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Synthetic approach and structural comparison of some novel phosphanes of the type $(C_5Me_5)_2PX$ (X = F, Cl, Br, I)

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Summary — The preparation of sterically highly strained phosphanes of the type Cp^*_2PX (X = F, I, Cp^* = pentamethylcyclopentadienyl) is described in detail. Protocols for the so far unknown congeners (X = F, Cl, Br, I), as well as improved procedures for the already described ones Cp^*_2PX (X = Cl, Br) are presented. Moreover, the molecular structures of three of these compounds in the solid state have been investigated on the basis of X-ray diffraction data.

phosphane / crystallographic structure / pentamethylcyclopentadienyl derivatives / halophosphane

Résumé — Procédé de synthèse et comparaison structurale de nouveaux phosphanes de type $(C_5Me_5)_2PX$ (X = F, I). Une synthèse de phosphanes de type Cp^*_2PX (X = F, Cl, Br, I, Cp^* = pentaméthylcyclopentadiényle) est décrite en détail. Des modes opératoires pour les analogues inconnus (X = F, I), de même que des méthodes plus efficaces pour les substances connues de type Cp^*_2PX (X = Cl, Br) sont présentés. De plus, les structures cristallographiques de trois de ces composés à l'état solide ont été recherchées par rayons X.

phosphane / structure cristallographique / dérivé pentaméthylcyclopentadiényl / halophosphane

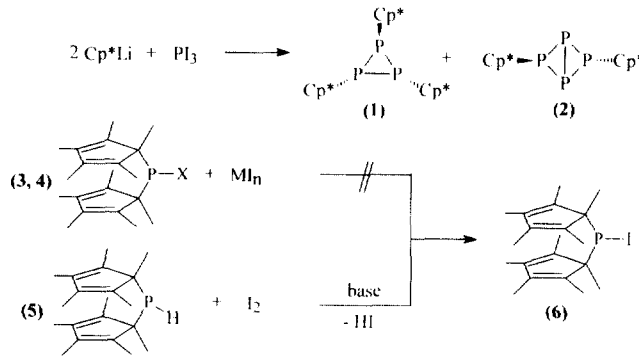
Introduction

In general halophosphanes are versatile synthons in phosphorus chemistry, due to the facile functionalisation of the halogen phosphorus bond by nucleophilic displacement [1]. A unique type of sterically highly crowded halophosphanes represent Cp*-halophosphanes and especially bis(Cp*)halophosphanes. In contrast to conventional halophosphanes the cleavage of the P–C(Cp*) bond is a common side reaction on nucleophilic attack. Therefore, a straightforward synthetic approach starting from the corresponding trihalophosphanes and two equivalents of Cp*Li is not successful in every case. Bis(Cp*)chloro and -bromo phosphane have been prepared by this method, although in moderate yield [2]. However, the analogous syntheses of the corresponding fluoro and iodo congeners fail.

Results and discussion

Reaction of PI_3 with two equiv of Cp*Li yields not the desired bis(Cp*)iodophosphane, but mono- and bicyclic polyphosphanes instead, of which **1** and **2** have been characterized by NMR spectroscopy [3]. The same products had been previously obtained by reduction of dichlorophosphane Cp^*PCl_2 with magnesium [4]. In extension of these findings we explored the preparation of Cp^*_2PI via functionalisation of other bis(Cp*)phosphanes. The formation of the P–I bond with common halogen exchange reagents such as sodium iodide, magnesium iodide and iodotrimethylsilane was not successful. A completely different approach represents the oxidation of phosphane Cp^*_2PH **5** [5] with elemental iodine. In order to neutralize the HI formed alongside the reaction is conducted in the presence of an equimolar amount of base. By this method Cp^*_2PI **6** could be obtained in high yield and purity (scheme 1).

