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

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The infrared spectra of $[Cl_2M\ Olefin]_2$ (olefin = vinyl alcohol, vinyl ethers, and their derivatives, M = Pt and Pd) have been studied in the 4000—100 cm^{-1} frequency region. A normal coordinate analysis of the coordinated vinyl alcohol indicated that the lone-pair electrons of oxygen conjugated with π-electrons of the double bond to some extent, even in the coordinated state. The coordination strengths of vinyl alcohol, vinyl ethers, and their derivatives have been examined by comparing the metal-olefin streching vibrations.

The synthesis of the vinyl alcohol complex, $[Cl_2Pt(CH_2{=}CHOH)]_2$, has been previously reported.[1] It does not contain organic moieties other than vinyl alcohol, so 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 the C=C stretching to the lower frequency. Nakamoto and Grogan analyzed the normal coordinate of the ethylene coordinated to platinum(II) and concluded that the force constant of the stretching of the

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[1] Y. Wakatsuki, S. Nozakura, and S. Murahashi, This Bulletin, **42**, 273 (1969).

double bond is 6.00 mdyn/Å, a value which is 19% smaller than that of free ethylene.[2] It may be thought that vinyl alcohol, like vinyl ethers, includes such a resonance structure as: $CH_2{=}CH{-}OH \longleftrightarrow \overset{-}{C}H_2{-}CH{=}\overset{+}{O}H$. However, the contribution of such a resonance form may be decreased upon 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 the C=C and C–O stretchings of the π-coordinated vinyl alcohol, the approximate in-plane normal coordinate analysis of the coordinated vinyl alcohol was carried out. It seemed that it might thereby be possible to determine whether or not the abovementioned resonance structures really exist and the coordination of the oxygen atom to the metal.

Nakamoto and Grogan analyzed the far-infrared spectra of Zeise's dimer, $[Cl_2Pt\ C_2H_4]_2$, and its palladium analog; they assigned the metal-ethylene stretching vibration to the absorption at 408 cm^{-1} of the Pt complex and to that at 427 cm^{-1} of the Pd complex.[3] In order to ascertain the coordination power of vinyl ethers to Pt(II) and Pd(II), we measured the far-infrared spectra of vinyl ether complexes of the Zeise dimer type in the range of 700—100 cm^{-1}, and compared the frequencies of the absorptions which are assignable to the metal-olefin stretching vibrations with each other. It has often been said that the magnitude of the shift upon coordination in the C=C stretching mode reflects the strength of the metal-olefin bond. Free vinyl ethers have, however, been found to complicate two or more absorptions in the C=C stretching region;[4] moreover, the C=C stretching vibration of the coordinated olefin may strongly couple with other vibrations, as in the case of the coordinated ethylene.[2] Thus, the shift of the C=C stretching vibration upon coordination cannot be taken as a measure of the coordination power. Accordingly, the direct measurement of the metal-olefin stretching vibration, described above, is desirable.

Experimental

The Preparation of Complexes. The preparation of Pt(II) and Pd(II) complexes with vinyl ethers and their derivativs has been described in a preceding paper.[5] Vinyl alcohol and propenyl alcohol complexes with Pt(II) were synthesized as has been described in another previous paper.[1] The platinum complex of $CH_2{=}CH{-}OD$ was obtained in a method similar to that used for the vinyl alcohol complex, that is, the hydrolysis of the silyl ether bond of the $CH_2{=}CH{-}OSiMe_3$ complex with a small amoun of heavy water.

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

Procedure of Calculatin. It is assumed that the vinyl alcohol molecule is planar and that this plane is retained even in its coordinated state. Vinyl alcohol has 15 ($3\times7-6$) fundamental vibrations; of these, 11 are in-plane vibrations and 4 are out-of-plan vibrations. In this study, only the in-plane vibrations are examined.

It is expected that the vibrations of the vinyl alcohol molecule coordinated to a metal couple extremely weakly with other vibrations such as those due to the Pt–Cl bond. Thus, an examination of only the vibration of the vinyl alcohol coordinated to a metal is permissible.

