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Transition Metal Complexes of Enol and Enol Derivatives

CONTENTS

INTRODUCTION

Direct synthesis of poly(vinyl alcohol) from acetaldehyde has been one of the important synthetic problems in high polymer chemistry. Only a few studies on this topics, however, have been made and the problem still remains unsolved.

It was shown that the magnitude of the heat of the hypothetical polymerization of acetaldehyde into amorphous poly(vinyl alcohol) is -14.9 Kcal/monomer unit.[1] According to Dolliver et al., the theoretical value for the heat of enolization of acetaldehyde is +10.0 Kcal/mole.[2] Consequently, the heat of the hypothetical polymerization of vinyl alcohol is -24.9 Kcal/monomer unit, as is shown in Fig. 1.
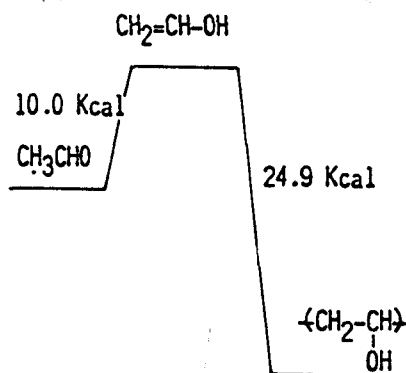

Fig. 1. Energy level diagram for vinyl alcohol.

These values are comparable to the heat of usual vinyl polymerizations (-15∼-25 Kcal/monomer unit). Poly(vinyl alcohol) could be synthesized via the vinyl polymerization of vinyl alcohol, therefore, if vinyl alcohol was stable enough. As is well known, this is not the case and vinyl alcohol could not be detected in acetaldehyde.[3] In order to realize the polymerization of vinyl alcohol, a catalyst is necessary to stabilize the enol from and to increase its concentration.

One of the possible way of stabilizing vinyl alcohol may be π-coordination to metals (Fig. 2).

In the present work, the coordination of vinyl ethers to platinum(II)

$$CH_3CHO \longrightarrow CH_2\text{=}CH\text{-}OH \longrightarrow \text{\textlparen} CH_2\text{-}CH \text{\textrparen}_n$$
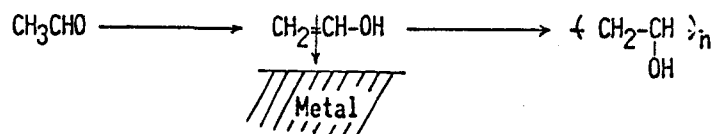
Fig. 2. Schematic route for the polymerization of acetaldehyde into poly(vinyl alcohol).

and palladium(II) has been investigated,since vinyl ethers can be regarded as model compounds of vinyl alcohol. In addition, vinyl esters have been shown to coordinate to rhodium(I). Platinum complex of vinyl alcohol itself has successfully been synthesized by an indirect method and studied spectroscopically.

Since only a little is known about π-complexes of those olefins which have oxygen next to the double bond, studies on these olefin π-complexes, especially on the role of oxygen in stabilizing complexes are an interesting problem in the view of organometallic chemistry.

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CHAPTER I

Synthesis of Platinum(II) and Palladium(II) Complexes of Vinyl Ethers;

Synthesis of Rhodium(I) Complexes of Vinyl Esters; Reactions of Vinyl

Ether Complexes with Acids and Bases

Introduction

Chatt's theory has been accepted in general, in which a metal-olefin bonding is described to be formed by both the electron donation from the olefin to the metal and the electron back-donation from the metal to the olefin.[1] The kind and valency of the metal involved may act an important role in determination of the stability of metal-olefin bonding. Almost all of the stable olefin π-complexes heretofore known are limited within those olefins having an electron-withdrawing substituent. Thus it has generally been thought that the back-donation contributes more efficiently than the donation to the formation of stable olefin-metal π bonding.

With respect to Pt(II), the mesurement of stability constants by Venanzi et al. afforded a conclusion that the π-accepting ability of the olefin is more important than the σ-donating ability.[2] In contrast, the mesurement of equilibrium constants by Orchin et al. of the coordinations of substituted styrenes with Pt(II) informed that the σ value of Hammett equation and the logarithm of the equilibrium constants are in a U shaped relation,[3] and consequently that the σ-donating ability, as well as π-accepting ability, takes part in the coordination. Moreover, the study of infrared spectra of the π-complexes by Nakamoto et al. suggests that the σ-donating ability may be more important for the coordination.[4]

Meanwhile, Cramer studied the influence of the substituent of the olefin on the equilibrium constants of the coordination of the olefin to Rh(I), and concluded that the olefins having stronger electron withdrawing substituent are more liable to be coordinated and that those having electron releasing substituent resist to be coordinated.[5]

In view of the metals with d^8 electron configuration, therefore, it is

still not clear that the substituent on the olefin to be coordinated should be electron withdrawing or releasing in order to form a stable π complex.

We have discovered that the olefins having a strong electron releasing substituent such as vinyl ethers form extremely stable complexes with Pt(II) and Pd(II). Vinyl esters, in the same way, form stable complexes by coordinating to Rh(I). With respect to the π coordinated complexes of vinyl e her and vinyl ester, there have simply been known that Fe(O) forms unstable complexes.[6]

The reaction of the coordinated vinyl ether with proton and hydroxy ion has been studied to see whether the similar reaction with that of Wacker Process does occur or not.

Experimental

The preparation of vinyl ethers and their derivatives.── Methyl vinyl ether, chloroethyl vinyl ether and 2,2,2-trifluoroethyl vinyl ether used are commercial reagents. Isopropyl and t-butyl vinyl ether were prepared by the alcohol exchange of isobutyl vinyl ether with isopropanol and t-butanol, respectively. Vinyl trimethylsilyl ether was prepared in accordance with the Nesmeyanov's method.[7] Preparation of propenyl ethers and 1,2-dimethoxyethylene are described in chapter IV. cis-β-Methoxy-styrene was prepared according to Miller's method.[8]

The preparation of vinyl esters.── Vinyl acetate was obtained commercially. Vinyl trifluoroacetate, vinyl monochloroacetate and ethyl vinyl carbonate were prepared by the known methods.[9][10] [11] Vinyl formate and vinyl isobutyrate were prepared by the ester exchange of vinyl acetate with formic acid and isobutyric acid, respectively.[12]

Platinum complexes.── 1,3-Bis(ethylene)-2,4-dichloro-μ-dichloro-di-platinum was prepared by Chatt's method.[1] A representative procedure of the preparation of the complexes is as follows: About 100 mg of Zeise's dimer, $[Cl_2PtC_2H_4]_2$, was suspended in 8 ml of dry toluene in nitrogen atmosphere and the suspension was cooled to -30° C or below. While stirring with a magnetic stirrer, about 0.05 ml of a vinyl ether was added dropwise with a syringe. Within a few minutes, the heterogeneous suspen-

sion turned to a yellow homogeneous solution. While maintaining this solu-
tion at -20° C or below, the excessive vinyl ether and solvent were evapo-
rated under reduced pressure. The residue was rinsed with petroleum ether
at a low temperature and warmed up to room temperature to obtain the desir-
ed yellow or orange powdery complex. If necessary, the thus obtained com-
plex may be purified by the reprecipitation from hot toluene-petroleum
ether.

Palladium complexes.—— Palladium complexes were prepared by the re-
action of $Cl_2Pd(PhCN)_2$ and olefin according to Kharasch's method.[13] The
reaction was carried out in toluene at room temperature.
About 200 mg of $Cl_2Pd(PhCN)_2$ was dissolved in 20 ml of dry toluene and the
undissolved material was removed by filtration under nitrogen atmosphere.
To this filtrate, 0.1 ml of vinyl ether was added and the solution was
stirred with a magnetic stirrer. Precipitation of the desired complex had
occured in 1 hour. The supernatant solution was removed by decantation and
the precipitate was washed with toluene for several times.

Rhodium complexes.—— μ-Dichlorotetraethylenedirhodium(I) was prepared
in accordance with Cramer's method.[14] On addition of vinyl esters to a
toluene solution of Rh(I)-ethylene complex, the coordinated ethylene was
easily displaced and vinyl ester complexes were obtained.

The reaction of t-butyl vinyl ether complex of Pd(II) with acid and
base.—— The Pd(II) complex of t-butyl vinyl ether (ca. 100 mg) was sus-
pended in an 45 % aqueous HF solution (ca. 10 ml) at room temperature,
then the suspension was allowed to stand overnight and the volatiles were
evaporated. The infrared spectrum of the residue did not show any change
of the palladium complex suspended.
An aqueous 45 % solution of sodium hydroxide (0.5 ml) was added to 228.8
mg (0.411 mmole) of $[Cl_2Pd(CH_2=CHOCMe_3)]_2$ in nitrogen atmosphere. A vigor-
ous reaction occurred and a black precipitate of palladium metal instantly educed.
When this reaction mixture was titrated with 1/10 N aqueous hydrochloric
acid solution, the quantitative amount of acetic acid (0.830 mmole) was
detected. The acetic acid was qualitatively confirmed by the color reaction
with ferric chloride. With respect to the alcohol produced, after the de-
composition of the complex with alkali, the liquid phase was distilled
under reduced pressure at room temperature and the distilate was analyzed

by means of glpc method (poly(ethylene glycohol) 1500, 0.75 m), giving
84 % of the theoretical amount of t-butanol.

