

co-workers.<sup>19</sup> However, the experiments<sup>17,18</sup> following Doering's early liquid-phase work showed a non-statistical insertion in the gas phase which was most pronounced in the case of insertion of CH<sub>2</sub> into isobutane.<sup>18</sup> It has been suggested by Frey and Kistiakowsky<sup>17</sup> that the indiscriminacy in the liquid phase is to be attributed to excited CH<sub>2</sub> which inserts before it can lose its energy. They observed a trend away from statistical when inert gas was added to remove the excitation from CH<sub>2</sub> and implied that thermal CH<sub>2</sub> discriminates in its insertion reactions. However, if CH<sub>2</sub> singlet is transformed by collision to the ground-state triplet, discriminate *abstraction* may be expected.<sup>2</sup> As a consequence association of methyl and alkyl radicals may produce the illusion of a more discriminate insertion by CH<sub>2</sub> as pointed out by Richardson and co-workers.<sup>20</sup> The elimination of this factor, of course, constitutes the basic reason for scavenging free radicals by addition of NO in the present work as well as in the recent work of Whitten and Rabinovitch<sup>9</sup> and by the addition of O<sub>2</sub> in the work of Carr.<sup>21</sup>

The present finding that  $k_1/k_2 \sim 0.43$  also lends support to the conclusion that insertion is relatively indiscriminate even when two different reactant molecules such as methane and propane are involved.

The present work is, therefore, in essential agreement with the conclusions of Carr<sup>21</sup> who found that the reaction of CH<sub>2</sub> with isopentane involved insertion of CH<sub>2</sub>

(19) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(20) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **83**, 1934 (1961).

(21) R. W. Carr, Jr., *J. Phys. Chem.*, **70**, 1970 (1966).

in a relatively indiscriminate fashion with a slight trend toward favoring insertion at the most highly substituted CH bond.

It is becoming increasingly clear<sup>22-28</sup> that both triplet and singlet CH<sub>2</sub> are formed in the photolysis of ketene. A very convincing demonstration that this is also true of the photolysis of diazomethane has recently been made by Bader and Generosa.<sup>29</sup> Carr<sup>26</sup> has deduced that about 15% of the CH<sub>2</sub> is triplet in the 3130-Å photolysis of ketene.

It may be said that it is the singlet species of CH<sub>2</sub> that inserts indiscriminately.<sup>30</sup> Our observation that CH<sub>2</sub> appears to carry over about 2.5 kcal mole<sup>-1</sup> in the insertion reaction suggests that the singlet CH<sub>2</sub> lies not more than about 2.5 kcal mole<sup>-1</sup> above the ground-state triplet assuming that the singlet CH<sub>2</sub> suffers many collisions before inserting and that these collisions result in a fully relaxed singlet CH<sub>2</sub>.

**Acknowledgment.** One of us (M. L. H.) gratefully acknowledges a summer (1966) research fellowship granted by the University of Missouri at Saint Louis.

(22) J. W. Simons and B. S. Rabinovitch, *ibid.*, **68**, 1322 (1964).

(23) F. H. Dorer and B. S. Rabinovitch, *ibid.*, **69**, 1964 (1965).

(24) S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

(25) H. M. Frey, *Chem. Commun.*, 260 (1965).

(26) R. W. Carr, Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966).

(27) C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 3179 (1966).

(28) C. McKnight and F. S. Rowland, *ibid.*, **89**, 469 (1967).

(29) R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965).

(30) D. F. Ring and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **88**, 4285 (1966).

## Homogeneous Catalysis in the Reactions of Olefinic Substances.<sup>1a</sup> VIII. Isomerization of 1,5-Cyclooctadiene with Dichlorobis(triphenylphosphine)platinum(II)<sup>1b</sup>

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*Contribution from the William Albert Noyes Laboratory of Chemistry,  
University of Illinois, Urbana, Illinois. Received January 27, 1967*

**Abstract:** Homogeneous catalytic isomerization of 1,5-cyclooctadiene has been effected by [PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in the presence of SnCl<sub>2</sub>·2H<sub>2</sub>O, under nitrogen or hydrogen gas. Isomerization occurs by stepwise migration of the double bonds. The effective reaction intermediate may be a hydridoplatinum-olefin complex which has been isolated from the reaction medium and characterized. The synthesis of such a tin-platinum-olefin hydride complex is reported for the first time. The kinetics of the reaction suggest that isomerization occurs in two consecutive reversible first-order reactions. The source of hydrogen for the formation of the metal hydride complex is investigated. Tin(II) chloride has been found essential for the isomerization process. Its role is investigated in detail, and it is suggested that it activates the platinum catalyst by being coordinated to it through the ligand SnCl<sub>3</sub><sup>-</sup> which is a strong  $\pi$  acceptor and a weak  $\sigma$  donor.

