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Novel Diastereotopic Isomerism of a Styrene Complex of Pt(II) Containing the η^3-Methallyl Ligand

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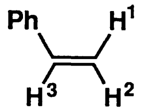
The ^{1}H NMR NOE experiments on Pt(η^3-CH_2CMeCH_2)(styrene)(C_6F_5) indicated that the configuration of the major isomer in $CDCl_3$ solution is similar to that in the solid state determined previously by X-ray analysis. The minor isomer corresponds to a diastereomer of the major isomer, where both isomers contain the C=C bond lying almost in the coordination plane. The interconversion between the two isomers was suggested to be an intramolecular process.

Olefin complexes of transition metals containing η^3-allyl ligands have received increasing attention from both coordination$^{1)}$ and synthetic$^{2)}$ chemical points of view. Very few works, however, paid attention to the structural aspect of these complexes in solution. Following the determination of the novel olefin geometry in Pt(η^3-CH_2CMeCH_2)(styrene)(C_6F_5) (1) *in the solid state*,$^{1a)}$ we thought it of special interest to examine detailed solution behaviors of 1 because the styrene ligand in this type of complex is expected to take multiple coordination geometries due to both rotational and diastereotopic isomerisms.$^{3)}$ Herein reported are new results concerning these aspects gained by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of 1 at 25 °C (Fig. 1a) shows the presence of two isomeric forms (1-maj and 1-min; relative ratio 3:1). All of the styrene and methallyl proton resonances could unambiguously be assigned as shown in 2 and 3 ($H^{1'} \sim H^{7'}$ for the minor isomer) on the basis of the following criteria; 1) the NOE experiments described later identify a pair of allylic anti and syn protons (H^4 and H^5, H^7 and H^6) attached to the same carbon; 2) the anti proton resonates at the higher field than the corresponding syn proton;$^{3b,4)}$ 3) the J_{Pt} values for the allylic protons well reflect the ligand trans-influence which is larger for C_6F_5 than olefinic ligands;$^{4,5)}$ thus, for example, J_{Pt-H^4} (61 Hz) is larger than J_{Pt-H^7} (40 Hz).

When crystals of 1 were dissolved in $CDCl_3$ at -60 °C, only a single set of resonances due to 1-maj was detected. Gradual isomerization of 1-maj to 1-min was observed, and an equilibrium mixture was obtained in ca. 8 h at 0 °C and within 5 min at 25 °C. The following NOE experiments strongly indicate that 1-maj assumes a configuration 4 which is similar to that determined by the X-ray diffraction. Thus, selective irradiation at H^3 and H^6 (Figs. 1b, 1c) resulted in small (3% and 1%), but distinct enhancement of the intensity of H^6 and H^3 resonances, respectively, suggesting a relatively short distance between H^3 and H^6. This distance is estimated ca. 2.6 Å by the X-ray analysis. The diastereoisomer of 4, namely 5 is



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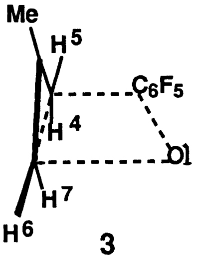

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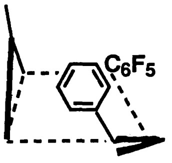

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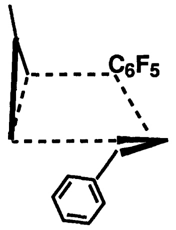

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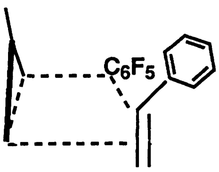

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also consistent with the NOE experiments. However, it seems natural to assume that the diastereomeric identity of the solid state structure is retained in **1**-maj as detected initially upon dissolution.

An alternative configuration **6** which also has a short H^3----H^6 distance can be ruled out,$^{6)}$ since this configuration should give any NOE enhancement not only for H^3 but also H^2 on irradiating H^6.$^{7)}$ Exclusion of **6** from possible configurations for the major isomer is also supported by the stability trend of an ortho-methylstyrene complex, $Pt(\eta^3\text{-}CH_2CMeCH_2)(CH_2{=}CHC_6H_4Me\text{-}o)(C_6F_5)$ (**7**); i.e. we found that the stability constant$^{8)}$ of **7** is considerably smaller than **1** (by 1/1.9) and $Pt(\eta^3\text{-}CH_2CMeCH_2)(CH_2{=}CHC_6H_4Me\text{-}p)(C_6F_5)$ (by 1/2.5). The reason may be that the ortho-methyl substituent would experience considerable steric interaction with H^6 in a geometry analogous to **4**; NOE confirmed a short distance between o-Me and H^6. If **6** were the actual solution configuration, the stability of **7** would be comparable to or greater than **1** and the para-methylstyrene analog, as was demonstrated previously in the authentic perpendicular olefin complexes.$^{1b)}$

