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Preliminary communication

MECHANISM OF THE ALKYLATION OF DIALKYLGOLD(III) COMPOUNDS WITH ALKYLGOLD(I) COMPLEXES

G.W. RICE and R.S. TOBIAS*

Department of Chemistry, Purdue University, W. Lafayette, Indiana 47907 (U.S.A.)

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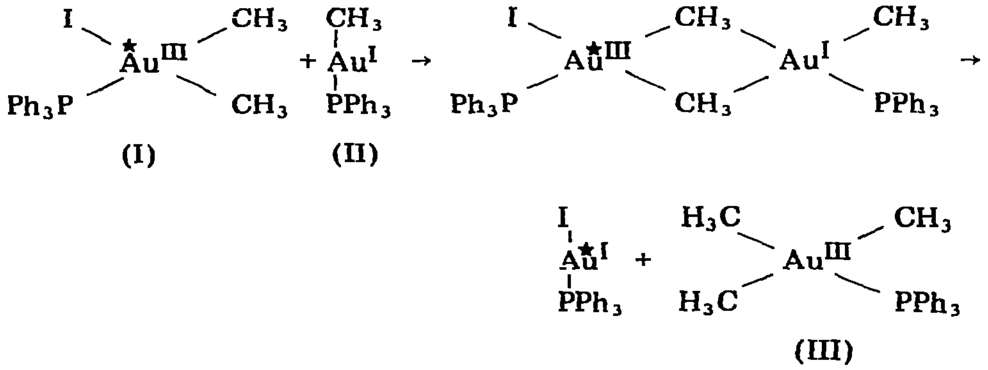
Summary

Reaction mechanisms and solvent effects of reactions of *cis*-$(CH_3)_2IAuPPh_3$ compounds with labeled alkylgold(I) complexes are discussed; the results are compared with those of reactions of similar mercury compounds.

In the course of studying oxidative addition reactions of alkylgold(I) complexes, Tamaki and Kochi [1] found that *cis*-$(CH_3)_2IAuPPh_3$ (I) reacted rapidly and quantitatively with CH_3AuPPh_3 (II) yielding $(CH_3)_3AuPPh_3$ (III) and $AuIPPh_3$. A deuteration study involving reaction of I and CD_3AuPPh_3 in neat methyl iodide was reported to result in the formation of CH_3AuPPh_3 as a metastable intermediate in the initial reaction mixture indicating scrambling of the methyl and perdeuteromethyl groups. After 50 minutes at 25°, only the trimethyl complex was present.

It is reasonable to assume that the Au^{I}—Au^{III} exchange reaction involves a binuclear intermediate. One possible mechanism, reaction I, would involve ligand transfer and a redox reaction of the gold center. It is analogous to the homolytic



(1)

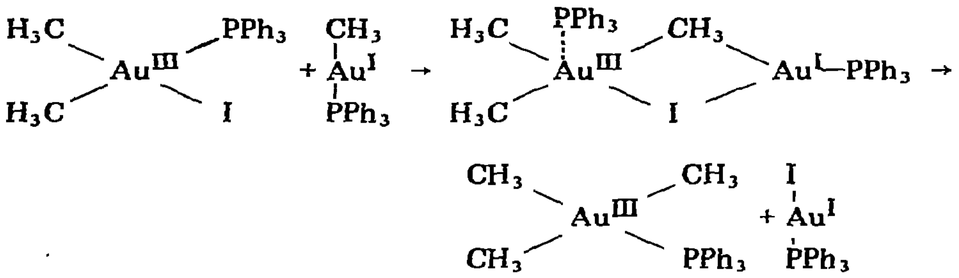

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TABLE 1

DISTRIBUTION OF THE ^{198}Au ACTIVITY AMONG REACTION PRODUCTS

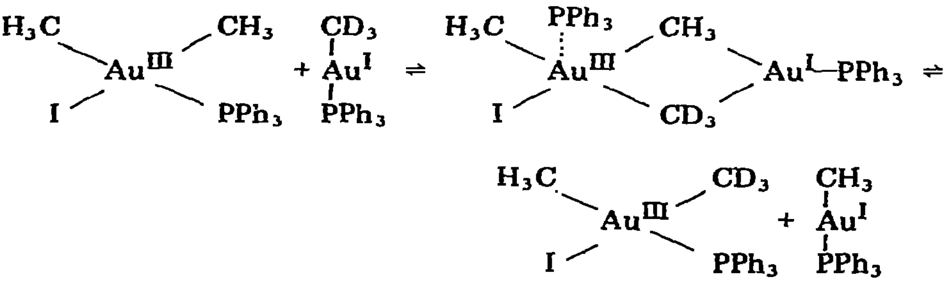
Complex	Sample wt. (g)	Activity ^{a} (cpm)	10^{-4} activity mmol^{-1} (cpm mmol^{-1})
CH_3AuPPh_3	0.0107	10300	46
$IAuPPh_3$	0.0106	9780	54
$(CH_3)_3AuPPh_3$	0.0159	1130	3.6

^{a} Corrected for background.

isotope exchange observed under mild conditions between metallic mercury and RHgX compounds [2]. Reaction 2 is a simple one alkyl exchange typical of many reactions employed in the synthesis of organometallic compounds. A reaction involving methyl radicals is very unlikely. since we observe no methane or ethane formation when the reaction takes place in chloroform, methylene chloride, or benzene.

