Journal of Fluorine Chemistry, 39 (1988) 197–216

Received: July 3, 1987; accepted: September 23, 1987

A NEW APPROACH TO THE SYNTHESIS OF ARYLDIFLUOROPHOSPHINES. FORMATION OF CIS-DICHLORO-BIS(ARYLDIFLUOROPHOSPHINE) PLATINUM(II) COMPLEXES *

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SUMMARY

Reaction of chlorodifluorophosphine with aryllithium compounds has been found to furnish aryldifluorophosphines. This type of reaction is applicable to any aromatic system for which a regioselective lithiation is possible. The most stable products are those in which the PF_2 group is protected by two neighbouring groups, in the 2- and 6- position of an aromatic ring. The ^{19}F- and ^{31}P- n.m.r. spectra of the aryldifluorophosphines are presented and discussed.

Evidence for several lines of spontaneous transformation of aryldifluorophosphines has been obtained: (i) scrambling reaction with formation of bis-aryl-fluorophosphines and phosphorus trifluoride, and (ii) redox disproportionation with formation of aryltetrafluorophosphoranes and cyclopolyphosphines, respectively. In both cases, the underlying reaction mechanism seems to be similar in nature. A number of cis-dichloro-bis-(aryldifluorophosphine)platinum(II) complexes, involving the new difluorophosphines, have been prepared. The ^{19}F- and ^{31}P - n.m.r. spectra of these complexes are discussed in relation to those of the uncoordinated ligands.

Also, the fragmentation pathway of the platinum(II) complexes in their mass spectra has been deduced and is discussed.

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* Diplomarbeit Lutz Heuer; Technische Universität, Braunschweig, 1986;

** Author to whom correspondence should be addressed. Part of this work has been presented to the 8th Winter Fluorine Conference of the American Chemical Society; St.Petersburg, Florida, U.S.A.; Jan. 26,1987.

0022-1139/88/$3.50

INTRODUCTION

Platinum(II) complexes with phosphorus(III) ligands involving aromatic groups bearing an ortho- substituent with potential donor atoms, e.g. N,O,S or Sb, have been studied; especially with a view of exploring their potential catalytic applications [1]. Furthermore, the antitumour properties of platinum(II) complexes, e.g. CISPLATIN® { cis-$[Cl_2(NH_3)_2Pt]$ } and related compounds , have generated an interest in such complexes, and have stimulated interesting chemical research [2], even though a real breakthrough in antitumour chemotherapy has not come about during the last 30 years [3].

Attempts at replacing the nitrogen- containing ligands in complexes of the type of CISPLATIN® have failed because phosphine ligands were found to exert a strong trans effect in dichloroplatinum(II) compounds [2c]. It was hoped, therefore, that employing difluorophosphines, as a result of their subtle σ - donor and π - acceptor properties, would give rise to improved antitumour effects.

RESULTS AND DISCUSSION

In a previous publication [4 a] we have described the synthesis of 2-methoxyphenyldifluorophosphine and of 2- dimethylaminophenyldifluorophosphine, by chlorine - fluorine exchange on the appropriate dichlorophosphines. The latter were obtained by the cleavage reaction with HCl of the aminophosphines, $ArP(NR_2)_2$. The overall yield in these reactions was of the order of 40% when distillation without further transformation reactions occurring was possible. A further complication arose on account of the reaction of HCl with an amino substituent in an aromatic aminophosphine of type $1\text{-}(R_2N)_2P\text{-}2\text{-}R'_2N\,C_6H_4$. When HF, instead of HCl, was allowed to react with an aminophosphine, the expected direct formation of a difluorophosphine was not observed [5,6] whereas ^{19}F- and ^{31}P- n.m.r. spectroscopic evidence has been obtained for the cleavage of one P-N bond in an arylaminophosphine of type, $ArP(NEt_2)_2$ with formation of the arylfluorodiethylaminophosphine, $ArP(F)(NEt_2)$ [6]. At elevated temperature, due to a different type of reaction, formation of the arylphosphine, $ArPH_2$, has been observed.

Lines and Centofanti [7] have reported a process for the synthesis of alkyl, alkenyl and alkinyl difluorophosphines by the reaction of solid organometallic reagents with halodifluorophosphines, XPF_2 (X = Cl,Br) between -78 °C and room temperature. Organo-lithium-, mercury- or magnesium- compounds were usually employed. Since $ClPF_2$, through a new synthesis [8], has become readily available, its reactions with some organometallic reagents were studied.

No formation of difluorophosphines was observed employing the reaction of $ClPF_2$ with Grignard reagents in ether or with solid aryl mercury compounds in the absence of solvents at different temperatures up to 70 °C , as well as with solutions of aryl mercury compounds in dichloromethane, up to 40 °C . Also, aryllithium compounds or arylaluminium compounds were allowed to react with $ClPF_2$ in non-polar media (e.g. petroleum ether (b.r. 60-80 °C) or n-hexane); instead of difluorophosphines tertiary phosphines were obtained [4,5].

Fair yields of aryldifluorophosphines were obtained, eventually, when a mixture of diethylether/ n-hexane was employed as a medium for the reaction of aryllithium compounds with $ClPF_2$. The lithiation of the aromatic precursors was conducted, following the procedures described by Slocum and Jennings [9a] and Reinhoudt et al. [9b], i.e.

$$ArH\ (ArBr) + {}^{n}BuLi \xrightarrow{Et_2O\ /Hexane} ArLi + BuH\ (BuBr) \qquad (1)$$

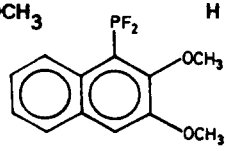
$$ArLi + ClPF_2 \xrightarrow{Et_2O\ /Hexane} ArPF_2 + LiCl \qquad (2)$$

(A r = aromatic group; see Table 1).

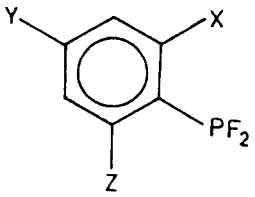
The new procedure has been applied to the synthesis of a total of 14 aryldifluorophosphines (Table 1).

