A ^{13}C AND ^{31}P N.M.R. INVESTIGATION OF RESTRICTED ROTATION IN [Pt(η^3-ALLYL){P(CYCLOHEXYL)$_3$}$_2$]$^+$[PF$_6$]$^-$ AND RELATED COMPOUNDS

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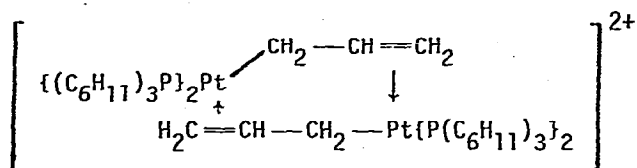C.N.R. Istituto di Chimica delle Macromolecole, Via E. Bassini 15,

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Summary

The dynamic behaviour of [Pt(η^3-allyl){P(cyclohexyl)$_3$}$_2$]$^+$[PF$_6$]$^-$ has been reinvestigated, and the earlier interpretation of restricted rotation about the Pt—P endorsed. The activation parameters were obtained. [Pt(η^3-allyl)(PPr^i$_3$)$_2$]$^+$[PF$_6$]$^-$ behaves similarly, while it has not proved possible to stop the rotation in [Pt(η^3-allyl){P(CH$_2$Ph)$_3$}$_2$]$^+$[PF$_6$]$^-$.

INTRODUCTION

As a result of work on Pd(PR$_3$)$_n$ [1] and Pt(PR$_3$)$_n$ [2], R = alkyl, phenyl, or p-tolyl; n = 2, 3, or 4, we have been interested in the inter-ligand interactions found in these compounds. The qualitative observation for [Pt(η^3-C$_3$H$_5$){P(C$_6$H$_{11}$)$_3$}$_2$]$^+$ of a dynamic process [3], which was attributed to restricted rotation about the platinum-phosphorus bond, offered the possibility of a further examination of this behaviour as a function of tertiary phosphine. It was not clear whether the dynamic process was really due to restricted rotation or to other causes, e.g.,

a structure, I, analogous to that found for [Pt(allyl)(acac)]$_2$ [4], had not

been unambiguously eliminated. Recently, there has been suggested an

$$\left[\begin{array}{c} \{(C_6H_{11})_3P\}_2Pt \overset{\displaystyle CH_2 - CH = CH_2}{\underset{\displaystyle H_2C = CH - CH_2 - Pt\{P(C_6H_{11})_3\}_2}{\Big\downarrow}} \end{array} \right]^{2+}$$

I

alternative interpretation of the dynamic process based on the presence of

two conformers in the crystal [5].

RESULTS AND DISCUSSION

In CD_2Cl_2/CH_2Cl_2 at room temperature, the ^{13}C n.m.r. spectrum gave the

expected spectrum for $[Pt(\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2]^+$ with signals due to the

allyl group at $\delta(^{13}CH_2)$ = 62.3, d, $|\underline{N}\{^2\underline{J}(^{31}P,\ ^{13}C)_{\underline{trans}} + ^2\underline{J}(^{31}P,\ ^{13}C)_{\underline{cis}}\}|$ =

29 Hz, $^1\underline{J}(^{195}Pt,\ ^{13}C)$ = 67 Hz, and $\delta(^{13}CH)$ = 113.8 (no resolved coupling)

and due to the tertiary phosphine, $\delta(^{13}C^1)$ = 37.8, d, $|\underline{N}\{\underline{J}(^{31}P,\ ^{13}C) +$

$^3\underline{J}(^{31}P,\ ^{13}C)\}|$ = 27 Hz, $^2\underline{J}(^{195}Pt,\ ^{13}C)$ = 34 Hz; $\delta(^{13}C^2)$ = 30.8,

$^3\underline{J}(^{195}Pt,\ ^{13}C)$ = 20 Hz; $\delta(^{13}C^3)$ = 27.9, $|\underline{N}\{^3\underline{J}(^{31}P,\ ^{13}C) + ^5\underline{J}(^{31}P,\ ^{13}C)\}|$ =

8 Hz; $\delta(^{13}C^4)$ = 26.5. On cooling to -80° to freeze out the dynamic

process, the changes in the allyl ligand signal are minimal. The $^{13}CH_2$

signal became a poorly resolved triplet which could be considered to

consist of two overlapping doublets at $\delta62.8$ and $\delta61.6$ while no significant

changes occurred to the allyl ^{13}CH signal at $\delta113.9$. Major changes

occurred to the $P(C_6H_{11})_3$ ^{13}C n.m.r. signal which became a mass of

overlapping signals, with a new signal at $\delta41.9$. It is clear that these

observations show that the solution structure is not I for three reasons.