Nakamoto *et al.* estimated that the C=C and C–H distances of the coordinated ethylene are 1.364 and 1.089 Å respectively.[2] In the case of the coordinated vinyl alcohol, these values are employed. With respect to the C–O an O–H distances, the values of 1.42 and 0.956 Å respectively are used. It is estimated that all the angles around the carbons are 120°, and that the COH angle is 110°. The conformation around the C–O bond is unclear; in this case, a trans planar conformation is assumed. Figure 1 illustrates the 13 internal coordinates employed for the calculation.

Table 1. Symmetry coordinates for the in-plane vibrations of the coordinated vinyl alcohol

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

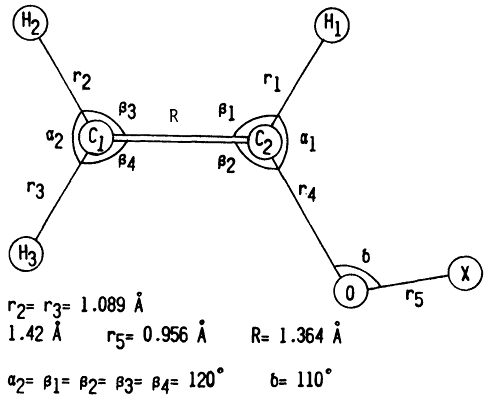

Fig. 1. Structure and internal coordinates of coordinated vinyl alcohol.

Table 1 lists the symmetry coordinates used in the present work.

The ***F*** matrix elements for the in-plane vibrations were expressed in terms of the Urey-Bradley force field.[6] A matrix secular equation of the $|GF-E\lambda|=0$[7] form was constrtcued and solved by using a NEAC 2203 computer.

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[2] M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, **88**, 5454 (1966).

[3] M. J. Grogan and K. Nakamoto, *ibid.*, **90**, 918 (1968).

[4] Y. Mikawa, This Bulletin, **29**, 110 (1956).

[5] Y. Wakatsuki, S. Nozakura, and S. Murahashi, *ibid.*, to be submitted.

[6] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

[7] E. B. Wilson, *ibid.*, **7**, 1047 (1939); **9**, 76 (1941).

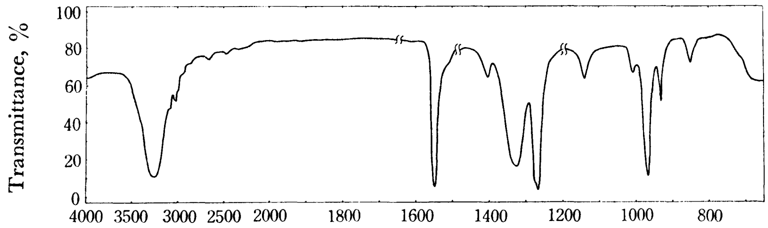

Fig. 2. IR spectrum of $[Cl_2Pt(CH_2=CH\text{-}OH)]_2$.
4000—1700 and 1500—1200 cm^{-1}; Hexachlorobutadiene mull.
1700—1500 and 1200—700 cm^{-1}; Nujol mull.

Results and Discussion

A. Normal Coordinate Analysis of Coordinated Vinyl Alcohol. The infrared spectrum of the coordinated vinyl alcohol is shown in Fig. 2, while the best sets of force constants for the coordinated vinyl alcohol are listed in Table 2.

TABLE 2. 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 3. VIBRATIONS OF COORDINATED VINYL ALCOHOL; $CH_2=CHOH$

Frequency, Obsd[a]	cm^{-1} Calcd	Assignment[b] (PED %)
3260 s	3345	ν(OH)(100)
3080 vw	3140	ν(CH)(99)
3020 vw	3019	ν_a(CH$_2$)(100)
	2916	ν_s(CH$_2$)(99)
1550 s	1567	ν(C=C)(45), δ(CH)(26), δ(CH$_2$)(12)
1405 w	1411	δ(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 934 m		Out-of-plane bending

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak.
b) ν, stretching; δ, bending; r, rocking; s, symmetric; and a, asymmetric.
PED, Potential Energy Distribution.

