Delhi University, for recording the ESR spectrum of the compound.

Registry No. $K_2Cr_2O_7$, 7778-50-9; hydrobromic acid, 10035-10-6; 2,2'-bipyridinium oxopentabromochromate(V), 57527-51-2.

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Isolation of Thermally Stable Compounds Containing the Dimethylaurate(I) and Tetramethylaurate(III) Anions[1]

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Lithium dimethylaurate(I) has been reported by Tamaki and Kochi to be quite stable in diethyl ether solution but to decompose at −78° when freed of ether and to yield rather unstable bis(pyridine) and 2,2'-bipyridyl adducts.[2,3] In a recent communication,[4] we found the corresponding gold(III) complex, lithium tetramethylaurate(III), to be equally stable in ether solution but also unstable when freed of ether. We now report the isolation of remarkably stable solid derivatives of both the permethylaurate(I) and -(III) moieties, obtained by complexing the lithium ion with the aprotic polyamine *N,N,N',N'',N''*-pentamethyldiethylenetriamine. Analogous reactions with polyethers also are discussed.

Experimental Section

Diethyl ether was distilled from CaH_2 under dry nitrogen immediately before use. All manipulations of methyllithium and permethylaurates were performed under dried argon using Schlenk-type glassware and syringe techniques. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by the departmental microanalytical laboratory or by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDT) was obtained from K & K Laboratories and used without further purification. Diethylene glycol dimethyl ether (diglyme) was distilled from metallic sodium under argon.

Synthesis of [Li(PMDT)][$(CH_3)_2Au$]. To $CH_3AuP(C_6H_5)_3$ was added with stirring slightly more than 1 equiv of halide-free CH_3Li prepared from $(CH_3)_2Hg$ and lithium sand. When dissolution of the solid was complete, PMDT was added dropwise. The mixture was slightly turbid until more than 1 equiv of PMDT had been added, when a fine white precipitate formed all at once. The precipitate was collected on a frit inside the apparatus, washed twice by slurrying with small portions of dry ether, and dried thoroughly under vacuum. The solid was crushed by manipulating the stirring bar with a hand-held magnet, and a portion of the resulting powder was shaken into an attached collection tube (Ace Glass "sample loader") which was then sealed off under vacuum. Other sampling devices were charged by transferring the apparatus to an argon-filled glovebag. Anal. Calcd for $C_{11}H_{29}N_3LiAu$: C, 32.4; H, 7.18; N, 10.3; Li, 1.70; Au, 48.4. Found (duplicate analyses): C, 32.2, 32.2; H, 7.33, 7.01; N, 10.5, 10.4; Li, 1.50, 1.51; Au, 48.8, 48.1; mp 120–123° dec. The compound decomposes in seconds upon exposure to moist air and upon contact with solvents such as water, methanol, and chloroform. Attempts to prepare Na[$(CH_3)_2Au$] from a solution containing a mixture of Li[$(CH_3)_2Au$] and $P(C_6H_5)_3$ in ether by addition of THF or pyridine solutions of $NaClO_4$ gave solutions which precipitated $CH_3AuP(C_6H_5)_3$ upon addition of methanol or water, whereas ether solutions of Li[$(CH_3)_2Au$] react violently with methanol or water to form only metallic gold.

Table I. Raman Frequencies of Permethylaurates

Compd	ν(Au–CH_3), cm^{-1}	δ_s(CH_3), cm^{-1}
Li[$(CH_3)_4Au$][a]	530 p, 522 dp, 484 dp	1212 p, 1176 dp
[Li(PMDT)]-[$(CH_3)_4Au$][b]	529, 520, 490	1208, 1168
Li[$(CH_3)_2Au$][a]	526, 490	1173
[Li(PMDT)]-[$(CH_3)_2Au$][b]	525, 492	1168

[a] Ether solution; from ref 4. [b] Microcrystalline solid.

Synthesis of [Li(PMDT)][$(CH_3)_4Au$]. This was prepared from $(CH_3)_3AuP(C_6H_5)_3$ by a procedure identical with that given above, except that the reaction mixture was permitted to stand 15 min prior to addition of PMDT to allow completion of the slower methylation. Anal. Calcd for $C_{13}H_{35}N_3LiAu$: C, 35.7; H, 8.07; N, 9.61; Li, 1.59; Au, 45.0. Found: C, 35.5; H, 8.00; N, 9.75; Li, 1.80; Au, 45.3. The compound melts at 86–88° with effervescence, but there is no discoloration until 185°. The compound decomposes only slowly upon exposure to moist air. It is not soluble in water and is not rapidly attacked by it. It dissolves readily in moist methanol, showing no evidence of colloidal gold for up to 30 sec.

