

Homogeneous Catalysis. II. The Mechanism of the Hydrosilation of Olefins Catalyzed by Group VIII Metal Complexes¹

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Platinum(II) and rhodium(I) olefin complexes have been studied as catalysts for the hydrosilation of olefins. The relative importance of hydrosilation and isomerization reactions was found to be dependent on the nature of the silane used. Alkyl phosphine complexes of platinum(II) were found to undergo reaction with trialkylsilanes to produce the corresponding platinum(II) hydride. Although no evidence was found for the formation of stable Pt-Si bonds, a phosphine complex of iridium(I) was found to cleave a variety of silicon hydrides, retaining both the silicon and the hydride fragments in its coordination sphere. On the basis of the known chemistry of *d⁸* metal complexes, a mechanism is suggested for the coordination-catalyzed hydrosilation of olefins which is very similar to that proposed for coordination-catalyzed hydrogenation reactions.

Introduction

In the first paper of this series,² we noted that transition metal olefin complexes may react catalytically with olefins in at least four important ways, leading to polymerization, addition, substitution, and double-bond migration. We described some systems in which double-bond migration was the dominant reaction and interpreted the reaction in terms of the chemistry of metal olefin complexes. In the present paper we shall describe some observations on the metal complex catalyzed hydrosilation of olefins, a system in which all four of the above-described reactions have been observed.³

The chloroplatinic acid catalyzed hydrosilation reaction has previously been studied in great detail by Speier, *et al.*⁴ Considerations of the mechanism, however, have been limited to the organic chemistry involved. This probably results from the inference that chloroplatinic acid acts as a catalyst by virtue of its reduction to platinum metal.⁵ In a recent paper, however, Speier⁶ noted that the chloroplatinic acid catalyzed addition of trichlorosilane to olefins was apparently homogeneous. If these catalyses are homogeneous, it would seem profitable to consider the mechanism in terms of the chemistry of group VIII metal complexes. This paper, therefore, concerns

firstly the noncatalytic reactions of silicon hydrides with group VIII metal phosphine complexes, then the study of olefin complexes as catalysts. The latter section is concerned more with the accompanying olefin isomerization than hydrosilation, the course of the latter being already well documented.⁴

Experimental

The olefins and metal catalyst complexes used in this work were the same as described previously.²

Trialkyl- and triarylsilanes were commercial products of Peninsular Chemresearch, Inc. Alkyl- and aryl-halosilanes were obtained as technical grade products from the Silicone Products Department, General Electric Company. Triethoxysilane was prepared as described by Shorr.⁶

The volatile silanes were purified by distillation. Triphenylsilane was used without further purification.

Preparation of Phosphine Complexes. Bis(tributylphosphine)- and bis(triphenylphosphine)dichloroplatinum(II) were prepared as described by Jensen.⁷ The former was obtained as the pure *cis* isomer as described by Chatt and Wilkins.⁸

A standard sample of bis(tributylphosphine)chlorohydridoplatinum(II) was prepared as described by Chatt and Shaw.⁹

Bis(triphenylphosphine)carbonylchloroiridium(I) was prepared as described by Vaska and DiLuzio.¹⁰

Reactions of Silanes with Phosphine Complexes. The following illustrate typical reactions: (1) Bis(tributylphosphine)dichloroplatinum(II) (0.1 g.) was refluxed with triethylsilane (2 g.) under nitrogen for 1 hr. The reaction vessel was evacuated and volatile components were removed by continuous evacuation. The residual viscous oil had infrared and n.m.r. spectra indistinguishable from those of an authentic sample of bis(tributylphosphine)chlorohydridoplatinum(II). Trihexyl-, tribenzyl-, and triphenylsilanes reacted more slowly giving products with infrared spectra consistent with their being mixtures of bis(tributylphosphine)chlorohydridoplatinum(II) ($\nu_{\text{Pt-H}}$ 2150 \pm 10 cm^{-1}) and the corresponding chlorosilane.

(2) Bis(triphenylphosphine)dichloroplatinum(II) (1.5 g.) was heated to 145° under nitrogen for 24 hr. with 2 ml. of trihexylsilane. The product was extracted with dry petroleum ether and then benzene. The petroleum ether solution on evaporation gave a product with an infrared spectrum similar to that of a mixture of trihexylsilane and trihexylchlorosilane. A chloride analysis showed that the mixture was ap-

(6) L. M. Shorr, *ibid.*, 76, 1390 (1954).

(7) K. A. Jensen, *Z. anorg. allgem. Chem.*, 229, 225 (1936).

