

Preliminary communication

Catalytic mechanism involving oxidative addition in the coupling of alkylgold(I) with alkyl halides

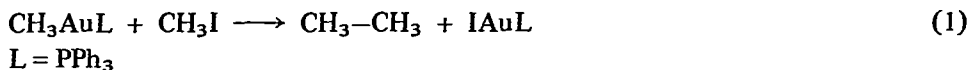
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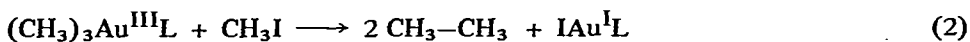
(Received April 24th, 1972)

We wish to report a novel catalytic mechanism for the coupling of organometals with alkyl halides which proceeds by oxidative addition^{1,2}. We chose organogold complexes for a mechanistic study since a variety of alkylgold(I) and alkylgold(III) complexes are known³⁻⁶, and their diamagnetism allows a direct and ready examination of these species as intermediates by NMR. Our conclusions about the intermediates and the mechanism of the coupling reaction differ from those reached in a recent report⁷ and, moreover, clarify the ambiguities contained therein.

The reaction between methyl(triphenylphosphine)gold(I) and methyl iodide produces ethane and iodo(triphenylphosphine)gold(I) according to the stoichiometry given in eq. (1) after 46 h at 25°. Examination of the NMR spectrum shows that $\text{CH}_3\text{Au}^{\text{I}}\text{L}$



(δ 1.35 ppm, doublet $J = 8.0$ Hz, relative to external TMS in CH_3I)⁵ disappears after 11 h and is replaced by $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{L}$ [$(\text{CH}_3)_2$, *cis* to L, δ 0.87 ppm, doublet, $J = 7.0$; CH_3 , *trans* to L, δ 1.92 ppm, doublet $J = 9.1$]⁴. Furthermore, $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{L}$ can be isolated in 87% yield together with $\text{IAu}^{\text{I}}\text{L}$ (91%) if the reaction is kept at 0° for 6 days and then carefully worked up. It is identical with that synthesized by an independent method⁴, and it reacts with methyl iodide according to the stoichiometry given in eq. (2).



The oxidation of $\text{CH}_3\text{Au}^{\text{I}}\text{L}$ to an alkylgold(III) intermediate is most readily accommodated by an oxidative addition of CH_3I , but we could find no evidence for the presence of the expected adduct, $(\text{CH}_3)_2\text{Au}^{\text{III}}\text{L}$. However, this dilemma is readily resolved by the observation that the NMR spectrum of independently synthesized⁶ *cis*- $(\text{CH}_3)_2\text{Au}^{\text{III}}\text{L}$ [CH_3 , *cis* δ 2.08 ppm, doublet, $J = 8.2$; CH_3 , *trans* δ 2.48 ppm, doublet,

$J = 9.0$] disappears completely in the presence of an equimolar amount of $\text{CH}_3\text{Au}^{\text{I}}\text{L}$ within half an hour at 25° , and it is replaced by the spectrum of $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{L}$. The latter together with $\text{IAu}^{\text{I}}\text{L}$ can be isolated in high yields from the reaction mixture. Separately, $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{L}$ and $(\text{CH}_3)_2\text{Au}^{\text{III}}\text{IL}$ decompose to ethane at much slower rates as shown in Table 1 than the exchange reactions described above[★].

These observations are consistent with the rather unusual catalytic mechanism given below^{★★}:

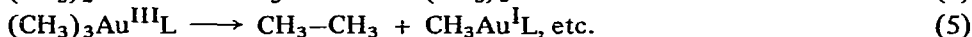
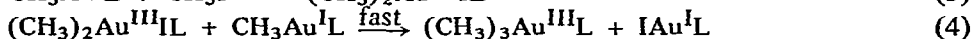


TABLE 1

RATES OF ETHANE FORMATION FROM VARIOUS METHYLGOLD COMPLEXES IN METHYL IODIDE AT 31° .

