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Ferrocenyldihalophosphanes[†]

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Summary — An improved synthesis for ferrocenyldichlorophosphane, $FcPCl_2$ ($Fc = C_5H_4FeC_5H_5$) is reported. The availability of this compound gives access to the other, previously unknown members of the homologous ferrocenyldihalophosphane series, $FcPX_2$ (X = F, Br, I). The latter are characterised by NMR and high-resolution mass spectroscopy. The class of ferrocenyldihalophosphanes is a valuable synthon for the generation of a large variety of ferrocenylphosphanes.

ferrocene / phosphane / ferrocenylphosphane / dihalophosphane / ferrocenyldihalophosphane

Résumé — **Ferrocenyldihalophosphanes.** Une synthèse de ferrocenyldichlorophosphane $FcPCl_2$ ($Fc = C_5H_4FeC_5H_5$) est décrite. La disponibilité de ce composé donne accès aux autres dérivés de la famille homologue de ferrocenyldihalophosphane, $FcPX_2$ (X = F, Br, I) jusqu'ici inconnus. Ces derniers sont caractérisés par RMN et spectrométrie de masse haute résolution. La classe des ferrocenyldihalophosphanes constitue un intermédiaire important pour la préparation d'une large variété de ferrocenylphosphanes.

ferrocene / phosphane / ferrocenylphosphane / dihalogénophosphane / ferrocenyldihalogénophosphane

Introduction

Although the first ferrocenyldihalophosphane $Fc-PCl_2$ (Fc = 1-ferrocenyl) was reported in 1962 by Sollot et al [1] its isolation and characterisation is unsatisfactory by modern standards. The same group reported [2] several improved routes to this compound starting from ferrocene, summed up in a reinvestigation by Pauson and coworkers in 1992, in which the former procedures are evaluated as 'inconsistent and not reproducable' [3]. In the same year, Ninfant'ev et al reported a reliable synthesis [4] of $Fc-PCl_2$ starting from monolithiated ferrocene [5]. The latter is available via metal–halogen exchange from Fc–Br, which itself is accessible in low yield from Fc–HgCl [6], which limits the synthetic scope of this route. By combining this route by Ninfant'ev et al and that to monolithiated ferrocene by Kagan et al [7] we developed a procedure for $Fc-PCl_2$ **2**, starting from ferrocene, which affords the desired product in 52% yield with respect to the lithiating reagent. Furthermore, we succeeded in synthesizing the other previously unknown ferrocenyldihalophosphanes $Fc-PF_2$ **1**, $Fc-PBr_2$ **3** and $Fc-PI_2$ **4** of this homologous series. The dihalophosphanes are ideal precursors for the synthesis of ferrocenylphosphanes [8] and phosphoranes [9], that contain a phosphorus atom either in regular or in low coordination. Furthermore, their availability gives access to unsymmetrically substituted ferrocenylphosphanes (scheme 1) [10].

Ferrocenyldichlorophosphane is synthesized by lithiating ferrocene with *tert*-BuLi at 0 °C, which in contrast to the lithiation with *n*-BuLi results in the predominant formation of monolithiated ferrocene. Subsequent treatment with chlorobis(diethylamino)phosphane prevents the formation of di- or triferrocenyl phosphanes. The resulting bis(diethylamino)-ferrocenylphosphane is converted into the desired dichlorophosphane with excess PCl_3, thus avoiding the use of etheric HCl. The Et_2N-PCl_2 formed may be reused for the synthesis of further $(Et_2N)_2PCl$. Unreacted ferrocene can be sublimed off from the resulting mixture. The remaining $Fc-PCl_2$ is purified by distillation in high vacuum, yielding the desired product as a dark red solid (scheme 2). This stands in contrast to Cowley's description [8a] of **2** as an orange oil [11].