Results and Discussion

Platinum complexes of vinyl ethers and their derivatives could be pre-
pared by displacing the coordinated ethylene of Zeise's dimer by vinyl
ethers or by their derivatives in accordance with the following formula:
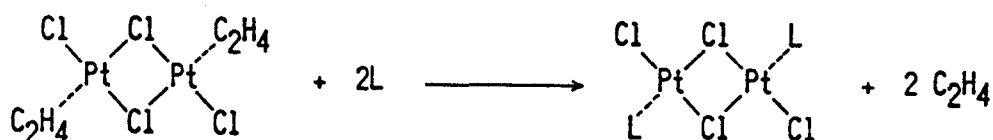
In general, if the reaction is carried out at room temperature, the
polymerization of vinyl ether occurs as a side reaction, and so the complex-
es cannot be obtained satisfactorily. This may be due to the inevitable in-
corporation of a trace amount of hydrogen chloride in the preparational
step of Zeise's dimer. The above-mentioned reaction must be carried out at
low temperatures. With respect to the olefins of low cationic polymeriz-
ability such as trifluoroethyl vinyl ether, 1,2-dimethoxyethylene, tri-
methylsilyl vinyl ether and trimethylsilyl propenyl ether, the complex may
be prepared at room temperature. The complexes are fairly stable, except
trimethylsilyl vinyl ether complex which reacts with moisture (see chapter
II), and even if they are allowed to stand in air for several hours no
change was recognizable.

The case of above-mentioned reaction, that is, whether the displacement
of coordinated ethylene does occur or not, may be in relation to the elec-
tron releasing property of the substituents on the olefins involved. In
the case of vinyl ethers, 2-butne, styrene, etc., the reaction proceeded
easily, but in the case of the olefins having an electron withdrawing sub-
stituent such as vinyl acetate, acrylonitrile, fumaronitrile, 1,2-dichloro-
ethylene, etc., the ligand substitution reaction did not occur. The high
electron density of the double bond of the attacking olefin may be neces-
sary for displacing the ethylene coordinated with Pt(II).

Table I. Analytical data and physical properties of $[Cl_2Pt \ Olefin]_2$.

Olefin used	Yield, %	Analysis, % (calcd.)	Decomp. temp,°C	IR ν(C=C) cm^{-1}
CH$_2$=CHOCH$_3$	80	C, 11.23(11.11) H, 1.91(1.87) Pt, 59.27(60.20)	123-124	1518
CH$_2$=CHOCH(CH$_3$)$_2$	68	C, 17.29(17.05) H, 2.88(2.86) Pt, 55.02(55.40)	90-100	1521
CH$_2$=CHOC(CH$_3$)$_3$	83	C, 19.75(19.68) H, 3.37(3.30) Pt, 52.80(53.28)	80- 90	1515
CH$_2$=CHOCH$_2$CH$_2$Cl	48	C, 12.87(12.90) H, 1.96(1.89) Pt, 51.88(52.36)	100-110	1516
CH$_2$=CHOCH$_2$CF$_3$	72	C, 12.01(12.19) H, 1.33(1.28) Pt, 50.59(49.50)	122-125	1510
CH$_2$=CHOSiMe$_3$		C, 15.77(15.71) H, 2.86(3.16) Cl, 19.13(18.55) Pt, 51.27(51.04)	120-122	1510
cis- CH$_3$CH=CHOCH$_3$	95	C, 14.84(14.21) H, 2.38(2.39) Pt, 57.21(57.70)	137-140	1520
trans- CH$_3$CH=CHOCH$_3$	16	C, 14.82(14.21) H, 2.41(2.39) Cl, 20.70(20.97) Pt, 57.21(57.70)	145-148	1533
cis- CH$_3$CH=CHOSiMe$_3$	71	C, 18.70(18.19) H, 3.55(3.56)	118-121	1507
trans- CH$_3$CH=CHOSiMe$_3$	65	C, 18.02(18.19) H, 3.42(3.56) Cl, 18.68(17.90)	121-123	(1507)
cis- CH$_3$OCH=CHOCH$_3$	82	C, 13.81(13.20) H, 2.29(2.21) Cl, 19.83(19.48) Pt, 53.04(53.58)	140-145	1562
trans- CH$_3$OCH=CHOCH$_3$		C, 13.91(13.20) H, 2.28(2.21) Cl, 20.17(19.48) Pt, 53.01(53.58)	143-145	1535
cis- C$_6$H$_5$CH=CHOCH$_3$	87	C, 27.03(27.01) H, 2.48(2.52) Pt, 48.08(48.75)	130-138	1518

Table I shows yield, elementary analysis, decomposition temperature and wave number of infrared C=C stretching vibration of the platinum complexes obtained.

All the palladium complexes were brown powder and were relatively stable even in air, as in the case of the platinum complexes.

Table II shows yield, elementary analysis, decomposition temperature and wave number of infrared C=C stretching vibration of the palladium complexes obtained.

In case silyl vinyl ether, chloroethyl vinyl ether or trifluoroethyl vinyl ether was employed as the olefin, the respective palladium complex was not obtained by this method.

Table II. Analytical data and physical properties of $[Cl_2Pd\ Olefin]_2$.

Olefin used	Yield, %	Analysis, % (calcd.)	Decomp. temp.°C	IR $v(C=C)$ cm^{-1}
$CH_2=CHOCH_3$	76	C, 14.67(15.31) H, 2.48(2.57) Cl, 30.29(30.13)	60-70	1538
$CH_2=CHOCH(CH_3)_3$	57	C, 23.33(22.80) H, 3.83(3.83)	63-71	1527
$CH_2=CHOC(CH_3)_3$	47	C, 26.19(25.97) H, 4.41(4.36)	64-67	1520
cis- $CH_3CH=CHOCH_3$		C, 19.50(19.26) H, 3.18(3.23)	65-75	1531
trans- $CH_3CH=CHOCH_3$	50		70-78	(1531)
cis- $CH_3OCH=CHOCH_3$	74		120-130	(1543)
trans- $CH_3OCH=CHOCH_3$	54	C, 19.08(18.10) H, 3.13(3.04)		1543
cis- $C_6H_5CH=CHOCH_3$	30	C, 34.24(34.70) H, 3.20(3.24)	105-112	1536

The yellow powder-like complexes of Rh(I)-vinyl esters have stability comparable to the vinyl ether complexes of platinum and palladium.

Table III shows wave numbers of C=C stretching vibrations in the infrared spectra of the rhodium complexes obtained.

Table III. The C=C stretching frequencies of Rh(I)-vinyl ester complexes: [L'_2Rh Cl]$_2$ (cm^{-1})
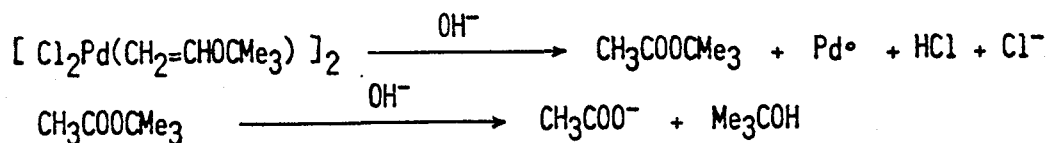
L'	$v(C=C)$ of free olefin	$v(C=C)$ of coord olefin	Magnitude of shift
$CH_2=CHOCOH$	1645	1495	150
$CH_2=CHOCOCH_3$	1650	1497	153
$CH_2=CHOCOCH(CH_3)_2$	1650	1500	150
$CH_2=CHOCOCH_2Cl$	1649	1502	147
$CH_2=CHOCOCF_3$	1652	1498	154
$CH_2=CHOCOCH_2CH_3$ (C=O)	1653	1502	151

Although the C=O stretching frequencies of the vinyl esters are almost unchanged by coordination, their C=C stretching frequencies are lowered about 150 cm^{-1}. However, a systematic influence of substituents was not recognized in these frequency shifts.

The palladium complex of t-butyl vinyl ether was found to be fairly stable towards 45 % hydrogen fluoride. This behavior is in contrast to the fact that free vinyl ether easily decomposes into acetaldehyde and alcohol in the presence of an acid and that some of ether linkages are easily cleaved by hydrogen fluoride.[15]

It was made clear that in contrast to the inertness of free vinyl ether against alkali the coordinated vinyl ether is easily attacked by OH$^-$ ion and consequently is oxidized by the similar reaction to that of the Wacker Process. We detected the theoretical amount of acetic acid and 84 % of the theoretical amount of t-butanol. Thus the occurence of the

following reaction may be deduced.

$$[Cl_2Pd(CH_2=CHOCMe_3)]_2 \xrightarrow{OH^-} CH_3COOCMe_3 + Pd^\circ + HCl + Cl^-$$

$$CH_3COOCMe_3 \xrightarrow{OH^-} CH_3COO^- + Me_3COH$$

This reaction clearly shows that, although the double bond of t-butyl vinyl ether in the free state is relatively electron rich, when coordinated to a metal it may be positively charged by the electron flow to the metal and becomes liable to be attacked by hydroxy ion.

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CHAPTER II

π Complexes of Vinyl Alcohol and Propenyl Alcohol with Platinum(II)

and Some Attempts for the Direct Preparation from Aldehydes

Introduction

Gero succeeded in mesuring the concentration of the enol form of various carbonyl compounds which are reluctant to enolize. However, he could not d cect vinyl alcohol in acetaldehyde even by his highly sensitive method and thus estimated the concentration of vinyl alcohol to be less than 10^{-5} %.[1] It is well established that the compounds otherwise inaccessible can be fixed as metal complexes, such as cyclobutadiene,[2] ketenimine,[3] trimethylene methane,[4] carbene,[5] orthquinodimethane[6] and benzyne.[7] Iron(II) complex of vinyl alcohol was also reported by Green and Ariyaratne; it was prepared by the protonation of an oxoalkyl-iron complex,[8] as shown below:

R: H or CH$_3$
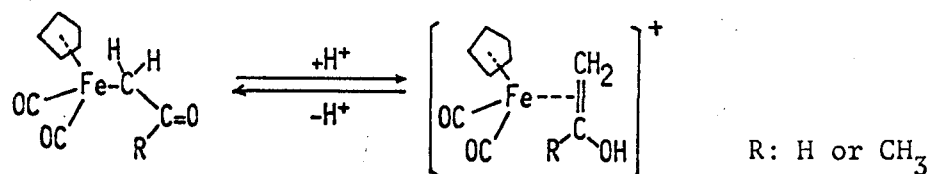
In this chapter the preparation of vinyl alcohol and propenyl alcohol complexes with platinum(II) in a completely different manner is described.

Some trials on coordinating the enol form of aldehydes to metals by adding aldehydes to the ethylene complex of platinum were undertaken but was unsuccessful.