TABLE 1

Aryldifluorophosphines

Compound number	X[a]	Y[a]	Z[a]
1	H	H	H
2	H	CH_3	H
3	OCH_3	H	H
4	$N(CH_3)_2$	H	H
5	OCH_3	H	OCH_3
6	OC_6H_5	H	OC_6H_5
7a	OCH_3	H	CF_3
7b	OCH_3	CF_3	H
8	OCH_3	H	$N(CH_3)_2$
9	OCH_3	H	$NCH_3(CH(CH_3)_2)$
10	OCH_3	H	$N(CH_2CH_2)_2NCH_3$
11	OCH_3	H	$N(CH_2CH_2)_2O$
12	OCH_3	H	$N(CH_2CH_2OCH_3)_2$
13			

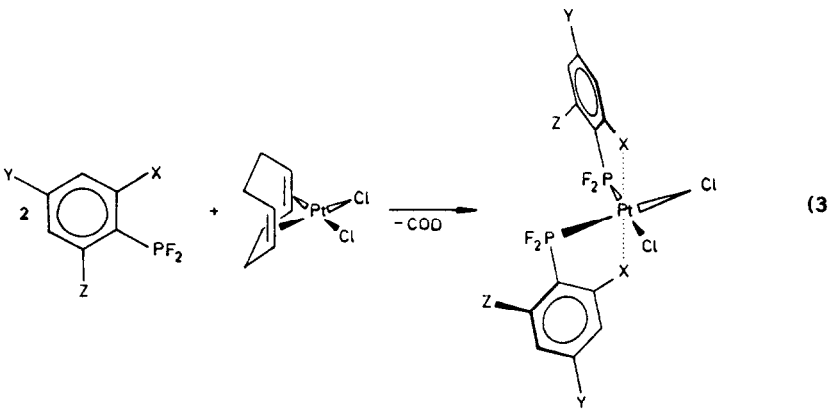
[a]X, Y and Z are substituents of the aromatic group in $ArPF_2$, as follows,



Compounds **1** [10,11], **2** [11], **3** [4], and **4** [4] have previously been described in the literature.

All aryldifluorophosphines were reactive liquids, and no attempt was made to isolate them in a pure state. Their stability, even in solution, was limited, and care had to be taken that their n.m.r. characterisation and subsequent reactions were carried out promptly. The aryldifluorophosphines could be stored without change at -20 °C for several days.

The aryldifluorophosphines, **1** , **5** , **6** , **7a**, **11** , and **13** were allowed to react with the platinum(II) complex , $Cl_2(C_8H_{12})Pt$ (cod $PtCl_2$) [12] in dichloromethane as a medium, to give complexes of type, $[Cl_2(ArPF_2)_2Pt]$ (eq. 3).



(3)

All the platinum(II) complexes, **14** - **19** , were obtained as crystalline white solids. According to their ^{31}P-n.m.r. spectra (^{1}J (PPt)) the platinum(II) complexes, **14** - **19** all have *cis* configurations [13]. They are poorly soluble in almost any solvent, except certain solvents of medium polarity, such as dichloromethane and chloroform in which, especially, compounds **14** and **16** , were found to be moderately soluble.

Crystallisation of the complexes, **14** - **19** was effected employing the diffusion method [14].

TABLE 2

Aryldifluorophosphine–Platinum(II) Complexes, $[Cl_2(ArPF_2)_2Pt]$

Compound number	Number of the ligand	X[a]	Y[a]	Z[a]
14	**1**	H	H	H
15	**5**	OCH_3	H	OCH_3
16	**6**	OC_6H_5	H	OC_6H_5
17	**7a**	OCH_3	H	CF_3
18	**11**	OCH_3	H	$N(CH_2CH_2)_2O$
19	**13**	(see above)		

a. see footnote to Table 1.

Spectroscopic investigations

N.m.r. spectra of aryldifluorophosphines and their platinum(II) complexes

N.m.r. spectra (^{19}F and ^{31}P) of all aryldifluorophosphines, **1 - 13** , were recorded on solutions of the crude products in $CDCl_3$. In the case of compounds, **1 - 4**, the data obtained are in good agreement with literature values.

All shifts and coupling constants were observed in the expected range. The variations in δP are somewhat larger than those in δF. The values observed vary between 197.1 and 216.2 p.p.m. and steric and electronic factors are thought to be responsible for these differences.

The largest variation in the values of ^1J (PF) for our aryldifluorophosphines amount to 70 Hz (^1J (PF) ranging between 1129 and 1199 Hz). Likewise, the variations in δ F are not significant; thus, δF is varying over a range of 9 p.p.m. only. In conjunction with ^1J (PF) δF values are, however, well suited to the characterisation of difluorophosphines.

For only one compound, **7a**, long range coupling, $^5J(FF)$ has been observed. This is due, presumably, to the proximity of the $-PF_2$ group to the $-CF_3$ substituent, and is suggested to be caused by through-space interactions which are larger than normally expected, considering the number of bonds between the coupling nuclei [15]. The value, e.g. of $^4J(PF)$ (58 Hz) compares to $^2J(PF)$ in CF_3PF_2 (87.2 Hz) [16].

The n.m.r. spectra of the aryldifluorophosphine- platinum(II) complexes are rather more complicated. Due to their limited solubility the complete characterisation of some of the platinum complexes , **14—19** , by n.m.r. spectroscopy was impossible. Recording ^{19}F-n.m.r. spectra, in particular, proved difficult because a Fourier transformation (Ft)-n.m.r. spectrometer for routine ^{19}F-n.m.r. spectroscopy was not available. The spin system for

cis-dichloro-bis(aryldifluorophosphine)platinum(II) complexes is represented by $[A[X]_2]_2M$ with A=P, X=F and M=Pt. Thus, the observed P-F coupling constant is composed of ^1J (PF) and ^3J(PF) [4,13], and the appearance of the ^{19}F- and ^{31}P- n.m.r. spectra is typical.

