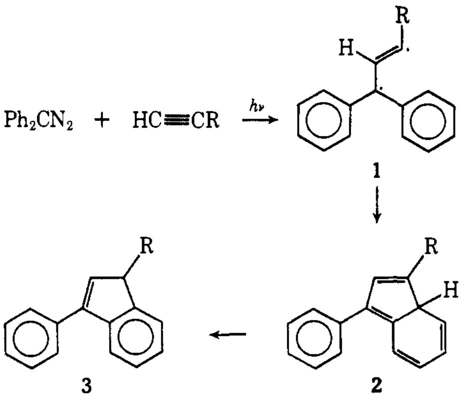
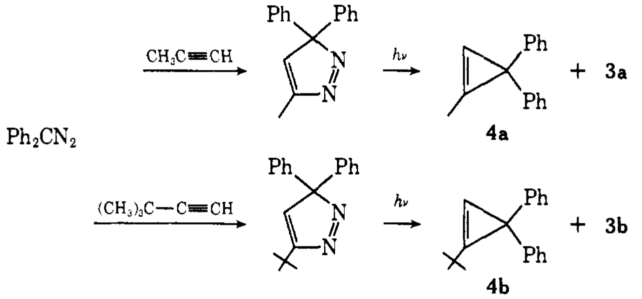
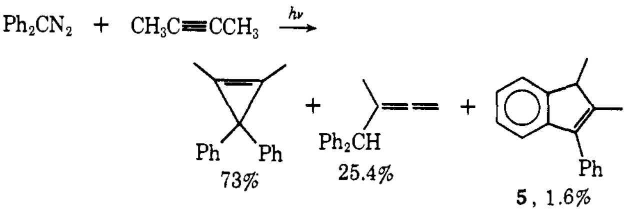


a, R = CH_3
b, R = $(CH_3)_3C$
c, R = Ph

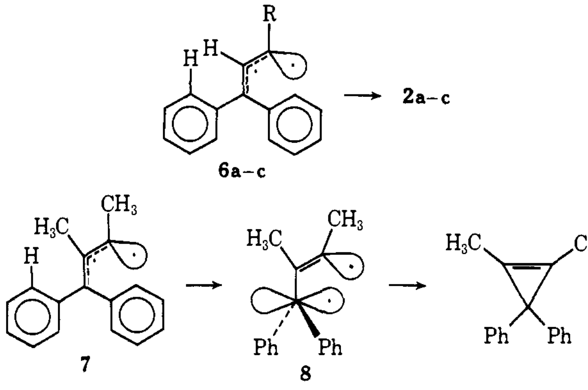
photochemical[12] reactions of this type are known. Although the temperatures involved in this work never exceeded room temperature and are thus far below the 190–200° necessary to convert tetraphenylcyclopropene to 1,2,3-triphenylindene,[11] a photochemical rearrangement seemed distinctly possible. Accordingly, we synthesized authentic cyclopropenes **4a** and **4b** by the photochemical decomposition of the corresponding 3*H*-pyrazoles.[13] These pyrazoles are potential intermediates in the formation of indenes from diphenyldiazomethane and acetylenes. However, under a variety of conditions, including both direct and sensitized decomposition, the pyrazoles always gave substantial (20–45%) amounts of cyclopropene. Thus they cannot be intermediates in the original decompositions in which no more than traces of cyclopropene can be formed. Cyclopropenes **4a** and **4b** are not converted to indenes either by direct or by sensitized irradiation. Both benzophenone and diphenyldiazomethane were tried as sensitizers. Thus, **3a–c** are primary products of the reaction.



