ELSEVIER

Journal of Fluorine Chemistry 83 (1997) 159–166

JOURNAL OF FLUORINE CHEMISTRY

Chemistry of bis(pentafluorobenzyl) phosphines and phosphine oxides. Single-crystal X-ray diffraction study of η^6-mesitylene-dichloro-[bis(pentafluorobenzyl)phosphinous acid]–ruthenium(II) and of 1,2-bis(pentafluorophenyl)ethane [1]

Roland Krafczyk, Holger Thönnessen, Peter G. Jones, Reinhard Schmutzler *

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany

Received 3 October 1996; revised 10 January 1997; accepted 10 January 1997

Abstract

The reaction of pentafluorobenzyl magnesium bromide with phosphorus trichloride in a 2:1 molar ratio led to the disubstituted product, bis(pentafluorobenzyl)bromophosphine **1**, which, upon reaction with lithium aluminium hydride, was converted to bis-(pentafluorobenzyl)phosphine **3**. The reaction of **3** with oxygen led to bis(pentafluorobenzyl)phosphine oxide **4**. The reaction of **1**, **3** and **4** with di-μ-chloro-bis-[(η^6-mesitylene)chloro-ruthenium(II)] **5** yielded the η^6-mesitylene-phosphinedichloro–ruthenium(II) complexes **6–8**.

Single-crystal X-ray structure determinations are described for the phosphinous acid–ruthenium(II) complex **8** and for the by-product 1,2-bis(pentafluorophenyl)ethane **2**, formed during the Grignard reaction of magnesium and pentafluorobenzylbromide. In **8**, the Ru–C bond lengths can be categorised as four short (219–222 pm) and two long (224–228 pm). A weak intramolecular P–OH···Cl contact (O···Cl, 304 pm) is observed. © 1997 Elsevier Science S.A.

Keywords: Fluorinated phosphines; Phosphine–ruthenium complexes; Single crystal; X-ray; Structure determination

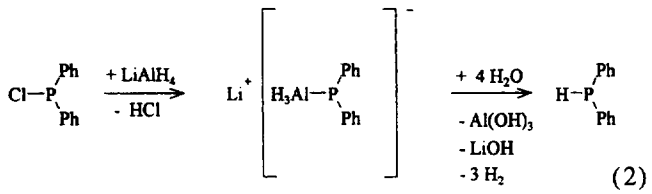
1. Introduction

The reaction of Grignard reagents with phosphorus trichloride leads to aryl and alkyl phosphines or halophosphines, depending on the reaction conditions and/or the ratio of the reactants (Eq. (1))

$$(3-n)\mathrm{RMgX} + \mathrm{PX_3} \rightarrow \mathrm{R}_{3-n}\mathrm{PX}_n + (3-n)\mathrm{MgX_2} \quad (\mathrm{R} = \text{aryl, alkyl};\ \mathrm{X} = \mathrm{Br, Cl};\ n = 0, 1, 2) \qquad (1)$$

The reaction of pentafluorophenyl magnesium bromide and phosphorus trichloride was investigated by Fild et al. in 1966 [1,2]. In a molar ratio of 2:1, the reaction led to bis(pentafluorophenyl)bromophosphine (as the major product) and small amounts of bis(pentafluorophenyl)-chlorophosphine. Similar reactions of the related pentafluorobenzyl Grignard reagent have not been reported.

The use of lithium aluminium hydride as a reducing agent was found to transform various organophosphorus compounds into the corresponding PH–phosphines [3]. The course of the conversion of diphenylchlorophosphine to diphenylphosphine was examined using ^{31}P NMR spectroscopy by Fluck and Binder [4]. They postulated the formation of an aluminium–phosphine complex, from which the phosphine was released upon hydrolysis (Eq. (2))



(2)

Compounds of the type $R_2P(:O)H$ (R = alkyl, aryl) are named phosphine oxides. They correspond to the tautomeric form of phosphinous acids [5]. The first derivatives of this class of compounds were synthesised by Williams and Hamilton [6]. The equilibrium can favour the phosphinous acid if the substituents at phosphorus are highly fluorinated or perfluorinated (Eq. (3)),

$$\mathrm{R_2P{-}OH} \underset{\mathrm{R = alkyl,\ aryl}}{\rightleftarrows} \mathrm{R_2P(:O)H} \qquad (3)$$

* Corresponding author.

[1] Dedicated to Professor Oskar Glemser on the occasion of his 85th birthday.

PII S0022-1139(97)00019-5

Accordingly, bis(trifluoromethyl)phosphinous acid exists as the acid tautomer [5,7,8]. The same was observed for bis(pentafluorophenyl)phosphinous acid [9]. Kleiner developed a synthesis of $(CH_3)_2P(:O)H$ and examined its reactivity [10]. A simple method of preparing phosphine oxides is the oxidation of secondary phosphines with air [3].

Phosphines are excellent ligands towards transition metals. The reaction of cyclohexa-1,3-diene with ethanolic ruthenium(III) trichloride was reported by Winkhaus and Singer to give a benzene complex of empirical formula $[RuCl_2(C_6H_6)]$ which, on reaction with tri-*n*-butylphosphine, gave the adduct $[RuCl_2(C_6H_6)(PBu^n_3)]$ [11]. In this research, we chose to study the complexation of the phosphines **1**, **3** and **4** in their reaction with di-μ-chloro-bis-[(η^6-mesitylene)chloro–ruthenium(II)] **5**.

