mined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters and the method of estimation of standard deviations have been described previously.[10] As a check on the stability of the instrument and the crystal, two reflections, the (200) and (002), were measured after every 30 reflections; no significant variation was noted.

One independent quadrant of data was measured out to $2\theta = 110°$; a total of 349 unique reflections $(I > 2\sigma(I))$ was obtained. The intensities were corrected for Lorentz and polarization effects but not for absorption, since the extreme values of the transmission factors were 0.90 and 0.95.

Fourier calculations were made with the ALFF[11] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[12] The function $w(|F_o| - |F_c|)^{13}$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber[14] for C and N; those for hydrogen were from "International Tables for X-ray Crystallography."[15] Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program.[16] Crystal structure illustrations were obtained with the program ORTEP.[17]

(10) J. L. Atwood and K. D. Smith, *J. Amer. Chem. Soc.*, **96**, 994 (1974).

(11) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, USAEC Report IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(13) J. M. Robertson and J. G. White, *J. Chem. Soc.*, 358 (1947).

(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(15) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(16) W. K. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(17) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794,

Structure Solution and Refinement. The structure was solved by the straightforward application of the direct methods program MULTAN.[18] Anisotropic refinement of the seven nonhydrogen atoms in the asymmetric unit with $1/\sigma^2$ weights gave agreement indices of 0.102 and 0.099. Inclusion of hydrogen atom contributions at calculated positions (C–H bond length assumed to be 0.95

$$R_1 = \sum|F_o| - |F_c|/\sum|F_o|$$

$$R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$$

Å) and further anisotropic refinement of the nonhydrogen atoms led to final values of $R_1 = 0.076$ and $R_2 = 0.073$. Unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final-difference Fourier map showed no feature greater than 0.2 e/Å^3. The final values of the positional and thermal parameters are given in the microfilm edition.[19,20]

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6132.

Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, p 70.

(18) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, *Sect. A*, **27**, 368 (1971).

(19) See paragraph at end of paper regarding supplementary material.

(20) The equation of the plane is $0.2830X - 0.8300Y - 0.4806Z - 1.0825 = 0$.

Studies Concerning Complexes of Ozone with Carbon π Systems

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Abstract: The formation and characterization of the first π complexes observed between ozone and aromatic or olefinic π systems are described. A correlation was made between the ionization potentials of a group of aromatic substrates and the wavelength of the absorption of their ozone complexes in the visible region. Two of the complexes were allowed to react with certain cis and trans olefins. The cis–trans ratios of the ozonides produced were different from those of the ozonides obtained by ozone alone in the cases of the *cis*- and *trans*-1,2-diisopropylethylenes. However, there was no appreciable difference in the results obtained using complexed or uncomplexed ozone with the less bulky *cis*- and *trans*-3-hexenes.

In previous communications[1,2] the formation of π complexes between ozone and 1-mesityl-1-phenylethylene, 1-mesityl-1-phenylethane, 1-methoxyl-1,2,2-trimesitylethylene, and mesitylene was reported. The present paper gives additional experimental details concerning the complexes already reported and extends the work to several new complexes, elucidation of their

(1) P. S. Bailey, J. W. Ward, and R. E. Hornish, *J. Amer. Chem. Soc.*, **93**, 3552 (1971).

(2) P. S. Bailey, J. W. Ward, R. E. Hornish, and F. E. Potts, III, *Advan. Chem. Ser.*, No. **112**, 1 (1972).

structures, and to ozonations of cis and trans olefins using two of the complexes as ozonating agents.

The discovery of the first complex ever observed between ozone and a carbon π system (that of 1-mesityl-1-phenylethylene)[1,2] resulted from a search for a possible precursor to the epoxide which is the major product of ozonation of 1-mesityl-1-phenylethylene at ordinary temperatures.[2,3] Ozonation of the olefin (with ozone–nitrogen) at $-120°$ still resulted in the

(3) P. S. Bailey and A. G. Lane, *J. Amer. Chem. Soc.*, **89**, 4473 (1967).

immediate formation of the epoxide and molecular oxygen. When the ozonation was carried out at −150 to −155°, in Freon 12 or isopentane, however, no molecular oxygen was evolved and the color of the complex appeared. The color was sometimes grey, greenish blue, or burgundy red. At lower temperatures and without excess ozone it was always burgundy red. At −150 to −155°, the color persists for at least 2 hr, although some epoxide begins to precipitate after about 30 min. If the temperature is allowed to rise to about −140°, the color of the complex disappears, molecular oxygen is evolved, and a heavy precipitate of the epoxide appears. In some of the experiments the molecular oxygen was shown to contain singlet oxygen.

