An Investigation by Nuclear Magnetic Resonance of the Effects of the Pentafluorophenyl Group on the Rotation of the Triethylphosphine Ligands in some Platinum(IV) Complexes

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The variable-temperature ^1H and ^{19}F n.m.r. spectra of *cis-cis-trans*-$[PtX_2(C_6F_5)_2(PEt_3)_2]$ and *mer-trans*- and *mer-cis*-$[PtX_3(C_6F_5)(PEt_3)_2]$ (X = Cl or Br) have been investigated. It is concluded that, at low temperatures, the rotation of the phosphine ligands is prevented by steric interaction with *cis*-pentafluorophenyl groups. Values of δ_P, δ_{Pt}, $^2J(PP)$, and $^1J(PtP)$ from heteronuclear INDOR measurements are reported.

THE structures proposed for the platinum(IV) complexes formed by the addition of chlorine or bromine to *cis*- and *trans*-$[PtX(C_6F_5)(PEt_3)_2]$ and *cis*-$[Pt(C_6F_5)_2(PEt_3)_2]$ (X = Cl or Br) were based on dipole-moment measurements.[1] Recently we have shown that a *trans*-P–Pt–P arrangement is distinguished by a large positive value of $^2J(PP)$ and that the latter can conveniently be determined by ^1H-$\{^{31}P\}$ INDOR.[2] Since the magnitude of $^1J(PtP)$ also gives a good indication of the *trans* ligand, we have now made detailed n.m.r. measurements on these complexes to confirm their stereochemistry. Our studies are confined to chlorides and bromides as the addition of iodine to solutions of pentafluorophenylplatinum(II) complexes gave no indication of the formation of platinum(IV) derivatives.

TABLE 1

N.m.r. parameters from ^1H spectra of *trans*-(pentafluorophenyl)bis(triethylphosphine)platinum complexes

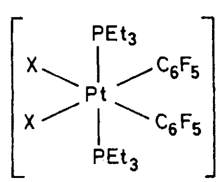
Complex	τ(CH_2) [a]	τ(CH_3)	δ_P [b]	$^2J(PP)$ [b]	$^1J(PtP)$ [b]	δ_{Pt} [c]
cis-cis-trans-$[PtCl_2(C_6F_5)_2(PEt_3)_2]$	7.81	8.82	−2.2	+510	1 463	*d*
cis-cis-trans-$[PtBr_2(C_6F_5)_2(PEt_3)_2]$ [e]	7.66	8.81	5.5	+507	1 462	1 382
cis-cis-trans-$[PtI_2(C_6H_5)_2(PEt_3)_2]$	7.76	9.05	21.7	+491	1 803	1 046
mer-trans-$[PtCl_3(C_6F_5)(PEt_3)_2]$	7.72	8.88	−4.1	+550	1 475	2 164
mer-trans-$[PtBr_3(C_6F_5)(PEt_3)_2]$	7.57	8.85	7.7	+547	1 481	1 235
trans-$[PtCl(C_6F_5)(PEt_3)_2]$	8.37	8.94	−14.9	+403	2 486	92
trans-$[PtBr(C_6F_5)(PEt_3)_2]$	8.36	8.96	−12.9	+379	2 456	−52
trans-$[PtI(C_6F_5)(PEt_3)_2]$	8.18	8.97	−8.9	+379	2 426	−310

[a] $|^2J(PH) + {}^4J(PH)| \approx {}^3J(HH) \approx \frac{1}{2}|^3J(PH) + {}^5J(PH)| \approx 8$ Hz. [b] From ^1H-$\{^{31}P\}$ INDOR; values ±0.2 p.p.m. or ±10 Hz. δ_P is the shift upfield of H_3PO_4. [c] In p.p.m. to high frequency of 21.4 MHz when corrected to $SiMe_4$ (δ 100 MHz). [d] Not measured. [e] At 310 K.

