

Preliminary communication

ON THE MOLECULAR STRUCTURES AND NMR SPECTRA OF
 $\text{PC}_6\text{F}_5(\text{CH}_3)_2$ COMPLEXES OF PLATINUM(II)

LJUBICA MANOJLOVIĆ-MUIR, KENNETH W. MUIR*, TIHOMIR SOLOMUN,

Chemistry Department, The University, Glasgow G12 8QQ (Great Britain)

DEVON W. MEEK and JAMES L. PETERSON

Chemistry Department, The Ohio State University, 140 W, 18th Avenue, Columbus, Ohio 43210 (U.S.A.)

(Received December 15th, 1977)

Summary

^1H and ^{31}P NMR parameters for *cis*- $[\text{PtX}_2\text{L}_2]$ and $[\text{PtXL}_3]^+$ complexes in which L is $\text{PC}_6\text{F}_5(\text{CH}_3)_2$ and X = a range of anionic ligands, together with crystal structure analyses of *cis*- $[\text{PtX}_2\text{L}_2]$, (I, X = Cl; II, X = CF_3) and $[\text{Pt}(\text{CH}_3)_3\text{L}_3][\text{PF}_6^-]$ (III), suggest that electron-withdrawal by C_6F_5 has only a limited effect on the metal—ligand bonding and that the *trans*-influences of CH_3^- and CF_3^- on Pt—P bonds are of similar magnitude. The dependence of ^{19}F NMR chemical shifts and coupling constants on the nature of the Pt—X bonding is also described.

As part of an investigation of the σ - and π -components of Pt—P bonds we have prepared *cis*- $[\text{PtX}_2\text{L}_2]$ and $[\text{PtXL}_3][\text{PF}_6^-]$ complexes where X is a variety of anionic ligands, including Cl^- , CH_3^- , and CF_3^- , and L is the novel phosphine ligand $\text{PC}_6\text{F}_5(\text{CH}_3)_2$ [1]. ^1H , ^{19}F , and ^{31}P NMR studies of a large number of these compounds and X-ray diffraction analyses of I, II and III permit us to compare the *trans*-influence and bonding to platinum (i) of L and monotertiary phosphines containing only alkyl or aryl substituents, and (ii) of CH_3^- and CF_3^- .

The crystal structures of I—III were determined from diffractometric intensity data corrected for absorption. *R* and the number of observed reflexions (in parentheses) are, for I, II, and III respectively, 0.025 (3859), 0.023 (2673), and 0.029 (5374). Selected structural and NMR parameters for I—III are given in Fig. 1*.

Differences in the intramolecular steric environments of chemically equi-

*I is monoclinic, a 11.318, b 14.056, c 13.914 Å, β 103.51°, space group $P2_1/c$, Z 4. II is monoclinic, a 12.460, b 8.276, c 22.343 Å, β 103.68°, space group $C2/c$, Z 4, molecular symmetry C_2 . III is monoclinic, a 13.973, b 14.101, c 16.827 Å, β 93.39°, space group $P2_1/n$, Z 4.

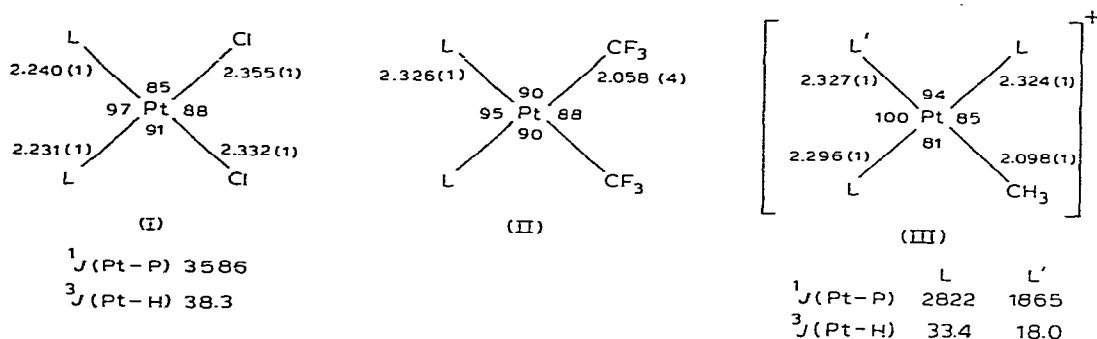


Fig. 1. Bond lengths (Å), angles ($^{\circ}$) and coupling constants (Hz) in I, II and III. $\text{L} = \text{L}' = \text{PC}_6\text{F}_5(\text{CH}_3)_2$. The insolubility of II in common solvents precluded NMR experiments.

valent ligands in III (and to a lesser extent in I) are reflected in variations of up to 0.03 Å in comparable metal–ligand bonds. Nevertheless, the mean Pt–P bond lengths in I–III lead to the expected *trans*-influence series

$\text{Cl}^- < \text{PC}_6\text{F}_5(\text{CH}_3)_2 \sim \text{CH}_3 \sim \text{CF}_3$. The corresponding $^1J(\text{Pt}-\text{P})$ and $^3J(\text{Pt}-\text{H})$ coupling constants give a similar series, but suggest a larger gradation between P- and C-donor ligands than do the bond lengths. The NMR results imply that in III the Pt–P(*trans* to C) bond has less *s*-character than the Pt–P(*trans* to P) bonds. Yet this difference is evidently not sufficiently large to produce detectable variations in the mean bond lengths.

