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Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. XII. Dissociation of the Olefin in *trans*-Dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II) Complexes[1)]

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The rates of dissociation of the olefin in the title compounds were determined by the dynamic NMR technique by taking advantage of the line shape change due to the isopropyl-methyl protons. The rates of dissociation were independent of concentration in bromoform-*d* solutions. The free energy of activation was between 17.0 and 19.1 kcal mol^{-1} at 353 K for the compounds, of which line shapes were fully analyzed, depending upon the substituent in the pyridine ring and electron-withdrawing substituents giving low activation energy. The solvent effect was noticed on the dissociation rates: Aromatic hydrocarbons give higher rates of dissociation than halogenated hydrocarbons. Although solvents of strong affinity toward platinum(II) tend to decompose the complex, tetrahydrofuran-d_8 was found to give definitely higher rates of dissociation of the olefin in *trans*-dichloro(4-methoxycarbonylpyridine 1-oxide)(3-methyl-1-butene)platinum-(II) than bromoform-*d*, when it was used as a solvent. The mechanism of dissociation was discussed from the available data.

The dynamic NMR technique has been proved useful in investigation of bond breaking-and-forming processes as well as intramolecular dynamics.[2,3)] The bond breaking-and-forming processes are of particular interest because by the investigation of the kinetics the process provides fundamental knowledge for the understanding of dissociation reactions in a sense that the phenomenon could be observed in the absence of any foreign materials in the dynamic NMR technique.

The technique requires some molecular features. The molecule to be studied should possess a pair of diastereotopic nuclei of which magnetic sites are exchanged by dissociation-and-combination and the time scale must fall within the range suitable for the technique, 10^0—10^3 s^{-1}, although the rates are adjustable to some extent by changing temperatures of observation. If a molecule meets the requirements, it is possible to observe various dissociation processes. We have reported the dissociation of an organic halide,[4)] an organic carboxylate,[5)] ammonium salts,[6,7)] and amine ligands from organometallic compounds.[8)] The olefin–metal complex also falls in the category that can be investigated by this technique because chirality is found according to the face of the olefin to which a metal is bonded,[9)] and racemization takes place when the olefin dissociates and reforming of the bond from the other face of the olefin after rotation takes place. The point is how to find a suitable compound for the investigation by the dynamic NMR technique.

Platinum(II)–olefin complexes are well-known and the racemization of their optically active members has been studied by the classical methods. They are usually stable enough to be isolated as chemical entities to mean that the complexes should be in general destabilized for the investigation by the dynamic NMR technique because the time scale of NMR spectroscopy is much faster than the classical laboratory time scale.

Platinum(II)–olefin complexes are known to exchange the olefin in the presence of the excess of an olefin. Potassium trichloro(ethylene)platinate(II) is known to undergo the olefin exchange in the presence of ethylene faster than the NMR time scale even at low temperatures.[10)] The ethylene ligand can also be exchanged by other olefins if the olefin is present.[11)] There is wealth of information on the exchange of olefins in the platinum(II)–olefin complexes.[12–17)]

In the absence of the excess of olefin, the dissociation of the olefin in platinum(II)–olefin complexes seems to be very slow. There are only a few reports that have dealt with the dissociation of the complexes in the absence of an olefin. Frits and Sellmann reported that the coupling of the olefin protons with ^{195}Pt disappeared on dissolution of dichloro(ethylene)(4-substituted pyridine)platinum(II) complexes in acetone, if the 4-substituent in the pyridine ring was electron-withdrawing.[18)] Kaplan et al. generalized the loss of coupling of olefinic protons with the platinum nucleus in *trans*-dichloro(olefin)-(substituted pyridine)platinum(II) complexes in acetone at ambient temperature for the compounds that carry an electron-withdrawing substituent.[19)] The latter authors suggested the role of pyridine base which was present in a minute amount in the system in the olefin exchange.[20)] However, they did not report the kinetic data for the exchange.