(8) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2532 (1951).

(9) J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).

(10) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 84, 679 (1962).

(1) This work was presented in part before the Division of Inorganic Chemistry, 141st National Meeting of the American Chemical Society, Washington, D. C., March 21-24, 1962, paper 67.

(2) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, 86, 1776 (1964).

(3) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 51.

(4) (a) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, 79, 974 (1957); (b) J. L. Speier and J. C. Saam, *ibid.*, 80, 4104 (1958); (c) *ibid.*, 83, 1351 (1961); (d) J. W. Ryan and J. L. Speier, *ibid.*, 86, 895 (1964).

(5) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, 83, 4385 (1961).

proximately 50% chlorosilane. The benzene solution on evaporation yielded a deep red powder (*Anal.* Found: C, 55.5; H, 4.2; P, 8.5; Cl, 2.8; Pt, 27; Si, 0). A benzene-insoluble residue was identified as unchanged bis(triphenylphosphine)dichloroplatinum(II).

(3) A sample of bis(triphenylphosphine)carbonylchloroiridium(I) (0.278 g.) was placed in a tube and evacuated on a vacuum transfer line. Triethoxysilane (2 g.) was distilled onto the iridium complex and the reactants were left at room temperature for 12 hr. During this time the yellow crystalline iridium(I) compound was transformed into a white powder, both the starting material and the product being insoluble in triethoxysilane. After completion of reaction, all volatile material was pumped off by prolonged evacuation at room temperature. The reaction tube was detached from the line and weighed to determine any increase in weight. The tube was then replaced on the vacuum line, evacuated, and heated for 2 hr. at 150°. A liquid distilled off into a liquid nitrogen trap leaving a yellow powder. Both products were weighed and examined by infrared.

Similar reactions with trichloro-, ethyldichloro-, and phenyldichlorosilane resulted in white powders; analyses were carried out on the first two only.

(a) Product from HSiCl_3 : *Anal.* Calcd. for $\text{IrCOCl}(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{HSiCl}_3$: C, 48.5; H, 3.4; Si, 3.1; Cl, 15.5; P, 6.8; Ir, 21.0. Found: C, 49.4; H, 3.7; Si, 2.8; Cl, 15.3; P, 6.7; Ir, 20.4.

(b) Product from $\text{C}_2\text{H}_5\text{SiCl}_2\text{H}$: *Anal.* Calcd. for $\text{IrCOCl}(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{C}_2\text{H}_5\text{SiCl}_2\text{H}$: C, 51.5; H, 4.0; Si, 3.1; Cl, 11.7; P, 6.8; Ir, 21.2. Found: C, 52.1; H, 4.5; Si, 2.1; Cl, 10.5; P, 7.0; Ir, 21.0.

Higher temperatures were required for decomposition, but volatile products were trapped and examined by infrared.

Infrared Spectra of Iridium Complexes. The infrared spectra of the iridium complexes were measured in KBr disks. Strong bands in the 1970–2040 cm^{-1} region were assigned to ν_{CO} of an iridium(III) carbonyl, while bands in the 2080–2180 cm^{-1} region were assigned to $\nu_{\text{Ir-H}}$ of an iridium(III) hydride.¹⁰ The spectra of solutions of iridium–silicon hydride adducts in benzene were measured in rock salt cells vs. pure solvent as reference.

Metal-Catalyzed Hydrosilation Reactions. The following illustrate typical hydrosilation reactions. (1) Phenyldichlorosilane (0.1 mole) was added to 1-hexene (0.15 mole) in which was dissolved dichlorobis(ethylene)- μ,μ' -dichlorodiridium(II) (10^{-5} M). The mixture was refluxed under nitrogen for 2 hr. and then distilled at reduced pressure to yield 20 g. (76%) of a clear liquid, b.p. 88–90° (0.1 mm.). *Anal.* Calcd. for $\text{C}_6\text{H}_5\text{SiCl}_2 \cdot \text{C}_6\text{H}_{13}$: C, 55.2; H, 6.95; Cl, 27.2. Found: C, 54.9; H, 6.86; Cl, 28.2.

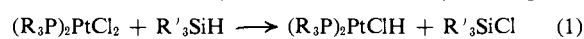
(2) Ethyldichlorosilane (0.1 mole) was added to 1-hexene (0.15 mole) in which was dissolved tetrakis(ethylene)- μ,μ' -dichlorodiridium(I) (10^{-4} M). The mixture was refluxed for 2 hr. under nitrogen and the product distilled at reduced pressure. A fraction (9 g.) boiling at 81–82° (7 mm.) was found by analysis to be $\text{C}_2\text{H}_5\text{SiCl}_2 \cdot \text{C}_6\text{H}_{13}$ (Calcd.: C, 45.0; H, 8.5; Cl, 33.3. Found: C, 44.97; H, 8.54; Cl, 29.9); yield, 50%.