RESULTS

$[PtX_2(C_6F_5)_2(PEt_3)_2]$ (X = Cl *or* Br).—The ^1H n.m.r. spectrum of the methyl groups of $[PtCl_2(C_6F_5)_2(PEt_3)_2]$ is the typical quintet of a *trans*-bis(triethylphosphine) complex[3] but the methylene protons are a broad unresolved hump. The methyl resonances of the bromo-derivative are noticeably broadened at room temperature but are much narrower at 40 °C. The relevant parameters from the ^1H and ^{31}P n.m.r. spectra (obtained by ^1H-$\{^{31}P\}$ INDOR measurements on the methyl peaks) are given in Table 1. The values of $^2J(PP)$ clearly indicate a linear P–M–P arrangement and the values of $J(PtP)$ agree with this.[2] The i.r. and Raman spectra of the chloro-complex both showed two PtCl stretching vibrations at the same wavenumbers (308, polarised for Raman spectrum of tetrahydrofuran solution, and 292 cm^{-1}). Thus the complexes have the *cis-cis-trans* structure (1).

On irradiation of the main ^{31}P resonance, the methylene resonances became partially resolved but the result was a quintet not a quartet. This suggested that the methylene protons were diastereotopic and the ^{19}F spectra showed the source of the asymmetry. Both complexes showed five ^{19}F resonances of equal intensity and ^{19}F-$\{^{19}F\}$ decoupling experiments on the bromide proved that all the five were linked by *ortho* couplings. The obvious conclusion is that the pentafluorophenyl groups are not free to rotate about the Pt–C bond. The obstruction is presumably the phosphine ligands; *e.g.* from models the *o*-fluorines would have to ap-



(1)

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[1] R. Usón, P. Royo, and J. Gimeno, *Rev. Acad. Cienc. Exactas, Fis.-Quim. Natur. Zaragoza*, 1973, **28** (3), 355.

[2] R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, 1974, 1676.

[3] F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1326.

proach to within *ca.* 220 pm of the phosphorus atom compared with the sum of van der Waals radii of 325 pm and the ethyl groups are likely to constitute an even greater

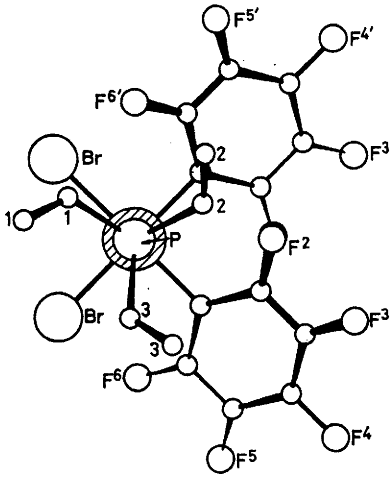

FIGURE 1 Suggested configuration of $[PtBr_2(C_6F_5)_2(PEt_3)_2]$ viewed down the P–Pt–P axis; the far PEt_3 group has been omitted

barrier. The situation and spectra are similar to those of the iridium complexes, $[IrXY(C_6F_5)(CO)(PPh_3)_2]$ (XY = Cl_2, Br_2, I_2, HCl, or HBr).[4] The chemical shift of the *o*-fluorines nearest to the halides (Figure 1, $F^6F^{6'}$) should alter much more on going from chloride to bromide than the other *o*-fluorines ($F^2F^{2'}$) and this and the decoupling experiments are the basis of the assignments in Table 2.

