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Preliminary communication

ON THE MOLECULAR STRUCTURE AND NMR SPECTRUM OF *cis*-[$PtPh_2(Ph_2PCH_2PPh_2)$]

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Summary

The X-ray crystal structure analysis of *cis*-[$PtPh_2(Ph_2PCH_2PPh_2)$] suggests that the unusually low Pt—P coupling constant is a consequence of distortion of the valency angles at the platinum and phosphorus atoms; the restrictive geometry of the chelate ring does not effect the lengths of the metal—ligand bonds.

Whilst 1,2-bis(diphenylphosphino)ethane (dpe) has been extensively used as a chelating ligand, complexes of bis(diphenylphosphino)methane (dpm) are less common. Nevertheless, examples of preferential unidentate [1] and bridging [2] coordination, as well as of the expected chelate formation [3, 4], have already been reported.

We find that the chemical and spectroscopic properties of dpm complexes of platinum are unusual. Thus $(dpm)_2Pt^0$ readily undergoes thermal decomposition at 400 K to release Ph_2MeP and Ph_3P. By contrast, we have observed that $(dpe)_2Pt^0$ is stable to 570 K, whereas it has been reported that $(dpm)_2Pd^0$ is stable in vacuo to 470 K [5]. Furthermore, reaction of $(dpm)PtCl_2$ and $(Me_3Si)_2Hg$ can lead to the unusual Pt^I complex $(dpm)_2Pt_2Cl_2$ [6], a product not observed in the analogous reaction of $(dpe)PtCl_2$ [7]. A novel reaction of dpm with aryl-copper compounds, involving replacement of a dpm methylene proton by copper, has also been described [8].

We have observed that the coupling constant $^1J(^{195}Pt—^{31}P)$ for $(dpm)PtPh_2$ (1491.8 Hz) is appreciably smaller than those for $(dpe)PtPh_2$ and *cis*-$(Ph_3P)_2PtPh_2$ (1748.7 and 1748.4 Hz, respectively). This result is significant in view of the recent suggestion that a correlation exists between $^1J(^{195}Pt—^{31}P)$ and Pt—P bond lengths in platinum(II) complexes containing mono(tertiary phosphine) ligands [9].

Since the restrictive geometry of the four-membered chelate ring (particularly at platinum) could effect the metal—ligand bonding and thus be responsible for some of these chemical and spectroscopic peculiarities, we have examined the crystal structure of $(dpm)PtPh_2$ by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, and there are four molecules in a cell of dimensions a = 15.390, b = 10.138, c = 22.380 Å, β = 119.4°. The structure has currently been refined to R = 0.068 and R' = 0.076, using 4299 independent diffractometric intensity data for which θ(Mo-K_α) $\leqslant$ 26°.

The crystal structure contains discrete molecules of *cis*-[$PtPh_2(Ph_2PCH_2PPh_2)$], in which dpm acts as a bidentate ligand. The platinum atom, and the carbon and phosphorus atoms directly bonded to it, are coplanar to within 0.03 Å. The methylene carbon atom is displaced by 0.17 Å from the platinum coordination plane. Mean values of chemically equivalent bond lengths and angles are shown in Fig. 1.

Despite the constraints imposed by the chelate ring the bond lengths agree well with those observed in mono(tertiary phosphine) complexes of platinum(II). Thus the mean Pt—P and Pt—C distances (2.30(1) and 2.05(1) Å) are close to the corresponding values (2.317(5) and 2.043(13) Å) found in *cis*-[$PtPh(GePh_2OH)(PEt_3)_2$] [10], and the P—C bond lengths are as expected (see e.g. ref. 11). The C—P—C angles (mean 106°) are also in the range typical of both free and coordinated mono(tertiary phosphine) [12]. The internal ring angles at platinum and phosphorus are about 15° less than the expected values for unconstrained P—Pt—P and Pt—P—C angles (respectively 90 and ca. 109°). The Pt—P—C(Ph) angles (mean 120°) are also rather larger than typical values in mono(tertiary phosphine) complexes (see ref. 12).

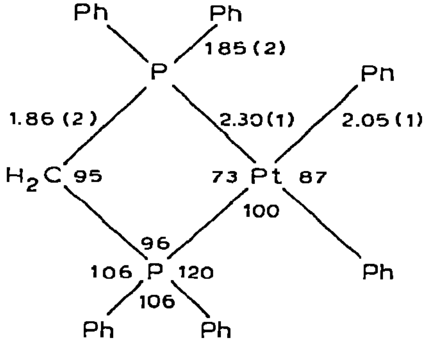

Fig. 1. Mean bond lengths (Å) and angles (degrees in) *cis*-[$PtPh_2(Ph_2PCH_2PPh_2)$]. Standard deviations of angles are $\leqslant 1^\circ$ except for C(sp^2)—P—C(sp^2) where the individual values are 103 and 108°.

The dimensions of the chelate ring in (dpm)$PtPh_2$ may be compared with those observed in the five-coordinate complex (dpm)$Fe(CO)_3$ [3] and the octahedral complex (dpm)$Mo(CO)_4$ [4], where the mean M—P bond lengths are 2.22 and 2.52 Å and the P—M—P angles are 74 and 64°, respectively. Since in none of the three compounds do the M—P bond lengths appear to be influenced by the chelating effects, it would seem that an explanation for the unusual behaviour of dpm complexes should be best sought in the distortions of the valency angles at the metal and phosphorus atoms. It thus follows that the abnormally low value of $^1J(^{195}Pt—^{31}P)$ for (dpm)$PtPh_2$, compared with those for (dpe)$PtPh_2$ and *cis*-[$(Ph_3P)_2PtPh_2$], where the P—Pt—P and Pt—P—C angles are expected to be closer to 90 and 109°* respectively, indicates that the coupling constants are strongly

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*Structural data for these compounds are not available. However, in [{$(CF_3)_2PCH_2CH_2PPh_2$}$PtCl_2$] the P—Pt—P and Pt—PPh_2—CH_2 bond angles are 86 and 108° [13].

influenced by the P—Pt—C and Pt—P—C angles. It would, therefore, be unrealistic to apply the suggested correlation [9] between coupling constants and Pt—P bond lengths to complexes in which the bond angles at the platinum or phosphorus atoms might be seriously distorted.

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