Starting from the dichlorophosphane, the other ferrocenyldihalophosphanes can be synthesized following standard procedures. While the dibromophosphane **3** is accessible by means of a scrambling reaction of **2** with PBr_3, halogen exchange with TmsI furnishes diiodophosphane **4**. Both compounds can be isolated and recrystallized from toluene/pentane. Similarily, reaction of **2** with SbF_3 in toluene solution yields difluorophosphane **1**. The isolation of the latter from minor byproducts was not successful, since upon attempted distillation **1** disproportionated or was oxidized by excess SbF_3. Both possibilities have been described previously for similar difluorophosphanes by Schmutzler [12]. Correspondingly, the tetrafluorophosphorane **5** formed in

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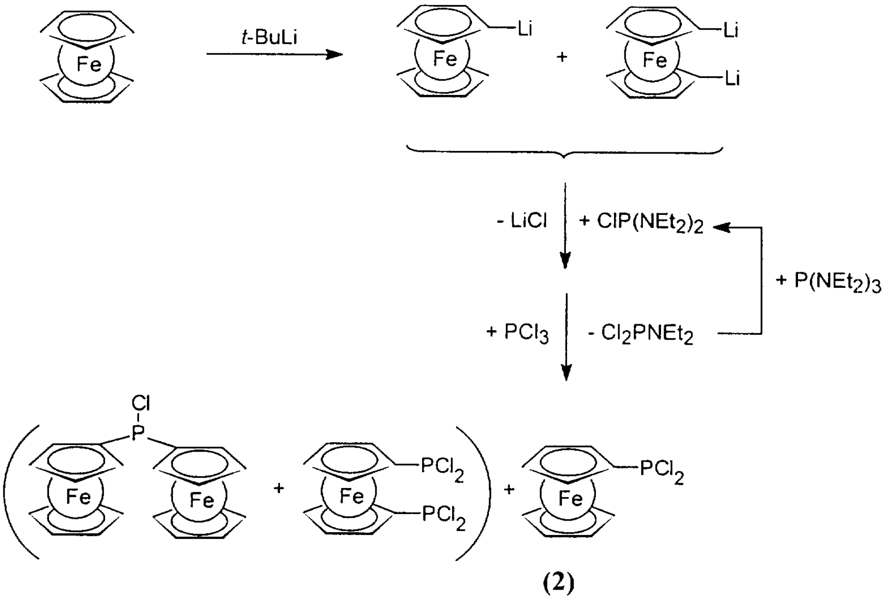
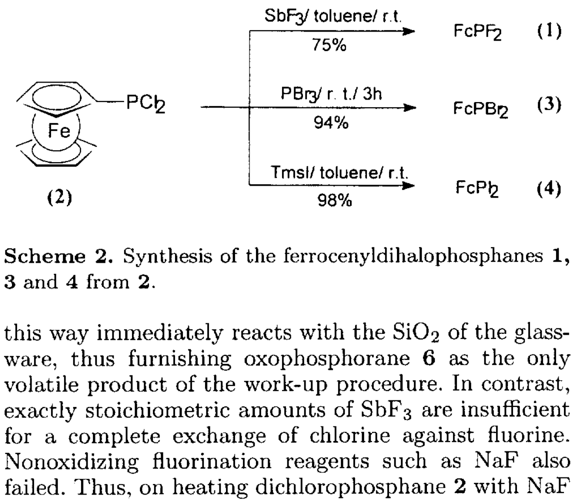
[†] Dedicated to Prof Dr Hans-Friederich Grützmacher on the occasion of his 65th birthday

* Correspondence and reprints



Scheme **1**. Synthesis of **2** starting from ferrocene.



Scheme 2. Synthesis of the ferrocenyldihalophosphanes **1**, **3** and **4** from **2**.

this way immediately reacts with the SiO_2 of the glassware, thus furnishing oxophosphorane **6** as the only volatile product of the work-up procedure. In contrast, exactly stoichiometric amounts of SbF_3 are insufficient for a complete exchange of chlorine against fluorine. Nonoxidizing fluorination reagents such as NaF also failed. Thus, on heating dichlorophosphane **2** with NaF and without solvent to about 100 °C under vacuum for several hours, no difluorophosphane is formed, which is expected to be the most volatile component of the mixture. Instead, **2** is recovered as the only product (scheme 3).