Methylgold complex	Conc. (M)	Rate constant ^a (min^{-1})	Time (h) for completion ^b
$\text{CH}_3\text{AuPPh}_3$	$3.4 \cdot 10^{-2}$	$5.0 \cdot 10^{-4}$	48 (100)
$(\text{CH}_3)_2(\text{I})\text{AuPPh}_3$	$2.0 \cdot 10^{-2}$	$4.3 \cdot 10^{-4}$	100 (100)
$(\text{CH}_3)_3\text{AuPPh}_3$	$2.14 \cdot 10^{-2}$	$2.10 \cdot 10^{-3c}$	40 (200)
	$3.29 \cdot 10^{-2}$	$1.51 \cdot 10^{-3}$	

^aApparent first order rate constant for first 20% reaction. ^bPercent yield of ethane liberated (in parentheses) based on gold. ^cApparent rate constant decreases with increasing concentration of trimethylgold (III) with inverse half-order dependence.

Oxidative addition in the first step (eq. 3) is followed by an alkyl transfer (eq. 4) which is too rapid to allow observation of the adduct. According to this mechanism, alkyl coupling derives from reductive elimination (eq. 5) of the alkylgold(III) intermediate to regenerate the alkylgold(I) species. The stereochemistries of oxidative addition (eq. 3) and reductive elimination (eq. 5) are difficult to observe since alkyl exchange is rapid under these conditions. Thus, an examination of the NMR spectrum of equimolar amounts of $(\text{CH}_3)_2\text{Au}^{\text{III}}\text{IL}$ and $\text{CD}_3\text{Au}^{\text{I}}\text{L}$ shows that $\text{CH}_3\text{Au}^{\text{I}}\text{L}$ is formed as a metastable intermediate whose concentration reaches a maximum within 10 min. After 50 min. the spectrum due to $(\text{CH}_3)_2\text{Au}^{\text{III}}\text{IL}$ also disappears and only the two new doublets due to *cis* and *trans* methyl groups in $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{L}$ remain. A similar scrambling of methyl groups is shown in the reaction between $\text{CH}_3\text{Au}^{\text{I}}\text{L}$ and CD_3I .

Support for this mechanistic scheme is also shown by the mixed reaction between $\text{CH}_3\text{CH}_2\text{Au}^{\text{I}}\text{L}$ and CH_3I at 31° , in which *n*-butane (91%) is preferentially

[★]The *trans*-dimethyl isomer of $(\text{CH}_3)_2\text{IAuPPh}_3$ or related derivatives are as yet unknown. The liberation of ethane from the thermolysis of $(\text{CH}_3)_3\text{AuPPh}_3$ in xylene is reported in reference 3.

^{★★}A similar mechanism has been speculatively postulated (see ref. 1b).

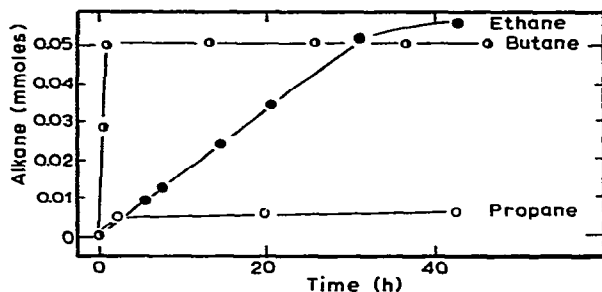


Fig. 1. Reaction of $\text{CH}_3\text{CH}_2\text{Au}^{\text{I}}\text{L}$ (0.113 mmole) with CH_3I at 31° ; \circ , n-butane; \bullet , ethane; \circ , propane. Yields based on the utilization of alkyl groups according to the text.

