

Preliminary communication

**FLUXIONAL FIVE-COORDINATE PLATINUM(II) COMPLEXES CONTAINING CHELATING TRIPHOSPHINE LIGANDS**

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Summary

Platinum(II) dimethyl complexes of the three triphosphines  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ ,  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ , and  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$  have been shown by  $^{31}\text{P}$  NMR to undergo exchange of the terminal phosphino groups. An exchange route involving a five-coordinate platinum(II) complex is proposed.

We have taken advantage of the strong covalent Pt—C bond and the strong coordination tendency of chelating triphosphine ligands to study a series of five-coordinate dimethylplatinum(II) complexes. The compounds were prepared by treating  $\text{Pt}(\text{CH}_3)_2(1,5\text{-COD})$  (COD = cyclooctadiene) [1] with each of the ligands  $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  (ttp),  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  (etp), and  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$  (dmetp).

Figure 1 shows the temperature dependence of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Pt}(\text{CH}_3)_2(\text{ttp})$ . The low-temperature limiting spectrum (obtained at  $0^\circ\text{C}$ ) is an [AB] pattern, together with the corresponding satellites due to the 33.6% natural  $^{195}\text{Pt}$ ; the spectrum is consistent with two bonded phosphorus nuclei and one uncoordinated, terminal phosphorus atom. At higher temperatures the peaks due to the two terminal phosphorus nuclei broaden and the coupling between the bonded terminal phosphorus nucleus and platinum is lost, whereas the Pt—P coupling to the central phosphorus atom is retained. The peaks assigned to the central phosphorus atom vary with temperature, indicating that the coupling constants between the central phosphorus nucleus and the two terminal ones change during the exchange process. One can stop the two terminal phosphino groups from undergoing exchange by removing the platinum-methyl groups and creating a vacant coordination site on the platinum atom. Thus, treatment of  $\text{Pt}(\text{CH}_3)_2(\text{ttp})$  with excess HCl (formed in situ by mixing acetyl chloride and methanol) gave  $[\text{PtCl}(\text{ttp})]\text{Cl}$ , whose  $^{31}\text{P}$

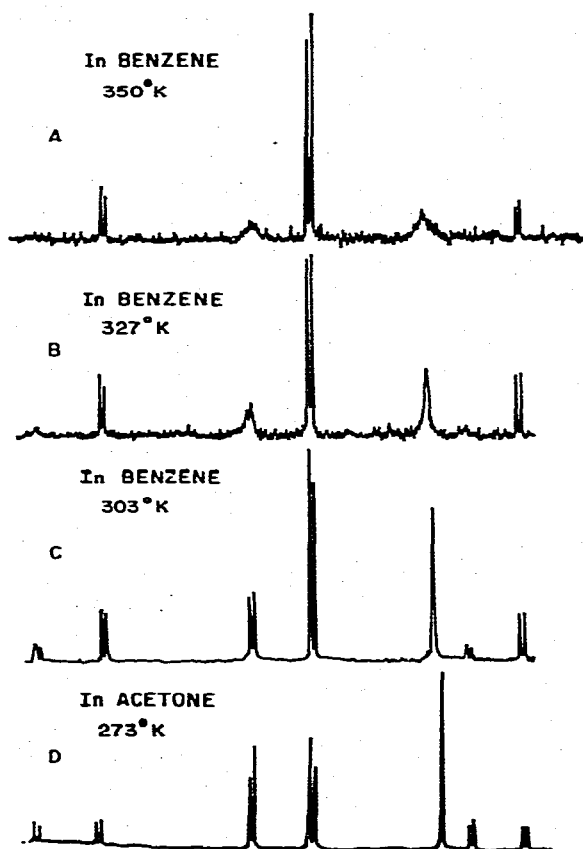


Fig. 1. Fourier-transform, proton-decoupled phosphorus-31 NMR spectra of  $\text{Pt}(\text{CH}_3)_2(\text{ftp})$  as a function of temperature.

NMR spectrum shows that all three phosphorus atoms are bonded in a square-planar platinum(II) complex [2].

The limiting  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (at  $-91^\circ\text{C}$ ) of  $\text{Pt}(\text{CH}_3)_2(\text{etp})$  (Fig. 2) demonstrates that *etp* also functions as a bidentate ligand toward  $\text{Pt}(\text{CH}_3)_2$  at low temperatures. At  $25^\circ\text{C}$  only a triplet with  $^{195}\text{Pt}$  satellites is seen; thus, the two terminal phosphorus nuclei become equivalent on the NMR time scale and couple equally to the central phosphorus nucleus. Similar behavior is observed in the variable temperature spectra of  $\text{Pt}(\text{CH}_3)_2(\text{dmetp})$ .

An interesting change in the magnitude of the P-P coupling constant was noted in the spectral data of these complexes. The P-P coupling constants for a 5-membered chelate ring is decreased, whereas that for the 6-membered chelate ring is increased compared to the  $J(\text{P}-\text{P})$  value of the free ligand. For example, the P-P coupling constants are 29 and 1 Hz in the *etp* and *ttp* ligands, respectively [3], and they are changed to  $\sim 0$  and 18 Hz in the corresponding dimethylplatinum(II) complexes. A similar effect has been observed