When the temperature was decreased, the features of the proton spectrum of $[PtBr_2(C_6F_5)_2(PEt_3)_2]$ became broad. At 220 K the spectrum again became sharp and, particularly with ^{31}P decoupling, four sets of lines can be distinguished (see Figure 2). ^1H-$\{^{31}P\}$ INDOR measurements using the three types of methyl group (one in area C and two in D) gave the same ^{31}P main resonance to within ± 1 Hz), and δ_P (+5.3 p.p.m.) and $J(PtP)$ (1 458 Hz) are very close to the values at 310 K. The ^{19}F spectrum was unchanged at 220 K. It follows that the two phosphines are still equivalent; only their ethyl groups become inequivalent at low temperature, *i.e.* they have ceased to rotate about the Pt–P bond. The areas A : B : C : D integrate in the ratio *ca.* 2 : 3 : 4 : 6. Area A clearly corresponds to one diastereotopic methylene group whilst D corresponds to two methyl groups. We are forced to the conclusion that the chemical-shift difference for one diastereotopic methylene group is so large that one half combines with the third methylene group to give area B whilst the other is in area C, under the third methyl group. ^1H-$\{^1H\}$ Decoupling showed that the methylene of area A was coupled to the methyl of area C but the other groups were too close for satisfactory decoupling experiments. However, the assignment of the lines of these methylene resonances and their relation to the methyl peaks was possible by ^1H-$\{^1H\}$ INDOR experiments using low irradiating powers and observing the lines of the methyl triplets (with ^{31}P decoupling). The INDOR spectra were typical of ethyl groups and implied that $^2J(HH)$ and $^3J(HH)$ had opposite signs. The appearance of the spectra, especially the methyl resonance, suggested that $^3J(HH)$ did not differ between the two protons of a methylene group or, in fact, between ethyl groups. As the condition $J_{AX} = J_{BX}$ greatly simplifies the analysis of the ABX_3 spin system,[5] we

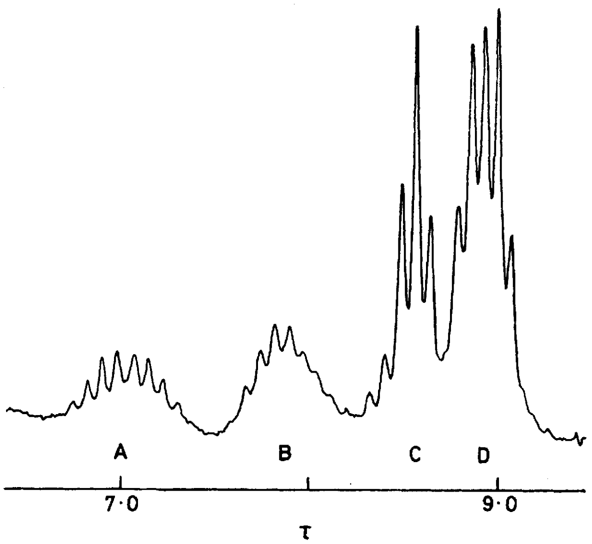

FIGURE 2 Hydrogen-1 n.m.r. spectrum of $[PtBr_2(C_6F_5)_2(PEt_3)_2]$ in $CDCl_3$ at 220 K with ^{31}P decoupling

TABLE 2

Fluorine-19 n.m.r. parameters

	Chemical shift/p.p.m.[a]					Coupling constants (*J*/Hz)							
Complex	F^2	F^6	F^3	F^5	F^4	PtF^2	PtF^6	PtF^3	PtF^5	PtF^4	F^2F^3	F^5F^6	$F^3F^4 \simeq F^4F^5$
cis-cis-trans-$[PtCl_2(C_6F_5)_2(PEt_3)_2]$ [b,c]	116.3	106.7	163.2	160.9	157.9	145	95	45	40	18	24	26	20
cis-cis-trans-$[PtBr_2(C_6F_5)_2(PEt_3)_2]$ [b,c]	115.9	100.8	163.1	160.7	157.8	136	102	45	40	19	25	25	21
mer-trans-$[PtCl_3(C_6F_5)(PEt_3)_2]$ [d]	111.5		162.8		159.0	85		39		20	22		21
mer-trans-$[PtBr_3(C_6F_5)(PEt_3)_2]$ [c]	106.5		161.4		157.3	93		38		18	22		21
mer-cis-$[PtCl_3(C_6F_5)(PEt_3)_2]$ [e] [f]	115.3	113.9	162.0	161.3	157.9	*ca.* 65	*ca.* 50	*h*		*h*	27	23	20
[g]	113.7		163.8		159.7	59		26		*h*	23		20
mer-cis-$[PtBr_3(C_6F_5)(PEt_3)_2]$ [e] [f]	108.4	105.6	162.1	161.4	157.9	*ca.* 85	*ca.* 60	*h*		*h*	29	29	22
[i]	106.3		163.5		159.5	63		*h*		*h*	24		21
cis-$[PtCl(C_6F_5)(PEt_3)_2]$ [e]	119.6		163.7		162.2	307		60		*h*	20		20
cis-$[PtBr(C_6F_5)(PEt_3)_2]$ [e]	119.0		164.3		162.8	309		62		*h*	21		20
cis-$[PtI(C_6F_5)(PEt_3)_2]$ [d]	116.5		165.0		163.9	311		61		*h*	23		20
cis-$[Pt(C_6F_5)_2(PEt_3)_2]$ [e]	117.6		163.7		163.0	354		68		13	*h*		20

