

sence of higher molecular weight materials, such as the dimer of the vinyl alcohol.

Comparison of Ozonation of Cis and Trans Olefins with Ozone and Complexed Ozone. The olefins ozonized were *cis*- and *trans*-1,2-diisopropylethylene, *cis*- and *trans*-3-hexene, and *cis*- and *trans*-di-*tert*-butylethylene. The complexes used were those of 1-mesityl-1-phenylethylene and the corresponding ethane. The ozonations were carried out in the two-compartment vessel. First, the ozone complex was produced in the left-hand compartment at -150° , after which a solution of the olefin to be studied was blown into the solution of the complex, at -150° . The resulting solution was allowed to stand at -150° for 2–3 hr after which it was allowed to rise slowly to room temperature. Analyses were by vpc, as described earlier.

Acknowledgment. This work was supported by grants from the Robert A. Welch Foundation (F-042) and the National Science Foundation (GP-28187) for which the authors are grateful. Acknowledgment also is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research. The authors also thank Drs. Ben A. Shoulders and Clifford A. Becker, for help and advice concerning the low-temperature nmr and visible spectra techniques, and Dr. Rex E. Hornish for characterizing one of the complexes.

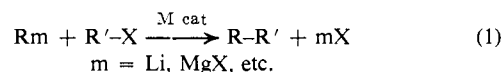
Catalysis by Gold. Alkyl Isomerization, Cis-Trans Rearrangement, and Reductive Elimination of Alkylgold(III) Complexes

A. Tamaki, S. A. Magennis, and J. K. Kochi*

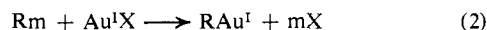
Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received March 28, 1974

Abstract: Gold is a particularly useful catalyst for mechanistic studies, since organogold intermediates can be readily probed by nmr studies in solution. Thus, trialkyl(triphenylphosphine)gold compounds undergo a variety of competing reactions including: (a) the isomerization of alkyl groups σ -bonded to gold(III), (b) the *cis*-*trans* rearrangement of the square planar complexes, and (c) the reductive elimination of two *cis*-alkyl groups as dialkyl to form alkylgold(I) species. Under proper conditions each of these processes can be studied independently. Alkyl isomerization and reductive elimination are found to proceed *via* a dissociative mechanism involving prior loss of the phosphine ligand. A mechanism is proposed in which the resultant metastable trigonal trialkylgold(III) species is a common intermediate which either undergoes β -hydrogen elimination and readdition on the route to alkyl isomerization or loss of two alkyl groups to effect *cis*-reductive elimination. On the other hand, the rate of *cis*-*trans* isomerization is unaffected by the presence of excess PPh_3 . A unimolecular mechanism is proposed in which the rearrangement proceeds *via* a spontaneous inversion of the configuration at the gold nucleus in the four-coordinate trialkyl(triphenylphosphine)gold species.

The facile coupling of Grignard and organolithium reagents [Rm] with alkyl halides is catalyzed by various metal complexes, especially those of copper¹ and gold.²



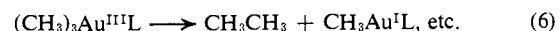
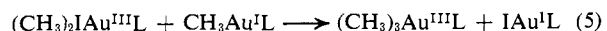
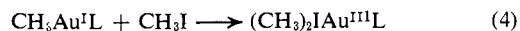
The catalytic process in eq 1 for $\text{M} = \text{Au}^{\text{I}}$ involves the prior alkylation of gold(I) as schematically represented in eq 2, followed by the reaction with alkyl halide in eq 3.²



The reaction of the alkylgold(I) species with alkyl halide in eq 3 is rate limiting. The previous study² showed that coupling of methyl groups in the catalytic

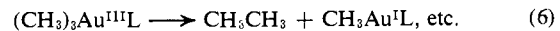
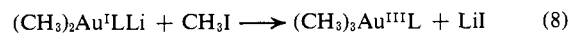
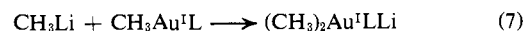
reaction of methyl(triphenylphosphine)gold and methyl iodide proceeded by a multistep sequence of reactions involving oxidative addition, alkyl exchange, and reductive elimination (Scheme I, eq 4–6, $\text{L} = \text{PPh}_3$).

Scheme I



Oxidative addition of alkyl halide to gold(I) can also be achieved *via* the more reactive dialkylaurate(I) species (Scheme II), *e.g.*,³

Scheme II



Trimethyl(triphenylphosphine)gold is the key intermediate in eq 6^{1,4} leading to the coupling of methyl groups, whether the reaction proceeds *via* methyl(triphenylphosphine)gold(I) or dimethylaurate(I) shown

(3) (a) A. Tamaki and J. K. Kochi, *J. Organometal. Chem.*, **51**, C39 (1973); **64**, 411 (1974); (b) *J. Chem. Soc., Dalton Trans.*, 2620 (1973); (c) *J. Organometal. Chem.*, **61**, 441 (1973).

(4) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

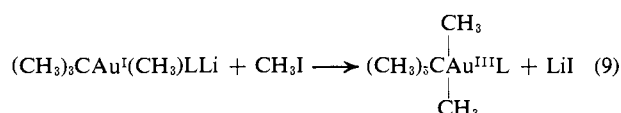
(1) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967); **90**, 5615 (1968); M. Tamura and J. K. Kochi, *ibid.*, **93**, 1485 (1971); *J. Organometal. Chem.*, **42**, 205 (1972); C. R. Johnson and G. A. Dutra, *J. Amer. Chem. Soc.*, **95**, 7783 (1973). For a review, see J. F. Normant, *Synthesis*, 63 (1972), and G. H. Posner, *Org. React.*, **19**, 1 (1972); A. E. Jukes, *Advan. Organometal. Chem.*, **12**, 215 (1974).

(2) A. Tamaki and J. K. Kochi, *J. Organometal. Chem.*, **40**, C81 (1972).

in Schemes I or II, respectively. It is, therefore, important to establish the mechanism of decomposition of trialkyl(triphenylphosphine)gold(III) species. Since they have square planar configurations, it is possible to examine the stereochemical requirements for reductive elimination of two alkyl groups. In the course of this study we noted the isomerization of alkyl groups attached to gold(III), as well as the *cis*-*trans* rearrangement of alkyldimethyl(triphenylphosphine)gold complexes. We find that these three phenomena are all interrelated, and to facilitate the presentation each of them will be discussed separately.

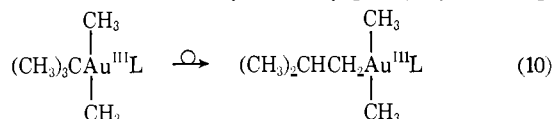
Results and Discussion

I. Spontaneous Isomerization of *tert*-Butylgold(III) to Isobutylgold(III). An unusually facile rearrangement of a *tert*-butyl group to the isobutyl isomer is observed when it is σ -bonded to gold(III). Thus, *trans-tert*-butyldimethyl(triphenylphosphine)gold is readily formed from lithium *tert*-butylmethyl(triphenylphosphine)aurate(I) and methyl iodide in diethyl ether solution at -78° by a reaction described previously (L = PPh₃).⁵



Lithium iodide was separated from the solution by adding dimethoxyethane (DME) and filtering off the precipitate. The presence of *tert*-butyldimethyl(triphenylphosphine)gold in DME solution is readily indicated by its ¹H nmr spectrum,⁴ [(CH₃)₂ *cis* to P, δ 0.03 ppm doublet, $J = 7.3$ Hz; (CH₃)₃C, δ 1.59 ppm doublet, $J = 11.4$ Hz; integration, *t*-Bu/Me = 1.5], provided the diethyl ether is first removed *in vacuo*, since the methyl group in the cosolvent obscures the *tert*-butyl resonance.

Attempts to purify *tert*-butyldimethyl(triphenylphosphine)gold led to its spontaneous conversion to the isomeric *trans*-isobutyldimethylgold(III) analog.



