Synthesis of some phospha-alkenes with the fluoromesityl ($2,4,6-(CF_3)_3C_6H_2$) group on phosphorus and of their complexes with $[PtCl_2(PEt_3)]_2$

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Abstract

The phospha-alkenes $ArP{=}CR^1R^2$, where $Ar = 2,4,6-(CF_3)_3C_6H_2$, and $R^1 = R^2 = Cl$ (**1**), $R^1 = SiMe_3$, $R^2 = H$ (**2**), or $R^1 = Ph$, $R^2 = H$ (**3**), have been synthesized. Compound **1** was isolated and fully characterized, but **3** could only be identified in solution. All three phospha-alkenes react with the dimeric species $[PtCl_2(PEt_3)]_2$ in a 2:1 ratio to form η^1-bonded platinum(II) complexes, the structures of which may be readily deduced from the nuclear magnetic resonance data.

Key words: Platinum; Phospha-alkenes; Fluoromesityl

1. Introduction

Many compounds containing the $-P{=}C\langle$ group (phospha-alkenes) have been prepared in recent years, and their coordination chemistry extensively investigated [1,2]. None has been described, however, with the fluoromesityl $2,4,6-(CF_3)_3C_6H_2$ (Ar) group attached to phosphorus. In a recent paper we reported the synthesis and characterization of some organometallic complexes of the symmetrical diphosphene ArP=PAr [3]. This compound is remarkably stable, even in air [3], and does not form an adduct with vanadocene [4], showing that the electron-withdrawing Ar groups are extremely effective in deactivating the diphosphene. It was therefore of considerable interest to synthesize phospha-alkenes with the Ar group on phosphorus, and to examine their stability and coordination chemistry.

2. Results and discussion

Three new phospha-alkenes $ArP{=}CR^1R^2$ have been prepared ($R^1 = R^2 = Cl$ (**1**)) ($R^1 = SiMe_3$; $R^2 = H$ (**2**)) ($R^1 = Ph$; $R^2 = H$ (**3**)), the first two of which were sufficiently stable to be isolated. Compound **3** was readily identifiable in solution from its ^{31}P nuclear magnetic resonance (NMR) spectrum, but could not be isolated in a pure state. The ^{31}P chemical shifts for all three compounds, together with other characterization data, are given in Section 3.

Attempts were also made to replace chlorine in $ArP{=}CCl_2$ (**1**) by other groups. BuLi was added to a solution of **1** in tetrahydrofuran (THF) at −78°C, but the solution blackened immediately, even at this temperature. Dropwise addition of a solution of Me_3SiCl in THF at this temperature, followed by warming of the mixture to room temperature, yielded no evidence for the formation of $ArP{=}C(Cl)SiMe_3$. Direct reaction of ArLi [3,5] with $ArP{=}CCl_2$ in a mixture of Et_2O and THF at −10°C also failed to generate $ArP{=}C(Cl)Ar$, the only ^{31}P signal arising from starting material, while the ^{19}F spectrum confirmed the formation of some ArCl [6]. This behaviour was not unexpected because of the low basicity of ArLi, as illustrated by the reaction $ArLi + CCl_4 \rightarrow ArCl$.

The coordination chemistry was investigated by treating each of the phospha-alkenes with 0.5 molar equivalent of the dimeric platinum(II) species $[PtCl_2(PEt_3)]_2$, which led to the formation of