[a] Relative to $CFCl_3$. [b] $J(F^2F^5)$, $J(F^3F^5)$, and $J(F^3F^6)$ *ca.* 5 Hz; $J(F^2F^4)$ and $J(F^4F^6)$ too small to be visible. [c] In $CDCl_3$. [d] In $(CD_3)_2CO$. [e] In CD_2Cl_2. [f] At 180 K. [g] At 300 K. [h] Coupling not identified in spectrum. [i] At 270 K.

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[4] R. L. Bennett, M. I. Bruce, and R. C. F. Gardner, *J.C.S. Dalton*, 1973, 2653.

[5] V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, 1960, **33**, 1794.

assumed this to be the case in evaluating the shifts in Table 3. Similar results were obtained for the chloro-complex at temperatures of *ca.* 30 K lower except that the shift between the methylene protons of ethyl(1) was too small to be identified.

The solid-state structures of some platinum(II) complexes of triethylphosphine [6] have one ethyl group pointing away from the metal. The other two methyl groups are directed away from the plane of the molecule with their carbon atoms somewhat nearer to the vertical axis than the methylene carbons. As the internuclear distance between these methyl carbon atoms and an atom such as chlorine placed on the vertical axis is only *ca.* 270 pm, such an arrangement is unlikely to persist on oxidation. Indeed, the chemical shifts of the methyl protons are much less sensitive than those of the methylene group to change of halide and to the magnetic anisotropy of the aryl rings, suggesting that all the methyl groups are directed away from the metal. A *cis*-M–X bond significantly affects the chemical shifts of the protons of co-ordinated PMe_3 *via* its electric dipole and magnetic anisotropy.[7] Since these effects depend on distance, they may be used here as a guide to the relative positions of the three ethyl groups.

TABLE 3

Hydrogen-1 n.m.r. parameters of low-temperature spectra of $[PtX_2(C_6F_5)_2(PEt_3)_2]$ and $[PtX_3(C_6F_5)(PEt_3)_2]$

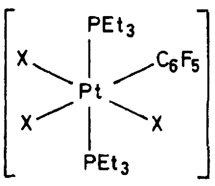
	Et(1)			Et(2)			Et(3)			
Complex	τ(CH_2)		τ(CH_3)	τ(CH_2)		τ(CH_3)	τ(CH_2)		τ(CH_3)	*T*/K
cis-cis-trans-$[PtCl_2(C_6F_5)_2(PEt_3)_2]$ *		*ca.* 7.31	8.57	7.80	8.07	8.85	7.86	8.54	9.00	220
cis-cis-trans-$[PtBr_2(C_6F_5)_2(PEt_3)_2]$ *	6.87	7.17	8.56	7.80	8.05	8.85	7.78	8.43	8.98	230
mer-trans-$[PtCl_3(C_6F_5)(PEt_3)_2]$		*ca.* 7.33	8.87		*ca.* 8.22	8.79	*ca.* 7.13	?	9.28	180
mer-trans-$[PtBr_3(C_6F_5)(PEt_3)_2]$		*ca.* 7.12	8.84		*ca.* 8.19	8.61	6.94	8.12	9.21	180

* ^2J(HH) 15 and ^3J(HH) 7 Hz for all the ethyl groups.