Nmr spectra of Freon-12 solutions of the unreacted olefin (−150°), the O_3–olefin complex (−150°), and of the latter solution warmed to −135° were taken and the bands are shown in Table I. The spectra of the

Table I. Ozonation of 1-Mesityl-1-phenylethylene. Nmr Bands (δ)[a]

Species	Phenyl protons	Mesityl ring protons	Vinyl or epoxide protons	Mesityl methyl protons
Olefin (−150°)	7.69, 7.09	6.74	5.92, 5.03	2.29, 2.06
Complex (−150°)	7.52, 6.96	6.58	5.79, 4.90	2.15, 1.97
Epoxide (−135°)	6.99	6.68	2.97	2.17, 2.04

[a] δ values in parts per million.

olefin and of the ozone–olefin complex contained the same bands, the only difference being that the complex peaks were very slightly upfield from those of the olefin (average of many spectra). Such was also found for π complexes of iodine or tetracyanoethylene with aromatic compounds.[4,5]

Conclusive evidence for the formation of a complex between ozone and mesitylphenylethylene was obtained from the visible spectrum taken on a frozen, clear-glass solution of the ozonized olefin in isopentane at −195°. In contrast to the characteristic doublet at 575–610 nm for ozone,[6] the complex absorbed strongly at 460 nm. Only a trace of the pure ozone absorption was present.

The other complexes reported earlier,[1,2] those of 1-mesityl-1-phenylethane, 1,2,2-trimesityl-1-methoxyethylene, and mesitylene were obtained and characterized similarly. At −120 to −150°, they were blue-black in color, but at −195°, they were brown. Their absorption in the visible region is shown in Table II.

The absorption in the visible region turned out to be the most important physical property of the complexes. Assuming that the absorption is due to the promotion of an electron from the highest occupied molecular orbital of the donor molecule to the lowest unoccupied molecular orbital of the acceptor molecule, there should be a correlation between the wavelength of absorption in the visible region and the ionization potential of the organic

(4) R. Foster and C. A. Fyfe, *Progr. Nucl. Magn. Resonance Spectrosc.*, 4, 1 (1969).

(5) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, Chapters 1–4.

(6) A. D. Kirshenbaum and A. G. Streng, *J. Chem. Phys.*, 35, 1440 (1961).

Table II. Visible Absorption Spectra of Ozone π Complexes (−195°)[a]

Compound	Ionization potential[b] (eV)	λ_{max} (nm)	Color
Toluene	8.82	383	Green
Ethylbenzene		382	Green
tert-Butylbenzene		375	Green
o-Xylene	8.56	410	Olive green
Mesitylene	8.40	441	Brown
1,2,2-Trimesityl-1-methoxyethylene		445	Brown
Mesitylphenylethane		450	Brown
Mesitylphenylethylene		460	Burgundy red
Pentamethylbenzene	7.92	541	Purple
Hexaethylbenzene		552	Purple

[a] In isopentane glass. [b] See ref 5.

π system. In order to test this possibility, complexes of a number of alkyl-substituted benzenes were prepared and their visible spectra taken at −195° in an isopentane glass solution. The results are listed in Table II which shows that as the ionization potential of the π system decreases, the absorption occurs at lower energy (higher wavelength) levels, as expected. The colors of the complexes progress from green to purple as the wavelength of the absorption increases. In addition to the compounds listed in Table II, the following compounds appeared to give ozone complexes, as indicated by the colors produced: benzene (pale green), anisole (olive green), *p*-dineopentylbenzene (green), 1-ethyl-2-iodobenzene (blue-green), and 1,4-dimethylnaphthalene (purple). Surprisingly, durene failed to give a complex.

The complexation with these compounds is reversible. For example, when the solution of the complex of ethylbenzene was allowed to warm from −195° to about −150°, the color changed from that of the pure complex to the blue of ozone. Upon recooling the solution to 195°, the color of the complex reappeared. In the case of the mesitylene and 1-mesityl-1-phenylethane complexes most of the ozone could be swept out of the systems at −100°.