The catalytic isomerization of monoolefins has formed the subject of many recent publications.<sup>2</sup> Only a few reports, however, have been devoted to the

(1) (a) Part VII: H. Itatani and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 1600 (1967). (b) This report is partly based on a portion of the Ph.D. Thesis by H. A. Tayim, University of Illinois, Feb 1967.

catalytic isomerization of polyolefins.<sup>3</sup> The isomerization of dienes was observed in the synthesis of some

(2) For a recent review of homogeneous catalysis, see J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

(3) R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

transition metal-olefin complexes.<sup>4,5</sup> We have observed that the hydrogenation of nonconjugated dienes to the monoenes with platinum and palladium complexes as catalysts proceeds *via* the formation of the conjugated dienes.<sup>6</sup> This prompted us to investigate, in some detail, the isomerization of some representative nonconjugated dienes. Another incentive for the investigation of the catalytic isomerization of polyolefins in general and 1,5-cyclooctadiene in particular is the controversy concerning the direction and path of the isomerization reaction.<sup>4b,5</sup> It has been reported that 1,3-cyclooctadiene was isomerized to 1,5-cyclooctadiene during an attempt to prepare an organometallic complex with 1,3-cyclooctadiene coordinated to the metal atom. It has also been suggested that the mechanism of isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene is not stepwise since 1,4-cyclooctadiene was not detected as an intermediate.

## Experimental Section

**1. Apparatus.** Infrared absorption spectra were measured in KBr disks using a Perkin-Elmer 521 infrared spectrophotometer. Nuclear magnetic resonance spectra were run on a Varian A-60 instrument in  $\text{CDCl}_3$  solution with trimethylsilane as an internal standard. An Industrial Instruments conductivity bridge, Model RC16B2, was used for conductance measurements. A bench-size, 300-ml stainless steel Magne-Drive autoclave was used when pressures higher than 1 atm were utilized. Reactions under a pressure of 1 atm were carried out in an erlenmeyer flask. The hydrocarbon reaction products were analyzed by a Varian Aerograph GC-1520B gas chromatograph employing a thermal conductivity detector. A 10 ft  $\times$  0.25 in. copper column with 20% diethylglycol adipate on 60-80 Chromosorb W was used, and the carrier gas was helium. Column temperatures and carrier gas flow rates were varied so as to give reasonable resolution of the components. Elemental microanalyses were carried out in the University of Illinois microanalytical laboratory.

**2. Preparation of Chemicals.** 1,4-Cyclooctadiene was prepared by reducing cyclooctatetraene by sodium metal in alcohol.<sup>7</sup> Indium(I) chloride,  $\text{InCl}$ , was prepared by treating indium metal with the calculated amount of mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ .<sup>8</sup> *trans*-Hydridochlorobis(triphenylphosphine)platinum(II),  $[\text{PtHCl}(\text{PPh}_3)_2]$ ,<sup>9,10</sup> and *cis*-dichlorobis(triphenylphosphine)platinum(II),  $[\text{PtCl}_2(\text{PPh}_3)_2]$ ,<sup>11,12</sup> were prepared by methods reported in the literature. We found that the complex  $[\text{PtCl}_2(\text{PPh}_3)_2]$  is quite soluble in dichlorohydrocarbons, particularly methylene chloride. This offers a more convenient method for purifying the complex without losing much of the yield, namely, by precipitating the complex from a methylene chloride solution by addition of *n*-hexane.

Bis{hydridotrichlorostannatobis(triphenylphosphine)}- $\mu$ -(1,5-cyclooctadiene)-diplatinum(II),  $[\{\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2\}_2(1,5\text{-COD})]$ , was prepared by stirring a mixture of 0.5 mmole of *trans*-hydridochlorobis(triphenylphosphine)platinum(II) and 5.0 mmoles of tin(II) chloride dihydrate,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , in excess (*ca.* 30 ml) 1,5-cyclooctadiene at room temperature for 1 hr. The yellow precipitate that separated was filtered and leached quickly with methylene chloride. The pure compound was precipitated from the yellow methylene chloride solution by the addition of low-boiling petroleum ether: mp 140° dec; molar conductance in nitrobenzene at 25°, 2.0  $\text{ohm}^{-1} \text{cm}^2$  (nonelectrolyte); mol wt (in methylene chloride, by osmometric method), 1880 (calcd 2000).

