Homogeneous Catalysis. I. Double Bond Migration in *n*-Olefins, Catalyzed by Group VIII Metal Complexes[1]

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It has been shown that the complexes of several group VIII metals can catalyze the migration of double bonds in linear olefins to yield an equilibrium distribution of isomers. The rate of the reaction, the need for cocatalysts, and the nature of the distribution of isomers in the course of the reaction was shown to be very sensitive to (i) the metal ion, (ii) the oxidation state of the metal ion, and (iii) the ligands present on the metal ion. The metal ion catalyzed isomerization is interpreted in terms of a reversible metalation of the double bond *via* a metal–olefin complex.

Introduction

In recent years many processes have been described in the literature in which an olefin is induced to undergo reaction in the presence of catalytic amounts of a transition metal complex. In many of these reactions the mediation of a transition metal–olefin complex has been postulated.[2-10]

Four principal types of reaction are encountered in these systems, namely, polymerization, molecular addition to a multiple bond, multiple bond migrations, and group substitution in the vicinity of multiple bonds. Usually one of these reactions will predominate, but frequently several may be observed to occur simultaneously. Our objective has been to seek a general mechanistic interpretation of the reactions of transition metal olefin complexes which is consistent with their extremely varied catalytic properties.

In the present paper we wish to describe some experiments in which a variety of group VIII metal complexes was used to catalyze the isomerization of *n*-olefins.

Experimental

The 1-hexene used in this work was Phillips Research Grade (~100 mole %). Both 2-heptene and 3-heptene were Phillips Technical Grade (95 mole % minimum). Chromatographic and infrared analyses showed both of these internal heptenes to be approximately equimolar *cis* and *trans* isomers.

Dichlorobis(ethylene)-μ,μ'-dichlorodiplatinum(II) was prepared as described by Chatt.[11] Bis(benzonitrile)dichloropalladium(II) was prepared as described by Kharasch.[12]

Rhodium heptanoate was prepared by precipitation from hot aqueous solution, using 4 moles of sodium heptanoate per mole of $RhCl_3 \cdot 3H_2O$. The yellow precipitate was filtered, washed with water, dried, and extracted with warm heptane. On evaporation *in vacuo* the heptane solution yielded an orange waxy solid. Infrared and elemental analyses of the product were consistent with its being predominantly $(C_6H_{11}COO)_3Rh$, admixed with a small quantity (<10 mole %) of basic heptanoates.

Tetrakis(ethylene)-μ,μ'-dichlorodirhodium(I) was prepared as described by Cramer.[13]

Isomerization of 1-Hexene by Platinum(II) Complexes.—Reactions were carried out *in vacuo* in sealed tubes. In a typical experiment a reaction tube was charged with a solution of di-

chlorobis(ethylene)dichlorodiplatinum(II) in 1-hexene (1 ml., 0.001 *M*) and enough cocatalyst to give a 0.2 *M* solution in the hexene. The tube was cooled in liquid nitrogen, evacuated to *ca*. 0.001 mm. pressure, and then sealed off. The reaction mixture was heated for the required time on a boiling water bath and the products analyzed by chromatography and infrared.

In experiments involving water, aqueous HCl, and aqueous Na_2CO_3, the reaction mixture remained as two phases throughout the reaction. In these experiments the quantity of aqueous reagent used was that which would yield a 0.2 *M* solution if the water and olefin were miscible.

Isomerization of Olefins by $RhCl_3 \cdot 3H_2O$.—All reactions catalyzed by $RhCl_3 \cdot 3H_2O$ were carried out at reflux under N_2. Standard reaction mixtures were prepared by dissolving $RhCl_3 \cdot 3H_2O$ (13 mg.) in 1 ml. of nucleophilic cocatalyst in a 25-ml. round-bottom flask and then adding the olefin (9 ml.) under nitrogen. The bulk of the catalyst solvent would usually dissolve rapidly in the olefin, leaving the catalyst as an oily residue at the bottom of the flask. As refluxing was commenced the rhodium complex gradually dissolved in the olefinic phase to give a yellow solution.

Samples of reaction mixture were analyzed periodically by infrared and chromatography.

Isomerization with Other Catalysts.—The previously described methods, *i.e.*, those used to study platinum–olefin complexes and $RhCl_3 \cdot 3H_2O$, will be referred to as methods A and B, respectively.