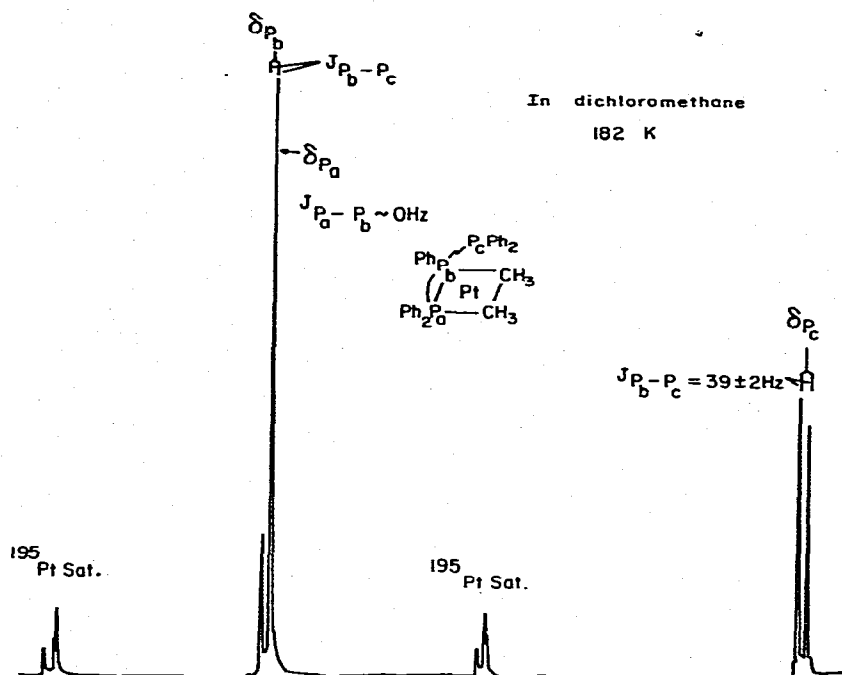
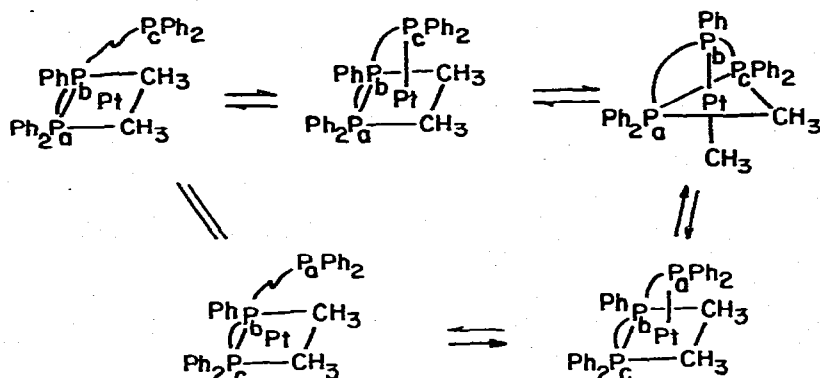


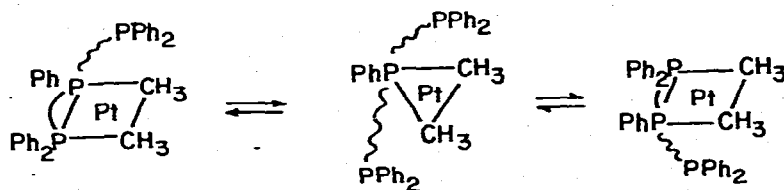
Fig. 2. Fourier-transform, proton-decoupled phosphorus-31 NMR spectrum of  $\text{Pt}(\text{CH}_3)_2(\text{etp})$  at 182 K in dichloromethane. Note that the chemical shifts of  $P_a$  and  $P_b$  are nearly coincidental.

previously [4,5]. This change on coordination may be rationalized as follows: (1) the  $J(\text{PP})$  value contains coupling contributions through both the hydrocarbon backbone and the metal center, i.e.  $J(\text{PP}) = {}^bJ(\text{PP}) + {}^mJ(\text{PP})$ ; and (2)  ${}^bJ(\text{PP})_{\text{complex}} = {}^bJ(\text{PP})_{\text{free ligand}}$  as suggested by Grim et al. [6]. In a five-membered chelate ring,  ${}^bJ(\text{PP})$  has a sign opposite to that of  ${}^mJ(\text{PP})$ , which leads to a smaller observed  $J(\text{PP})$  value.

From the spectral data we conclude that these  $\text{Pt}(\text{CH}_3)_2(\text{triphosphine})$  complexes undergo exchange of the bonded and free terminal phosphino groups via an intramolecular bond breaking process. Two such schemes can be constructed to explain the  ${}^{31}\text{P}\{^1\text{H}\}$  NMR spectra. Scheme 1 involves an associative process with two equivalent terminal phosphino groups in a five-coordinate intermediate, which is present in very small concentrations and is not detected by  ${}^{31}\text{P}$  NMR. Scheme 2 requires a dissociative process to form a three-coordinate platinum(II) intermediate. Three-coordinate platinum(II) intermediates have been suggested in the uncatalyzed *cis*  $\leftrightarrow$  *trans* isomerization of  $\text{PtRX}(\text{PEt}_3)_2$  complexes [7,10], in the thermal decomposition of  $\text{Pt}(\text{n-C}_4\text{H}_9)_2(\text{PPh}_3)_2$  [8], and in the mechanism of olefin insertion into a platinum-hydrogen bond [9,10]. We tend to favor Scheme 1 and the five-coordinate intermediate on the basis of precedent in cases where a platinum(II) complex is present with excess ligand, e.g., the dangling phosphino group. For

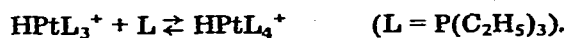


SCHEME 1



SCHEME 2

example, Jesson et al. [11] recently presented NMR spectroscopic evidence for a five-coordinate intermediate in the reaction



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