Syntheses of Cp^*_2PF **8** by direct conversion of trifluorophosphane with Cp*Li are problematic, since the reactivity of PF_3 is drastically reduced compared to its

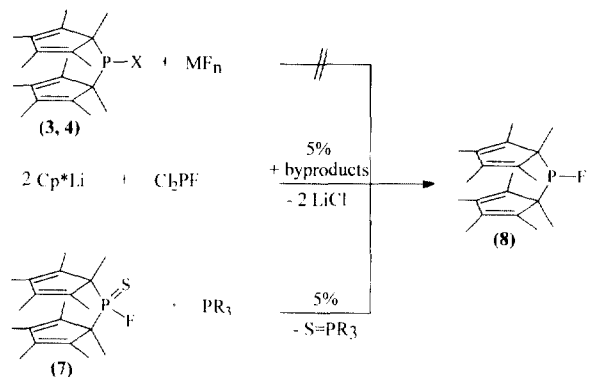


Scheme 1

* Correspondence and reprints

higher congeners, due to the strong P–F bond [6, 7]. As described by Schmutzler et al these difficulties can be overcome by the use of PCl_2F instead, which provides two activated reaction sites in the molecule [6, 7]. Indeed Cp^*_2PF could be identified as a minor product among others following this method, although the low yield and purity of the product made an improved procedure desirable.

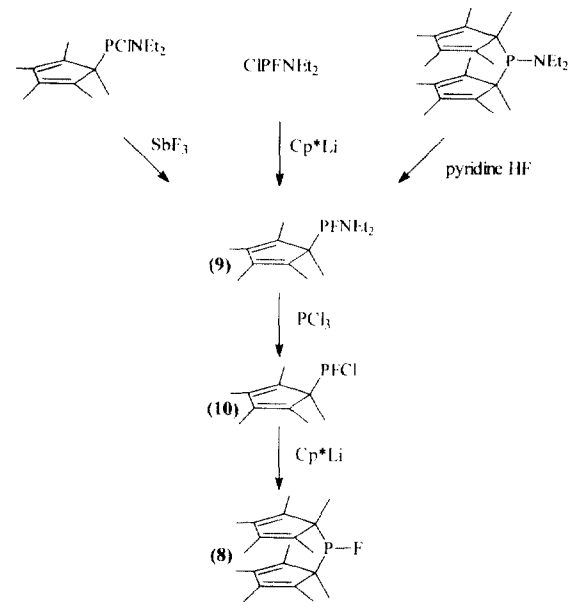
However, the direct halogen exchange of other bis(Cp*)halophosphanes Cp^*_2PX (X = Br, Cl) **3**, **4** with various fluorinating agents (eg, AgF, SbF_3, NaF, KHF_2, etc) fails. In contrast with the corresponding phosphorane Cp^*_2PSCl under similar conditions the exchange of chlorine by fluorine readily takes place, thus furnishing Cp^*_2PSF **7**. Finally a reductive desulfuration of the latter with different phosphanes PR_3 (R = Ph, Bu, OPh, NEt_2) affords the desired fluorophosphane **8** (scheme 2).



Scheme 2

While the number of byproducts in this reaction is reduced compared to the sequence starting from PCl_2F, the yield (5%) still remains unsatisfactory. Since we assumed that the reason for the incomplete conversion of the latter substrate was the steric hindrance at the phosphorus center, we were encouraged to synthesize a precursor which already contained the P–F bond besides only one Cp*-group and a further reactive site. Therefore we made efforts to obtain the so far unknown mixed halogen species Cp*PClF **10** as a suitable precursor. Indeed the latter can be obtained by scrambling reaction of **9** with PCl_3. The aminophosphane **9** itself turned out to be accessible on three different routes, that are summarized in scheme 3.

