

N.M.R. Studies of Ligand Exchange on Acetylacetonatotrimethylplatinum(IV)

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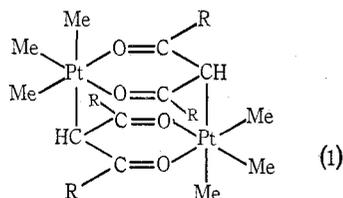
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Abstract

A quantitative analysis of the variable-temperature ¹H n.m.r. spectra of acetylacetonatotrimethylplatinum(IV) has been made. In CDCl₃ solution the exchange of acetylacetonate ligands is a first-order reaction and proceeds predominantly by dissociation of the dimer into two separated five-coordinate activated complexes. The activation energy is 61.5 ± 0.8 kJ mol⁻¹.

Introduction

The compound PtMe₃(di-n-butyrylmethane) has been shown to be dimeric in the solid state,^{1,2} with the β-diketone ligand coordinated through two oxygen atoms to one platinum atom and through the central (γ) carbon atom to the second platinum atom, as shown (1; R = Pr). A number of complexes of the type PtMe₃(β-dicarbonyl) have been prepared and shown to be dimeric in benzene solution,^{3,4} which suggests that in each case a structure similar to that of (1) persists in solution.



In the ¹H n.m.r. spectra of trimethylplatinum(IV) compounds, the proton chemical shifts of the methyl groups bonded to platinum and the ¹⁹⁵Pt-¹H coupling constants (¹⁹⁵Pt, *I* = 1/2, 34% abundance) have been found to depend on the ligands in the *trans* positions.⁵⁻⁷ In principle, then, for [PtMe₃(acac)]₂ (1; R = Me) two methylplatinum resonances in the intensity ratio of 2 : 1 with different chemical shifts and different ¹⁹⁵Pt-¹H coupling constants would be expected. However, at 60 MHz the methylplatinum spectrum of [PtMe₃(acac)]₂ at 303 K in both benzene and CDCl₃

¹ Swallow, A. G., and Truter, M. R., *Proc. Roy. Soc. A*, 1960, **254**, 205.

² Hargreaves, R. N., and Truter, M. R., *J. Chem. Soc. A*, 1969, 2282.

³ Chatterjee, A. K., Menzies, R. C., Steel, J. R., and Youdale, F. N., *J. Chem. Soc.*, 1958, 1706.

⁴ Hall, J. R., and Swile, G. A., *J. Organometal. Chem.*, 1970, **21**, 237.

⁵ Kite, K., Smith, J. A. S., and Wilkins, E. J., *J. Chem. Soc.*, 1966, 1744.

⁶ Clegg, D. E., and Hall, J. R., *Aust. J. Chem.*, 1967, **20**, 2025.

⁷ Clegg, D. E., Hall, J. R., and Swile, G. A., *J. Organometal. Chem.*, 1972, **38**, 403.

was found to consist of a single 1 : 4 : 1 triplet.⁵ Variable-temperature n.m.r. spectra in CDCl_3 solution of several compounds of the type $[\text{PtMe}_3(\beta\text{-dicarbonyl})]_2$ indicated that a kinetic process involving a rapid breaking of the Pt-C $_{\gamma}$ bond was responsible for the simpler spectra observed at higher temperatures.⁴

The present paper describes a quantitative analysis of this exchange process for $[\text{PtMe}_3(\text{acac})]_2$ based on the resonances of the platinum-methyl protons and the acetylacetonate γ -proton.

Experimental

$[\text{PtMe}_3(\text{acac})]_2$ was prepared by reaction of $\text{Na}(\text{acac}) \cdot 2\text{H}_2\text{O}$ with $[\text{PtMe}_3]_2 \text{SO}_4 \cdot 4\text{H}_2\text{O}$ in ethanol as described previously.⁸ ^1H n.m.r. spectra were run in CDCl_3 at 90 MHz on a Bruker spectrometer fitted with a variable-temperature probe. The solution (concentration 0.088M) was internally referenced with Bu^tOH ; the chemical shifts were as reported previously.⁴

Results and Discussion

At 249 K the ^1H n.m.r. spectrum of $[\text{PtMe}_3(\text{acac})]_2$ in CDCl_3 showed two methyl-platinum triplets in the intensity ratio of 2 : 1 with a chemical shift difference of 0.1 p.p.m. between the main peaks. The values of $^2J(^{195}\text{Pt}-\text{CH}_3)$ are 75.1 and 73.3 Hz respectively. The methyl protons on the acetylacetonate ligand show no observable coupling with either of the ^{195}Pt nuclei or the central (γ) proton. However, the γ -proton is coupled to the nearer ^{195}Pt nucleus and the spectrum indicates that $^2J(^{195}\text{Pt}-\text{CH}_{\gamma})$ has a magnitude of 42 Hz.