Curiously, irradiation of diphenyldiazomethane in dimethylacetylene produced a mixture of cyclopropene and indene strongly favoring (*ca.* 45:1) cyclopropene. The presence of the known[14] indene **5** was inferred from appropriate peaks in the nmr spectrum of the crude reaction mixture. We attribute this startling change in reaction course to a steric effect. In particular, we suspect that the intermediates responsible for indene



formation are well described by **6a–c**. Rotation of one phenyl ring[15] allows formation of **2** but cyclopropenes cannot easily be produced. The diradical **7**, analogous to **6**, but formed from a disubstituted acetylene, suffers an alkyl–hydrogen interaction which is missing in **6**, and which apparently requires rotation to **8**, which is a suitable intermediate for cyclopropene



formation.

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(12) D. J. Keyton, J. J. Brophy, G. W. Griffin, B. Halton, M. Kulig, and M. A. Battiste, Abstracts, 160th National Meeting of the American Chemical Society, Sept 1970, ORGN 91.

(13) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968).

(14) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970).

(15) Triplet fluorenylidene, which would produce an intermediate in which this rotation is impossible, forms only cyclopropenes.

(16) National Science Foundation Predoctoral Fellow, 1967–1971.

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Nuclear Magnetic Resonance Spectra and Ligand Substitution Reactions of Methylgold and Trimethylgold Complexes

Sir:

Our recent spectroscopic studies of the classical organogold compounds trimethylphosphinemethylgold (**1**) and trimethylphosphinetrimethylgold (**2**) have revealed some interesting phenomena, which shed new light on the relative reactivities of gold(I) and gold(III) complexes in ligand substitution processes. Compound **1**

$$\underset{\mathbf{1}}{CH_3Au\leftarrow P(CH_3)_3} \qquad \underset{\mathbf{2}}{(CH_3)_3Au\leftarrow P(CH_3)_3}$$

was obtained following the procedure described for the triethylphosphine complex by Coates and Parkin[1] and identified by its elemental analysis[2] and infrared, proton magnetic resonance, and mass spectra.

Solutions of this monomeric compound in pure anhydrous benzene exhibit the expected two proton resonances in the pmr spectra, both signals being split

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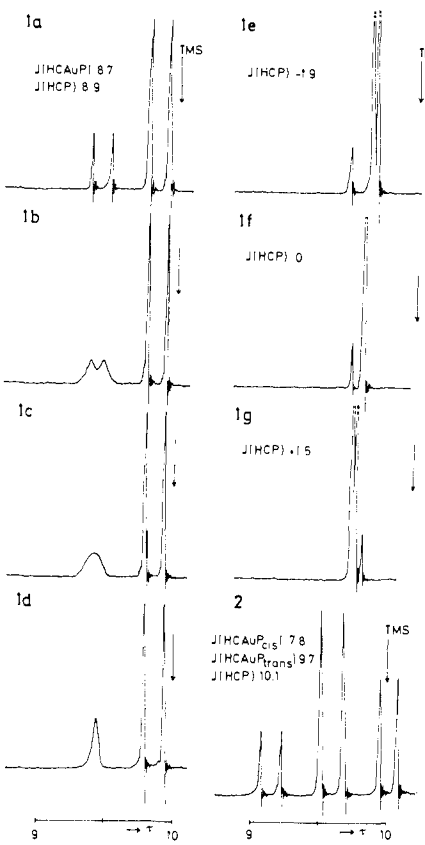
(1) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 3220 (1962).

(2) Compound **1**, mp 70–71°. *Anal.* Calcd for $C_4H_{12}AuP$ (288.1): C, 16.70; H, 4.20. Found: C, 16.60; H, 4.06; mol wt (mass spectrum) 288 (no melting point, analysis, or molecular weight reported in ref 1).