The availability of **10** by the described routes made the investigation of its conversion to the desired fluorophosphane Cp^*_2PF possible. According to our synthetic concept, the reaction of **10** with Cp*Li indeed readily furnishes **8** in high yield (91%) and purity. The phosphorus nucleus shows a coupling to the fluorine nucleus ($^1J_{PF}$: 900 Hz) and appears exceptionally deshielded ($\delta(^{31}P)$: 230 ppm) compared to the corresponding difluorophosphane (Cp^*PF_2: $\delta(^{31}P)$ = 159 ppm ($^1J_{PF}$: 1160 Hz)) [8]. The opposite would have been expected, since a high field shift of fluorophosphanes FPR_2 with respect to their related difluorophosphanes F_2PR is the rule for common alkyl and aryl substituents [9]. The significant deshielding of the phosphorus atom in **8** may be ascribed to a partial ionic character of the P–F bond.



Scheme 3

X-ray diffraction studies

In order to investigate the influence of the halogen atom onto the bonding situation within the series Cp^*_2PX, X-ray diffraction studies have been performed for X = I (**6**), Br (**3**) and Cl (**4**) in the solid state. Suitable single crystals could be obtained by recrystallisation at −30 °C from toluene for **3** and from a toluene/pentane mixture for **4**. The same procedure worked well for **6** with pentane as solvent, while **8** remained microcrystalline under various crystallisation conditions in the common solvents.

In the solid state all the three congeners **3**, **4** and **6** (figs 1–3) adopt the same conformation, in which the Cp*-rings show a parallel arrangement. As expected, the phosphorus center reveals a pyramidalized geome-

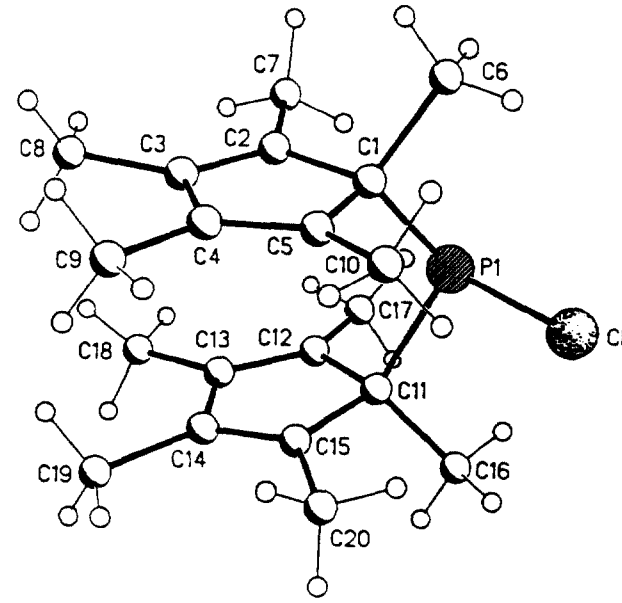


Fig 1. Molecular structure of **4**.

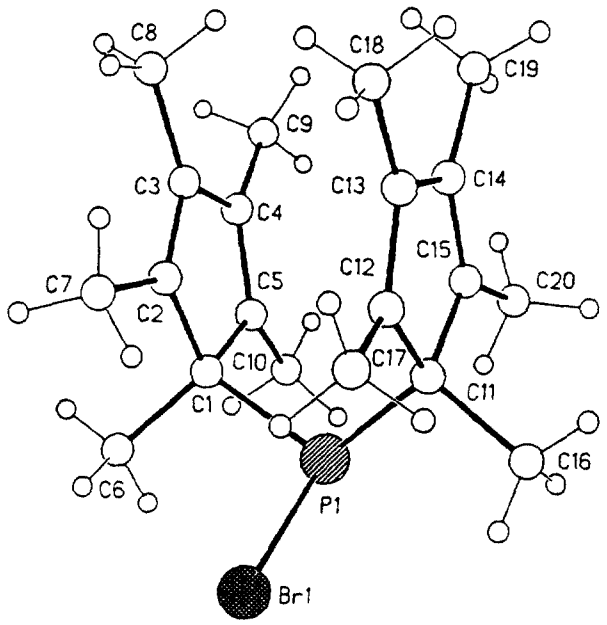


Fig 2. Molecular structure of **3**.