Experimental

The preparation of vinyl trimethylsilyl ether and propenyl trimethyl-
silyl ether are described in chapter I and IV, respectively.

The preparation of complexes.—— To a suspension of Zeise's dimer,
$[Cl_2PtC_2H_4]_2$, in 5 ml of toluene, there was added about 0.1 ml of vinyl
trimethylsilyl ether. The mixture turned orange and became homogeneous
shortly after the addition. The toluene and the excess of vinyl trimethyl-
silyl ether were then evaporated at room temperature to give a yellow
powder of $[Cl_2Pt(CH_2=CHOSiMe_3)]_2$, which decomposed under nitrogen at 120-
122° C. Found: C, 15.77; H, 2.86; Cl, 19.13; Pt, 51.27 %. Calcd. for C_5H_{12}
Cl_2OSiPt: C, 15.71; H, 3.16; Cl, 18.55, Pt, 51.04 %.

This powder was dissolved in 10 ml of benzene containing about 200 ppm
of water. When the solution was allowed to stand overnight at room tem-
perature, fine ywllow crystals of the vinyl alcohol complex precipitated
in a 68 % yield; these crystals decomposed at 127-131° C.
Found: C, 7.91; H, 1.33; Cl, 22.77; Pt, 62.77 %. Calcd. for $C_2H_4Cl_2OPt$:
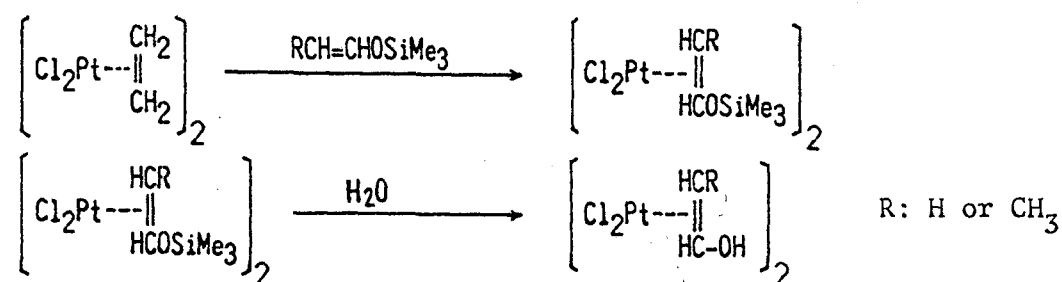C, 7.75; H, 1.30; Cl, 22.87; Pt, 62.92 %.

A similar reaction of propenyl trimethylsilyl ether gave an orange
yellow powder of $[Cl_2Pt(CH_3CH=CHOSiMe_3)]_2$ which decomposed at 118-121° C.
Found: C, 18.02; H, 3.42; Cl, 18.68 %. Calcd. for $C_3H_6Cl_2OPt$: C, 18.19;
H, 3.56; Cl, 17.90 %. The hydrolysis was carried out similarly in moist
benzene to give yellow crystals of the propenyl alcohol complex after
10 days at room temperature. The yield was 61 %. It decomposed at 118-
121° C.
Found: C, 11.28; H, 1.84; Cl, 22.37; Pt, 60.22 %. Calcd for $C_3H_6Cl_2OPt$:
C, 11.12; H, 1.87; Cl, 21.88; Pt, 60.20 %.

Results and Discussion

Indirect preparation of the vinyl and propenyl alcohol complexes.

As is shown below, 1,3-bis-(alkenyl trimethylsilyl ether)-2,4-dichloro-μ-dichlorodiplatinum was synthesized by the replacement of ethylene by alkenyl trimethylsilyl ether (c.f. chapter I), and the Si-O bond was hydrolyzed to give alkenyl alcohol complexes.

$$\left[Cl_2Pt \text{---} \parallel \begin{array}{c} CH_2 \\ CH_2 \end{array} \right]_2 \xrightarrow{\ RCH=CHOSiMe_3\ } \left[Cl_2Pt \text{---} \parallel \begin{array}{c} HCR \\ HCOSiMe_3 \end{array} \right]_2$$

$$\left[Cl_2Pt \text{---} \parallel \begin{array}{c} HCR \\ HCOSiMe_3 \end{array} \right]_2 \xrightarrow{\ H_2O\ } \left[Cl_2Pt \text{---} \parallel \begin{array}{c} HCR \\ HC\text{-}OH \end{array} \right]_2 \qquad R: \ H \ or \ CH_3$$

Since the Si-O bond of the vinyl trimethylsilyl ether complex is extremely sensitive to moisture, the vinyl alcohol complex was formed when the complex was treated with wet benzene. It was also formed when the vinyl trimethylsilyl ether complex was exposed to air (70% humidity) at room temperature for about 10 minutes.

On the decomposition of the vinyl alcohol complex with pyridine, acetaldehyde was liberated and was detected by gas chromatography.

Infrared spectra of the vinyl and propenyl alcohol complexes are shown in Fig. 1. Specific absorptions of $\nu(OH)$ and $\nu(C=C)$ are obvious and no carbonyl absorptions are found in both complexes. The detailed study on the infrared spectum of the vinyl alcohol complex is described in chapter III.
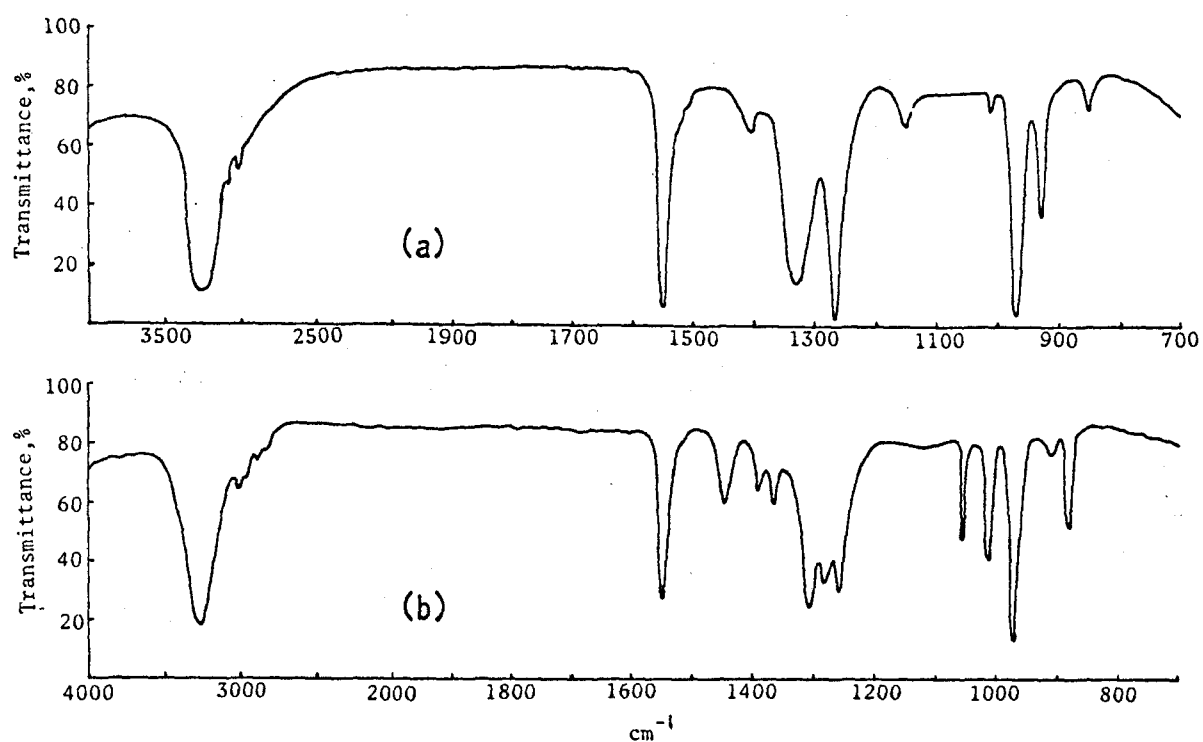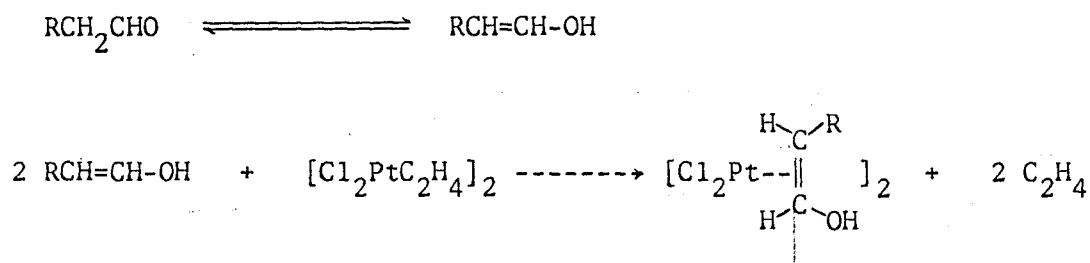
Fig. 1. Infrared spectra of (a) vinyl alcohol and (b) propenyl
alcohol coordinated to platinum(II). (Nujol mull and Hexachloro-
butadiene mull method.) Nujol and Hexachlorobutadiene peaks are
excluded.

Attempts on the direct preparation of the enol complexes.

Enol form of an aldehyde or ketone may be able to replace the ethylene of $[Cl_2PtC_2H_4]_2$ to give the enol complex.

$$RCH_2CHO \rightleftharpoons RCH=CH-OH$$

$$2\ RCH=CH-OH\ +\ [Cl_2PtC_2H_4]_2 \dashrightarrow [Cl_2Pt{-}{-}\underset{H-\overset{C}{C}-OH}{\overset{H\diagdown C \diagup R}{\|}}]_2\ +\ 2\ C_2H_4$$

To check the possibility of the reaction mentioned above, the following experiment was performed.

