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Preliminary communication

Dialkylaurate(I) complexes and the synthesis of trialkylgold(III) compounds

A. TAMAKI and J.K. KOCHI

Department of Chemistry, Indiana University, Bloomington, Indiana, 47401 (U.S.A.)

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We wish to present the preparation of novel★ dialkylaurate(I) species and their use in the facile synthesis of a variety of new mixed trialkylgold(III) complexes. A colorless homogeneous solution was obtained when methylgold(I) (CH_3AuL, L = $(C_6H_5)_3P$) was treated with an equimolar amount of methyllithium in ether or dimethoxyethane, the PMR spectrum of which showed a methyl singlet [δ–0.19 ppm, external TMS] corresponding to 6 protons.

$$CH_3AuL + CH_3Li \rightarrow \underset{(I)}{(CH_3)_2Au^IL^-Li^+} \qquad (1)^{\star\star}$$

When successively more than 1 equiv. of CH_3Li was present, the PMR spectra simply consisted of the superposition of I and CH_3Li [δ–1.89 ppm] indicating that reversal of Eq. 1 is not rapid on the NMR time scale. The singlet absorption, which broadened slightly but remained unresolved down to –70°, suggests, however, that there is exchange of groups in I, especially in view of the methyl doublets observed in the PMR spectra (in dioxane) of CH_3AuL (δ 0.65 ppm, J 8.0 Hz) and $(CH_3)_3AuL$[$(CH_3)_2$, *cis* to L, δ 0.17 ppm, J 7.0 Hz; CH_3 *trans* to L, δ 1.26 ppm, J 9.1 Hz] due to coupling with the phosphorus nuclei[2,3]★★★.

I could be isolated as a colorless crystalline solid when a concentrated solution (or one diluted with hexane) was chilled to –78°, but the recrystallized sample decomposed when removed from the ethereal environment. However, an air-sensitive bis-pyridine derivative was isolated, when two equivalents of pyridine were added to I, and characterized by

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★ Hitherto there have been only sporadic reports of unsaturated or undefined aurate complexes[1a-1c], for "ate" complexes see also ref. 1d.

★★ Aurate(I) complexes are probably four-coordinate, and the presence of a coordinated solvent molecule is implied in I (*vide infra*).

★★★ Several mechanisms involving the exchange of either the solvent derived or PPh_3 ligands are possible, and may be resolved by a phosphorus NMR study.

$$(CH_3)_2AuL^-Li^+ + 2\,Py \rightarrow (CH_3)_2AuPy_2{}^-Li^+ + L \qquad (2)$$

(I)

elemental (Au, Li) analysis and by its PMR spectrum, in which the integrated intensities of the methyl and pyridine resonances appeared in the ratio of 6/10. Attempts to prepare the bis(triphenylphosphine) analog were unsuccessful.

A variety of unsymmetrical dialkylaurate(I) complexes were also prepared by either of two procedures, *e.g.*:

$$CH_3AuL + (CH_3)_3CLi \xrightarrow{a} (CH_3)_3CAu(CH_3)L^-Li^+ \xleftarrow{b} (CH_3)_3CAuL + CH_3Li \qquad (3)$$

These aurate species undergo rapid oxidative addition with various alkyl halides to form trialkylgold(III) complexes in excellent yields. The process constitutes an improved and

$$R^1R^2Au^IL^-Li^+ + R^3{-}X \rightarrow R^1R^2R^3Au^{III}L + LiX \qquad (4)$$

convenient method of preparing trialkylgold(III) complexes[2-7] as well as new mixed alkyl analogs as described below.

Dialkylaurate complexes are potent nucleophiles. For example, oxidative addition of a stoichiometric amount of methyl iodide to I occurs on mixing at 0° in ether. In contrast, the same trimethylgold(III) is generated from the neutral CH_3AuL by the rate-limiting

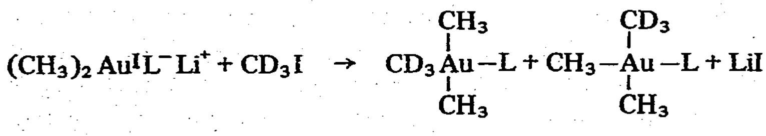
$$(CH_3)_2Au^IL^-Li^+ + CH_3I \rightarrow (CH_3)_3Au^{III}L + LiI \qquad (5)$$

reaction 6 only after a week at 0° with CH_3I as solvent[8].

$$CH_3AuL + CH_3I \rightarrow (CH_3)_2Au^{III}IL \qquad (6)$$

$$(CH_3)_2AuIL + CH_3AuL \xrightarrow{fast} (CH_3)_3Au^{III}L + IAuL \qquad (7)$$

The stereochemistry of the oxidative addition (Eq.5) to the aurate complex was examined with CD_3I and shown to proceed to a mixture containing the *trans* isomer predominantly*.