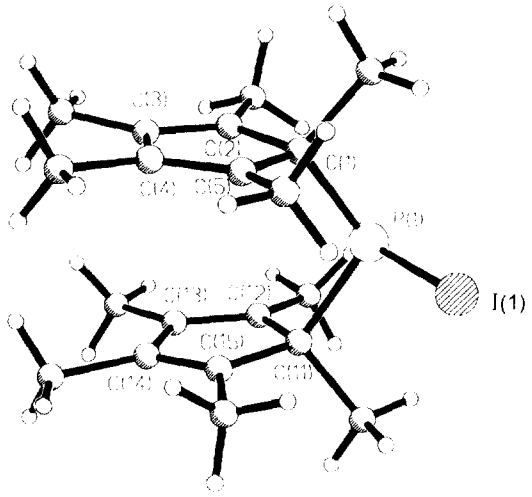


Fig 3. Molecular structure of **6**.

try. This pyramidalisation correlates qualitatively well with the electronegativity of the halogen substituent, in accordance with Bent's rule. The major contribution to this effect arises from the C–P–X angles, while the C–P–C angles in all three compounds are nearly the same. The bond lengths to the phosphorus atoms are slightly elongated throughout with respect to standard single bonds. This observation may be assigned to the sterically highly crowded situation at the phosphorus center. Selected geometric parameters of this series are summarized in table I and crystallographic data in table II.

Experimental section

All steps were carried out under exclusion of air and moisture under an atmosphere of dried argon; glassware, reagents and solvents have been prepared likewise.

Table I. Comparison of characteristic bond lengths [pm] and angles [°] for compounds **4**, **3** and **6**.

X =	*Cl* (**4**)	*Br* (**3**)	*I* (**6**)
P(1)–X(1)	208.4 (1)	226.9 (2)	249.4 (1)
P(1)–C(1)	188.9 (2)	189.1 (6)	189.3 (3)
P(1)–C(11)	188.5 (2)	188.5 (6)	189.6 (3)
C(1)–P(1)–C(11)	111.7 (1)	111.8 (3)	111.3 (1)
C(1)–P(1)–X(1)	101.7 (1)	102.9 (2)	104.4 (1)
C(11)–P(1)–X(1)	102.0 (1)	102.1 (2)	104.0 (1)
Σ∠P(1)	314.8 (1)	316.8 (2)	319.7 (1)

^{31}P NMR: Bruker AMX 300 (121.5 MHz); external standard 85% H_3PO_4.

^{13}C NMR: Bruker AMX 300 (75.5 MHz); external standard tetramethylsilane.

^{1}H NMR: Bruker AMX 300 (300 MHz); external standard tetramethylsilane.

^{31}P and ^{13}C NMR spectra have been recorded with ^{1}H-decoupling. A positive sign means low field with respect to the standard.

MS: Kratos MS 50 and VG instruments VG 12-250 (EI, direct inlet). The given m/z^+ values refer to the isotope of highest abundance for each element.

Melting points: measured without correction in sealed capillaries in a melting point apparatus supplied by Büchi, Flawil/Switzerland.

Elemental analyses: Heraeus CHN-O-Rapid. The literature procedure [2] for the syntheses of the bis(Cp*)halogenophosphanes **3** and **4** has been modified.

Bis(pentamethylcyclopentadienyl)bromo- and -chlorophosphane ***3*** *and* ***4***

24 mmol (3.4 g) of Cp*Li is suspended in 30 mL of pentane and 10 mmol of phosphorus trihalide (PBr_3: 0.95 mL, PCl_3: 0.88 mL) is added slowly at ambient temperature. After completed addition, the mixture is stirred vigorously for 12 h. The mixture is then diluted with further 50 mL of pentane and filtered. The residue is extracted three times with 50 mL of pentane and the combined fractions are concentrated to a volume of 20 mL. From this solution the product crystallizes on cooling to −80 °C. Yield: **3** 2.21 g (82%)/**4**: 1.20 g (87%). ^{31}P-{^{1}H}-NMR (pentane): **3**: δ = 166.8/**4**: δ = 163.3.

