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The Preparation and Some Reactions of Platinum(II) and Palladium(II) Complexes of Vinyl Ethers[1]

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Stable complexes with the general formula $[Cl_2ML]_2$ (M=Pt, Pd; L=vinyl ethers, propenyl ethers, 1,2-dimethoxyethylene) have been prepared. The IR spectra of $[Cl_2Pt(\textit{trans}\text{-}CH_3CH{=}CHOCH_3)]_2$ showed a change which was attributed to the *trans—cis* isomerization of the coordinated olefin. A similar *cis—trans* isomerization was also suggested for the other propenyl ether and 1,2-dimethoxyethylene complexes. The palladium complex of vinyl *t*-butyl ether was found to react with aqueous NaOH in a way similar to the Wacker process.

Although many transition metal–olefin complexes are known, few reports have appeared concerning complexes of olefins with strong electron-releasing substituents such as vinyl ethers; indeed, it has only been known that Fe(0) forms a very unstable complex with vinyl ethyl ether.[2] Such olefins will form unstable complexes with low valent transition metals because they have a strong σ-donating ability, but a poor π-accepting ability. In Pt(II) and Pd(II) complexes of ethylene, the contribution of the back donation has been emphasized, as in the case of the Zeise salt.[3] A detailed study of IR spectra has, however, shown that σ-donation from the olefin plays an important role in these complexes, while back-donation from the metal is of little importance.[4] Vinyl ethers can be expected, therefore, to form stable complexes with Pt(II) and Pd(II). Also, coordinated vinyl ethers might show an unusual behavior as a result of the interaction of lone-pair electrons of the oxygen atom with the metal. In this work, Pt(II) and Pd(II) complexes of vinyl ethers and their derivatives will be prepared, and the properties of the novel complexes will be studied by means of IR spectroscopy.

Results and Discussion

The analytical data and some physical properties of the novel complexes obtained by the following reactions are listed in Tables 1 and 2.

$$[Cl_2PtC_2H_4]_2 + 2\text{olefin} \longrightarrow [Cl_2Pt\text{olefin}]_2 + 2C_2H_4$$

$$2Cl_2Pd(PhCN)_2 + 2\text{olefin} \longrightarrow [Cl_2Pd\text{olefin}]_2 + 4PhCN$$

As expected, all the complexes are moderately stable in air at room temperature except for the vinyl trimethylsilyl ether complex, which is moisture-sensitive.[5] They can be stored at −20°C for months.

The last columns in Tables 1 and 2 show the configuration of the coordinated olefin, as determined by IR spectroscopy.

Figure 1 shows the IR spectra of the platinum complex of propenyl methyl ether. The spectrum of the freshly-prepared complex of *trans*-propenyl methyl ether (I) is shown at the top (a). When the solid sample, I, was allowed to stand under argon at 70°C for 48 hr, the spectrum changed to (b), indicating that the change takes place even in a solid state, while the sample I dissolved in toluene at 70°C for several hours showed the spectrum at the bottom (c). The spectrum (c) was also obtained when the complex (II) was prepared from the *cis*-isomer. The dotted line in Fig. 1-(c) shows the spectrum of the palladium analog (III); it was virtually identical with that of the platinum complex. As will be described later, the decomposition of the sample III with pyridine yielded almost pure *cis*-propenyl methyl ether. These facts indicate that the sample I was a mixture of *cis*- and *trans*-olefin complexes,

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TABLE 1. ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF [ClPt$_2$olefin]$_2$

