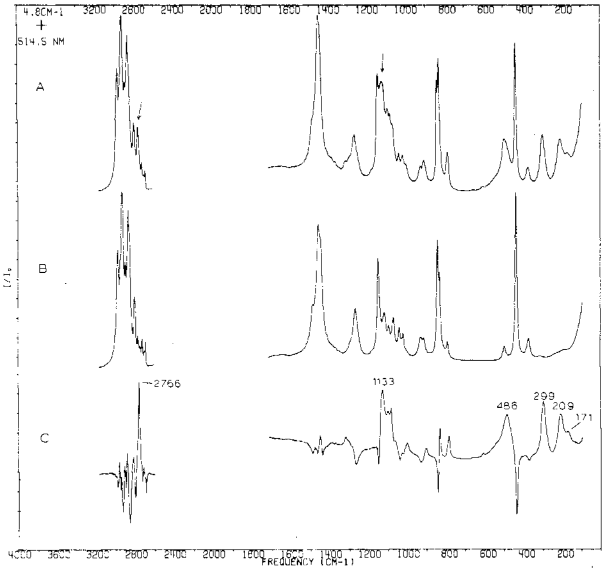


Figure 4. Raman spectrum of methyllithium. A, halide-free CH_3Li in diethyl ether; B, diethyl ether; C, Raman difference spectrum (A – B).

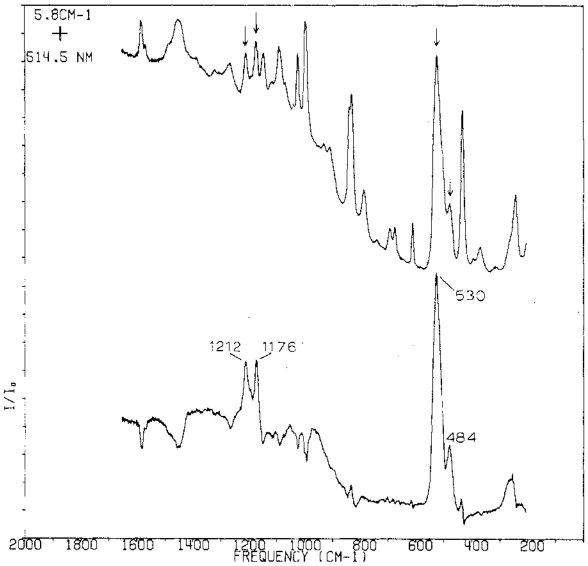


Figure 5. Raman spectrum of $Li[(CH_3)_4Au]$: top, $(CH_3)_3AuP(C_6H_5)_3$ (0.3 *M*) + CH_3Li (0.3 *M*) in diethyl ether; bottom, difference spectrum [$(CH_3)_3AuP(C_6H_5)_3$ (0.3 *M*) + CH_3Li (0.3 *M*) + $(C_2H_5)_2O$] – [$P(C_6H_5)_3$ (0.3 *M*) + $(C_2H_5)_2O$].

Krohmer and Goubeau[13] for methyllithium containing LiCl.

When $(CH_3)_3AuP(C_6H_5)_3$ is reacted with CH_3Li, the band characteristic of bound phosphine at 1100 cm^{-1} [14] decreases to 1091 cm^{-1}, again indicating displacement of the phosphine upon alkylation of the gold center. The intense ν(Au–C) bands of $(CH_3)_3AuP(C_6H_5)_3$ at 506 and 538 cm^{-1} are replaced by an intense band at 530 cm^{-1} and a much weaker band at 484 cm^{-1}. The $\delta(CH_3)$ frequencies are almost unchanged from the values of $(CH_3)_3AuP(C_6H_5)_3$. The solution spectrum and the difference spectrum in which the ether and $P(C_6H_5)_3$ contributions have been subtracted are illustrated in Figure 5. The anomalous base line results from the deposition of material on the sample cell wall at the solution–wall interface where the laser beam passed through the wall; this occurs only in samples containing uncoordinated phosphine. The difference spectrum shows only two bands in the (Au–C) stretching region and two in the $\delta_s(CH_3)$ region. These bands appear at the same positions when the tetramethylaurate(III) solutions are prepared from $K[AuCl_4]$ with no $P(C_6H_5)_3$ present.