In contrast to *cis*-[PtCl₂{(CF₃)₂PCH₂CH₂P(C₆H₅)₂}], where electron-withdrawal by CF₃ substantially shortens both the adjacent Pt–P bond and the *trans*-Pt–Cl bond [2], the structures and NMR spectra of I–III indicate that L is little different electronically from monotertiary phosphines with alkyl or aryl substituents, such as PC₆H₅(CH₃)₂. Thus the $^1J(\text{Pt}-\text{P})$ coupling constants for I–III are typically only 3% larger than those for analogous complexes of PC₆H₅(CH₃)₂. The mean Pt–P and Pt–Cl distances in I (2.236(6) and 2.344(12) Å) are shorter, but only slightly, than corresponding values (Pt–P 2.248(9)–2.259(3) Å, Pt–Cl 2.361(6)–2.376(12) Å) in *cis*-[PtCl₂L'₂] complexes where L' = P(CH₂CH₃)₃ [3], PC₆H₅(CH₃)₂ [4], and P(CH₃)₃ [5]. Our results thus tend to confirm the conclusion that the group electronegativity of C₆F₅ is only slightly greater than that of C₆H₅ (ca. 2.7 versus 2.4 on the Pauling scale) [6].

The narrowing of the C–C–C angle at the phenyl carbon atom attached to phosphorus in the L ligands of I–III (mean 115.5(2)) is indicative of greater P→C₆F₅ inductive electron release than occurs in P–C₆H₅ systems [7]. However, the mean P–C₆F₅ bond length of 1.836(3) Å agrees well with the corresponding mean of 1.828(3) Å [7] for P–C₆H₅ bonds.

The Pt–CF₃ distance in II is 0.040(7) Å shorter than the Pt–CH₃ distance in III. Similar, though larger differences (ca. 0.1 Å) have been found between fluorocarbyl- and hydrocarbyl-metal bond lengths for other transition metal ions and various rationalisations have been offered [8]. Here we believe that enhancement of the C(2s) component of the Pt–C bond in II compared with III affords the most plausible explanation. The mean Pt–C–F and F–C–F angles (114.8(7) and 103.6(4) $^{\circ}$) are consistent with this view, as is the similarity in

trans-influence on Pt—P bond lengths displayed by CF₃ and CH₃. We have recently shown that the *trans*-influence of σ -hydrocarbyl ligands on Pt—Cl bonds is insensitive to the hybridisation of the donor carbon atom [9].

The ¹⁹F NMR spectra of L—Pt(II) complexes are sensitive indicators of the bonding properties of the other ligands. Thus, for the L ligand *trans* to X in both *cis*-[PtX₂L₂] and [PtXL₃]⁺ complexes, the chemical shift of F (*para* to P) follows the π -acceptor order of X, as does the *J*(F—F) coupling constant between the fluorine atoms respectively *ortho* and *para* to phosphorus.

Acknowledgements

We thank N.A.T.O. for financial support and the University of Glasgow for a scholarship (to T.S.).

References

- 1 J.L. Peterson, Ph.D. Dissertation, The Ohio State University, 1973.
- 2 I. Macleod, Lj. Manojlović-Muir, D. Millington, K.W. Muir, D.W.A. Sharp and R. Walker, *J. Organometal. Chem.*, **97** (1975) C7.
- 3 Lj. Manojlović-Muir, K.W. Muir and T. Solomun, unpublished work.
- 4 R.W. Baker, M.J. Braithwaite and R.S. Nyholm, *J. Chem. Soc. Dalton*, (1972) 1924.
- 5 G.G. Messmer, E.L. Amma and J.A. Ibers, *Inorg. Chem.*, **6** (1967) 725.
- 6 J.M. Holmes, R.D. Peacock and J.C. Tatlow, *Proc. Chem. Soc. London*, (1966) 108.
- 7 A. Domenicano, A. Vaciago and C.A. Coulson, *Acta Crystallogr. B*, **31** (1975) 1630.
- 8 M.R. Churchill, *Perspectives in Structural Chem. Vol. 3*, 1970, p. 91.
- 9 C.J. Cardin, D.J. Cardin, M.F. Lappert and K.W. Muir, *J. Chem. Soc. Dalton*, in the press.