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^{31}P NMR STUDIES ON THE *MER–FAC* ISOMERIZATION OF $Pt(S_4N_4)Cl_2(PMe_2Ph)$

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Abstract—When heated in chloroform the meridional $S_4N_4^{2-}$ complex, $Pt(S_4N_4)Cl_2(PMe_2Ph)$, readily isomerizes, giving a product which has, on the basis of ^{15}N-labelling studies, been identified as the facial isomer.

Previously we have reported on the preparation of $Pt(S_4N_4)Cl_2(PMe_2Ph)$ (**1**), from the reaction of S_4N_4 with $[PtCl_2(PMe_2Ph)]_2$.[1] The product is only the second example of a complex of $S_4N_4^{2-}$, and the first to display a meridional coordination geometry i.e. with the coordinating atoms (two sulphurs and one nitrogen) in the same plane.

Here, we report on investigations into the isomerization of **1**. Although we have as yet been unable to grow crystals of the isomeric species, **2**, suitable for X-ray crystallographic confirmation, we have assigned a facial conformation on the basis of the ^{31}P NMR spectra of 99% ^{15}N-labelled samples of **1** and **2**, which show greatly contrasting magnitudes of ^{15}N–^{31}P coupling constants.

EXPERIMENTAL

General reaction conditions were as described previously; $[PtCl_2(PMe_2Ph)]_2$ was prepared by reaction of *cis*-$PtCl_2(PMe_2Ph)_2$ with $PtCl_2$ in xylene at $\approx$ 160°C.[2]

IR spectra were obtained using a PE 1720X instrument. ^{31}P NMR spectra were obtained (in $CDCl_3$) using a JEOL FX90Q operating at 36.21 MHz and are referred to 85% H_3PO_4. Microanalyses were performed by the Imperial College Service.

In a typical reaction a sample of *mer*-$Pt(S_4N_4)Cl_2(PMe_2Ph)$ (**1**) was prepared, as described previously, by reaction of S_4N_4 (70 mg, 0.38 mmol) with $[PtCl_2(PMe_2Ph)]_2$ (150 mg, 0.19 mmol) in CH_2Cl_2. Precipitation with hexane yielded the crude product (197 mg, 88%); it did not prove necessary to purify the compound before use (which can be done by elution on a Bio-beads gel-permeation column) since identical results were obtained using crude and purified samples. Compound **1** was dissolved in $CHCl_3$ ($\approx$ 25 cm^3) and the red solution heated to 75–80°C (under a nitrogen pressure of *ca* 5 psi); at intervals, ^{31}P NMR was used to assess the degree of isomerization by measuring the ratio of **1** (δ 5.2 ppm) to the isomer **2** (δ −9.4 ppm, $^1J(^{195}Pt–^{31}P)$ 2453 Hz). After 20 min the ratio of **1**:**2** was $\approx$ 3:1; after 40 min 1:1, after 90 min 1:4 and after 3 h the reaction had effectively gone to completion. Also present in the ^{31}P NMR of the product was a singlet at δ −21 ppm ($^1J(^{195}Pt–^{31}P)$ 3411 Hz), indicative of $Pt(S_2N_2H)Cl(PMe_2Ph)$[3] [Fig. 1(b)], and a compound revealed by a singlet at δ −18.0, ^1J 1995 Hz. The ratio of the complex at δ −9.4 to the combined amounts of the other two species was approximately 4:1.

The $CHCl_3$ was removed *in vacuo* and the product redissolved in CH_2Cl_2 (10 cm^3) then placed on a Bio-beads gel-permeation column and eluted with CH_2Cl_2. The sample separated into a number of bands; a fast moving brown band followed by a green and a red–orange fraction. The latter was collected, reduced in volume and a brown–red solid was obtained by addition of hexane (yield, 80 mg). The ^{31}P NMR spectrum of the product revealed the presence of the species at δ −9.4, together with a small amount of δ −21 and a trace of the species at δ −18. Slow diffusion of hexane into a CH_2Cl_2 solution yielded a crop of small clustered red crystals interspersed with white needles. The red crystals were separated by hand and redissolved in CH_2Cl_2.