Both coupling constants and chemical shift values for complexes, **14** through **19**, are as expected [4]. Since ^2J(PP) coupling is not seen, and because of the magnitude of ^1J(PPt) [13], *cis*- geometry for these square-planar platinum(II) complexes is indicated [13,17].

TABLE 3

^{19}F- and ^{31}P- N.m.r. Data for Aryldifluorophosphines, $ArPF_2$

Compound number	δF (ppm)	^1J(FP) (Hz)	δP (ppm)	^1J(PF) (Hz)
1	-91.9	1171	207.4	1169
Lit. [10]	-92.3	1173	207.0	1166
2			208.9	1163
Lit. [11]			205.3	1130
3	-99.7	1163	208.4	1175
Lit. [4]	-99.5	1166	208.3	1176
4	-100.4	1138	197.1	1149
Lit. [4]	-100.5	1164	197.1	1147
5	-97.7	1151	215.7	1163
6	-95.9	1170	209.0	1177
7a	-95.9	1193	205.7	1199
	(CF_3) -54.8	^4J(FP) = 57; ^5J(FF) = 13		^4J(PF) = 58
7b	-100.1	1186	202.7	1190
	(CF_3) -63.2	^6J(FP)= 22		
8	-93.9	1138	202.5	1151
9	-93.6	1139	201.3	1142
10	-93.2	1135	201.3	1155
11	-93.9	1143	201.1	1153
12	-93.9	1129	206.5	1137
13	-92.5	1131	216.2	1145

TABLE 4

^{19}F- and ^{31}P- N.m.r. Data for Aryldifluorophosphine–Platinum(II) Complexes, $[Cl_2(ArPF_2)_2Pt]$

Compound number	δF (ppm)	$\lvert {}^1J(PF) + {}^3J(PF) \rvert$ (Hz)		δP (ppm)	$^1J(PPt)$ (Hz)
14	[a]	1132		137.3	5039
15	[a]	[b]		130.4	[b]
16	-55.8	1148[c]	1151[d]	130.6	5435[e]
17	[a]	1142		129.0	5474
18	[a]	1129		123.7	5600
19	[a]	1139		133.8	5453

[a] ^{19}F- n.m.r. spectra not recorded. [b] Compound poorly soluble; no coupling was resolved; [c] from ^{19}F- n.m.r; [d] from ^{31}P- n.m.r.; [e] $^2J(FPt) = 512.4$ Hz.

Mass spectra of the platinum complex, 14 - 19

The spectra were obtained by E.I. mass spectrometry, and parent peaks were observed, in some cases. The pathway for the fragmentation could be deduced in all cases. Some selected fragments observed in the mass spectra of **14** - **19** are listed in Table 5. Aside from the normal fragments [18], e.g. $[M-Cl]^+$, $[M-Cl-HCl]^+$ (for all complexes) and $[M-CH_3-Cl]^+$ in the case of **15**, **17**, and **19**, fragments such as $[M-HF]^+$, $[M-PF_2]^+$, $[M-ligand]^+$, and some of their combinations were observed. In every case strong peaks (20-100% relative intensity) [5] are due to the loss of ligands from the complexes. As previously reported by Miller [18b] for $C_6F_5PF_2$ similar fragmentations have been observed for our aryldifluorophosphines.

In the case of **14**, a melting range, 115-118°C is observed while decomposition does not occur below 230 °C. Thus, intense signals due to important fragment ions, including the molecular peak, were observed. The mass spectrum of **14** is shown in Fig. 1, the calculated and observed data for the isotopic distribution of the molecular peak of **14** are presented in Fig. 2. The same kind of agreement between observed and calculated values has been noted for peaks corresponding to $[M-Cl]^+$, $[M-HCl-Cl]^+$, $[M-C_6H_5PF_2-HCl-Cl]^+$, and for the fragment ion, $[C_6H_4Pt]^+$.

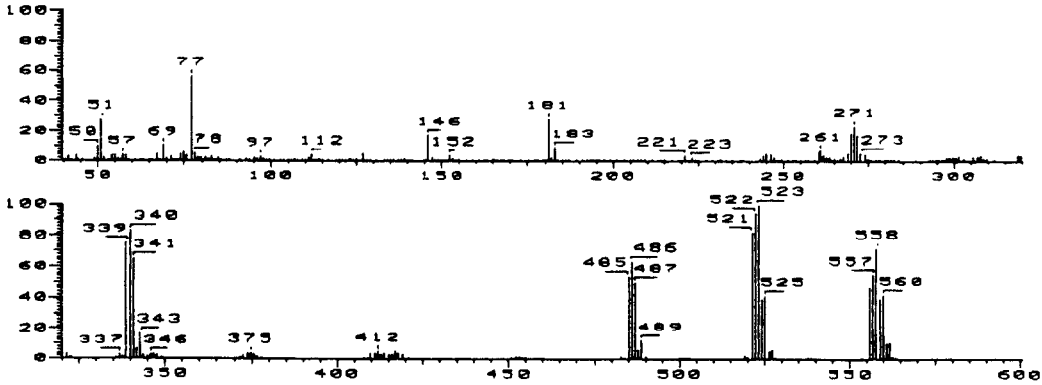


Fig. 1. Mass spectrum of 14- (120 °C).