At first sight it would appear that the 1-mesityl-1-phenylethylene–ozone complex is less stable than the others, since all color disappears at about −140°, whereas the other complexes appear still to exist, in equilibrium with ozone, at considerably higher temperatures. This is not a measure of stability, however, but of susceptibility to other reactions of ozone: epoxide formation and/or ozonolysis. This greater susceptibility of the mesitylphenylethylene system to further ozone attack also makes it appear that in this case complexation is not reversible. Most likely it is reversible in all cases. At this stage in the study of ozone complexation it is not certain whether the complex is a precursor to other intermediates in epoxidation and/or ozonolysis, or whether it is purely incidental and dissociation occurs prior to further ozone attack.

The wavelength of the absorption indicates that the 1-mesityl-1-phenylethylene–ozone complex is actually slightly stronger than that of mesitylene or 1-mesityl-1-phenylethane (Table II). This fact may be significant in regard to the seat of the complexation in the case of 1-mesityl-1-phenylethylene. Molecular models show that the styrene system of mesitylphenylethylene can be

Table III. Ozonolyses of Cis and Trans Olefins with Complexed and Uncomplexed Ozone[a]

Expt	R in RCH=CHR	Config	Solvent	Complex	Cis/trans[b] ratio	Yield (%) ozonide
1	i-Pr	Trans	CF₂Cl₂	None	50/50	33–42
2	i-Pr	Trans	CF₂Cl₂	A[c]	40/60	6
3	i-Pr	Cis	CF₂Cl₂	None	50/50	69–85
4	i-Pr	Cis	CF₂Cl₂	A[c]	69/31	5–8
5	i-Pr	Trans	Isopentane	None	43/57	28
6	i-Pr	Trans	Isopentane	B[c]	48/52	32
7	i-Pr	Cis	Isopentane	None	66/34	82
8	i-Pr	Cis	Isopentane	B[c]	56/44	85
9	Et	Trans	CF₂Cl₂	None	38/62	32
10	Et	Trans	CF₂Cl₂	A[c]	40/60	4
11	Et	Cis	CF₂Cl₂	None	60/40	32
12	Et	Cis	CF₂Cl₂	A[c]	57/43	10
13	Et	Trans	Isopentane	None	50/50	55
14	Et	Trans	Isopentane	B[c]	48/52	48
15	Et	Cis	Isopentane	None	49/51	83
16	Et	Cis	Isopentane	B[c]	52/48	70

[a] A comparison is made of the cis/trans ozonide ratios obtained using ozone alone and ozone complexed with the π system designated. All reactions were carried out at $-155 \pm 5°$ using solutions in the range 0.01–0.05 M. See Experimental Section for techniques used. [b] Cis/trans ozonide ratios were determined by vpc, as described in the Experimental Section. Some of the values are the average of two or three experiments which varied by more than $\pm 1\%$. [c] A is 1-mesityl-1-phenylethylene; B is 1-mesityl-1-phenylethane.

planar, but that the mesityl group can not be coplanar with the olefinic double bond. The ionization potentials of mesitylene and styrene are very close, with that of styrene being slightly lower;[5] in addition, the nonconjugated olefinic double bond should increase the ionization potential of the mesityl group over that of mesitylene itself. Therefore, it seems likely that in the case of the mesitylphenylethylene, complexation involves the conjugated styrene system rather than the mesityl group. Upon decomposition of the complex, epoxidation then occurs. With the other complexes, of course, the aromatic system has to be the center of complexation. Even in the case of 1,2,2-trimesityl-1-methoxyethylene, complexation must involve a mesityl group since molecular models show that the olefinic double bond is completely inaccessible. The aromatic rings do not undergo further ozone attack until higher temperatures are reached.

Incidental to the above, it is seen in Table I that there are two phenyl proton peaks in the $-150°$ nmr spectrum of 1-mesityl-1-phenylethylene. The room temperature spectrum only has one phenyl proton peak (at about δ 7.20). One possible explanation is that the phenyl group rotates freely at room temperature, but is frozen at $-150°$.

In our studies no evidence for ozone complexes of purely aliphatic π systems was obtained. However, the ionization potentials of these systems would be so high that absorption would probably not occur in the visible region. Using a different technique, Heicklen and coworkers[7] have obtained infrared spectral evidence for the formation of ozone complexes of simple olefins, including propene, isobutene, cis- and trans 2-butene, trimethylethylene, tetramethylethylene, cyclopentane, and cyclohexene. They, as did we, also observed an ozone–toluene complex.

