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Determination of Rates of Dissociation of an Olefin Ligand in an Olefin-Platinum Complex by Dynamic NMR Spectroscopy[1)]

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The double-doublet signal due to isopropyl-methyl protons in trans-dichloro(4-methyl-1-pentene)(4-methoxycarbonylpyridine 1-oxide)platinum(II) shows the change in line shapes at high temperatures in its ^1H NMR spectra, owing to the racemization process, which involves the dissociation of the olefin. The activation parameters were obtained for $CDBr_3$ solutions as follows: $\Delta H^{\ddagger}$ 17.6 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ -2.7 ± 1.3 cal mol^{-1} K^{-1}. Incidentally, this is the first observation of the racemization of an olefin-metal complex by the dynamic NMR method.

Dynamic NMR lends help in studying the dynamic process occurring in organic compounds as well as in inorganic compounds.[2,3)] We have shown that this technique is useful in studying the rates of dissociation of a proton from ammonium salts,[4,5)] that of a carbocation from quaternary ammonium salts,[1)] and amine ligands from coordination compounds.[6)]

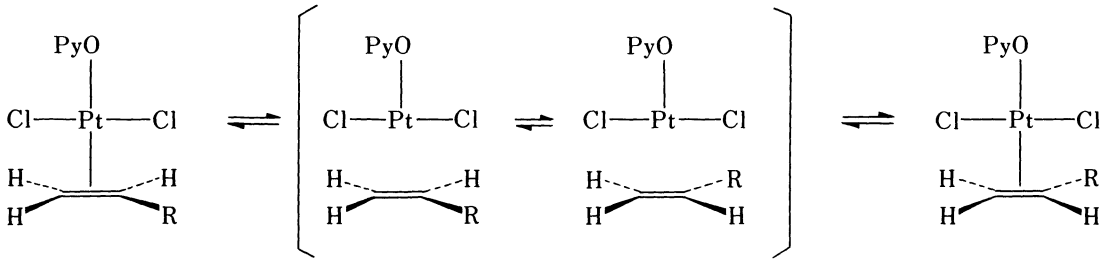
The feature of the technique is to observe the spin exchange taking place in a system due to the dissociation of a chemical bond. The exchange of spins is manifested when there is a pair of diastereotopic nuclei and racemization or topomerization[7)] takes place. Since the elements of chirality involve center, axis, and plane, it will be worthwhile to seek examples of application of the dynamic NMR technique to the chiral elements other than the center.

Olefin-metal complexes are well known to be chiral, if the olefin is properly substituted. Since this chirality is manifested by virtue of the fact that the metal sits above or below the plane of the olefin, this group of optical isomers may be taken as the examples of the plane asymmetry, though the Cahn-Ingold-Prelog system recommends to take this type of compounds as the chirality about a center.[8)] In order to search suitable compounds for the dynamic NMR spectroscopy, we have launched a project to study a series of platinum-olefin complexes. This paper is to report a preliminary result of such investigations.

Although the olefin exchange in complexes of the Zeise salts is fast in the presence of an olefin,[9)] if the olefin is absent, it is very slow.[10,11)] In order to fulfill the requirement by the dynamic NMR technique, the rates of the dissociation must be increased. Literature search reveals that there are two ways to enhance the rates of racemization of the olefin complexes of Pt(II): 1)

electron-poor olefins give higher rates of racemization than the electron-rich,[12] and 2) weak bases bound to the trans position of the olefin in a complex tends to give higher rates than strong bases.[13] In addition, solvents might play an important role in determining the rates of racemization because a solvent molecule might associate with the complex to facilitate the dissociation of an olefin molecule.

We chose 4-methyl-1-pentene as an olefin for two reasons. Firstly, it possesses a pair of diastereotopic methyl groups when it coordinates to a platinum atom. Secondly, it gives an advantage that the observation of coalescence of the spectral lines is possible at the lower temperatures owing to a small chemical shift difference between the protons on the two methyl groups. The second point was important because complexes of this type tend to decompose on prolonged heating. 4-Methoxycarbonylpyridine 1-oxide was chosen as the base trans to the olefin in a complex because pyridine 1-oxides are known to be much weaker bases than pyridines.[14] Thus we are able to determine rates of racemization without any appreciable decomposition of trans-dichloro(4-methyl-1-pentene)(4-methoxycarbonylpyridine 1-oxide)platinum(II) with the use of a JEOL GX-270 machine which operates at 270 MHz.



Scheme 1. Idealized topomerization process of trans-dichloro(4-methyl-1-pentene)(4-methoxycarbonylpyridine 1-oxide)platinum(II): R = isobutyl, PyO = 4-methoxycarbonylpyridine 1-oxide

The idealized dissociative process for the racemization is shown in Scheme 1. Here, if the olefin dissociates and rotates with respect to its olefinic plane to allow the platinum ion to coordinate from the back side, then the inversion of stereochemistry completes. From the NMR point of view, the isopropyl-methyl protons are diastereotopic as far as the olefin does not dissociate, but they lose the diastereotopicity if the racemization rates become large enough on the NMR time scale. The observed spectra of the protons in the isopropyl-methyl groups are shown in Fig. 1 together with calculated ones. The calculation was performed with the DNMR3 program.[15] Chemical shift differences and T_2 were treated as reported before.[2] The rate constants thus obtained were put into the Eyring equation to afford the activation parameters compiled in Table 1.