Thus, removal of the ethereal solvent in reaction 9 at low temperatures afforded a colorless solid from which the *tert*-butylgold(III) complex could be separated from lithium iodide by extraction with *n*-pentane. However, it could not be isolated from the pentane extract in pure form despite careful efforts, since the nmr spectrum always showed the presence of the isobutyl isomer.

Authentic isobutyldimethyl(triphenylphosphine)gold was independently synthesized from isobutyldimethylaurate(I) and methyl iodide.⁴ It was readily recrystallized from pentane and identified by elemental analysis and by its ¹H nmr spectrum ((CH₃)₂ *cis* to P, δ 0.27 ppm doublet, $J = 7.4$ Hz; CH₂ δ 2.07–2.29 multiplets, (CH₃)₂C δ 1.27 doublet, $J = 6.6$ Hz; CH $\delta \approx 1.3$ ppm multiplet; with the correct intensity ratios relative to Ph₃P).

The isomerization of *tert*-butyldimethyl(triphenyl-

phosphine)gold was examined at room temperature in diethyl ether solution by ¹H nmr, using the well-resolved *cis*-(CH₃)₂ resonances. As the rearrangement progressed, the doublet at δ 0.27 ppm increased monotonically and that at δ 0.03 ppm decreased concomitantly. Integration showed that the sum of the intensities of the two signals always remained constant (and equal to 6 relative to the 15 aromatic protons), from which we conclude that the isomerization proceeds quantitatively. Finally, removal of the solvent afforded, after recrystallization, pure isobutyldimethyl(triphenylphosphine)gold in high yield.

The rearrangement appears to be irreversible, although isotopic labeling studies will establish this point. At this juncture, however, it is clear that if such an equilibrium were established, it would lie overwhelmingly toward the isobutyl side. Furthermore, the observation of only *trans*-isobutyldimethyl(triphenylphosphine)gold and none of the *cis* isomer from the rearrangement of *trans-tert*-butyldimethyl(triphenylphosphine)gold is consistent with its greater thermodynamic stability (*vide infra*). Kinetic processes leading to the *cis*-isobutyl compound, if any exist, are not distinguished by the data on hand.

The kinetics of isomerization in DME solution were first order in *tert*-butyldimethyl(triphenylphosphine)gold. The first-order rate constants obtained at various temperatures are listed in Table I. We calculate

Table I. Temperature Dependence of the Isomerization of *tert*-Butylgold(III)^a

[(CH ₃) ₂ CAu-(CH ₃) ₂ L] ^b , M	Temp, °C	Rate constant (sec ⁻¹)
0.50	27	1.2 × 10 ⁻⁶
0.50	36	1.1 × 10 ⁻⁴
0.50	45	2.5 × 10 ⁻⁴
0.50	52	8.9 × 10 ⁻⁴

^a In 1,2-dimethoxyethane solution. ^b Initial concentration, L = PPh₃.

the apparent activation parameters for isomerization to be $\Delta H^\ddagger = 29$ kcal mol⁻¹ and $\Delta S^\ddagger = 16$ eu. The rearrangement was not materially affected by the presence of a threefold excess of propylene or a 25-fold excess of 1-butene.

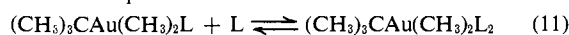
The observed first-order rate constant for the rearrangement of *tert*-butyldimethyl(triphenylphosphine)gold, however, decreased with increasing amounts of added triphenylphosphine as shown in Table II.

Table II. Effect of Triphenylphosphine on the Rate of Isomerization of *tert*-Butyldimethylgold(III)L^a

(CH ₃) ₂ CAu-(CH ₃) ₂ L (mmol)	Added L (mmol)	L/R ₂ AuL (mmol/mmol)	Rate constant (sec ⁻¹)
0.44	0	0	1.1 × 10 ⁻⁵
0.44	0.097	0.22	5.5 × 10 ⁻⁶
0.44	0.28	0.63	2.5 × 10 ⁻⁶
0.44	0.61	1.4	1.5 × 10 ⁻⁶

^a In DME solutions at 25°, L = PPh₃.

The retardation in rate by added PPh₃ cannot be due to an associative process such as



(5) A. Tamaki and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 423 (1973).

Table III. Isomerization of Propyl Groups During Reductive Elimination of Propyldimethyl(triphenylphosphine)gold Isomers^a

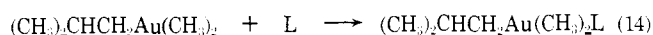
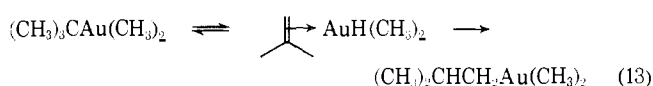
R =	R(CH ₃) ₂ AuPPh ₃		Temp, °C	Alkane (mol %) ^b		
	(10 ³ mmol)	Added PPh ₃ (10 ³ mmol)		RCH ₃	R'CH ₃	% Rgt. ^c
<i>trans-n</i> -Propyl	50	0	70	65	5	7
<i>trans-i</i> -Propyl	50	51	90	60	5	8
<i>cis-n</i> -Propyl	50	0	70	55	5	8
<i>cis-i</i> -Propyl	51	51	90	50	4	7
<i>trans</i> -Isopropyl	50	0	70	60	38	39
<i>trans</i> -Isopropyl	50	50	90	55	21	28
<i>cis</i> -Isopropyl	51	0	70	45	26	37
<i>cis</i> -Isopropyl	50	51	90	53	21	29

^a In decalin solutions. ^b R' is the isomer of R. ^c Rearrangement based on isomeric alkanes produced and intended as qualitative indication of rates only.

since phosphorus nmr studies show no indication of the presence of any phosphine adducts in sufficient concentrations to cause rate decreases of the magnitudes shown in Table II. Furthermore, successive additions of PPh₃ to a DME solution of isobutyldimethyl(triphenylphosphine)gold under the conditions of the isomerization do not alter the phosphorus nmr spectrum. The spectra simply consist of the superpositions of the phosphorus resonances due to the organogold(III) species and free triphenylphosphine. At low concentrations of triphenylphosphine, however, only the line due to PPh₃ is broadened but largely unshifted, probably due to a slight degree of association. Similar results were also observed in benzene solutions.

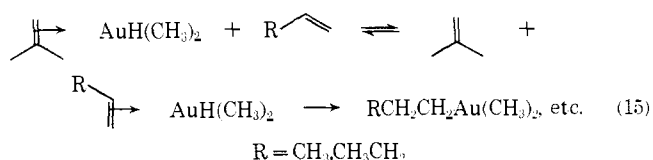
The following mechanism (Scheme III) is proposed

Scheme III



based on the observed kinetic parameters, the phosphorus nmr studies and the trapping experiments, which suggest that the rearrangement is dissociative and intramolecular.

According to this mechanism, the rearrangement of the *tert*-butyl group occurs *via* a hydridogold species (to which isobutylene is π -complexed) followed by readdition as indicated in eq 13. The driving force for β elimination may be steric in origin.⁶ There is no evidence, however, that isobutylene is kinetically free since incorporation of olefin could not be effected, even when it was used in large excess. A similar lack of olefin exchange was noted in the reversible addition-



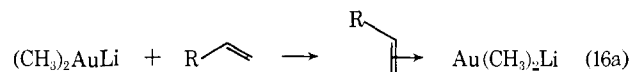
elimination sequence during reductive elimination of di-*n*-butylbis(triphenylphosphine)platinum.⁷

The formulation in Scheme III is not without its difficulties. Thus, attempts to generate π -complexed

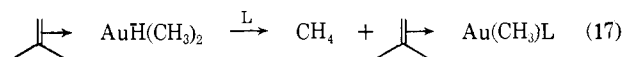
(6) Cf. R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, **26**, 101 (1971); P. S. Braterman and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 657 (1972); S. Ohtuska, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Amer. Chem. Soc.*, **95**, 3180 (1973).