Firstly, the σ-bonded CH_2 group in I would be expected to occur between

$\delta0$ and $\delta30$ [6]. Secondly, for the σ-bonded CH_2 group in I, $^1\underline{J}(^{195}Pt,\ ^{13}C)$

would be expected to be larger than 400 Hz. As the averaged $^1\underline{J}(^{195}Pt,\ ^{13}C)$

is 67 Hz, this would require $^1\underline{J}(^{195}Pt,\ ^{13}C)$ for the π-bonded olefinic CH_2

group to be more negative than -250 Hz, an improbable requirement. Thirdly, $J(^{195}Pt, ^{13}C)$ is observed at room temperature for both the allyl and $P(C_6H_{11})$ groups. Consequently both allyl and $P(C_6H_{11})_3$ exchange must be slow on the n.m.r. time scale. This requires that the break-up of I into monomers is slow, yet the X-ray structure [5] shows the structure to be monomeric. Consequently it can be concluded that I is not significantly present in solution.

The remaining two interpretations of the dynamic process are readily resolved by ^{31}P n.m.r. spectra. At room temperature, the $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Pt(\eta^3-C_3H_5)\{P(C_6H_{11})_3\}_2]^+[PF_6]^-$ consists of a singlet at $\delta28.4$ with $^1J(^{195}Pt, ^{31}P)$ = 3777 Hz and a septet due to the $[PF_6]^-$ anion. On cooling to -74°C, the signals broaden, separate, and finally gives an AB spectrum with ^{195}Pt satellites, see Figure 1. The two ^{31}P signals are at
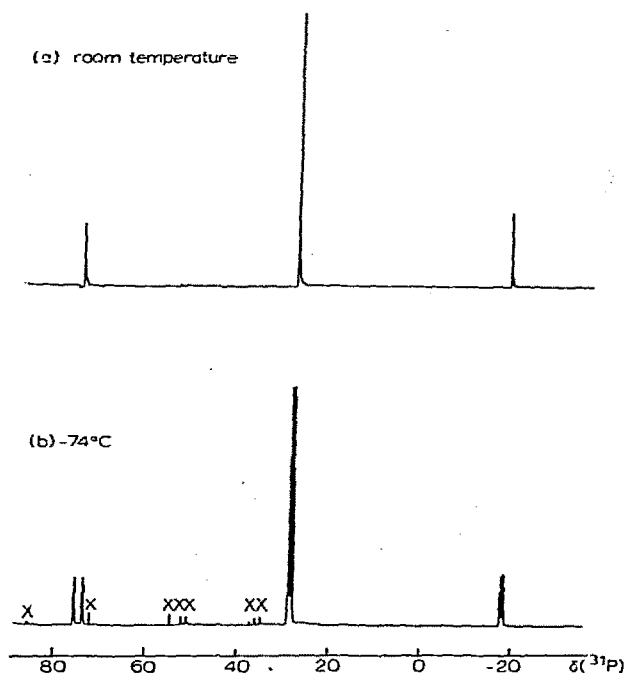

Figure 1. The ^{31}P n.m.r. spectrum of $[Pt(\eta^3-C_3H_5)\{P(C_6H_{11})_3\}_2]^+$ in CH_2Cl_2 at (a) room temperature and (b) -74°C. Note that at -74°C some impurity signals (x) are visible.

$\delta 28.4$, $^1J(^{195}Pt, {}^{31}P) = 3804$ Hz, and $\delta 27.7$, $^1J(^{195}Pt, {}^{31}P) = 3705$ Hz. The observation of $^2J(^{31}P, {}^{31}P) = 6$ Hz clearly shows that the two phosphorus environments are within the same molecular ion. This observation is completely consistent with the original interpretation in terms of rotamers [3], and is completely inconsistent with the recent interpretation in terms of two conformers [5]. A full variable temperature ^{31}P n.m.r. study was performed. The most easily followed lineshape changes occurred in the high frequency ^{195}Pt satellites, see Figure 2. A lineshape analysis of the AB exchange problem was performed for each set of three signals to give the rates:- $-60°C$, 21 s^{-1}; $-49.5°C$, 48 s^{-1}; $-38°C$, 135 s^{-1}; $-27°C$, 442 s^{-1}; $-19°C$, 720 s^{-1}; and $-11°C$, 1650 s^{-1}. An Eyring rate plot gave $\Delta \underline{G}^{\dagger}_{240} = 11.3$ kcal mole^{-1}, $\Delta \underline{H}^{\dagger} = 9.4 \pm 0.5$ kcal mole^{-1}, and $\Delta \underline{S}^{\dagger} = -7.9 \pm 1.7$ cal deg^{-1} mole^{-1}, one standard deviation being given.