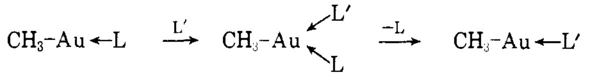
Figures 1 and 2. Proton magnetic resonance spectra of trimethylphosphinemethylgold (**1**) and trimethylphosphinetrimethylgold (**2**) in benzene solution at various molar ratios of complex and free ligand: (1a) pure **1**, (1b) compound **1**/ligand = 1000:1, (1c) 350:1, (1d) 100:1, (1e) 1:1.5, (1f) 1:3.5, (1g) 1:9, (2) pure compound **2**. Spectra were run at 60 MHz and 30°. Initial concentration 10% (w/w) compound **1** or **2** in benzene. This concentration drops as phosphine is added to the solution. τ values are in parts per million relative to external TMS.

into a doublet by $^1HC^{31}P$ and $^1HCAu^{31}P$ coupling,[3] respectively (Figure 1a). However, this picture is obtained only if all traces of free ligand are rigorously excluded from the solution. Successive addition of very small amounts of trimethylphosphine (the solutions thus being 10^{-3}–10^{-2} *M* in phosphine per mole of complex) to the sample leads to a collapse of the CH_3Au doublet, which is finally replaced by a sharp, unshifted singlet (Figures 1b–d).

Further addition of trimethylphosphine affects only the $(CH_3)_3P$ doublet, which experiences a decrease in its $^1HC^{31}P$ coupling constant and a shift toward the value of the free ligand (Figure 1e). In the special case when the complex and the ligand are present in a molar ratio of 1:3.4, a sharp singlet with a zero $^1HC^{31}P$ coupling is observed (Figure 1f). With a greater excess of phosphine this singlet again becomes split (Figure 1g) and the coupling constant approaches a final value close to that reported for pure trimethylphosphine in benzene: |2.6| Hz,[4] while a concentration shift causes the $(CH_3)_3P$ and CH_3Au signals to change positions.

These nmr phenomena can be understood in terms of a rapid ligand exchange process at the CH_3Au center, the rate of which is strongly dependent on the concentration of the free ligand. In the absence of the latter this process is slow on the nmr time scale and high preexchange lifetimes, τ, of the phosphine at the gold atom warrant a $^1HCAu^{31}P$ coupling. With phosphine concentrations >1%, the exchange reaction becomes rapid enough to reduce the τ value beyond the experimental limit, which is estimated[5] to be 2.5×10^{-2} sec at 30°. At still higher phosphine concentrations the phosphine resonance represents the weighted average in chemical shift and coupling constant of the resonances of complexed and free phosphine, owing to rapid exchange conditions. The observation of a zero coupling $^1HC^{31}P$ at a certain molar ratio of reactants is evidence for *opposite signs* of $J(^1HC^{31}P)$ in the free phosphine and its complex. As $J(^1HC^{31}P)$ is known[4] to be positive in $(CH_3)_3P$, it must be negative in the complex, in line with findings for other coordination compounds of phosphines.[4]

The mechanism of ligand exchange at the CH_3Au moiety is believed to be associative and to include an intermediate with sp^2-hybridized gold atoms of coordination number three.



$$CH_3{-}Au \leftarrow L \xrightarrow{L'} CH_3{-}Au\begin{matrix} \swarrow L' \\ \nwarrow L \end{matrix} \xrightarrow{-L} CH_3{-}Au \leftarrow L'$$

$L = L' = P(CH_3)_3$

The concentration dependence of the nmr spectra is consistent with this proposal. In preparative experiments it could be shown that compound **1** undergoes a spontaneous reaction with an excess of triethylphosphine at room temperature to give quantitative yields of the known[1] compound $CH_3AuP(C_2H_5)_3$ and $(CH_3)_3P$.

The compound $[(CH_3)_3AuP(CH_3)_3]$, **2**, was synthesized as described by Coates and Parkin;[6] all properties of the sample obtained were in full agreement with the data given by these authors. Mass spectra indicated the presence of monomeric species in the vapor phase. The proton nmr spectrum consists of three signals with relative intensities 1:2:3. Each of these is split into a 1:1 doublet with different spacings of the lines (Figure 2). This pattern confirms a square-planar arrangement of the ligands at the gold atom.[6,7] The doublets are easily assigned to the *trans*- and *cis*-CH_3Au groups and the $(CH_3)_3P$ ligand, according to their intensities. The large difference in δ and *J* values between *trans*- and *cis*-CH_3Au groups is noteworthy with respect to the trans effect of the ligand.