Isomerization of Olefins by Silanes in the Presence of Hydrosilation Catalysts. The methods of analysis for following the isomerization of olefins were the same as those described previously.² (1) 1-Hexene was treated with a variety of halo- and alkoxy-silanes by refluxing under nitrogen in the presence of 10^{-6} M Pt(II) added as dichlorobis(ethylene)- μ,μ' -dichlorodiplatinum(II). The initial molar ratio of olefin to silane was always 4:1. The disappearance of silane was checked periodically by analysis of the $\nu_{\text{Si-H}}$ band in the 2200– cm^{-1} region of the infrared.

(2) Triethylsilane was treated by a stepwise addition to 1-hexene. Aliquots of triethylsilane (1 ml.) were added periodically to a 10^{-6} M solution of Pt(II) in hexene (20 ml.). The retention time for the silane on the g.p.c. column was of the same order of magnitude as those for the isomeric hexenes, and, consequently, all components of the mixture, except the addition product, could be analyzed in a single operation.

Results

Reaction of Silanes with Phosphine Complexes. The reactions of Pt(II) phosphine complexes with silanes fell into three categories: (a) no reaction, as found with all except the trialkyl- and triarylsilanes; (b) meta-theoretical exchange between chloride and hydride, as found with bis(tributylphosphine)dichloroplatinum(II) and trialkyl- and triarylsilanes, according to eq. 1;

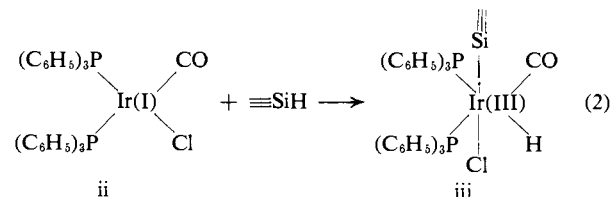


(R = alkyl, R' = alkyl or aryl)

and (c) the reaction between bis(triphenylphosphine)-dichloroplatinum(II) (i) and trialkyl- or triarylsilanes. The brown product of this reaction gave no indication of Pt–H in either infrared or n.m.r. spectra, and elemental analysis indicated complete absence of silicon. The empirical formula corresponded closely to $\text{Pt}_2[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Cl}$.

The experiment was repeated with triphenyl-, tribenzyl-, and trihexylsilanes and all gave similar results. Reactions of i with electronegatively substituted silanes, such as halosilanes and alkoxy-silanes, yielded only starting materials under the conditions described above. In none of these reactions was there any evidence for the formation of stable metal–silicon bonds.

The reactions of bis(triphenylphosphine)carbonylchloroiridium(I) with silanes were remarkably different from those of the isoelectronic platinum(II) complexes. With iridium(I) it was the silane with electronegative substituents which reacted with great facility, even at room temperature, whereas the trialkyl- and triarylsilanes did not react at all. In keeping with the known chemistry of the iridium(I) complex,¹⁰ it was expected that a homolytic cleavage would occur, as illustrated in eq. 2.



For the reaction with triethoxysilane described in the Experimental section, the weight increment (0.057

g.) corresponded closely to that expected for a 1:1 adduct between ii and triethoxysilane (expected 0.058 g.). Thermal decomposition of the adduct *in vacuo* yielded the original weight of pure ii. The volatile product, 0.052 g., was successfully trapped and identified as triethoxysilane. Dissolution of the adduct in benzene and evaporation to dryness yielded pure ii. An infrared spectrum of a concentrated solution of the adduct in benzene showed the presence of free triethoxysilane in solution, together with a mixture of iridium(I) and iridium(III) complexes.

Similar results were found with HSiCl_3 , $\text{C}_2\text{H}_5\text{SiCl}_2\text{H}$, and $\text{C}_6\text{H}_5\text{SiCl}_2\text{H}$. Adducts were formed at room temperature but did not dissociate until somewhat higher temperatures (150–200°) were reached. These reactions were complicated by the presence of small amounts of HCl, which also forms an adduct. However, weight increments were within 10% of those expected for 1:1 adducts and analyses gave reasonable agreement. Both ethyl- and phenyldichlorosilane were isolated, and identified by infrared, on heating their adducts. No adducts were formed below 50° with tetraethoxysilane or tetrachlorosilane, indicating that the adduct formation is peculiar to the Si–H bond.