Bis(benzonitrile)dichloropalladium(II) was studied both in the presence and absence of cocatalysts by both methods A and B. To obtain an initially homogeneous system it was necessary to predissolve the palladium complex in benzene. Standard composition for reaction mixtures was olefin: benzene = 9:1 and a palladium concentration of 0.001 *M*.

In a high purity experiment method A was slightly modified. The palladium complex was placed in a reaction tube and pumped out to *ca*. 10^{-4} mm. Dry benzene was distilled onto the complex *in vacuo* by cooling the reaction tube in liquid nitrogen. The tube was warmed to room temperature to allow the complex to dissolve, then cooled again, and hexene distilled in. Finally the tube was sealed off and heated in a boiling water bath for 2 hr., and the reaction products were analyzed.

The catalytic activities of rhodium heptanoate, iridium trichloride, and tetrakis(ethylene)-μ,μ'-dichlorodirhodium(I) were all studied by both methods A and B.

Diagnostic Reaction for Catalytic Activity.—A few milligrams of complex was dissolved in 0.1 ml. of ethanol and the solution was boiled for 10 min. with 1-octene (1 ml.). At the end of reaction the olefin was examined by infrared for the presence of the characteristic *trans* band at 960 cm.$^{-1}$.

Positive results were obtained by this test for all complexes of Pt(II), Pd(II), Rh(III), and Ir(III). Negative results were obtained for chloro and carboxylate complexes of Fe(III), Co(II), Ni(II), and Ru(III).

Analysis of Olefins.—Primary analysis of isomeric olefin mixtures was effected by partial resolution on a 20-ft., β,β'-oxydipropionitrile column at 27° and a helium flow rate of 50 ml. per min. Under these conditions the column resolved hexenes and heptenes into three fractions which were shown to be the (1 + *trans*-3), (*cis*-3 + *trans*-2), and (*cis*-2) isomers in order of increasing retention time.

A secondary analysis was performed by collecting the three fractions from the chromatograph and analyzing their infrared spectra. The components of the first two fractions were readily distinguishable in their infrared spectra and a rough estimate of

(1) This work was presented in part before the 141st National Meeting of the American Chemical Society, Washington D. C., March 21-24, 1962.

(2) *Chem. Eng. News*, **39**, No. 15, 43 (1961).

(3) M. Orchin and G. L. Karapinka, *J. Org. Chem.*, **26**, 4187 (1961).

(4) C. S. Marvel and J. R. Rogers, *J. Polymer Sci.*, **49**, 335 (1961).

(5) H. Klopfer, *Angew. Chem.*, **61**, 266 (1949).

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(8) J. Smidt, *Chem. Ind.* (London), 54 (1962).

(9) R. F. Heck and D. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(10) J. Speier, J. A. Webster, and G. H. Barnes, *ibid.*, **79**, 974 (1957).

(11) J. Chatt, "Inorganic Syntheses," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1957, p. 210.

(12) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

(13) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

the relative proportions of *trans* isomers mixed with either *cis* or terminal isomer was obtained by comparison of bands in the 960 (*trans*), 1640 (*cis* or terminal), and 700–750 cm.$^{-1}$ (*cis* or terminal) regions.

Results

Isomerization of 1-Hexene by Platinum(II) Complexes.

—A series of experiments showed that platinum–olefin complexes would catalyze the migration of olefinic double bonds to equilibrium in the presence of certain nucleophilic cocatalysts. The results of these experiments are indicated in Table I.

TABLE I

Cocatalyst	Isomerization	Observations
None	No	...
C$_2$H$_5$OH	Yes	Homogeneous throughout
(CH$_3$)$_2$CHOH	Yes	Homogeneous throughout
(CH$_3$)$_3$COH	Yes	Homogeneous throughout
HAc	Yes	Homogeneous throughout
H$_2$O	No	Two phases; metal pptd. slowly in aq. phase
Aq. Na$_2$CO$_3$	No	Two phases; metal pptd. rapidly in aq. phase
Aq. HCl	No	Two phases; no metal pptd.
(C$_2$H$_5$)$_3$N	No	Dark oily ppt. slowly formed