NMR spectroscopic properties

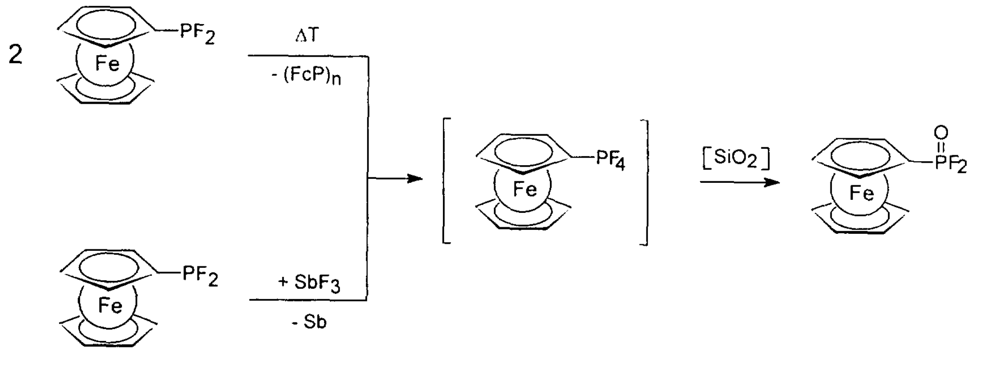
The NMR data of the ferrocenyldihalophosphanes show some interesting trends depending on the electronegativity of the halogen atom. Thus, the ^{31}P-resonance of the phosphorus atom is shifted to low field, in the order iodine to fluorine. As in the cases of methyl- or phenyl-substituted dihalophosphanes (when plotted against electronegativity) the phosphorus in difluorophosphanes resonates at higher field than would be expected from a linear regression of the higher homologues (fig 1).

This observation is usually explained by the better π-donating ability of fluorine compared to the higher halogens. While in the older literature this is assumed to proceed by d_π–p_π interaction [13] it is considered nowadays that the acceptor properties of a phosphanyl group are primarily due to low-lying σ^* orbitals, which corresponds to the concept of negative hyperconjugation [14].

The chemical shift of the phosphorus nucleus depends also on the geometric features of the molecule. An increase of the electronegativity of the halogen atom should result in a decrease of the bond angles at phosphorus, thus enhancing the s-character of the phosphorus lone pair (Bent's rule). Consequently, on decreasing the bond angles X–P–X an upfield shift is observed. However, this steric contribution does not seem to be of great importance in our case, since a similar effect for chlorine to fluorine should be observed as for iodine to bromine. The fact that only the fluoro derivatives exhibit a less unshielded phosphorus atom, as expected by comparison with the other dihalophosphanes, corroborates the interpretation that this is mainly due to the resonance interaction as outlined above.

Compared to other dihalophosphanes, the ferrocenyl-substituted dihalophosphanes resonate at higher field than the corresponding methyl-substituted ones, but unexpectedly the resonances appear at lower field than the phenyl-substituted ones. Due to the better σ-donating ability of the ferrocenyl group with respect to the phenyl group the opposite would have been expected.

The ^{13}C NMR spectra of the dihalophosphanes show similar trends, depending on the electronegativity of the substituent on phosphorus (table I). In the order iodine to chlorine, the ipso carbon atom resonates at



(1) (5) (6)

Scheme 3. Decomposition of 1 on attempted distillation.