2. Results and discussion

2.1. Synthesis of bis(pentafluorobenzyl)bromophosphine 1

The Grignard reagent, pentafluorobenzyl magnesium bromide, was prepared by reaction of pentafluorobenzyl bromide with an excess of magnesium turnings in diethyl ether. It was added dropwise to a solution of phosphorus trichloride in diethyl ether in a molar ratio of 2:1, in order to prevent threefold substitution. After removing the magnesium salts and further work-up, **1** was isolated as a solid (Eq. (4)),

$$2C_6F_5CH_2MgBr + PCl_3 \xrightarrow[-MgBrCl,\ -MgCl_2]{} \underset{\mathbf{1}}{(C_6F_5CH_2)_2PBr} \quad (4)$$

In contrast to the results of Fild et al. [1], the formation of the corresponding chloride was not observed. During work-up, 1,2-bis(pentafluorophenyl)ethane **2** was isolated. Compound **2** was first described by Bruce in 1967 [12]. He observed its formation during the decomposition of the complex $[CpFe(CO)_2CH_2C_6F_5]$.

The identity of **1** and **2** was established by NMR spectroscopy (^1H, ^{13}C, ^{19}F, ^{31}P) and mass spectrometry, and, in the case of **2**, by a single-crystal X-ray structure determination. **2** was formed in a Wurtz-type reaction of the Grignard reagent with pentafluorobenzyl bromide [13] (Eq. (5)),

$$C_6F_5CH_2MgBr \xrightarrow[-MgBr_2]{+C_6F_5CH_2Br} \underset{\mathbf{2}}{C_6F_5CH_2CH_2C_6F_5} \quad (5)$$

The ^1H NMR spectrum of **1** exhibits an unresolved multiplet ($\delta(^1H) = 3.3$–3.6 ppm) for the CH_2 protons. For **2**, a singlet ($\delta(^1H) = 3.0$ ppm) was observed. A pseudo-quintet ($\delta(^{31}P) = 86.6$ ppm, $^4J(PF) = 19$ Hz) appeared in the ^{31}P NMR spectrum of **1**.

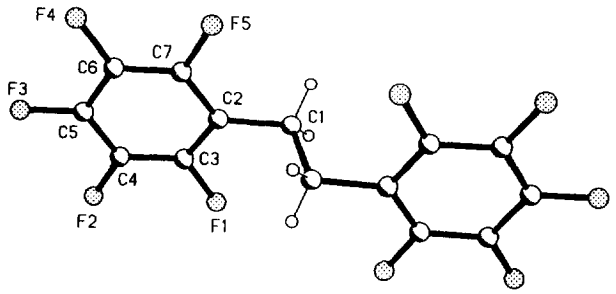


Fig. 1. The molecule of compound **2** in the crystal. Radii are arbitrary. Only the asymmetric unit is numbered.

2.2. X-ray crystal structure determination of 2

The molecule of **2** possesses crystallographic inversion symmetry, with the inversion centre at the midpoint of the C1–C1′ bond. The pentafluorophenyl groups, which show only a slight mean deviation from planarity (1.4 pm), are thus exactly parallel. The bond lengths and angles are as expected, e.g. C1–C2, 150.8(3) pm; C1–C1′, 154.2(4) pm; C2–C1–C1′, 111.2(2)° (Fig. 1).

2.3. Synthesis of bis(pentafluorobenzyl)phosphine 3 and bis(pentafluorobenzyl)-phosphine oxide 4

The reaction of bis(pentafluorobenzyl)bromophosphine **1** with lithium aluminium hydride in diethyl ether gave **3**

$$\underset{\mathbf{1}}{4(C_6F_5CH_2)_2PBr} \xrightarrow[2.\ +H_2O/HCl]{1.\ +LiAl/H_4} \underset{\mathbf{3}}{4(C_6F_5CH_2)_2PH} \quad (6)$$

A ^{31}P NMR spectroscopic examination showed that **3** was formed directly, before hydrolysis. The aluminium–phosphine complex, as proposed by Fluck and Binder [4] for the system diphenylchlorophosphine/lithium aluminium hydride, was not observed.

Bis(pentafluorobenzyl)phosphine oxide **4** was formed by stirring a solution of **3** in dichloromethane in an open flask for several hours (Eq. (7)),

$$\underset{\mathbf{3}}{(C_6F_5CH_2)_2PH} \xrightarrow{+0.5O_2} \underset{\mathbf{4}}{(C_6F_5CH_2)_2P(:O)H} \quad (7)$$

After work-up, **3** and **4** were characterised by NMR spectroscopy (^1H, ^{13}C, ^{19}F, ^{31}P) and mass spectrometry. Unexpectedly, the formation of the phosphinous acid tautomer, which was predicted in the case of fluorinated substituents at the phosphorus atom, was not observed. The phosphine oxide tautomer was present instead.

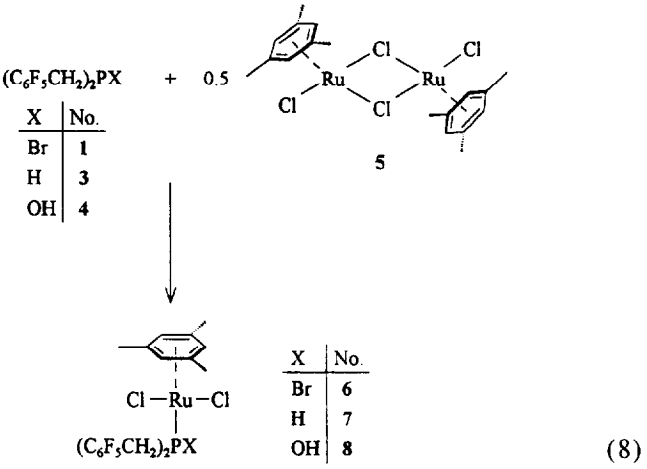
The ^1H NMR spectra of **3** and **4** were found to exhibit doublets in the range 3.2–4.6 ppm for the CH_2 group. The P<u>H</u> resonance of **3** and the P(:O)<u>H</u> resonance of **4** were observed as doublets (**3**: $\delta(^1H) = 5.3$ ppm, $^1J(HP) = 195$ Hz;

4: $\delta(^1H) = 7.1$ ppm, $^1J(HP) = 498$ Hz). In the ^{31}P NMR spectra of **3** and **4**, doublets of multiplets (**3**: $\delta(^{31}P) = -59.1$ ppm, $^1J(PH) = 195$ Hz; **4**: $\delta(^{31}P) = 22.5$ ppm; $^1J(PH) = 498$ Hz) were observed. The presence of the phosphine oxide tautomer **4** was confirmed by the $\delta(^{31}P)$ value and the large $^1J(PH)$ coupling constant.