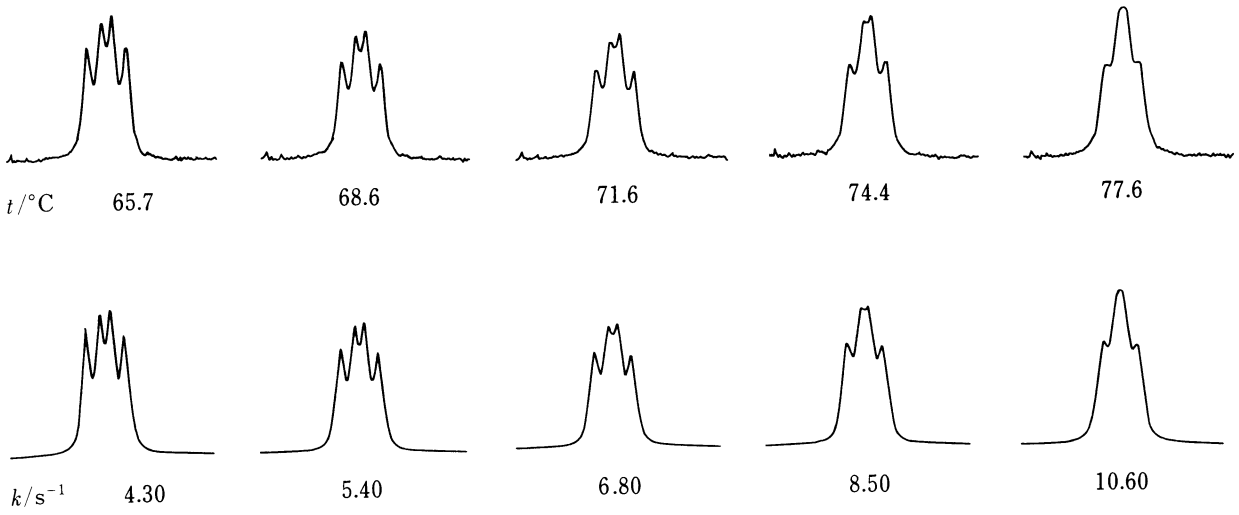


Fig. 1. Observed (top) and calculated (bottom) line shapes for the isopropyl-methyl protons in trans-dichloro(4-methyl-1-pentene)(4-methoxycarbonylpyridine 1-oxide)platinum(II) at various temperatures

The interesting point here is that we do not observe significant solvent effects on the rate of dissociation and consequently on the activation parameters. Therefore, we prefer to postulate that the dissociation of the olefin takes place here in a dissociative manner. Incidentally some of the reactions of the square planar platinum(II) complexes are known to take dissociative processes, though many of them proceed in associative manner.[16] The entropy of activation might support the above postulate, because in the associative reactions the entropy of activation is known to be large negative,[13] whereas the observed ones are close to zero, in addition to the fact that Romeo et al. observed small positive entropy of activation for dissociative reactions.[17] However, we wish to defer the

Table 1. Kinetic parameters for the racemization of trans-dichloro-(4-methyl-1-pentene)(4-methoxycarbonylpyridine 1-oxide)platinum(II) in two solvents[a)]

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{323}$/kcal mol^{-1}
$CDBr_3$	17.6 ± 0.5	-2.7 ± 1.3	18.4
$C_2D_2Cl_4$	19.0 ± 0.5	2.7 ± 2.7	18.2

a) 1 cal = 4.184 J

detailed discussion on the entropy of activation until some more data are accumulated, because literature values of entropy of activation are sometimes positive for the associative reactions,[12] and sometimes negative for the dissociative reactions.[18]

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References

1) Part XI of the series, Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation: for Part X, see T. Morita and M. Ōki, Bull. Chem. Soc. Jpn., 59, 3605 (1986).
2) "Dynamic Nuclear Magnetic Resonance Spectroscopy," ed by L. M. Jackman and F. A. Cotton, Academic Press, New York (1975).
3) M. Ōki, "Applications of Dynamic NMR Spectroscopy to Organic Chemistry," VCH Publishers, Deerfield Beach (1985).
4) M. Ōki, M. Ohira, Y. Yoshioka, T. Morita, H. Kihara, and N. Nakamura, Bull. Chem. Soc. Jpn., 57, 2224 (1984).
5) M. Ōki and M. Ohira, Bull. Chem. Soc. Jpn., 57, 3025 (1984).
6) M. Ōki and M. Ohira, Bull. Chem. Soc. Jpn., 57, 3117 (1984).
7) G. Binsch, E. L. Eliel, and H. Kessler, Angew. Chem., Int. Ed. Engl., 10, 570 (1971).
8) R. S. Cahn, C. Ingold, and V. Prelog, Angew. Chem., Int. Ed. Engl., 5, 385 (1966).
9) R. Cramer, Inorg. Chem., 4, 445 (1965).
10) G. Paiaro and A. Panunzi, J. Am. Chem. Soc., 86, 5148 (1964).
11) A. Panunzi and G. Paiaro, J. Am. Chem. Soc., 88, 4843 (1966).
12) S. Miya, K. Kashiwabara, and K. Saito, Inorg. Chem., 19, 98 (1980).
13) K. Konya, J. Fujita, H. Kido, and K. Saito, Bull. Chem. Soc. Jpn., 45, 2161 (1972).
14) H. H. Jaffe and G. O. Doak, J. Am. Chem. Soc., 77, 4441 (1955).
15) G. Binsch, Top. Stereochem., 3, 97 (1968).
16) G. K. Anderson and R. J. Cross, Chem. Soc. Rev., 9, 185 (1980).
17) G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, J. Chem. Soc., A, 1971, 1877.
18) K. Romeo, D. Minniti, and M. Trozzi, Inorg. Chem., 15, 1134 (1976).

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