*Anal.* Calcd for  $\text{C}_{80}\text{H}_{74}\text{P}_4\text{Cl}_6\text{Sn}_2\text{Pt}_2$ : C, 48.04; H, 3.73; Cl, 10.64. Found: C, 47.93; H, 3.86; Cl, 10.82.

(4) (a) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961); (b) R. E. Rinehart and J. S. Lasky, *ibid.*, **86**, 2516 (1964).

(5) H. Frye, E. Kuljian, and J. Viebrock, *Inorg. Chem.*, **4**, 1499 (1965).

(6) H. Itatani and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 1600 (1967).

(7) L. E. Craig, R. M. Eloffson, and I. J. Rossa, *ibid.*, **75**, 480 (1953).

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(12) A. Grinberg and Z. A. Razumova, *Zh. Prikl. Khim.*, **27**, 105 (1954).

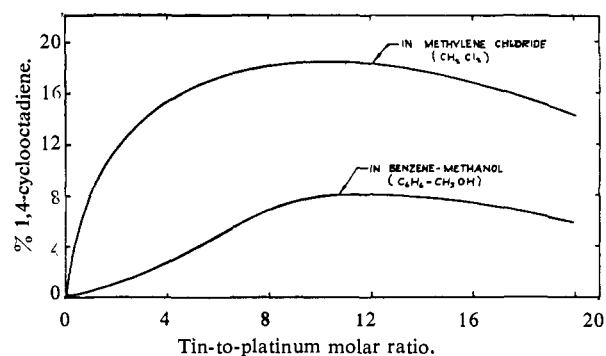


Figure 1. Effect of cocatalyst-to-catalyst ratio on the catalytic isomerization of 1,5-cyclooctadiene.

Proton nmr chemical shifts (ppm) relative to a scale on which trimethylsilane has a shift of 10 ppm are 2.60 (15), 4.45 (1), 7.65 (2);  $\nu_{\text{Pt-H}}$  2200 (m) and 2100 (m)  $\text{cm}^{-1}$ ;  $\text{SnCl}_3^-$ , 350 (s)  $\text{cm}^{-1}$ .

Dichloro-1,5-cyclooctadieneplatinum(II),  $[\text{PtCl}_2(1,5\text{-COD})]$ , was prepared by the reaction of 1,5-cyclooctadiene with a platinum(II) complex which was prepared *in situ* by the reduction of potassium chloroplatinate(IV). A suspension of 5.0 mmoles of  $\text{K}_2\text{PtCl}_6$  in 100 ml of water was treated with excess 1,5-cyclooctadiene and then with 2.5 mmoles of  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$  which was added slowly and with continuous stirring. The mixture was stirred at room temperature for 3 hr. The creamy white precipitate that separated was filtered, washed successively with alcohol and ether, and dried in air, mp 235°.

*Anal.* Calcd for  $\text{C}_8\text{H}_{12}\text{Cl}_2\text{Pt}$ : C, 25.68; H, 3.23; Cl, 18.86. Found: C, 25.98; H, 3.31; Cl, 18.41. Infrared spectrum: 3020 (s), 3000 (s), 2930 (m), 2900 (s), 2830 (s), 2800 (s), 1492 (s), 1470 (vs), 1445 (s), 1420 (s), 1370 (w), 1335 (vs), 1305 (s), 1268 (m), 1235 (s), 1220 (s), 1200 (s), 1170 (vs), 1100 (w), 1082 (s), 1070 (sh), 1000 (vs), 900 (s), 865 (vs), 825 (vs), 800 (s), 772 (vs)  $\text{cm}^{-1}$  (s = strong, m = medium, w = weak, vs = very strong, sh = shoulder).

