Stereochemistry and Absolute Signs of $^3J_{P-H}$ Nuclear Spin Coupling Constants in Methyl Platinum(II) Complexes containing Tertiary Phosphines

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Absolute signs for $^3J_{P-H}$ nuclear spin coupling constants of the methyl protons in some methylplatinum(II) tertiary phosphine complexes are positive for phosphorus atoms *cis* to the methyl group and negative for a phosphorus atom *trans* to methyl. Negative signs have been found for the coupling of platinum to methyl protons, $^2J_{Pt-H}$, in these complexes and to olefin protons in dimethyl-[2-vinylphenyl(diphenyl)phosphine]platinum(II). The geminal olefin protons in this compound have a positive-signed coupling with phosphorus. Platinum and phosphorus chemical shifts and coupling constants obtained from INDOR spectra are reported.

THE two different nuclear spin couplings between phosphorus and the protons of the methyl groups attached to platinum in *cis*-dimethylbis(triethylphosphine)platinum(II) have opposite signs.[1] In this complex, the spin system is essentially $AA'X_3X_3'$,[2] in which it is not possible to determine from single resonance spectra which ^3J coupling is which. These two couplings have similar magnitudes of a few Hz in many examples of platinum complexes with tertiary phosphines.[3]

We have used heteronuclear double-resonance techniques to obtain the relative signs of $^1J_{Pt-P}$, $^3J_{P-H}$, and $^2J_{Pt-H}$. By using McFarlane's absolute sign determination[4] of $^1J_{Pt-P}$, we have obtained the absolute signs of these two ^3J couplings, thus identifying which has the *trans*-route and which the *cis*. This assignment may prove to be the basis of a method for determining the stereochemistry of alkyl groups relative to phosphines generally. Although the magnitude of $^1J_{Pt-P}$ is diagnostic of the group *trans* to the phosphorus atom,[1] our ^3J sign determination provides a simple basis for assigning stereochemistry in mixed alkyl complexes of platinum with a phosphorus-bonded ligand.

We have examined complexes (1)—(3).* Complex (1) alone provided the answer to the sign question; complexes (2) and (3) gave corroborative evidence. N.m.r. data necessary for the sign determination are given in the top section of Table 1, other data collected incidentally being in the bottom section. Vinyl ^1H n.m.r. data are in Table 2.

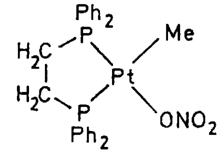
TABLE 1

^1H N.m.r. and INDOR data for complexes (1)—(3) [a]

Parameter	$PtMe(NO_3)(dpe)$ (1)	PtClMe(sp) (2)	$PtMe_2(sp)$ (3)
$^1J_c(Pt-P)/Hz$	$+4510 \pm 40$	$+4270 \pm 10$	—
$^1J_t(Pt-P)/Hz$	$+1820 \pm 20$	—	$+1731 \pm 6$
$^2J_c(Pt-H)/Hz$	$-48{\cdot}5 \pm 0{\cdot}5$	$-72{\cdot}5 \pm 0{\cdot}2$	$-86{\cdot}5 \pm 0{\cdot}5$
$^2J_t(Pt-H)/Hz$		—	$-67{\cdot}0 \pm 0{\cdot}5$
$^3J_c(P-H)/Hz$	$+2{\cdot}0 \pm 0{\cdot}3$	$+3{\cdot}4 \pm 0{\cdot}2$	$+7{\cdot}5 \pm 0{\cdot}3$
$^3J_t(P-H)/Hz$	$-7{\cdot}5 \pm 0{\cdot}3$	—	$-7{\cdot}8 \pm 0{\cdot}3$
$\Xi P_t/Hz$	$21,400,605 \pm 50$	$21,407,961 \pm 50$	$21,412,462 \pm 13$
$\Xi P_c/Hz$	$40,482,114 \pm 5$	$40,481,710 \pm 5$	$40,482,084 \pm 3$
$\Xi P_t/Hz$	$40,482,754 \pm 5$	—	
δ_c-CH_3/p.p.m.	$0{\cdot}48 \pm 0{\cdot}01$	$1{\cdot}13 \pm 0{\cdot}01$	$1{\cdot}19 \pm 0{\cdot}01$
δ_t-CH_3/p.p.m.			$0{\cdot}74 \pm 0{\cdot}01$
Solvent (saturated at 32 °C)	CD_2Cl_2	$CDCl_3$	$CDCl_3$