Thus, comparing the shifts of the methylene protons in chloro- and bromo-complexes, ethyl(1) is clearly nearest to the halides whilst ethyl(2) is furthest away, *i.e.* in the PtC_2 quadrant. From models, it appears that there is only room for one of the methylene protons of ethyl(2) between the nearest fluorine atoms (F^2 and $F^{6'}$) and, according to which of the methylene protons it is, the C–C bond will lie approximately parallel to or perpendicular to the $C_6F_5{}'$ ring. It is presumably the interaction of this methylene proton and the *o*-fluorine atoms that provides the barrier to rotation and when the triethylphosphine groups cease to rotate it seems unlikely that the partial rotation of ethyl(2), which would exchange the methylene proton between F^2 and $F^{6'}$, can occur either. It is not obvious why one of the two possible orientations should be preferred but this is presumably the case since only one form of the complexes is observed and this has both sets of ethyl groups in the same orientation. Changing halide has an almost equal effect on the shifts of the two methylene protons of ethyl(3), suggesting that both are reasonably near to the halides in which case the methyl group must point away from the halides. If, to lessen the steric interactions within the triethylphosphine group, all the methyl groups point in the same direction, then the configuration will be approximately that of Figure 1.

We also studied the phenyl complex $[PtI_2Ph_2(PEt_3)_2]$ which has the same structure.[8] The triethylphosphine resonances did not separate on lowering the temperature although the P–H and H–H splitting became unresolved at low temperature.

mer-trans-$[PtX_3(C_6F_5)(PEt_3)_2]$ (X = Cl *or* Br).—The platinum(IV) complex formed by the addition of the appropriate halogen to *trans*-$[PtX(C_6F_5)(PEt_3)_2]$ (X = Cl or Br) must have the *trans* disposition of the phosphine ligands as in structure (2) to account for the values of ^2J(PP) and ^1J(PtP) (Table 1).



(2)

At room temperature, the methylene resonances of $[PtBr_3(C_6F_5)(PEt_3)_2]$ were the usual pattern for a *trans*-bis(triethylphosphine) complex and do not appear to be diastereotopic. However, on cooling they broadened and then separated as did the methyl resonances (Figure 3). Unfortunately, even with ^{31}P irradiation, the features were not well resolved and the methylene resonances appeared as two broad humps each corresponding to three protons. ^1H-{^1H} INDOR observing the high-field methyl resonance showed that the related methylene group contributed one proton to each of these features. INDOR likewise identified the methylene group related to the middle methyl signal, but the third methylene resonance is assigned by elimination because it was too close to the low-field methyl band for

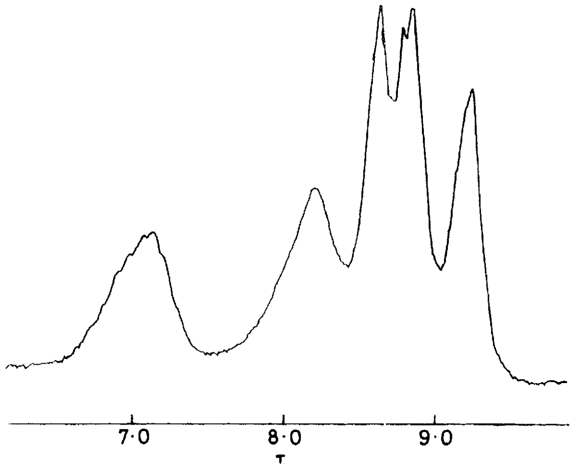


FIGURE 3 Hydrogen-1 n.m.r. spectrum of *mer-trans*-$[PtBr_3(C_6F_5)(PEt_3)_2]$ in CH_2Cl_2 at 180 K with ^{31}P decoupling

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[6] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1775; D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlovic-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

[7] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, 2134.