**3. Isolation of Reaction Intermediates.** After each isomerization experiment, the cool reaction mixture was filtered and concentrated to about one-third of its volume by evaporation under reduced pressure. The concentrated solution was filtered again, and the filtrate was treated with enough low-boiling petroleum ether to effect partial precipitation. The supernatant solution was decanted and the residue was washed several times with petroleum ether. The residue was then purified by dissolution in methylene chloride followed by precipitation by petroleum ether. The process of purification was repeated several times until a pure compound having a consistent elemental analysis and sharp melting or decomposition point was obtained. Following the above procedure, a compound having chemical and physical properties identical with those of the complex  $[\{\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2\}_2(\text{COD})]$ , synthesized above, was obtained.

## Results

Isomerization of 1,5-cyclooctadiene was effected by dichlorobis(triphenylphosphine)platinum(II) in the presence of tin(II) chloride dihydrate. Control experiments using the platinum complex alone or the cocatalyst ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) alone showed that no isomerization was effected in either case, nor could isomerization be effected by using  $[\text{PtHCl}(\text{PPh}_3)_2]$  or  $[\text{PtCl}_2(1,5\text{-COD})]$  without a cocatalyst. That the water of crystallization in  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  had no effect on the rate of isomerization is shown by the fact that identical results were obtained in two similar experiments with the dihydrate as a cocatalyst in one case and anhydrous  $\text{SnCl}_2$  in the other.

The effect on the catalytic activity of varying the ratio of the cocatalyst to the catalyst is shown in Figure 1. The results illustrated in the figure refer to the isomerization of 2.0 g of 1,5-cyclooctadiene in 50 ml of methylene chloride or 2:3 methanol-benzene solution using 0.5 mmole of  $[\text{PtCl}_2(\text{PPh}_3)_2]$  as a catalyst and

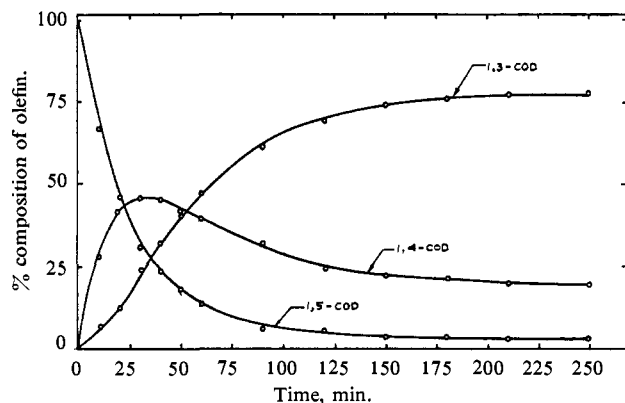


Figure 2. Catalytic isomerization of 1,5-cyclooctadiene in benzene-methanol solution under 1 atm of nitrogen at 60°.

varying amounts of the cocatalyst,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , under 500 psi of hydrogen at 20° for 2 hr. The most effective ratio is found to be 10. The figure also shows that isomerization proceeds at a greater rate in methylene chloride than in a 3:2 benzene-methanol solvent.

In order to study the function of the cocatalyst, salts of different metals were investigated. The results of varying the cocatalyst on the efficiency of isomerization are shown in Table I.

Table I. Isomerization of 1,5-Cyclooctadiene (3.0 g) Using 0.5 mmole of  $[\text{PtCl}_2(\text{PPh}_3)_2]$  and Various Cocatalysts (5.0 mmoles)<sup>a</sup>

| Cocatalyst                                | Composition of product, % |         |         |
|---|---------------------------|---------|---------|
|   | 1,3-COD                   | 1,4-COD | 1,5-COD |
| $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ | 32                        | 45      | 23      |
| $\text{GeCl}_2$                           | ..                        | 15      | 85      |
| $\text{PbCl}_2$                           | ..                        | 6       | 94      |
| $\text{PbCl}_4$                           | ..                        | 1       | 99      |
| $\text{AsCl}_3$                           | ..                        | 2       | 98      |
| $\text{SbCl}_3$                           | 5                         | 30      | 65      |
| $\text{BiCl}_3$                           | ..                        | 4       | 96      |
| $\text{GaCl}_3$                           | ..                        | 7       | 93      |
| $\text{InCl}_3$                           | 3                         | 10      | 87      |
| $\text{TiCl}_4$                           | ..                        | 3       | 97      |
| $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ | 12                        | 47      | 41      |
| $\text{PF}_5$                             | 3                         | 8       | 77      |
| $\text{CO}$                               | ..                        | 9       | 91      |

<sup>a</sup> In 50 ml of  $\text{CH}_2\text{Cl}_2$  under 500 psi of hydrogen at 50° for 2 hr.