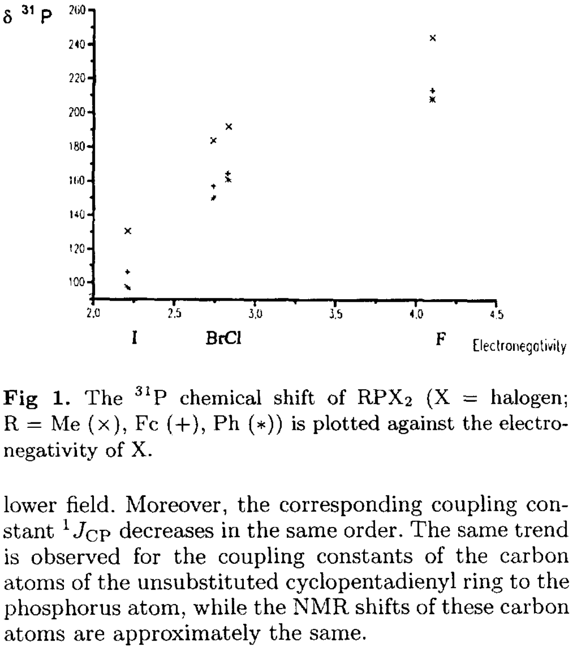


Fig 1. The ^{31}P chemical shift of RPX_2 (X = halogen; R = Me (×), Fc (+), Ph (*)) is plotted against the electronegativity of X.

lower field. Moreover, the corresponding coupling constant $^1J_{CP}$ decreases in the same order. The same trend is observed for the coupling constants of the carbon atoms of the unsubstituted cyclopentadienyl ring to the phosphorus atom, while the NMR shifts of these carbon atoms are approximately the same.

Experimental section

General procedure

All steps were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried and freshly distilled from Na/K alloy before use. NMR spectra were recorded on a Bruker AMX 300 spectrometer. ^{31}P NMR spectra were recorded at 121.5 MHz using 85% H_3PO_4 as external standard, ^1H and ^{13}C NMR spectra with tetramethylsilane as external standard at 300 MHz and 75.5 MHz respectively.

- *Ferrocenyldichlorophosphane 2*

To a solution of 37.2 g (0.2 mol) of ferrocene in 300 mL of THF cooled to 0 °C, 116 mL (0.186 mol) of a solution of *tert*-BuLi in hexane is added slowly, while the temperature is maintained. After stirring for half an hour, 39.2 g (0.186 mol) of $ClP(NEt_2)_2$ dissolved in 300 mL THF is added at the same temperature. The resulting mixture is treated after further stirring for 1 h with 65.6 mL (0.75 mol) of PCl_3. After stirring for another 2 h at room temperature, the solvent and excess PCl_3 and Cl_2PNEt_2 are evaporated under vacuum using a steam bath. The residue is heated under 10^{-3} Torr at 80 °C until all the unreacted ferrocene is sublimed off. Under these conditions the product can be distilled at 98 °C, as a dark red viscous oil, that solidifies at room temperature (yield: 16.8 g, 58.6 mmol, 52% relative to *tert*-BuLi).

Mp: 39 °C.

^1H NMR (C_6D_6): H_α (2H) 4.44; H_β (2H) 4.24; Cp′ (5H) 4.08.

^{13}C NMR (C_6D_6): C_{ipso} 80.14 (d, $^1J_{CP}$ = 52.76 Hz); C_α 73.4 (d, $^2J_{CP}$ = 4.58 Hz); C_β 71.3 (d, $^3J_{CP}$ = 22.89 Hz); Cp′ 70.78 (d, $^3J_{CP}$ = 1 Hz).

^{31}P NMR (toluene): 164.7 ppm.

MS (EI, eV): 286, M^+ (^{56}Fe), 100%; 283.9204 (found), 283.9215 (calc), M^+ (^{54}Fe, 2 ^{35}Cl), 6.8%; 251, M^+ - Cl, 52%; 156, $CpFeCl^+$, 80%; 95, CpP, 68%; 56, Fe, 27%.

- *Ferrocenyldibromophosphane 3*

To 0.49 g (1.7 mmol) $FcPCl_2$ an excess (5 mL) of PBr_3 is added, and the mixture is stirred at room temperature for 3 h. Then the volatile byproducts are removed under vacuum on a steam bath. The residue is dissolved in toluene and filtered. After evaporation of the solvent, spectroscopically pure $FcPBr_2$ is obtained (0.6 g, 1.6 mmol, 94.1%), which can be recrystallized from toluene/pentane at 4 °C.

