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Preliminary communication

THE PREPARATION, NMR SPECTRA, AND STRUCTURE OF UNSYMMETRICAL DITERTIARY PHOSPHINE COMPLEXES OF PLATINUM(II)

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Summary

The ${}^1J$(Pt—P) coupling constants in the complexes *cis*-$PtCl_2(R_2PCH_2CH_2PPh_2)$, where R = CF_3, C_6F_5, and the bond lengths in the complex with R = CF_3 indicate that the metal—ligand bonding is strongly influenced by the substituents on phosphorus.

We have recently described the synthesis of the novel diphosphine ligand L, $Ph_2PCH_2CH_2P(CF_3)_2$, and the structure of the palladium(II) complex $[PdCl_2L]$ [1]. This work indicated that the electronic properties of the substituents on phosphorus exert a profound influence upon the metal—ligand bonds. We have now prepared analogous platinum(II) complexes. The considerable amount of comparative structural data available for platinum(II)—phosphine complexes and the proposed correlation between ${}^1J$(Pt—P) coupling constants and Pt—P bonds lengths [2] suggested that a more critical evaluation of the nature of the metal—phosphine bonding might be possible for these platinum(II) compounds. Moreover, the bonding in analogous complexes of second and third row transition metals is sometimes markedly different, especially when π-acid ligands are involved [3].

The ligand L′, $Ph_2PCH_2CH_2P(C_6F_5)_2$, was prepared by addition of $(C_6F_5)_2PH$ to $Ph_2PCH{=}CH_2$ in the presence of a radical initiator and precipitated from refluxing methanol. The complexes $[PtCl_2L]$ and $[PtCl_2L']$ were obtained by reaction of the appropriate diphosphine with $[PtCl_2(CNPh)_2]$ in refluxing benzene. The compounds were fully characterised by analytical and spectroscopic methods (Table 1). Crystals of $[PtCl_2L]$ are nearly isomorphous with those of the palladium analogue [1], and contain four molecules in a monoclinic cell of dimensions $a = 10.062$, $b = 13.690$, $c = 15.930$ Å, $\beta = 108.66°$, the space group being $P2_1/c$. The

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TABLE 1

NMR AND IR SPECTRA OF THE DIPHOSPHINE LIGANDS AND THEIR PLATINUM(II) COMPLEXES

Chemical shifts, δ, are in ppm downfield of H_3PO_4, J are in Hz, and ν in cm^{-1}, R = CF_3 or C_6F_5.

Compound	$\delta(PPh_2)$	$\delta(PR_2)$	$^1J(Pt—PPh_2)$	$^1J(Pt—PR_2)$	$^3J(P—P)$	$^2J(P—F)$	$^5J(P—F)$	$\nu(Pt—Cl)$
L[a]	−13.1	2.3	—	—	42	70		—
L′[b]	−12.69	−44.36	—	—	42.2	25.5	1.4	—
$[PtCl_2L]$[b]	45.1	62.5	3120	4013	< 8	85		298,339
$[PtCl_2L']$[b]	42.16	14.33	3445	3845	< 8			300,335

[a] Measured on a saturated solution in $CDCl_3$ at 24.3 MHz. [b] Measured on a saturated solution in $CDCl_3$ at 40.5 MHz using a Varian XL 100 FT spectrometer.

structure was solved by the heavy atom method and refined to $R = 0.04$ using 3354 diffractometric intensity data corrected for absorption $[\theta(\text{Mo-}K_\alpha) \leqslant 27^\circ]$. Pertinent bond lengths and angles are displayed in Fig. 1.

The most noteworthy feature of the molecular structure is the extreme shortness both of the Pt—P(CF_3)$_2$ bond and of the *trans*-Pt—Cl bond. Prior to this, the shortest Pt—P(phosphine) distance observed in the 56 monomeric platinum(II)—phosphine complexes for which structural data are available was that of 2.215(4) Å in the anion $[PtCl_3(PEt_3)]^-$ [4]. The short Pt—Cl distance suggests that the *trans* influence of the CF_3-substituted phosphorus atom is substantially less than that of a trialkyl- or triaryl-phosphine and is comparable with that of chlorine or isocyanide [5]. The Pt—PPh_2 and Pt—Cl(*trans* to PPh_2) distances are normal, being equal, within experimental error, to comparable values in at least five other complexes of the type *cis*-$PtCl_2L(PR_3)$, R = aryl or alkyl, L = phosphine, isocyanide or carbenoid [6].

The trend in the Pt—P bond lengths in $[PtCl_2L]$ is reflected in the ^1J(Pt—P) coupling constants which differ by ca. 900 Hz. This difference decreases to 400 Hz in $[PtCl_2L']$. We suggest that the observed increase of the coupling constants along the series $PPh_2 < P(C_6F_5)_2 < P(CF_3)_2$ may be related to increased electron-withdrawing ability of the substituents on phosphorus [7].

We consider that the bond lengths in $[PtCl_2L]$ can not be satisfactorily explained solely in terms of differences in the Pt—P σ-bonds. Rather, we conclude that the shortness of the Pt—P(CF_3)$_2$ bond is a consequence of substantial backdonation from platinum to phosphorus. Synergic enhance-

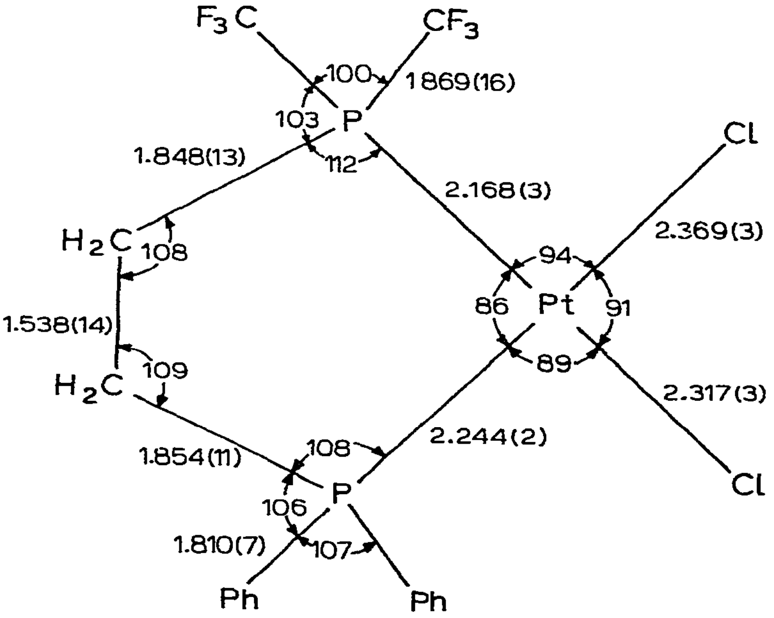

Fig. 1. Bond lengths (Å) and bond angles (°) in $[PtCl_2L]$. Standard deviations of angles are less than 1°. Chemically equivalent bond lengths and angles have been averaged. The Pt—P—CF_3 angles are 116 and 120°, and the Pt—P—Ph angles are 108 and 117°.

ment of the σ-bonding would then explain the high coupling constant. The unusually small *trans* influence of the $P(CF_3)_2$ group would also be expected, since an analogy can be drawn with carbon-donor ligands which diplay a substantial drop in *trans* influence if backdonation is at all extensive [5].

We also note that the Pd—$P(CF_3)_2$ bond length [2.192(1) Å] in [$PdCl_2$ L] is 0.024(4) Å longer than the corresponding value in the platinum complex. The other comparable bond lengths and angles in the two complexes are equal within the limits of experimental errors.

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