We also carried out similar NOE experiments for **1**-min (e.g. Fig. 1d) to find a short distance between $H^{3'}$ and $H^{6'}$. It thus seems unlikely that **1**-min corresponds to a rotamer of **4** in which the C=C bond in **4** has rotated by 180° about the Pt-olefin bond axis. Presence of another rotamer **6** may also be excluded$^{6)}$ by the result of Fig. 1d showing no NOE enhancement of $H^{2'}$. Moreover, molecular models suggested non-existence of any sufficiently high energy transition state during the rotation from **4** to **6** as to allow the appearance of two separate resonances due to **4** and **6** at 25 °C. We now suggest that **5** is the structure of **1**-min. The unusually high field shift of the $H^{7'}$ resonance in the minor isomer is also consistent with the structure **5**, since in this configuration $H^{7'}$ would lie in a region where it experiences the diamagnetic shielding effect of the phenyl ring of styrene.

It seems of further interest to note that the rate of isomerization from **1**-maj to **1**-min, at both 0 °C and 25 °C, was not affected by adding free styrene (2 equiv.), and much faster than the intermolecular olefin ligand exchange in the presence of comparable amounts of the free olefin.$^{9)}$ This is somewhat unusual, since the rate of interconversion between the isomers arising from coordination of prochiral olefins in the traditional Pt(II) complexes was strongly enhanced by the addition of free olefin.$^{10)}$ The above evidence strongly suggests that the isomerization between **1**-maj and **1**-min does not proceed via dissociation of the coordinated styrene, but through intramolecular mechanism(s).

A few mechanisms are possible which lead to an apparent diastereotopic interconversion of **1** (**4**$\rightleftharpoons$**5**); 1) a 180° rotation of the methallyl plane about the Pt-allyl bond axis; 2) temporary η^3-allyl to η^1-allyl conversion at either of the η^3-allyl