The pmr spectrum of compound **2** is *unaffected* by the addition of various quantities of the free ligand to the solution. The ligand exchange at the $(CH_3)_3Au$ species therefore appears to be a *slow* process on the nmr time scale even in the presence of excess ligand. Though this is still true at +60° (the upper limit of thermal stability for the compound in solution), the substitution reaction may be conducted on a preparative scale if the necessary reaction periods are allowed for.

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(3) A similar $^1HCAu^{31}P$ coupling has recently been detected in triphenylphosphinetrimethylsilylmethylgold: A. Shiotani and H. Schmidbaur, *J. Amer. Chem. Soc.*, **92**, 7003 (1970). In a cationic system, $CH_3Hg \leftarrow P(CH_3)_3^-$, which is isoelectronic with compound **1**, a coupling $J(^1HCHg^{31}P) = 6.2$ Hz has been observed: H. Schmidbaur and K. H. Räthlein, unpublished results.

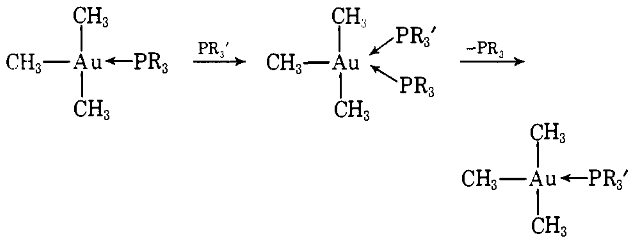
(4) G. Mavel, *Progr. Nucl. Magn. Resonance Spectrosc.*, **1**, 251 (1966).

(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

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

(7) B. Armer and H. Schmidbaur, *Angew. Chem.*, **82**, 120 (1970); *Angew. Chem., Int. Ed., Engl.*, **9**, 101 (1970).

Thus, compound **2** may be converted into the corresponding triethylphosphine complex simply by mixing it with excess $(C_2H_5)_3P$. After 1 day at 50°, $(CH_3)_3AuP(C_2H_5)_3$ is obtained in 80% yield. The most likely mechanism[8,9] for this reaction is again an associative process, now involving a *pentacoordinate* intermediate with gold in a dsp^3 state.



The difference in reaction rates for compounds **1** and **2** is probably due to the variation in the Au–P bond energies. It is also significant that $|J(^1HC^{31}P)|$ appears to be greater for compound **2** than for compound **1**, confirming a stronger Au–P interaction in the former. Finally, in ir spectra reported by Coates, *et al.*,[6] the Au–P stretching frequencies show a higher value for Au^{III} than for Au^{I} compounds. According to molecular models, steric factors are not likely to play a decisive role.

[8] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 18.

[9] C. D. Falk and J. Halpern, *J. Amer. Chem. Soc.*, **87**, 3003 (1965); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1968, p 357 ff.

[10] Visiting scholar supported by UBE Industries Ltd., Tokyo, Japan.

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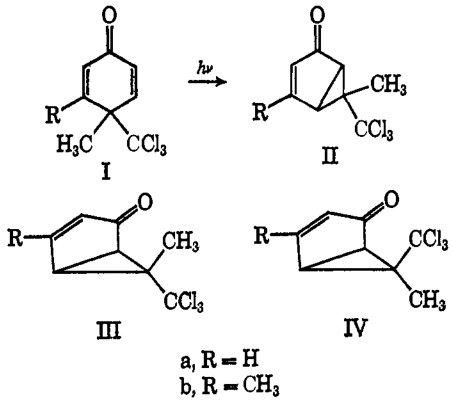
Stereoselectivity in the Photochemical Rearrangement of 3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadienone[1,2]

Sir:

