# Pentafluorophenyl Derivatives of Phosphorus, Arsenic, and Antimony and their Complexes with Rhodium, Palladium, and Platinum

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The compounds  $(C_{6}F_{5})_{n}Ph_{3-n}X$  (X = P, As, or Sb; n = 1, 2, or 3) have been prepared in high yield by an improved method using pentafluorophenyl-lithium. The reactions of these ligands with various rhodium, palladium, and platinum compounds have been investigated and displacement reactions indicate that the complexes  $\begin{array}{l} L_2PtCl_2 \text{ increase in stability in the order of ligands (L), & Me_2S < (C_6F_5)_3P < (C_6F_5)Ph_2As < (C_6F_5)_2PhP < tris(2,6-di-fluorophenyl)phosphine < cyclo-octa-1,5-diene < Ph_3As < (C_6F_5)Ph_2P < Ph_3P < (PhO)_3P. \end{array}$ 

The i.r. spectra (400-200 cm.-1) and <sup>19</sup>F n.m.r. spectra of the compounds are reported.

In a previous paper <sup>1</sup> we have described rhodium complexes of trispentafluorophenylphosphine and the phosphines (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PhP and (C<sub>6</sub>F<sub>5</sub>)Ph<sub>2</sub>P. Herein we describe rhodium, palladium, and platinum complexes of the phosphines, arsines, and stibines  $(C_6F_5)_nPh_{3-n}X$ (n = 1, 2, or 3; X = P, As, or Sb).

A summary of the reactions of the ligands,  $(C_{6}F_{5})_{n}Ph_{3-n}X$  with some rhodium, palladium, and platinum compounds is given in Table 1. The palladium and platinum complexes isolated are all of the type  $L_2MX_2$  (M = Pd or Pt; X = Cl, Br, or I) and since the i.r. spectra (400-200 cm.<sup>-1</sup>) of the chloride and bromide complexes (Table 2) only exhibit one metal-halogen stretching frequency they presumably have a transconfiguration. The range of frequencies found for these metal-halogen stretching vibrations is in agreement with

<sup>1</sup> R. D. W. Kemmitt, D. I. Nichols, and R. D. Peacock, Chem. Comm., 1967, 599; J. Chem. Soc. (A), 1968, 1898.

those found for other *trans*-complexes of this type.<sup>2</sup> The metal-iodine frequencies of the complexes L<sub>2</sub>MI, have not been located but the complexes are presumably trans.

TABLE I							
Ligand	$K_2$ PtCl <sub>4</sub>	$PtI_{2}$	$RhCl_3, xH_2O$	RhCl <sub>2</sub> (C <sub>2</sub> H	$_{4}$ ) <sub>4</sub> Rh <sub>2</sub> (CO) <sub>4</sub> Cl <sub>2</sub>		
$(C_{6}F_{5})_{3}P$	a	а	a	а	а		
$(C_6F_5)_2PhP$	а	a	a	a	a		
$(C_6F_5)Ph_2P$	а	а	a	а	a		
$(C_6F_5)_3As$	ь	b	b	b	b		
$(C_6F_5)_2$ PhAs	b	b	b	ь	ь		
$(C_6F_5)Ph_2As$	a	а	b	ь	a		
$(C_6F_5)_3Sb$	с	$\mathbf{b}$	С	с	b		
$(C_6F_5)_2$ PhSb	с	b	с	с	b		
$(C_6F_5)Ph_2Sb$	с	ь	с	с	b		
$(C_6H_3F_2)_3P$	a	a	a	ь	с		
$(C_6H_3F_2)_3As$	ь	b	b	ь	b		
a, Complex not attempted	formed. 1.	b,	No complex	formed.	c, Reaction		

<sup>2</sup> D. M. Adams, 'Metal-Ligand and Related Vibrations,' Arnold, London, 1967.