The products of the ozonation of mesitylphenyl-ethylene at $-150°$, after decomposition of the complex, were the same as at $-78°$. The yield of epoxide and/or rearrangement products appeared to be somewhat lower in the $-150°$ experiments, but this was perhaps

(7) L. A. Hull, I. C. Hisatsune, and J. Heicklen, *J. Amer. Chem. Soc.* **94,** 4856 (1972).

due largely to differences inherent in the experimental procedures. When ozone was applied directly at $-150°$, it tended to condense before entering the reaction mixture. This not only causes uncertainty as to whether or not all of the ozone reacted, but also as to whether or not some reacted locally, not only with the starting material but also with the products. By the other technique, the solution of the olefin was blown into a solution of ozone. Again, the initial concentration of ozone is higher than in the usual procedure at $-78°$, and side reactions involving initial products could occur. Another possibility is that some of the complex decomposed, even at $-150°$, to mesitylphenyl-vinyl alcohol which reacted with ozone to give a radical which dimerized. Mass spectral data indicated that higher molecular weight products than obtained at higher temperatures were produced, possibly including the dimer of the vinyl alcohol. The production of dimers *via* low-temperature ozonization of vinyl alcohols will be discussed in a later paper.

We next turned our attention to the interesting question as to whether ozonation of cis and trans olefins with ozone π complexes afforded the same stereochemical results, in regard to the ozonides produced, as ozonation of the same olefins with unbound ozone. The results are shown in Table III. Two different complexes were used. The first was ozone–mesitylphenylethylene. With this complex the yields of the foreign ozonides were very low because most of the complexed ozone reacted with the olefinic double bond of the mesitylphenylethylene system itself. This difficulty was overcome by using the mesitylphenylethane complex. In this case reaction with the foreign olefin is much faster than with the aryl groups of the mesitylphenylethane.

It can be seen that appreciably different stereochemical results are obtained with the cis- and trans-diisopropylethylenes, but not with the cis- and trans-3-hexenes, depending on whether complexed or uncomplexed ozone was employed. This indicates that in the reactions of olefins having bulky substituents at the double bond, at least, the entire ozone complex is involved in the step which determines the stereochemistry. The mechanism must, therefore, be different from that of

ozonolysis with ozone alone, in which it is believed that the stereochemistry is determined during decomposition of the initial ozonide (1,2,3-trioxolane) and recombination of the Criegee moieties.[8,9] Perhaps the 3-hexenes, being less hindered than the diisopropylethylenes, are more reactive and rob the complex of the ozone, reacting directly with it by the normal mechanism. We attempted to study the more highly hindered cis- and trans-1,2-di-tert-butylethylenes, but the ozonations were too slow at $-150°$. Differences in stereochemical results using complexed vs. uncomplexed ozone were more pronounced with the cis- than the trans-diisopropylethylene, perhaps again emphasizing the importance of steric factors.

It can be seen from Table III that the results using the mesitylphenylethylene complex (expt 1–4) were quite different from those using the mesitylphenylethane complex (expt 5–8), in comparison to the results using uncomplexed ozone. The differences were greater with the mesitylphenylethylene complex than with the mesitylphenylethane complex and in opposite directions. However, the solvents were different in the two cases and it is highly possible that this is more important than the fact that the two complexes were different. Much more work is necessary in order to settle such questions. Until then, it does not appear fruitful to speculate on the mechanism involved using complexed ozone. The observation that there are very real differences in results with complexed and uncomplexed ozone, however, assumes considerable importance.

Aside from the contrast of results with complexed and uncomplexed ozone, it is somewhat difficult to compare results of uncomplexed ozone at $-150°$ and higher temperatures, because the solutions employed at the higher temperatures were generally much more concentrated.[8] However, it appears that there is no important temperature effect with any of the four compounds studied in hydrocarbon solvents (isopentane and pentane, cf. ref 8) using ozone itself. One interesting observation is that in Freon 12 at the low temperature and low concentration, the cis–trans ozonide ratios, using ozone alone, were identical starting from either the cis- or the trans-diisopropylethylene; these ratios were quite different, on the other hand, in isopentane solution. With the cis- and trans-3-hexenes, however, the results were exactly the opposite in the two solvents. The significance of this is difficult to assess at the present time.