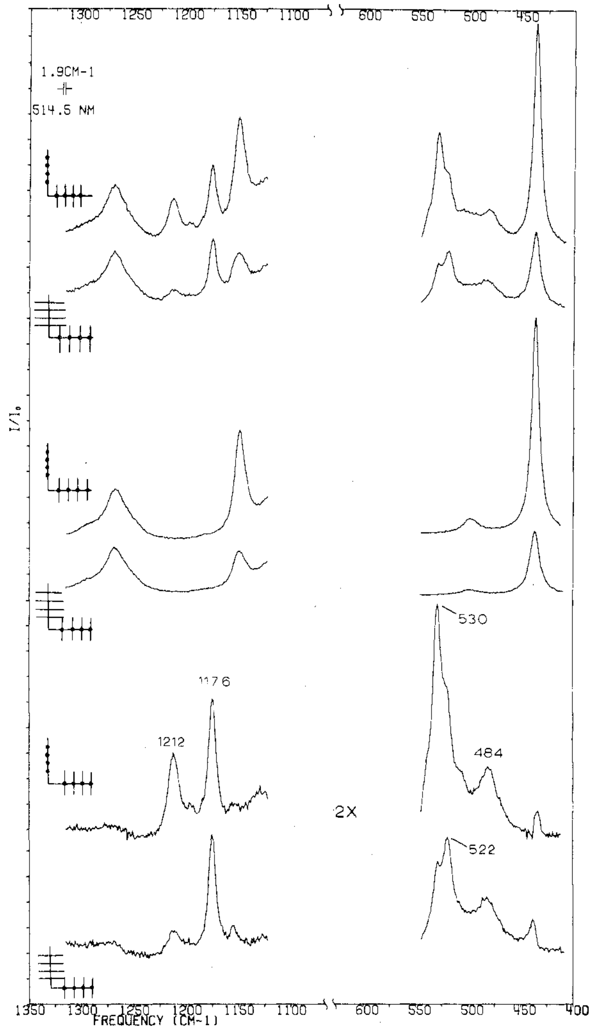


Figure 6. Determination of the depolarization ratios for $Li[(CH_3)_4Au]$. The geometry is such that ρ for a depolarized band is 6/7. A (top), $Li[(CH_3)_4Au]$ + $P(C_6H_5)_3$ + $(C_2H_5)_2O$; B (center), $(C_2H_5)_2O$; C (bottom), Raman difference spectrum (A – B).

Table II. Raman Frequencies of Lithium Tetramethylaurate(III), Lithium Dimethylaurate(I), and Related Compounds in Diethyl Ether Solution

Compd	$\nu(Au-CH_3)$, cm^{-1}	$\delta_s(CH_3)$, cm^{-1}
$Li[(CH_3)_4Au]$	530 p, 522 dp, 484 dp	1212 p, 1176 dp
$Li[(CD_3)_4Au]$	485[a]	922, 903[c]
$(CH_3)_3AuP(C_6H_5)_3$	538 p, 506 dp	1210 p, 1176 dp
$(CD_3)_3AuP(C_6H_5)_3$	492, 464	928, 903[c]
$Li[(CH_3)_2Au]$	526	1173
$Li[(CD_3)_2Au]$	477	908[c]
$CH_3AuP(C_6H_5)_3$	539[b]	1167[d]
$CD_3AuP(C_6H_5)_3$	492[d]	912[d]

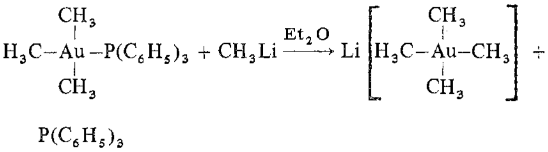
[a] Other bands obscured by solvent. [b] 544 cm^{-1} for a powder sample. [c] Uncertainties are rather large because of the presence of weak solvent bands at ca. 913 and 933 cm^{-1}. [d] Crystalline sample.

Figure 6 illustrates the data for determining the state of polarization of the Raman bands in the ν(Au–C) and $\delta_s(CH_3)$ regions. These show that the 1212 cm^{-1} methyl deformation is totally symmetric as is the 530 cm^{-1} ν(Au–C) stretch. It also is seen from these higher resolution measurements that the 530 cm^{-1} band overlaps a depolarized band at 522 cm^{-1}.

The Raman data are collected in Table II. Frequencies also are given for the perdeuterio compounds. The (Au–C) totally symmetric stretching frequencies measured for these compounds agree well with values calculated from the light hydrogen analogs treating the methyl groups as point masses. Ideally the A_{1g} frequencies would differ by $(6/5)^{1/2} = 1.095$; observed, $Au(CH_3)_2^-$, 1.10_5; $Au(CH_3)_4^-$, 1.09_1.