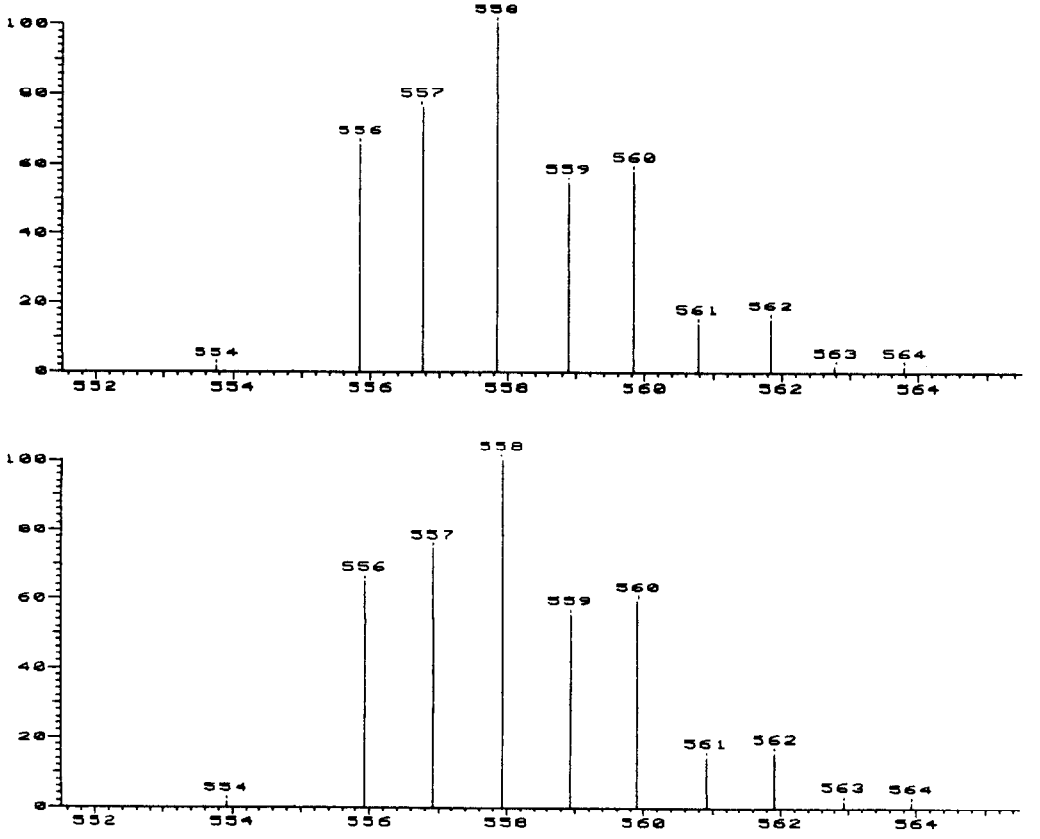


Fig. 2. Molecular peak of 14; observed (above), calculated (below).

TABLE 5

Relative Intensities of Selected Peaks in the Mass Spectra of cis- Dichloro-bis(aryldifluorophosphine) platinum(II) Complexes[a]

Compound number	Molecular Peak	[M-Cl] [M-HCl]	[M-HF]	[M-Cl-HCl]	[M-Cl-MeCl]	[L]
14	77	base peak	>1	62	--	33
15	1	base peak	3	14	38	20
16	--	62 ($-H_2Cl$)	--	2	--	base peak
17[b]	--	72	5	4	10	54
18[b]	--	24 ($-H_2Cl$)	--	3	--	82 (L-H)
19[b]	--	2 ($-H_2Cl$)	--	1	5	54

[a]Relative intensities in %; all peaks displayed typical isotopic distributions. [b]In this case small fragments have been observed as base peaks.

Transformation Reactions of the Aryldifluorophosphines

As against dichlorophosphines, representatives of which have been in the literature since the 19th century [19a] , difluorophosphines have become known only relatively recently. This is due, not so much to synthesis problems but to the inherent instability of fluorophosphines, see, e.g. [4,5,19c,d,e,h]. Only difluorophosphines with highly electronegative substituents are sufficiently stable to be stored at room temperature for extended periods of time. In some cases the spontaneous transformation reactions of difluorophosphines provide useful approaches to the synthesis of cyclopolyphosphines. Tetrafluorophosphoranes, besides polyphosphines, are the products of the redox disproportionation of difluorophosphines. The reaction is catalyzed by hydrogen fluoride [19h].

The course of this disproportionation reaction may be rationalized in terms of both the acceptor and donor properties of these phosphorus(III) compounds [19]. It has been observed that the stability of difluorophosphines increases in the presence of tertiary amines, e.g. triethylamine or N,N- dimethylaniline [5,20].* Because of the *decrease* in their Lewis acid character no redox disproportionation has been observed in these cases. Similar arguments may be invoked in the case of difluorophosphines with electronegative substituents [21]. Here, again no spontaneous redox disproportionation takes place, due to the *increase* in Lewis acidity of the P(III) compound. In both cases the disproportionation reaction proceeds slowly or cannot be observed.

In some cases the detailed course of such redox disproportionation reactions has been investigated, and oxidation-reduction, scrambling and thermolytically induced reactions are suggested to occur. In Fig. 3 the proposed interrelationsship between the various reaction pathways is shown.

* A mixture of **5** with triethylamine or N,N-dimethylaniline in $CDCl_3$, maintained at 70°C for 8 days, did not show any formation of tetrafluorophosphorane in the ^{19}F-n.m.r. spectrum.

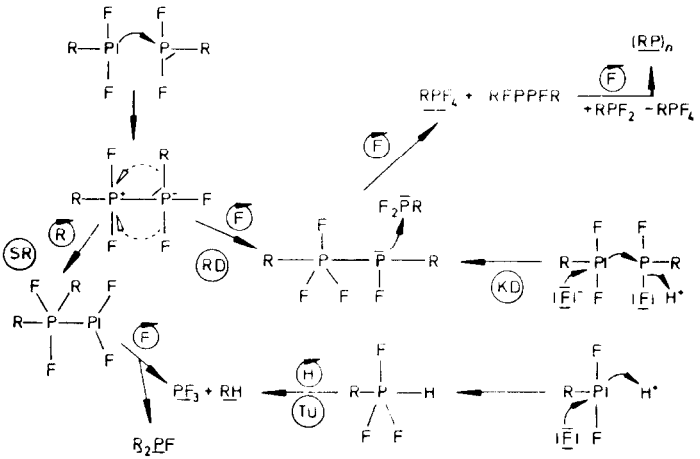


Fig. 3. Suggested pathways for the transformation of aryldifluorophosphines (KD = catalytic redox disproportionation; RD = redox disproportionation; SR = scrambling reaction; TU = thermal displacement reaction; (F)→, migration of fluorine; (H)→, migration of hydrogen).