There are two strategies to facilitate racemization of the platinum(II)–olefin complexes, as judged from the literatures. One is to use a less basic base to the trans position of an olefin: The strong base stabilizes the olefin complex by the trans influence.[21)] And the other is to use a solvent of strong affinity towards the

platinum(II) ion. On the basis of NMR point of view, it is also important to render the chemical shift difference of the two exchanging protons small in order that we observe the exchange process at low temperatures.

We started from *trans*-dichloro(olefin)(pyridine)-platinum(II) where the olefin was 3-methyl-1-butene that possesses the potential diastereotopic protons. It was not possible to observe the change in line shapes of the signals due to the diastereotopic protons in the olefin in nonpolar solvents and the complex decomposed in polar solvents. In order to facilitate the racemization, pyridine 1-oxide was introduced to the trans position of 3-methyl-1-butene. Although this compound showed a sign of racemization, namely line-broadening of the signals due to the isopropyl-methyl protons, it was not stable enough to survive the measurements at 100 °C or higher temperatures that were needed for the line shape analyses: The situation was improved relative to the pyridine case but was still not good enough for the dynamic NMR work. Finally we introduced 4-methyl-1-pentene as an olefin and 4-methoxycarbonylpyridine 1-oxide as a base in the trans position to the olefin to find that the complex was suitable for the NMR work. This paper reports the results of such investigations and discusses the substituent effects in the pyridine ring and the solvent effects on the rates of racemization as well as the mechanism of dissociation.

Results

The syntheses of the complexes used in this study were carried out in the following way. Potassium trichloro(ethylene)platinate(II)[22] was dimerized by acidification[23] and the dimer **1** was treated with 4-methyl-1-pentene to replace the ethylene ligand. The resulted olefin complex **2** was then treated with 4-substituted pyridine 1-oxide to give the desired compound **3**.[24]

The kinetic parameters obtained as the results of the line shape analysis are given in Tables 1—3. The feature of the data is that the electron-donating substituent in the 4-position of the pyridine ring reduces the rates of racemization considerably and we found that only line broadening to a small extent for the methyl and unsubstituted compounds. The plot of the free energy of activation for racemization at 353 K against pK_a values of the pyridine 1-oxide[25] gave a straight line, the correlation coefficient being

Table 1. The Effect of Concentration on the Kinetic Parameters for Dissociation of the Olefin in *trans*-Dichloro(4-methyl-1-pentene)(4-methoxycarbonyl-pyridine 1-oxide)platinum(II) in Bromoform-*d*

Concentration / 10^{-2} mol L^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1} [a]	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1} [a]	$\Delta G^{\ddagger}_{353}$/kcal mol^{-1} [a]	r [b]
1.8	17.4±0.6	−3.2±1.9	18.5	0.9996
3.4	17.6±0.5	−2.7±1.3	18.5	0.9998
5.0	17.2±0.4	−3.6±1.1	18.5	0.9998

a) 1 cal=4.184 J. b) Correlation coefficient.

Table 2. Substituent Effects on the Kinetic Parameters for Dissociation of the Olefin Ligand in *trans*-Dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II) in Bromoform-*d* at ca. 40 mmol L^{-1}