The infrared spectrum of **4** showed absorptions at $\tilde{\nu} = 2362$ cm^{-1}, due to the P–H group and $\tilde{\nu} = 1189$ cm^{-1}, due to the P(:O) group.

2.4. Synthesis of the ruthenium(II) complexes 6–8

Refluxing **5** with the ligands **1**, **3** and **4** in dichloromethane led to the corresponding ruthenium(II) complexes **6–8**



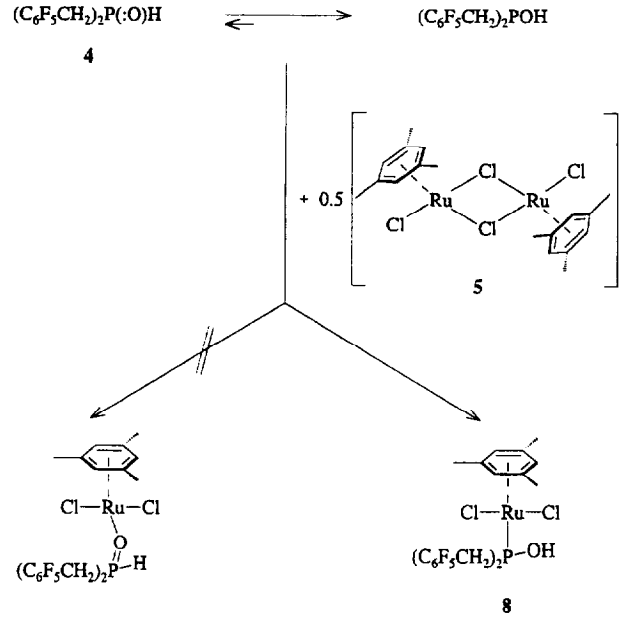
(8)

In contrast to the starting phosphorus(III) compounds **1**, **3** and **4**, the complexes formed were neither air- nor moisture-sensitive. The identity of compounds **6–8** was established by infrared and NMR spectroscopy (^1H, ^{13}C, ^{19}F, ^{31}P), mass spectrometry and elemental analysis, and, in the case of **8**, by a single-crystal X-ray structure determination.

For **6**, bromine–chlorine exchange led to the formation of a mixture of three isomers in a ratio 6:5:2 (^1H, ^{13}C and ^{31}P NMR evidence). An attempt at a single-crystal X-ray structure analysis of **6** was unsuccessful, because of the associated disorder.

Whereas free **4** exists as the phosphine oxide tautomer, after its complexation to ruthenium in **8** it is, necessarily, present as the phosphinous acid tautomer. Infrared spectroscopy and a single-crystal X-ray structure analysis confirmed the structure of **8** (Scheme 1).

The ^1H NMR spectra of **6–8** were found to exhibit multiplets ($\delta(^1H) = 3.20$–4.70 ppm) for the CH_2 protons of the benzyl group. In the ^1H NMR spectrum of **6**, three sets of signals, due to three isomers, were observed. The resonances of the mesitylene–$C\underline{H}_3$ groups were observed as singlets at $\delta = 2.17$ **a**, 2.22 **b** and 2.11 **c** ppm, the mesitylene ring–$\underline{H}$ protons as singlets at $d = 5.02$ **a**, 5.08 **b** and 4.98 **c** ppm. Their ratio was **a**:**b**:**c** = 6:5:2. In the ^1H NMR spectrum of **7**, the mesitylene signals were observed as singlets at $\delta = 2.20$ and 4.99 ppm, and the resonance of the P–$\underline{H}$ proton as a doublet of multiplets at $\delta = 5.21$ ppm with $^1J(HP) = 382.90$ Hz. In



Scheme 1. The complexation of phosphine oxide **4** to ruthenium in **8** as phosphinous acid tautomer.

comparison with the uncoordinated ligand **3**, the $^1J(HP)$ coupling constant was doubled after complexation. In the ^1H NMR spectrum of **8**, the mesitylene signals were observed as singlets at $\delta = 2.25$ and 5.05 ppm, and the P–O$\underline{H}$ proton resonance as a multiplet at $\delta = 7.95$ ppm.

The ^{31}P NMR spectrum of **6** was found to exhibit three singlets at $\delta = 106.12$ **a**, 102.94 **b** and 108.01 **c** ppm, due to three isomers. In the ^{31}P NMR spectrum of **7**, a doublet at $\delta = 10.37$ ppm with $^1J(PH) = 382.90$ Hz was observed. The ^{31}P NMR spectrum of **8** showed a singlet at $\delta = 117.07$ ppm, due to the P–O$\underline{H}$ group of the phosphinous acid tautomer. For the presence of the phosphine oxide tautomer, a doublet for the resonance of the P(:O)$\underline{H}$ group would be expected.

Table 1 lists the ^{31}P NMR resonances of the ligands **1**, **3** and **4**, compared to those of their ruthenium complexes **6–8**.

The infrared spectrum of **6** showed an absorption at $\tilde{\nu} = 499$ cm^{-1}, due to P–Br. In the infrared spectrum of **7**, the P–H absorption was observed at $\tilde{\nu} = 2426$ cm^{-1}. For **8**, the O–H vibration was observed at $\tilde{\nu} = 3300$ cm^{-1} and the P–O vibration at $\tilde{\nu} = 1127$ cm^{-1}.