In Fig. 1 a profile of isomer distributions *vs.* time for the ethanol cocatalyzed isomerization of 1-hexene is shown. The main characteristics of the reaction are autocatalysis and the preferential formation of *cis*-2 isomer in the early stages of reaction, relative to the equilibrium ratio of *cis*-2:*trans*-2 isomers. Using the data of Pines[14] this ratio should be 0.22. At the
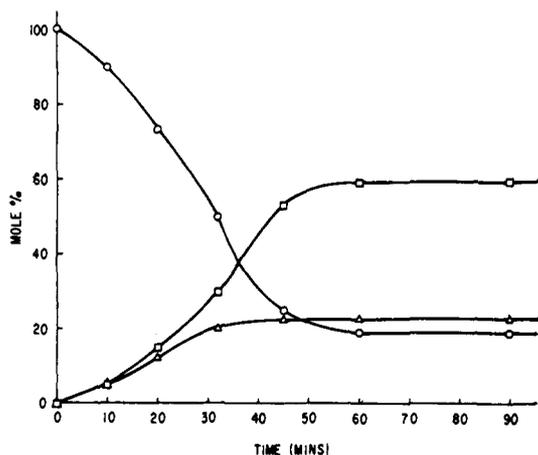

Fig. 1.—Isomerization of 1-hexene by Pt(II)–C$_2$H$_5$OH catalyst at 100°: O, 1-hexene + *trans*-3; □, *trans*-2 + *cis*-3; △, *cis*-2.

end of the reaction neither 1-hexene nor *cis*-3-hexene was detectable by infrared spectroscopy, as would be expected if they were approaching their equilibrium concentrations.

Similar results were obtained using isopropyl alcohol, *t*-butyl alcohol, and glacial acetic acid as cocatalysts. The composition profiles were identical, within the limits of experimental error, with regard to composition, but there was a small variation in rate with the different cocatalysts. The rate of reaction decreased slightly in the series: C$_2$H$_5$OH > (CH$_3$)$_2$CHOH > (CH$_3$)$_3$COH ≈ CH$_3$COOH.

Isomerization of Olefins by RhCl$_3$·3H$_2$O.

—Initial qualitative experiments showed that an alcoholic

(14) H. Pines, *Advan. Catalysis*, **12**, 117 (1960).
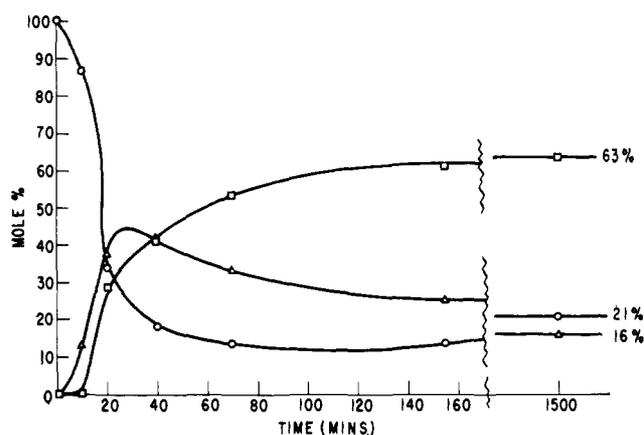
Fig. 2.—Isomerization of 1-hexene by RhCl$_3$·3H$_2$O–C$_2$H$_5$OH at 63–67° (legend as for Fig. 1).
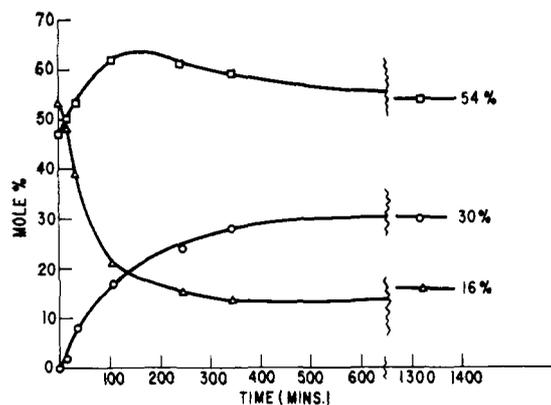
Fig. 3.—Isomerization of *cis*- and *trans*-2-heptene by RhCl$_3$·3H$_2$O–C$_2$H$_5$OH at 98° (legend as for Fig. 1).

solution of RhCl$_3$·3H$_2$O is a very potent catalyst for the isomerization of olefins. The composition profile for the isomerization of 1-hexene by an ethanolic solution of RhCl$_3$·3H$_2$O is shown in Fig. 2. The most outstanding feature of this reaction is the very high preference with regard to formation of the *cis*-2 isomer, both in terms of the over-all maximum concentration and in terms of its concentration relative to that of the *trans*-2 isomer. Analysis of the (1-hexene + *trans*-3-hexene) fraction, between 40 and 100 min. reaction time, showed the concentration of 1-hexene dropping rapidly to the detectable limit while the *trans*-3 isomer gradually increased. The minimum in the curve for these two isomers occurs at the point where the rate of disappearance of one equals the rate of appearance of the other.