Synthesis of [Li(PMDT)][I]. This was prepared by addition of 1 equiv of PMDT to anhydrous LiI in ether and was collected and washed in the same manner as the aurates. Anal. Calcd for $C_9H_{23}N_3LiI$: C, 35.3; H, 7.55; N, 13.7. Found: C, 34.9; H, 7.76; N, 13.4.

Attempted Synthesis of [Li(diglyme)][$(CH_3)_2Au$] and [Li(diglyme)][$(CH_3)_4Au$]. The syntheses described above were repeated substituting diglyme for PMDT. The addition of diglyme to ether solutions of $Li(CH_3)_2Au$ or $Li(CH_3)_4Au$ gave white precipitates. The gold(III) compound developed a purple color due to some decomposition on washing with ether, but neither showed further decomposition when sealed off under vacuum. These are nonstoichiometric and appear to contain ca. 1.5 mol of diglyme/mol of Li^+.

Raman Spectra. Spectra of solids were obtained with a Jarrell-Ash 25-300 spectrophotometer using 632.8-nm He–Ne excitation. Samples were contained in sealed capillaries, and the transillumination technique was employed. The frequencies of sharp bands should be accurate to ±2 cm^{-1}.

Results and Discussion

The observed Raman bands of [Li(PMDT)][$(CH_3)_4Au$] and [Li(PMDT)][$(CH_3)_2Au$] are collected in Table I along with those from the previously reported[4] anion spectra for diethyl ether solutions. The spectra indicate that the change in state has little effect on the structure of the aurates. Presumably the interaction of a permethylaurate anion with $Li(PMDT)^+$ in the crystal is comparable to the interaction with solvated Li^+ via ion pairing in ether solution. In all cases, the anions are perturbed from the expected symmetries of the free ions, and the number of Raman bands in the ν(Au–C) region is greater than predicted for D_{4h} and $D_{\infty h}$ symmetry. The solid-state spectra confirm conclusions drawn from the solution Raman and proton NMR spectra.[4] The assignments of the solid-state spectra are unambiguous because of the very weak scattering of PMDT which was studied with [Li(PMDT)][I].

The [Li(PMDT)][$(CH_3)_nAu$] complexes are extemely stable gold alkyls, though quite reactive ones. Both are stable for months at room temperature, and they do not photolyze either in fluorescent lighting for that time or in periods of up to 20-hr exposure to ~25-mW helium–neon laser radiation. In this respect, the permethylaurates are more stable than the parent compounds $CH_3AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_6H_5)_3$, which slowly deposit gold at room temperature both in solutions and in the solid state. The increase in intrinsic stability upon replacement of phosphine by the methyl group is accompanied by an increase in reactivity, however, due to the increased electron density at the gold center. This is shown by comparisons of oxidative addition to $CH_3AuP(C_6H_5)_3$ and $(CH_3)_2Au^-$ [2,3] and by the deposition of metallic gold when the permethylaurates are exposed to air or protic solvents.

Recent discussions of transition metal alkyls[5-7] have pointed out that stabilization by phosphines has little to do with π-acceptor characteristics of the ligand but is primarily due to coordinative saturation of the metal. Mechanistic studies have indicated that $CH_3AuP(C_6H_5)_3$ and $(CH_3)_3AuP(C_6H_5)_3$ have as the first step in their decompositions the dissociation of phosphine.[8,9] The increased thermal stability upon replacement of the phosphine with an additional methyl group would appear to be due to the less ready dissociation of a methyl group from a permethylaurate than that of phosphine from a neutral complex. This also would explain the instability of $Li[(CH_3)_2Au]$ and $Li[(CH_3)_4Au]$ in the solid state; the bare lithium cation should interact strongly with the methyls, promoting their dissociation from gold, whereas the interaction of etherated lithium in solution or PMDT-chelated lithium in the solid state should be weak. It appears that Li^+ is more effectively chelated, as expected, by one pentamethyldiethylenetriamine ligand than by the analogous oxygen ligand diethylene glycol dimethyl ether.