## TABLE 2

I.r. spectra of the complexes  $(410-200 \text{ cm})^{-1}$ (Metal-halogen frequencies are in italics)

$[(C_6F_5)_3P]_2PtCl_2$	395w, 366w, 351ms, 338s, 317m, 284w, 240ssh 236s
$[(C_6F_5)_3P]_2PdCl_2\dots\dots$	<b>393</b> w, <i>365</i> s, 336s, 317m, 284w, 240s, 236sh
$[(C_6F_5)_3\mathrm{P}]_2\mathrm{PtBr}_2\ldots\ldots\ldots$	394w, 366w, 337s, 317s, 282m, 255s, 241s 236s
$[(C_6F_5)_3P]_2PdBr_2$	391w, 365w, 343msh, 337s, 315m,
$[(C_6F_5)_3P]_2PtI_2$	396w, 343msh, 338s, 317m, 283w,
$[(C_6F_5)_2PhP]_2PtCl_2\dots$	253501, 200ml 383m, 369m, 347ssh, 341sbr, 318m, 286w 243c 236c
$[(C_6F_5)_2PhP]_2PdCl_2$	382m, 357s, 344s, 337s, 317m, 285w, 242s 235s
$[(C_6F_5)_2PhP]_2PtBr_2$	382m, 369m, 343s, 337s, 318m, 285w, 255s, 244s, 236s
$[(C_6F_5)_2PhP]_2PdBr_2 \dots$	381m, 368m, 343s, 337s, 316m, 282sbr, 244m, 235m
$[(C_6F_5)_2PhP]_2PtI_2$	392m, 344ms, 338s, 317m, 245m, 237m, 228ms, 209w
$[(C_6F_5)_2PhP]_2PdI_2$	389m, 344s, 337s, 316m, 280w, 245ms, 225ms
$[(C_{e}F_{e})Ph_{e}P]_{e}PtCl_{e}$	346ssh 343s 316w 234m
[(C.F.)Ph.P] PdCl	350c 343c 316ur 943ur 993ur
I(C E) DE DI DE D	950, 944, 910, 254, 205, 1, 205
$[(C_6F_5)Pn_2P]_2PtBr_2 \dots$	370m, 344s, 318w, 254s, 237mbr, 227w
$[(C_6F_5)Ph_9P]_9PdBr_9\dots$	343s, 316w, 278s, 233w, 223w
C.F.)Ph.Pl.PtL	343s 316w 236m
$\int (C \mathbf{E}) \mathbf{D} \mathbf{E} $	0403, 010W, 200m
$[(C_6\Gamma_5)P\Pi_2P]_2P\Pi_2\dots$	343s, 310w, 245m, 227ms, 224wsh
$[(C_6F_5)Ph_2As]_2PtCl_2 \dots$	387s, 358m, 340s, 330s, 323s, 316ms,
_	301s 282w 248m 233m 224m 203w
$[(C_6F_5)Ph_2As]_2PtBr_2 \dots$	387s, 357m, 330s, 323s, 316s, 299s, 282w, 248s, 232m, 224m, 203w
$[(C_6F_5)Ph_2As]_2PtI_2$	387s, 355m, 327sbr, 316msh, 295s, 280msh, 235m, 222m, 203m
$[(C_6F_5)Ph_2As]_2RhCOCl$	385s, 357m, 326s, 320s, 314s, 297s, 282m, 246m, 232m, 222m, 193m
$[(C,H,F_{1}),P],PtCL$	364s 353s 348s 340s 395m
$[(C \sqcup E) D] D D D_{2}$	264+ 252+ 240- 206- 040-
$[(\bigcirc_{6}^{11}3^{12})_{3}^{r}]_{2}^{r}(D_{12}^{r})_{2}$	3048, 3338, 3488, 32011, 2488
$(C_{6}F_{5})_{3}P$	394w, 377vw, 371vw, 356vw, 328s,
	314m, 284w, 236msh, 230s
(C.F.),PhP	393s 330shr 313m 234msh 225m
$(C \mathbf{F})$ Dh D	201abr 272mab 240a 214m 025m
$(C_6\Gamma_5)\Gamma\Pi_2\Gamma$	214m
$(C_6F_5)_3$ As	393s, 386s, 373s, 353w, 313m, 283m, 256sbr, 228s, 220s
$(C_6F_5)_2$ PhAs	386s, 377s, 354w, 313m, 303s, 284s, 271s, 252s, 228m, 223msh
$(C_6F_5)Ph_2As$	383s, 354w, 310sbr, 284m, 271m, 253w, 232s
$(C_6F_5)_3Sb$	374s, 368s, 364msh, 348w, 331s, 280m, 225sbr
$(C_6F_5)_2$ PhSb	394w, 369s, 364s, 349w, 312m, 280m, 256s, 233s, 204m
$(C_6F_5)Ph_2Sb$	364s, 350w, 314m, 294m, 263s, 253s, 231s, 220msh
(C, H, F)	405m 35leeb 346e 334e 305m
$(C_6H_3F_2)_3As$	329s, 319m, 277m, 255s, 243, 227m