During this same time period the *cis*-3 isomer was observed to increase and decay again below the detectable limit in the (*trans*-2 + *cis*-3) fraction. The composition profile for the isomerization of approximately equimolar *cis*- and *trans*-2-heptene by ethanolic RhCl$_3$·3H$_2$O is shown in Fig. 3. As expected, the *cis*-2 isomer decayed fairly rapidly to approximately its equilibrium concentration, while *trans*-3 isomer accumulated in the system. Analysis of the (*trans*-2 + *cis*-3) fraction revealed the origin of the maximum in that curve to be an accumulation followed by a decay of the *cis*-3 isomer, indicating a similar specificity to that observed for the migration of the hexene double bond from the 1- to the 2-position.

It may be noted that migration from the 2- to 3-position is considerably slower than from the 1- to 2-,
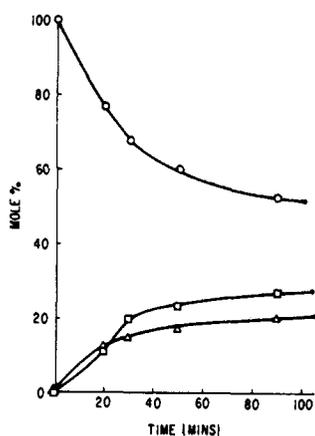
Fig. 4.—Isomerization of 1-hexene by Pd(II)–olefin-chloro complex at 63–67° (legend as for Fig. 1).

in spite of the fact that heptenes have a higher reflux temperature than hexenes by $ca.$ 30°.

With an equimolar mixture of cis- and $trans$-3-heptene, no significant isomerization occurred in 24 hr. under reflux.

A large number of cocatalysts was used with the $RhCl_3 \cdot 3H_2O$–hexene system, including secondary and tertiary alcohols, ethers, ketones, carboxylic acids, and water. Of the cocatalysts used, only water was ineffective. This observation, and the fact that isopropyl alcohol and t-butyl alcohol, which are better cosolvents for catalyst and olefin than ethanol, gave considerably higher rates than the latter, suggested strongly that in fact $RhCl_3 \cdot 3H_2O$ was an intrinsic catalyst for double bond migration and that the function of the "cocatalyst" was in fact that of cosolvent for catalyst and substrate. Thus, water was ineffective since it was not an adequate solvent for the olefin.

A solution of rhodium heptanoate in boiling 1-hexene was found to be inactive as an isomerization catalyst in the absence of added cocatalysts. In the presence of ethanol or isopropyl alcohol a very slow reaction occurred. Using experimental method A, with ethanol and rhodium heptanoate, results very similar to the platinum(II) reaction were obtained, both with respect to rate and composition profile.

Tetrakis(ethylene)-μ,μ'-dichlorodirhodium(I) showed no catalytic activity either in the presence or absence of cocatalysts.
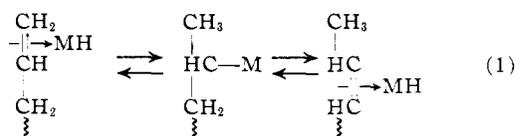
Other Isomerization Catalysts.—Reactions involving palladium(II) complexes were made difficult to study by the inevitable precipitation of palladium metal. Palladium–olefin complexes react extremely easily with strong nucleophiles to yield the metal.[7,8] Even in the high purity experiment where great care was taken to avoid contamination of the reaction mixture with moisture or air, palladium metal was precipitated in the course of the reaction. Nevertheless, under the cleanest reaction conditions used, the palladium(II) complexes catalyzed the isomerization of 1-hexene at about the same rate as that observed for the ethanol-cocatalyzed platinum(II) reaction and gave very similar isomer distributions. In the presence of deliberately added nucleophiles, such as ethanol, the palladium system immediately gave the metal. However, a small amount of isomerization was always initially observed, but the rate of reaction rapidly dropped to

zero as catalyst was reduced to metal. A composition profile for the isomerization of 1-hexene by palladium-(II) is shown in Fig. 4. The rapid decline in rate was coincident with the precipitation of metal.

Iridium trichloride was briefly investigated by experimental method A and gave results very similar to those obtained with platinum(II). The iridium(III) complex was not active in the absence of cocatalysts.