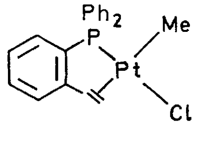
[a] The subscripts *c* and *t* indicate the relative *cis*- or *trans*-stereochemistry of a phosphorus atom and a methyl group. Errors quoted are estimated standard deviations.

The ^1H n.m.r. spectrum of the methyl group of complex (1) was a doublet of doublets due to the two phosphorus couplings, with satellites from molecules



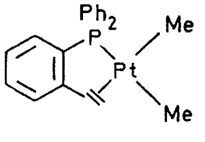
$PtMe(NO_3)(dpe)$

(1)



PtClMe(sp)

(2)



$PtMe_2(sp)$

(3)

with the magnetic isotope ^{195}Pt (34% abundance). ^1H-$\{^{31}P\}$ INDOR on the central four peaks established

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* The abbreviation (sp) is used for 2-vinylphenyl(diphenyl)-phosphine, which has been named *o*-styryldiphenylphosphine in previous papers dealing with this ligand.

[1] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[2] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[3] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087 and references therein.

[4] W. McFarlane, *Chem. Comm.*, 1967, 772.

that the two phosphorus nuclei were chemically shifted by 640 Hz at 40·48 MHz and that the $^{2}J_{\mathrm{P-P}}$ coupling was less than 20 Hz. (We have therefore used first-order spectral analysis.) ^{1}H-{^{31}P} INDOR, the high-field satellite peaks being monitored, established that the phosphorus nucleus with the larger $^{1}J_{\mathrm{Pt-P}}$ had the smaller $^{3}J_{\mathrm{P-H}}$. We have thus shown, on the grounds that the larger $^{1}J_{\mathrm{Pt-P}}$ must come from the phosphorus *trans* to the nitrato-group, that the *cis*-coupling constant, $|^{3}J_{\mathrm{P-H}}|$, is 2·0 Hz. The *trans* $|^{3}J_{\mathrm{P-H}}|$ is 7·5 Hz. Since ^{1}H-{^{31}P} of the two higher-frequency platinum-caused satellites (in the indirectly observed phosphorus spectrum) decoupled the low-frequency satellite in the proton spectrum, $^{2}J_{\mathrm{Pt-H}}$ and $^{1}J_{\mathrm{Pt-P}}$ have opposite signs. On the basis of McFarlane's determination of the absolute sign of $^{1}J_{\mathrm{Pt-P}}$ as positive, and the assumption that this is always positive (there is no evidence of sign reversal), $^{2}J_{\mathrm{Pt-H}}$ is negative. The signs of the $^{3}J_{\mathrm{P-H}}$ couplings were established by ^{1}H-{^{195}Pt} INDOR. Irradiation of the highest frequency of the four broad platinum transitions collapsed the second-lowest-frequency peak of the four peaks of each satellite in the proton spectrum. This experiment alone established the $^{3}J_{\mathrm{P-H}}$ signs as +2·0 Hz and −7·5 Hz, that is, the *cis*-coupling route gives the positive sign and the *trans*-route the negative sign. We completed the other three ^{1}H-{^{195}Pt} INDOR experiments, each of which confirmed the assignment.

