Stereochemistry and Absolute Signs of ${}^{3}J_{P,H}$ Nuclear Spin Coupling Constants in Methylplatinum(IV) Tertiary Phosphine Complexes

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Abstract

¹H–{³¹P} and ¹H–{¹⁹⁵Pt} INDOR spectra have been recorded for PtMe₃(acac)PPh₃. The stereochemical dependence of the absolute signs of ${}^{3}J_{P,H}$ for the platinum methyl protons has been determined. An earlier suggestion of the value of such signs in structural studies of alkylplatinum(II) tertiary phosphine complexes has been extended to such complexes of platinum(IV).

In an earlier paper,¹ absolute signs of the two ${}^{3}J_{P,H}$ nuclear spin coupling constants of the methyl protons in some methylplatinum(II) tertiary phosphine complexes were determined. On this basis, it was suggested that absolute sign determination in such platinum(II) complexes may provide a means of establishing the position of alkyl groups relative to phosphorus atoms, particularly for mixed alkyl complexes where the magnitude of ${}^{1}J_{Pt,P}$ may not be diagnostic. We here extend the earlier work to a complex of platinum(IV) and show that the ${}^{3}J_{P,H}$ absolute signs have the same stereochemical dependence as observed for the platinum(II) complexes.

The preparation of $PtMe_3(acac)PPh_3$ (acac = acetylacetonate) has been described in another paper² which also gave nuclear spin Hamiltonian parameters determined directly from proton magnetic resonance spectra. Its structure may be presumed to be that in which the three platinum methyl groups are mutually *cis*. All trimethylplatinum compounds of known crystal structure have this *cis* methyl arrangement.³⁻⁵

We have recorded the ${}^{1}H-{}^{31}P$ and ${}^{1}H-{}^{195}Pt$ INDOR spectra of this compound in CDCl₃ solution at 34°C using procedures described before.¹ Both ${}^{1}H-{}^{31}P$ and ${}^{1}H-{}^{195}Pt$ experiments gave ${}^{1}J_{Pt,P}$ (the latter one more precisely) as 964 Hz with an estimated precision of measurement of ± 4 Hz. Recalling the well established correlation of ${}^{1}J_{Pt(II),P}$ with the ligand *trans* to this bond^{6,7} and the fact that the ratio of ${}^{1}J_{Pt(IV),P}$ to ${}^{1}J_{Pt(II),P}$ is generally close^{6,8} to 3/5, the value confirms the structure as having the phosphine *trans* to a strong *trans*-effect ligand, that is, methyl rather than an oxygen of the chelate. The coupling constants of particular interest are ${}^{3}J_{P,H}$ of

¹ Bennett, M. A., Bramley, R., and Tomkins, I. B., J. Chem. Soc., Dalton Trans., 1973, 166.

² Hall, J. R., and Swile, G. A., J. Organometal. Chem., 1973, 47, 195.

³ Thayer, J. S., Organometal. Chem. Rev. A, 1970, 5, 53.

⁴ Adamson, G. W., Bart, J. C. J., and Daly, J. J., J. Chem. Soc. A, 1971, 2616.

⁵ Casalone, G., and Mason, R., Inorg. Chim. Acta, 1973, 7, 429.

⁶ Pidcock, A., Richards, R. E., and Venanzi, L. M., J. Chem. Soc. A, 1966, 1707.

⁷ Allen, F. H., and Sze, S. N., J. Chem. Soc. A, 1971, 2054.

⁸ Allen, F. H., and Pidcock, A., J. Chem. Soc. A, 1968, 2700.

the platinum methyl protons. Their signs relative to that of ${}^{1}J_{Pt,P}$ were shown by ${}^{1}H-{}^{195}Pt$ INDOR to be the same for the two methyl groups *cis* to phosphorus, but opposite for the methyl group *trans* to phosphorus. Similarly the relative signs of ${}^{2}J_{Pt,H}$ and ${}^{1}J_{Pt,P}$ were shown to be opposite for both *cis* and the *trans* methyl groups by ${}^{1}H-{}^{31}P$ experiments. The absolute sign of ${}^{1}J_{Pt,P}$ has been shown to be positive⁹ and thus the analogy with the earlier platinum(II) compounds is complete. Each ${}^{2}J_{Pt,H}$ is negative; more especially, ${}^{3}J_{P,Pt,C,H}$ is positive for the *cis* coupling route and negative for the *trans* coupling route. In the course of this work we recorded INDOR spectra and determined that $\Xi_{Pt} = 21446063 \pm 2$ Hz and that $\Xi_{P} = 40480869 \pm 10$ Hz.



Fig. 1. Computer averaged (63 scans) ${}^{1}H{-}{}^{195}Pt$ INDOR spectrum of PtMe₃(acac)PPh₃, monitoring the proton transition at lowest field. The upper trace is an inverted computer simulation with half-height linewidth 9 Hz and ${}^{2}J_{Pt,C,H}$ values of (-) 74.2 Hz (two *cis* Me groups) and (-) 60.4 Hz (*trans* Me group).

The phosphorus resonance is thus $3 \cdot 2$ p.p.m. to low field of phosphoric acid.¹⁰ The well resolved INDOR spectrum (Fig. 1) demonstrates that coupling to all ligand

¹⁰ McFarlane, W., Ann. Rev. N.M.R. Spectrosc., 1968, 1, 148.

⁹ McFarlane, W., J. Chem. Soc., Chem. Commun., 1967, 772.

The possible stereochemical value of absolute sign determination of ${}^{3}J_{P,Pt,C,H}$ coupling constants suggested for platinum(II) complexes may well apply also to complexes of platinum(IV).

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