As the temperature is raised the two CH_3 -Pt peaks merge, until at about 303 K there is a single main methyl-platinum resonance with averaged satellite peaks; the relative intensities are 1 : 4 : 1 and $^2J(^{195}\text{Pt}-\text{CH}_3)$ is equal to 74.8 Hz. Analysis of the averaging of the CH_3 -Pt peaks was made analogously to that used for exchange of aqua groups on the aquabipyridinetrimethylplatinum(IV) cations,⁹ i.e. by using a superposition of three separate two-site exchanges (weights 0.66, 0.17, 0.17) between pairs of sites whose relative populations are 2/3 (methyl groups *trans* to O) and 1/3 (methyl groups *trans* to CH). Computer-simulated spectra were calculated and the methyl pre-exchange lifetimes, τ_{Me} , were obtained by visual comparison of experimental and computed spectra.

For the γ -proton, the 1 : 4 : 1 pattern broadens as the temperature is raised, and gradually the satellites coalesce under the central peak, which reaches a maximum width of 11 Hz at about 300 K. As the temperature is raised further the main peak sharpens again but without satellites. This behaviour is consistent with a random intermolecular exchange process between the γ -carbon of the acetylacetonate ligand and Pt nuclei in different magnetic states (spin quantum numbers +1/2, -1/2 for spin one-half ^{195}Pt nuclei and 0 for spin zero Pt nuclei). The exchange-modified Bloch equations for this system have been used to derive computer-simulated spectra as a function of τ_{γ} , the pre-exchange lifetime for the C $_{\gamma}$ -Pt bond dissociation. Visual comparison of spectra yielded τ_{γ} values over the temperature range 273-330 K. Since $[\text{PtMe}_3(\text{acac})]_2$ has an unfavourable temperature coefficient of solubility, the order of the reaction was studied at 313 K. At this temperature the γ -proton signal has started to sharpen again, but its width (6.5 Hz) is still large enough for accurate τ_{γ} values (see

⁸ Hall, J. R., and Swile, G. A., *J. Organometal. Chem.*, 1973, **47**, 195.

⁹ Clegg, D. E., Hall, J. R., and Ham, N. S., *Aust. J. Chem.*, 1970, **23**, 1981.

Fig. 1). When the concentration was halved, the line-width of the γ -proton peak was unchanged; τ_γ is thus independent of concentration and we conclude that the reaction is of the first order.

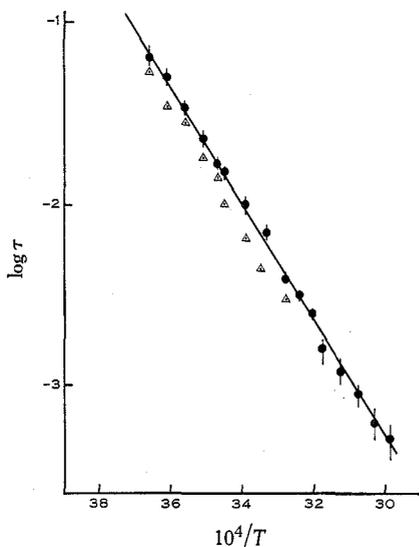


Fig. 1. Arrhenius plot for ligand exchange reaction of acetylacetonatotrimethylplatinum(IV) in CDCl_3 :
 Δ , τ_{Me} ;
 \bullet , τ_γ .
 Solid line from least-squares fit using τ_γ values; activation energy $61.5 \pm 0.8 \text{ kJ mol}^{-1}$.
 Error bars on τ_γ points are from $\pm 0.25 \text{ Hz}$ estimated error in the line-width of broadened peaks.

The methyl-platinum group pre-exchange lifetimes and the pre-exchange lifetimes obtained from the γ -carbon proton are shown in an Arrhenius plot in Fig. 1. From τ_γ values the reaction activation energy is 61.5 kJ mol^{-1} with a standard deviation of $\pm 0.8 \text{ kJ mol}^{-1}$. Because of the small chemical shift difference between the methyl-platinum peaks, τ_{Me} was available for a smaller temperature range than τ_γ .

It has been established previously⁴ that the exchange process occurring in a number of β -dicarbonyl complexes of trimethylplatinum(IV) involves breaking of the Pt-C $_\gamma$ bonds. The first-order reaction implies that the reaction proceeds by the dissociation of the platinum dimer into two separated five-coordinate activated complexes, with the consequence that there is a negligible chance of one ruptured Pt-C $_\gamma$ bond reforming at the same Pt and C $_\gamma$ atoms. Thus each dissociation leads to intermolecular exchange between the Pt atoms, and it follows that the methyl and γ -proton pre-exchange lifetimes should be the same and equal to the reciprocal of the rate constant k_1 for dimer dissociation. After allowing for experimental error it is observed that τ_γ is somewhat greater than τ_{Me} , so that it seems that there is a small contribution from another mechanism which can render the methyl groups equivalent. Such a mechanism might involve dissociation of the dimer to a solvent-caged monomer pair, followed by recombination before the monomers diffuse apart. Alternatively some intramolecular rearrangement could also occur following breaking of only one Pt-C $_\gamma$ bond.

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