Discussion

Since the tetramethylaurate(III) does not bind triphenylphosphine and there are no low frequency modes suggestive of any type of cluster, the ion would be expected to have a square planar skeletal structure formed according to reaction 2. The ^1H NMR spectra are entirely consistent with the



$$\begin{matrix} & CH_3 & \\ & | & \\ H_3C- & Au & -P(C_6H_5)_3 \\ & | & \\ & CH_3 & \end{matrix} + CH_3Li \xrightarrow{Et_2O} Li\left[\begin{matrix} & CH_3 & \\ & | & \\ H_3C- & Au & -CH_3 \\ & | & \\ & CH_3 & \end{matrix}\right] + P(C_6H_5)_3 \qquad (2)$$

occurrence of this reaction. The (Au–C) coordinates of a square planar structure will transform as $A_{1g} + B_{1g} + E_u$. Only the A_{1g} and B_{1g} modes should be Raman active. The symmetric methyl deformations transform according to the same representation, so only two should be Raman active. The survey spectrum, Figure 5, shows two bands in the $\delta_s(CH_3)$ and two in the ν(Au–C) regions plus a broad band at ca. 260 cm^{-1} assigned to δ(C–Au–C). Careful measurements using difference spectra of the depolarization ratio of the 530 cm^{-1} band reveal that it consists of a 530 cm^{-1} polarized component plus a 522 cm^{-1} depolarized component. Since the dielectric constant of diethyl ether is 4.4 at 20°,[15] it probably is too much to hope that the tetramethylaurate(III) will obey free ion selection rules.

Although ether has a low dielectric constant, it is a reasonably good donor solvent, and Li^+ is likely to be strongly solvated. This is indicated by the high solubility of many ionic compounds in diethyl ether; for example, anhydrous $LiClO_4$, LiBr, and LiI are soluble to more than 1 *M* which corresponds to more than 10 mol % solute. Consequently, solvent-separated ion pairs might be expected. In general planar anions appear particularly susceptible to perturbation by ion pairing.[16] Clearly, the 530 cm^{-1} band arises from the A_{1g} mode. Either the 522 or the 484 cm^{-1} band should correspond to the B_{1g} mode. The third mode could arise from the Raman forbidden E_u (D_{4h} selection rules) (Au–C) stretching mode allowed by a lowering of the symmetry from that of the free ion. Moreover, a square planar tetramethylaurate(III) will not obey D_{4h} selection rules exactly, although they would be expected to be a good approximation with free rotation of the methyl groups. An examination of the vibrations of the isoelectronic $[Pt(NH_3)_4]^{2+}$ [17] shows that the skeletal stretches all occur in a narrow range: $A_{1g} \sim 538$, B_{1g} 526, $E_u \sim 510$, while the skeletal deformation is at 270 cm^{-1}. This comparison suggests that the 522 cm^{-1} band is due to the B_{1g} aurate mode.

Replacement of the phosphine of $(CH_3)_3AuP(C_6H_5)_3$ by CH_3^- has practically no effect on the symmetric methyl deformation region, but the effect on (Au–C) stretching modes is more significant. A normal coordinate analysis of $(CH_3)_3AuP(CH_3)_3$ [18] indicated that the higher frequency Raman band at 540 cm^{-1} corresponds primarily to motion of the unique methyl group, while the lower frequency band at 512 cm^{-1} results from in-phase stretching of the mutually trans methyl groups. A significant trans–trans interaction force constant of 0.20 mdyn $Å^{-1}$ was necessary to fit the data. Coordination of the fourth methyl group to $(CH_3)_3AuP(C_6H_5)_3$ causes the highest frequency ν(Au–C) band to decrease by 8 to 530 cm^{-1}.

Displacement of $P(C_6H_5)_3$ from $CH_3AuP(C_6H_5)_3$ by CH_3^-, reaction 3, again causes little change in the methyl deformation

$$CH_3\text{-}Au\text{-}P(C_6H_5)_3 + LiCH_3 \rightarrow Li[CH_3\text{-}Au\text{-}CH_3] + P(C_6H_5)_3 \qquad (3)$$