(7) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

hydridogold species from dimethylaurate(I) have been unsuccessful despite varied approaches,^{3b} *e.g.*



Furthermore, if such species were discrete intermediates during the rearrangement, it is not clear why a competing process involving the reductive elimination of methane was not observed.⁸ Moreover, their steady

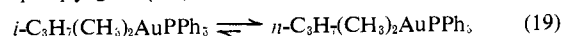


state concentration must be low, since the nmr spectra of the solution taken during isomerization showed no evidence of their presence.

The isopropylgold(III) analog, *i*-Pr(CH₃)₂AuPPh₃, does not rearrange under the same conditions, and the use of higher temperatures causes reductive elimination. The decomposition of trialkyl(triphenylphosphine)gold will be discussed later, but suffice it to mention at this point that two alkyl groups are reductively eliminated by an intramolecular process. The hydrocarbon



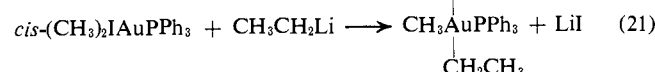
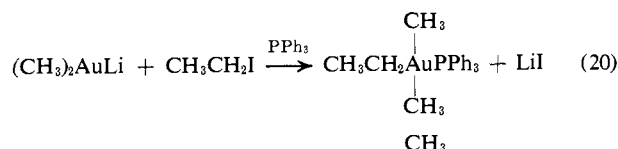
products (RCH₃ and R'CH₃ in Table III) consisting of isomeric butanes from the decomposition of propyldimethyl(triphenylphosphine)gold isomers indicate that isopropyl and *n*-propyl groups are interconverted during the course of reductive elimination. Thus, either *cis*- or *trans-i*-Pr(CH₃)₂AuPPh₃ affords *n*-butane in addition to the expected isobutane. Similarly, *cis*- or *trans-n*-Pr(CH₃)₂AuPPh₃ produces significant amounts of isobutane together with *n*-butane. Examination of the nmr spectra during the course of decomposition indicates that the isomerization of propyl groups does occur, but the rates are not fast enough to compete effectively with decomposition. Consequently, high steady state concentrations of the isomeric compound are not built up, and changes are difficult to measure by nmr. However, from the yields of rearranged products shown in Table III, we deduce that isopropylgold(III) is more extensively converted to the *n*-propylgold(III) isomer than *vice versa*.



(8) (a) The reductive elimination of alkane from hydridogold(III) is rapid.^{3b} (b) Cf. A. Johnson, R. J. Puddephatt, and J. L. Quirk, *J. Chem. Soc., Chem. Commun.*, 938 (1972); (c) R. Hüttel and H. Reinheimer, *Chem. Ber.*, **99**, 2778 (1966).

There are other examples of the rearrangement of *tert*-butyl groups attached to the main group elements, boron and aluminum; but these occur only at elevated temperatures (190 and 120° (30%), respectively).⁹ Among the few known examples of *tert*-alkyl derivatives of transition metals, there are no reports of rearrangement, although there is recent evidence which indirectly suggests the isomerization of *sec*-alkyliridium(III) and nickel(II) complexes.¹⁰

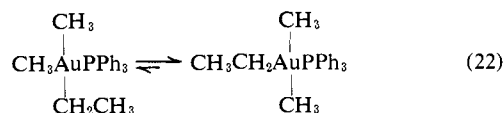
II. Cis-Trans Isomerization of Alkyldimethyl(triphenylphosphine)gold. *trans*-Ethyl dimethyl(triphenylphosphine)gold was synthesized by oxidative addition of ethyl iodide to lithium dimethylaurate(I). The corresponding cis isomer was prepared by stereospecific



alkyl exchange between *cis*-iododimethyl(triphenylphosphine)gold and ethyllithium.³

The pair of $\text{Et}(\text{CH}_3)_2\text{AuPPh}_3$ isomers were readily distinguished by their proton nmr spectra. The two equivalent CH_3 groups *cis* to P in the *trans* isomer consisted of doublets (δ 0.29 ppm, $J = 7.0$ Hz) which were well-resolved from the doublet splitting due to the single CH_3 group *cis* to P in the *cis* isomer (δ 0.15 ppm, $J = 6.9$ Hz) as well as an additional doublet splitting (δ 1.31 ppm, $J = 1.31$ Hz) due to the other CH_3 group which is *trans* to P.

A solution of *cis*-ethyl dimethyl(triphenylphosphine)gold in benzene at 70° rearranged to the *trans* isomer in the presence of an equimolar amount of added triphenylphosphine as shown in Figure 1. Similarly starting with pure *trans*-ethyl dimethyl(triphenylphosphine)gold, under the same conditions it equilibrated to



the same mixture consisting of 70% of the *trans* isomer. Isomerization was complete since the combined integrations of all the proton resonances due to $\text{CH}_3\text{-Au}$ relative to those of triphenylphosphine showed no significant decrease during the course of these changes.

If less than 20 mol % of added triphenylphosphine was present, at 70°, some decomposition accompanied the isomerization. Similar results of *cis-trans* equilibration were obtained with both isomers of *n*-propyl dimethyl(triphenylphosphine)gold. However, *cis*-isopropyl dimethyl(triphenylphosphine)gold rearranged completely to the *trans* isomer. The position of equi-

(9) (a) H. Lehmkuhl, *Angew. Chem.*, **76**, 817 (1964); *Justus Liebigs Ann. Chem.*, **719**, 40 (1968); (b) W. Gerrard and H. R. Hudson, *Chem. Rev.*, **65**, 697 (1965).

(10) (a) W. Kruse, *J. Organometal. Chem.*, **42**, C39 (1972); (b) W. P. Giering and M. Rosenblum, *ibid.*, **25**, C71 (1970); (c) R. P. A. Sneeden and H. H. Zeiss, *ibid.*, **26**, 101 (1971); (d) B. K. Bower and H. Tennent, *J. Amer. Chem. Soc.*, **94**, 2512 (1972); (e) D. F. Gill and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, **65** (1972); (f) F. R. Jensen and D. H. Buchanan, *ibid.*, 153 (1973); (g) M. A. Bennett and R. Charles, *J. Amer. Chem. Soc.*, **94**, 666 (1972); (h) K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, *ibid.*, **94**, 9269 (1972).

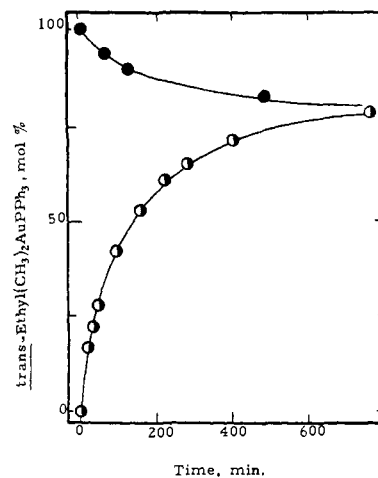
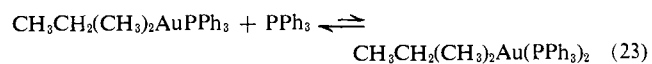


Figure 1. Equilibration of *cis*- $\text{Et}(\text{CH}_3)_2\text{AuPPh}_3$ (●) and *trans*- $\text{Et}(\text{CH}_3)_2\text{AuPPh}_3$ (○) in benzene at 70° in the presence of triphenylphosphine (see text).

librium must heavily favor *trans*-isopropyl dimethyl(triphenylphosphine)gold, since it remained unchanged under the same conditions. After a prolonged period, however, it decomposed slightly.

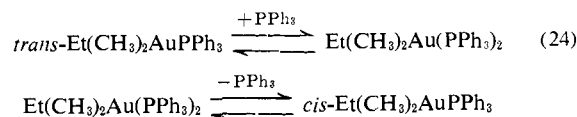
The *cis-trans* isomerization of alkyldimethyl(triphenylphosphine)gold compounds was unaffected by the addition of successively more triphenylphosphine. Since the rates of alkyl isomerization and reductive elimination (*vide infra*) are adversely affected by excess PPh_3 , the *cis-trans* rearrangement could be readily studied separately under these conditions.