$$(CH_3)_2Au^IL^-Li^+ + CD_3I \rightarrow CD_3\underset{CH_3}{\overset{CH_3}{Au}}{-}L + CH_3{-}\underset{CH_3}{\overset{CD_3}{Au}}{-}L + LiI \qquad (8)$$

(I) (73%) (13%)

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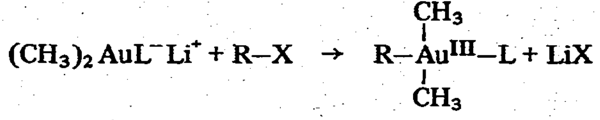
* *Cis* and *trans* methyl groups (relative to Ph_3P) in these and related methylgold(III) compounds are easily distinguished by their PMR chemical shifts[2,3a] in ethereal solvents δ(*cis*-CH_3), −0.1 to 0.3 ppm doublet, δ(*trans*-CH_3), 1.0 to 1.3 ppm doublet (dioxane).

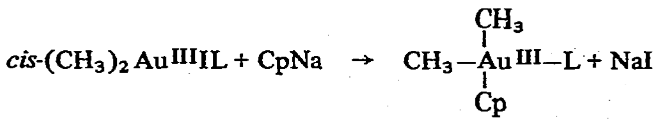
Other alkyl halides also reacted readily with I to afford *trans* alkyldimethylgold(III) compounds in high yields. Among n-butyl derivatives the rates of reaction 9 increased in the



$$\mathrm{(CH_3)_2AuL^-Li^+ + R{-}X \rightarrow R{-}\overset{CH_3}{\underset{CH_3}{Au^{III}}}{-}L + LiX} \qquad (9)$$

$R = C_2H_5, n\text{-}C_4H_9, i\text{-}C_4H_9$

order: $Cl < Br < I$, and among alkyl iodides the rates decreased in the order: $CH_3 > C_2H_5 > n\text{-}C_4H_9$ (*cf.* Fig. 1). The formation of *trans* adducts in oxidative addition (Eq.9) contrasts with the retention of stereochemistry observed in the substitution of the dimethyliodogold(III) complex to form the *cis* product by Tobias *et al.* [7], *e.g.:*



$$cis\text{-}\mathrm{(CH_3)_2Au^{III}IL + CpNa \rightarrow CH_3{-}\overset{CH_3}{\underset{Cp}{Au^{III}}}{-}L + NaI} \qquad (10)$$

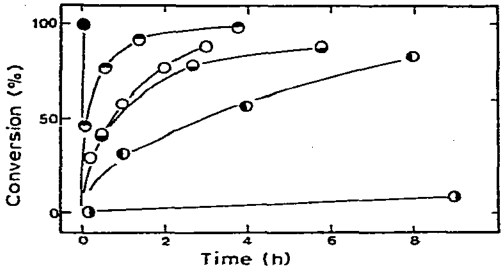
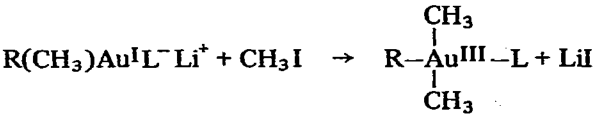


Fig.1. Reaction of alkyl halides with $(CH_3)_2AuPPh_3Li$ at 25° in ether. ●, CH_3I; ◒, C_2H_5I; ○, $n\text{-}C_4H_9I$; ◓, C_6H_5I; ◐, $n\text{-}C_4H_9Br$; ◑, $n\text{-}C_4H_9Cl$.

Although the reactions of secondary and tertiary alkyl halides with I were too slow to be observed, the highly substituted alkylgold(III) complexes could be readily prepared from the mixed dialkylaurate complex and CH_3I, *e.g.:*



$$\mathrm{R(CH_3)Au^IL^-Li^+ + CH_3I \rightarrow R{-}\overset{CH_3}{\underset{CH_3}{Au^{III}}}{-}L + LiI} \qquad (11)$$

Only the *trans* isomer was found in reaction 11 when $R = i\text{-}C_3H_7$, $t\text{-}C_4H_9$ or neo-C_5H_{11}, and suggests that steric effects are also important in the oxidative addition. Interestingly, the stereoselectivity of reaction 11 is lower than that of reaction 9, since approximately 30% of the *cis* isomer was found when R = ethyl. Only the *cis* isomer was observed when either phenyl iodide reacted with I or $Ph(CH_3)AuL^-Li^+$ reacted with CH_3I. In addition to *cis*-$Ph(CH_3)_2AuL$, a significant amount of $(CH_3)_3AuL$ was formed in both reactions. The route by which the latter is generated is not yet clear.

The preparation of these trialkylgold(III) complexes will allow the examination of the stereochemistry and the mechanism of the reductive elimination given in Eq.12 and reported in an earlier study[8]. Oxidative addition of aurate(I) complexes, employing sub-

$$R_3Au^{III}L \rightarrow R{-}R + RAu^{I}L \qquad (12)$$

strates other than alkyl halides, will also be described later.

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