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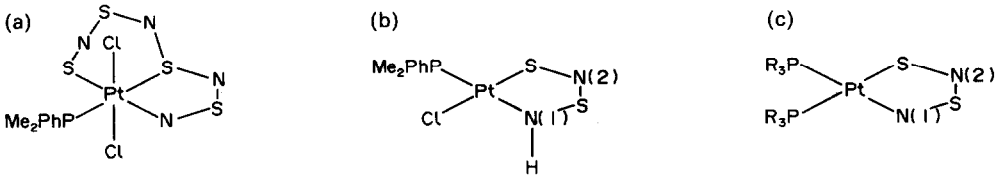

Fig. 1. Structures and numbering schemes of **1** and related compounds.

Slow hexane diffusion yielded poorly formed red crystals which were free of the white impurity. The ^{31}P NMR spectrum of these crystals revealed that they were the species responsible for the peak at δ −9.4 ppm, and they analysed correctly for $PtCl_2(S_4N_4)(PMe_2Ph)$; Found: C, 16.4; H, 1.6; N, 9.5. Calc.: C, 16.3; H, 1.9; N, 9.5%.

The reaction of $S_4^{15}N_4$ (19 mg, 0.1 mmol) with $[PtCl_2(PMe_2Ph)]_2$ (40 mg, 0.05 mmol) was performed as above and, after measurement of the ^{31}P NMR spectrum of the initial products, the chloroform solution was heated to 95°C for 3 h and the spectrum of the isomer recorded. No attempt was made to purify a sample of the ^{15}N-labelled species.

RESULTS AND DISCUSSION

The dimeric, chloro-bridged species $[PtCl_2(PMe_2Ph)]_2$ reacts with S_4N_4 at room temperature, in CH_2Cl_2, to give the platinum(IV) species $PtCl_2(S_4N_4)(PMe_2Ph)$ (**1**)[1] which contains a meridionally-coordinated tridentate $S_4N_4^{2-}$ ligand. This bonding mode is substantially different to that observed in $Ir(CO)Cl(S_4N_4)(PPh_3)$,[4] the only other $S_4N_4^{2-}$ complex known, in which the ligand adopts a facial geometry. In the light of this contrast in geometries we have attempted to assess the potential for isomerization within **1**. We have found that upon standing in solution for a number of days, or refluxing in chloroform for a few hours, **1** does indeed isomerize to a species which we believe contains a facial $S_4N_4^{2-}$ ligand.

If the chloroform solution of **1** is heated to $\approx$ 90°C, and the nature of the species in solution assessed by ^{31}P NMR, the amount of **1** present is seen to decrease and a new species, **2**, revealed by a singlet at δ −9.4 ($^1J(^{195}Pt–^{31}P)$ 2453 Hz), appears. After 3 h at this temperature there is complete conversion of **1** to **2**, together with small amounts of $Pt(S_2N_2H)Cl(PMe_2Ph)$ (**3**) (Fig. 1) and a complex at δ −18.0 (^1J 1995 Hz). Purification using a Biobeads gel-permeation column with CH_2Cl_2 as eluent, allows isolation of **2** along with traces of a colourless impurity. We have yet to fully characterize this impurity; its mass spectrum contains peaks at m/z 154 ($[\{PMe_2Ph\}NH_2]^+$), 293 ($[\{PMe_2Ph\}_2NH_3]^+$) and 307 ($[\{PMe_2Ph\}_2N_2H_3]^+$) with no evidence of the presence of sulphur.

We have not been able to grow crystals of **2** of sufficient quality to allow X-ray study, although they analyse correctly for $PtCl_2(S_4N_4)(PMe_2Ph)$, confirming that **2** is indeed an isomer of **1**. Furthermore, attempts to prepare crystalline samples of analogues of **1** and **2** ($PR_3 = PPh_2Me$, PEt_3) have been unsuccessful, the products (which by ^{31}P NMR are of the same type as **1** and **2**) being obtained as oils.