In the  $(C_6F_5)_2PhP$  complexes and in  $[(C_6F_5)_3P]_2PtX_2$ (X = Br or I) an additional band is observed on the high frequency side of the 338 cm.<sup>-1</sup> ligand band at ca. 343 cm.<sup>-1</sup> which is not observed in the free phosphines Table 2). The complexes of tris-2,6-difluorophenylphosphine also show a band at 364 cm.<sup>-1</sup> which is absent in the free phosphine. These additional frequencies could be due to overtone or combination bands or to a change in configuration of the ligand when it is complexed to the metal. This effect is not observed in the complexes of  $(C_6F_5)Ph_2P$  although additional bands in

<sup>3</sup> S. Ahrland, J. Chatt, and N. R. Davies, Quart. Rev., 1958, **12**, 265.

the region 400-800 cm.<sup>-1</sup> not present in the free ligands are observed for all the complexes.

$$L_2 PtCl_2 + 2L' \Longrightarrow L'_2 PtCl_2 + 2L \qquad (1)$$

Qualitative displacement reactions of the type illustrated in equation (1) where  $L_2$  or  $L'_2$  is one molecule of a bidentate ligand or two molecules of a unidentate ligand have been investigated. The displacement reactions indicate that the complexes increase in stability in the order of ligands  $Me_2S < (C_6F_5)_3P < C_6F_5$  $(C_6F_5)Ph_2As < (C_6F_5)_2PhP < tris-2,6-diffuorophenyl$  $phosphine < cyclo-octa-1,5-diene < Ph_3As < (C_6F_5)Ph_2P$  $< Ph_3P < (PhO)_3P$ . None of the reactions is reversible, and in no case was the equilibrium displaced by the precipitation of a product. However, in the reaction of  $(C_6F_5)_3P$  with  $cis-(Me_2S)_2PtCl_2$  the dimethyl sulphide released escapes from the reaction mixture and so might displace any equilibrium. The effect of solvent on these displacement reactions has not been investigated.

In agreement with earlier work <sup>3</sup> phosphines are stronger ligands than arsines of similar structure. Thus, Ph<sub>3</sub>P displaces Ph<sub>3</sub>As from its complex and (C<sub>6</sub>F<sub>5</sub>)Ph<sub>2</sub>P displaces (C<sub>6</sub>F<sub>5</sub>)Ph<sub>2</sub>As. In view of this it is not surprising that complexes of  $(C_6F_5)_2$ PhAs have not been isolated. It should also be noted that displacement of triphenylphosphine by triphenylphosphite has been observed several times previously.4,5

Change in the oxidation state of the central metal atom has also been found to alter the ligand displacement order <sup>3</sup> and we find that  $(C_6F_5)Ph_2P$  will displace  $Ph_3As$ from (Ph<sub>3</sub>As)<sub>2</sub>PtCl<sub>2</sub> but not from (Ph<sub>3</sub>As)<sub>4</sub>Pt.