region, and a frequency decrease of 11 cm^{-1} occurs in the totally symmetric (Au–C) vibration. The normal modes of $[M(CH_3)_2]^z$ species have been discussed.[19] The (Au–C) coordinates of a linear $(CH_3)_2Au^-$ species will transform as $A_{1g} + A_{2u}$, and the symmetric methyl deformations transform according to the same representations. Accordingly, one stretching mode and one symmetric methyl deformation should be Raman active. The survey spectrum shows bands at 526 and 1173 cm^{-1} as expected. Once more, the difference spectra also indicate the presence of additional weak bands at 490 and 1205 cm^{-1}. These may result from perturbations of solvent bands or they may arise from the formation of different types of ion pairs. There are no modes indicating cluster formation. This coupled with the observation that phosphine is released upon alkylation suggests that the aurate(I) anion is monomeric. The $\delta_s(CH_3)$ and ν(Au–C) modes of $(CH_3)_2Au^-$ correlate smoothly with the corresponding vibrations of other isoelectronic $[M(CH_3)_2]^z$ species as illustrated in Figure 7. Unfortunately only three modes can be assigned with confidence for the aurate(I) because of interference by the ether solvent and triphenylphosphine, especially in the infrared.

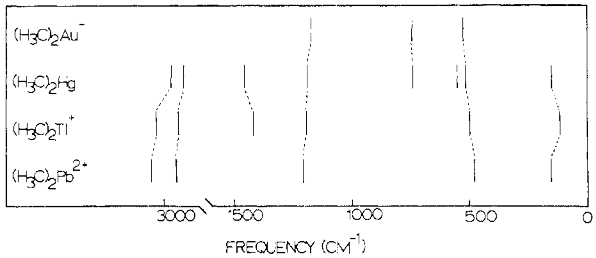


Figure 7. Correlation diagram for the modes of linear $[(CH_3)_2M]^z$ species.

Table III. Raman-Active Modes of $[AuX_n]^-$ Systems ($n = 2$ and 4)

X	$\nu[AuX_2^-]\Sigma_g^+$, cm^{-1}	$\nu[AuX_4^-]A_{1g}$, cm^{-1}
Cl^-	324–334[a]	350[b]
Br^-	208–209[a]	215[b]
I^-	156–158[a]	148[b]
CN^-	450[c]	461[c]
CH_3^-	526	530

[a] Reference 21. Multiple bands occur in the solid state spectra. [b] Reference 22. [c] Reference 23.

The (Au–C) stretching frequencies of $(CH_3)_4Au^-$ and $(CH_3)_2Au^-$ are very similar, and this appears to be typical of gold complexes which have the same ligands but gold in the 1+ and 3+ oxidation states. This is illustrated by the data in Table III for the totally symmetric vibrations. This also has been discussed for the methylgold(I) and trimethylgold(III) phosphine complexes,[18] and the effect can be seen in the data, Table II. A similar effect is noted in AuF_4^-, $\nu_1 = 588$, and AuF_6^-, $\nu_1 = 595$ cm^{-1}.[20]

In the equimolar mixtures of $CH_3AuP(C_6H_5)_3$ or $(CH_3)_3AuP(C_6H_5)_3$ with an equivalent amount of CH_3Li, no vibrations characteristic of unreacted methyllithium are observed. The spectrum of CH_3Li itself in ether shows a series of bands similar in number but somewhat lower in frequency than the cluster modes reported for $(t\text{-}C_4H_9Li)_4$ dissolved in methylcyclohexane.[24] Methyllithium is known in the crystalline state to have a regular tetrahedron of lithium atoms with triply bridging methyl groups above the tetrahedral faces.[25] Assuming that the structure persists in ether solution, four totally symmetric modes would be expected below 1300 cm^{-1}.[26] The frequencies assigned by Scovell et al.[24] to cluster modes give a pattern similar to that of $(CH_3Li)_4$, although the latter frequencies are somewhat lower. The only discrepancy is that the mode observed by Scovell et al. at 1133 cm^{-1} for $(t\text{-}C_4H_9Li)_4$ which was assigned primarily to (C–C) stretching cannot give rise to the increase in scattering observed in the $(CH_3Li)_4$ case at ca. 1125 cm^{-1}. The usual assignment of the vibrations in this region is to the symmetric (HCH) deformations. Scovell et al.,[24] in fact, noted that their (C–C) stretching force constant needed to calculate the 1133 cm^{-1} mode was unreasonably high. They attributed this to contributions from angle bending involving (C–H) bonds in this normal mode. Since their calculation was concerned only with the cluster modes, only the Li_4C_{16} unit without hydrogens was used in the calculation. In the presence of halide ions, the clusters are altered or broken down, and these bands all disappear. NMR studies of CH_3Li–LiI mixtures in the range −50 to −90° suggest that $Li_4(CH_3)_4$, $Li_4(CH_3)_3I$, and $[LiI]_n$ clusters exist.[27] It is possible that dissociation occurs upon warming to 25°, the temperature of the Raman measurements.