2.5. X-ray crystal structure determination of 8

The X-ray crystal structure of **8** (Fig. 2) confirms the coordination of the ligand **4** as the phosphinous acid tautomer. The coordination geometry of the central ruthenium atom can be compared to that in the complex $C_6H_6RuCl_2(PMePh_2)$ [14].

The distance ruthenium–(mesitylene ring centre) is 171.6 pm. The average Ru–C bond length (222.3(5) pm) differs insignificantly from that in $C_6H_6RuCl_2(PMePh_2)$ (221.7(10) pm). As in the benzene complex, the individual Ru–C bond lengths are significantly different. Four short and two long distances can be observed: Ru–C17 (220.6(5) pm),

Table 1
^{31}PNMR data of the ligands **1**, **3** and **4**, compared with those of their ruthenium complexes **6–8**

^{31}PNMR	**1**	**3**	**4**
Uncoordinated ligand	$R_2\underline{P}$–Br	$R_2\underline{P}$–H	$R_2\underline{P}$(:O)–H
δ/ppm	86.63	−59.10	22.50
	quint	dm	dm
$^1J(PH)$/Hz	–	195.41	498.61
	6	**7**	**8**
Complex	[Ru(R_2P–Br)]	[Ru(R_2P–H)]	[Ru(R_2P(:O)H)]
δ/ppm	106.12 **a**	10.37	117.07
	102.94 **b**		
	108.01 **c**		
	s	d	s
^1J(HP)/Hz	–	382.90	–

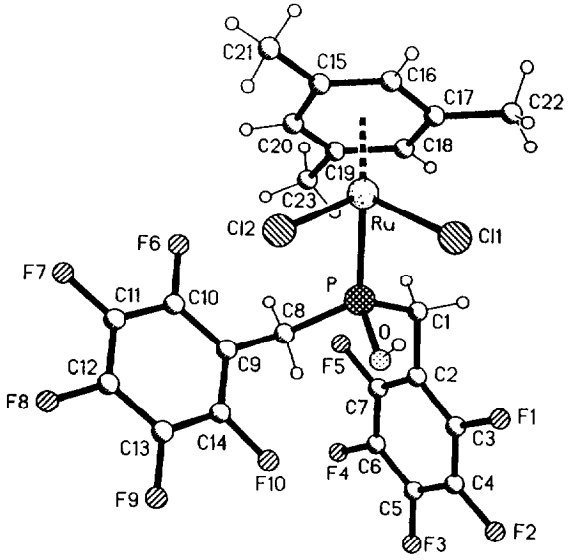


Fig. 2. The molecule of compound **8** in the crystal. Radii are arbitrary.

Ru–C18 (219.5(4) pm), Ru–C20 (219.3(5) pm) and Ru–C19 (222.0(4) pm); Ru–C16 (224.8(4) pm) and Ru–C15 (227.8 (4) pm). As previously suggested [14], the reason may be the *trans* bond-weakening property of the tertiary phosphine.

As in $C_6H_6RuCl_2(PMePh_2)$ (P–Ru–Cl1, 84.3(4)°; P–Ru–Cl2,86.6(4)°; and Cl1–Ru–Cl2, 87.5(4)°), all angles at ruthenium between chlorine and phosphorus are acute (P–Ru–Cl1, 84.35(4)°; P–Ru–Cl2, 86.07(5)°; and Cl1–Ru–Cl2, 85.26(4)°). The Ru–Cl1 (242.11(12) pm) and Ru–Cl2 (240.19(12) pm) bond lengths are essentially the same as in the benzene complex (Ru–Cl1, 241.0(3) pm; Ru–Cl2, 240.9(3) pm). Because of the different substitution at the phosphorus atom, the Ru–P bond length (229.08(14) pm) should not be compared with that of $C_6H_6RuCl_2(PMePh_2)$ (Ru–P, 233.5(3) pm).

The phosphorus atom displays distorted tetrahedral coordination geometry, with the largest deviations from ideal angles for O–P–C8 (100.0(2)°) and C8–P–Ru (121.5(2)°). The P–C1 bond (185.7(4) pm) is insignificantly longer than the P–C8 bond (183.2(5) pm).

The mesitylene ring is planar (mean deviation 2.1 pm) and subtends interplanar angles to the pentafluorophenyl rings of 58° (C2 to C7, mean deviation 0.3 pm) and 89° (C9 to C14, mean deviation 0.8 pm). The dihedral angle between the two pentafluorophenyl rings is 90°. A weak intramolecular contact P–OH···Cl1 is observed, with O···Cl1, 304 pm, H···Cl1, 237 pm and O–H···Cl1, 138°.

3. Experimental details

All experiments were carried out with the exclusion of air and moisture; solvents were purified and dried according to the usual methods [15]. "In vacuo" (i.v.) refers to a pressure of 0.1 mm Hg at 25 °C, unless stated otherwise.

Di-μ-chloro-bis-[(η^6-mesitylene)chloro-ruthenium(II)] **5** was synthesized, following literature procedures [16,17].

3.1. NMR

Bruker AC 200 (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz; ^{19}F, 188.3 MHz; ^{31}P, 81.0 MHz); reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C), and $CFCl_3$ ext. (^{19}F), 85% H_3PO_4 ext. (^{31}P); high-field shifts were given negative signs, low-field shifts positive signs; the assignment of the aromatic ^{13}C and ^{19}F resonances is explained in Fig. 3. MS: Finnigan MAT 8430; IR: Nicolet 320 FT-IR spectrometer; elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen.

3.2. Crystal structure analyses (see Tables 2–4)

3.2.1. Data collection and reduction

Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 for **2**, and Siemens P4 for **8**, both with LT-2 low-temperature attachment). The cell constants for **2** were refined from $\pm\omega$ angles of 50 reflections in the 2θ range 20–23°. The orientation matrix for **8** was refined from setting angles of 50 reflections in the 2θ range 10–25° (monochromated Mo Kα radiation).