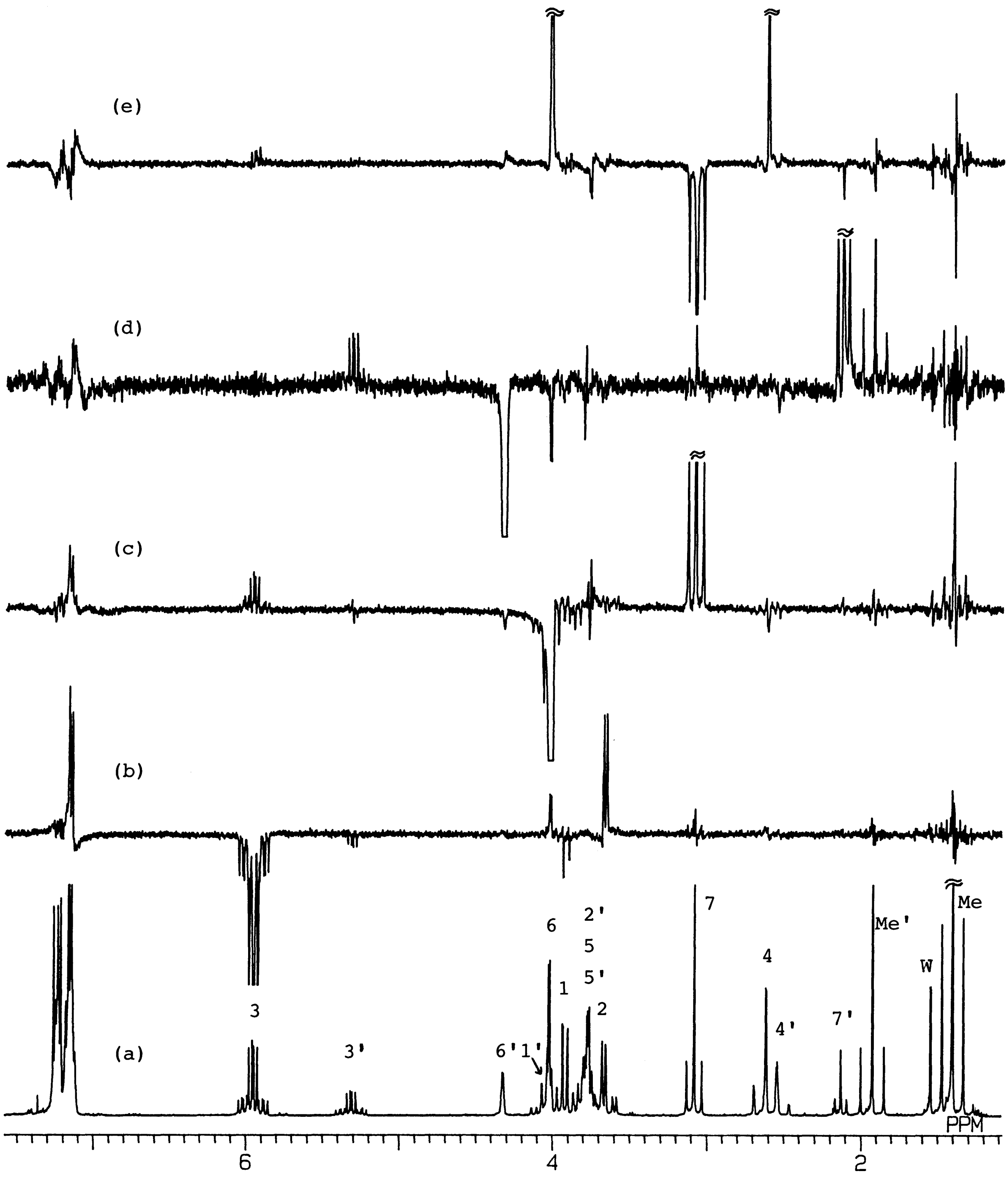

Fig. 1. 400 MHz ^1H NMR (a) and NOE difference (b-e) spectra of $\underset{\sim}{1}$ in $CDCl_3$ at 25°C. Selective irradiation at H^3 (b), H^6 (c), $H^{6'}$ (d), and H^7 (e). Overlapping $H^{2'}$, H^5, and $H^{5'}$ could be assigned by NOE difference spectra irradiating at $H^{3'}$, H^4, and $H^{4'}$, respectively. ^{195}Pt satellites are recognized except for $H^{2'}$, H^5, $H^{5'}$, H^6, and $H^{6'}$. W denotes H_2O.

terminals, followed by re-coordination of the C=C bond using an enantioface opposite to the original one; 3) enantioface inversion of the styrene ligand itself through an η^1-olefin intermediate (Pt-terminal carbon bonding). The possibility 1 can easily be excluded, since the NOE experiments exhibiting weak spin saturation transfer phenomena (e.g. $H^7 \rightarrow H^{7'}$ in Fig. 1e) suggest that there occurs chemical exchange between H^7 and $H^{7'}$, but not between H^7 and $H^{4'}$, the latter exchange being expected from the mechanism 1. Further studies are in progress to elucidate the precise mechanism of the present isomerization reaction.

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3) The X-ray analyses revealed that the conformations of styrene in **1**[1a)] and Pt(η^3-CH_2CMeCH_2)(styrene)($SnCl_3$)[3b)] are related to each other by an approximately 180° rotation about the Pt-olefin bond axis; b) A. Musco, R. Pontellini, M. Grassi, A. Sironi, S. V. Meille, H. Ruegger, C. Ammann, and P. S. Pregosin, Organometallics, 7, 2130 (1988).

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6) Extended Hückel MO calculations on a model Pt(η^3-CH_2CHCH_2)(CH_2=CH_2)(CH_3) suggested[1a)] that the energy of the configuration having ethylene within the coordination plane is almost the same as that having ethylene perpendicular to the plane, but the bond strength between Pt and ethylene is somewhat larger in the in-plane than the perpendicular configuration. We assume that the latter calculation better simulates the relative stability (i.e. **4** more stable than **6**).

7) The X-ray result shows that H^6 is located almost on the coordination plane.

8) The stability constant is defined as the equilibrium constant of the equilibrium between [**1** + substituted styrene] and [substituted styrene complex + styrene].

9) As in the slow ligand exchange observed at 25 °C,[1a)] we also found that at 0 °C substitution of para-chlorostyrene for styrene in **1** was only ca. 10% complete at 5 h after adding para-chlorostyrene (1 equiv.) to a $CDCl_3$ solution of **1**.

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