Acetaldehyde (the enol content is known to be less than 10^{-5}%[1]), propionaldehyde, phenylacetaldehyde, phenylacetone (the enol content 2.9 %[1]) or acetylacetone (the enol content 76.4% [1]) was added at room temperature to the ethylene complex of platinum or its toluene suspension. The mixture turned yellow and homogeneous shortly after the addition. After a few hours or more, most of the toluene was removed by evaporation and then petroleum ether was added to the mixture to precipitate the complex. The resulting yellow powder was found by infrared spectroscopy to be the unchanged ethylene complex in all cases and no enol complex was detected. When the mixture was allowed to stand for a long period of time, a side reaction, probably aldol condensation of the carbonyl compound, occurred and the platinum(II) complex decomposed gradually.

By the reasons stated in chapter I, the enol form of acetylacetone is supposed to have no ability to replace the ethylene coordinated to platinum(II) owing to the strong electron-attracting property of the carbonyl group. On the other hand, judging from the fact that trifluoroethyl vinyl ether react readily with Zeise's dimer, vinyl alcohol and propenyl alcohol probably have the ability to replace the coordinated ethylene. However, the concentration of these enols in acetaldehyde and propionaldehyde, respectively, seem to be too low to make the reaction appreciable.

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CHAPTER III

Infrared Spectroscopic Study of Enol and Enol Derivatives Coordinated
to Platinum(II) and Palladium(II)

Introduction

The vinyl alcohol complex, $[Cl_2Pt(CH_2=CHOH)]_2$, described in chapter II
does not contain organic moieties other than vinyl alcohol so that the
analysis of its infrared spectrum is relatively easy.

The double bond of coordinated olefin, in general, approaches a single
bond to some extent, as is confirmed by the shift of C=C stretching to the
lower frequency. Recently Nakamoto et al. analyzed the normal coordination
of the ethylene coordinated to platinum(II) and concluded that the force
constant of the stretching of the double bond is 6.00 mdyn/Å which is 19
% smaller than that of free ethylene.[1] It may be thought that vinyl
alcohol, as vinyl ethers, includes such resonance structure as;

$$CH_2=CH-O-H \longleftrightarrow \overset{-}{C}H_2-CH=\overset{+}{O}-H$$
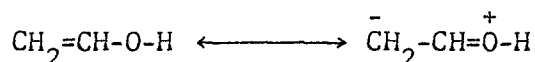
However, the contribution of such resonance form may be decreased upon
π-coordination to a metal since the double bond character of coordinated
olefin is smaller than that of free olefin.
In order to obtain the force constants of C=C and C-O stretchings of the
π-coordinated vinyl alcohol, approximate in-plane normal coordinate analysis
was carried out. It may be thereby possible to estimate whether there exist
or not the above-mentioned resonance structure and the coordination of the
oxygen atom to the metal.

Meanwhile, Nakamoto et al. also analyzed the far infrared spectra of
Zeise's dimer, $[Cl_2PtC_2H_4]_2$, and its palladium analog and assigned the
metal-ethylene stretching vibration to the absorption at 408 cm^{-1} of the
platinum complex and to that at 427 cm^{-1} of the palladium complex.[2]
In order to know the coordination power of vinyl ethers to platinum(II)
and palladium(II), we mesured the far infrared spectra of vinyl ether

complexes of the Zeise's dimer type in the range of 700-100 cm^{-1}, and com-
pared the frequencies of the absorptions, which are assignable to the
metal-olefin stretching vibrations, each other.

It has often said that the magnitude of shift upon coordination in C=C
stretching mode reflects the strength of metal-olefin bond. Free vinyl
ethers have, however, complicated two or more absorptions in the C=C
stretching region,[3] and moreover, the C=C stretching vibration of ,the
coordinated olefin, as in the case of coordinated ethylene,[1] may strongly
couple with other vibrations. Thus, the shift width of C=C stretching vibra-
tion by coordination cannot be taken to be a mesure of coordination strength.
Accordingly, the direct mesurement of metal-olefin stretching vibration as
mentioned above is desirable.

Experimental

Preparation of complexes.—— Preparation of platinum and palladium
complexes are described in chapter I and II. Platinum complex of CH_2=CHOD
was obtained in a similar method to that of the vinyl alcohol complex
mentioned in chapter II, that is, the hydrolysis of the silyl ether bond
of trimethylsilyl ether complex with a small amount of heavy water.

Spectral mesurements.—— Spectra were obtained mainly by means of the
Nujol mull technique using a Hitachi EPI-2 (4000—700 cm^{-1}), a Japan
Spectroscopic DS-402G (700— 500 cm^{-1}) and a Hitachi FIS-1 (500—100 cm^{-1})
spectrometer.

Procedure of calculation.—— It is assumed that vinyl alcohol molecule
is planer and that this plane is retained even in its coordinated state.
Vinyl alcohol has 15 (3×7-6) fundamental vibrations and of these, 11 are
in-plane vibrations and 4 are out-of-plane vibrations. In this study, only
the in-plane vibrations are examined.

It is expected that the vibrations of the vinyl alcohol molecule co-
ordinated to platinum couple extremely weakly with other vibrations such
as those due to Pt-Cl bond. Thus, the single examination of the vibration
of vinyl alcohol coordinated to a metal may be righteous.

Nakamoto et al. estimated that the C=C and C-H distances of the co-ordinated ethylene are 1.364 Å and 1.089 Å, respectively.[1] In the case of the coordinated vinyl alcohol, these values are employed. With respect to C-O and C-H distances, 1.42 Å and 0.956 Å, respectively, are used. It is estimated that all the angles around the carbons are 120° and that the angle $\angle$COH is 110°. The geometric relation between the O-H bond and the C=C double bond is unclear, and in this case it is assumed to be trans. Fig. 1 illustrates 13 internal coordinates employed for the calculation.

$r_1 = r_2 = r_3 = 1.089$ Å
$r_4 = 1.42$ Å $r_5 = 0.956$ Å $R = 1.364$ Å

$\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = \beta_3 = \beta_4 = 120°$ $b = 110°$
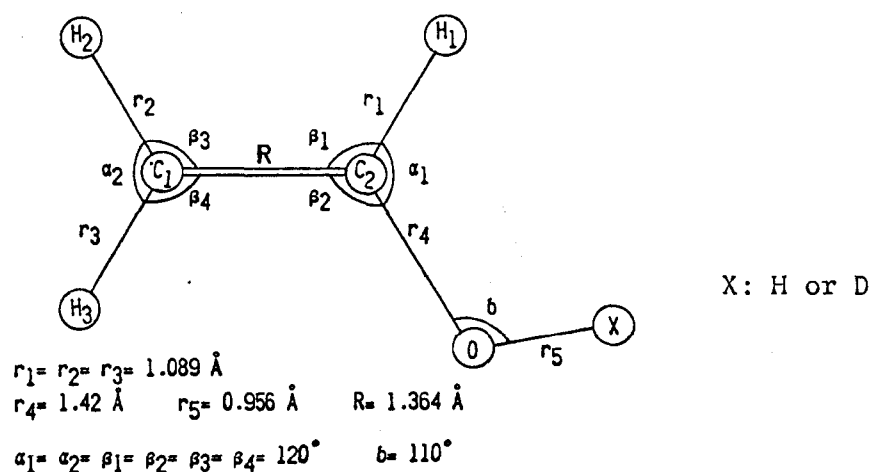
X: H or D

Fig. 1. Structure and internal coordinates of coordinated vinyl alcohol.

Table I lists the symmetry coordinate used in the present work.

The F matrix elements for the in-plane vibrations were expressed in terms of the Urey-Bradley force field.[4] A matrix seqular equation of the form | GF-Eλ |=0 [5] was constructed and solved using a NEAC 2203 computer.

Table I. Symmetry coordinates for the in-plane vibrations of the
          coordinated vinyl alcohol.

Symmetry coordinate	Vibrational mode [a]
$S_1 = \Delta r_1$	$\nu(CH)$
$S_2 = 1/\sqrt{2}(\Delta r_2 - \Delta r_3)$	$\nu_a(CH_2)$
$S_3 = 1/\sqrt{2}(\Delta r_2 + \Delta r_3)$	$\nu_s(CH_2)$
$S_4 = \Delta r_4$	$\nu(CO)$
$S_5 = \Delta r_5$	$\nu(OH)$
$S_6 = \Delta R$	$\nu(C=C)$
$S_7 = 1/\sqrt{6}(2\Delta\beta_2 - \Delta\alpha_1 - \Delta\beta_1)$	$\delta(CCO)$
$S_8 = 1/\sqrt{2}(\Delta\beta_1 - \Delta\alpha_1)$	$\delta(CH)$
$S_9 = 1/\sqrt{6}(2\Delta\alpha_2 - \Delta\beta_3 - \Delta\beta_4)$	$\delta(CH_2)$
$S_{10} = 1/\sqrt{2}(\Delta\beta_3 - \Delta\beta_4)$	$r(CH_2)$
$S_{11} = \Delta b$	$\delta(OH)$
$S_{12} = 1/\sqrt{3}(\Delta\alpha_1 + \Delta\beta_1 + \Delta\beta_2)$	Redundant
$S_{13} = 1/\sqrt{3}(\Delta\alpha_2 + \Delta\beta_3 + \Delta\beta_4)$	Redundant

a) ν_s and ν_a, symmetric and asymmetric stretching; δ, bending;
r, rocking.

Results and Discussion

A. Normal coordinate analysis of coordinated vinyl alcohol.

The best sets of force constants for the coordinated vinyl alcohol
are listed in Table II.

Table III and IV compares the observed frequencies with those cal-
culated for coordinated vinyl alcohol and its deuterio analog by using
those sets of force constants.

Table II. Force constants for vinyl alcohol coordinated to Pt(II). (mdyn/Å)

Stretching	K(C-H)	4.63
	K(C=C)	5.85
	K(C-O)	5.00
	K(O-H)	6.00
Bending	H(HCH)	0.37
	H(HCC)	0.15
	H(CCO)	0.32
	H(HCO)	0.22
	H(COX)	0.47
Repulsive	F(H⋯H)	0.00
	F(H⋯C)	0.30
	F(C⋯O)	0.70
	F(H⋯O)	1.00
	F(C⋯X)	0.50

Table III. Vibrations of coordinated vinyl alcohol; CH_2=CH-OH.