Bis(pentamethylcyclopentadienyl)iodophosphane ***6***

A solution of 1.56 mmol (0.47 g) Cp^*_2PH dissolved in 10 mL of ether is treated with a solution of 1.56 mmol iodine in 2 mL of toluene at ambient temperature. To the reaction mixture 1.56 mmol (0.22 mL) of triethylamine are added immediately. After precipitation of solid white to reddish triethylammonium iodide the solvent is evaporated in vacuum. The remaining residue is extracted with 10 mL of pentane and filtered. After concentration to 2 mL, 4 mL of toluene are added to the solution. Crystallisation at −30 °C yields the product as orange crystals. Yield: 0.58 g (87%), Mp: 84–86 °C.

^{31}P NMR (C_6D_6): δ = 139.6 (s).

MS (15 eV, 300 °C): 429, $[M]^+$, 0.5%; 301, $[M - I]^+$, 22%; 293, $[Cp^*PI]^+$, 100%; 166, $[Cp^*P]^+$, 23%; 134, $[Cp^*–H]^+$, 15%.

Anal [%]: C: 56.08; H: 7.06 (calc). C: 56.79; H: 7.91, (found).

Table II. Crystallographic data and summary of data collection and refinement.

	3	***4***	***6***
Formula	$C_{20}H_{30}PBr$	$C_{20}H_{30}PCl$	$C_{20}H_{30}PI$
M_r	381.3	336.9	428.3
Dimensions [mm]	0.30 × 0.40 × 0.45	0.10 × 0.35 × 0.40	0.80 × 1.00 × 1.60
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no 14)	$P2_1/c$ (no 14)	$P2_1/n$ (no 14)
a [Å]	13.719(2)	8.373(1)	13.502(6)
b [Å]	10.026(1)	15.467(3)	10.360(3)
c [Å]	14.590(2)	15.313(2)	14.416(4)
β [°]	99.49(1)	101.93(1)	98.89(3)
V [Å^3]	1979.3(4)	1940.3(5)	1992.4(12)
Z	4	4	4
ρ [g cm^{-3}]	1.28	1.15	1.43
μ [mm^{-1}]	3.536	2.461	1.684
$F(000)$	800	728	872
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	CuKα	CuKα	MoKα
λ [Å]	1.54178	1.54178	0.71073
T [K]	208(2)	200(2)	193(2)
$2\theta_{max}$ [°]	120	120	50
	$-15 \leqslant h \leqslant 15$	$-9 \leqslant h \leqslant 9$	$0 \leqslant h \leqslant 21$
	$0 \leqslant k \leqslant 11$	$-17 \leqslant h \leqslant 0$	$-16 \leqslant h \leqslant 0$
	$-16 \leqslant h \leqslant 0$	$0 \leqslant h \leqslant 17$	$-22 \leqslant h \leqslant 22$
No of measured data	3124	3003	3896
No of unique data	2944	2881	3427
No of obs data for ($I > 2\sigma(I)$)	2533	2575	3261
R_{int}	0.037	0.053	0.037
Refinement on	F^2	F^2	F^2
No of parameters	110	209	210
R [for $I > 2\sigma(I)$]	0.097	0.046	0.053
w$R2$ (all data)	0.273	0.130	0.115
Max/Min			
Difference peak [e/Å^3]	1.94/−1.12	0.43/−0.39	1.43/−0.78

Bis(pentamethylcyclopentadienyl)thiophosphinic acid fluoride ***7***

A suspension of 3 mmol (0.23 g) potassium hydrogen difluoride (KHF_2) in 2 mL of toluene is treated with 1 mmol (0.36 g) bis(pentamethylcyclopentadienyl)thiophosphinic acid chloride dissolved in 3 mL of toluene. The mixture is heated to reflux for 24 h. Afterwards the solvent is removed under vacuum and the residue is extracted with 20 mL of pentane and filtered. Exchange from pentane by toluene and cooling to −30 °C yields the product as colourless crystals. Yield: 0.31 g (88%), Mp: 178–180 °C.