[8] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

double-resonance work. The C_6F_5 group is not asymmetric, even at low temperature (^{19}F n.m.r. parameters in Table 2). The chloro-complex behaved similarly but the low-temperature features were less well resolved at 180 K. The n.m.r. parameters (Table 4) are less informative on the low-temperature conformation than for the bis(pentafluorophenyl) complexes but are consistent with an arrangement like that of Figure 1 in which C_6F_5' is replaced by bromide.

mer-cis-$[PtX_3(C_6F_5)(PEt_3)_2]$(X = Cl *or* Br).—The product of the reaction of chlorine with *cis*-$[PtCl(C_6F_5)(PEt_3)_2]$ had Pt–Cl stretching vibrations typical of a *mer*-$[PtCl_3]$ unit [9] (i.r. 344s, 325m, and 281s; Raman 326s and 279s cm^{-1}). The n.m.r. spectra showed two types of triethylphosphine groups with parameters (Table 4) as expected for structure (3). The product isolated from the analogous reaction of bromine with *cis*-$[PtBr(C_6F_5)(PEt_3)_2]$ was identified as *mer-trans*-$[PtBr_3(C_6F_5)(PEt_3)_2]$ [structure (2)] from its spectra. When the reaction was carried out in dichloromethane, the n.m.r. spectra recorded *in situ* paralleled those of the chloro-complex but considerable isomerisation occurred within 1 h at room temperature.

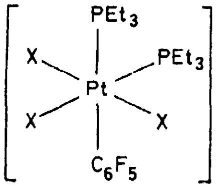
TABLE 4

N.m.r. parameters from ^1H spectra of *cis*-(pentafluorophenyl)bis(triethylphosphine)platinum complexes

	PEt$_3$ *trans* to C_6F_5				PEt$_3$ *trans* to halide				
	$\tau(CH_2)$ [a]	$\tau(CH_3)$	δ_P [b]	$^1J(PtP)$ [b]	$\tau(CH_2)$	$\tau(CH_3)$	δ_P [b]	$^1J(PtP)$ [b]	δ_{Pt} [c]
mer-cis-$[PtCl_3(C_6F_5)(PEt_3)_2]$	7.69	8.67	12.5	1 336	7.57	8.80	−9.8	2 103	2 038
mer-cis-$[PtBr_3(C_6F_5)(PEt_3)_2]$	7.54	8.65	26.6	1 351	7.48	8.77	0	2 043	*d*
cis-$[Pt(C_6F_5)_2(PEt_3)_2]$	8.32	8.88	−1.7	2 356					−135
cis-$[PtCl(C_6F_5)(PEt_3)_2]$	7.97	8.82	−10.2	2 186	8.30	8.92	−4.4	3 763	−2
cis-$[PtBr(C_6F_5)(PEt_3)_2]$	7.89	8.83	−7.1	2 197	8.31	8.92	−4.6	3 744	−127
cis-$[PtI(C_6F_5)(PEt_3)_2]$	7.76	8.85	−2.6	2 216	8.32	8.93	−2.6	3 636	−358

[a] $^2J(PH) \approx \frac{1}{2}\{^3J(PH)\} \approx {}^3J(HH) \approx 8$ Hz. [b–d] as in Table 1.

At normal temperature the ^{19}F n.m.r. spectra corresponded to a symmetric pentafluorophenyl group. However, on cooling, the *o*- and *m*-fluorine resonances broadened and then each divided into two so that they resembled those of the asymmetric C_6F_5 groups of $[PtX_2(C_6F_5)_2(PEt_3)_2]$. (The assignments in Table 2 are based on this analogy.) The proton resonances of the phosphine *cis* to C_6F_5 first broadened when the temperature was decreased and then separated to give a broad band, equivalent to one methylene group at low field (τ 6.77, X = Cl; 6.63, Br) and another unresolved feature to high field (τ 8.02, X = Cl; 7.99, Br) which probably extends under the resonances of the other phosphine and corresponds to the remaining two methylene groups. The methyl resonances of this phosphine also separated at low temperature, one going markedly to high field [*ca.* τ 8.7 (twice) and 9.03, X = Cl; 8.61, 8.69, and 8.96, Br]. Because the resonances were broad at 190 K, attempts at ^1H-$\{^1H\}$ INDOR measurements were not satisfactory and we did not obtain any information relating the methylene groups to their respective methyl groups. The resonances of the phosphine *trans* to C_6F_5 did not separate at low temperature although the lines broadened such that, at 180 K, signs of P–H coupling had almost disappeared.