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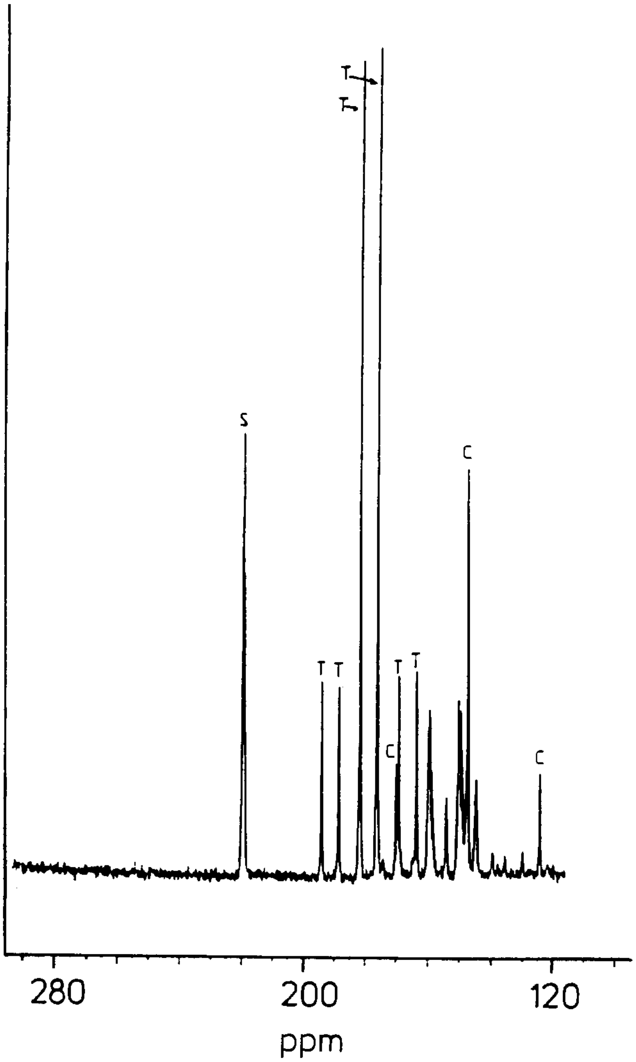

Fig. 1. High frequency region of the ^{31}P NMR spectrum from the reaction of 3 with $[PtCl_2(PEt_3)]_2$: S, starting material (3); T, *trans* isomer; C, *cis* isomer.

monomeric η^1-bonded complexes in each case, as shown by the magnitude of the $^1J_{P-Pt}$ values (see Section 3). Interestingly, however, only the thermodynamically more stable *cis* isomer [7,8] was observed for **1**, as shown by the very small $^2J_{PP}$ coupling between the phosphorus (P_B) of the PEt_3 group and P_A in the phospha-alkene ligand [7,8], while **2** formed the *trans* isomer, stable for at least 6 h. Compound **3** initially yielded a mixture of the *cis* and *trans* isomers, both clearly detectable in the spectrum recorded after 30 min (Fig. 1), but, after 2 h, only the *cis* isomer was present.

These results indicate that the substituents on carbon have a significant influence on the nature of the product. It seems probable that in all cases the formation of the *trans* complex is kinetically favoured, but that the thermodynamically stable species will be the *cis* isomer [8,9]. For phospha-alkene **1** the *trans* complex was not detected, indicating that conversion to the *cis* analogue is very rapid in this instance. Compound **3** provided conclusive NMR evidence for the coexistence of both isomers of the platinum(II) complex in solution, although conversion of the *trans* isomer to its *cis* analogue was complete after 2 h, whereas the *trans* derivative of **2** was stable for at least 6 h. While more prolonged studies would be necessary to clarify whether the complex of **2** ultimately reverts to the expected *cis* form, the results allow the relative rates of isomerization to be compared.

3. Experimental details

All manipulations, including NMR sample preparation, were carried out either *in vacuo* or under dry nitrogen. ^{31}P and ^{19}F NMR spectra were recorded on a Bruker AC250 instrument at 101.256 MHz (^{31}P) and 235.360 MHz (^{19}F). Chemical shifts are measured relative to external 85% H_3PO_4 and $CFCl_3$ respectively, with the high frequency (downfield) direction taken as positive. C and H analyses were obtained by microcombustion on a Perkin–Elmer 240 instrument. The UV–visible spectra were recorded for solutions in CCl_4 (**1** and **2**) or THF (**3**) in quartz cells, with the solvent system in the reference beam, between 200 and 450 nm. Mass spectra were recorded on a VG Analytical 7070E instrument, operating in the electron impact (EI) mode.

3.1. Preparation of $ArP{=}CCl_2$ (1)

Two procedures, shown in the following equations, were used to synthesize the precursor phosphine $ArP(CHCl_2)Cl$, the second equation giving higher yields:

$$CHLiCl_2 + ArPCl_2 \rightarrow ArP(CHCl_2)Cl \xrightarrow{DBU} ArP{=}CCl_2 \qquad (1a)$$

$$CHLiCl_2 \xrightarrow[(2)\,ArPCl_2]{(1)\,\frac{1}{2}CdCl_2} ArP(CHCl_2)Cl \xrightarrow{DBU} ArP{=}CCl_2 \qquad (1b)$$