Experimental Section

Materials. 1-Mesityl-1-phenylethylene,[10] the corresponding ethane,[11] and 1-methoxy-1,2,2-trimesitylethylene[2] were prepared by previously published methods. The cis- and trans-1,2-disubstituted ethylenes used in the cis–trans ozonide ratio studies were 99% pure materials obtained from Chemical Samples Co. The isopentane and dichlorodifluoromethane (Freon 12) were pure solvents obtained from the Matheson Coleman and Bell Chemical Co. The other hydrocarbons, etc.. ozonized were all high quality chemicals obtained commercially.

(8) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, J. Amer. Chem. Soc., 90, 1822 (1968), and references therein.

(9) R. P. Lattimer, R. L. Kuckowski, and C. W. Gillies, J. Amer. Chem. Soc., 96, 348 (1974).

(10) R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley, J. Amer. Chem. Soc., 66, 681 (1944).

(11) E. M. Terent'eva, P. I. Sanin, T. G. Stepantseva, M. M. Kusakov, N. A. Skimanko, and V. I. Stidorenko, Neftekhimiya, 1, 141 (1961); Chem. Abstr., 57, 9698b (1962).

Ozonation Procedures. The ozonator was a Welsbach Model T 816. Direct ozonations were by usual procedures described in preceding papers,[12] using either nitrogen or oxygen as a carrier, even at $-150°$. For ozonations involving the addition of a cold solution of a substrate to an ozone solution or to a solution of an ozone-π complex, a special two-chambered vessel. described in an earlier publication,[13] was used. The -150 to $-160°$ temperature was reached using an isopentane–liquid nitrogen bath. For the low-temperature solvent either isopentane or Freon 12 was used. Nmr and visible spectra were obtained on solutions ozonized directly in the respective tubes, using approximately 0.1 and 0.01 M solutions, respectively.

Spectra and Chromatography. The low-temperature nmr spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe and using cyclopropane as an internal standard and Freon 12 as a solvent. The visible spectra were recorded with a Cary-14 spectrophotometer, using a rectangular quartz reaction tube and a special dewar flask equipped with a quartz window. The complex was produced in the reaction tube at $-150°$ using isopentane as solvent. The solution was then frozen to a glass at $-195°$ (liquid N_2) in the dewar flask and the spectrum taken. Gas chromatographic analyses were performed with a Varian Aerograph 1520 B dual column chromatograph equipped with a flame ionization detector and temperature programming. For the mesitylphenylethylene ozonation products a 3-ft 5% SE-30 on Chromosorb P column was used at an injection temperature of 180°. column temperature of 165°, and a detector temperature of 240°. Total ozonide yields were determined on a 5-ft SE-30 column (injection and column temperatures, 60°. detector temperature, 195°). Cis–trans ozonide ratios were determined on a 20-ft 20% Cyanosilicone Fluid XF 1150 on Chromosorb P column (injection temperature. 70°: column. 65°: detector, 195°).

Formation of π Complexes. Ozonation of 1-Mesityl-1-phenylethylene. Freon 12 solutions (0.1 M) were made by adding the olefin to the reaction vessel, condensing in the vessel a volume of cyclopropane equal to approximately twice the olefin volume and enough of Freon 12 to give the desired total volume. Isopentane reaction mixtures were approximately 0.02 M. The ozonations were carried out at $-150°$ with an equivalent of ozone using either nitrogen or oxygen carrier. Some difficulty was encountered with the ozone condensing just before it entered the reaction vessel. but it eventually was always carried over by the carrier gas. The complex color usually formed immediately in the case of mesitylphenylethylene in Freon 12. In isopentane, sometimes only a grey color was observed at $-150°$ and the true complex color did not appear until lower temperatures were reached. In some mesitylphenylethylene experiments. using nitrogen carrier. molecular oxygen was determined as a product.[12] No molecular oxygen was evolved as long as the color of the complex persisted. Above about $-140°$. the color disappeared and at $-110°$. molecular oxygen was rapidly evolved. The yield varied from 60 to 65%. compared to 80% yields at $-78°$. It was shown in a separate experiment that all dissolved molecular oxygen could be purged from Freon 12 solutions at $-150°$. Therefore, the oxygen evolved at $-110°$ came from decomposition of the complex. The molecular oxygen evolved was shown to contain singlet oxygen in a separate experiment. A cold ($-150°$) Freon 12 solution of the complex was purged of ozone by a nitrogen stream (30 min). The red solution was then removed from the bath while still being purged with nitrogen. The red color disappeared. The exit gases were passed through a very short piece of Tygon tubing into a solution of rubrene. The rubrene solution was immediately bleached: the bleached rubrene solution was quickly evaporated and a mass spectrum of the residue showed a peak with an m/e value of 548, which is correct for the singlet oxygen–rubrene product.[14] Nmr and visible spectra were recorded as described above. Gas chromatographic analysis of the products from decomposition of the mesitylphenylethylene complex were performed as described earlier. The yield of epoxide and/or mesitylphenylvinyl alcohol ranged from 58 to 65%. compared to 80–90% from ozonations at $-78°$.[3] Other products were mesityl phenyl ketone and ozonation products of the mesitylphenylvinyl alcohol.[3] In addition. mass spectral data indicated the pre-