Evidence that the 1:1 adducts, obtained through reaction of silicon hydrides with ii, were octahedral complexes of iridium(III) was provided by the infrared spectra of the adducts. The carbonyl ν_{CO} absorption in such complexes is very sensitive to the charge of the central metal ion, moving to higher frequencies as the positive charge on the metal ion increases. Such a strengthening of the C–O bonding is expected since increasing positive charge on the metal tends to reduce donation by the metal into the antibonding π -orbital of the carbonyl group. The absorption frequencies for $\nu_{\text{Ir-H}}$ and ν_{CO} of a variety of hydride adducts of compound ii are listed in Table I, together with

Table I

Addend	$\nu_{\text{Ir-H}} (\pm 2)$, cm.^{-1}	$\nu_{\text{SiH}} (\pm 5)$, cm.^{-1}	$\nu_{\text{CO}} (\pm 2)$, cm.^{-1}
...	1950
H_2^a	2190, 2100	...	1970
HCl^b	2240	...	2025
Cl_3SiH	2100 (m), 2100 (sh)	2275	2020 (s), 2000 (s)
$\text{C}_2\text{H}_5\text{Cl}_2\text{SiH}$	2110 (m)	2190	2035 (s), 2020 (s)
$\text{C}_6\text{H}_5\text{Cl}_2\text{SiH}$	2145 (m)	2205	2025 (s), 2010 (sh)
$(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$	2080 (m)	2195	1975 (s), 1970 (s)
$(\text{C}_2\text{H}_5)_3\text{SiH}$...	2100	...

^a Bis(triphenylphosphine)carbonylchloroiridium(I). ^b From data of Vaska and DiLuzio.¹⁰

$\nu_{\text{Si-H}}$ for the free silanes. The adducts were insufficiently soluble in suitable solvents to obtain evidence of metal hydride bonds by n.m.r. In all of the silane adducts, bands were observed which were attributed to an iridium hydride and to a carbonyl attached to iridium(III). Because the interaction between the silicon and metal is an unknown quantity, meaningful correlations between shifts and electronic structure are difficult to obtain. However, the trichlorosilane adduct was found experimentally to have a higher thermal stability than that of triethoxysilane. Thus a temperature of 200° was necessary to dissociate the former

significantly. This difference in stability was reflected in the carbonyl-stretching frequency, that of the triethoxysilane adduct being much closer to the value for iridium(I).

Olefin Complexes as Catalysts for the Hydrosilation of Olefins. The olefin complexes of both platinum(II) and rhodium(I) were found to be very effective catalysts for the addition of silanes to olefinic compounds. In all reactions studied, a control using chloroplatinic acid as catalyst was found to give essentially the same result as the platinum-olefin complexes in terms of rate, yield, and product. A strict comparison of rates proved to be impossible since at the low concentration of catalyst ($\sim 10^{-6}$ M) at which rates became low enough to study isothermal reactions, impurity interference was found to be a dominating influence on the rate of reaction.

The results of hydrosilation reactions were found to be much more dependent on the nature of the substrates than on the nature of the catalyst. Thus, it was found that both platinum(II)- and rhodium(I)-olefin complexes catalyzed the reduction of allyl chloride and allyl acetate to propylene in the presence of silanes and catalyzed the addition of silanes to internal olefins to yield terminal products, as previously observed by Speier, *et al.*, using chloroplatinic acid as catalyst.⁴

Relative Rates of Hydrosilation and Isomerization. Under the conditions used for studying isomerization (reflux under nitrogen with 10^{-6} M Pt(II)), 1-hexene, a typical α -olefin, gave rise to three types of reaction dependent on the silane.

(a) Hydrosilation proceeded rapidly to completion without any observable isomerization, either before or after completion of the addition reaction. The reaction mixture remained colorless throughout the reaction. This type of behavior was observed with trimethoxy- and triethoxysilane.

(b) Hydrosilation proceeded rapidly to completion with concurrent extensive isomerization of excess olefin. The initially colorless reaction mixture darkened slowly during the addition reaction. This was the most commonly observed behavior and was exemplified by the reactions of trichloro-, ethyldichloro-, and phenyldichlorosilane.

(c) Hydrosilation proceeded rapidly at first with concurrent isomerization, but the rates of both processes fell rapidly to zero. The reaction mixture was dark brown from the moment the silane and catalyst were contacted. This type of behavior was observed with triethyl-, tribenzyl-, and triphenylsilane.