The phosphorus nmr spectrum of *cis*-ethyl dimethyl(triphenylphosphine)gold in benzene solution consist of a single sharp resonance (δ 29.3 ppm relative to external H_3PO_4). Free triphenylphosphine under the same conditions exhibits a singlet resonance further upfield (δ -5.6 ppm). The ^{31}P nmr spectrum of an equimolar mixture of the two shows the coordinated phosphine to be unchanged, and the resonance due to the free ligand only moves slightly downfield (δ -5.0 ppm) and broadens slightly. Neither the ^{31}P nor ^1H nmr spectrum shows the presence of any new species even at relatively high PPh_3 concentrations. We conclude, therefore, that association of triphenylphosphine with ethyl dimethyl(triphenylphosphine)gold to form a five-coordinate species is not kinetically important. Simi-



lar conclusions were deduced from the proton nmr spectra of trimethyl(triphenylphosphine)gold.¹¹

The kinetic results also indicate that the *cis-trans* isomerizations of ethyl dimethyl(triphenylphosphine)gold do not proceed *via* an associative mechanism shown in eq 24, since the rate is not accelerated by added tri-



phenylphosphine. Indeed, the fact that the rate of isomerization is relatively unaffected by added tri-

(11) A. Shiotani, H. F. Klein, and H. Schmidbaur, *J. Amer. Chem. Soc.*, **93**, 1555 (1971); *Chem. Ber.*, **104**, 2831 (1971).

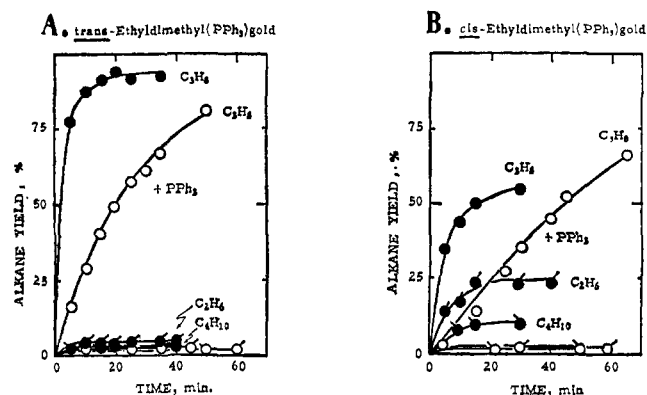
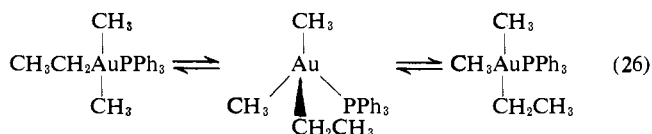


Figure 2. Thermal decomposition of (A) *trans*-ethyl dimethyl-(triphenylphosphine)gold and (B) *cis*-ethyl dimethyl-(triphenylphosphine)gold in decalin solution at 90° is shown in dark circles: ●, propane; ○, ethane; ◐, *n*-butane. The same reaction carried out in the presence of excess PPh₃ is in open circles: ○, propane; ◊, ethane; ◑, *n*-butane.

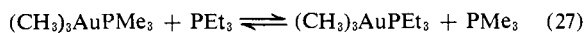
phenylphosphine supports a unimolecular process such as those presented in eq 25 and 26 (Scheme IV).

Scheme IV



According to those mechanisms, isomerization takes place *via* an intramolecular rearrangement. A tetrahedral intermediate may be involved as in eq 26, since dynamic equilibria between planar diamagnetic configurations and paramagnetic pseudotetrahedral forms are well established with nickel(II) complexes.¹² However, there are no examples of similar interconversions with gold(III) complexes, and it leaves open the alternative possibility that a tetrahedral transition state rather than an intermediate is involved as in eq 25.

Recently, Schmidbaur and coworkers¹¹ reported extensive ligand exchange between trimethyl(trimethylphosphine)gold and triethylphosphine after 1 day at 50°. An associative mechanism similar to that presented in eq 24 was suggested.^{12b} However, in view



of our foregoing results, it is possible that the phosphine substitution proceeds *via* a dissociative process. We hope that this problem will be resolved later by kinetic studies.

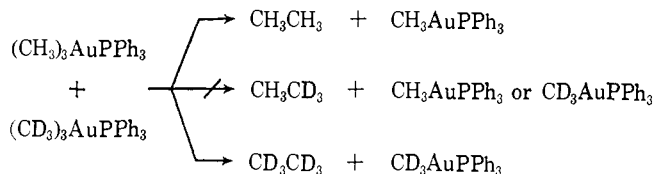
III. Reductive Elimination of Alkyldimethyl(triphenylphosphine)gold Complexes. The thermal decomposition of trimethyl(triphenylphosphine)gold in *tert*-butylbenzene solutions proceeds smoothly by reductive elimination of ethane at 80° according to eq 28.^{2,4}



The intramolecular nature of the decomposition was examined using an equimolar mixture of (CH₃)₃Au-

(12) (a) G. N. La Mar and E. O. Sherman, *J. Amer. Chem. Soc.*, **92**, 2691 (1970); L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *ibid.*, **92**, 1855 (1970); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 423 ff; (c) solvent may be involved; cf. D. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).

PPh₃ and (CD₃)₃AuPPh₃, which was decomposed for approximately one half-life. The isotopic analysis of ethane was based on the known mass spectral cracking patterns¹³ of CH₃CH₃, CH₃CD₃, and CD₃CD₃, and it indicated that CH₃CH₃ and CD₃CD₃ were formed in roughly equal amounts. Significantly, less than 5% of the cross-over product, CH₃CD₃, was formed judging by the normalization of the mass spectrum to a synthetic one, especially with regard to the minimal level of the unique *m/e* peak at 33. The foregoing results

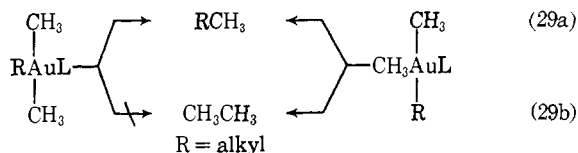


thus demonstrate that reductive elimination from trialkylgold(III) complexes proceeds mainly *via* an intramolecular route.

Similarly, *cis*-ethyl dimethyl(triphenylphosphine)gold in benzene solution decomposed readily at 70° in the absence of added triphenylphosphine. Examination of the nmr spectrum of the solution during this process showed that only very small nonequilibrium amounts (<10%) of *trans*-ethyl dimethyl(triphenylphosphine)gold were present at any time in the decomposing mixture. In other words, the reductive elimination of *cis*-Et(CH₃)₂AuPPh₃ proceeded at a rate faster than that of *cis*-*trans* rearrangement but only in the absence of added triphenylphosphine.

The decomposition of *trans*-Et(CH₃)₂AuPPh₃ in decalin solution afforded high yields of mainly propane as shown in Figure 2a. On the other hand, the decomposition of *cis*-Et(CH₃)₂AuPPh₃, which proceeded at significantly slower rates under the same conditions, produced a mixture of both propane and ethane as shown in Figure 2b. The formation of propane and ethane apparently proceeded *via* a common precursor, since the ratios of these alkanes remained invariant to moderate conversions of *cis*-Et(CH₃)₂AuPPh₃. The rate of decomposition of *cis*-Et(CH₃)₂AuPPh₃ decreased progressively as the temperature was lowered to 80 and 70° (Figure 3), and it was slightly slower in aromatic solvents such as *tert*-butylbenzene, *p*-xylene, or cumene. The relative amounts of propane and ethane varied only slightly with temperature and solvent. The rates of decomposition could be readily followed under these conditions by gas chromatographic analysis of the liberated alkanes or by the disappearance of alkyl(CH₃)₂AuPPh₃ by nmr. However, the kinetics were not established due to the extreme sensitivity of the rate to triphenylphosphine liberated during the decomposition (*vide infra*).