The course of the disproportionation reaction of difluorophosphines was followed by ^{31}P- n.m.r. spectroscopy in sealed n.m.r. tubes at 70°C. In most cases the observed spectra displayed a large number of signals of which only the most intense ones are considered.

From the data in Table 6 it is noted that in the case of the derivatives of aniline the same decomposition pathway is always followed. For the aniline derivatives only the thermolytically induced reaction is conceivable, because the other pathways are blocked by the internal amino function.

EXPERIMENTAL

All the experiments described in the following were conducted with careful exclusion of air and moisture. Solvents were dried using standard procedures.

N.M.R.- and Mass-spectrometric Instruments and Conditions

JEOL JNMR-60: ^{19}F (56.4 MHz) (compounds **1** through **13**);
Varian EM 390: ^{19}F (84.6 MHz) (compound **16**);
Bruker WM 400: ^{31}P (162.0 MHz) (all compounds); ^{1}H (400 MHz); ^{13}C (100.6 MHz);
Hitachi-Perkin Elmer R 24B: ^{1}H (60 MHz).

TABLE 6

Transformation Reactions of Aryldifluorophosphines

Difluorophosphine, $ArPF_2$	Proposed Pathway of Transformation[a]	Products and Conditions	N.M.R. - Data and Remarks
1	RD or KD	$[PhP]_5$ and $PhPF_4$	see Lit. [10]
3	RD or KD	2-$(CH_3O)C_6H_4PF_4$ and	see Lit. [4]
		$[2\text{-}(CH_3O)C_6H_4P]_4$	see Lit. [4]
	SR	$[2\text{-}(CH_3O)C_6H_4]_2PF$	^{31}P (162 MHz), d
		(3 h / 70°; *ca.* 5 %)	δ 204.7; $^1J(PF)$ 1107
4 and **8 - 12**	TU	PF_3	reaction rate very
		(70°; *ca.* 2 % per month)	slow
5	RD or KD	$2,6\text{-}(CH_3O)_2C_6H_3PF_4$	^{31}P (162 MHz), quint.
			δ -39.3; $^1J(PF)$ 975
		(8 d / 70°; *ca.* 95 %)	^{19}F (56.4 MHz), d
			δ -42.0; $^1J(FP)$ 972
	SR	$[2,6\text{-}(CH_3O)_2C_6H_3]_2PF$	^{31}P (162 MHz), d
		(2 d / 70°; *ca.* 5 %)	δ 207.4; $^1J(PF)$ 1107
6	RD or KD	$2,6\text{-}(C_6H_5O)_2C_6H_3PF_4$	^{31}P (162 MHz), quint.
		(7 months/70°; *ca.* 12 %)	δ -41.3; $^1J(PF)$ 977
		$[2,6\text{-}(C_6H_5O)_2C_6H_3P]_4$	^{31}P (162 MHz), s
		(7 months/ 70°; *ca.* 6 %)	δ - 59.5
	SR	$[2,6\text{-}(C_6H_5O)_2C_6H_3]_2PF$	^{31}P (162 MHz), d
		(7 months / 70°; *ca.* 6 %)	δ 201.2; $^1J(PF)$ 1117
		PF_3	
		(7 months / 70°; *ca.* 2 %)	
7a	SR	$[2\text{-}CH_3O\text{-}6\text{-}CF_3C_6H_3]_2PF$	^{31}P (162 MHz), d
		(6 d / 70°; *ca.* 25 %)	δ 197.6; $^1J(PF)$ 1135
			$^4J(PF)$ 63
		PF_3	
		(6 d / 70°; traces)	
13	SR	$[2,3\text{-}(CH_3O)_2C_{10}H_5]PF$	^{31}P (162 MHz), d
		(6 d / 70°; *ca.* 26 %)	δ 196.2; $^1J(PF)$ 1064
		PF_3	
		(6 d / 70°; *ca.* 28 %)	

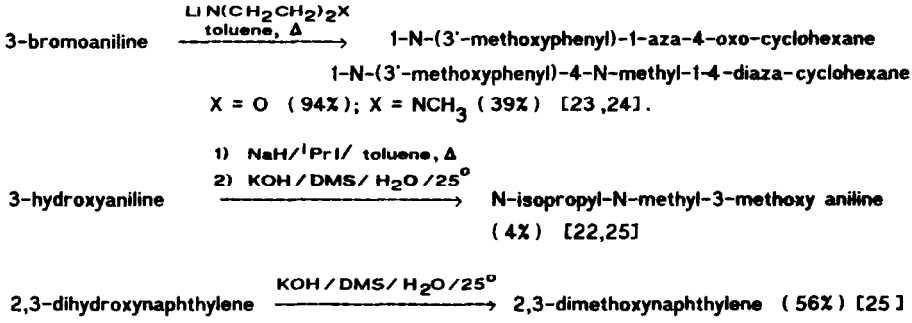
[a] RD = redox disproportionation; KD= catalytic redox disproportionation; SR = scrambling reaction; TU = thermal rearrangement.

References: CCl_3F external (^{19}F); 85% H_3PO_4 external (^{31}P); $(CH_3)_4Si$ (TMS) internal (^1H and ^{13}C). Absorptions to low field of reference signals are assigned positive chemical shift values. All spectra were recorded in solutions in $CDCl_3$, with proton- decoupling.
The following abbreviations are used to denote the multiplicity of signals: s = singlet, "s" = pseudo singlet, d = doublet, t = triplet, etc.
Mass spectra (E.I.) were recorded on a Finnigan MAT 8430 instrument at 70 eV.
Melting points were determined, using a Büchi 510 instrument, in 0.1 mm capillaries.