Frequency, cm⁻¹		Assignment
Obsd	Calcd	(PED %)
3260 s	3345	ν(OH)(100)
3080 vw	3140	ν(CH)(99)
3020 vw	3019	$\nu_a(CH_2)$(100)
	2916	$\nu_s(CH_2)$(99)
1550 s	1567	ν(C=C)(45), δ(CH)(26), $\delta(CH_2)$(12)
1405 w	1411	$\delta(CH_2)$(65), δ(CH)(20), δ(OH)(11)
1330 s	1340	δ(OH)(48), ν(CO)(34),
1270 vs	1264	δ(CH)(43), ν(CO)(21), δ(OH)(13)
1145 w	1099	ν(C=C)(33), ν(CO)(27)
850 w	834	$r(CH_2)$(78)
497 s	495	δ(CCO)(82)

Frequencies not calculated

1013 vw	⎫
968 vs	⎬ Out-of-plane bending
934 m	⎭

-22-

Table IV. Vibrations of coordinated vinyl alcohol; CH_2=CH-OD.

Frequency, cm^{-1}		Assignment b)
Obsd a)	Calcd	(PED %)
3078 w	3141	ν(CH)(99)
3015 w	3019	ν_a(CH$_2$)(100)
	2916	ν_s(CH$_2$)(99)
2420 m	2436	ν(OD)(100)
1527 vs	1551	ν(C=C)(47), δ(CH)(26), δ(CH$_2$)(15)
1405 w	1401	δ(CH$_2$)(63), δ(CH)(33)
1270 vs	1284	ν(CO)(60), δ(CH)(14)
1220 s	1169	ν(C=C)(24), δ(CH)(23), ν(CO)(18)
940 m	919	δ(OD)(76)
850 w	831	r(CH$_2$)(73)
490 s	490	δ(CCO)(82)

Frequencies not calculated

1013 w
985 s
973 sh
800 vw
} Out-of-plane bending

a) vs, very strong; s, strong; m, medium; w,-weak; vw, very weak; sh, shoulder.   b) ν, stretching; δ, bending; r, rocking; s, symmetric; and a, asymmetric.

The product rule for isotopic frequencies[6] works extremely well in this case and thus it supports the righteousness of the assignment made.

Table II shows that the force constant of C=C stretching is slightly smaller than that of the coordinated ethylene (6.00 mdyn/Å), and that the force constant of its C-O stretching is relatively larger than that of methanol (2.43 mdyn/Å)[7] or diethyl ether (4.38 mdyn/Å).[8] These figures reasonably imply that such resonance structure as CH_2=CH-OH ⟷ $\bar{C}H_2$-CH=$\overset{+}{O}$H exists to relatively large extent, and simultaneously that the lone pair electrons of the oxygen do not interact with platinum.

B. Metal-olefin stretching vibratios.

Fig. 2 shows far infrared spectra of the complexes of the type $[Cl_2M\ Olefin]_2$ in which M represents platinum or palladium.
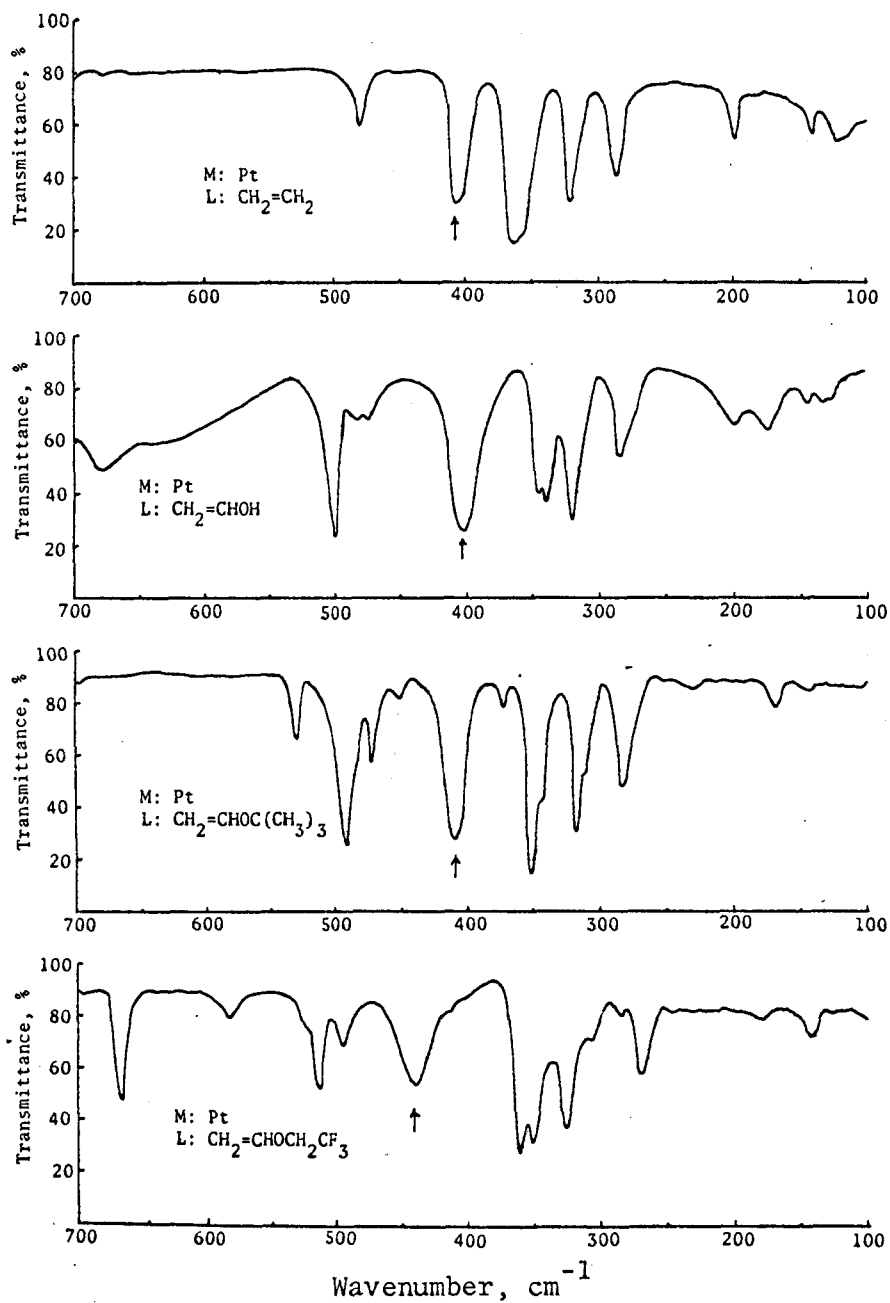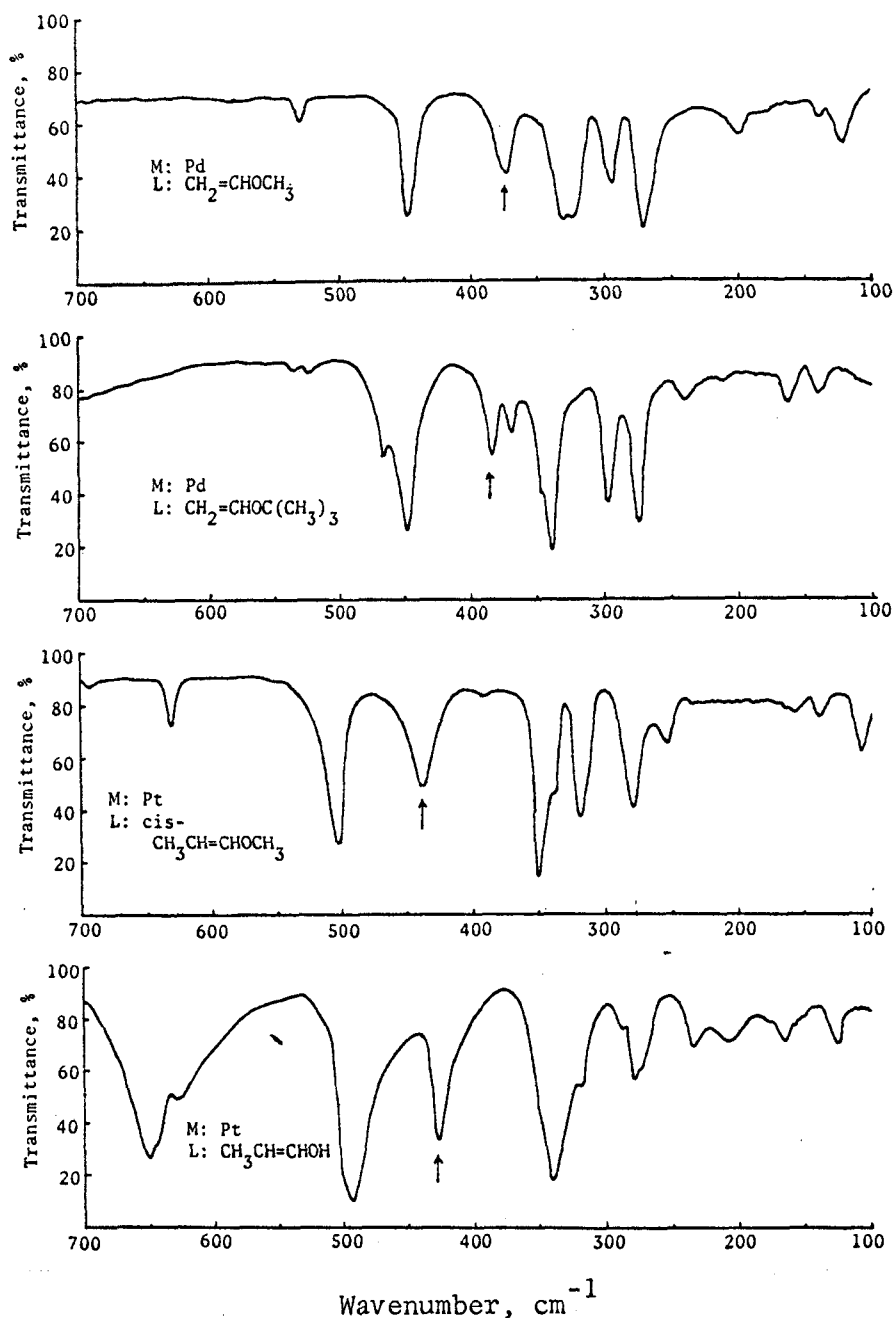

Fig. 2. Infrared spectra of $[Cl_2M\ L]_2$

Fig. 2 (continued). Infrared spectra of $[Cl_2M \; L]_2$.