Similar results were also obtained with *cis*- and *trans*-*n*-propyldimethyl(triphenylphosphine)gold and isopropyldimethyl(triphenylphosphine)gold as shown in Table IV. In every case, products are consistent



(13) "Eight Peak Index of Mass Spectra," Vol. I, 1st ed, Mass Spectral Data Center.

Table IV. Decomposition of Isomeric Alkyldimethyl(triphenylphosphine)gold^a

	R(CH ₃) ₂ AuPPh ₃		T, °C	Time, ^b min	Alkane (mol %) ^{c,d}		
	(10 ³ mmol)	PPh ₃ (10 ³ mmol)			RCH ₃	CH ₃ CH ₃	RR
<i>trans</i> -Ethyl	70	0	70	75	83	3	2
	51	0	90	45	93	3	2
	49	57	90	180	96	2	2
<i>cis</i> -Ethyl	44	0	70	100	58	28	4
	51	0	90	80	54	29	8
	56	55	90	150	86	3	2
<i>trans</i> - <i>n</i> -Propyl	50	0	70	60	65 ^e	6	
	50	51	90	170	80 ^e	3	
<i>cis</i> - <i>n</i> -Propyl	50	0	70	200	60 ^e	45	
	51	51	90	300	60 ^e	4	
<i>trans</i> -Isopropyl	50	0	70	13	95 ^f	10	
	50	50	90	25	75 ^g	1	
<i>cis</i> -Isopropyl	51	0	70	75	70 ^h	45	
	50	51	90	60	85 ⁱ	1	

^a Decalin solution. ^b Time required for major decomposition (arbitrary). ^c Yields relative to R(CH₃)₂AuPPh₃ charged. ^d Yields in excess of 100% due to additional ethane formed by decomposition of CH₃AuPPh₃ in the absence of added PPh₃ (see text). ^e Including isobutane, 5%. ^f *n*-Butane, 40%. ^g *n*-Butane, 20%. ^h *n*-Butane, 25%. ⁱ *n*-Butane, 20%, yields relative to R(CH₃)₂AuPPh₃.

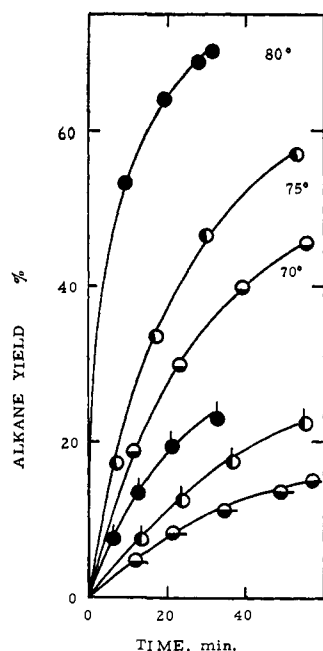
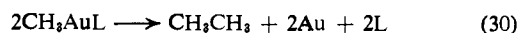


Figure 3. Temperature dependence of the reductive elimination of *cis*-ethyldimethyl(triphenylphosphine)gold in decalin solution (temperature, in propane, in ethane): 80°, ●, ○; 75°, ○, ○; 70°, ○, ○.

with an intramolecular process involving a rather stereospecific *cis* elimination. Significantly, during the reductive elimination of *cis*-alkyldimethyl(triphenylphosphine)gold isomers, it is either the ethyl or propyl group rather than the methyl group which is preferentially lost.

Decomposition of (alkyl)(CH₃)₂AuPPh₃ under these conditions is slightly complicated by the slow further decomposition of CH₃AuPPh₃ to deposit a gold mirror and to liberate additional ethane.



No metallic gold is deposited, however, when the reductive elimination of alkyldimethyl(triphenylphosphine)gold is carried out in the presence of added (>20 mol %) triphenylphosphine. The reaction stops cleanly after the first stage, *i.e.*

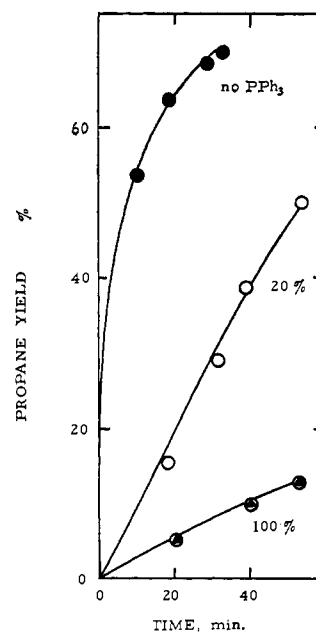
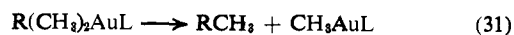


Figure 4. The thermal decomposition of *cis*-diethyldimethyl(triphenylphosphine)gold in decalin solutions at 70° in the presence of ●, no, ○, 20%, and ●, 100%, molar excess of triphenylphosphine. For clarity the formation of ethane is not included.

since CH₃AuPPh₃ is stabilized by added triphenylphosphine and can be recovered from the reaction mixture.³⁰

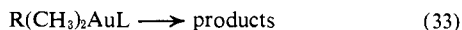
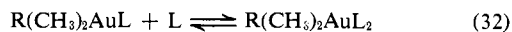
The rates of decomposition of both *trans*- and *cis*-Et(CH₃)₂AuPPh₃ are also retarded by added triphenylphosphine as shown in Figures 2a and 2b, respectively. The extent of retardation increases but is not strictly proportional to the amounts of added triphenylphosphine. The rate of decomposition is severely affected by an equimolar excess of triphenylphosphine (Figure 4). Strikingly, propane is the only major product obtained from both *cis*- and *trans*-Et(CH₃)₂AuPPh₃ in the presence of added triphenylphosphine. As shown earlier, the latter is readily attributable to the competing configurational equilibration of *cis*- to *trans*-Et(CH₃)₂AuPPh₃, which is less susceptible to retardation by added PPh₃ than the reductive elimination.

It is noteworthy that alkenes derived by β -elimination (*i.e.*, ethylene from ethyl or propylene from propyl

groups) are not important products under these conditions. Furthermore, simple alkanes generated by hydrogen transfer (*i.e.*, methane from methyl, ethane from ethyl, or propane from propyl groups) are also unimportant products.

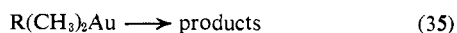
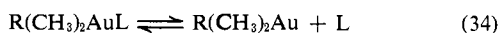
The retardation of the decomposition of alkyl-dimethyl(triphenylphosphine)gold by added PPh_3 can be accounted for by either of two mechanisms: (i) a pre-equilibrium formation of an inactive five-coordinate bis-phosphine adduct (Scheme VA), or (ii) a reversible

Scheme VA



dissociation of PPh_3 (Scheme VB). The associative

Scheme VB

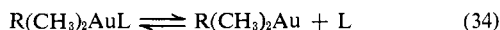


mechanism in Scheme VA can be readily dismissed by ^{31}P nmr studies, which show that successive additions of PPh_3 do not alter the nmr spectrum of ethyldimethyl(triphenylphosphine)gold. Furthermore, the ^{31}P and ^2H nmr spectra show no indication of any new phosphine adducts in sufficient concentrations to cause rate decreases of the magnitudes obtained. We conclude, therefore, that the decomposition (eq 31) of trialkyl(triphenylphosphine)gold proceeds *via* the dissociative mechanism shown in Scheme VB.

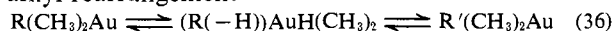
The exchange of alkyl groups between gold(III) and gold(I) species² accounts for some of the minor anomalies observed during the decomposition. Thus, the formation of minor amounts of *n*-butane from $\text{Et}(\text{CH}_3)_2\text{AuPPh}_3$ suggests that diethylgold(III) species are present.² Even more important, however, is the isomerization of alkyl groups, as shown in Table IV by the formation of isobutane from the *cis* and *trans* isomers of $n\text{-Pr}(\text{CH}_3)_2\text{AuPPh}_3$ and *n*-butane from the isopropyl analogs. Both cases can be traced to the interconversion of isopropylgold(III) and *n*-propylgold(III) discussed in section I.