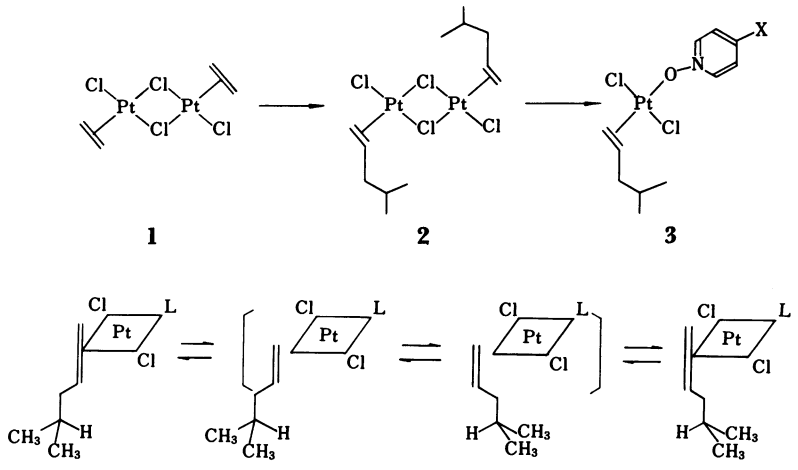
Substituent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{353}$/kcal mol^{-1}	r [b]
CH_3			20.4[b]	
H			19.6	
Cl	18.1±0.6	−2.8±1.9	19.1	0.9996
CH_3OCO	17.6±0.5	−2.7±1.3	18.5	0.9998
NO_2	13.8±0.7	−9.0±2.1	17.0	0.9994[c]

a) Correlation coefficient. b) At 363 K. c) 14 mmol L^{-1} in chloroform-*d*.

Table 3. Solvent Effects on the Kinetic Parameters for Dissociation of the Olefin Ligand in *trans*-Dichloro(4-methyl-1-pentene)(4-methoxycarbonylpyridine 1-oxide)platinum(II)

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{323}$/kcal mol^{-1}	r [a]
$CDBr_3$	17.6±0.5	−2.7±1.3	18.4	0.9998
$C_2D_2Cl_4$[b]	19.0±0.9	2.7±2.7	18.2	0.9994
C_6D_6	16.3±0.5	−3.8±1.4	17.5	0.9998
$C_6D_5CD_3$	16.7±0.3	−3.1±1.7	17.7	0.9997

a) Correlation coefficient. b) 1,1,2,2-Tetrachloroethane-d_2.



L=pyridine 1-oxide

Scheme 1.

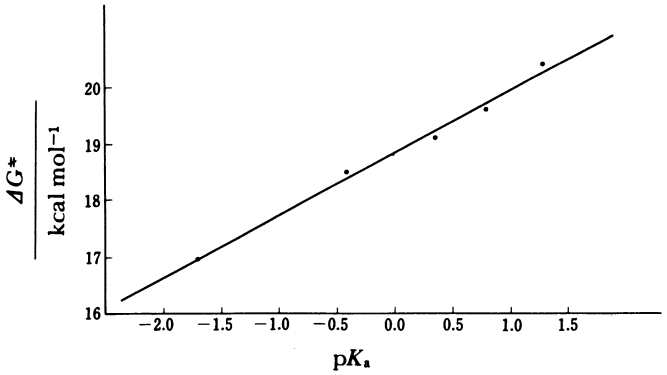


Fig. 1. Relationship between pK_a's of 4-substituted pyridine 1-oxide and free energies of activation for the dissociation of the olefin in *trans*-dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)-platinum(II) at 353 K.

0.995, when $\Delta G^{\ddagger}$ for the methyl compound at 363 K is included (Fig. 1). We believe the inclusion of the latter data is permissible because the entropy of activation is small for other compounds in the series examined, rendering the change in the free energy of activation from 353 K to 363 K small.

Discussion

The results in Table 1 clearly indicate that the rates of racemization are not affected by the concentration of the substrate. This will exclude the mechanisms that involve the catalytic action of the free pyridine oxide that is present in a minute amount, though this mechanism was suggested by Kaplan et al.[20] Then we can assume the process be unimolecular, although solvent assistance in the dissociation is not ruled out. Then over simplified mechanism of the racemization can be written as in Scheme 1, where the species shown in the brackets are the intermediates that are not observed. The results in Table 2 together with the fact that the complex that contains pyridine to the trans position of the olefin ligand shows much slower rates of racemization than those listed in Table 2 are examples of typical trans effects.[26]