Reactions of the first group were typified by very high yields of recoverable terminal hydrosilation product (>90% based on silane), and excess terminal olefin was recovered with no detectable (<1% of recovered olefin) internal isomers.

Reactions of the second group usually gave yields in the range of 50–80% after 2 hr. of reaction under reflux. By periodic analysis of silane concentration, it was shown that the lower yields with these silanes were due to the slowness of the reactions and not to catalyst deactivation.

The third group of silanes was characterized by extremely poor yields of addition products (<20%) obtained at reflux temperatures, in spite of an initial rapid, exothermic reaction. In this case the low yields

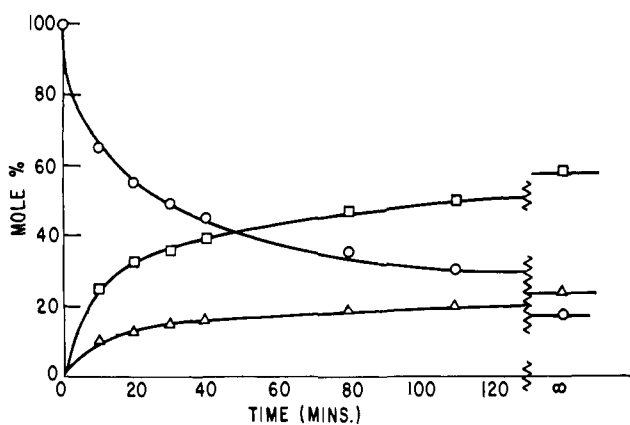


Figure 1. Isomerization of 1-hexene by $C_6H_5SiCl_2H-Pt(II)$ at $65-70^\circ$ under N_2 : silane:olefin = 1:4; $[Pt] = 10^{-6} M$. \circ , terminal- + *trans*-3; \square , *cis*-3 + *trans*-2; \triangle , *cis*-2.

were undoubtedly due to thermal deactivation of the catalyst,¹¹ as will be demonstrated in the next section.

No system was found in which palladium-olefin complexes would catalyze the addition of a silicon hydride to an olefin. In most systems the palladium complex was reduced to the metal very rapidly by the silane, but even in the few cases where reduction did not occur, no catalysis was observed.

The complexes of Pt(II) and Rh(I) with chelating diolefins, such as 1,5-cyclooctadiene, were considerably less active than the complexes of monoolefins.

Isomerization of Olefins during Hydrosilation. The composition profile for the hexenes present in the course of an addition of phenyldichlorosilane to 1-hexene (mole ratio 1:4), catalyzed by $10^{-6} M$ Pt(II), is shown in Figure 1. This profile is substantially different from those described previously for the isomerization of hexene by platinum(II)-olefin complexes in the presence of cocatalysts.² There is no indication of autocatalysis, suggesting that the silane reacts very rapidly to yield the species responsible for isomerization. The isomerization rate asymptotically approaches zero in such a way that the *cis*-2 isomer does not approach its equilibrium value. This kinetic limitation is due to the decay of silane to the point where the rate becomes silane dependent. The silane was no longer detectable after 50 min. of reaction time, but even at that concentration the silane was probably more abundant than the catalyst by several orders of magnitude. After many hours of reaction, the addition of more catalyst had no effect on the isomer distribution. The addition of more silane caused further slight changes in distribution.

Another exceptional feature of Figure 1 is the fact that the ratio of *cis*-2:*trans*-2 isomers remains essentially constant throughout the course of the reaction at a value of 0.40. This contrasts with the previously studied systems where there was invariably a high initial preference for the formation of the *cis* isomer, which declined markedly as the reaction progressed.

Other halosilanes were found to exhibit the same behavior as phenyldichlorosilane, except for variations in the *cis*:*trans* ratio. For ethyldichloro- and -trichloro-

(11) More recently we have found that high yields may be obtained with these silanes if the reaction is carried out slowly at room temperature.