Olefin used	Yield, %	Analysis, % (Calcd)	Decomp. temp., °C	IR ν(C=C) cm^{-1}	Configuration of coordinated olefin
$CH_2=CHOCH_3$	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	
$CH_2=CHOCH_2CH_2Cl$	48	C, 12.87 (12.90) H, 1.96 (1.89) Pt, 51.88 (52.36)	100—110	1516	
$CH_2=CHOCH_2CF_3$	72	C, 12.01 (12.19) H, 1.33 (1.28) Pt, 50.59 (49.50)	122—125	1510	
$CH_2=CHOSi(CH_3)_3$		C, 15.77 (15.71) H, 2.86 (3.16) Cl, 19.13 (18.55) Pt, 51.27 (51.04)	120—122	1510	
cis-$CH_3CH=CHOCH_3$	95	C, 14.84 (14.21) H, 2.38 (2.39) Pt, 57.21 (57.70)	137—140	1520	*cis*
trans-$CH_3CH=CHOCH_3$	16	C, 14.82 (14.21) H, 2.41 (2.39) Cl, 20.70 (20.97) Pt, 57.21 (57.70)	145—148	1533 1520	*cis-trans* mixture
cis-$CH_3CH=CHOSiMe_3$	71	C, 18.70 (18.19) H, 3.55 (3.56)	118—121	1507	*cis*
trans-$CH_3CH=CHOSiMe_3$	65	C, 18.02 (18.19) H, 3.42 (3.56) Cl, 18.68 (17.90)	121—123	(1507)a)	*cis*
cis-$CH_3OCH=CHOCH_3$	82	C, 13.81 (13.20) H, 2.29 (2.21) Cl, 19.83 (19.48) Pt, 53.04 (53.58)	140—145	1562 1535	*cis-trans* mixture
trans-$CH_3OCH=CHOCH_3$		C, 13.91 (13.20) H, 2.28 (2.21) Cl, 20.17 (19.48) Pt, 53.01 (53.58)	143—145	1535	*trans*
cis-$C_6H_5CH=CHCH_3$	77	C, 28.40 (28.14) H, 2.57 (2.62) Pt, 50.14 (50.78)	135—140	1512	*cis*
trans-$C_6H_5CH=CHCH_3$	76		120—130	1523	*trans*

a) Isomerization had been finished before IR spectrum was taken.

TABLE 2. ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF [Cl$_2$Pdolefin]$_2$

Olefin used	Yield, %	Analysis, % (Calcd)	Decomp. temp., °C	IR ν(C=C) cm^{-1}	Configuration of coordinated olefin
$CH_2=CHOCH_3$	76	C, 14.67 (15.31) H, 2.48 (2.57) Cl, 30.29 (30.13)	60—70	1538	
$CH_2=CHOCH(CH_3)_2$	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	*cis*
trans-$CH_3CH=CHOCH_3$	50		70—78	(1531)a)	*cis*
cis-$CH_3OCH=CHOCH_3$	74		120—130	(1543)a)	*trans*
trans-$CH_3OCH=CHOCH_3$	54	C, 19.08 (18.10) H, 3.13 (3.04)		1543	*trans*

a) Isomerization had been finished before IR spectra were taken.

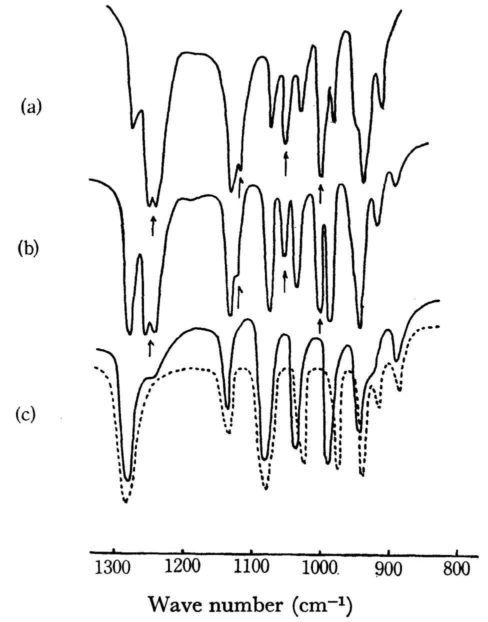


Fig. 1. IR spectra of $[Cl_2Pt(CH_3CH{=}CHOCH_3)]_2$ (Nujol mull)

(a) Complex prepared from *trans*-$CH_3CH{=}CHOCH_3$ (sample I).

(b) Sample I isomerized in a solid state.