It was reported some years ago that the photochemical rearrangement of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (Ia) in a variety of solvents gave only one of the two possible stereoisomeric lumiketones IIa.[3] In the absence of the second diastereomer, no definite assignment of stereochemistry to the product was possible, although structure IVa was preferred on the basis of spectral data.[3] The presence of the larger substituent in the endo orientation as in IVa would be consistent with observations made in several other dienone–lumiketone photorearrangements,[4,5] for which a rationalization has been provided by Rodgers and Hart.[5]



The photochemistry of the methyl homolog of Ia, cyclohexadienone Ib, has now been studied, and it is found that both stereoisomeric lumiketones IIIb and IVb are formed. The stereochemistry of these bicyclic ketones has been unequivocally established on the basis of spectral data, and ultimately X-ray crystallographic analysis of one of the isomers. Photolysis of Ib at 2537 Å in *tert*-butyl alcohol, followed by chromatography on silica gel, led to isolation of IIIb, mp 69–71°, and IVb, mp 91–93°. Analysis of the crude photolysate by glpc indicated they are formed initially in the ratio of 15:1, respectively. The isomers have similar mass spectra, except for the relative intensity of some peaks and the absence of a molecular ion at m/e 238 in the case of IIIb;[6] in both cases the base peak was at m/e 203 (M − Cl). Their ir spectra are similar, featuring a carbonyl band at 1710 cm^{-1} in both cases. Whereas IIIb showed uv absorption (EtOH) at 257 ($\log \epsilon$ 3.57) and 208 nm ($\log \epsilon$ 3.79), that for IVb was slightly shifted to 266 ($\log \epsilon$ 3.56) and 212 nm ($\log \epsilon$ 3.79). From their nmr spectra a stereochemical assignment is possible. Whereas both isomers show resonances for the vinyl proton at δ 5.64 ppm (broad multiplet) and a vinyl methyl at δ 2.14 ppm (d), the other methyl group is shielded in IIIb (δ 1.54) compared with IVb (δ 1.62),[7] while the cyclopropyl-H resonances are correspondingly deshielded (δ 2.74, m) in IIIb compared with IVb (δ 2.42, m). In addition, the *endo*-methyl resonance in IIIb is broadened compared with IVb, consistent with long-range coupling with the cyclopropane protons according to the familiar W plan.[8]

No interconversion of the lumiketones IIIb and IVb is observed on heating or irradiation of either stereoisomer.[9] Such treatment leads, as in the parent case,[3] to other compounds whose structures are currently being elucidated.

The configuration of IIIb has been established absolutely by X-ray crystallographic analysis. The compound crystallized in the monoclinic space group

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[1] Part XXIX of a series on the photochemistry of unsaturated ketones in solution. Part XXVIII: D. I. Schuster and B. M. Resnick, *J. Amer. Chem. Soc.*, **92**, 7502 (1970).

[2] This research was supported at New York University by the National Science Foundation under Grants GP-7433 and GP-10828.

[3] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **88**, 1825 (1966); D. J. Patel and D. I. Schuster, *ibid.*, **90**, 5137 (1968).

[4] (a) T. Matsuura, *Bull Chem. Soc. Jap.*, **37**, 564 (1964); (b) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **89**, 1678 (1967); (c) B. Miller, *ibid.*, **89**, 1690 (1967); (d) K. Ogura and T. Matsuura, *Bull. Chem. Soc. Jap.*, **43**, 2891 (1970).

[5] T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 4845 (1969).

[6] The elemental composition of IIIb is based on a satisfactory elemental analysis as well as the mass spectral fragmentation.

[7] Shielding of *endo*- relative to *exo*-6-methyl groups in bicyclo[3.1.0]hexenones has been suggested earlier[4,5] and used to assign stereochemistry. See also D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).

[8] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 334 ff.

[9] In other investigations,[10] interconversion of epimeric lumiketones was also not observed. This appears to be a general observation in these systems.

[10] (a) H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **89**, 5163 (1967); (b) D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).