3.2.2. Structure solution and refinement

The structures were solved by direct methods and refined anisotropically on $\underline{F}^2$ (program system: SHELXL-93, G.M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups; the hydroxyl H of **8** was identified in a difference synthesis and refined in terms of a rigid OH group. The weighting scheme was of the

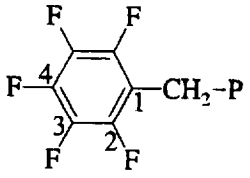


Fig. 3. The assignments of the aromatic ^{13}C and ^{19}F NMR signals.

Table 2
Crystal data for compounds **2** and **8**

Compound	**2**	**8**
Formula	$C_{14}H_4F_{10}$	$C_{23}H_{17}Cl_2F_{10}OPRu$
M_r	362.17	702.31
Crystal habit	Colourless tablet	Red prism
Crystal size/mm	0.5×0.4×0.2	0.42×0.25×0.1
Temperature/°C	−130	−100
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Cell constants		
a/pm	877.4(2)	774.09(12)
b/pm	579.97(12)	1360.15(14)
c/pm	1246.2(3)	2436.0(3)
β/°	90.97(3)	
U/nm^3	0.6341(2)	2.5648(6)
Z	2	4
D_x/Mg m^{-3}	1.897	1.819
μ/mm^{-1}	0.214	0.971
$F(000)$	356	1384
$2\theta_{max}$/°	50	50
No. of reflns.:		
measured	2219	4112
independent	1121	3836
R_{int}	0.057	0.019
$wR(F^2$, all refl.)	0.093	0.055
$R(F, > 4\sigma(F))$	0.035	0.032
No. of parameters	109	347
S	1.073	0.889
Max. Δ/σ	<0.001	<0.001
Max. $\Delta\rho$/e nm^{-3}	194	484

form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$. The absolute structure of **8** was determined using the method of Flack [18]; the final x value was −0.06(3). Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD 405149 and CSD 405150.

3.3. *Bis(pentafluorobenzyl)bromophosphine 1 and 1,2-bis(pentafluorophenyl)ethane 2*

To a mixture of 1.00 g (41.1 mmol) of magnesium turnings and 2 ml of diethyl ether was added, dropwise with stirring, 3.55 g (13.6 mmol) of pentafluorobenzyl bromide at room temperature. During the formation of the Grignard reagent, 15 ml of diethyl ether were added. The reaction was exothermic and therefore the reaction mixture was temporarily cooled, using an ice bath. It was then allowed to warm up to room temperature; unreacted magnesium turnings were removed by filtration, and the solution was added at 0 °C to a solution of 0.93 g (6.8 mmol) of phosphorus trichloride in 80 ml of diethyl ether. The mixture was stirred at 0 °C for 15 min and the precipitate formed was collected by filtration. The solvent and all volatile components were removed i.v. The residue was stirred with 50 ml of *n*-hexane (in order to separate the by-product **2** from **1**). After filtration, **1** was dried i.v. Storing the mother liquor at −30 °C for 3 days resulted in the precipitation of **2** as a colourless solid, which was filtered off and dried i.v.

1: Yield: 0.94 g (29%), m.p. 130°C. ^{1}H NMR ($CDCl_3$): δ=3.32–3.65 ppm [m, 4H, 2x $C\underline{H}_2$]. ^{13}C NMR ($CDCl_3$): δ=27.42 [d, $^1J(CP)$=39.28 Hz, 2C, 2x $\underline{C}H_2$]; 102.68 [m, 2C, 2x aromatic C-1]; 138.10 [dm, $^1J(CF)$=253.74 Hz, 4C, 4x aromatic C-3]; 141.85 [dm, $^1J(CF)$=257.23 Hz, 2C, 2x aromatic C-4]; 145.19 ppm [dm, $^1J(CF)$=239.70 Hz, 4C, 4x aromatic C-2]. ^{19}F NMR ($CDCl_3$): δ=−161.65 [m, 4F, 4x aromatic F-3]; −155.12 [m, 2F, 2x aromatic F-4]; −140.88 ppm [m, 4F, 4x aromatic F-2]. ^{31}P NMR ($CDCl_3$): δ=86.63 ppm [quint, $^4J(PF)$=19.33 Hz, 1P]. EI-MS, m/z (%): 474 (10) $[M]^+$, 293 (4) $[M-(C_6F_5CH_2)]^+$, 181 (100) $[C_6F_5CH_2]^+$. $C_{14}H_4BrF_{10}P$ (473.04).

2: Yield: 0.96 g (39%), m.p. 90°C. ^{1}H NMR ($CDCl_3$): δ=3.01 ppm (s, 4H, 2x $C\underline{H}_2$). ^{13}C NMR ($CDCl_3$): δ=21.86 (s, 2C, 2x $\underline{C}H_2$); 112.76 (m, 2C, 2x aromatic C-1); 137.69 (dm, 2C, $^1J(CF)$=263.80 Hz, 2x aromatic C-4); 140.10 (dm, 4C, $^1J(CF)$=244.79 Hz, 4x aromatic C-3); 145.14 ppm (dm, 4C, $^1J(CF)$=246.33 Hz, 4x aromatic C-2). ^{19}F NMR ($CDCl_3$): δ=−162.51 (m, 2F, 2x aromatic F-3); −156.33 (m, 1F, aromatic F-4); −144.75 ppm (m, 2F, 2x aromatic F-2). EI-MS, m/z (%): 362 (22) $[M]^+$, 181 (100) $[C_6F_5CH_2]^+$. $C_{14}H_4F_{10}$ (362.17).