(c) Sample I isomerized in a solution.
Complex prepared from *cis*-$CH_3CH{=}CHOCH_3$ (sample II). ------Pd analog (sample III)

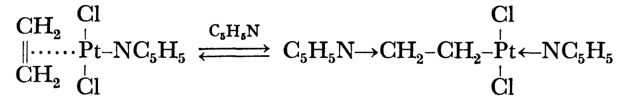
whereas the sample II was a pure *cis*-olefin complex and coordinated propenyl methyl ether was isomerized from *trans* to *cis*.

In the case of the 1,2-dimethoxyethylene coordinated to platinum, a similar isomerization in a solid state was followed by studying the IR spectra; however, the isomerization was from *cis* to *trans* in this case.

The platinum complex of propenyl trimethylsilyl ether and palladium complexes of propenyl methyl ether and 1,2-dimethoxyethylene all showed one kind of IR spectrum independent of the olefin isomers used. The configuration of the coodinated olefins in these complexes was determined by comparing the IR spectra with those of platinum complexes.

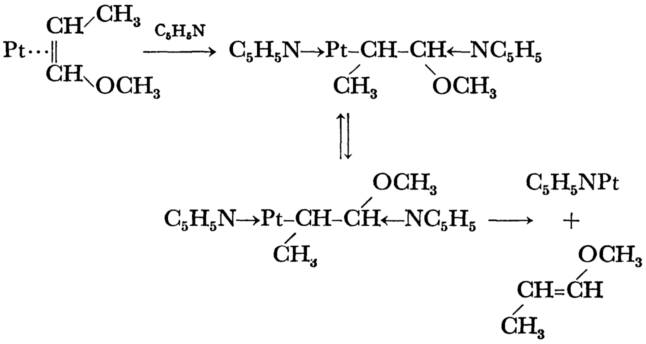
To compare these olefins with those having no oxygen atoms among their substituents, platinum complexes of *cis*- and *trans*-2-butene and *cis*- and *trans*-β-methylstyrene were prepared; however, they did not show any isomerization. The results with the 2-butene complex are in agreement with those reported by Jonassen and Kirsch.[6] The fact that coordinated propenyl ethers and 1,2-dimethoxyethylene isomerized readily under the conditions under which coordinated 2-butene and β-methylstyrene did not isomerize at all suggests that the contribution of the oxygen atom in the vinyl ether derivatives is essential for the isomerization. The most probable explanation may be some kind of interaction of the oxygen atom with the metal, thus stabilizing the transition state.

cis-Propenyl methyl ether coordinated to palladium or platinum was displaced with pyridine, and the propenyl methyl ether thus liberated was analyzed by glc. Propenyl methyl ether of the *cis*/*trans* ratio of 45 : 1 was liberated from the palladium complex, but the ratio was 3.1 : 1 when it was displaced from the platinum complex, indicating that a considerable amount of the *trans*-isomer was formed in the course of the displacement reaction. Orchin and his co-workers suggested that the displacement of coordinated ethylene by pyridine may proceed by a prior $\pi\rightarrow\sigma$ rearrangement:[7]



$$\overset{CH_2}{\underset{CH_2}{\|}}\cdots\cdots\overset{Cl}{\underset{Cl}{Pt}}\text{-}NC_5H_5 \overset{C_5H_5N}{\rightleftarrows} C_5H_5N\rightarrow CH_2\text{-}CH_2\text{-}\overset{Cl}{\underset{Cl}{Pt}}\leftarrow NC_5H_5$$

An analogous σ-bonded intermediate may account for the observation that the *trans*-isomer is formed during the *cis*-propenyl ether displacement by pyridine:



If the olefin molecule, which is about to leave the metal, spends enough time in 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 conformations of the σ-complex as well as by relative rate of its decomposition.

