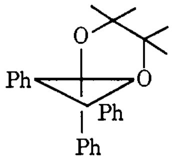
electronegativities on phosphorus would never occur without the constraint of the small ring.



1

The preparation of an epoxide has been reported by the use of singlet oxygen on an olefin in pinacolone as a solvent,[10] in analogy to the isolation of dioxetanes from the action of ozone on olefins in the same solvent.[11] In each of these cases it has been postulated that the monodeoxygenation involves the removal of coordinate oxygen from a perepoxide[10] or perdioxetane (Staudinger molozonide) intermediate[12a] through Baeyer–Villiger attack on pinacolone. The present report represents the first instance of reduction of a dioxetane to an epoxide through initial insertion of the oxygen acceptor into the ring. We shall report shortly on some metal insertions into the dioxetane ring followed by reductive fragmentation, which provide models for the extremely rapid catalytic dioxetane decompositions recently observed.[13]

Acknowledgments. This work was supported by grants from the National Science Foundation and the National Institutes of Health. We thank Charles L. Lerman for arousing our interest in the reactions of dioxetanes with trivalent phosphorus compounds.

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Rearrangement and Decomposition of Trialkylgold(III) Complexes

Sir:

Trialkylgold(III) species are the key intermediates in the catalytic coupling of alkyl groups from organogold(I) complexes and alkyl halides.[1] They are also rather unique among transition metal alkyls in undergoing reductive elimination by alkyl coupling rather than by disproportionation.[2] Thus, ethyl groups are coupled in high yields during the decomposition of diethyl(methyl)(triphenylphosphine)gold,[1,3] *e.g.*

$$(CH_3CH_2)_2CH_3Au^{III}PPh_3 \longrightarrow CH_3CH_2CH_2CH_3 + CH_3Au^{I}PPh_3 \qquad (1)$$

Various isomeric trialkyltriphenylphosphinegold complexes can now be obtained, which have square-planar configurations characteristic of four-coordinate gold(III).[4] The known stereochemical structures of these complexes[4,5] allowed us to examine the stereochemistry and the manner in which alkyl groups are reductively eliminated from alkylgold(III) species, and they have provided mechanistic insight into the coupling process.

trans-Ethyldimethyl(triphenylphosphine)gold was synthesized by oxidative addition of ethyl iodide to lithium dimethyl(triphenylphosphine)aurate(I).[6] The corresponding cis isomer was prepared by stereospecific alkyl exchange between *cis*-dimethyliodotriphenylphosphinegold and ethyl Grignard.[4c] Other analogs in Table I were synthesized by similar procedures. The stereoisomeric pairs are readily distinguished by their proton nmr spectra.[4,6] Molecular weight measurements by vapor pressure osmometry indicated that these alkyldimethyltriphenylphosphine gold complexes are monomeric in solutions of benzene as well as *n*-heptane.

Table I. Decomposition of Stereoisomeric Alkyldimethyl(triphenylphosphine)gold[a]

R(CH₃)₂AuPPh₃	(10³ mmol)	PPh₃ (10³ mmol)	*T*, °C	Time,[b] min	Alkane (mol %)[c,d] RCH₃	CH₃CH₃	RR
trans-Ethyl	70	0	70	75	83	3	2
	51	0	90	45	93	3	2
	49	57	90	180	96	2	2
cis-Ethyl	44	0	70	100	58	28	4
	51	0	90	80	54	29	8
	56	55	90	150	86	3	2
trans-*n*-Propyl	50	0	70	60	65[e]	6	
	50	51	90	170	80[e]	3	
cis-*n*-Propyl	50	0	70	200	60[e]	45	
	51	51	90	300	60[e]	4	
trans-Isopropyl	50	0	70	13	95[f]	10	
	50	50	90	25	75[g]	1	
cis-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 $R(CH_3)_2AuPPh_3$ charged. [d] Yields in excess of 100% due to additional ethane formed by decomposition of CH_3AuPPh_3 in the absence of added PPh_3 (see text). [e] Including isobutane 5%. [f] *n*-Butane, 40%. [g] *n*-Butane, 20%. [h] *n*-Butane, 25%. [i] *n*-Butane, 20%, yields formed relative to $R(CH_3)_2AuPPh_3$.

The decomposition of *trans*-$CH_3CH_2(CH_3)_2AuPPh_3$ afforded high yields of only propane. On the other hand, the decomposition of *cis*-$CH_3CH_2(CH_3)_2AuPPh_3$, which proceeded at significantly slower rates under the same conditions, produced a mixture of pro-

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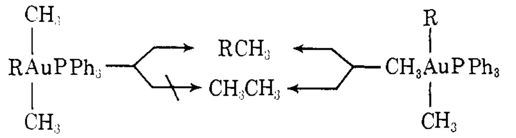
pane and ethane (see Table I). These results are consistent with an intramolecular process, involving a rather stereospecific cis elimination. Similar results were obtained with *cis*- and *trans*-*n*-propyl- and -isopropyldimethyltriphenylphosphinegold as shown in



(2a)
(2b)

$R = C_2H_5, n\text{-}C_3H_7, i\text{-}C_3H_7$

Table I. Decomposition under these conditions is slightly complicated by the slow further decomposition of CH_3AuPPh_3 to deposit a gold mirror and liberate additional ethane[7]

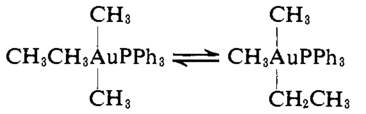
$$2CH_3AuPPh_3 \longrightarrow CH_3CH_3 + 2Au^0 + 2PPh_3 \quad (3)$$

No metallic gold is deposited, however, when the reductive elimination of alkyldimethyl(triphenylphosphine)gold is carried out in the presence of added PPh_3. The rate of decomposition of alkyldimethyl(triphenylphosphine)gold is increasingly retarded by successive amounts of added PPh_3. The reaction under these conditions stops cleanly after the first stage

$$R(CH_3)_2Au^{III}PPh_3 \longrightarrow RCH_3 + CH_3Au^{I}PPh_3 \quad (4)$$

since the slower decomposition of CH_3AuPPh_3 is severely retarded by PPh_3,[7] and CH_3AuPPh_3 can be readily observed in the reaction mixture by nmr.