Preparation of the starting materials

The following compounds were obtained from commercial sources or were prepared by the literature procedures indicated:
2-Bromo-N,N-dimethylaniline [22], 2-bromoanisole, 3-bromoanisole, bromobenzene, 4-bromotoluene , cis-dichloro-(η^4-1,5-cyclooctadiene) platinum [12], 2,3-dihydroxy-naphthalene, 3-hydroxyaniline, 3- methoxyaniline, resorcinol diphenylether, 3-(1,1,1- trifluoro-methyl)anisole.

Some precursor compounds were synthesized following procedures indicated in the literature:



NaH = sodium hydride; DMS = dimethyl sulfate.

Preparation of 3-Methoxy-bis[N,N-(2-methoxyethyl)] aniline

a. 3-Methoxy-bis[N,N-(2-hydroxyethyl)] aniline [26]

A mixture of 50 g (0.406 mole) of m-anisidine and 25 mL of water was placed in a 700 mL heavy-wall glass tube, and was cooled to -196°C. Ethylene oxide (36.5 g; 0.829 mole) was then condensed into the tube which was sealed (TEFLON® stopcock). The mix-

ture was stirred for 45 h at room temperature, and 1 h at 70°C. Ether (200 mL) was added to the liquid reaction mixture which was subsequently extracted with six 150 mL portions of diethyl ether. The extracted products were combined and dried over potassium carbonate. The aniline derivative was obtained upon fractional distillation of the residue remaining after the ether had been removed; b.p. 185–191°C (0.45 mm); yield 83.2 g (97 %). Anal. $C_{11}H_{17}NO_3$ (211.26); Found (Calc.): C, 62.36 (62.53); H, 8.27 (8.11); N, 6.51 (6.63).

^{1}H n.m.r. spectrum (at 60 MHz): δH (aromat.) 7.3–6.9 [m; 1H] and 6.4–6.2 [m; 3H]; δ_{OCH_3} 3.9 [s; 3H]; δ_{CH_2} 4.0–3.5 [m; 8H]. Two protons (at δ *ca.* 4.1) could be exchanged by deuterium upon interaction with D_2O.

b. 3-Methoxy-bis[N,N-(2-methoxyethyl)] aniline

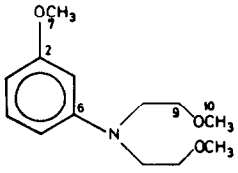
A mixture of 5 g (0.167 mole) of sodium hydride (as an 80 % suspension in paraffin oil) and 200 mL of toluene was placed in a r.b. flask. After 16 g (0.076 mole) of 3-methoxy-bis[N,N-(2-hydroxyethyl)] aniline had been added during 30 min with magnetic stirring the reaction mixture was refluxed for 10 min. Dimethyl sulfate (10 g; 0.079 mole) was then added at such a rate that gentle reflux was maintained. After the addition of dimethyl sulfate had been completed the mixture was refluxed for another 2 h. The reaction mixture was cooled to room temperature, and 10 mL of water and 100 mL of an aqueous solution (50 %) of potassium hydroxide were added with vigorous stirring. The mixture was extracted with six 150 mL portions of diethyl ether. Subsequently, the ether extracts were combined, and volatile products were removed in vacuo (*ca.* 15 mm). The higher-boiling residue was fractionally distilled. B.p. 130–131°C (0.6 mm); yield 17.1 g (94 %).

Anal. $C_{13}H_{21}NO_3$ (239.31); Found (Calc.): C, 66.03 (65.24); H, 9.12 (8.84); N, 5.71 (5.85).

^{1}H n.m.r. spectrum (at 400 MHz): δ_{H4} 7.07 ["t", ^{3}J(HH) 8.2; 1H]; δ_{H5} 6.31 ["d", ^{3}J(HH) 8.2; 1H]; δ_{H1} 6.25 ["d", ^{4}J(HH) 2.5; 1H]; δ_{H3} 6.22 ["d", ^{3}J(HH) 8.2; 1H]; δ_{H7} 3.73 [s; 3H]; $\delta_{H8,9}$ 3.51 ["s", 8H]; δ_{H10} 3.31 [s, 6H].

The single peak, due to the methylene protons (8,9) corresponds to an AA'BB' spectrum; in this case the product of frequency and chemical shift approximates to zero. When measured on a 60 MHz instrument a significant broadening of this signal was noted. If the ^{1}H n.m.r. spectrum of this compound was recorded in $CDCl_3$ (containing trifluoroacetic acid) the signal was split into the expected AA'- and XX'- parts (at 400 MHz). This observation was caused by the protonation of the nitrogen atom which invalidates the above mentioned approximation of the product of frequency and chemical shift to zero.

^{13}C n.m.r. spectrum (at 400 MHz): C1 98.4 [d]; C2 160.7 [s]; C3 100.7 [d]; C4 129.7 [d]; C5 104.8 [d]; C6 149.1 [s]; C7 58.6 [q]; C8 50.9 [t]; C9 70.0 [t]; C10 54.7 [q].



Preparation of aryldifluorophosphines from aryllithium compounds and PF_2Cl

In compounds **1** - **4** bromine/ lithium exchange furnished the lithiated aromatic systems under the same conditions as in the experiment described. The aryldifluorophosphines, **1** - **4**, were distilled and the distillate was a mixture of the n-butyl derivatives of the aromatic precursor and of the aryldifluorophosphines. For reaction conditions, see Table 7. The synthesis of 2.6-dimethoxyphenyldifluorophosphine, **5**, is described as a typical example. In this case a direct lithiation between the two methoxy substituents of the aromatic nucleus occurred.