The dimethylaurate(I) anion has been reported to form bis(pyridine) and 2,2′-bipyridyl adducts which precipitate from solution as the lithium salt but not to form any stable phosphine adducts.[3,4] This observation seemed surprising, because gold(I) shows little tendency to increase its coordination number beyond two. In addition, the gold center in the dimethylaurate(I) is already quite electron rich as shown by its potent nucleophilicity in reactions with electrophiles.[4] The anomaly seems to have been resolved by the observation that a stoichiometric adduct LiI·2py can be precipitated from an ether solution of anhydrous LiI by addition of 2 equiv of pyridine. The reaction of pyridine with lithium dimethylaurate(I) therefore appears to involve coordination of the pyridine to the lithium cation rather than to the gold center. The solvation of lithium ion in pyridine[28] and dipyridyl[29] has been discussed and several crystal structures have been reported for salts which have nitrogen and oxygen donors coordinated to lithium.[30–32] Since these were found generally to involve four coordination of the lithium ion, the adducts of lithium dimethylaurate(I) may involve some type of lithium–methyl interaction in the solid state.

The appreciable stability of lithium tetramethylaurate(III) is not too surprising in view of the existence of the dimethylaurate(I) complex which was found to be stable indefinitely in ether solution at room temperature when air is excluded.[4] The tetramethylaurate(III) solutions appear to be at least as stable. This is consistent with the behavior of the corresponding halogenoaurates, where salts of the AuX_2^- type are air stable but found to disproportionate in the presence of water to gold metal plus the air and water stable AuX_4^- ions. Solutions of $Li[(CH_3)_4Au]$ appear to be stable indefinitely in ether solution, while $(CH_3)_3AuP(C_6H_5)_3$ under the same conditions (no CH_3Li present) decomposes to deposit a gold mirror within a few days. The presence of the powerful reducing agent CH_3Li *prevents* reduction of $(CH_3)_3AuP(C_6H_5)_3$ through formation of $(CH_3)_4Au^-$ which does not undergo reductive elimination readily.

The stability found for $Li[(CH_3)_4Au]$ is in marked contrast to that reported[10] for trimethylgold(III) in ether where the solution decomposed at −40°, although the $(CH_3)_3Au$ could be stabilized somewhat by a number of neutral donor ligands. It seems likely that reaction of CH_3Li and $AuBr_3$ in the synthesis of trimethylgold(III) would lead to the formation of $[(CH_3)_3AuBr]^-$. This species apparently is not stable in view of the observed behavior. In general, gold(III) species with even numbers of alkyl groups seem to be more stable than those with odd numbers. For example, the $[(CH_3)_2AuX_2]^-$ anions are well characterized for X = Cl, Br, and I[33], while the $[CH_3AuX_3]^-$ anions do not appear to exist.

Both $[(CH_3)_2Au]^-$ and $[(CH_3)_4Au]^-$ appear to be coordinatively saturated in view of the absence of any measurable binding of $P(C_6H_5)_3$. The dimethylaurate(I) can easily expand its coordination number upon reaction with saturated molecules by oxidative addition. With the tetramethylaurate(III) no such path for reaction is available. This probably is one of the reasons for the considerable stability of the tetramethylaurate(III). No tendency for the reductive elimination of ethane from this anion at room temperature was observed.

It is interesting to note that stabilization of trimethylgold(III) by the addition of tertiary phosphines to an ether solution at −80° generally has been attributed to delocalization of charge from the gold center via $d\pi$–$d\pi$ back bonding. Obviously no such effect can be operative in $[(CH_3)_4Au]^-$, and this is but another example of the declining significance of "back bonding".

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Registry No. $Li[(CH_3)_4Au]$, 55822-64-5; $Li[(CD_3)_4Au]$, 55822-65-6; $(CH_3)_3AuP(C_6H_5)_3$, 33635-47-1; $(CD_3)_3AuP(C_6H_5)_3$, 55822-66-7; $Li[(CH_3)_2Au]$, 53863-37-9; $Li[(CD_3)_2Au]$, 55822-67-8; $CH_3AuP(C_6H_5)_3$, 23108-72-7; $CD_3AuP(C_6H_5)_3$, 55822-68-9; CH_3Li, 917-54-4; LiI·2py, 55822-69-0.

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