It can be seen from the displacement series that as the number of pentafluorophenyl groups increases in the series  $(C_6F_5)_n Ph_{3-n}P$  (n = 0, 1, 2, or 3) the ligand properties of the phosphine become weaker. Similarly, tris-2,6difluorophenylphosphine is a poorer ligand than triphenylphosphine.

The position of the <sup>19</sup>F chemical shift  $(\delta p)$  of the para-fluorine in transition-metal complexes of the

TABLE 3

 $\delta p$  For the *para*-fluorine measured in p.p.m. upfield from benzotrifluoride (internal reference)

		_	
L	$L_2PtCl_2$	L	Difference
$(C_6F_5)Ph_2P$	85.9	87.1	-1.2
$(C_6F_5)_2PhP$	$83 \cdot 3$	86.8	-3.5
$(C_6F_5)Ph_2As$	85.8	88.3	-2.5
$(C_6F_5)_3P$	80.9	85·3 ª	-4.4

" H. J. Emeléus and J. M. Miller, J. Inorg. Nuclear Chem., 1966, 28, 662.

phosphines  $(C_6F_5)_nPh_{3-n}P$  (n = 1, 2, or 3) has been related to the  $d\pi$ - $d\pi$  bonding between the metal and the phosphorus.<sup>1,6</sup> The <sup>19</sup>F n.m.r. data for the parafluorines in the complexes  $L_2PtCl_2$  [L =  $(C_6F_5)_nPh_{3-n}P$ (n = 1, 2, or 3) together with those of the free phos-

<sup>4</sup> L. Vallarino, J. Chem. Soc., 1957, 2287, 2473.

<sup>5</sup> L. Malatesta and C. Cariello, J. Chem. Soc., 1958, 2323.
<sup>6</sup> M. G. Hogben, R. S. Gay, and W. A. G. Graham, J. Amer.

Chem. Soc., 1966, 88, 3457.

TABLE	4
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	Storting			Found			Required		
Product	Yield (%)	material	M.p.	c	H	M	C	H	$\overline{M}$
$(C_{a}F_{5})_{3}P^{a,b}\dots$	85	PCl <sub>3</sub>	$115-116^{\circ}$			<b>540</b>			532
$(C_{\mathfrak{s}}F_{\mathfrak{s}})_{\mathfrak{s}}PhP \circ \dots$	75	PhPCl,	68 - 70			436			442
$(C_{6}F_{5})$ Ph <sub>2</sub> P <sup>c</sup>	75	Ph,PCI	6870			358			352
$(C_{\beta}F_{\delta})_{3}As^{a}$	75	AsČl <sub>a</sub>	104106			570			576
$(C_6F_5)_2$ PhAs	50	PhAsCl <sub>2</sub>	73 - 75	<b>44</b> ·0	1.0	484	44.4	1.0	486
$(C_6F_5)Ph_2As$	55	Ph <sub>2</sub> AsCl	63 - 64	$55 \cdot 1$	$2 \cdot 7$	403	54.6	$2 \cdot 6$	396
$(C_6F_5)_3Sb^a$	75	SbČl <sub>3</sub>	73 - 75			617			622
$(C_6F_5)_2$ PhSb	50	PhSbCl <sub>2</sub>	8991	<b>40</b> ·0	$1 \cdot 0$	516	40.2	1.0	532
$(C_6F_5)Ph_2Sb$	<b>25</b>	Ph <sub>2</sub> SbCl	30 - 33	<b>48·4</b>	$2 \cdot 3$	460	48.7	$2 \cdot 3$	442
$(C_6H_3F_2)_3P$	70	$PCI_3$	128 - 130	58.2	2.5	368	58.6	$2 \cdot 5$	370
$(C_6H_3F_2)_3$ As	75	AsCl <sub>3</sub>	105 - 106	51.4	$2 \cdot 4$	412	$52 \cdot 2$	$2 \cdot 2$	414

<sup>e</sup> M. Fild, O. Glemser, and G. Cristoph, Angew. Chem., Internat. Edn., 1964, 3, 801. <sup>b</sup> L. A. Wall, R. E. Donadio, and W. J. Pummer, J. Amer. Chem. Soc., 1960, 82, 4846. <sup>c</sup> M. Fild, O. Glemser, and I. Hollenberg, Naturwiss., 1965, 52, 590.