Preparation of 2,6-dimethoxyphenyldifluorophosphine, **5**

The experiment was conducted in an atmosphere of dry nitrogen in a 300 mL heavy-wall glass tube, fitted with a TEFLON® stopcock. To a solution of 5 g (0.036 mole) of resorcinol dimethylether in 20 mL of ether were added 13.5 g of a 15% solution of n-butyllithium in n-hexane (corresponding to 0.037 mole of $^{n}BuLi$), and the tube was sealed. After 20 h of stirring (using a magnetic stirrer) at room temperature ($\hat{=}$ 25 °C) precipitation of a white solid was noted. The suspension was cooled to -196°C and 4.2 g (0.04 mole) of PF_2Cl was added (at a pressure of 10^{-2} mm). The tube was sealed again, and its contents were allowed to warm to room temperature during 15 min. Lithium chloride was found to be precipitated. About half of the solvent was removed *in vacuo*, and the residue was then centrifuged (*ca.* 6000 rpm). The decanted clear liquid was subsequently kept in vacuo (*ca.* 0.1 mm) until all the solvent was removed. The crude yield of **5** was 5.8 g. From the ^{1}H-n.m.r. spectrum the intensity ratio of the CH_3O-protons in both starting material and product was found to be 1:1.1 which corresponds to a yield of *ca.* 39 %.

The product, **5**, was found to undergo decomposition upon warming above 30°C, and its distillation was not attempted. All n.m.r. spectroscopic investigations were conducted, therefore, on the crude product, obtained as described above.

Preparation of cis-dichloro-bis(aryldifluorophosphine) platinum(II) complexes

The synthesis of the bis-aryldifluorophosphine complexes is described by way of a typical experiment. Dichloro(η^4 -1,5-cyclooctadiene) platinum(II) [12] was dissolved in a small amount of dichloromethane (500 mg cod$PtCl_2$ in *ca.* 35 mL). The clear solution was degassed and the flask was sealed in an atmosphere of nitrogen. Now the calculated amount of the ligand in dichloromethane was added in one portion. After the time stated in Table 8 the cis-dichloro-bis(aryldifluorophosphine) platinum(II) complex was filtered off, washed with small amouts of dichloromethane, and dried in vacuo (10^{-2} mm). All yields are based on the amount of (cod)$PtCl_2$ complex.

TABLE 7

Preparation of aryldifluorophosphines, $ArPF_2$ from the reaction of aryllithium compounds with $ClPF_2$

Compound number	Reactants	g ; mole	Reaction time of lithiation (temp.)	Yield of $ArPF_2$ g (%), from ^1H - n.m.r.
1	PhBr	15,0 ; 0.096	48 h (25°)	2.5 g (18)
	$^nBuLi^a$	35.5 ; 0.097		
	Ether	60 mL		
	PF_2Cl	10.5 ; 0.1		
2	$4\text{-}CH_3C_6H_4Br$	15.0 ; 0.087	120 h (25°)	1.5 g (11)
	$^nBuLi^a$	33.0 ; 0.090		
	Ether	60 mL		
	PF_2Cl	10.0 ; 0.096		
3	$2\text{-}CH_3OC_6H_4Br$	15.0 ; 0.080	96 h (25°)	7.3 g (52)
	$^nBuLi^a$	30.0 ; 0.082		
	Ether	60 ml		
	PF_2Cl	9.9 ; 0.095		
4	$2\text{-}(CH_3)_2NC_6H_4Br$	15.0 ; 0.075	96 h (25°)	5.8 g (41)
	$^nBuLi^a$	28.0 ; 0.076		
	Ether	60 mL		
	PF_2Cl	8,3 ; 0.08		
5	$1,3\text{-}(CH_3O)_2C_6H_4$	5.0 ; 0.036	20 h (25°)	2.9 g (39)
	$^nBuLi^a$	13.5 ; 0.036		
	Ether	20 mL		
	PF_2Cl	4.2 ; 0.040		
6	$1,3\text{-}(PhO)_2C_6H_4$	4.8 ; 0.018	23 h (33°)	4.5 g (75)
	$^nBuLi^a$	6.7 ; 0.018		
	Ether	30 mL		
	PF_2Cl	2.0 ; 0.019		

(continued)

TABLE 7 *(cont.)*

Compound number	Reactants	g ; mole	Reaction time of lithiation (temp.)	Yield of $ArPF_2$ g (%)
7a	3-$CH_3OC_6H_4CF_3$	5.0 ; 0.028	20 h (30°)	3.7 g (54)[b]
7b	^nBuLi[a]	11.0 ; 0.030		2.2 g (32)[b]
	Ether	40 mL		
	PF_2Cl	4.0 ; 0.038		
8	3-$CH_3OC_6H_4N(CH_3)_2$	7.0 ; 0.046	35 h (30°)	3.2 g (31)
	^nBuLi[a]	17.0 ; 0.046		
	Ether	40 mL		
	PF_2Cl	10.0 ; 0.096		
9	3-$CH_3OC_6H_4NMe^iPr$	2.3 ; 0.013	50 h (30°)	1.0 g (24)
	^nBuLi[a]	4.7 ; 0.013		
	Ether	20 mL		
	PF_2Cl	2.0 ; 0.019		
10	3-$CH_3OC_6H_4N(CH_2CH_2)_2NMe$	6.0 ; 0.029	45 h (33°)	1.5 g (19)
	^nBuLi[a]	11.0 ; 0.030		
	Ether	40 mL		
	PF_2Cl	10.0 ; 0.096		
11	3-$CH_3OC_6H_4N(CH_2CH_2)_2O$	10.0 ; 0.052	50 h (30°)	2.8 g (21)
	^nBuLi[a]	19.0 ; 0.053		
	Ether	40 mL		
	PF_2Cl	6.6 ; 0.063		
12	3-$CH_3OC_6H_4N(CH_2CH_2OMe)_2$	10.0 ; 0.042	56 h (30°)	5.9 g (46)
	^nBuLi[a]	15.5 ; 0.042		
	Ether	40 mL		
	PF_2Cl	4.7 ; 0.045		
13	2,3-$(CH_3O)_2C_{10}H_6$	10.0 ; 0.053	20 h (30°)	6.2 g (46)
	^nBuLi[a]	20.0 ; 0.055		
	Ether	50 mL		
	PF_2Cl	6.5 ; 0.062		

[a] n-Butyl lithium was employed as a 15 % solution in n-hexane; the amounts given refer to the weight of this solution;

[b] from ^{31}P- and ^{19}F- n.m.r. spectra.