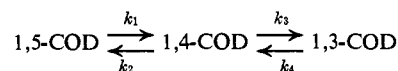
Table II illustrates the effect of varying the nature of the ambient gas and the catalyst in an attempt to locate the source of the hydride in the metal hydride complex formed as a reaction intermediate. To complete the information provided by Table II, it should be stated that 1,5-cyclooctadiene under conditions identical with those mentioned in the table but with  $\text{CH}_2\text{Cl}_2$  as solvent and  $[\text{PtCl}_2(\text{PPh}_3)_2]$  as catalyst yielded 100% 1,3 isomer.

Table II. Isomerization of 1,5-Cyclooctadiene (30 ml) without Solvent Using Some Platinum Complexes (1.0 mmole) and 5.0 mmoles of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ <sup>a</sup>

| Platinum complex                  | Gas          | Composition of product, % |         |         |
|-----------------------------------|--------------|---------------------------|---------|---------|
|                                   |              | 1,3-COD                   | 1,4-COD | 1,5-COD |
| $[\text{PtCl}_2(\text{PPh}_3)_2]$ | $\text{H}_2$ | 100                       | ...     | ...     |
| $[\text{PtHCl}(\text{PPh}_3)_2]$  | $\text{H}_2$ | 100                       | ...     | ...     |
| $[\text{PtHCl}(\text{PPh}_3)_2]$  | $\text{N}_2$ | 59                        | 31      | 10      |
| $[\text{PtCl}_2(\text{PPh}_3)_2]$ | $\text{N}_2$ | ...                       | 11      | 89      |

<sup>a</sup> Under 600 psi of nitrogen or hydrogen at 90° for 5 hr.

The kinetics of the isomerization of 1,5-cyclooctadiene (2.0 g) were investigated under 1 atm of nitrogen, using  $[\text{PtHCl}(\text{PPh}_3)_2]$  (0.5 mmole) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (5.0 mmoles) in 3:2 benzene-methanol solution (50 ml) at 60°. The circles in Figure 2 refer to the experimental results, while the solid lines refer to a hypothetical system of consecutive reversible first-order reactions



with the rate constants ( $\text{sec}^{-1}$ )  $k_1 = 7.0 \times 10^{-4}$ ,  $k_2 = 1.0 \times 10^{-4}$ ,  $k_3 = 4.0 \times 10^{-4}$ , and  $k_4 = 1.0 \times 10^{-4}$ . The rate equations can be written as shown in eq 1-3,

$$dx/dt = -xk_1 + yk_2 \quad (1)$$

$$dy/dt = xk_1 - yk_2 - yk_3 + zk_4 \quad (2)$$

$$dz/dt = yk_3 - zk_4 \quad (3)$$

where  $x$ ,  $y$ , and  $z$  represent the concentrations (expressed in per cent) of 1,5-COD, 1,4-COD, and 1,3-COD, respectively, in the reaction mixture at time  $t$ . The equations yield the solutions<sup>13</sup> given in eq 4-6.

$$x = 100 \left[ \frac{k_2 k_4}{n_2 n_3} + \frac{k_1 (n_2 - k_3 - k_4)}{n_2 (n_2 - n_3)} e^{-n_2 t} + \frac{k_1 (k_3 + k_4 - n_3)}{n_3 (n_2 - n_3)} e^{-n_3 t} \right] \quad (4)$$

$$y = 100 \left[ \frac{k_1 k_4}{n_2 n_3} + \frac{k_1 (k_4 - n_2)}{n_2 (n_2 - n_3)} e^{-n_2 t} + \frac{k_1 (n_3 - k_4)}{n_3 (n_2 - n_3)} e^{-n_3 t} \right] \quad (5)$$

$$z = 100 \left[ \frac{k_1 k_3}{n_2 n_3} + \frac{k_1 k_3}{n_2 (n_2 - n_3)} e^{-n_2 t} - \frac{k_1 k_3}{n_3 (n_2 - n_3)} e^{-n_3 t} \right] \quad (6)$$

$$n_2 = \frac{1}{2}(p + q) \quad n_3 = \frac{1}{2}(p - q)$$

$$p = k_1 + k_2 + k_3 + k_4$$

$$q = p^2 - 4(k_1 k_3 + k_2 k_4 + k_1 k_4)^{1/2}$$

A reasonable value for the value of  $k_1$  was first determined from the approximately first-order nature of the early part of the curve for the disappearance of 1,5-COD. The curve representing the concentration of 1,4-COD shows a maximum at  $t = 30$  min. Thus  $dy/dt = 0$  at  $t = 30$  min. Moreover, the exponential terms in eq 4-6 become negligible at high values of  $t$ , corresponding to the flat parts of the curves. All these features simplify the determination of the values of the  $k$ 's by a trial and error method. The above values of the  $k$ 's were arrived at by utilizing such simplifications.