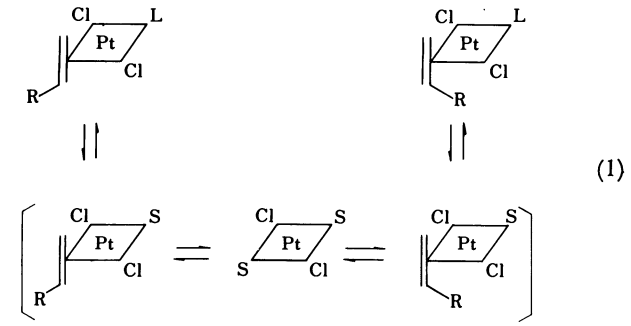
Since the role of solvent molecules is important in racemization of the olefin complexes, it will be of interest to see the solvent effect on the rates of racemization. Table 3 clearly indicates that, whereas halogenated hydrocarbons, $CDBr_3$ and $C_2D_2Cl_4$, give about the same free energy of activation, the aromatic solvents do again about the same free energy of activation, the aromatic solvents giving definitely larger rates of dissociation of the olefin. It is interesting to note that the rates of dissociation are not dependent on the polarity of the solvent molecules. Rather they seem to indicate that the affinity of the solvent molecule towards platinum(II) is important.

For further understanding we have changed solvents to see the effects on the rates of dissociation. However, the complexes tend to decompose in solvents such as dimethyl-d_6 sulfoxide, nitromethane-d_3, acetonitrile-d_3, methanol-d_4, and *N*,*N*-dimethylformamide-d_7. In tetrahydrofuran-d_8, the complex also decomposed at high temperatures. However, *trans*-dichloro(4-methoxycarbonylpyridine 1-oxide)(3-methyl-1-butene)platinum(II) was found to survive to afford kinetic data for dissociation at one point of temperature: 16.4 kcal mol^{-1} at 300 K.[27] Comparing the results with the fact that dissociation of the olefin was not detectable in the same complex in bromoform-*d* at 330 K, we conclude that solvent molecules coordinate to the platinum ion before ligand dissociation.

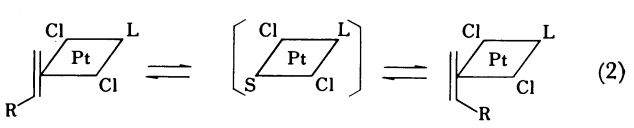
The entropy of activation should reflect the mechanism, dissociative or associative. Although it is known that the entropy of activation is large negative if a solvent molecule participate in an associative reaction,[17] the entropy of activation shown in Tables 1—3 are all close to zero except one case which is still closer to zero than −10 cal mol^{-1} K^{-1}. Recently, the

entropy of activation of dissociative reactions in platinum complexes has been reported to be small positive.[28,29] This quantity of entropy of activation agrees with those obtained for extrusion of a particle from an organic compound.[30] Thus interpretation of these results is difficult in a straightforward manner. It is also true that the entropy of activation should be discussed with care because some dissociative reactions are known to give negative entropy of activation[31] and associative reactions give positive entropy of activation.[16] It might even be the quality of kinetic data that give confusing results in entropy of activation or the randomly dispersing data of the entropy of activation might reflect factors that have not been considered. Therefore, we should like to defer further discussion on the quantity of entropy of activation except mentioning on one point. The participation of the solvent molecule in dissociation of the olefin ligand is apparent from the data given above. It is possible that in these cases of square planar complexes, to which a solvent molecule loosely associates even at the ground state, the entropy of activation could be near zero even in associative reactions, because acquiring freedom of motion by the olefin ligand in the transition state could be important. Further study on this point is awaited.

Admitting the participation of the solvent molecule in the dissociation of the olefin ligand, we can write two mechanisms. One is the process which proceeds via substitution of the solvent for the pyridine oxide ligand followed by the dissociation of the olefin ligand (Eq. 1). The other is the process in which the solvent assists directly the dissociation of the olefin without affecting the pyridine oxide ligand (Eq. 2).