Rearrangement and Reductive Elimination of Alkyl-dimethyl(triphenylphosphine)gold. Three separate reactions can be independently observed with alkyl-dimethyl(triphenylphosphine)gold complexes: (i) alkyl isomerization, (ii) *cis*-*trans* rearrangement, and (iii) reductive elimination. The rates of alkyl isomerization and reductive elimination are retarded by added triphenylphosphine, and both processes proceed *via* a dissociative mechanism. We infer that they involve a common trigonal intermediate formed by loss of a phosphine ligand as shown in Scheme VI.

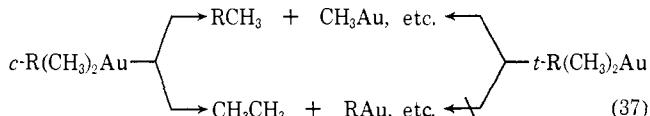
Scheme VI



(i) alkyl rearrangement



(iii) reductive elimination



Reductive elimination proceeds by loss of two *cis*-

alkyl groups from the trialkylgold(III) intermediate (eq 37). The geometric arrangement of the alkyl groups in this intermediate is unknown at present. However, a geometry is required for the trigonal intermediate in which the three alkyl groups are not symmetrically placed relative to each other, *i.e.*, the two methyl groups in the *cis*-alkyldimethyl(triphenylphosphine)gold isomer remain inequivalent.¹⁴ The latter is required by the observation of a rather stereospecific *cis* elimination (*cf.* eq 29). The ready isomerization of alkyl groups σ -bonded to gold(III) occurs in the order *tert*-butyl > isopropyl > *n*-propyl, and it is in accord with the facility with which β -elimination occurs with other transition metal alkyls.^{6,15} On the other hand, *cis*-*trans* rearrangement of alkyldimethyl(triphenylphosphine)gold is relatively unaffected by the presence of excess triphenylphosphine, and it suggests that the rearrangement is a unimolecular process involving the undissociated trialkyl(triphenylphosphine)gold species.

Experimental Section

Materials. Diethyl ether and 1,2-dimethoxyethane (DME) were dried with sodium benzophenone ketyl. After refluxing, the ethers were distilled under nitrogen.

Methylithium (Foote Chemical Co.) was recrystallized three times from ether. A DME solution of methylithium was prepared by drying the recrystallized material *in vacuo* and redissolving it in the solvent. The concentrations of methylithium were determined by acidimetric titration with standard hydrochloric acid solution. An aliquot was also hydrolyzed and the liberated methane determined quantitatively by glc using the internal standard method. Ethyllithium in benzene and *tert*-butyllithium in *n*-pentane were from Foote Chemical Co. and used as such. Alkyl halides were commercial samples (Eastman White Label or Aldrich Chemical Co.) and dried over phosphorus pentoxide and transferred *in vacuo*.

Hydrogen tetrachloroaurate(III) [$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$] was prepared from 99.95% gold by dissolution in aqua regia¹⁶ and converted in 96% yield to chlorotriphenylphosphinegold(I) according to the procedure described by Gregory and Ingold, mp 242–243° (lit 248–249°).¹⁷

Methyltriphenylphosphinegold(I). A Grignard reagent prepared from methyl iodide (2.5 ml, 40 mmol) and magnesium (1.0 g, 43 mmol) in 15 ml of ether was added dropwise to a suspension of ClAuPPh_3 (3.00 g, 6.06 mmol) in 25 ml of ether under nitrogen at -5° during 15 min. The mixture was refluxed for an hour, and then added to 150 ml of ice-cold 0.5% H_2SO_4 . Ether (20 ml) was added and the mixture was filtered. The solid was washed three times with benzene (100 ml each). The ether layer and the benzene washings were combined, washed with water, dried with Na_2SO_4 , and evaporated to about 80 ml. Pentane (200 ml) was then added and the mixture was chilled at -20° . Colorless fine crystals were obtained, 2.23 g (78% yield). A crystallized sample had melting point 167–168° (lit. 175°, 173–175°, 172–174°¹⁸); molecular weight (vpo) 475, theoretical 474; analysis Au, 40.9, 40.5, 40.8, calcd, 41.5; nmr in CDCl_3 δ , 1.10 ppm, $J = 8.0$ Hz (room temperature) [lit. δ 0.67 ppm, $J = 8.0$ Hz (35°)].¹⁹

Ethyl(triphenylphosphine)gold. A Grignard reagent prepared from 3.0 ml of ethyl bromide (40 mmol) and 1.15 g of Mg (47 mmol) in 50 ml of ether was added dropwise to a suspension of ClAu -

(14) (a) T-shaped trigonal intermediates are favored over Y-shaped ones, unless a phosphine ligand is present in the outer-coordination sphere. (b) The presence of an activation energy for interconversion of a *cis*-like and *trans*-like three-coordinate intermediate has also been proposed in the isomerization of the isoelectronic Pt(II) system which proceeds by a dissociative mechanism (G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc. A*, 1877 (1971)).

(15) For a review, M. Hancock, M. N. Levy, and M. Tsutsui, *Organometal. React.*, 4, 1 (1972).

(16) O. Glemser and H. Sauer, "Handbook of Preparative Inorganic Chemistry," Vol. II, 2nd ed, G. Brauer, Ed., Academic Press, New York, N. Y., 1965, p 1057.

(17) B. J. Gregory and C. K. Ingold, *J. Chem. Soc. B*, 276 (1969).

(18) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 3220 (1962).

(19) H. Schmidbaur and A. Shiotani, *Chem. Ber.*, 104, 2821 (1971).

PPh_3 (2.66 g, 514 mmol) in 20 ml of ether under nitrogen at -10° . The mixture was stirred for 2 hr at room temperature, and then added to 800 ml of 0.5% aqueous H_2SO_4 at 0° . The ether layer was separated and the aqueous layer was extracted with 200 ml of ether. The combined ether solution was dried with Na_2SO_4 , treated with active carbon, concentrated to about 150 ml, added to 100 ml of pentane, and chilled to -20° . Crystals separated, which were filtered and dried under vacuum, 1.30 g (49% yield), mp $134.5\text{--}135.5^\circ$ dec (lit. $150\text{--}152^\circ$ dec,¹⁷ ca. 130° dec¹⁸). *Anal.* Calcd for $\text{C}_{20}\text{H}_{20}\text{PAu}$: C, 49.2; H, 4.14; P, 6.35. Found: C, 49.06; H, 4.08; P, 6.09.

***n*-Propyl(triphenylphosphine)gold.** A Grignard reagent prepared from 4.0 ml of *n*-propyl bromide (44 mmol) and 1.12 g of Mg (46 mmol) in 30 ml of ether was added to a suspension of ClAuPPh_3 (3.02 g, 6.1 mmol) in 20 ml of ether between -11 and -5° during 20 min. The mixture was stirred at room temperature for an hour and added to 400 ml of 0.5% H_2SO_4 at 0° . Ether (100 ml) was added and the ether layer was separated. It was washed with water, dried with Na_2SO_4 , treated with active carbon, and evaporated until almost dry. The residue was recrystallized with a 1:1 mixture of ether and pentane and afforded almost colorless crystals, 1.91 g (62%), mp $77.5\text{--}79.0^\circ$ dec.