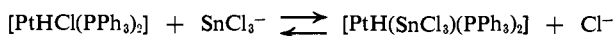
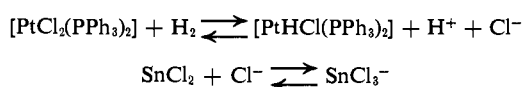
## Discussion

**1. Metal Hydride Complex Formation.** The isolation of a hydridoplatinum-olefin intermediate suggests (but does not necessarily prove) that metal hydride and metal-olefin complex formation are important steps in the mechanism of isomerization. However, the formation of neither complex alone represents the rate-determining step in the isomerization reaction.

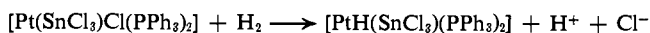
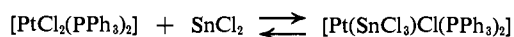
(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 8.

This is suggested by the fact that isomerization proceeds at comparable rates with  $[\text{PtCl}_2(\text{PPh}_3)_2]$ ,  $[\text{PtHCl}(\text{PPh}_3)_2]$ , or  $[\text{PtCl}_2(1,5\text{-COD})]$  as catalysts under identical conditions. However, a reaction involving the hydrido-platinum-olefin complex may be the rate-determining step. In order to find the possible source of hydrogen for the formation of the metal hydride complex, the experiments reported in Table II were performed. Thus, catalytic isomerization of 1,5-cyclooctadiene was tried (a) under nitrogen using  $[\text{PtCl}_2(\text{PPh}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  solution, (b) under hydrogen using  $[\text{PtCl}_2(\text{PPh}_3)_2]$  without a solvent, (c) under nitrogen using  $[\text{PtCl}_2(\text{PPh}_3)_2]$  without a solvent, and (d) under nitrogen using  $[\text{PtHCl}(\text{PPh}_3)_2]$  without a solvent. In all the systems except c, almost complete isomerization of the diene to the conjugated isomer took place. System c gave a small yield of 1,4-cyclooctadiene and no detectable 1,3-cyclooctadiene. This shows that, while molecular hydrogen and the solvent may supply hydride ions, the olefin cannot be a significant source of hydrogen.

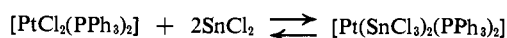
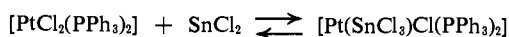
Formation of the hydride complex from the solvent is understandable in terms of oxidation of the solvent, say alcohol to aldehyde or ketone. In systems where the solvent is not easily oxidized or in systems without a solvent, the situation is not as clear. Homolytic fission of hydrogen as occurs in the well-known reaction  $2[\text{Co}^{\text{II}}(\text{CN})_5]^{3-} + \text{H}_2 \rightarrow 2[\text{Co}^{\text{III}}\text{H}(\text{CN})_5]^{3-}$ , or insertions as in  $[\text{Ir}^{\text{I}}\text{Cl}(\text{CO})(\text{PPh}_3)_2] + \text{H}_2 \rightarrow [\text{Ir}^{\text{III}}\text{H}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ , would involve the oxidation of platinum(II) to platinum(IV). This is unlikely under the reaction conditions. As a matter of fact, reduction to platinum(0) rather than oxidation to platinum(IV) was sometimes observed. Tin(II) chloride may be suggested as the reducing agent. The use of tin(IV) chloride as a cocatalyst, however, gave results comparable to those of tin(II) chloride cocatalyst, thus ruling out this possibility. It is plausible, therefore, to suggest that hydrogen is activated by heterolytic fission by replacing one of the ligands on the platinum atom. Thus



or



**2. The Role of Tin(II) Chloride.** Catalytic isomerization and hydrogenation of olefins by  $[\text{PtCl}_2(\text{PPh}_3)_2]$  are peculiar in that they cannot be effected in the absence of  $\text{SnCl}_2$ . The activity of the catalyst increases with increasing tin-to-platinum ratio to a maximum corresponding to a tin-to-platinum ratio of 10, then declines at a much slower rate. However, the maximum ratio of tin to platinum in any of the isolated intermediates was 2. These observations can be understood in terms of the reversibility of the insertion of  $\text{SnCl}_2$  into the platinum complex