In both cases, $CHLiCl_2$ (11.8 mmol) was prepared in THF : Et_2O : light petroleum (4 : 1 : 1 v/v/v) at −130°C (pentane–liquid nitrogen slush bath), as described previously [10]. In the first method, this reagent was added to a stirred solution of $ArPCl_2$ (13.0 mmol) in Et_2O at −140°C. The mixture, which turned red, was allowed to warm to room temperature. The white precipitate was filtered off and the solvent removed *in vacuo* to yield a yellow oil. The ^{31}P NMR spectrum showed the presence of some unchanged $ArPCl_2$ ($\delta = 145.4$ ppm), the required ArP(CHCl$_2$)Cl (δ = 63.6 ppm) and ArP(CHCl$_2$)$_2$ (δ = 6.5 ppm). The tertiary phosphine ArP(CHCl$_2$)$_2$ was removed as a solid by crystallization from Et$_2$O at −40°C, and the product ArP(CHCl$_2$)Cl was obtained by distillation at 68°C (0.1 Torr) as a clear oil, with a 41% yield. Anal. Found: C, 27.3; H, 1.08%. $C_{10}H_3Cl_3F_9P$ calc.: C, 27.8; H, 0.70%. ^{31}P NMR: 63.6 (septet, $^4J_{PF}$ = 49.8 Hz) ppm. ^{19}F NMR: −54.7 (d, 6F); −64.8 (s, 3F) ppm.

The alternative route to this chlorophosphine involved the addition of CdCl$_2$ (5.9 mmol) directly to the stirred solution of CHLiCl$_2$ in Et$_2$O at −130°C. The reaction mixture was allowed to warm to 0°C and stirred for 1 h; this was followed by the addition in one portion of ArPCl$_2$ (12 mmol) in Et$_2$O. The solution was refluxed for 1 h, allowed to cool to room temperature, filtered and concentrated *in vacuo*. The ^{31}P NMR spectrum showed that the product was exclusively the desired product ArP(CHCl$_2$)Cl, which was isolated as above with a 65% yield.

In both cases an equimolar quantity of DBU in THF was then added dropwise during 5 min to a stirred solution of ArP(CHCl$_2$)Cl in THF at 0°C. The solution was allowed to warm to room temperature, and the white precipitate of DBU.HCl filtered off. The THF was removed by distillation at atmospheric pressure, and the product **1** distilling at 76°C (0.7 Torr) was collected as a clear oil with a 60% yield. Anal. Found: C, 30.6; H, 0.92%. $C_{10}H_2Cl_2F_9P$ calc.: C, 30.4; H, 0.51%. UV-visible (CCl$_4$): λ_{max} = 327, 227 nm, MS (EI): 394 (13.1%, ArP=CCl$_2^+$), 359 (100%, ArP = CCl$^+$). ^{31}P NMR (CDCl$_3$): 202.9 (septet, $^4J_{PF}$ = 21.4 Hz) ppm. ^{19}F NMR (CDCl$_3$): −61.0 (d, 6F, $^4J_{PF}$ = 21.4 Hz): −65.1 (s, 3F) ppm.

3.2. Preparation of ArP=C(SiMe$_3$)H (2)

The preparation was carried out according to:

$$Me_3SiCH_2MgBr \xrightarrow[(2)\,ArPCl_2]{(1)\,\frac{1}{2}CdCl_2} ArP(CH_2SiMe_3)Cl \xrightarrow{DBU} ArP{=}C(SiMe_3)H \quad (2)$$