(3)

Platinum(II) *Complexes*.—Hopton *et al.*[3] reported details of the platinum(II) precursors of the platinum(IV) complexes described above. In view of the effect of temperature on the spectra of the latter, we made similar measurements on some of the platinum(II) complexes. For *cis*-$[PtX(C_6F_5)(PEt_3)_2]$ (X = Cl and I), *trans*-$[PtI(C_6F_5)(PEt_3)_2]$, and *cis*-$[Pt(C_6F_5)_2(PEt_3)_2]$, there was no significant difference between the spectra at room temperature and at 180 K. The lines of the proton spectra of these and *trans*-$[PtCl(C_6F_5)(PEt_3)_2]$ did no more than broaden at 180 K. The latter effect seems to be general for the triethylphosphine complexes studied here and probably reflects a barrier to rotation within the PEt$_3$ group. Some ^{31}P and ^{195}Pt parameters from INDOR measurements are recorded in Tables 1 and 4, and the ^{19}F parameters for some *cis* complexes which were not reported previously or for which the values are markedly different are given in Table 2. The resonances of the *o*-fluorines of *cis*-$[PtX(C_6F_5)(PEt_3)_2]$ (X = Cl, Br, or I) showed an additional splitting of 16 Hz which must be due to coupling from the phosphorus *trans* to the C_6F_5 group, as a corresponding coupling was not observed for the *trans* isomers where both phosphines are *cis* to the C_6F_5 group. A similar coupling of 10 Hz was observed on the *m*-fluorine resonances. The platinum(IV) complex *mer-cis*-$[PtCl_3(C_6F_5)(PEt_3)_2]$ showed a coupling of 11 Hz from phosphorus to the *m*-fluorines but, surprisingly, no observable coupling to the *o*-fluorines. As in the spectra of the platinum(IV) complexes, the resonances of the *p*-fluorine of *trans*-$[PtX(C_6F_5)(PEt_3)_2]$ (X = Cl, Br, or I) had satellites corresponding to $^5J(PtF)$ 20 Hz.

DISCUSSION

Although we have suggested that interaction between the ethyl groups and *cis* halides in *trans*-$[PtX_4(PEt_3)_2]$ results in weakening of the Pt–P bond,[2] any such interaction does not result in a barrier sufficient to inhibit the rotation of the phosphine at low temperature. However, rotation can be stopped if there is a *cis*-C_6F_5 group. In the platinum(II) complexes, the pentafluorophenyl group can lie perpendicular to the Pt–P bond with the *o*-fluorine atoms above and below the plane of the complex, and in this position will have very little interaction with the alkyl groups of the phosphine. In $[PtX_2(C_6F_5)_2(PEt_3)_2]$, the aryl rings must be tilted out of the plane perpendicular to the Pt–P bond in order to accommodate the *o*-fluorine atoms on adjacent rings, and in *mer-cis*-$[PtX_3(C_6F_5)(PEt_3)_2]$ the difference in the effect of change of halide on the two types of *o*-fluorine observed at low

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[9] P. L. Goggin and J. R. Knight, *J.C.S. Dalton*, 1973, 1489.

temperature suggests that the ring is tilted here also. Such tilting of the rings brings the *o*-fluorine atoms much closer to the phosphines, so providing the barrier to rotation. For all the three types of complex studied the temperature required to affect rotation of the phosphine is lower for chlorides than bromides. This would be expected if steric interaction between *o*-fluorine atoms and adjacent halides contributed to the tilting of the rings, the amount of tilting being greater for the bulkier halide. As a consequence of the symmetry, the tilting of the aryl group in *mer-trans*-$[PtX_3(C_6F_5)(PEt_3)_2]$ does not render the *o*-fluorine atoms inequivalent.

Previous examples of restricted rotation usually involve asymmetric phosphines with bulky substituents, *e.g.* *trans*-$[RhCl(CO)(PRBu^t{}_2)_2]$.[10] For the pentafluorophenyl complexes studied here we have found restricted rotation of a symmetric phosphine containing the sterically less demanding ethyl group. In contrast to $[RhCl(CO)(PRBu^t{}_2)_2]$, only one conformer was found in each case.