The palladium complex of vinyl *t*-butyl ether was treated with an aqueous hydrogen fluoride and with an aqueous sodium hydroxide. The complex was recovered unchanged from a suspension in 45% aqueous hydrogen fluoride; this is in contrast to the fact that free vinyl ethers are readily hydrolyzed into aldehyde and alcohol in an acid. On the other hand, the complex reacted vigorously with a 45% aqueous sodium hydroxide to yield palladium metal and a quantitative amount of the acetate ion; furthermore, about 84% of the theoretical amount of *t*-butyl alcohol was detected by glc. By analogy with the Wacker process, the reaction may be described as follows:

$$\frac{1}{2}[Cl_2Pd(CH_2{=}CHOCMe_3)]_2 \xrightarrow{OH^-} CH_3COOCMe_3 + Pd^0 + HCl + Cl^-$$

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

Experimental

Solvents. The toluene and petroleum ether (bp 30—50°C) were purified by the ordinary method and were dried by refluxing over sodium for several days. They were freshly distilled before use.

Olefins. The vinyl methyl ether, vinyl 2-chloroethyl

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[6] H. B. Jonassen and W. B. Kirsch, *J. Amer. Chem. Soc.*, **79**, 1279 (1957).

[7] P. D. Kaplan, S. Schmist, and M. Orchin, *ibid.*, **90**, 4175 (1968).

ether, vinyl 2,2,2-trifluoroethyl ether, and 2-butene were commercial reagents. The other olefins were prepared by the known methods.[9-12] The *cis*- and *trans*-isomers of propenyl ethers were separated by fractional distillation and were confirmed by studying their NMR coupling constants. The *cis*- and *trans*-isomers of 1,2-dimethoxyethylene were separated by fractional distillation and were identified by dipole-moment measurements in benzene (*cis*, 2.00D; *trans*, 1.83D).

[Cl$_2$Ptolefin]$_2$. This complex was prepared simply by the addition of an olefin to a suspension of $[Cl_2PtC_2H_4]_2$ in toluene. The complexes of vinyl 2,2,2-trifluoroethyl ether, 1,2-dimethoxyethylene, and β-methylstyrene were prepared at room temperature, but the reactions of the other olefins were carried out at low temperatures in order to prevent side reactions. The preparation of the propenyl methyl ether complex will be described as an example; about a 100 mg portion of $[Cl_2PtC_2H_4]_2$ was suspended in 10 m*l* of toluene under a nitrogen atmosphere, and then the suspension was cooled in a dry ice–methanol bath. About 0.2 m*l* of propenyl methyl ether was added, and the mixture was stirred for about 1 hr. The heterogeneous mixture gradually turned homogeneous as the reaction proceeded. The toluene and the excess of propenyl methyl ether were evaporated at −35°C under reduced pressure. The resulting yellow powder of the complex was recrystallized, if necessary, from hot toluene–petroleum ether.

[Cl$_2$Pdolefin]$_2$. This complex was prepared by the reaction of $Cl_2Pd(PhCN)_2$ and an olefin according to Kharasch's method.[13] The reaction was carried out in toluene at room temperature. The preparation of 1,2-dimethoxyethylene complex was as follows: about a 200 mg portion of $Cl_2Pd(PhCN)_2$ was dissolved in 20 m*l* of toluene under a nitrogen atmosphere, after which the undissolved material was removed by filtration. To this filtrate, 0.05 m*l* of 1,2-dimethoxyethylene was added, and then the solution was continuously stirred. The precipitation of the desired complex occurred within 1 hr. The supernatant solution was removed by decantation, and the precipitate was washed with toluene several times.

Decomposition of the Complexes with Pyridine. The platinum and palladium complexes of propenyl methyl ether were decomposed with pyridine, thus liberating the original olefin without forming any by-product. For example, to 200 mg of [Cl$_2$Pt *cis*-$CH_3CH{=}CHOCH_3$]$_2$ we added 1 m*l* of toluene containing a calculated amount of pyridine. The complex dissolved immediately, and there precipitated within 1 hr white crystals which appeared to be $[Pt\ Py_4]Cl_2$. The supernatant solution was analyzed by glc (tricresyl phosphate, 1.5 m, 40°C).

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11) H. Baganz, K. Praefcke, and J. Rost, *Chem. Ber.*, **96**, 2657 (1963).

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