Discussion

There is little doubt that the susceptibility of olefinic double bonds to nucleophilic attack is greatly enhanced when they are coordinated to a transition metal.[7,8,15] The isomerization of olefins in the hydroformylation reaction has been discussed by Orchin and Karapinka[3] and Heck and Breslow[9] in terms of a reversible nucleophilic attack on a coordinated olefin by hydride. Such a process is illustrated schematically in eq. 1 where M

$$
\begin{array}{ccc}
\underset{\text{CH}_2}{\overset{\text{CH}_2}{\underset{|}{\overset{||\rightarrow\text{MH}}{\text{CH}}}}} & \underset{\text{CH}_2}{\overset{\text{CH}_3}{\underset{|}{\overset{|}{\text{HC—M}}}}} & \underset{\text{HC}}{\overset{\text{CH}_3}{\underset{|}{\overset{|}{\text{HC}}}}} \\
\end{array} \qquad (1)
$$

is a transition metal ion.

The same mechanism is sufficient to account for the present results on olefin isomerization. However, the wide variety of conditions under which isomerization was observed and the varying degrees of stereospecificity shown lead to the conclusion that the reaction is very sensitive to both the metal ion and the source of hydride. The hydride ion may originate from the cocatalyst, its anion, or the carbanion resulting from an initial nucleophilic attack on the coordinated olefin.

In the case of palladium, where no cocatalyst is required, hydride ion must originate from the olefin. However, it is unlikely that a C–H bond on a coordinated olefin is broken under such mild conditions. A more reasonable hypothesis is that here, chloride ion is the nucleophile which attacks coordinated olefin and that hydride is then released from the resulting carbanion. Of the cocatalysts listed in Table I for platinum(II), the alcohols have all been found to give metal hydrides when reacted with platinum group metal complexes stabilized by phosphines.[16,17] Hydride could, however, originate from the metal alkyl resulting from alkoxide attack on coordinated olefin since under much milder conditions alcohols add to platinum–olefin complexes to give platinum alkyls.[18] Further, acetate is a less likely source of hydride than the carbanion which would result from its attack on coordinated olefin. Acetate attacks coordinated olefins very readily.[7] In the case of palladium, the resulting alkyl undergoes a shift of hydride before decomposing to palladium metal and a substituted vinyl product.[19] Whether the hydride shift occurs via a palladium hydride complex or by a direct hydride shift within the carbanion has not been determined.

The mechanism for olefin isomerization in eq. 1 could also involve a direct hydride ion transfer between the alkyl and olefin groups of an alkyl–olefin complex.

(15) J. Chatt, J. Chem. Soc., 2496 (1957).
(16) J. Chatt and B. L. Shaw, Chem. Ind. (London), 931 (1960).
(17) L. Vaska and J. W. DiLuzio, J. Am. Chem. Soc., 83, 1262 (1961).
(18) J. Chatt, J. Chem. Soc., 2496 (1957).
(19) E. W. Stern, Proc. Chem. Soc., 111 (1963).

Direct evidence on such points is lacking, but for platinum(II) it is known that an excess of olefin inhibits reduction of olefin complexes to the metal by nucleophiles. Parallel with this stabilization is the formation of a bis(olefin) complex with excess olefin.[20,21] These results suggest the possibility of an alkyl–olefin complex as an intermediate.

The rate of formation of the various olefin isomers from a mechanism similar to that of eq. 1 will depend on the rate of isomerization of olefin coordinated to the metal ion *vs.* the rate of exchange of free for coordinated olefin. The former process may be expected to be governed by the stabilities of the various alkyl and olefin complexes involved. The stepwise formation of products from terminal olefins suggests that olefin exchange is comparable in rate or faster than the isomerization. This is the same conclusion reached by Johnson[22] for the isomerization of 4-methylpent-1-ene by cobalt hydrocarbonyl, but contrary to Manuel's[23] conclusions using iron carbonyls as catalysts. Manuel found that hexene-2 was isomerized very slowly to hexene-3, but hexene-1 rapidly isomerized to hexene-2 and -3. To explain this result it was suggested that hexene-1 was isomerized to hexene-3 within the metal complex. While the present results substantiate Manuel's findings, we do not agree with his conclusion. Alternative explanations are possible; for example, the isomerization of hexene-2 to hexene-3 and *vice versa* may be catalyzed by an intermediate such as the platinum alkyl formed from hexene-1. Such an intermediate would be the alkyl–olefin complex suggested earlier; we are presently seeking evidence on this point.