TABLE 8

Preparation of cis-dichlorobis(aryldifluorophosphine) platinum(II) complexes

Compound number Melting point	Reactants	(g ; mmole)	Reaction time Yield (mg , %) Molecular Weight	Empirical formula Analysis (C , H , P) (Found ; Calculated)
14 (115-118°; >230° dec.)	**1** (cod)$PtCl_2$ CH_2Cl_2	(0.76 ; 5.4) (1.00 ; 2.7) (10 mL)	12 h[a] 1270 mg (85) (558.15)	$C_{12}H_{10}Cl_2F_4P_2Pt$[b] F : C: 25.7; H: 1.8; P: 11.1 C: C: 25.8; H: 1.8; P: 11.1
15 (212° dec.)	**5** (cod)$PtCl_2$ CH_2Cl_2	(0.91 ; 4.4) (0.75 ; 2.0) (55 mL)	24 h 960 mg (71) (678.25)	$C_{16}H_{18}Cl_2F_4O_4P_2Pt$ F : C: 28.7; H: 2.8; P: 9.2 C: C: 28.3; H: 2.7; P: 9.1
16 (201/8° dec.)	**6** (cod)$PtCl_2$ CH_2Cl_2	(1.80 ; 5.5) (1.00 ; 2.7) (40 mL)	340 h[a] 1830 mg (71) (926.54)	$C_{36}H_{26}Cl_2F_4O_4P_2Pt$[c] F : C: 47.5 ; H: 3.1; P: 6.7 C: C: 46.7; H: 2.8; P: 6.7
17 (223/4° dec.)	**7** (cod)$PtCl_2$ CH_2Cl_2	(1.43 : 5.9) (1.00 ; 2.7) (40 mL)	190 h 1270 mg[d] (91) (754.20)	$C_{16}H_{12}Cl_2F_{10}O_2P_2Pt$[e] F : C: 25.6; H: 1.7; P: 8.1 C: C: 25.5; H: 1.6; P: 8.2
18 (214/8° dec.)	**11** (cod)$PtCl_2$ CH_2Cl_2	(0.77 ; 2.9) (0.50 ; 1.3) (60 mL)	120 h[a] 320 mg (31) (790.43)	$C_{22}H_{30}Cl_2F_4N_2O_4P_2Pt$ F: C: 32.5; H: 3.6; N: 3.4 C: C: 33.4; H: 3.8; N: 3.5
19 (218° dec.)	**13** (cod)$PtCl_2$ CH_2Cl_2	(1.54 ; 6.0) (1.00 ; 2.7) (50 mL)	24 h 1640 mg (79) (778.37)	$C_{24}H_{22}Cl_2F_4O_4P_2Pt$ F : C: 36.3 ; H: 2.8; P: 8.2 C: C: 37.0 ; H: 2.9; P: 8.0

[a] The crystallisation was effected by ether diffusion [14]; [b] F: Cl: 12.6; C: Cl: 12.7; [c] the complex was obtained with *ca.* 1 mole of ether. The m.p. was 195°C, and was found to rise to the number given during drying for 20 h at 10^{-2} mm. The amount of ether was then found to decrease to *ca.* 0.6 mole; [d] the yield is based on the isomer isolated (63%, based on the ligand mixture); [e] F : F: 25.0; C: F: 25.2 ;

These reactions were followed by ^{19}F- and ^{31}P- n.m.r. spectroscopy, on samples diluted with $CDCl_3$ (*ca.* 1:10) , and sealed into n.m.r. tubes which were heated to the temperatures and for the periods of time indicated in Table 6 . As a rule, signals due to numerous products were observed in the n.m.r. spectra. Only those products are listed whose identity could be established with certainly. The yields specified, due to the small quantities of products, are only approximate.

ACKNOWLEDGEMENTS

We are indebted to BASF AG, Bayer AG, Hoechst AG, Chemetall, and DEGUSSA for gifts of chemicals. The support of Fonds der Chemischen Industrie is gratefully acknowledged.

We wish to thank Professor L.Ernst and Dr.V.Wray, Gesellschaft für Biotechnologische Forschung mbH, Braunschweig -Stöckheim, and Prof.O.Stelzer, Wuppertal for contributing some n.m.r. spectra, and Dr.H.M.Schiebel, Institut für Organische Chemie der Technischen Universität Braunschweig, for the mass spectra.

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6 A mixture of 2-methoxyphenyl-bis(N,N-diethylamino) phosphine and an excess of HF/pyridine (Janssen Chimica) showed, after 2 h at room temperature, in the ^{31}P-n.m.r. spectrum a doublet at 149.1 ppm, ^{1}J(PF) = 950 Hz and a doublet at -127.9 ppm in the ^{19}F-n.m.r. spectrum ^{1}J(FP) = 947 Hz; indicating the formation of 2-methoxyphenyl-(N,N-diethylamino)- fluorophosphine (E.Niecke, R.Rüger and W.Güth, *Z.Naturforsch.*, **40b** (1985) 1049). Heating of 2-methoxyphenyl-bis(N,N-diethylamino) phosphine in sulfolane as a solvent up to 200°C with an excess of HF/pyridine in a glass flask yielded *ca.* 80% 2- methoxyphenyl phosphine. The reaction pathway postulated is: cleavage of the P-N bond led to the formation of the P-F bond, hydrolysis of the P-F bond by H_2O (from the reaction of HF with the glass flask), and thermolytic decomposition of the 2-methoxyphenyl phosphorous acid formed. (L.Maier in: G.M. Kosolapoff and L.Maier (Eds), Organic Phosphorus Compounds, Vol.1, Wiley- Interscience, New York, 1972, p.9). The phosphine showed in the ^{31}P-n.m.r. spectrum a triplet at -139.0 ppm, ^{1}J(PH) = 202 Hz, which collapsed to a singlet by proton decoupling. These spectra were recorded on the JEOL n.m.r. spectrometer (see Experimental).

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