(12) A. M. Reader, P. S. Bailey, and H. M. White, J. Org. Chem., 30, 784 (1965), and references therein.

(13) P. S. Bailey, T. P. Carter, Jr., C. M. Fischer, and J. A. Thompson, Can. J. Chem., 51, 1278 (1973). .

(14) R. W. Murray, W. C. Lumma, Jr., and J. W. P. Lin, J. Amer. Chem. Soc., 92, 3205 (1970).

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.

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

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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 copper[1] and gold.[2]
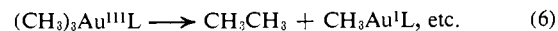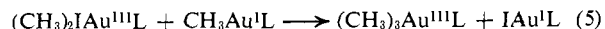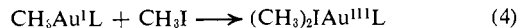
$$Rm + R'-X \xrightarrow{\text{M cat}} R-R' + mX \qquad (1)$$
$$m = Li, MgX, \text{etc.}$$
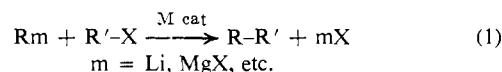
The catalytic process in eq 1 for M = Au[I] involves the prior alkylation of gold(I) as schematically represented in eq 2, followed by the reaction with alkyl halide in eq 3.[2]

$$Rm + Au^IX \longrightarrow RAu^I + mX \qquad (2)$$
$$RAu^I + R'-X \longrightarrow R-R' + Au^IX, \text{etc.} \qquad (3)$$
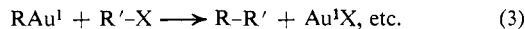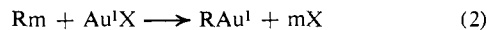
The reaction of the alkylgold(I) species with alkyl halide in eq 3 is rate limiting. The previous study[2] showed that coupling of methyl groups in the catalytic
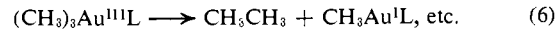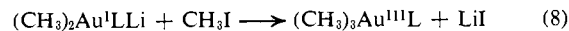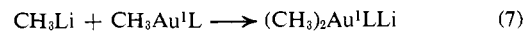
reaction of methyl(triphenylphosphine)gold and methyl iodide proceeded by a multistep sequence of reactions involving oxidative addition, alkyl exchange, and reductive elimination (Scheme I, eq 4–6, L = PPh_3).

Scheme I

$$CH_3Au^IL + CH_3I \longrightarrow (CH_3)_2IAu^{III}L \qquad (4)$$
$$(CH_3)_2IAu^{III}L + CH_3Au^IL \longrightarrow (CH_3)_3Au^{III}L + IAu^IL \qquad (5)$$
$$(CH_3)_3Au^{III}L \longrightarrow CH_3CH_3 + CH_3Au^IL, \text{etc.} \qquad (6)$$

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

$$CH_3Li + CH_3Au^IL \longrightarrow (CH_3)_2Au^ILLi \qquad (7)$$
$$(CH_3)_2Au^ILLi + CH_3I \longrightarrow (CH_3)_3Au^{III}L + LiI \qquad (8)$$
$$(CH_3)_3Au^{III}L \longrightarrow CH_3CH_3 + CH_3Au^IL, \text{etc.} \qquad (6)$$

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

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