3.4. *Bis(pentafluorobenzyl)phosphine 3*

To a mixture of 1.00 g (2.1 mmol) of **1** and 50 ml of diethyl ether was added 0.08 g (2.1 mmol) of lithium aluminium hydride at 0 °C. The reaction mixture was allowed to warm up to room temperature. After stirring for 2 h at room temperature, 10 ml of hydrochloric acid (10%) were added at 0 °C. The reaction mixture was allowed to warm up to room temperature, and after stirring for 10 min, the ether layer was separated. After removing the solvent and all volatile components i.v., **3** was left as a colourless solid.

Yield: 0.46 g (55%), m.p. 38 °C. ^{1}H NMR ($CDCl_3$): δ=3.95–4.10 [m, 4H, 2x $C\underline{H}_2$]; 5.27 ppm [d, $^1J(HP)$=195.41 Hz, 1H, P$\underline{H}$]. ^{13}C NMR ($CDCl_3$): δ=22.78 [d, $^1J(CP)$=60.32 Hz, 2C, 2x $\underline{C}H_2$]; 103.59 [m, 2C, 2x aromatic C-1]; 136.61 [dm, $^1J(CF)$=253.11 Hz, 4C, 4x aromatic C-3]; 141.46 [dm, $^1J(CF)$=254.55 Hz, 2C, 2x aromatic C-4]; 144.11 ppm [dm, $^1J(CF)$=241.73 Hz, 4C, 4x aromatic C-2]. ^{19}F NMR ($CDCl_3$): δ=−162.30 [m, 4F, 4x aromatic F-3]; −157.17 [m, 2F, 2x aromatic F-4]; −143.56 ppm [m, 4F, 4x aromatic F-2]. ^{31}P NMR ($CDCl_3$): δ=−59.10 ppm [dm, $^1J(PH)$=195.41 Hz, 1P]. EI-MS, m/z (%): 394 (22) $[M]^+$, 213 (8) $[M-(C_6F_5CH_2)]^+$, 181 (100) $[C_6F_5CH_2]^+$. $C_{14}H_5F_{10}P$ (394.15).

3.5. *Bis(pentafluorobenzyl)phosphine oxide 4*

1.50 g (3.8 mmol) **3** was dissolved in 20 ml of dichloromethane and stirred for 5 h at room temperature in an open

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2**. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
F(1)	1077.5(13)	3146(2)	3272.6(10)	34.7(3)
F(2)	1834.2(13)	2040(2)	1252.0(10)	39.9(4)
F(3)	842.4(14)	−2011(2)	374.6(9)	40.9(4)
F(4)	−965.5(14)	−4863(2)	1526.9(10)	38.7(4)
F(5)	−1700.0(13)	−3779(2)	3549.1(10)	36.8(4)
C(1)	−674(2)	322(4)	4624.3(14)	26.6(5)
C(2)	−336(2)	−269(3)	3474.4(15)	23.6(4)
C(3)	557(2)	1144(3)	2852(2)	24.7(5)
C(4)	944(2)	615(4)	1815(2)	26.2(5)
C(5)	439(2)	−1430(4)	1370(2)	28.4(5)
C(6)	−465(2)	−2881(3)	1960(2)	26.4(5)
C(7)	−831(2)	−2294(4)	2997(2)	24.3(5)

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **8**. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Ru	6278.8(5)	8799.2(3)	2357.0(2)	21.1(1)
Cl(1)	3353.6(14)	8170.8(9)	2332.2(6)	38.3(3)
Cl(2)	7033.0(14)	7204.2(8)	2705.8(5)	29.4(3)
P	5629(2)	9196.4(9)	3247.2(5)	24.4(3)
O	4226(4)	8508(2)	3534.1(12)	34.3(9)
F(1)	1448(4)	10083(2)	3826.6(11)	51.6(8)
F(2)	658(5)	10612(3)	4854.0(14)	67.6(11)
F(3)	3045(5)	11510(2)	5492.1(12)	78.0(14)
F(4)	6218(6)	11926(2)	5076.4(13)	78.9(12)
F(5)	6965(4)	11469(2)	4031.1(13)	54.4(10)
F(6)	10304(4)	8373(2)	3316.5(11)	47.2(9)
F(7)	11689(5)	6672(3)	3647(2)	80.0(12)
F(8)	10131(6)	5586(3)	4436(2)	97(2)
F(9)	7213(5)	6283(3)	4923(2)	89.5(13)
F(10)	5866(4)	8005(3)	4609.2(12)	65.1(10)
C(1)	4685(6)	10446(3)	3316(2)	30.1(12)
C(2)	4224(6)	10735(4)	3899(2)	28.9(12)
C(3)	2653(7)	10532(4)	4128(2)	36.0(13)
C(4)	2242(8)	10802(4)	4658(2)	45(2)
C(5)	3435(9)	11267(4)	4974(2)	47.0(15)
C(6)	5013(9)	11483(4)	4760(2)	50(2)
C(7)	5383(7)	11230(4)	4227(2)	37.6(13)
C(8)	7291(6)	9214(3)	3783(2)	29.9(12)
C(9)	8028(6)	8242(4)	3950(2)	29.2(12)
C(10)	9522(7)	7869(4)	3716(2)	32.5(13)
C(11)	10235(7)	6986(5)	3879(2)	43.7(15)
C(12)	9453(10)	6446(4)	4276(3)	56(2)
C(13)	7955(9)	6789(5)	4519(2)	52(2)
C(14)	7287(7)	7676(4)	4355(2)	39.7(14)
C(15)	8162(6)	8572(3)	1650(2)	28.1(12)
C(16)	6578(6)	8852(4)	1440(2)	29.7(11)
C(17)	5685(6)	9713(4)	1633(2)	31.4(12)
C(18)	6496(6)	10299(3)	2031(2)	27.3(11)
C(19)	8130(6)	10032(3)	2254(2)	23.5(11)
C(20)	8905(6)	9152(3)	2084(2)	26.0(11)
C(21)	9061(7)	7655(3)	1472(2)	37.6(14)
C(23)	9048(6)	10700(3)	2651(2)	37.8(12)
C(22)	3956(7)	9987(4)	1400(2)	46.1(15)

flask. The solvent was removed i.v., and **4** was left as a colourless solid.