The large difference in the chemical shifts of the phosphine groups in **1** and **2**, 5.2 and −9.4 ppm, respectively, is indicative of a substantial change in geometry within the complexes, as is the fact that the IR spectrum of **2** contains strong peaks at 794 and 812 cm^{-1}, which are absent from the spectrum of **1**. Figure 2 illustrates some of the structures which **2** could, conceivably, adopt.

Insight into the structure of **2** can be obtained from the ^{31}P NMR spectrum of the ^{15}N-labelled complex. Figure 3 compares the ^{31}P spectrum of ^{15}N-labelled **1** with that of the isomer, **2**. As there is only one phosphine group present in **1** or **2**, the ^{31}P NMR of the unlabelled complexes are singlets, with appropriate ^{195}Pt satellites (for **1** and **2**,

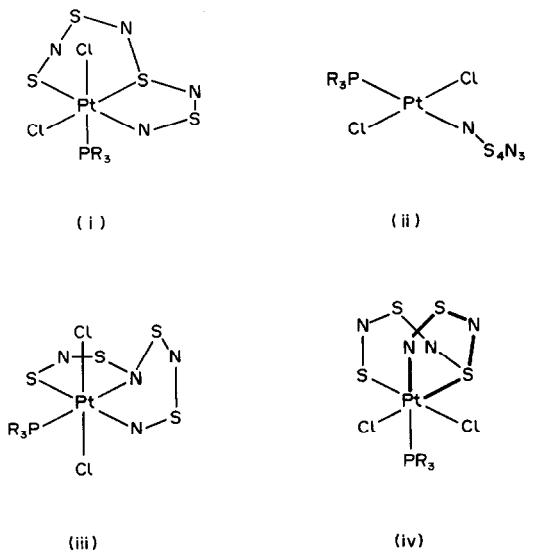

Fig. 2. Possible structures of **2**.

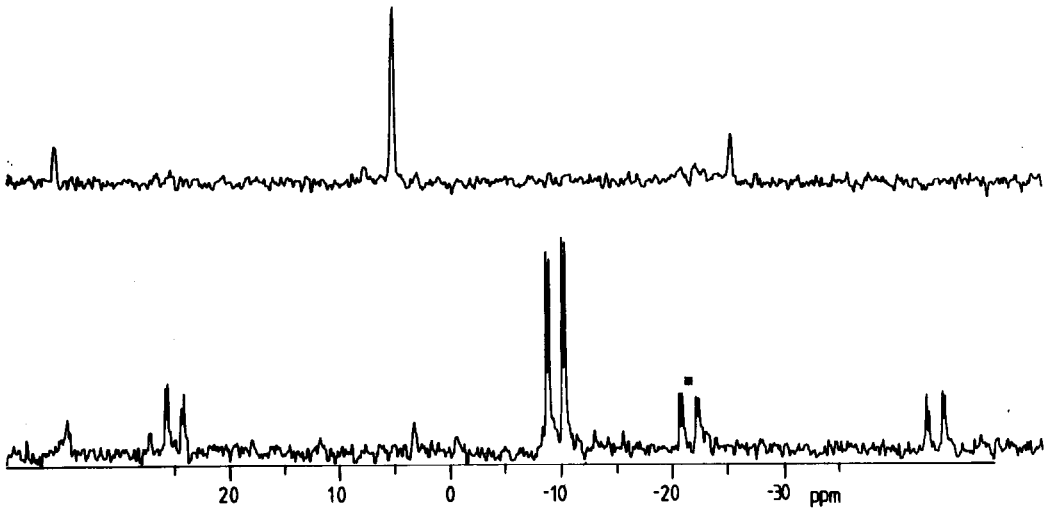

Fig. 3. 36.21 MHz ^{31}P-{^1H} NMR spectrum (in $CDCl_3$) of ^{15}N-labelled **1** (upper) and **2** (lower). The asterisk marks the peaks due to ^{15}N-labelled $PtCl(S_2N_2H)(PMe_2Ph)$.