# TABLE 5

Microanalytical data of the complexes

			Found (%)		Required (%)	
Compound	Colour	M.p.*	c	Hal	c	Hal
$[(C_{e}F_{e})_{2}P]_{e}PtCl_{e}$	Yellow	225—235° d.	32.7	5.3	$32 \cdot 5$	$5 \cdot 3$
$[(C_{\mathfrak{s}}F_{\mathfrak{s}})_{\mathfrak{s}}P]_{\mathfrak{s}}PtBr_{\mathfrak{s}}$	Orange yellow	293–298 d.	30.6	11.2	30.4	11.3
(C <sub>s</sub> F <sub>5</sub> ),P],PtI,	Pink	220-240 d.	28.6	16.2	28.5	16.7
$[(C_{a}F_{5}),P],PdCl,$	Yellow	230—240 d.	35.2	5.6	$34 \cdot 8$	5.7
$[(C_{\mathfrak{s}}F_{\mathfrak{s}})_{\mathfrak{s}}P]_{\mathfrak{s}}PdBr_{\mathfrak{s}}$	Orange	241—245 d.	32.7	11.9	32.5	12.1
	0		С	н	С	н
$[(C_{\mathfrak{s}}F_{\mathfrak{s}}), PhP], PtCl_{\mathfrak{s}}$	Pale yellow	268 - 270	$37 \cdot 1$	0.94	37.6	0.87
$[(C_6F_5)_2PhP]_2PtBr_2$	Cream	260 - 263	$35 \cdot 2$	0.83	34.8	0.86
$[(C_6F_5)_2PhP]_2PtI_2$	Pink	267 - 272	$32 \cdot 1$	0.80	32.4	0.75
$[(C_6F_5)_2PhP]_2PdCl_2$	Yellow orange	245 - 250	40.4	0.97	40.8	0.95
$[(C_6F_5), PhP]_2PdBr_2$	Orange	255 - 260	36.9	0.83	37.6	0.87
$[(C_{\mathfrak{s}}F_{\mathfrak{s}})_{\mathfrak{s}}PhP]_{\mathfrak{s}}PdI_{\mathfrak{s}}$	Yellow brown	222 - 225	34.6	0.82	34.8	0.80
$[(C_6F_5)Ph_2P]_2PtCl_2$	Pale yellow	225 - 226	44.4	$2 \cdot 19$	44.6	2.06
$[(C_6F_5)Ph_2P]_2PtBr_2$	Yellow	222 - 225	40.7	1.98	40.7	1.89
$[(C_6F_5)Ph_2P]_2PtI_2$	Orange	241 - 243	37.8	1.91	37.4	1.83
$[(C_6F_5)Ph_2P]_2PdCl_2$	Yellow orange	192-194	49.2	2.33	48.9	2.27
$[(C_6F_5)Ph_2P]_2PdBr_2$	Orange	215 - 218	<b>44</b> ·8	2.22	44.6	2.16
$[(C_6F_5)Ph_2P]_2PdI_2$	Brown	226 - 229	40.5	1.90	<b>4</b> 0·6	1.88
$[(C_6F_5)Ph_2As]_2PtCl_2$	Pale yellow	201 - 206	41.1	1.92	40.9	1.91
$[(C_6F_5)Ph_2As]_2PtBr_2$	Light orange	203-210	37.5	1.75	37.8	1.77
$[(C_6F_5)Ph_2As]_2PtI_2$	Pink	216-230	34.6	1.63	35.0	1.63
$[(C_6F_5)Ph_2As]_2RhCOC1$	Yellow	138 - 144	46.5	$2 \cdot 21$	46.4	2.10
$[(C_6H_3F_2)_3P]_2PtCl_2 \qquad \dots \qquad $	Light yellow	300—310 d.	42.3	1.80	42.9	1.79
$[(C_6H_3F_2)_3P]_2PtBr_2$	Yellow	300—310 d.	$39 \cdot 2$	1.61	39.5	1.65

\* d. = decomp.

phines, are given in Table 3, and they suggest that there is a decrease in  $\pi$ -bonding between the phosphines and the metal as the number of  $C_6F_5$ -groups increases. Since the basicity of the phosphines also decreases as n becomes larger both these effects correlate with the positions of these phosphines in the displacement series.