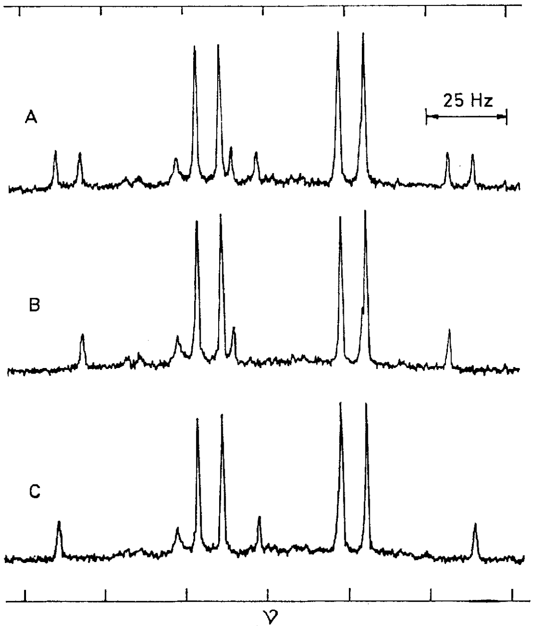
TABLE 2

Vinyl group ^{1}H n.m.r. parameters for $CDCl_3$ solutions of PtClMe(sp) and $PtMe_2$(sp). Coupling constants are all ±0·5 Hz, unless otherwise noted. The assignment of *cis*- and *trans*-geminal protons is based on their coupling constants with H_{α}. Signs are given only where determined in this work

	PtClMe(sp)	$PtMe_2$(sp)
δH_{α}	6·09	5·37
δH_{β}(*cis*)	5·21	4·42
δH_{β}(*trans*)	3·76	3·29
J_{cis}/Hz	9·0	8·4 ± 0·3
J_{trans}/Hz	14·5	13·4 ± 0·3
J_{gem}/Hz	1·3	<1
$J(H_{\alpha}-Pt)$/Hz	31·0	−32·9
$J(H_{\beta cis}-Pt)$/Hz	36·6	−45·3
$J(H_{\beta trans}-Pt)$/Hz	−31·6	−38·5
$J(H_{\alpha}-P)$/Hz	<1	<1
$J(H_{\beta cis}-P)$/Hz	<1	+2·8
$J(H_{\beta trans}-P)$/Hz	1·5	+4·5

Compound (2) was assigned the structure shown on the grounds of the large $^{1}J_{\mathrm{Pt-P}}$ coupling. ^{1}H-{^{31}P} and H^{1}-{^{195}Pt} INDOR established the signs given in Table 1. We were able to show that the geminal olefin proton (with the large, *trans*-proton coupling) in (2) had $^{2}J_{\mathrm{Pt-H}}$ −32 ± 1 Hz, by assuming that the larger of the two olefin couplings was the *trans*-interaction. Although the other two olefinic protons were coupled to platinum, they showed no resolved phosphorus coupling.

Complex (3) provided the most spectacular evidence for the opposite signs of the two $^{3}J_{\mathrm{P-H}}$ interactions. In a ^{1}H-{^{195}Pt} selective decoupling experiment, irradiation of the lower-frequency platinum transition (broad) collapsed the lower-frequency proton satellites of the high-frequency (low field) methyl proton resonance and the higher-frequency proton satellite of the low-frequency methyl resonance (Figure C). The low-field methyl group can thus be assigned to be *cis* to the phosphorus atom, having the positive ^{3}J coupling. We completed all possible ^{1}H-{^{31}P} and ^{1}H-{^{195}Pt} INDOR experiments to produce the data in Table 1. Using the same techniques, we were able to show that all three platinum-to-olefin proton coupling constants were negative,* and that phosphorus-to-olefin proton couplings were positive for the two geminal protons.