^{31}P NMR (C_6D_6): δ = 133,5 (d, sp; $^1J_{PF}$: 1086.5 Hz; $^3J_{PH}$: 17.2 Hz).

^{1}H NMR ($CDCl_3$): δ (Me 1) = 1.81 (d, $^3J_{HP}$: 17.6 Hz), δ (Me 2,5) = 1.71 (m)/1.69 (m), δ (Me 3.4) = 1.35/1.28.

^{13}C-{^{1}H,^{31}P}-NMR ($CDCl_3$): 19.6 (d, $^3J_{CF}$: 1.7 Hz), (Me 1): 12.3 (d, J_{CF}: 1.9 Hz) / 12.0 (s) 11.9 (s) / 11.8 (d, J_{CF}: 3.4 Hz), (Me 2–5); 63.7 (d, $^2J_{CF}$: 11.1 Hz), (C 1); 139.7 (s) / 139.3 (d, J_{CF}: 2.3 Hz) (C 2–5): 136.7 (d, J_{CF}: 1.9 Hz) / 134.2 (d, J_{CF}: 1.9 Hz).

^{13}C-{^{1}H}-NMR ($CDCl_3$): (Me 1), 19.6 (dd, $^2J_{CP}$: 8.1 Hz, $^3J_{CF}$: 1.5 Hz); (Me 2–5), 12.3 (d, J_{CF}: 1.9 Hz) / 11.8 (d, J_{CF}: 3.4 Hz): 12.0 (d, J_{CP}: 1.1 Hz) / 11.9 (d, J_{CP}: 0.8 Hz); (C 1), 63.8 (dd, $^1J_{CP}$: 48.4 Hz, $^2J_{CF}$: 11.1 Hz), (C 2–5), 139.7 (d, J_{CP}: 8.4 Hz), 139.3 (dd, J_{CP}: 9.3 Hz, J_{CF}: 2.3 Hz); 136.7 (ψ-t, $J_{CP} = J_{CF}$: 1.9 Hz); 134.5 (dd, J_{CP}: 3.0 Hz, J_{CF}: 1.9 Hz).

MS (70 eV, 200 °C): 352, 5%, $[M]^+$; 320, 1%, $[M - S]^+$; 217, 70%, $[M - Cp^*]^+$; 186, 30%, $[Cp^*PF]^+$; 167, 1%, $[Cp^*P]^+$; 135, 100%, $[Cp^*]^+$. High resolution: 352.1793 (found); 352.1790 (calc) $C_{20}H_{30}FPS$.

Diethylamino-fluoro-(pentamethylcyclopentadienyl)-phosphane ***9***

(1) To 3.66 mmol (1.0 g) of Cp^*NEt_2PCl [10], 1.75 mmol (0.32 g) of antimony trifluoride is added in small portions under vigorous stirring. After 4 h, 5 mL of toluene are added and the mixture is stirred for further 12 h. The conversion can be monitored by ^{31}P NMR. In case of incomplete reaction further 0.32 g SbF_3 is added and stirring is continued for 24 h. Subsequently, all volatile components are removed under vacuum and the residue is extracted several times with 10 mL of pentane followed by filtration. The solvent of the solution is evaporated and the resulting yellow oil is distilled under vacuum.

Remark: Upscaling of the reaction prolongs the reaction time significantly.