TABLE 4. VIBRATIONS OF COORDINATED VINYL ALCOHOL; $CH_2=CHOD$

Frequency, Obsd[a]	cm^{-1} Calcd	Assignment[b] (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	ν(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.
PED, Potential Energy Distribution.

In Tables 3 and 4 the observed frequencies are compared with those for coordinated vinyl alcohol and its deuterio analog calculated by using those sets of force constants.

The product rule for isotopic frequencies[8] works extremely well in this case; thus, it supports the validity of the assignments made.

Table 2 shows that the force constant of the C=C stretching is slightly smaller than that of the coordinated ethylene (6.00 mdyn/Å),[2] and that the force constant of its C–O stretching is relatively larger than those of methanol (2.43 mdyn/Å)[9] or diethyl ether (4.38 mdyn/Å).[10] These values reasonably imply that such a resonance structure as $\overset{-}{C}H_2\text{–}CH\text{=}\overset{+}{O}H$ exists to some extent even in the coordinated state. The larger value of the force constant of the C–O stretching also indicates that the lone-pair electrons of the oxygen atom do not interact with platinum.

B. Metal-olefin Stretching Vibrations. Figure 3 shows the far-infrared spectra of the complexes of the

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[8] E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, N. Y., (1955), p. 182.

[9] S. Mizushima and T. Shimanouchi, "Infrared and Raman Effect," Kyoritsu, Tokyo (1958), p. 229.

[10] M. Hayashi, *Nippon Kagaku Zasshi*, **78**, 222 (1957).