(1)



(2)

If the first possibility is the case that we observe, the rate-determining step must be the dissociation of the pyridine oxide ligand, because, if the dissociation of the olefin were rate-determining, we could not explain the substituent effects seen in the dissociation of the olefin. If the second case is the one we observe, we may have to assume that, although the pyridine oxide ligand dissociates faster than the olefin ligand, there are species that permit dissociation of the olefin ligand, without affecting the pyridine oxide ligand.

It is difficult to determine which is the real case at present but we are inclined to conclude that the second is more likely to be the case for the following reasons. Firstly, although it is still to be confirmed, less basic ligands in the platinum complexes will dissociate more easily than the more basic. Since pyridine 1-oxides are weaker bases than pyridines and the dissociation of the pyridine base from platinum(II) complexes are known,[18–20] it is natural to assume that pyridine 1-oxides will dissociate much more easily than monosubstituted olefins. Therefore, that the rate-determining step in the dissociation of the olefin is the dissociation of the pyridine oxide ligand is less likely. Secondly, although more of the molecules are in the process of dissociation of the pyridine oxide ligand than those in the process of the dissociation of the olefin, we do not observe the dissociated or solvent-ligated molecules to mean that the concentration of the complex is practically the same during the process observed by the dynamic NMR spectroscopy. Therefore, the slow dissociation of the olefin and the fast dissociation of the pyridine oxide ligand do not hamper the Eq. 2 for being the true mechanism of the reaction.

Finally we should like to mention on another possibility of the racemization mechanism which had been proposed in a literature.[32] That is, a platinum–olefin complex would racemize via a sigma-complex. In this mechanism, the process has to pass a transition state or an intermediate which has charge separation. Should this situation take place, it is expected that solvents that stabilize ionic species should enhance the reaction rates. In spite of this expectation, aromatic hydrocarbons show lower barrier to the transformation than halogenated hydrocarbons, although every solvent parameter suggests that the latters should more stabilize ionic species than the formers.[33] Thus the possibility of intervention of a sigma-bonded intermediate (or transition state) is less likely. We favor the solvent assisted mechanism over the sigma-complex mechanism.

Experimental

Dynamic NMR Measurements and Analyses of the Data. The ^{1}H NMR spectra were obtained on a JEOL GX-270 spectrometer which operates at 270 MHz. Samples were dissolved to make up ca. 50 mmol L^{-1} solutions in appropriate solvents except for the determination of the effects of concentration (Table 1) on the rates and for 4-nitropyridine 1-oxide complex which was sparingly soluble in $CDCl_3$. In the latter case, the concentration was

14 mmol L^{-1}. Temperature was measured directly by a thermometer. The chemical shift differences of the signals due to isopropyl-methyl protons drifted when temperature was varied. The drift was measured at several points in the slow exchange limit and the linear relation between the temperature and the chemical shift difference was obtained as shown in Table 4. The chemical shift difference at the temperature of simulation was obtained by extrapolation with the use of the equations. The coupling constants between the methyl protons and the methine proton were independent of temperature (6.6—6.8 Hz), though small differences were noted from condition to condition. T_2's were determined by considering the line shapes in the slow exchange limit and were used throughout the temperature range examined. They were 0.08—0.17 s. The spectra were analyzed as the exchange $A_3B_3X \rightleftharpoons B_3A_3X$ with the use of DNMR 3 program.[34] The rate constants thus obtained were doubled to obtain rates of dissociation in order to accommodate the fact that the rates of racemization is twice of those of dissociation. The rate constants of dissociation are summarized in Table 5.

For the calculation of the line shapes of the complexes with 4-methyl and unsubstituted pyridine 1-oxide, the observed chemical shift difference, 10.7 and 11.1 Hz, respectively, were directly used. T_2's were 0.12 and 0.14 s, respectively, for the former and the latter. For the complex with 3-methyl-1-butene, the chemical shift difference, T_2, and rate constant at 300 K were 104.1 Hz, 0.10 s, and 6.7 s^{-1}, respectively.