N.M.R. Parameters.—The electron-withdrawing effect of the fluorines in C_6F_5 should result in a lower σ-donor ability than Ph or Me. Thus, in *cis*-$[PtCl(C_6F_5)(PEt_3)_2]$, ^1J(PtP) for the phosphine *trans* to C_6F_5 is much less than when *trans* to chloride {3 520 Hz in *cis*-$[PtCl_2(PEt_3)_2]$ [11]}, but not nearly so low as when *trans* to methyl {1 719 Hz in *cis*-$[PtCl(Me)(PEt_3)_2]$ [12]}. The presence of a methyl substituent in a *cis* position produces a large increase in ^1J(PtP). Pentafluorophenyl also produces an increase but it is much less than for methyl in the platinum(II) complexes and minimal in the platinum(IV) ones. The ^{195}Pt chemical shifts of the pentafluorophenylplatinum(II) complexes are not far removed from those of the analogous methyl complexes [13,14] suggesting that the difference in σ-donating and π-accepting properties of these two organic ligands either does not greatly affect δ_{Pt} or that the effects of these differences largely cancel each other out. The difference between the platinum shifts of related chloro- and bromo-complexes usually reflects the *trans* influence of the ligand opposite the halide.[13] However, the small difference in this respect between CH_3 and C_6F_5 contrasts with their relative *trans* influences, *e.g.* the behaviour of ^1J(PtP) above.

Since coupling from ^{195}Pt to the *o*-fluorines involves three bonds, it will not necessarily show a simple relation to the Pt–C bond strength, despite which, for *cis*-$[PtX(C_6F_5)(PEt_3)_2]$, there is a good correlation between ^3J(PtF) and the expected *trans* influence of the *trans* ligand.[3] The much greater reduction in ^3J(PtF) (*ca.* 1 : 5) on oxidation compared to ^1J(PtP) (*ca.* 2 : 3) indicates a weaker Pt–C bond in the higher oxidation state if this correlation extends to the comparison of oxidation states. On the basis that the electron density on the *p*-fluorine will be affected both by π donation from the metal to the ring and by σ donation from the ring to the metal, whereas the electron density on the *m*-fluorine atoms will only be affected by the latter, Hopton *et al.*[3] used the difference between the ^{19}F chemical shifts of the *p*- and *m*-fluorines to evaluate the degree of π bonding to the aryl ring. For all the platinum(IV) complexes here, this difference is close to −4.1 p.p.m. which is more negative than for the related platinum(II) complexes (*ca.* −1.5 p.p.m.),[3] which is the predicted result if there is less π donation from the metal in the higher oxidation state.

EXPERIMENTAL

The ^{19}F n.m.r. spectra were recorded on a JEOL PFT 100 Fourier-transform spectrometer, using an internal deuterium lock. Proton and double-resonance spectra were obtained with a Varian Associates HA 100 spectrometer as previously described.[15] Except where otherwise indicated, samples were as *ca.* 0.1 mol dm^{-3} solutions in dichloromethane.

The chloro- and bromo-complexes were those of ref. 1. We attempted to prepare analogous iodoplatinum(IV) complexes by addition of iodine to solutions of platinum(II) complexes. Even after 1 d, the ^{1}H and ^{19}F n.m.r. spectra of an equimolar mixture of $[Pt(C_6F_5)_2(PEt_3)_2]$ and I_2 in dichloromethane showed no feature additional to those of the initial platinum(II) complex and the colour of the solution was still violet. The n.m.r. parameters, especially ^1J(PtP), for an equimolar mixture of *cis*-$[PtI(C_6F_5)(PEt_3)_2]$ and I_2 in dichloromethane fit a *trans*-platinum(II) rather than a platinum(IV) complex. The brown colour of the solution and the differences in the ^{31}P and ^{195}Pt n.m.r. parameters from those of *trans*-$[PtI(C_6F_5)(PEt_3)_2]$ probably indicate that there is a small amount of the platinum(IV) complex present in rapid equilibrium with the platinum(II) complex, *cf.* the reaction of iodine with $[PtI_2(PMe_3)_2]$.[16]

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