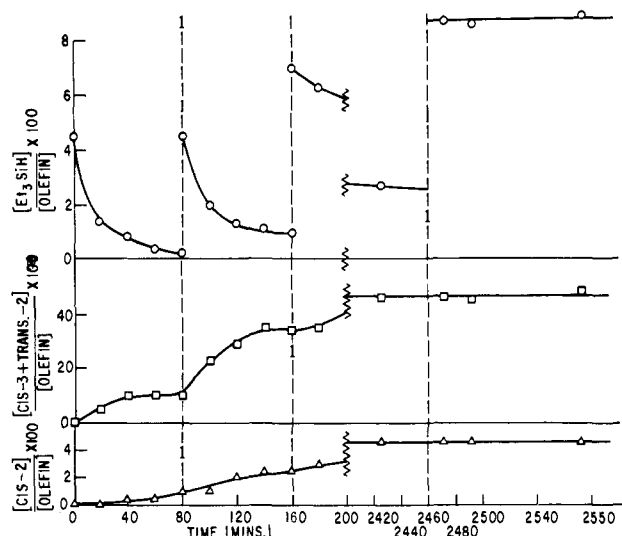


Figure 2. Reaction of $(C_2H_5)_3SiH$ with 1-hexene, catalyzed by Pt(II) at $65-70^\circ$ under N_2 : $[Pt] = 10^{-6} M$ (composition changes for various components expressed relative to total olefin).

silane the ratios were found to be 0.53 and 0.31, respectively.

The compositional changes resulting from a stepwise hydrosilation of 1-hexene with triethylsilane are illustrated in Figure 2. The dependence of isomerization rate on silane concentration was very apparent in this system. The ratio of *cis*-2:*trans*-2 isomers again remained fairly constant at a value of *ca.* 0.1, the lowest value for any of the silanes studied. Thirdly, there was a gradual decline in catalyst efficiency until, by the time of the fourth addition, there was still an abundance of 1-hexene remaining in the system. A calculation of the extents of hydrosilation *vs.* isomerization based on Figure 2 showed that by the end of the reaction for every mole of silane added to hexene, approximately 5 moles of 1-hexene was converted to internal isomers. This may be compared with the phenyldichlorosilane system, where less than 2 moles of olefin was isomerized per mole of silane added, by the time the silane became undetectable. The formation of internal isomers was a conversion-limiting process because, in the case of triethylsilane, the hydrosilation of internal olefins was slow compared to the rate of deactivation of the catalyst.

Discussion

A reaction closely related to the metal-catalyzed hydrosilation of olefins is the metal-catalyzed hydrogenation of olefins. It is of interest that the latter reaction also was considered solely heterogeneous at first. However, recent work has clearly demonstrated instances of homogeneous catalysis.^{12,13} Our preliminary investigations revealed that hydrosilation of olefins by chloro- and alkoxy-silicon hydrides catalyzed by chloroplatinic acid also takes place in optically clear, colorless solutions. Additions of alkyl- and arylsilanes are accompanied by some reduction to the metal, but this also results in some deactivation of catalyst.

(12) J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

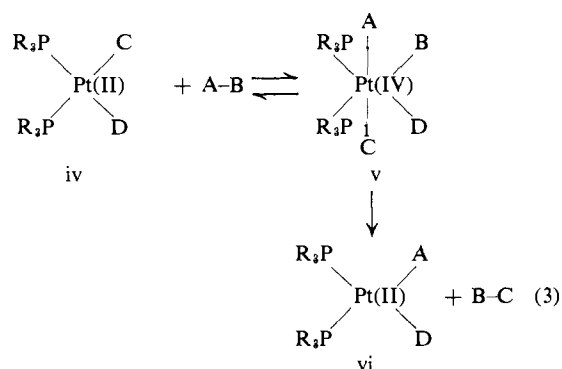
(13) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963).

The mechanism advanced for the hydrogenation reaction requires that the metal ion both coordinate olefin and cleave the bond of molecular hydrogen.¹² We, therefore, expected olefin coordination and Si-H bond cleavage to be probable functions of the metal catalyst in the hydrosilation reaction.

A case of Si-H cleavage was discovered for the iridium(I) complex used; these reactions parallel its reaction with hydrogen¹⁰ to form octahedral iridium(III) complexes. An alternative structure for the adducts would be that in which the silane as a whole adds as a single ligand, both the silicon and the iridium becoming pentacoordinate. Although such a structure does not seem to us to be very plausible *per se*, it can, in fact, be considered as a severely distorted case of the octahedral structure resulting from cleavage of the silicon hydride by iridium.

From Table I it appears that there is a rough correlation between the $\nu_{\text{Si-H}}$ of the free silane and the stability of the adduct formed, leading to the apparently anomalous conclusion that the stronger the Si-H bond, the more stable the complex derived from it. This anomaly is readily resolved if one concludes that the influences leading to a strengthening of the Si-H bond are even more effective in bonding the silicon to iridium.^{13a} In any event, one would expect the presence of electronegative substituents to enhance the stability of a silyl-like ligand by raising the effective positive charge on the metal ion.