With respect to the ethylene complexes with platinum and palladium, Nakamoto et al. reported that the metal-ethylene stretching vibrations are well isolated and thus their frequencies by themselves reflect the strength of coordination.[2] The infrared spectra of many platinum and

palladium complexes of vinyl ethers, as is shown by the figures, satisfactorily correspond to that of the ethylene complexes at the low frequency region, and the absorption with an arrow sign can be assigned to the stretching frequency between metal and olefin. Although this absorption is not so isolated as in the case of ethylene, it may be regarded as the semi-quantitative measure of the coordination strength of vinyl ethers. Table V lists the stretching vibrations of metal-olefin bonds thus obtained.

Table V. Metal-olefin stretching frequencies of $[Cl_2M\ Olefin]_2$. (M= Pt,Pd)

Olefin	Metal	
	Pt	Pd
$CH_2=CH_2$	408	427 cm^{-1}
$CH_2=CHOCH_3$	(410 ?)	376
$CH_2=CHOC(CH_3)_3$	408	384
$CH_2=CHOCH_2CF_3$	440	–
$CH_2=CHOH$	402	–
cis-$CH_3CH=CHOCH_3$	438	404
cis-$CH_3CH=CHOSiMe_3$	430	–
$CH_3CH=CHOH$	427	–

This table introduces the following conclusions with respect to the coordination strength of vinyl ethers:

a) The coordination strength of vinyl ethers to palladium is far weaker than that to platinum. If they were comparable in magnitude, the absorption of the palladium complex should be at about 20 cm^{-1} higher than that of platinum complex due to the mass effect.

b) The coordination strength of vinyl alcohol with platinum is almost equal to that of ethylene.

c) Propenyl ethers are fairly stronger than the corresponding vinyl

ethers in the coordination strength.

 d) 2,2,2-Trifluoroethyl vinyl ether is much larger than alkyl vinyl ethers in the coordination strength.

 The conclusions c and d imply a U-shaped relationship between the electron-releasing property of substituents and the coordination.strength in the coordination of vinyl ethers. The methyl group at the β position may consequently increase the coordination strength by its electron releasing property, in spite of the fact that it may sterically interferes the coordination.

 Okamura et al. calculated the energy levels of methyl vinyl ether and methyl propenyl ether by means of the extended Hükel method, and suggested that the energy levels of the lowest vacant orbital and the highest filled orbital of methyl propenyl ether are respectively higher than those of methyl vinyl ether owing to the β methyl group.[9] In the coordination of propenyl ethers, therefore, the σ-donation from the olefin to the metal may play a predominant role.

 The low cationic polymerizability of 2,2,2-trifluoroethyl vinyl ether is well known[10] and is explained by the electron-withdrawing effect of fluorine atoms. The energy levels of the lowest vacant orbital and the highest filled orbital of trifluoroethyl vinyl ether are probably lower than those of alkyl vinyl ethers due to the inductive effect of fluorine. It is supposed that these energy level lowering by fluorine is convenient for the coordination by favoring the back donation from the metal to the olefin.

 However, d-orbital energy levels of platinum(II) or palladium(II), which are employed for the coordination with olefin, are not determined so that the relationship between the energy levels of these ligands and metals cannot be shown clearly.

Acknowledgment

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CHAPTER IV

Cis-trans Isomerization of Internal Olefins Coordinated to Platinum(II)

and Palladium(II)

Introduction

Double bond migration of olefin in the presence of catalytic amounts of a transition metal complex has been studied extensively.[1)-3)] This reaction, postulated to proceed via a metal-olefin complex followed by either the metal hydride addition to the double bond or the formation of π-allyl metal hydride, necessarily accompanies cis-trans interconversion of the olefin. However, only a few studies have been made about cis-trans isomerization of the olefin which is coordinated to a transition metal.

Jonassen and Kirsh investigated the infrared spectra of $[Cl_2Pt\ L]_2$ (L= cis- and trans-2-butene), concluding that no cis-trans isomerization of 2-butene takes place.[4)] Joy and Orchin obtained the same result with L= 4-methyl-2-pentene; they also found that the 4-methyl-cis-2-pentene complex is about twice as stable as the trans isomer.[5)]

In this chapter, we wish to describe the first example of cis-trans isomerization of internal olefin coordinated to transition metals. Olefin complexes examined are Zeise's dimer type, $[Cl_2Pt\ Olefin]_2$, where olefins are propenyl methyl ether, propenyl trimethylsilyl ether, 1,2-dimethoxy-ethylene, β-methylstyrene and 2-butene. Palladium complexes, $[Cl_2Pd\ Olefin]_2$ in which olefins are propenyl methyl ether and 1,2-dimethoxyethylene, were also studied.

Experimental

Solvents.—— Toluene and petroleum ether were purified by the ordinary method and dried by refluxing over sodium for several days. They were freshly distilled before use.

Preparation of olefins.—— Propenyl methyl ether was prepared by the pyrolysis of propionaldehydedimethylacetal.[6] Cis and trans isomer were separated by fractional distillation through a spinning band column of 1.5 m long and confirmed to be pure by glc analysis (Tricresyl phosphate, 1.5 m). bp cis 45.0°C, trans 48.0°C   NMR coupling constant, J_{cis} = 6.5, J_{trans} = 12.5 cps.

Propenyl trimethylsilyl ether was prepared according to Petrov's method[7] from acrolein and trimethylsilane. Cis and trans isomer were separated by fractional distillation. The cis isomer fraction contained about 10% of hexamethyldisiloxane as an impurity. The trans isomer was found to be pure by glc (Silicon DC 550, 1.5 m).   bp cis 97°C, trans 104°C   NMR coupling constant, J_{cis} = 6.0, J_{trans} = 12.0 cps.

1,2-Dimethoxyethylene was prepared, as described by Baganz et al.,[8] by dechlorination of 1,2-dichloro-1,2-dimethoxyethane with magnesium. Cis and trans isomer were separated by fractional distillation. Baganz and his cowarkers measured the dipole moment of 1,2-diethoxyethylene and obtained the following result; cis 2.57 D (bp 134.7°C), trans 1.82 D (bp 132.4°C).[8] We measured the dipole moment of 1,2-dimethoxyethylene in benzene and obtained the value 2.00 D for the higher boiling (97°C) isomer and 1.83 D for the lower boiling (93°C) one. The data of dipole moment, together with the result of Baganz and his coworkers for diethoxyethylene, proved that the higher boiling isomer is cis and the lower boiling one is trans.

Cis-β-methylstyrene was prepared according to Foltz and Witkop by stereospecific reduction of phenylmethylacetylene.[9] bp 47-48°C/10.5 mmHg, pure gaschromatographycally (Silicon DC 550, 1.5m)

Trans-β-methylstyrene was prepared by dehydration of phenylethylcarbinol with Al_2O_3 at 350°C and fractionally distilled. bp 68.5-69°C/18 mmHg, gaschromatographycally pure (Silicon DC 550, 1.5 m).

Syntheses of [Cl_2Pt Olefin]$_2$ and [Cl_2Pd Olefin]$_2$.—— Detail of the syntheses of platinum and palladium complexes with vinyl ether derivatives[11] are described in chapter I. Platinum complexes of cis- and trans-2-butene[4]

and cis- and trans-β-methylstyrene were prepared in a similar way.

Cis-trans isomerization.—— The isomerization of olefin in the co-
ordinated state was observed by means of infrared spectroscopy. The spectra
were recorded using the nujol mull or potassium bromide pellet technique
with a Hitachi model EPI-2 or a Japan Spectroscopic DS-402G spectrophoto-
meter.

.In chapter I, it was shown that the platinum complex of propenyl tri-
methylsilyl ether can be prepared at room temperature and that the reaction
mixture is homogeneous.[12] The change of cis/trans ratio of propenyl trimethyl-
silyl ether in the presence of the complex was followed by gaschromatography
as described below.   Fifty mg of $[Cl_2PtC_2H_4]_2$ was suspended in 4ml of
toluene and the temperature of the suspension was kept at 50°C. Propenyl
trimethylsilyl ether (1 ml) was then added and a small amount of the re-
action mixture was withdrawn periodically to be analyzed for the cis/trans
ratio by gaschromatography (Silicon DC 550, 1.5 m, 85°).

Decomposition of the complexes with pyridine.—— Platinum and palladium
complexes of propenyl methyl ether can be decomposed with pyridine, liberat-
ing the original olefin without forming any by-product.
For example, to 200 mg of $[Cl_2Pt(CH_3CH=CH-OCH_3)]_2$, was added 1 ml of toluene
containing caluculated amount of pyridine. The complex dissolved immediate-
ly and within 1 hour there precipitated white crystals which appered to be
$[PtPy_4]Cl_2$. The supernatant solution was analyzed by gaschromatography
(Tricresyl phosphate, 1.5 m, 40°C) to determine the cis/trans ratio of
the liberated propenyl methyl ether.