Yield: 1.56 g (100%), m.p. 152 °C. ^{1}H NMR ($CDCl_3$): δ=3.25–4.60 [m, 4H, 2x $C\underline{H}_2$]; 7.14 ppm [d, $^1J(HP)$=498.61 Hz, 1H, P$\underline{H}$]. ^{13}C NMR ($CDCl_3$): δ=23.83 [d, $^1J(CP)$=60.52 Hz, 2C, 2x $\underline{C}H_2$]; 104.74 [m, 2C, 2x aromatic C-1]; 137.92 [dm, $^1J(CF)$=256.70 Hz, 4C, 4x aromatic C-3]; 140.98 [dm, $^1J(CF)$=255.70 Hz, 2C, 2x aromatic C-4]; 145.18 ppm [dm, $^1J(CF)$=253.16 Hz, 4C, 4x aromatic C-2]. ^{19}F NMR ($CDCl_3$): δ=−160.60 [m, 4F, 4x aromatic F-3]; 153.41 [m, 2F, 2x aromatic F-4]; −141.12 ppm [m, 4F, 4x aromatic F-2]. ^{31}P NMR ($CDCl_3$): δ=22.50 ppm [dm, $^1J(PH)$=498.61 Hz, 1P]. EI-MS, m/z (%): 410 (20) $[M]^+$, 394 (2) $[M-O]^+$, 229 (12) $[M-(C_6F_5CH_2)]^+$, 181 (100) $[C_6F_5CH_2]^+$. IR (KBr): $\tilde{\nu}$=2934 (w) (C–H); 2362 (w) (P–H); 1657 (w) (aromatic deform.); 1525 (vs) (aromatic deform.); 1189 (s) (P(:O)); 964 cm^{-1} (s) (C–F). $C_{14}H_5F_{10}OP$ (410.15): calcd., C 40.99, H 1.23%; found, C 40.95, H 1.38%.

3.6. Ruthenium complexes 6–8

A mixture of **1**, **3** or **4** with **5** was refluxed in 20 ml of dichloromethane for 4 h. The solution was filtered, and the volume was reduced to 5 ml i.v. Addition of 30 ml of *n*-hexane resulted in the precipitation of a red solid, which was filtered, washed with diethyl ether and dried i.v.

6: Yield: 0.30 g (93%), ratio of the isomers *a*:*b*:*c*=6:5:2 (see Section 2.4), m.p. 138–140 °C (dec.). ^{1}H NMR ($CDCl_3$): δ=2.11 c, 2.17 a, 2.22 b [s, 9H, 3x mes-C$\underline{H}_3$]; 3.70–4.70 [m, 4H, 2x C$\underline{H}_2$]; 4.98 c, 5.02 a, 5.08 b ppm [s, 3H, 3x mes-H]. ^{13}C NMR ($CDCl_3$): δ=19.31 c, 19.60 a, 19.81 b [s, 3C, 3x mes-$\underline{C}H_3$]; 30.63 c, 30.94 b, 31.24 a [m, 2C, 2x $\underline{C}H_2$]; 83.03 c, 84.21 a, 85.52 b [s, 3C, 3x mes-$\underline{C}H$]; 104.21 a, 105.21 c, 106.13 b [m, 2C, 2x aromatic C-1]; 106.86 b, 107.88 a, 108.58 c [s, 3C, 3x mes-$\underline{C}CH_3$]; 134.92–147.96 ppm [m, 10 C, 4x aromatic C-2, 4x aromatic C-3, and 2x aromatic C-4]. ^{19}F NMR ($CDCl_3$): δ=−161.44 [m, 4F, 4x aromatic F-3]; −153.47 [m, 2F, 2x aromatic F-4]; −136.57 ppm [m, 4F, 4x aromatic F-2]. ^{31}P{^{1}H} NMR ($CDCl_3$): δ=102.94 b, 106.12 a, 108.01 c ppm [s, 1P]. EI-MS, m/z (%): 428 (22) $[(C_6F_5CH_2)_2PCl]^+$, 393 (2) $[(C_6F_5CH_2)_2P]^+$, 181 (100) $[C_6F_5CH_2]^+$. IR (KBr): $\tilde{\nu}$=2927 (w) (C–H); 1656 (w) (aromatic deform.); 1522 (vs) (aromatic deform.); 970 (s) (C–F); 499 cm^{-1} (m) (P–Br). $C_{23}H_{16}BrCl_2F_{10}PRu$ (765.22): calcd., C 36.10, H 2.11%; found, C 35.82, H 2.14%.