Since there are only two chloride ions per platinum atom in the starting material, only two  $\text{SnCl}_2$  molecules can react to form  $\text{SnCl}_3^-$  ligands. When a large excess of  $\text{SnCl}_2$  is present, it will not only drive the above reactions toward the formation of a tin-rich complex, but may also block some of the sites on the platinum atom which would otherwise be available for coordination with the olefin. This may explain the slight decrease in the latter part of the curves in Figure 1.

In order to elucidate the function of  $\text{SnCl}_2$ , or rather the ion  $\text{SnCl}_3^-$ , salts having some chemical properties in common with  $\text{SnCl}_2$  were investigated. Thus, isomerization reactions were carried out using halides of other group IV elements, halides of group V and group III elements, and finally CO as cocatalysts. The results, shown in Table I, indicate that  $\text{SnCl}_2$  is almost unique in its "cocatalytic" properties. It does not exhibit its activation effects in virtue of the fact that tin is a member of group IV, nor are they due to the presence of an inert electron pair. Comparison with CO and  $\text{PF}_3$ , which are known to be  $\pi$  acceptors- $\sigma$  donors, shows that if  $\text{SnCl}_3^-$  utilizes the  $\pi$ -accepting  $\sigma$ -donation properties, it still differs from these two ligands in some respect. It is interesting to notice that antimony trichloride,  $\text{SbCl}_3$ , is a fairly good cocatalyst. Both Sn(II) and Sb(III) have vacant 5d orbitals of size and energy comparable to those of the filled 5d orbitals of platinum. These observations therefore suggest that  $\text{SnCl}_2$  functions through its complex ligand,  $\text{SnCl}_3^-$ , which is strong  $\pi$  acceptor (stronger than CO or  $\text{PF}_3$ ) and weak  $\sigma$  donor (weaker than CO or  $\text{PF}_3$ ) and which has vacant 5d orbitals of the right size and energy to accept electrons from the filled 5d orbitals of platinum. By doing so the ligand  $\text{SnCl}_3^-$  reduces the electron density on the platinum atom, thus making it susceptible to attack by nucleophiles like hydride ion or the carbon-carbon double bond of an olefin. The strong  $\pi$ -accepting capacity of  $\text{SnCl}_3^-$  also stabilizes hydrido and metal-olefin complexes once they are formed and prevents reduction of the platinum(II) atom.

**3. Over-all Reaction Mechanism.** The stepwise nature of the reaction is demonstrated by the results shown in Figure 2. A plausible mechanism is the hydride addition-abstraction mechanism originally suggested for the catalytic isomerization of olefins in the hydroformylation reaction<sup>14,15</sup> and later invoked by several authors to account for the isomerization of olefins by various catalysts.<sup>16</sup> Using these ideas, the reaction steps are as shown in Scheme I.

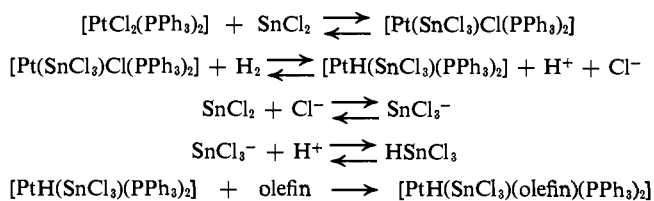
The olefin adds to the platinum atom to form the five-coordinate hydridoplatinum-olefin intermediate. It is the ability of  $d^8$  transition metal atoms to expand their coordination spheres that makes them effective catalysts. Although the achievement of the complete shell configuration is the driving force toward the formation of the five-coordinate intermediate, this intermediate is not very stable with respect to the four-coordinate, square-planar complex because the fifth d orbital in question is of higher energy than the other occupied d orbitals. This drives the reaction toward the formation of the four-coordinate complex through rearrangement to a metal-alkyl complex. The latter