The stepwise formation of products is particularly marked in the stereospecificity shown by the formation of super-equilibrium amounts of *cis* isomer during the early stages of the reaction. In the case of platinum this was manifested by an unusually high ratio of *cis* to *trans* isomers; but in the exceptional case of $RhCl_3 \cdot 3H_2O$, *cis*-hexene-2 was observed to rise to almost half the total reaction mixture in the early stages of the reaction.[24] It should also be noted that the stereospecificity is that to be expected if, as we have assumed, the olefin displacement step is comparable in rate to the isomerization of the complexed olefin. This implies that in the initial stages of isomerization of terminal olefin the isomer ratio appearing in solution will be favored by the more stable olefin complex which is the *cis*.[25]

The $RhCl_3 \cdot 3H_2O$ system must be regarded as exceptional, both with regard to reaction rates and stereo-

specificity. The inactivity of tetrakis(ethylene)-μ,μ'-dichlorodirhodium(I) as a catalyst excludes the possibility that $RhCl_3 \cdot 3H_2O$ is active by virtue of its reduction to the simple olefin–chloro complex. Attempts to characterize the recovered rhodium complexes from reaction mixtures thus far have not met with success. The recovered rhodium is usually a mixture of complexes, but the persistence of bands in the 1500–1600 cm.$^{-1}$ region of the infrared (the region in which double bond stretching is usually observed in metal–olefin complexes[26]) indicates that complexed olefin is an important component of the mixture. Bands attributable to metal carbonyl have also been observed in certain fractions of this material.

In sharp contrast to $RhCl_3 \cdot 3H_2O$, rhodium(III) heptanoate was not an intrinsic catalyst and even in the presence of cocatalysts such as alcohols the activity and stereospecificity of the heptanoate were low compared to $RhCl_3 \cdot 3H_2O$. An additional complication in the reactions of rhodium(III) as compared to platinum(II) is that the complexes of the former undergo reduction to rhodium(I) under the conditions of the isomerization reaction. For the case of ethylene the reaction may be written[13]

$$2RhCl_3 \cdot 3H_2O + 6C_2H_4 \longrightarrow$$
$$(C_2H_4)_4Rh_2Cl_2 + 2CH_3CHO + 4HCl + 4H_2O \quad (2)$$

It seems likely that this reaction also involves a nucleophilic attack on olefin and that reduction occurs due to the instability of the resulting metal alkyl. Isomerization is then to be expected if ethylene is replaced by a higher olefin. In view of the inactivity of simple rhodium(I)–olefin complexes, it seems likely that intermediates in reaction 2 are the most likely source of catalytic activity of $RhCl_3 \cdot 3H_2O$.

Finally, it should be mentioned that Milgrom and Urry[27] have reported the isomerization of olefins by platinum(II) complexes in acid media. These workers observed that weakly basic solvents, such as ethanol, inhibit the reaction and they suggested a carbonium ion intermediate as the active isomerizing species. Whether such an intermediate should be considered a carbonium ion attached to Pt^{n+} or a carbanion attached to $Pt^{(n+2)+}$ may be a matter of semantics. A negatively charged ligand would seem more logical. However, the isomerization in acid solution does not appear to proceed *via* the same route as in neutral or basic conditions. Thus, we found that aqueous hydrochloric acid was relatively ineffective as a cocatalyst and inhibited the alcohol-cocatalyzed reaction. The latter effect is to be expected if the reaction is initiated by alkoxide attack. Consistent with this interpretation is the fact that in the preparation of platinum(II)–olefin complexes it is necessary to acidify alcoholic solutions to prevent reduction to the metal.

(20) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).

(21) Unpublished results of the authors.

(22) M. Johnson, *J. Chem. Soc.*, 4859 (1963).

(23) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962). We wish to thank a referee for bringing these references to our notice.

(24) A referee has indicated that a similar excess of *cis* isomers was noted in a paper by Sparke on olefin isomerization by palladium complexes at the recent London IUPAC Meeting.

(25) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

(26) J. Chatt and D. Adams, *Chem. Ind.* (London), 149 (1960); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2821 (1962).

(27) J. Milgrom and W. H. Urry, Abstracts, Proceedings of the Seventh Intern. Conf. on Coordination Chem., Stockholm, Sweden, 1962, p. 264.