Results

Complexes of propenyl methyl ether.—— The infrared spectra of the
propenyl methyl ether-Pt(II) complex are shown in Fig. 1. The spectrum
of the freshly prepared complex of trans-propenyl methyl ether already
contained the absorptions which are specific to cis-propenyl methyl ether
complex (Fig.1-a). A part of the complex was allowed to stand under argon
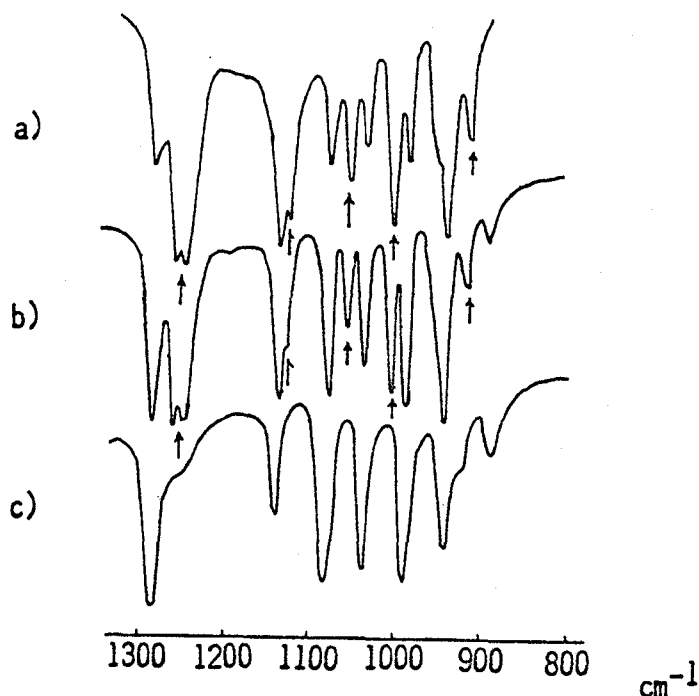at 70°C for 48 hours. The other was dissolved in toluene and kept at 70°C

Fig.1. ir spectra of [Cl$_2$ Pt (CH$_3$CH=CHOCH$_3$)]$_2$

a) Complex prepared from trans CH$_3$CH=CHOCH$_3$

b) Sample isomerized in a solid state

c) Sample isomerized in a soln.
   Complex prepared from cis CH$_3$CH=CHOCH$_3$

overnight. The spectrum of the latter became equal to the spectrum obtained from cis isomer (Fig. 1-c) while that of the former showed that the isomerization was incomplete (Fig. 1-b). These facts indicate that the isomerization is easier in a solution rather than in a solid state.

When the propenyl methyl ether was displaced with pyridine from the complex which showed the spectrum of Fig. 1-c, propenyl methyl ether of cis/trans ratio=3.1 was yielded. As is discussed afterwards, the cis/trans ratio of olefin in the decomposition product does not necessarily represent the cis/trans ratio in the complex. So far as one judged from infrared spectra, the trans isomer completely changed to the cis isomer in the complex.

The infrared spectra of palladium(II) complexes with propenyl methyl

ether were similar to the spectrum shown in Fig. 1-c, independent of the olefin isomers used. This indicates that propenyl methyl ether is apt to have the cis configuration in palladium complex as well as in platinum complex and the rate of isomerization appers to be much faster in palladium complex than in platinum complex.

The palladium complex prepared from trns-propenyl methyl ether was decomposed with pyridine and the cis/trans ratio of the liberated propenyl methyl ether was found to be about 45. In case of palladium complex, the cis/trans ratio in the decomposition product seems to be nearly equal to the cis/trans ratio in the complex.

When the propenyl methyl ether complex with platinum or palladium was decomposed with pyridine, only propenyl methyl ether was liberated and no allyl methyl ether was detected. We tried to synthesize allyl methyl ether complex of platinum by the reaction of $[Cl_2PtC_2H_4]_2$ and allyl methyl ether. Although the reaction did occur, isolation of the complex was unsuccessful owing to instability of the complex.

From the facts described above, it was concluded that propenyl methyl ether isomerizes from trans to cis in the coordinated state without formation of allyl methyl ether.

Platinum(II) complexes of propenyl trimethylsilyl ether.—— Complexes obtained from cis- and trans-propenyl trimethylsilyl ether gave identical infrared spectra. The 1300-900 cm^{-1} range of the spectra quite resembles that of cis-propenyl methyl ether complex, except the peak at 1255 cm^{-1} which is attributed to $-Si(CH_3)_3$ group, indicating that propenyl trimethylsilyl ether also adopts the cis form when coordinated to platinum(II).

In Fig. 2, the change of cis/trans ratio of propenyl trimethylsilyl ether with time in the presence of $[Cl_2PtC_2H_4]_2$ is shown. At point A in the figure, some quantity of trans isomer was added to the mixture to disturb the equilibrium but in less than 1 hour the cis/trans ratio again attained the constant value of about 2.8. The deviation of cis/trans ratio in the reaction mixture from that in the complex is discussed later.
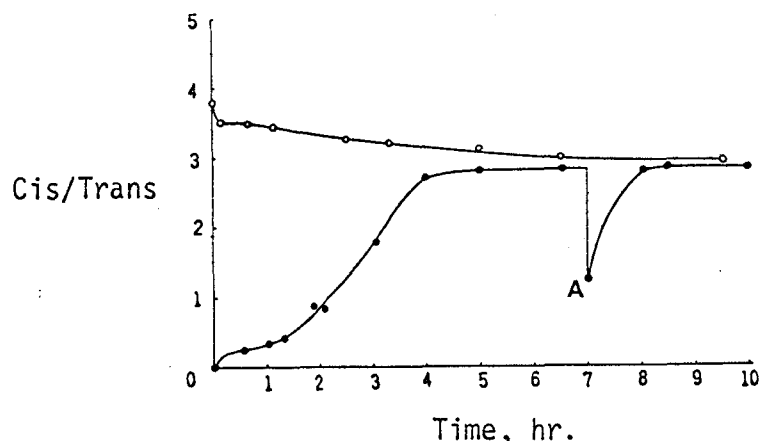
Fig. 2. The change of cis/trans ratio of $CH_3CH=CHOSi(CH_3)_3$ catalyzed by $[Cl_2PtC_2H_4]_2$ in toluene at 50°C.

1,2-Dimethoxyethylene complexes.—— C=C stretching frequency on the infrared spectra of 1,2-dimethoxyethylene which is coordinated to platinum(II) is 1562 cm^{-1} for the cis isomer and 1535 cm^{-1} for the trans isomer. The trans isomer complex has characteristic absorptions at 928 cm^{-1} (medium) and 880 cm^{-1} (weak) although other absorptions in 4000-650 cm^{-1} region are almost equal to those of the cis isomer complex. The isomerization was best observed by the change of peak intensities at 1562 cm^{-1} and 1535 cm^{-1}. The change of optical density ratio of these bands with time is shown in Fig. 3.
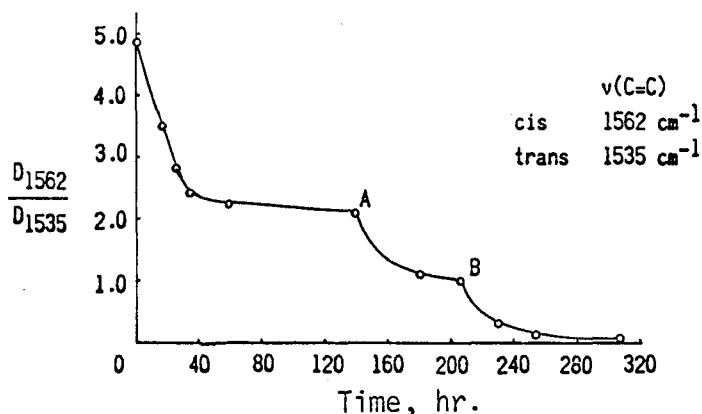

Fig. 3. The change of D_{1562}/D_{1535} on the IR spectra of $[Cl_2Pt(CH_3OCH=CHOCH_3)]_2$

The freshly prepared cis-1,2-dimethoxyethylene complex already contained the trans isomer in about 20% (see Fig.3 time=0). The content of the trans isomer increased rapidly at first stage but became constant after about 50 hours. At point A, the nujol mulled sample was exposed to air for 5 minutes and the change started again. At point B the sample was again exposed to air for 10 minutes. After 300 hours, only a strong peak at 1535 cm^{-1} was observed and the band at 1562 cm^{-1} disappeared. The acceleration of the change at point A and B is, as is discussed afterwards, supposed to be caused by moisture in air, which acted as a catalyst of the isomerization. The saturation of the change (Fig. 3) may be attributed to limited diffusion of the water since the spectra were observed using a solid state sample as a nujol mull.

Palladium complexes of 1,2-dimethoxyethylene were prepared from the cis and trans isomers and both showed the same infrared spectra. Comparing the spectra with that of the platinum complexes, it was infered that 1,2-dimethoxyethylene takes trans form also in palladium complex.

On the bases of these facts, it was concluded that 1,2-dimethoxyethylene isomerizes from cis to trans form when coordinated to platinum(II) or palladium(II).