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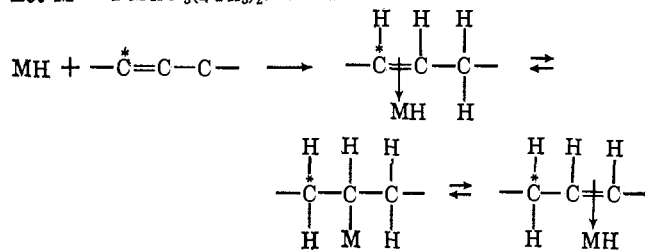
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## Scheme I



Let  $M = \text{PtSnCl}_3(\text{PPh}_3)_2$ . Thus



may be of a transitory existence because the metal-

carbon bond is weak in this complex because of the lack of back electron donation and  $\pi$  bonding. It therefore rearranges to a hydridometal-olefin complex by the abstraction by the metal atom of a hydrogen atom, possibly from a location that leads to double-bond migration. These processes may be repeated several times. At some stage in the process, the isomerized coordinated olefin exchanges with the unisomerized olefin in solution. Exchange reactions continue, and an equilibrium mixture of isomers is obtained. In dienes, conjugated isomers are expected to be the major isomerization products since they are stabilized by resonance relative to the nonconjugated isomers.

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## The Structure of a Trigonal-Bipyramidal Nickel(II) Cyanide Complex Containing the Tetradentate Ligand Tris(3-dimethylarsinopropyl)phosphine

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**Abstract:** A structural determination of  $[\text{Ni}(\text{TAP})\text{CN}^+]\text{ClO}_4^-$  (where TAP = tris(3-dimethylarsinopropyl)phosphine) was undertaken in order to study the coordination of a tetradentate ligand to a Ni(II) atom. This complex crystallizes with four formula species in an orthorhombic unit cell of symmetry  $P2_12_12_1$ , and of dimensions  $a = 10.27$  Å,  $b = 14.04$  Å, and  $c = 17.79$  Å. The configuration of the idealized cation,  $[\text{Ni}(\text{TAP})\text{CN}^+]$ , is a trigonal bipyramid in which the central nickel atom is surrounded by three arsenic atoms at equatorial sites and a phosphorus atom and a cyanide group in apical positions; each arsenic atom is connected to the apical phosphorus atom by a trimethylene chain such that the cation possesses a pseudo-threefold axis. The absolute conformation of the cation in the crystal examined was determined from anomalous dispersion effects.

In recent years a substantial number of five-coordinate Ni(II) complexes which contain mono-, bi-, tri-, or tetradentate donor ligands comprised of nitrogen, phosphorus, sulfur, or arsenic atoms have been synthesized and characterized both by chemical and physical means.<sup>2-8</sup> One such series of Ni(II) complexes possessing a mixed arsenic-phosphorus donor system was prepared by Benner, Hatfield, and Meek<sup>5</sup> through the reaction of nickel(II) salts with tris(3-dimethylarsinopropyl)phosphine (TAP). Five-coordinate metal cations of general formula  $[\text{Ni}(\text{TAP})\text{X}^+]$  (where  $\text{X} = \text{Cl}$ ,

$\text{Br}$ ,  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{SCN}$ , or  $\text{SC}_2\text{H}_5$ ) were postulated by these workers from magnetic susceptibility, electronic absorption, and conductivity measurements. Although stereochemical considerations indicate that the tetradentate ligand TAP can coordinate to four of the five bonding sites of either a square-pyramidal or trigonal-bipyramidal configuration, Meek and co-workers<sup>5</sup> assigned a trigonal-bipyramidal structure to the diamagnetic  $[\text{Ni}(\text{TAP})\text{X}^+]$  cations on the basis of the close similarity of their electronic spectra to those of the  $[\text{Ni}(\text{QAS})\text{X}^+]$  and  $[\text{Pt}(\text{QAS})\text{I}^+]$  cations (where QAS = tris(*o*-diphenylarsinophenyl)arsine); the platinum complex had been previously shown by an X-ray structural determination<sup>9</sup> to possess a trigonal-bipyramidal configuration. A single-crystal X-ray diffraction study of  $[\text{Ni}(\text{TAP})\text{CN}^+]\text{ClO}_4^-$  was undertaken not only to determine the over-all configuration and thereby to establish which of the three possible geometrical isomers of a trigonal-pyramidal cation is actually formed but also to obtain

(1) This paper is based in part on a dissertation submitted by D. L. Stevenson to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1967.

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