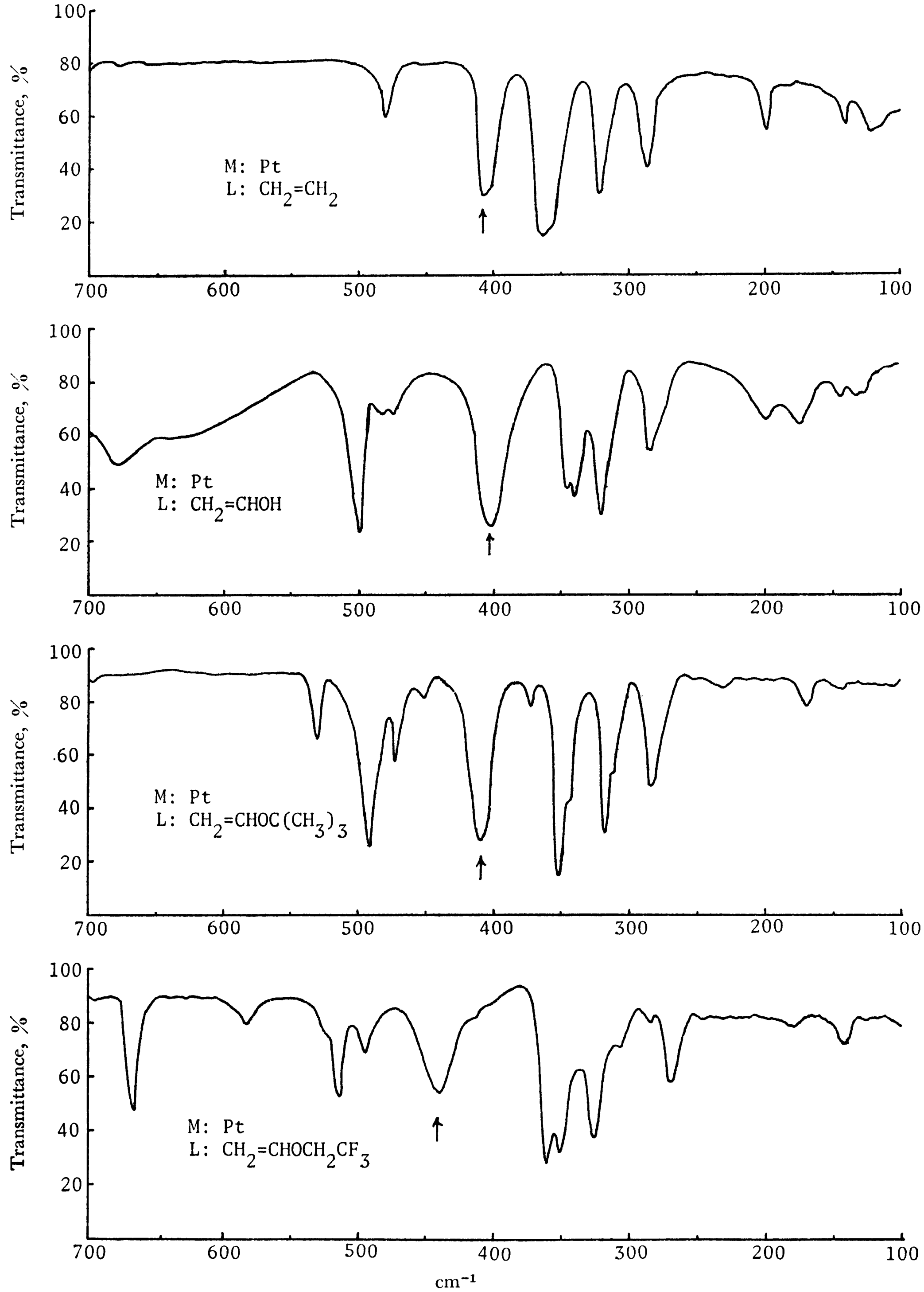

Fig. 3. Infrared spectra of [Cl$_2$ML]$_2$.

[Cl$_2$M Olefin]$_2$ type, in which M represents platinum or palladium.

With respect to the ethylene complexes with platinum and palladium, Nakamoto has reported that the frequency of a metal-ethylene stretching vibration is a better measure of the coordination strength than the shift width of the C=C stretching upon coordination.[3,11]

The infrared spectra of many platinum and palladium complexes of vinyl ethers, as is shown in the figure, satisfactorily correspond to the ethylene complex in 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, and hence has the possibility of coupling strongly with other vibrations, it may be regarded as a semi-quantitative measure of the coordination strength of vinyl ethers. Table 5 lists

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[11] M. Tsutsui, "Characterization of Organometallic Compounds," Part I, John Wiley & Sons, N. Y. (1969), p. 110.