#### EXPERIMENTAL

All operations involving n-butyl-lithium or pentafluorophenyl-lithium were carried out in dry apparatus using an atmosphere of dry oxygen-free nitrogen. Pentafluorophenyl-lithium was prepared from butyl-lithium and pentafluorobenzene.7 Sodium-dried tetrahydrofuran was redistilled from lithium aluminium hydride immediately before use. Molecular weights were determined on a Mechrolab vapour-pressure osmometer using chloroform solutions. M.p.'s were determined on a Reichert hotstage microscope and are uncorrected.

Analyses

Ph2AsCl,<sup>8</sup> PhAsCl<sub>2</sub>,<sup>8</sup> Ph2SbCl,<sup>9</sup> PhSbCl<sub>2</sub>,<sup>9</sup> and 2,6-difluorophenyl-lithium,<sup>10</sup> were prepared by literature methods.

Preparation of Pentafluorophenyl Derivatives of Phosphorus, Arsenic, and Antimony.—Pentafluorophenyl derivatives of phosphorus,<sup>11-13</sup> arsenic,<sup>12</sup> and antimony<sup>12</sup> have

- <sup>11</sup> M. Fild, O. Glemser, and I. Hollenberg, Naturwiss., 1965,
- 52, 590. <sup>12</sup> M. Fild, O. Glemser, and G. Cristoph, Angew. Chem., Internat. Edn., 1964, 3, 801.
- <sup>13</sup> L. A. Wall, R. E. Donadio, and W. J. Pummer, J. Amer. Chem. Soc., 1960, 82, 4846.

<sup>&</sup>lt;sup>7</sup> R. J. Harper, E. J. Soloski, and C. Tamborski, J. Org. Chem., 1964, 29, 2385.

<sup>&</sup>lt;sup>8</sup> A. B. Bruker and N. M. Nikiforova, J. Gen. Chem. (U.S.S.R.), 1958, 28, 2445. <sup>9</sup> F. F. Blicke, U. O. Oakdale, and F. D. Smith, J. Amer.

Chem. Soc., 1931, 53, 1025.

<sup>&</sup>lt;sup>10</sup> A. M. Roe, personal communication.

been prepared in low yield using pentafluorophenylmagnesium bromide. The use of pentafluorophenyllithium, however, gives high yields at lower cost since pentafluorobenzene is the ultimate starting material. A typical reaction is described below.

Phenylbispentafluorophenylphosphine.—A 500-ml. threenecked flask fitted with an oil-sealed paddle stirrer was flushed with nitrogen for 10 min. 1·1M-Butyl-lithium (91 ml.) was added and the flask was cooled to  $-78^{\circ}$ . A solution of pentafluorobenzene (16·7 g.) in dry ether (40 ml.) was then added dropwise during 15 min. and the mixture was stirred for 2 hr. at  $-78^{\circ}$ . Dichlorophenylphosphine (9·0 g.) in dry ether (30 ml.) was added dropwise and the mixture was allowed to warm to room temperature. The reaction mixture was filtered and the filtrate was evaporated to dryness, the solid was crystallised from alcohol (or hexane) to yield phenylbispentafluorophenylphosphine (17 g., 75%), m.p. 68—70° (lit. <sup>11</sup> 69—70°).