The motion of $[Pt(\eta^3-C_3H_5)(PPr^i_3)_2]^+$ proved to be more difficult to freeze out, but at $-101°C$, the ^{31}P n.m.r. spectrum in CD_2Cl_2/CH_2Cl_2 gave an AB n.m.r. spectrum with signals at $\delta 38.2$, $^1J(^{195}Pt, {}^{31}P) = 3728$ Hz and $\delta 37.7$, $^1J(^{195}Pt, {}^{31}P) = 3830$ Hz $^2J(^{31}P, {}^{31}P) = 7$ Hz. At room temperature, the ^{31}P n.m.r. spectrum consists of a singlet at $\delta 39.3$ with
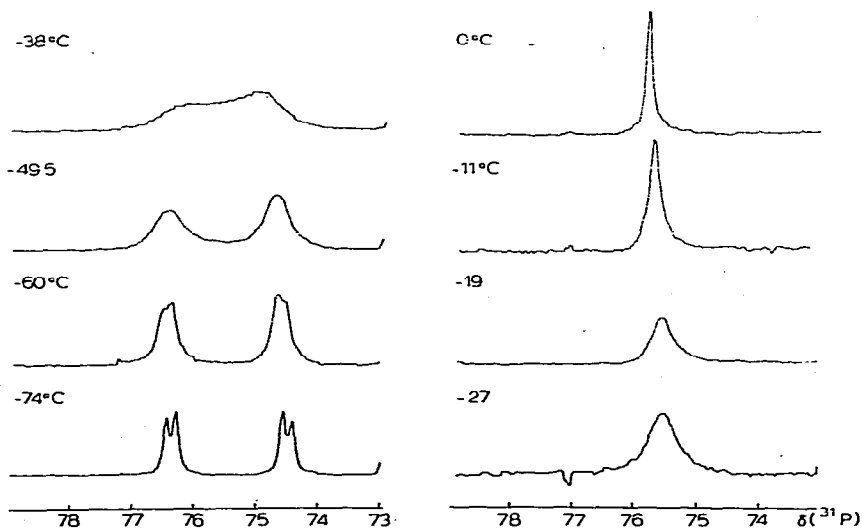

Figure 2. The variable temperature ^{31}P n.m.r. spectrum of the high frequency satellites of $[Pt(\eta^3-C_3H_5)\{P(C_6H_{11})_3\}_2]^+$ in CH_2Cl_2.

$^1\underline{J}(^{195}Py, {}^{31}P)$ = 3812 Hz. A complete variable temperature ^{31}P n.m.r. investigation was not performed, but $\Delta\underline{G}^{\dagger}_{194}$ = 8.9 kcal mole^{-1}. No effects attributable to restricted rotation was observed in the low temperature ^{31}P n.m.r. spectrum of $[Pt(n^3-C_5H_5)\{P(CH_2Ph)_3\}_2]^+[PF_6]^-$. This would suggest a somewhat lower value of $\Delta\underline{G}^{\dagger}$ in this case.

The nature of the dynamic process is not proven by this work, but the most reasonable interpretation is the one given earlier by Clark [3], namely restricted rotation about the platinum-phosphorus bond. This explanation appears to be very reasonable in view of the crystal structure which shows two different $P(C_6H_{11})_3$ rotamers in each molecular ion. Other explanations such as different rotamers about the phosphorus-carbon bond, a cyclohexyl ring being in the boat conformation, or the allyl group being skewed with respect to the P, Pt, P plane appear to be unlikely.

The measured interactions is that between the ground state and a twisted excited state. The tricyclohexylphosphine ligand is far from spherical, and the cyclohexyl groups intermesh in the ground state [5]. As interaction potentials increase rapidly as atoms approach one another, it is reasonable to suppose that the ground state inter-ligand repulsion energy is probably considerably smaller than the found $\Delta\underline{H}^{\dagger}$, i.e., not more than a few kilocalories per mole. This view is consistent with the interpretation of the instability of $Pt\{P(C_6H_{11})_3\}_3$ given previously [7].

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