A, Methyl ^{1}H n.m.r. spectrum (at 100 MHz) of $PtMe_2$(sp) with central doublets at δ 1·19 and 0·74, from molecules with non-magnetic platinum nuclei; B, ^{1}H-{^{195}Pt} INDOR irradiation Ξ = 21,413,327 Hz; C, ^{1}H-{^{195}Pt} INDOR irradiation at Ξ = 21,411,597 Hz

The complex PtClMe(dpe), from which the nitrato-complex (1) is formed, was obtained in an impure state by treating (1,5-cod)PtClMe with dpe [(1,5-cod) = cyclo-octa-1,5-diene and dpe = bis-(1,2-diphenylphosphino)ethane]. Its ^{1}H n.m.r. parameters agree well with those previously reported,[5] and the signs of the coupling constants were the same as those of complex (1).

Conclusions.—We have determined the absolute signs of $^{3}J_{\mathrm{P-H}}$ couplings in the methyl platinum(II) tertiary phosphine complexes and thereby have provided a means of establishing the position of alkyl groups relative to phosphorus atoms in such complexes. This will be particularly valuable for mixed alkyl

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* *Note added in proof.* This agrees with the results for compounds of the type PtCl(acac)(olefin), see C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1653.

[5] K. A. Hooton, *J. Chem. Soc.* (*A*), 1970, 1896.

complexes where ${}^1J_{\text{Pt-P}}$ may not be diagnostic. Absolute signs have also been determined for some platinum and phosphorus couplings to the olefin protons of co-ordinated 2-vinylphenyl(diphenyl)phosphine.

EXPERIMENTAL

All experiments were performed in the frequency sweep mode of a Varian HA-100 spectrometer with a double-tuned transmitter coil, the spectrometer carrier frequency being phase-locked to the frequency synthesiser used for the INDOR irradiation. Ξ values are resonant frequencies in a field in which protons of an internal tetramethylsilane lock would resonate at exactly 100 MHz. Although it was possible to *decouple* the platinum transitions (that is, to produce singlet peaks), we preferred to avoid the heating problems caused by this and to use lower power and *collapse* the satellites in the proton spectrum. Decoupling phosphorus from protons presented no problem because of the comparatively weaker coupling involved.

I.r. spectra were recorded on a Perkin-Elmer model 457 spectrophotometer, with Nujol and hexachlorobutadiene mulls and caesium iodide windows. All solvents (A.R. grade) were dried over sieves (B.D.H. 4A) before use. Analyses were by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates).

*Dichloro(cyclo-octa-*1,5-*diene)platinum*(II) [(1,5-cod)$PtCl_2$].—Anhydrous platinum(II) chloride (0·5 g) was refluxed with excess of cyclo-octa-1,5-diene (2 ml) in chloroform for one week. The solution was filtered hot, the solvent removed under vacuum, and the off-white crystalline product washed with n-pentane (2 × 10 ml) and dried at the pump (yield = 0·64 g, 91%). The product is identical with that obtained from Na_2PtCl_4 and the diene in propan-1-ol.[6]

*Dimethyl(cyclo-octa-*1,5-*diene)platinum*(II) [(1,5-cod)-$PtMe_2$].—This was prepared from (1,5-cod)$PtCl_2$ by treatment with excess of methylmagnesium iodide in diethyl ether, as described.[7] From 0·6 g of (1,5-cod)$PtCl_2$, 0·54 g of (1,5-cod)$PtMe_2$ was obtained (96%).