The permethylaurates may be compared to trimethylphosphonium–methylide compounds recently reported by Schmidbaur and coworkers,[10-12] of which the closest analogues to the aurates are $CH_3AuCH_2P(CH_3)_3$[11] and $(CH_3)_3AuCH_2P(CH_3)_3$.[12] As the aurates, these are thermally stable to above 100°, and the stability was attributed to the stabilizing effect of the onium center on the gold–carbon bonds.[12] In view of the comparable thermal stability of the permethylaurates, however, it would appear that while the positive center may well reduce the susceptibility of the compounds to electrophilic attack by decreasing the electron density on the gold atom, their thermal stability is the result of introducing an additional gold–carbon bond to the CH_3Au^I and $(CH_3)_3Au^{III}$ units. It is becoming apparent that stabilization of the gold methyls is not dependent upon special ligands such as phosphines but upon coordinative saturation of the gold center by any ligand which is strongly bound; methyl groups appear to be quite good as "stabilizing ligands".

The isolation of compounds containing the tetramethylaurate(III) would appear to complete the series of R_nAu^{III} compounds that began with the preparation of $(C_2H_5)_2AuBr$ in 1907[13] and continued with the synthesis of unstable[14] and stable[15] $(CH_3)_3Au^{III}$ compounds in 1943 and 1963, respectively.

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Registry No. $CH_3AuP(C_6H_5)_3$, 23108-72-7; $(CH_3)_3AuP(C_6H_5)_3$, 33635-47-1; $[Li(PMDT)][(CH_3)_2Au]$, 57444-57-2; $[Li(PMDT)][(CH_3)_4Au]$, 57444-55-0; $[Li(PMDT)][I]$, 52451-34-0.

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Reaction of Some Boron Halide Compounds with Platinum(0) and Platinum(II) Species

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The ability of many transition metal compounds to act as Lewis bases toward boron halides and related compounds is well established, and compounds of the types $(C_5H_5)_2WH_2{\cdot}BF_3$[1], $[(C_6H_5)_3P]_2Rh(CO)Cl{\cdot}BX_3$ (X = Cl or Br)[2], and $[(C_6H_5)_3P]_2Ir(CO)Cl{\cdot}xBF_3$ (x = 1 or 2)[3,4] have been reported. More recently the type of compound resulting from the action of BCl_3 on phosphineplatinum(0) derivatives has been shown to be very dependent upon the choice of starting materials and conditions.[5] Thus when $[(C_6H_5)_3P]_3Pt$ is treated with BCl_3 vapor, $[(C_6H_5)_3]_3Pt{\cdot}2BCl_3$ is formed, but in benzene 3 mol of the trichloride is consumed and the proposed products are $[(C_6H_5)_3P]Pt{\cdot}BCl_3$ (1 mol) and $(C_6H_5)_3P{\cdot}BCl_3$ (2 mol). The exposure of solid $[(C_6H_5)_3P]_4Pt$ to the trichloride vapor also results in the formation of $[(C_6H_5)_3P]_3Pt{\cdot}2BCl_3$ in addition to 1 mol of $(C_6H_5)_3P{\cdot}BCl_3$. The only reported route to the bis(phosphine) adduct, $[(C_6H_5)_3P]_2Pt{\cdot}BCl_3$, is the displacement of silicon tetrafluoride from $[(C_6H_5)_3P]_2Pt{\cdot}SiF_4$ by BCl_3.[5] We now report the results of our experiments involving the action of a variety of boron halide compounds on similar phosphineplatinum(0) derivatives.

Results and Discussion

The nature of the reaction between boron halides and phosphineplatinum(0) compounds is dependent upon both the halogen atom present and the type of boron halide compound used. It is convenient, therefore, to discuss the results separately, dealing first with the boron trihalides BX_3 (X = F, Cl) and then with the alkyl or aryl derivatives R_2BX (R = C_6H_5, CH_3; X = Cl, Br). In general two stoichiometries were found for the products, 1:1 and 1:2, and the results are summarized in Table I. The solid adducts are hydrolyzed in air with the exception of the adduct $[(C_6H_5)_3P]_2Pt{\cdot}2BF_3$.

A tensimetric titration shows that when tetrakis(triphenylphosphine)platinum is treated with boron trifluoride (in toluene), 4 mol of the latter is consumed per mole of platinum compound. However, the white precipitate is a mixture which we were unable to separate into its constituent compounds. We consider it unlikely that all the phosphine ligands are removed from the metal to form 4 mol of $(C_6H_5)_3P{\cdot}BF_3$ since there is no evidence for the existence of metallic platinum in the precipitate. A much simpler reaction occurs when $[(C_6H_5)_3P]_2Pt(C_2H_4)$ is treated with boron trifluoride; the ethylene is liberated quantitatively and 2 mol of boron trifluoride is consumed as shown tensimetrically. This adduct appears to be a four-coordinate Pt(0) species (I) rather than

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