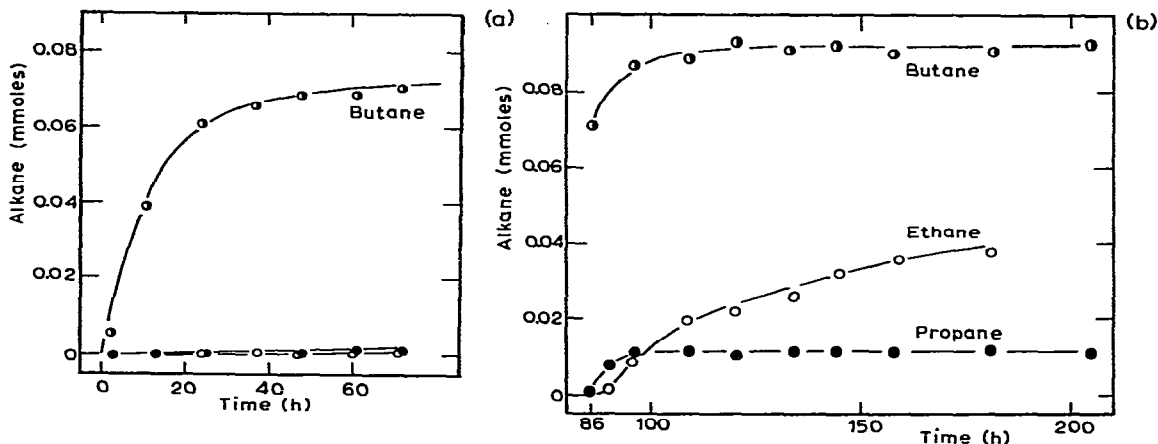
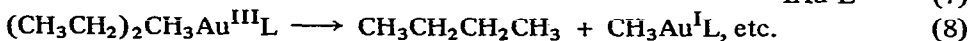
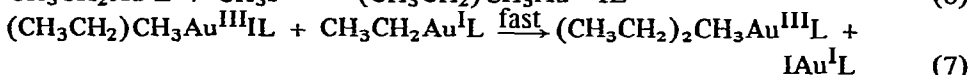
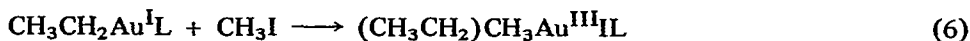


Fig. 2. (a) Reaction of $\text{CH}_3\text{CH}_2\text{AuL}$ (0.197 mmole) and CH_3I at 0° . (b) Continuation of (a) at 25° . \circ , n-butane; \circ , ethane; \bullet , propane.

formed (Fig. 1), followed by the slower evolution of ethane (95%). The two coupling processes can be well separated if the same reaction is first carried out at 0° , so that only n-butane (71%) is formed as shown in Fig. 2(a). On subsequent warming (after 86 h) of the mixture to 25° , additional n-butane (19%) as well as propane (11%) are formed, followed slowly by ethane as shown in Fig. 2(b). More of the cross coupled propane is formed under the latter conditions, but it is still a minor product. Reductive elimination



from the alkylgold(III) intermediate^{*} is expected to liberate ethyl (eq. 8) in preference to

^{*}Reductive elimination from $(\text{CH}_3\text{CH}_2)_2\text{Au}^{\text{III}}\text{IL}$ is also a possibility, although the analogous reaction does not contribute in the reactions of the methyl analog.

methyl groups^{*}. Similar reactions would afford n-propane via $\text{CH}_3\text{CH}_2(\text{CH}_3)_2\text{Au}^{\text{III}}\text{L}$ in slower subsequent steps. Indeed, the NMR spectrum at intermediate stages show the presence of $\text{CH}_3\text{Au}^{\text{I}}\text{L}$ and $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{L}$, as well as a new species which we tentatively ascribe to $\text{CH}_3\text{CH}_2(\text{CH}_3)_2\text{Au}^{\text{III}}\text{L}$. The lability of ethyl groups is also shown by the formation of n-butane in principal amounts together with smaller quantities of propane and ethane when $\text{EtAu}^{\text{I}}\text{L}$ and $(\text{CH}_3)_2\text{Au}^{\text{III}}\text{L}$ react at -20° . Furthermore, it should be emphasized that in the absence of alkyl exchange this system would have afforded mainly propane.

ACKNOWLEDGEMENT

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^{*}Based on the thermal stabilities of alkylgold(I)phosphine complexes (ref. 9).

Erratum

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The second line below eqn.(12) should read:

(0.98 mole) and Ph_3SiOPh (0.97 mole per mole of initial (III)), indicating the complete

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