Strikingly, propane is the only major product obtained from *both cis*- and *trans*-$CH_3CH_2(CH_3)_2AuPPh_3$ in the presence of added PPh_3 as shown in Table I. Separate nmr studies established that at slightly lower temperatures (where the decomposition is slower), *cis*- and *trans*-$CH_3CH_2(CH_3)_2AuPPh_3$ are readily interconverted to an equilibrium mixture favoring the trans isomer. The rate of cis–trans isomerization is relatively insensitive to the concentration of added PPh_3, although we were unable to study the isomerization at very low concentrations of PPh_3 due to the onset of the competing decomposition described above. Thus, the rate of cis–trans isomerization in eq 5 is clearly faster than the rate of decomposition in eq 4, in the *presence of added PPh*$_3$. Under these conditions, the preponderant formation of only propane from either *cis*- or *trans*-ethyldimethyl(triphenylphosphine)gold (see Table I) is readily attributable to rapid cis–trans isomerization followed by the preferential decomposition of the more labile trans isomer.[8]



$$\underset{\text{(trans)}}{CH_3CH_3\overset{CH_3}{\underset{CH_3}{Au}}PPh_3} \rightleftharpoons \underset{\text{(cis)}}{CH_3\overset{CH_3}{\underset{CH_2CH_3}{Au}}PPh_3} \quad (5)$$

(trans) (cis)

The retardation of the decomposition of alkyldimethyl(triphenylphosphine)gold by added PPh_3 can be accounted for by either of two mechanisms: (i) a preequilibrium formation of an inactive five-coordinate bisphosphine adduct

$$R(CH_3)_2AuPPh_3 + PPh_3 \rightleftharpoons R(CH_3)_2Au(PPh_3)_2 \quad (6)$$

$$R(CH_3)_2AuPPh_3 \longrightarrow \text{products} \quad (7)$$

or (ii) a reversible dissociation of PPh_3

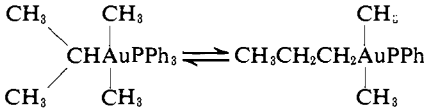
$$R(CH_3)_2AuPPh_3 \rightleftharpoons R(CH_3)_2Au + PPh_3 \quad (8)$$

$$R(CH_3)_2Au \longrightarrow \text{products} \quad (9)$$

The associative mechanism in eq 6 and 7 can be readily dismissed by ^{31}P nmr studies, which show that successive additions of PPh_3 do not alter the spectrum of $C_2H_5(CH_3)_2AuPPh_3$. The ^{31}P nmr spectra of *trans*-$C_2H_5(CH_3)_2AuPPh_3$ and free PPh_3 both consist of singlets, the chemical shifts of which are unchanged with various amounts of added PPh_3. Furthermore, the ^{31}P and ^1H 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 decomposition (eq 4) of trialkyl(triphenylphosphine)gold proceeds *via* a dissociative process involving a three-coordinate trialkylgold(III) intermediate such as that described in eq 8 and 9. Furthermore, the trigonal intermediate must maintain sufficient stereochemical integrity to allow for cis elimination of alkyl groups in the absence of added PPh_3 (*cf.* eq 2).[9,10] It is noteworthy that no significant amounts of alkenes are formed during the decomposition of any of these trialkylgold(III) compounds.

The exchange of alkyl groups between gold(III) and gold(I) species[1] accounts for some of the minor anomalies observed during the decomposition. Thus, the formation of small amounts of *n*-butane from $CH_3CH_2(CH_3)_2AuPPh_3$ suggests that diethylgold(III) species are present.[1] Even more important, however, is the isomerization of alkyl groups, as shown in Table I by the formation of isobutane from the cis and trans isomers of $CH_3CH_2CH_2(CH_3)_2AuPPh_3$ and *n*-butane from the isopropyl analogs. Both cases can be traced to the interconversion of isopropylgold(III) and *n*-propylgold(III) species, *e.g.*



(10)

the mechanism of which is analogous to the spontaneous rearrangement of *trans*-*tert*-$Bu(CH_3)_2AuPPh_3$ to the isobutyl isomer.[11] The latter has also been shown to occur *via* a trigonal intermediate formed by the same dissociative route presented in eq 8 and 9.

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[9] A geometry for the cis isomer is required in which the CH_3 groups are inequivalent. The presence of PPh_3 in the outer coordination sphere is not excluded.

[10] It is possible that cis–trans isomerization of trialkyl(triphenylphosphine)gold also proceeds by eq 8 and 9, if isomerization of the trigonal intermediate occurs faster than PPh_3 return. Nmr studies show that in the absence of PPh_3, *cis*-ethyl$(CH_3)_2AuPPh_3$ at 60° undergoes rearrangement and decomposition at competitive rates. The selective decompositions observed at higher temperatures (Table I) is consistent with this observation if the activation energy for reductive elimination from the trigonal intermediate is higher than that for rearrangement. Further studies are in progress.

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