A similar reaction might be expected for an isoelectronic square-planar Pt(II) complex cleaving a bond A-B to give an octahedral Pt(IV) complex. A large number of such reactions of bis(phosphine)-platinum(II) complexes have been studied by Chatt, *et al.*¹⁴ However, while a stable intermediate *v* is



formed in some cases, it may decompose thermally to either *iv* or *vi*. Sometimes *v* is so unstable with respect to *vi* that *iv* appears to react with A-B to yield *vi* directly.

The reaction of trialkylsilanes with bis(trialkylphosphine) complexes of platinum(II) appears to fall into the latter category. Whether *v* is an unstable intermediate or a genuine transition-state complex will depend very much upon the specific nature of the reacting groups. In the special case of very strong interaction between B and C, the transition state would approximate that proposed for the heterolysis of molec-

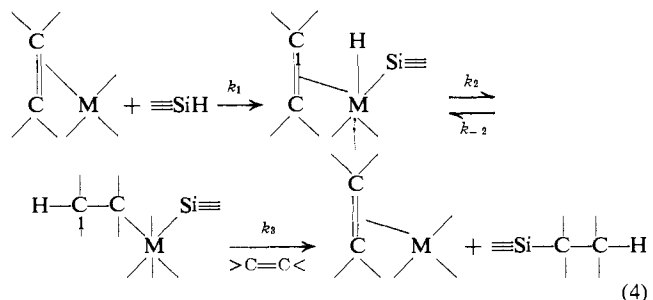
(13a) NOTE ADDED IN PROOF. A possible additional contribution to the stability of transition metal silyls is $d_{\pi}-d_{\pi}$ bonding, analogous to that encountered in the isoelectronic phosphine complexes of the transition metals.

(14) J. Chatt, *J. Chem. Soc.*, 2301 (1950); J. Chatt and B. L. Shaw, *ibid.*, 4020 (1959).

ular hydrogen by transition metal ions.¹⁵ It is quite conceivable that the affinity of an incipient silyl group for a halide ligand is so great in the case of silanes reacting with a platinum(II)-chloro complex that the octahedral intermediate *v* is never formed.

The reaction between trialkylsilanes and bis(tri-phenylphosphine)dichloroplatinum(II) is apparently complicated further by the thermal instability of the primary reaction products.¹⁶

In view of the results obtained by Speier, *et al.*,⁴ using simple chloro complexes of platinum(II) and -(IV), the finding that platinum(II)-olefin complexes are similarly active catalysts for hydrosilation was not totally unexpected. However, the high solubility of these complexes in olefins, and their relatively simple chemical nature, allows greater confidence in the hypothesis that the catalytic activity is a function of the metal ion and not some other property of the catalyst, *e.g.*, the strongly acid character of chloroplatinic acid. The identity of results obtained with platinum(II)-olefin complexes to control experiments using chloroplatinic acid indicates that both catalysts operate through very similar intermediates. It, therefore, becomes pertinent to inquire into what would happen if the phosphine ligands were replaced by olefinic ligands in a complex structurally analogous to *iv* in eq. 3. We have previously noted the enhanced susceptibility of coordinated olefins to attack by nucleophiles,² and we would expect at least the hydride fragment from silane cleavage to be particularly effective in attacking an olefinic ligand. To explain the observed variations in the isomerization which occur concurrently with hydrosilation, it is necessary to invoke two special cases for the addition of the silicon hydride fragments to the double bond. In the first case, the rates at which the silicon fragment and the hydride fragment attack the olefin are comparable, and there is effectively a concerted addition of the silane to the olefin. This situation would not be expected to lead to isomerization. In the second case, the rate at which the silicon fragment attacks the olefin is much less than the rate of hydride attack, and the lifetime of the hydride-olefin complex is long enough for a reversible alkyl-olefin equilibrium to lead to isomerization of the olefin.² The situation is illustrated schematically in eq. 4. In the case where $k_3 > k_{-2}$,



no isomerization would be expected, but if $k_{-2} > k_3$, isomerization will occur.

(15) J. Halpern, *Advan. Catalysis*, 11, 301 (1959).

(16) The brown product of this reaction appears to be the same as an uncharacterized compound we have obtained by thermal decomposition of tetrakis(tri-phenylphosphine)platinum(0).¹⁷ The chlorine in the analysis results from contamination by unchanged starting material.

(17) L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963).

Another criterion which must be satisfied before the catalytic cycle can be closed is that both k_2 and k_3 must be large compared to the rate at which the metal ion M may be reduced to metal by the strongly reducing ligands.