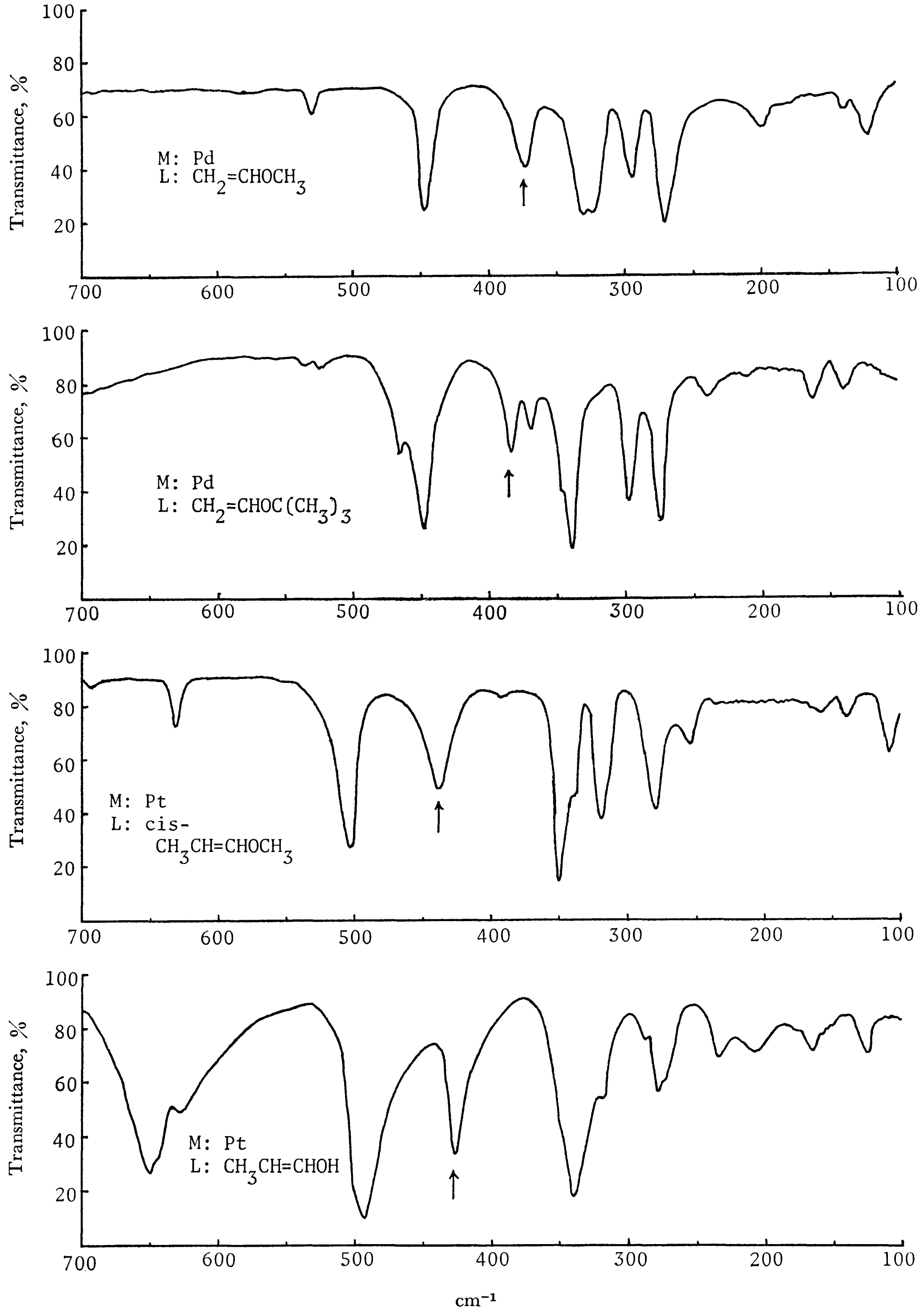

Fig. 3. Infrared spectra of $[ClM_2L]_2$.

the stretching vibrations of the metal-olefin bond thus obtained. This table suggests the following facts with respect to the coordination strength of vinyl ethers and their derivatives:

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

b) The coordination strength of vinyl alcohol and that of vinyl alkyl ether are almost equal to that of ethylene in the platinum complex.

c) Propenyl ethers are considerably stronger than the corresponding vinyl ethers in their coordination strength in spite of the fact that β-methyl group of the propenyl ethers may sterically interfere with the coordination, as is the case with 2-pentene.[12]

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[12] J. R. Joy and M. Orchin, *J. Amer. Chem. Soc.*, **81**, 310 (1959).

Table 5. 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-$CH_3CH=CHOCH$	438	404
cis-$CH_3CH=CHOSiMe_3$	430	—
$CH_3CH=CHOH$	427	—

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

As for the metal-olefin bonding, Chart and Duncanson's theory[13] has generally been accepted, in which the bonding is explained by a combination of the electron donation from the olefin to the metal and the electron back-donation from the metal to the olefin. The electron donation from the olefin to the metal is supposed to play an important role when the olefin has a strong electron-releasing substituent, as in the case of vinyl ethers or propenyl ethers. However, steric interactions between other ligands and a substituent on the olefin may also affect the coordination strength of the olefin; thus, the problem is complicated. At present, it seems to be difficult to interpret the relative coordination strengths of ethylene, vinyl alcohol, vinyl ethers, and their derivatives by means of a simple description.

The authors wish to express their thanks to Dr. Masamichi Kobayashi for his valuable suggestions on the analysis of the infrared spectra.

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13) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, **1953**, 2939.