Syntheses. Pyridine 1-oxide, 4-nitropyridine 1-oxide, 3-methyl-1-butene, and 4-methyl-1-pentene were available from Tokyo Kasei, Co. 4-Methoxycarbonylpyridine 1-oxide[35] and 4-chloropyridine 1-oxide[36] were prepared as were reported in literatures. The following is the typical method of synthesis of the complexes. The yields were 65—88%.

***trans*-Dichloro(4-methyl-1-pentene)(pyridine 1-oxide)platinum(II).** To a solution of 0.10 g (0.17 mmol) of tetrachlorobis(ethylene)diplatinum(II)[23] in 5 mL of dichloromethane was added 1 mL of 4-methyl-1-pentene and the whole was stirred for several minutes at room temperature. The volatile materials were evaporated and the residue was recrystallized from hexane to give 0.11 g of tetrachlorobis(4-methyl-1-pentene)diplatinum(II) as orange crystals. The crystals were dissolved in 5 mL of dichloromethane and stirred with 30 mg (0.32 mmol) of pyridine 1-oxide for 10 min. Evaporation of the solvent followed by recrystallization of the residue from dichloromethane–hexane afforded 89 mg (65%) of pale yellow crystals.

The melting point of this compound and analytical data are given in Table 6 together with those for other *trans*-dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)-platinum(II) complexes. ^1H NMR data are given in Table 7.

trans-Dichloro(4-methoxycarbonylpyridine 1-oxide)(3-methyl-1-butene)platinum(II), mp 121—122 °C (decomp), was similarly prepared as described for the preparation of the 4-methyl-1-pentene complexes. Found: C, 29.36; H, 3.49; N, 2.73%. Calcd for $C_{12}H_{17}Cl_2NO_3Pt$: C, 29.46; H, 3.50;

Table 4. Temperature Dependence of the Chemical Shift Differences between the Diastereotopic Pairs of Methyls in *trans*-Dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II)

Substituent	Solvent	Correlation[a]	r[b]
Cl	$CDBr_3$	$-0.05956t+16.15$	0.9929
CH_3OCO[c]	$CDBr_3$	$-0.06413t+16.35$	0.9968
CH_3OCO[d]	$CDBr_3$	$-0.07172t+16.69$	0.9995
CH_3OCO[e]	$CDBr_3$	$-0.06245t+16.24$	0.9982
CH_3OCO	$C_2D_2Cl_4$[f]	$-0.07468t+16.38$	0.9969
CH_3OCO	C_6D_6	$-0.05901t+10.11$	0.9994
CH_3OCO	$C_6D_5CD_3$	$-0.05832t+9.33$	0.9972
NO_2	$CDCl_3$	$-0.07857t+14.98$	0.9930

a) The correlation is given by $\Delta\nu=At+B$, where t is temperature in °C. b) Correlation coefficient. c) Concentration 34 mmol L^{-1}. d) Concentration 18 mmol L^{-1}. e) Concentration 50 mmol L^{-1}. f) 1,1,2,2-Tetrachloroethane-d_2.

Table 5. The Rates of Dissociation of the Olefin Ligand in *trans*-Dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II)

