Restricted Rotation and Preferred Conformations in Tris(pentafluorophenyl)phosphine Platinum(II) Complexes; the Mechanism of Helicity Reversal in a Co-ordinated Triarylphosphine

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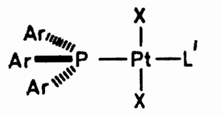
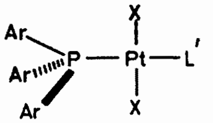
Summary Variable temperature ^{19}F and ^{31}P n.m.r. studies of some tris(pentafluorophenyl)phosphine platinum complexes show restricted rotation at low temperatures about the Pt–P and C(1)–P bonds with a preferred conformation in which none of the C(1)–P bonds lie in the platinum co-ordination plane; the mechanism of helicity reversal of the propeller-shaped ligand is a two-ring flip.

Triarylphosphines acting as ligands have non-planar propeller-like arrangements of aryl rings about the phosphorus[1] with two possible helical forms. We now report variable temperature ^{19}F and ^{31}P n.m.r. studies of the conformational behaviour in solution of platinum(II) complexes containing tris(pentafluorophenyl)phosphine, (L), $(C_6F_5)_3P$, as a ligand.

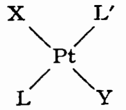
Kemmitt *et al.*[2] observed temperature dependent n.m.r. signals for the *ortho*-fluorines of L in the *trans*-platinum(II) complexes (**1**)—(**3**) and suggested that there was restricted rotation about P–Pt and C(1)–P bonds but did not investigate the complete nature of these effects.



1(A)



1(B)



$L=(C_6F_5)_3P$

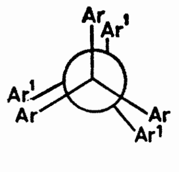
	L'	X	Y
(**1**)	$(C_6F_5)_3P$	Cl	Cl
(**2**)	$(C_6F_5)_3P$	Br	Br
(**3**)	$(C_6F_5)_3P$	I	I
(**4**)	PPh_3	Cl	Cl
(**5**)	PMe_2Ph	Br	Br
(**6**)	$PMePh_2$	Ph	Cl

We have now shown that in (**4**) and (**5**) (*trans* from the large values of $^2J_{PP}$) at −60 °C there are three *ortho*- (intensity 2:2:2), three *meta*- (intensity 2:2:2), and two *para*- (intensity 2:1) ^{19}F n.m.r. signals implying that two of the three aryl rings are equivalent with the two *ortho*-fluorines on the unique ring equivalent but the two *ortho*-fluorines on the equivalent rings non-equivalent [see 1(A) or 1(B)].

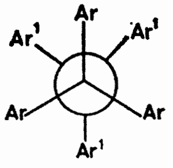
The above observations can be interpreted as representing the spectra of two propeller conformations of opposite helicity with rapid interconversion between conformers. Free rotation of the unique ring cannot be excluded by these observations alone and restricted rotation of L about the Pt–P bond is not required by the above observation (see below).

In the present work the low temperature ^{19}F n.m.r. spectra of (**1**) show two sets of three equal *ortho*-signals in the ratio *ca.* 3:1. The corresponding peaks for the *meta*- and *para*-fluorines are not completely resolvable at this temperature. The low temperature ^{31}P n.m.r. spectrum of (**1**) shows two signals (with ^{195}Pt satellites) in a 3:1 ratio, the value of $^1J_{PPt}$ showing that both species have *trans*-phosphines. The di-iodo complex (**3**) shows similar spectra at room temperature. Complexes (**1**) and (**3**) show simple spectra at 25 and 50 °C, respectively, the larger size of the iodide giving larger steric effects. We interpret these observations in terms of strongly hindered rotation about the Pt–P bonds at low temperature and the presence of two rotomers 2(A) and 2(B) which are eclipsed and staggered with respect to the aryl groups. The observation of rotational isomers for (**1**) and (**3**) but not for the triphenylphosphine complex (**4**) shows the greater barrier to rotation about the Pt–P bond in tris(pentafluorophenyl)phosphine complexes probably arising from larger C–P–C bond angles in the latter complexes.

In the ^{19}F n.m.r. spectrum of (**6**) the broad signal observed for the *ortho*-fluorines at room temperature separates into six equal signals at low temperature implying complete inequality of all *ortho*-fluorines and restricted rotation of each aryl group about its C(1)–P bond. The preferred conformation relative to the platinum co-ordination sphere must be with one aryl above the plane and two below as in 1(A) rather than as 1(B) which would continue to have equivalent aryl groups.



2(A)



2(B)

Helicity reversal in hindered propeller-like species may occur in four ways, called the zero-, one-, two-, and three-ring flip mechanisms by Kurland *et al.*,[3] depending upon the number of aryl rings which pass through a C(1)–P–Pt plane during the process. Mislow[4] has shown that the two-ring flip mechanism operates in triarylmethanes and triarylboranes with planar skeletons. The low temperature ^{19}F n.m.r. spectrum of (**4**) at −60 °C suggests an average of two propeller conformations of opposite helicity interconverting by the two-ring flip. The six *ortho*-signals of (**6**) are equally sharp at −80 °C but at −50 °C four are broadened whereas those at −121·2 and −125·4 p.p.m. remain sharp (see Table). This suggests that two of the rings have a lower barrier to rotation than the third.

Table[a]. N.m.r. parameters

		δ(^{19}F)/p.p.m.				L		L′			
		o	*m*	*p*	Temperature /°C	δ(^{31}P) /p.p.m.	*J*(PPt) /Hz	δ(^{31}P) /p.p.m.	*J*(PPt) /Hz	*J*(PP) /Hz	Temperature /°C
(1)	major	−119·8	−156·6			−26·9	3073				−80
				−141·6							
		−130·0	−157·2								
		−128·4	−158·3	−143·1	−65						
	minor	−120·9				−26·3	3081				
		−130·0									
		−127·2									
(3)	major	−115·6	−156·8			−42·3	2987				25
				−142·5							
		−130·3	−157·8								
		−124·1	−158·3	−143·6							
	minor	−115·8			−65	−41·5	2988				
		−130·3									
		−123·5									
(4)		−120·4	−157·5		−65	−20·6	2492	20·6	3089	573	25
				−143·4							
		−130·0	−158·1								
		−127·4	−158·7	−145·2							
(5)[b]		−119·1	−157·6			−23·7	2315	−10·7	2865	578	25
				−143·5							
		−130·0	−158·0		−65						
		−126·0	−158·5	−145·1							
(6)		−118·6	−156·0	−142·0		−19·7	2950	9·5	3630	527	25
		−121·2	−156·6	−144·2	−80						
		−123·0	−156·9	−144·6							
		−125·4	−157·2								
		−128·3	−158·1								
		−133·1	−158·9								

[a] All spectra recorded in $CDCl_3$ at 94·15 MHz (^{19}F) and 40·5 MHz (^{31}P); shifts are positive to low field w.r.t. external $CFCl_3$ and H_3PO_4. [b] Relative assignments of ^{19}F signals in (**5**) made by homonuclear selective irradiation.

It is noted that $^1J_{PtP}$ for co-ordinated tris(pentafluorophenyl)phosphine is lower than for co-ordinated triphenylphosphine, contrary to the trends which might be expected on electronegativity grounds[5] but consistent with an increase in CPC bond angles in the fluorinated ligand and thus lower *s*-character in the P–Pt bond.

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