7: Yield: 0.28 g (77%), m.p. >200 °C (dec.). ^{1}H NMR ($CDCl_3$): δ=2.20 [s, 9H, 3x mes-C$\underline{H}_3$]; 3.20–3.75 [m, 4H, 2x C$\underline{H}_2$]; 4.99 [s, 3H, 3x mes-H]; 5.21 ppm [dm, 1H, $^1J(HP)$=382.90 Hz, P$\underline{H}$]. ^{13}C NMR ($CDCl_3$): δ=17.62 [d, 2C, $^1J(CP)$=22.32 Hz, 2x $\underline{C}H_2$]; 19.12 [s, 3C, 3x mes-$\underline{C}H_3$]; 82.18 [s, 3C, 3x mes-$\underline{C}H$]; 106.14 [s, 3C, 3x mes-$\underline{C}CH_3$]; 109.67 [m, 2C, 2x aromatic C-1]; 137.68 [dm, 4C, $^1J(CF)$=258.31 Hz, 4x aromatic C-3]; 140.46 [dm, 2C, $^1J(CF)$=252.27 Hz, 2x aromatic C-4]; 144.94 ppm [dm, 4C, $^1J(CF)$=243.78 Hz, 4x aromatic C-2]. ^{19}F NMR ($CDCl_3$): δ=−161.44 [m, 4F, 4x aromatic F-3]; −154.60 [m, 2F, 2x aromatic F-4]; −140.76 ppm [m, 4F, 4x aromatic F-2]. ^{31}P NMR ($CDCl_3$): δ=10.37 ppm [d, $^1J(PH)$=382.90 Hz, 1P]. EI-MS, m/z (%): 686 (1) $[M]^+$, 394 (40) $[(C_6F_5CH_2)_2PH]^+$, 292 (2) $[M-(C_6F_5CH_2)_2PH]^+$, 181 (100) $[C_6F_5CH_2]^+$. IR (KBr): $\tilde{\nu}$=2924 (w) (C–H); 2426 (w) (P–H); 1656 (w) (aromatic deform.); 1522 (vs) (aromatic deform.); 970 cm^{-1} (s) (C–F). $C_{23}H_{17}Cl_2F_{10}PRu$ (686.32): calcd., C 40.25, H 2.50%; found, C 40.36, H 2.59%.

8: Yield: 0.44 g (90%), m.p. 186 °C (dec.). ^{1}H NMR ($CDCl_3$): δ=2.25 [s, 9H, 3x mes-C$\underline{H}_3$]; 3.30–3.90 [m, 4H, 2x C$\underline{H}_2$]; 5.05 [s, 3H, 3x mes-H]; 7.95 ppm [m, br, 1H, O$\underline{H}$]. ^{13}C NMR ($CDCl_3$): δ=22.77 [s, 3C, 3x mes-$\underline{C}H_3$]; 28.00 [d, 2C, $^1J(CP)$=23.08 Hz, 2x $\underline{C}H_2$]; 82.14 [s, 3C, 3x mes-$\underline{C}H$]; 107.02 [m, 2C, 2x aromatic C-1]; 107.85 [s, 3C, 3x mes-$\underline{C}CH_3$]; 135.00–147.89 ppm [m, 10 C, 4x aromatic C-2, 4x aromatic C-3 and 2x aromatic C-4]. ^{19}F NMR ($CDCl_3$): δ=−162.18 [m, 4F, 4x aromatic F-3]; −154.95 [m, 2F, 2x aromatic F-4]; −140.07 ppm [m, 4F, 4x aromatic F-2]. ^{31}P NMR ($CDCl_3$): δ=117.07 ppm [s, 1P]. EI-MS, m/z (%): 702 (3) $[M]^+$, 410 (11) $[(C_6F_5CH_2)_2POH]^+$, 257 (8) $[M-(C_6F_5CH_2)_2POH-Cl]^+$, 181 (100) $[C_6F_5CH_2]^+$. IR (KBr): $\tilde{\nu}$=3300 (w, br) (O–H); 2933 (w) (C–H); 1656 (w) (aromatic deform.); 1522 (vs) (aromatic deform.); 1127 (m) (P–O); 957 cm^{-1} (s) (C–F). $C_{23}H_{17}Cl_2F_{10}OPRu$ (702.32): calcd., C 39.33, H 2.44%; found, C 39.29, H 2.55%.

Acknowledgements

This research was supported by generous supplies of chemicals by HOECHST AG and DEGUSSA AG. The following are thanked for helpful discussions: Dr. H.-J. Kleiner, (HOECHST AG); Dr. I. Neda, Professor M. Fild, Dr. H.-M. Schiebel (mass spectra), Professor L. Ernst (NMR) (all of this Institute). The continuing support of Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] M. Fild, O. Glemser, I. Hollenberg, Z. Naturforsch. 21b (1966) 920.
[2] M. Fild, O. Glemser, Fluorine Chemistry Reviews, Vol. 3, Marcel Dekker, New York and London, 1969, p. 129ff.
[3] L. Maier, in: G.M. Kosolapoff, L. Maier (Eds.), Organic Phosphorus Compounds, Vol. 1, Wiley-Interscience, New York, London, Sydney, Toronto, 1972, p. 17ff.

[4] E. Fluck, H. Binder, Z. Naturforsch. 22b (1967) 1001.
[5] L.A. Hamilton, P.S. Landis, in: G.M. Kosolapoff, L. Maier (Eds.), Organic Phosphorus Compounds, Vol. 4, Wiley-Interscience, New York, London, Sydney, Toronto, 1972, p. 463ff.
[6] R.H. Williams, L.A. Hamilton, J. Am. Chem. Soc. 74 (1952) 5418.
[7] J.E. Griffiths, A.B. Burg, J. Am. Chem. Soc. 82 (1960) 1507.
[8] J.E. Griffiths, A.B. Burg, J. Am. Chem. Soc. 84 (1962) 3442.
[9] D.D. Magnelli, G. Tesi, J.U. Lowe, Jr., W.E. McQuistion, Inorg. Chem. 5 (1966) 547.
[10] H.-J. Kleiner, Liebigs Ann. Chem. (1974) 751.
[11] G. Winkhaus, H. Singer, J. Organomet. Chem. 7 (1967) 487.
[12] M.I. Bruce, J. Organomet. Chem. 10 (1967) 495.
[13] Autorenkollektiv, Organikum, 17th. edn., VEB Deutscher Verlag der Wissenschaften, Berlin, 1988, p. 496.
[14] M.A. Bennett, G.B. Robertson, A.K. Smith, J. Organomet. Chem. 43 (1972) C42.
[15] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd edn., Pergamon Press, Oxford, New York, Beijing, Frankfurt, Sao Paulo, Sydney, Tokyo, Toronto, 1988.
[16] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.
[17] J.W. Hull, Jr., W.L. Gladfelter, Organometallics 3 (1984) 605.
[18] H.D. Flack, Acta Cryst. A39 (1983) 876.