*Nitrato(methyl)[bis-(*1,2-*diphenylphosphino)ethane]platinum*(II) [PtMe(NO_3)(dpe)] (1).—A solution of (1,5-cod)-$PtMe_2$ (0·15 g, 0·45 × 10^{-3} mol) in benzene (15 ml) was treated dropwise with a 0·082N solution (5·5 ml) of HCl in diethyl ether (0·45 × 10^{-3} mol) with stirring during 5 min. A solution of bis-(1,2-diphenylphosphino)ethane (0·18 g, 0·45 × 10^{-3} mol) in benzene (5 ml) was added dropwise with stirring. After addition of the ligand was complete, the solution was gently refluxed for 5 min, filtered hot, and the impure PtClMe(dpe) precipitated by addition of n-hexane. The supernatant liquid was decanted, and the colourless complex was washed with n-pentane (2 × 5 ml) and dried at the pump (yield 0·25 g). The impure complex (*ca.* 30 mg) was dissolved in CD_2Cl_2 (0·5 ml) in an n.m.r. tube, and three drops of water were added, followed by an excess of solid silver nitrate. The mixture was left overnight, and was then filtered to remove excess of solid silver nitrate and precipitated silver chloride. After the ${}^1H$ n.m.r. and INDOR spectra had been measured, n-pentane was added to the solution to give colourless crystals of the *complex* in essentially quantitative yield. These were dried at the pump (Found: C, 47·4; H, 4·0; P, 8·6; N, 2·2. $C_{27}H_{27}NO_3P_2Pt$ requires C, 48·4; H, 4·1; P, 9·2; N, 2·1%). Bands typical of unidentate NO_3 [8] appeared at 1370 cm^{-1} (s) and at 1480—1500 cm^{-1} (broad, shoulder on ligand band at 1468 cm^{-1}). The i.r. spectrum in a KBr disc showed a band at 1385 cm^{-1} due to ionic NO_3, presumably formed by exchange in the disc.

The complex PtClMe(dpe) had been prepared[5] by pyrolysis of the ionic triethylphosphine complex [PtMe-(PEt_3)(dpe)]Cl. In our preparations, the low-field satellite of the methyl resonance of this product was always masked by another quartet, which had its high-field satellite under the methyl resonance of PtClMe(dpe). The analyses of PtClMe(dpe) were always low in C, P, and Cl, although our impure chloro-species showed ν(Pt–Cl) at 291 cm^{-1}, in agreement with that reported.[5] Recent work (by Dr. T. G. Appleton) has shown that the impurity is PtIMe(dpe). This arises from the complex (1,5-cod)PtIMe which is formed in small amounts together with (1,5-cod)$PtMe_2$ in the reaction of an excess of methylmagnesium iodide with (1,5-cod)$PtCl_2$. Pure (1,5-cod)$PtMe_2$ can be obtained by using an excess of methyl-lithium in place of methylmagnesium iodide and the dimethyl complex can be converted into pure (1,5-cod)PtClMe and PtClMe(dpe) as described above.

*Dimethyl-[*2-*vinylphenyl(diphenyl)phosphine]platinum*(II) [$PtMe_2$(sp)] (3).—A solution of (1,5-cod)$PtMe_2$ (0·22 g, 0·67 × 10^{-3} mol) in n-hexane (30 ml) was heated with 2-vinylphenyldiphenylphosphine (sp) (0·19 g, 0·67 × 10^{-3} mol) under reflux for 1 h. The solution was cooled to room temperature, and the insoluble *product* was filtered off, washed with ice-cold n-hexane (2 × 5 ml), and dried at the pump (yield 0·26 g, 76%) (Found: C, 52·4; H, 4·6; P, 6·3. $C_{22}H_{23}PPt$ requires C, 51·5; H, 4·5; P, 6·0%).

*Chloro(methyl)-[*2-*vinylphenyl(diphenyl)phosphine]platinum*(II) [PtClMe(sp)] (2).—A solution of $PtMe_2$(sp) (0·066 g, 1·29 × 10^{-4} mol) in benzene (10 ml) was treated with 0·074N-HCl (1·74 ml) in diethyl ether (1·3 × 10^{-4} mol) with stirring. The solvent was removed under vacuum, and the residue recrystallised from benzene–ethanol giving white crystals (0·055 g, 80%) (Found: C, 47·4; H, 3·7. $C_{21}H_{20}ClPPt$ requires C, 47·2; H, 3·8%); ν(Pt–Cl) 298 cm^{-1} (Nujol mull).

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