To test these different mechanisms, we have carried out reactions both with ^{198}Au labeled CH_3AuPPh_3 and with CD_3AuPPh_3. When *cis*-$(CH_3)_2AuIPPh_3$ and $CH_3{}^{198}AuPPh_3$ labeled by neutron activation are allowed to react in CH_2Cl_2 at room temperature for 16 h followed by removal of the solvent and extraction of $(CH_3)_3AuPPh_3$ into hot hexane, the radioactivity is found to reside almost entirely in the $IAuPPh_3$ product. The data are collected in Table 1. Formation of minor amounts of metallic gold through decomposition contributed a small fraction of the activity in both samples. Clearly, from these results, a redox reaction such as 1 can be ruled out.

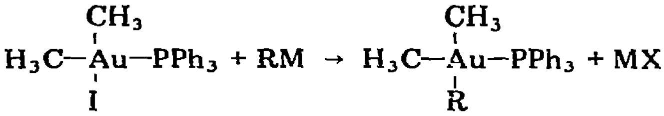
Exchange of methyl groups between I and CD_3AuPPh_3 would appear to require either the presence of methyl radicals in solution or a binuclear complex as in reaction 3. If 3 is relatively fast, it could account for the build-up of


(3)

CH_3AuPPh_3 which then would be removed by the slower process 2. The perdeuteromethyl group in $(CH_3)(CD_3)AuIPPh_3$ should be scrambled between the two non-equivalent positions, because halides and neutral ligands exchange rapidly on dimethylgold(III) compounds [3]. Since reaction 2 is essentially quantitative, the rate of the back reaction should be too slow to account for the accumulation of CH_3AuPPh_3. In addition, no exchange occurs when CD_3AuPPh_3 and III are mixed together.

As Tamaki and Kochi observed for solutions of I and II in CH_3I, we found a methyl proton resonance characteristic of CH_3AuPPh_3 (τ 9.52 ppm, $^2J(^{31}P—^1H)$ 8.0 Hz in CD_2Cl_2) when $CHCl_3$, CH_2Cl_2 or CD_2Cl_2 were used as the solvent. This signal amounted to about 10% of the initial methylgold(I) concentration. Solutions in benzene or NMR quality $CDCl_3$ showed no measurable quantity of the CH_3AuPPh_3. We are unable to explain this solvent effect, but the results are reproducible.

Exchange of perdeuteromethyl groups between I and II should lead to scrambling of the perdeuteromethyl group between non-equivalent positions on III as well as to the formation of some $(CH_3)(CD_3)_2AuPPh_3$ and $(CH_3)_3AuPPh_3$. This would be in contrast to the stereo-specific alkylations observed in the reactions of I with cyclopentadienylsodium [4] or alkyllithium reagents (eqn. 4) [5, 6].



$$H_3C—\overset{CH_3}{\underset{I}{Au}}—PPh_3 + RM \rightarrow H_3C—\overset{CH_3}{\underset{R}{Au}}—PPh_3 + MX \qquad (4)$$

When equimolar amounts of I and CD_3AuPPh_3 are allowed to react in $CDCl_3$ at 40°, the perdeuteromethyl group is inserted preferentially, though not exclusively, *cis* to the phosphine. The product PMR spectrum exhibits a ratio of 1.6/1 for methyl protons *cis* to phosphine (τ 10.08)/*trans* to phosphine (τ 8.92 ppm). Under similar conditions, the ratio is 1.4/1 in benzene and 1.7/1 in CH_2Cl_2. The presence of excess CD_3AuPPh_3 lowers the ratio markedly; the ratios are 1.29/1 and 1.03/1 for $CD_3AuPPh_3/(CH_3)_2AuIPPh_3$ mole ratios of 1.8 and 2.9, respectively. Stereospecific *cis* alkylation would require a 1/1 ratio, while complete scrambling would lead to a 2/1 ratio.

These results suggest that di-μ-methido bridged intermediates do lead to some methyl exchange. The principal reaction is a normal one alkyl exchange in which II simply acts as a fast and efficient alkylating agent. The variation in the *cis/trans* proton ratios with solvent and concentration indicates that the alkylation reaction 1 is stereospecific, and the observed scrambling must be due to the process shown in eqn. 3. The preferential substitution *cis* to the phosphine also indicates that the reaction is not one involving simply methyl radicals. With other strongly electrophilic metal complexes, II also is an effective methylating agent. For example, it reacts rapidly with $HgCl_2$, $HgBr_2$, HgI_2, $Hg(OAc)_2$, CH_3HgCl, CH_3HgBr, CH_3HgI, and CH_3HgOAc in solution by bimolecular processes [6]. There are a number of similarities in the bond strengths and reactions of CH_3Hg^{II} and $(CH_3)_2Au^{III}$ compounds [3], and it appears that the reaction with the $(CH_3)_2Au^{III}$ electrophile is very similar to the ones with CH_3Hg^{II}.

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