Substituent	Solvent	k/s^{-1}(temperature/°C)
CH_3	$CDBr_3$	4.2 (90.4)
H	$CDBr_3$	5.8 (80.4)
Cl	$CDBr_3$	4.0 (67.4), 5.4 (71.0), 7.0 (74.7), 9.6 (78.4), 13.0 (82.3), 17.0 (86.2)
CH_3OCO[a]	$CDBr_3$	6.6 (62.6), 8.6 (65.7), 10.8 (68.6), 13.6 (71.6), 17.0 (74.5), 21.2 (77.6)
CH_3OCO[b]	$CDBr_3$	6.4 (62.4), 8.6 (65.5), 10.6 (68.5), 13.4 (71.5), 16.8 (74.5), 20.6 (77.5)
CH_3OCO[c]	$CDBr_3$	7.0 (62.5), 8.8 (65.4), 11.2 (68.5), 13.8 (71.4), 17.4 (74.5), 22.0 (77.4)
CH_3OCO	$C_2D_2Cl_4$[d]	6.2 (56.5), 8.6 (59.7), 11.0 (62.7), 14.4 (65.6), 18.2 (68.4), 23.2 (71.6)
CH_3OCO	C_6D_6	6.4 (45.0), 8.2 (48.0), 10.6 (50.9), 14.0 (54.6), 17.2 (57.3), 22.4 (60.5)
CH_3OCO	$C_6D_5CD_3$	6.3 (48.9), 8.6 (52.5), 11.2 (55.5), 13.8 (58.3), 17.6 (61.5), 22.0 (64.4)
NO_2	$CDCl_3$	6.4 (28.1), 8.8 (32.3), 12.0 (36.0), 14.8 (38.6), 18.2 (41.8), 22.0 (44.5)

a) Concentration 34 mmol L^{-1}. b) Concentration 18 mmol L^{-1}. c) Concentration 50 mmol L^{-1}. d) 1,1,2,2-Tetrachloroethane-d_2.

Table 6. Melting Points and Analytical Data of *trans*-Dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II)

Substituent	Found/%			Calcd/%			Mp[a]
	C	H	N	C	H	N	θ_m/°C
CH_3	31.18	4.16	3.05	31.38	4.17	3.05	131—135
H	29.43	4.00	3.13	29.67	3.85	3.15	119—123
Cl	27.27	3.14	2.90	27.54	3.36	2.92	146—148
CH_3OCO	30.78	3.77	2.81	31.02	3.81	2.78	128—129
NO_2	26.84	3.20	5.56	26.95	3.29	5.71	153—154

a) With decomposition.

Table 7. ^{1}H NMR data (δ) of *trans*-Dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II) in $CDCl_3$ at 270 MHz at 22 °C

Substituent	Signal due to olefin					Signal due to pyridine		
	methyl[a]	methine	methylene	terminal CH_2[b]	α-H[b]	3,5-H	2,6-H	others
CH_3	0.96 (d) 1.01 (d)	1.95 (m)	1.52 (m) 2.19 (m)	4.18—4.29 (m)	5.00 (m)	7.47 (d) (J=6.7 Hz)	8.46 (d)	2.67 (s) (3H)
H	0.98 (d) 1.03 (d)	1.99 (m)	1.55 (m) 2.24 (m)	4.27—4.36 (m)	5.14 (m)	7.66 (t) (J=6.9 Hz)	8.59 (d)	7.89 (t) (1H)
Cl	0.97 (d) 1.03 (d)	1.97 (m)	1.52 (m) 2.19 (m)	4.26—4.38 (m)	5.07 (m)	7.71 (d) (J=7.0 Hz)	8.60 (d)	
CH_3OCO	0.99 (d) 1.04 (d)	2.00 (m)	1.53 (m) 2.22 (m)	4.33—4.44 (m)	5.21 (m)	8.17 (d) (J=7.0 Hz)	8.64 (d)	4.02 (s) (3H)
NO_2	1.01 (d) 1.07 (d)	2.07 (m)	1.47 (m) 2.22 (m)	4.40—4.68 (m)	5.41 (m)	8.23 (d) (J=7.5 Hz)	8.50 (d)	

a) The coupling constants were all 6.6 Hz except for the methyl compound (6.5 Hz). b) The coupling with ^{195}Pt was observed.

N, 2.86%. ^{1}H NMR ($CDCl_3$) δ=1.13 (3H, d, J=6.8 Hz), 1.55 (3H, d, J=6.4 Hz), 2.18 (1H, m), 4.02 (3H, s), 4.28—4.35 (2H, m), 5.01 (1H, m), 8.17 and 8.63 (4H, ABq, J=7.0 Hz).

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