^1J = 2170 and 2453 Hz, respectively). In the case of **1** [Fig. 3(a)] the only effect that introducing ^{15}N into the system appears to have is a slight broadening of this singlet, suggesting that none of the ^{15}N nuclei present couple to the phosphorus to any great degree. Results obtained previously for labelled complexes of the type $Pt(S_2^{15}N_2)(PR_3)_2$ (**4**)[5] (Fig. 1) show that the phosphorus *trans* to sulphur couples only to N(1), and that this coupling is small (5 Hz). Comparison of the structure of **1** with that of the aforementioned $S_2N_2^{2-}$ complexes suggests that the only ^{15}N–^{31}P coupling one would expect to see in ^{15}N-labelled **1** would be from N(1), and that this too would be weak. Hence it is this coupling that manifests itself as the slight broadening of the main peak.

In contrast, the ^{31}P NMR spectrum of ^{15}N-labelled **2** [Fig. 3(b)] shows much more fine structure; the original singlet is split into a pair of doublets. This is consistent with the presence of two ^{15}N–^{31}P couplings, of magnitude $\approx$ 57 and 8 Hz, and is almost identical to the pattern observed for $Pt(S_2^{15}N_2H)Cl(PMe_2Ph)$ [as seen in the small amount of impurity in the spectrum in Fig. 3(b)] in which the couplings are 54 and 7 Hz.[3] Therefore, we propose that the phosphine group in **2** must be in a similar environment to that in $Pt(S_2N_2H)Cl(PMe_2Ph)$, since, on the basis of our previous results, a ^{15}N–^{31}P interaction as large as 54 Hz could only be the result of a ^2J (^{31}P–^{15}N) coupling from a ^{15}N *trans* to phosphorus.[5] On this basis we can rule out structure (i) since this would require phosphorus *trans* to chlorine. The conversion of **1** to structure (ii) would require the oxidation of the $S_4N_4^{2-}$ ligand to neutral S_4N_4 and corresponding reduction of the platinum to platinum(II); this is somewhat unlikely in itself since any reduction at platinum would lead to species such as **3** or **4** and, although the value of the $^1J(^{195}Pt$–$^{31}P)$ coupling constant (2453 Hz) could be indicative of platinum(II), past results show such a small coupling is only observed for phosphorus *trans* to sulphur. Of the two remaining potential structures (iii) is unlikely since the presence of a nitrogen *cis* to the phosphorus would result in, at the least, a broadening of the lines, as seen in Fig. 3(a) (previously we have observed ^2J *cis* couplings of *ca* 5 Hz in **4**). Hence the only reasonable structure for **2** would appear to be (iv), that is a facial coordination, analogous to that seen in $Ir(CO)Cl(S_4N_4)(PPh_3)$. The use of ^{31}P–^{15}N coupling constants to identify the structure of **2** is clearly inferior to single crystal X-ray studies since other isomers could be possible. However, on the basis of the data that we have been able to obtain we believe structure (iv) to be the most likely.

We have yet to determine the mechanism of the *mer–fac* isomerization. Dissociation of the phosphine (*trans* to sulphur), rotation of the chlorides and nitrogen in a five-coordinate intermediate, followed by reassociation of the phosphine (*trans* to nitrogen) appears to be the most reasonable route. For comparison, it is interesting to note that in the isomerization of *trans*-$[PtBr_2(S_2N_2H)(PMe_2Ph)_2]^+$ to the *cis* form it is the phosphine *trans* to sulphur which is rotated.[6] We have yet to ascertain the nature of the species with δ −18.0, which is formed as a minor product during the isomerization of **1**. It is present in the green band which separates on Bio-beads; concentrated $CDCl_3$ solutions of this fraction deposit an insoluble red microcrystalline

product which can be shown by IR to contain PMe_2Ph, and which analyses as $[Pt(S_2N_2)(PMe_2Ph)]_2 \cdot 2CDCl_3$ (Found: C, 19.4; H, 2.1; N, 5.4. Calc.: C, 19.8; H, 2.0; N, 5.1%), suggesting that the red solid may be the PMe_2Ph analogue of $[Pt(S_2N_2)(PPh_3)]_2 \cdot CH_2Cl_2$, which we have previously reported.[7]

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