The unusual reaction which allyl chloride and allyl acetate undergo, reduction to propylene, has been the subject of some speculation. Eaborn has suggested that the catalyst may promote the normal ability of silicon hydrides to reduce organic halides.¹⁸ Speier has suggested that reduction results from an unusual addition to the double bond to give β -acetoxyalkylsilanes which yield propylene by β -elimination.^{4a} While silane addition in this sense is unusual, it is evident from the above mechanism that hydride addition must occur in this less favored manner to give a secondary carbanion in order to give rise to isomerization in terminal olefins. Following hydride addition to allyl chloride or acetate to give a secondary carbanion, it is only necessary to eliminate chloride or acetate ion to give propylene. Thus propylene and the silyl chloride or acetate could result without the necessity of ever forming β -acetoxyalkylsilanes. That it is the addition to the double bond of allyl chloride in the less-favored sense which leads to the formation of propylene may be inferred from recent work by Speier.^{4d} Thus, trichlorosilane-*d* gave 3-chloropropyl-2-*d*₁-trichlorosilane, but also propylene-3-*d*₁, on treatment with allyl chloride.

The mechanism proposed in eq. 4 requires that a catalyst be capable of the following.

(a) Activation of the silane (Si-H bond cleavage). This is probably the least critical requirement since a large number of transition metal ions react readily

(18) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 53.

with silanes,¹⁹ a larger number, for example, than those which activate hydrogen.

(b) Activation of the olefin. By this we imply the weakening of the C=C bond resulting from coordination. This is particularly marked for Pt(II).²⁰ Phosphine complexes of Pt(II) and Ir(I) which satisfy requirements (a) and (c) are ineffective as catalysts, presumably because of the inability of the olefin to coordinate.

(c) Resistance to destructive reduction of the metal ion. Palladium complexes are in general readily reduced to the metal by silicon hydrides even in the presence of excess olefin. This is at least one cause of their inability to catalyze homogeneous hydrosilylation reactions. The dark color of reaction mixtures and the decline in catalyst activity observed with the platinum(II)-trialkylsilane system are also presumably due to irreversible reduction of the catalyst.

The square-planar to octahedral transformation required by the proposed mechanism is particularly satisfied by the d^8 ions of group VIII, and the exceptional activity of platinum and rhodium ions may be in part due to this effect.

Finally, it should be pointed out that the mechanism proposed for this reaction is of the same general type as that proposed for Ziegler catalysis, the "Oxo" reaction, and many other reactions of unsaturated compounds catalyzed by transition metal ions. The similarities in the mechanisms of these reactions were clearly recognized at the Symposium on Homogeneous Catalysis at the 139th National Meeting of the American Chemical Society.²¹

(19) H. H. Anderson, *J. Am. Chem. Soc.*, **80**, 5083 (1958).

(20) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); J. Chatt, L. A. Duncanson, and R. G. Guy, *Chem. Ind. (London)*, 430 (1959).

(21) *Chem. Eng. News*, **39**, 43 (1961).

Chelate Chemistry. II.¹ Hydrolysis of Metal Tropolonates

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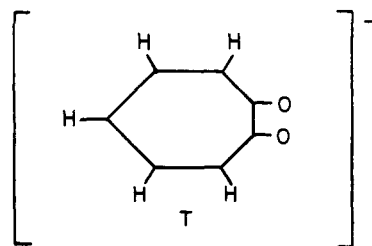
Tracer studies with O^{18} -enriched water have shown in the base hydrolysis of metal tropolonates that (1) initial attack occurs primarily on the chelate ligand rather than on the central metal atom for four- and six-coordinate cationic chelates, i.e., T_2B^+ , T_3Si^+ , T_3Ge^+ , and T_3P^{2+} ; (2) no significant attack of ligand takes place in neutral metal chelates; and (3) more than one mechanism is operative for the eight-coordinate cations T_4Nb^+ and T_4Ta^+ . Chelates derived from β -diketones seem to behave analogously to those derived from tropolone.

Introduction

In the first paper of this series,¹ a number of chelates

(1) Paper I: E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964).

derived from the tropolone anion, T, were described. These chelates exhibited coordination numbers of four



(T_2B^+), six (T_3La and T_3Si^+), and eight (T_4Zr). More recently we have prepared² eight-coordinate cations, T_4Nb^+ and T_4Ta^+ , as well as new octahedral chelates,²

(2) Paper III: E. L. Muetterties and C. M. Wright, to be published.