Isopropyl(triphenylphosphine)gold. A Grignard reagent, prepared from isopropyl bromide (3.5 ml) and Mg (1.0 g) in 30 ml of ether in an atmosphere of He, was added dropwise to a suspension of ClAuPh_3 (3.013 g, 6.09 mmol) in 100 ml of ether at -10° during 15 min. Triphenylphosphine (1.610 g, 5.91 mmol) was then added. The mixture was added to 400 ml of 0.5% H_2SO_4 at 0° . The ether layer was separated. The aqueous layer was twice extracted with 150 ml of ether each time. The combined ether extracts were then dried over Na_2SO_4 , treated with an active carbon, filtered, and concentrated to about 5 ml. Pentane (5 ml) was added and the solution was chilled to -26° , whereupon 2.623 g of slightly brown crystals were obtained, crude yield 86%. *Anal.* (on recrystallized sample): Calcd for $\text{C}_{21}\text{H}_{22}\text{PAu}$: C, 50.25; H, 4.43; P, 6.19; Au, 39.3. Found: C, 50.99; H, 4.41; P, 6.00; Au, 38.5. Molecular weight in benzene solution (vpo) 487, 493 (calcd 502); mp $150\text{--}151^\circ$ dec; nmr in CH_2Cl_2 δ 1.54, broad singlet, 6 H (taking the phenyl signal as 15 H).

***tert*-Butyl(triphenylphosphine)gold.** A Grignard reagent prepared from *tert*-butyl chloride (4.0 ml) and Mg, 1.0 g in 30 ml of ether, was added dropwise to a suspension of ClAuPPh_3 (2.005 g, 4.05 mmol) in 50 ml of ether at -20° during 25 min. Triphenylphosphine (1.070 g) was then added, and the mixture was stirred for 1.5 hr at -10° and 1.5 hr at room temperature. The mixture was added to 400 ml of 0.05% H_2SO_4 at 0° . The ether layer was separated and the aqueous layer was extracted with 150 ml of ether. The combined ether solution was dried, treated with active carbon, and concentrated at reduced pressure to about 20 ml. It was then chilled to -26° overnight. Colorless crystals (618 mg) were obtained (30%) which melted at $139\text{--}142^\circ$ dec, vapor pressure osmometry molecular weight 494, 516 (calcd 516). *Anal.* Calcd for $\text{C}_{22}\text{H}_{24}\text{PAu}$: C, 51.15; H, 4.7; P, 6.0; Au, 38.1. Found: C, 51.20; H, 4.58; P, 5.63; Au, 39.2. The nmr spectrum in dioxane solution showed a broad doublet at δ 1.35 ppm which had nine protons, taking phenyl signal (δ 7.48 ppm) as 15 protons. In benzene solution, it showed a sharp doublet (δ 1.97 ppm, J = 6.5 Hz).

***trans*-Ethylidimethyl(triphenylphosphine)gold.** A solution of dimethylaurate(I) prepared from 474 mg (1.00 mmol) of methyl(triphenylphosphine)gold and 1.00 mmol of methyl lithium in 1.86 ml of ether was treated with 1.25 mmol of ethyl iodide at room temperature for 20 hr. The solvent was removed *in vacuo* and the residue was extracted with 100 ml of pentane. The pentane extract was concentrated to 20 ml and chilled to -20° , whereupon a 56% yield of ethylidimethyl(triphenylphosphine)gold was obtained as colorless crystals. *Anal.* Calcd for $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{AuPPh}_3$: Au, 38.0. Found: Au, 37.5. In the nmr spectrum (dioxane solution), the two methyl groups appeared as a doublet (δ 0.29 ppm, J = 7.0 Hz) and the ethyl and phenyl groups as multiplets between δ 0.9–2.4 and 7.4–8.1 ppm, respectively, with the correct intensity ratio, molecular weight in *n*-heptane (vpo) 528 (calcd 518). *Anal.* Calcd for $\text{C}_{22}\text{H}_{26}\text{PAu}$: C, 50.97; H, 5.07. Found: C, 50.58; H, 4.95.

***trans*-*n*-Propylidimethyl(triphenylphosphine)gold** was obtained in 42% yield from dimethylaurate and *n*-propyl iodide: nmr (dioxane) $(\text{CH}_3)_2\text{Au}$ δ 0.22 ppm, J = 7.1 Hz, *n*-Pr 1.0–2.4 multiplet; molecular weight in *n*-heptane (vpo) 538 (calcd 532). *Anal.* Calcd for $\text{C}_{23}\text{H}_{28}\text{AuP}$: C, 51.9; H, 5.31. Found: C, 52.2; H, 5.50.

***trans*-Isobutyldimethyl(triphenylphosphine)gold** was obtained from either dimethylaurate and isobutyl bromide (after 9 days at room temperature) or isobutyl iodide (3 days). It was isolated as a colorless crystalline solid in 42% yield from pentane: nmr (dioxane) $(\text{CH}_3)_2\text{Au}$ δ 0.27 ppm, J = 7.4 Hz, $(\text{CH}_3)_2\text{C}$ 1.27, J = 6.6 Hz. *Anal.* Calcd for $\text{C}_{23}\text{H}_{30}\text{AuP}$: C, 52.8; H, 5.54. Found: C, 53.4; H, 5.81.

***trans*-Isopropylidimethyl(triphenylphosphine)gold** was prepared from lithium isopropylmethyl(triphenylphosphine)aurate(I) and methyl iodide in 33% yield: nmr (dioxane) $(\text{CH}_3)_2\text{Au}$ δ 0.14 ppm, J = 6.9 Hz, $(\text{CH}_3)_2\text{CH}$ 1.56 doublet (J = 12.4 Hz) of doublets (J = 6.4 Hz); (in benzene) $(\text{CH}_3)_2\text{Au}$ 0.37, J = 7.0 Hz, $(\text{CH}_3)_2\text{CH}$ 1.50, J = 7.0 Hz, doublet (J = 12.7 Hz) of doublets (J = 6.9 Hz).

***trans*-*tert*-Butyldimethyl(triphenylphosphine)gold.** A mixture of 2.03 g of methyl(triphenylphosphine)gold was treated with 3.64 ml of a solution of 1.18 *M tert*-butyllithium and 5 ml of diethyl ether and stirred at room temperature until it became homogeneous. It was then cooled to -78° and 0.27 ml of methyl iodide was added. The solution was allowed to warm up to room temperature and kept for 2 days. The solvent was removed *in vacuo* and the solid residue was taken up in 1:1 v/v ether-pentane. After recrystallization from pentane, 0.91 g of *trans*-isobutyldimethyl(triphenylphosphine) gold was obtained, which in comparison with the sample prepared from lithium dimethyl(triphenylphosphine)aurate and isobutyl iodide showed them to be the same.

The procedure was repeated with 836.5 mg of *tert*-butyl(triphenylphosphine)gold and 1.18 ml of 1.39 *M* methyl lithium in 2 ml of ether. The reactants were mixed at -78° and allowed to warm to room temperature with stirring until homogeneous. The solution was re-chilled to -78° and 1.18 ml of a 1.39 *M* solution of methyl iodide in ether was added at -78° . Dimethoxyethane (0.5 ml) was then added and the ether was removed *in vacuo*. Additional DME (0.5 ml) was added to the residue and the mixture was warmed to room temperature. After filtration to remove lithium iodide, the proton nmr spectrum of the solution showed a doublet resonance due to $(\text{CH}_3)_2$ cis to P (δ 0.03 ppm, J = 7.3 Hz), a *tert*-butyl doublet (δ 1.59 ppm, J = 11.4 Hz) with integrated intensities of 4.7 H and 7.0 H ($\text{CH}_3/t\text{-Bu}$ = 0.67) relative to phenyl = 15.0 H indicating some rearrangement. On standing overnight, the nmr of this solution was the same as that of *trans*-isobutyldimethyl(triphenylphosphine)gold. Attempts to isolate crystalline *trans*-*tert*-butyldimethyl(triphenylphosphine)gold always resulted in a sample contaminated with the isobutyl isomer.