^1H NMR (C_6D_6): H_α (2H) 4.43; H_β (2H) 4.25; Cp′ (5H) 4.06.

^{13}C NMR (C_6D_6): C_{ipso} 78.13 (d, $^1J_{CP}$ = 61.06 Hz); C_α 74.55 (d, $^2J_{CP}$ = 3.82 Hz); C_β 72.94 (d, $^3J_{CP}$ = 21.36 Hz); Cp′ 70.98 (d, $^3J_{CP}$ = 1.14 Hz).

^{31}P NMR: 157.1 ppm.

MS (EI, eV): M^+, 373.8157 (found), 373.8158 (calc), 13.1%; M^+ - Br, 60.3%; $CpFeBr^+$, 30.5%; 121 (33.7%), $CpFe^+$; 95 (100%), CpP^+; 56 (50.3%) Fe^+.

- *Ferrocenyldiiodophosphane 4*

0.88 g (4.4 mol) TmsI diluted with 8 mL toluene are treated with 0.58 g (2 mmol) of $FcPCl_2$ at room temperature. After stirring for 2 h, under exclusion of daylight, the solvent and the TmsCl formed are removed under vacuum. The product

Table I. ^{31}P and ^{13}C NMR data of **1–4**.

	$\delta(^{31}P)$	$\delta(^{13}C)$ - C_{ipso}	$^1J_{CP}$ (C_{ipso})	$\delta(^{13}C)$ - Cp'	$^3J_{CP}$ (Cp')
Fc–PF$_2$ **1**	213.6	–	–	–	–
Fc–PCl$_2$ **2**	164.7	80.14	52.76	70.78	< 1
Fc–PBr$_2$ **3**	157.1	78.13	61.06	70.98	1.14
Fc–PI$_2$ **4**	106.2	74.73	64.50	70.97	1.52

is obtained as a dark red oil (0.92 g, 1.96 mmol, 98%), which can be recrystallized from toluene/pentane at 4 °C, yielding **4** as dark platelets.

^{1}H NMR (C_6D_6): H_α (2H) 4.43; H_β (2H) 4.25; Cp′ (5H) 4.06.

^{13}C NMR (C_6D_6): C_{ipso} 74.73 (d, $^1J_{CP} = 64.5$ Hz), C_α 74.58 (d, $^2J_{CP} = 5.7$ Hz), C_β 74.50 (d, $^3J_{CP} = 16.8$ Hz); Cp′ 70.97 (d, $^3J_{CP} = 1.52$ Hz).

^{31}P NMR: 106.2 ppm.

MS (EI, eV): M^+ 469.7891 (found), 469.7881 (calc) 7.4%; (15.0%) M^+ – 58; (100.0%) M^+ – I; (85.0%) FcP^+; (25.9%) I^+; (28.2%) $CpFe^+$; (15.0%) CpP^+; (26.3%) Fe^+.

- *Ferrocenyldifluorophosphane* **1**

0.21 g (1.2 mmol) of SbF_3 suspended in 5 mL of toluene is treated with 0.35 g (1.2 mmol) of $FcPCl_2$ at room temperature. After stirring for 3 h $FcPF_2$ is formed in 75% yield, as determined by NMR spectroscopy. All attempts to isolate and purify the product by distillation failed and resulted in the formation of the corresponding oxophosphorane $FcPOF_2$ **6**.

1: ^{31}P NMR: 213.6 ppm (t, $^1J_{PF} = 1147$ Hz).

MS: 254, M^+, 5%; 252, M^+ – 2H, 100%; 121, $CpFe^+$, 10%; 65, Cp^+, 4%; 56, Fe^+, 1%.

6: $\delta(^{31}P)$: 23.0 ppm (t, $^1J_{PF} = 1082$ Hz).

MS: 270, M^+, 100%; 252, M^+–H_2O, 63%; 121, $CpFe^+$, 78%; 56, Fe^+, 18%.

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