Discussion

Cis-trans isomerization of olefins coordinated to platinum(II).—— The most accepted mechanism for the double bond migration of olefins catalyzed by transition metal complexes is addition-elimination of metal hydride to the double bond.[2)3)] The double bond migration reaction of 1-hexene in alcohol or acetic acid in the presence of $[Cl_2PtC_2H_4]_2$ was studied by Harrod and Chalk.[13)] The alcohol or acetic acid was postulated to be the source of hydride. Chatt and his coworkers investigated thermal decomposition of the complex trans-$[Pt(Et)Br(PEt_3)_2]$ and suggested the reversible reaction[14)]

$$Pt(C_2H_5)Br(PEt_3)_2 \rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} -\text{-PtHBr}(PEt_3)_2$$

In the present work the cis-trans isomerization of the coordinated olefins is also explicable by the addition-elimination mechanism of platinum hydride.

$$\quad\quad\quad (1)$$

(I)   (II)   (III)
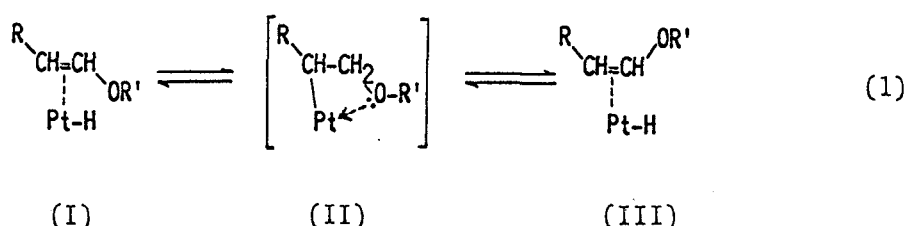
As is shown in Fig. 3 the rate of isomerization increased when the sample was exposed to air. This is probably caused by water in air, which reacted as the source of hydride. The role of water as the source of hydride is known in the preparation of cobalt cyanide hydrides.[15)16)] In the present case, the formation of platinum hydride from a trace amount of water in the solvent or in the air would proceed by the same mechanism as that of rhodium hydride from acidic proton.[3)]

$$Pt^{II} \;+\; H^{+} \;\rightleftharpoons\; Pt^{IV}\!-\!H \quad\quad\quad (2)$$
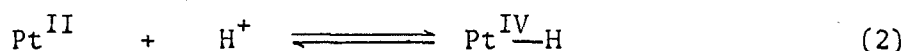
As we have seen, coordinated β-methylstyrene and 2-butene do not undergo the cis-trans isomerization whereas coordinated propenyl ethers and 1,2-dimethoxyethylene isomerize very easily. This can be interpreted by two reasons. First, the double bond of propenyl ethers and 1,2-dimethoxyethylene are supposed to be more electron rich than that of 2-butene and β-methylstyrene because of the conjugation with the lone-pair electrons on the oxygen atom. Accordingly, the platinum atom coordinated by propenyl ethers or 1,2-dimethoxyethylene should have more electron to reduce the proton (eq.2) than the platinum coordinated by 2-butene or β-methylstyrene. Secondly, a transition state such as (II) in eq. 1 would be stabilized by weak coordination of oxygen to fill up the coordination sites around the metal.

It has been known that cis olefin can coordinate more easily than the corresponding trans isomer[5)17)] probably because steric interactions between olefin and metal is greater in the trans form. In a free state,

however, a trans olefin is thermodynamically more stable than the cis
isomer although the reverse is true for some dihalogenoethylenes.[18]
Consequently, which of (I) and (III) in eq. 1 will be a predominant prod-
uct is governed by relative importance of these two factors . In case of
propenyl ethers, a steric interaction between propenyl ether and the metal
seems to be the major factor, favoring cis form in the isomerization. On
the other hand, 1,2-dimethoxyethylene isomerizes from cis to trans proba-
bly because the dipole-dipole repulsion between two methoxy groups is
severe in its cis form.

In the isomerization of propenyl methyl ether, allyl methyl ether was
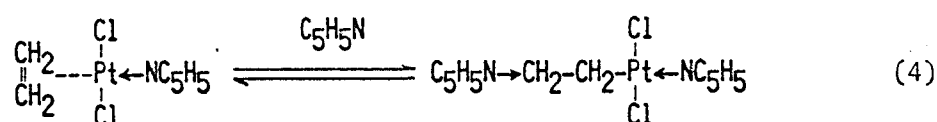not formed. This may be attributed to the instability of allyl methyl ether
complex of platinum.

Cis-trans isomerization of olefins coordinated to palladium(II).——
Isomerization of propenyl methyl ether and 1,2-dimethoxyethylene had been
accomplished before the infrared spectra of the palladium complexes were
observed. Since spectra were recorded immediately after the preparation
of the complexes, the isomerization must be fairly rapid.

The potential required to oxidize palladium(II) to palladium(IV) is so
high that hydride formation according to the reaction similar to eq. 2 is
unlikely. On the other hand, it has been known that Pd-Cl bond is reactive
enough to add to butadiene[19] and allen.[20] Considering these facts, we
suggest the following mechanism for the cis-trans isomerism of propenyl
methyl ether and 1,2-dimethoxyethylene on palladium(II).
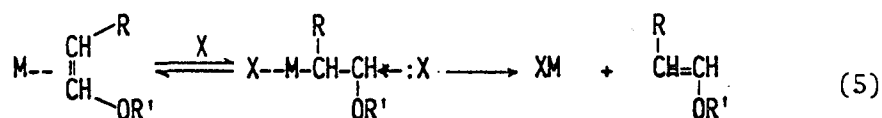

$$(3)$$
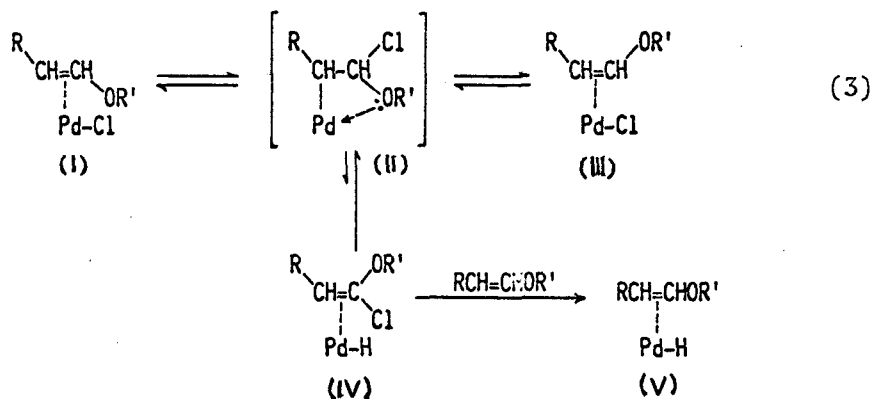
The possibility of forming hydride complex such as (V) was excluded by elemental analysis of the complex. Also, the complex like (IV) was not found in infrared spectra. Therefore, the isomerization would proceed via (I)—(II)—(III)

The cis/trans ratio of olefins in the presence of a catalytic amount of complexes.—— Recently, Orchin and his coworkers suggested that displacement of coordinated ethylene by pyridine may proceed by prior $\pi{\rightarrow}\sigma$ rearrangement.[21]

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}\text{---}\overset{\overset{\displaystyle Cl}{|}}{Pt}\underset{\underset{\displaystyle Cl}{|}}{\leftarrow}NC_5H_5 \quad \underset{\xrightleftharpoons{\hspace{1.5cm}}}{\overset{\displaystyle C_5H_5N}{}} \quad C_5H_5N{\rightarrow}CH_2\text{-}CH_2\text{-}\overset{\overset{\displaystyle Cl}{|}}{Pt}\underset{\underset{\displaystyle Cl}{|}}{\leftarrow}NC_5H_5 \qquad (4)$$

In the present work the isomerization of the coordinated olefin was almost complete so far as one judges from infrared spectra. Whereas decomposition of the propenyl methyl ether complex of platinum with pyridine gave free propenyl methyl ether of the cis/trans ratio=3.1. Futhermore, the cis/trans ratio of propenyl trimethylsilyl ether in the solution in the presence of the platinum complex reached a constant value of about 2.8. These phenomena will be explicable if a σ-bonded state analogous to eq. 4 is assumed as an intermediate of olefin displacement either by pyridine or by other propenyl ether molecule.

$$M\text{--}\begin{array}{c} CH \\ \| \\ CH \end{array}\!\!\begin{array}{c} {\nearrow}R \\ \\ {\searrow}OR' \end{array} \quad \underset{\xrightleftharpoons{\hspace{0.8cm}}}{\overset{\displaystyle X}{}} \quad X\text{--}M\text{-}CH\text{-}\overset{\overset{\displaystyle R}{|}}{CH}\underset{\underset{\displaystyle OR'}{}}{\leftarrow}:X \xrightarrow{\hspace{1cm}} XM \;+\; \overset{\overset{\displaystyle R}{|}}{CH}\underset{\underset{\displaystyle OR'}{|}}{=CH} \qquad (5)$$

X: pyridine(N) or olefin (O)

If the olefin molecule which is about to leave the metal, spend enough time on the σ complex state to allow rotation around the C-C bond, the cis/trans ratio of the liberated olefin will be controlled by the conformation of the σ complex.

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SUMMARY

Acetaldehyde is a potential starting monomer for the preparation of
poly(vinyl alcohol) so long as one judges from its energy level relation-
ships. The present work has been performed to find out some clue as to
the possibility of enolization-polymerization of aldehydes.

Vinyl ethers and their derivatives are regarded as enol derivatives;
the preparation of their complexes with platinum(II) and palladium(II) are
described in chapter I. In addition, it was shown that coordinated vinyl
ether reacts readily with hydroxy ion, in the same way as the Wacker Process,
to produce acetic ester.

In chapter II, synthesis of platinum(II) complexes with enol itself
(vinyl alcohol and propenyl alcohol) is described. Attempt has been made
to realize the enolization-coordination of aldehydes or ketones but so far
unsuccessful.

The enol and enol derivative complexes of platinum(II) or palladium(II)
thus obtained were studied by means of infrared spectroscopy in chapter III,
and the following conclusions were deduced:
a) Coordinated vinyl alcohol includes such a resonance form as
   $CH_2=CH-OH \longleftrightarrow \bar{C}H_2-CH=\overset{+}{O}H$ to a relatively large extent.
b) Vinyl alcohol coordinates with platinum(II) with almost the equal
   strength to that of ethylene.
c) Platinum(II) coordinates with vinyl ethers much more strongly than
   palladium(II) does.
d) Propenyl ethers are far stronger than the corresponding vinyl ethers in the
   coordination strength although the β-methyl group may interfere sterically
   the coordination.
e) 2,2,2-trifluoroethyl vinyl ether has much stronger coordination power
   than alkyl vinyl ethers.

In chapter IV, we describe the discovery that propenyl ethers and 1,2-
dimethoxyethylene isomerize readily in the coordinated state. Propenyl
ethers were found to isomerize from trans to cis in contrast with the
observation that 1,2-dimethoxyethylene isomerize from cis to trans. It was

confirmed that 2-butene and β-methylstyrene do not isomerize at all under the same condition used. A transition state was suggested, in which the oxygen atom weakly coordinates to metal and π-coordinated vinyl ether. derivatives undergo conversion into a σ-bonded structure.

Thus, useful informations on enol and enol derivatives in the coordinated state have been obtained.