(2) A solution of 1.4 mmol (0.52 g) $Cp^*_2PNEt_2$ [5] in 10 mL of pyridine is cooled to −40 °C and treated dropwise with 1.4 mmol (0.36 mL) hydrogen fluoride-pyridine complex (70% HF) dissolved in 2 mL pyridine. It is essential to maintain the temperature in a range from −38 °C to −42 °C. After completed addition the mixture is stirred at that temperature for further 2 h and is warmed afterwards very slowly to ambient temperature. The volatile components of the mixture are removed under vacuum and the remaining yellow oil is fractioned over a Vigreux column.

(3) To a suspension of 1.1 mmol (0.16 g) Cp^*Li in 10 mL of pentane a solution of 1 mmol (0.15 g) Et_2NPClF [11]

in 5 mL of pentane is added dropwise at −20 °C. After warming to ambient temperature the mixture is stirred for 6 h. Subsequent filtration and evaporation of the solvent yields the crude product, which can be purified by vacuum distillation. Bp: 58–62 °C (0.01 Torr).

Yields: (1) 0.28 g (31%); (2) 0.24 g (67%); (3) 0.19 g (74%).

^{31}P NMR (C_6D_6): δ = 179.9 (d, $^1J_{PF}$: 949.8 Hz).

MS (25 eV, 200 °C): 257, 16%, $[M]^+$; 238, 3%, $[M - F]^+$; 185, 4%, $[Cp^*PF]^+$; 134, 100%, $[Cp^* - H]^+$.

Chloro-fluoro-(pentamethylcyclopentadienyl)-phosphane ***10***

1 mmol (0.26 g) Cp^*NEt_2PF in 5 mL toluene is treated dropwise with 1.1 mmol (0.1 mL) of phosphorus trichloride at ambient temperature over a period of 30 min. Eventually, the volatile components are removed under vacuum. The remaining crude product is purified by vacuum distillation over a 10 cm Vigreux-column. Yield: 0.15 g (68%). Bp: 43–45 °C (0.01 Torr).

^{31}P NMR (C_6D_6): δ = 159.8 (d, $^1J_{PF}$: 1111.3 Hz).

^{1}H NMR (C_6D_6): (Me 1–5) = 1.76 (s).

^{13}C-{^{1}H}-NMR (C_6D_6): (Me 1–5), 14.3 (d, J_{CP}: 4.9 Hz); (C 1–5), 138.6 (d, J_{CP}: 34.9 Hz).

MS (25 eV, 25 °C): 220, 100%, $[M]^+$; 201, 10%, $[Cp^*PCl]^+$; 185, 100%, $[Cp^*PF]^+$; 135, 100%, $[Cp^*]^+$. High resolution: 220.0579 (found); 220.0584 (calc) $C_{10}H_{15}ClFP$.

Bis(pentamethylcyclopentadienyl)fluorophosphane ***8***

A solution of 1.13 mmol (0.25 g) Cp^*PClF in 5 mL of pentane is slowly added to a suspension of 1.4 mmol (0.2 g) Cp^*Li in 10 mL of pentane at 0 °C. The mixture is warmed to ambient temperature and stirred for 6–8 h. Subsequently, the residue is extracted several times with pentane and after filtration, the solvent is removed. The crude product is recrystallized from 2 mL of toluene at −30 °C. Yield: 0.33 g (91%), Mp: 90–92 °C.

^{31}P NMR (C_6D_6): 230.2 (d, $^1J_{PF}$: 899.6 Hz).

MS (25 eV, 200 °C): 320, 2%, $[M]^+$; 185, 100%, $[Cp^*PF]^+$; 165, 3%, $[Cp^*P - H]^+$; 134, 100%, $[Cp^* - H]^+$.

X-ray structure determination of ***3***, ***4*** *and* ***6***

The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. In **3** only the phosphorus and bromine atoms were refined anisotropically due to the absorption effects. The hydrogen atoms were refined using a riding model. In **3** and **4** an empirical absorption correction [12] and in **3** and **6** an extinction correction were applied. Further details of the crystal structure investigations may be obtained from the director of the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Telefax +44-1223-336033; E-mail: deposit@ccdc) on quoting the depository number CCDC-100818.

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