The other pentafluorophenyl derivatives were prepared in a similar manner. Details are summarised in Table 4. In some preparations an oil was obtained when the reaction mixture was finally evaporated to dryness. Crystallisation of the oil was effected by addition of a little absolute alcohol. The alcohol was removed under reduced pressure and the oil which remained was set aside until it crystallised.

Complexes of Rhodium, Palladium, and Platinum.— The results of attempts to prepare rhodium, palladium, and platinum complexes of the ligands are summarised in Table 1. Microanalytical data for the complexes isolated are given in Table 5.

Palladium and Platinum Complexes.—Complexes of the type  $L_2PtCl_2$  were prepared by dropwise addition of an aqueous solution of  $K_2PtCl_4$  to the ligand in warm alcohol. The complex which was precipitated was filtered off and recrystallised from chloroform–ethanol.  $L_2PtBr_2$ ,  $L_2PdCl_2$ , and  $L_2PdBr_2$  were prepared in a similar manner using aqueous solutions of  $K_2PtBr_4$ ,  $Na_2PdCl_4$ , and  $K_2PdBr_4$  respectively. The complexes  $L_2PdI_2$  were prepared from sodium iodide and the corresponding chloro-complexes in acetone solution. The complexes  $L_2PtI_2$  were prepared as follows. Platinum iodide and an excess of the ligand were heated under reflux overnight in xylene. The mixture was filtered hot, and the filtrate was evaporated to dryness. The solid was washed with hexane and recrystallised from chloroform–ethanol.

Rhodium Complexes.—Complexes of the type  $L_2RhCOCl$  were prepared by mixing a benzene solution of  $Rh_2(CO)_4Cl_2$ 

and the ligand. Effervescence occurred in all successful experiments and after this had subsided the mixture was evaporated to dryness. The residue was recrystallised from chloroform-ethanol.

In the reactions attempted between  $(C_2H_4)_4Rh_2Cl_2$  and the ligands,  $(C_2H_4)_4Rh_2Cl_2$  was added to a degassed solution of the ligand in methanol. The mixture was heated under reflux for 1 hr. and the complex, if formed, was slowly precipitated. This was filtered off, washed with alcohol and ether, and dried *in vacuo*. In some reactions a brownish solution was obtained from which no pure compounds could be isolated.

In the reactions between the ligands and hydrated rhodium trichloride, ethanolic solutions of  $RhCl_{3,x}H_2O$  and the ligand were heated under reflux for a few hours. when the complex was precipitated; this was filtered off, washed with alcohol and ether, and dried *in vacuo*. In some experiments the initial red colour of the solution slowly faded and a black insoluble residue formed.

Displacement Reactions .-- Weighed quantities of the reactants were added to the solvent (ca. 20 ml.) and the mixture was heated under reflux overnight. In reactions involving cyclo-octa-1,5-diene, xylene was used as solvent since the higher reaction temperature ensured complete displacement in a few hours. Chloroform was used for the other reactions. In a typical experiment cyclo-octa-1,5-diene (0.11g.) and trans-dichlorobis(tris-2,6-difluorophenylphosphine)platinum(II) (2:1 mole ratio) were heated under reflux in xylene (20 ml.) for 10 hr. The yellow complex slowly dissolved and gave a colourless solution. This was evaporated to dryness and the residue was washed with ether. The i.r. spectrum of the residue was identical to that of (cyclo-octa-1,5-diene)PtCl<sub>2</sub>. Recrystallisation from chloroform gave white needles, m.p. 230-280° (decomp.) (lit.,<sup>14</sup> 220-278°).

Since the products isolated were characterised by i.r. spectroscopy, as much as 25% of the starting materials could have been present in them.

We thank the S.R.C. for a grant (to D. I. N.), Imperial Smelting Corp. Ltd., for a generous gift of pentafluorobenzene and Johnson Matthey Ltd., for generous loans of platinum, palladium, and rhodium compounds.

## [8/294 Received, February 28th, 1968]

<sup>14</sup> J. Chatt, L. M. Vallarino, and L. M. Venanzi, J. Chem. Soc., 1957, 2496.