***cis*-Ethylidimethyl(triphenylphosphine)gold** was prepared by mixing equimolar amounts of *cis*-dimethyliodo(triphenylphosphine)gold and ethyllithium in ether until the exchange was complete. The mixture was poured into water and extracted several times with ether. The combined ethereal extracts after washing with water and drying over sodium sulfate were evaporated. *cis*-Ethylidimethyl(triphenylphosphine)gold (67%) was recrystallized from pentane: nmr (dioxane) CH_3 cis to P δ 0.15 ppm, J = 6.9 Hz, CH_2 trans to P 1.31, J = 9.0 Hz, *cis*- CH_3CH_2 1.04, multiplet; molecular weight in *n*-heptane (vpo) 526 (calcd 518). *Anal.* Calcd for $\text{C}_{22}\text{H}_{26}\text{AuP}$: C, 50.97; H, 5.07. Found: C, 50.40; H, 4.97.

***cis*-*n*-Propylidimethyl(triphenylphosphine)gold** was prepared by a similar procedure in 62% yield: nmr CH_3 cis to P: δ 0.17 ppm, J = 6.9 Hz; CH_2 trans to P 1.32, J = 8.9 Hz, *n*-Pr 0.5–2.0 multiplet; molecular weight in *n*-heptane (vpo) 522 (calcd 532). *Anal.* Calcd for $\text{C}_{23}\text{H}_{28}\text{PAu}$: C, 51.9; H, 5.31. Found: C, 52.2; H, 5.71.

***cis*-Isopropylidimethyl(triphenylphosphine)gold** was prepared by treating *cis*-iododimethyl(triphenylphosphine)aurate(I) with an equimolar amount of isopropyllithium in ether. The mixture was then poured into water and extracted with ether. Removal of the ether afforded *cis*-isopropylidimethyl(triphenylphosphine)gold in 44% yield: nmr CH_3 cis to P δ 0.13 ppm, J = 7.2 Hz, CH_2 trans to P and $(\text{CH}_3)_2\text{CH}$ 1.0–1.3 multiplets.

Thermolysis of Alkyldimethyl(triphenylphosphine)gold. A two-neck F round bottom flask was equipped with a rubber septum cap and a glass spoon which could be rotated in the ground glass joint without exposing the contents to air. Solvent (5 ml) was added and a weighed amount of alkylgold complex was placed on the spoon. The sealed vessel was swept with helium and a known amount of marker gas added *via* a hypodermic syringe. The vessel was placed in the bath and the reaction was started by rotating the spoon in the ground glass joint so that the contents dropped into the magnetically stirred solvent. Similar results were obtained when the one-neck vessel containing solvent was swept with helium and the sample quickly added to the preequilibrated solvent as the rubber septum was put in place.

In order to determine the possible effects of adventitious oxygen on the rate of decomposition, a benzene solution of *cis*-Et(CH₃)₂-AuPPh₃ containing *tert*-butylbenzene as an internal standard was placed in an nmr tube, rigorously degassed three times using freeze-pump-thaw cycle, and then sealed. The rates of decomposition were followed by nmr and shown to be the same within $\pm 10\%$ of comparable reactions carried out in air. The rates of thermal decomposition carried out in decalin solutions were difficult to reproduce even after careful purification and manipulation of the solvent in the absence of air. The formation of propane and ethane, however, showed little variation. The effect of peroxidic contaminants was examined by the deliberate addition of *tert*-butyl hydroperoxide or *tert*-butyl peroxyoxalate and will be reported separately at a later time. Water at low concentrations had no noticeable effect on the rate. The addition of up to equimolar amounts of CH₃AuPPh₃ also exerted a minimal effect on the rate of decomposition of *cis*-Et(CH₃)₂AuPPh₃.

Analysis. The gold content was determined gravimetrically by digesting the sample in concentrated sulfuric acid.²⁰ Other meth-

(20) C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Vol. IC, Elsevier, Amsterdam, 1961, p 390.

ods involving iodometry or complete thermolysis followed by gravimetry did not afford accurate analyses.

The hydrocarbon gases were analyzed by gas chromatography (hydrogen flame, Aerograph 500, 50 cm Porapak Q column at 90° or a 20 ft ODPN column). Quantitative analysis was effected by the internal standard method after careful calibration under reaction conditions. The latter was especially important when solvent was present due to differential solubility of gases. The analyses were reproducible to $\pm 2\%$.

The molecular weights in benzene solutions were carried out with a Mechrochrom 301A vapor pressure osmometer at 37° using benzil or benzophenone as calibrant. The pmr spectra were obtained on a Varian HA 100 spectrometer with variable temperature control or routinely on a Varian EM-360 spectrometer. All chemical shifts were measured (± 0.05 ppm) relative to external TMS. Phosphorus nmr spectra were taken on a Varian XL-100 Fourier transform spectrometer using H₃PO₄ as an external reference.

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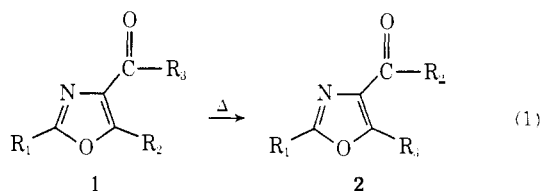
The Cornforth Rearrangement

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Abstract: The rates of Cornforth rearrangements of 2-aryl-5-methoxyoxazole-4-carboxylic amides have been studied. Variation of substituents in the 2-phenyl group indicates that a small positive charge develops at the adjacent carbon on passing to the transition state. Similar variation of substituents in a phenyl group attached to the amide nitrogen indicates that a similar small negative charge develops in the amide moiety. The effect of changes in the solvent also indicates that the transition state is not strongly polar. Either the transition state must occur early in the reaction or the open chain intermediate must be less polar than a classical zwitterionic structure would suggest.

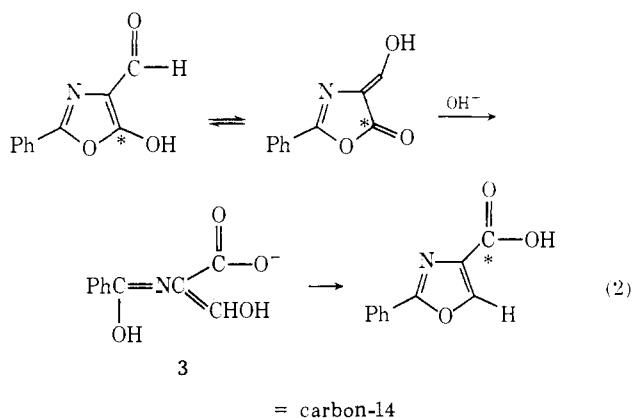
The thermal rearrangement of 4-carbonyl substituted oxazoles was first observed by Cornforth.¹ The general reaction is given in eq 1.



An analogous reaction, the base-induced rearrangement of 4-hydroxymethylene-5-oxazolones (*i.e.*, **1**, R₂ = OH; R₃ = H) to oxazole-4-carboxylic acids, has been investigated by isotopic labeling experiments.² When the carbonyl carbon of the oxazolone ring was labeled with carbon-14 and the compound was subjected to treatment with base, the rearranged oxazole-4-carboxylic acid was labeled only at the carboxyl carbon atom. The authors propose initial attack of hydroxide ion at the 2-position of the oxazolone ring with subsequent ring opening to **3** and ring closure to yield the ¹⁴C labeled acid (eq 2).

(1) J. W. Cornforth in "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p 700.

(2) C. G. Stuckwisch and D. D. Powers, *J. Org. Chem.*, **25**, 1819 (1960).



The thermal rearrangement of 4-carbonyl substituted 5-oxazolones to oxazoles has been studied for its synthetic utility since the oxazoles produced are intermediates in the synthesis of substituted amino acids.³

The mechanisms which have been proposed^{2,3c,4} are interrelated in that they involve the ring opening of the oxazole or oxazolone derivative to a zwitterionic inter-

(3) (a) W. Steglich and G. Hofte, *Chem. Ber.*, **102**, 883, 899 (1969); (b) *Tetrahedron Lett.*, 4727 (1970); (c) *Chem. Ber.*, **104**, 1408 (1971).

(4) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949.