A solution of Me$_3$SiCH$_2$MgBr (40 mmol) in Et$_2$O was added dropwise during 5 min to a solution of CdCl$_2$ (20.1 mmol) in Et$_2$O at 0°C, and the mixture stirred at this temperature for 1 h. The resulting pale-yellow solution was added in one portion to a stirred solution of ArPCl$_2$ (43.8 mmol) in Et$_2$O at room temperature, and the whole brought gradually to reflux and kept there for 4 h. The precipitate was filtered off and the solvent removed *in vacuo* to yield a yellow oil, which was purified by vacuum distillation. The first fraction consisted of unchanged ArPCl$_2$ (boiling point (b.p.), 62°C (0.5 Torr)), and the product ArP(Cl)(CH$_2$SiMe$_3$) was isolated as a very pale-yellow oil, (b.p., 84°C (0.5 Torr)) with a 53% yield. Anal. Found: C, 36.5; H, 3.30%. $C_{13}H_{13}ClF_9PSi$ calc.: C, 35.9; H, 3.01%. ^{31}P NMR (CDCl$_3$): 92.1 (septet, $^4J_{PF}$ = 51.8 Hz) ppm. ^{19}F NMR (CDCl$_3$): −54.7 (d, 6F, $^4J_{PF}$ = 51.8 Hz); −64.0 (s,3F) ppm. A solution of DBU (3.5 mmol) in THF was then added dropwise during 5 min to a stirred solution of ArP(Cl)(CH$_2$SiMe$_3$) (3.5 mmol) in THF at 0°C. The precipitate formed was filtered off, and the solvent removed *in vacuo* to give **2** as a yellow oil, (crude yield, 77%). UV-visible (CCl$_4$): λ_{max} 325, 260 nm. ^{31}P NMR (CDCl$_3$): 287.9 (septet, $^4J_{PF}$ = 26.5 Hz) ppm. ^{19}F NMR (CDCl$_3$): −56.7 (d, 6F, $^4J_{PF}$ = 26.5 Hz); −64.1 (s, 3F) ppm.

3.3. Preparation of ArP=C(H)Ph (3)

The precursor of this phospha-alkene, ArP(CH$_2$Ph)-Cl, was prepared by two different methods, as shown in the following equations, either directly by the action of ArLi [5] on PhCH$_2$PCl$_2$, or via the organocadmium reagent (PhCH$_2$)$_2$Cd:

$$ArLi + PhCH_2PCl_2 \longrightarrow ArP(CH_2Ph)Cl \xrightarrow{DBU} ArP{=}C(H)Ph \quad (3a)$$

$$PhCH_2MgBr \xrightarrow[(2)\,ArPCl_2]{(1)\,\frac{1}{2}CdCl_2} ArP(CH_2Ph)Cl \xrightarrow{DBU} ArP{=}C(H)Ph \quad (3b)$$

In the first procedure, ArLi (11.5 mmol) in Et$_2$O was added dropwise during 5 min to a stirred solution of PbCH$_2$PCl$_2$ (11.3 mmol) in Et$_2$O at −78°C. The mixture was allowed to warm to room temperature, the LiCl filtered off, and the filtrate concentrated *in vacuo* to yield a yellow oil, which was further purified by vacuum distillation. A colourless oil was collected at 122°C (0.3 Torr) with a 75% yield. Anal. Found: C, 43.8; H, 2.00%. $C_{16}H_9ClF_9P$ calc.: C, 43.8; H, 2.07%. ^{31}P NMR (CDCl$_3$): 86.4 (septet, $^4J_{PF}$ = 52.3 Hz) ppm. ^{19}F NMR (CDCl$_3$): −54.2 (d, 6F, $^4J_{PF}$ = 52.3 Hz); −64.6 (s, 3F) ppm. In the second method a solution of PhCH$_2$MgBr (11.0 mmol) in Et$_2$O was added dropwise during 5 min to a stirred suspension of CdCl$_2$ (5.5 mmol) in Et$_2$O at 0°C. The solution was stirred at this temperature for 1 h, and this was followed by addition in one portion of ArPCl$_2$ (11.1 mmol) in Et$_2$O. The mixture was brought to reflux, kept there for 4 h, and then allowed to cool to room temperature. The compound was isolated, purified as above, and obtained with a 64% yield. The second procedure has the advantage that the reaction can be carried out at a higher temperature, although yields are somewhat lower.

A solution of DBU (2.2 mmol) in THF was added during 5 min to a stirred solution of ArP(CH$_2$Ph)Cl (2.2 mmol) in THF at 0°C. The mixture was allowed to warm to room temperature, and the resulting precipitate removed. The ^{31}P NMR spectrum of the filtrate showed only one septet signal, at 218.1 ppm ($^4J_{PF}$ = 23.7 Hz) attributed to ArP=CH(Ph), formed with an apparently quantitative yield. UV–visible (THF): λ_{max} 327, 225 nm. The compound decomposed when the THF was removed *in vacuo*, the ^{31}P spectrum showing only the presence of decomposition products. It was used *in situ*, however, to yield the derivative with $[PtCl_2(PEt_3)]_2$.

3.4. *Preparation of the complexes of 1–3 with $[PtCl_2(PEt_3)]_2$*

The following reaction was used:

$$\mathrm{ArP{=}CR^1R^2} + \tfrac{1}{2}[\mathrm{PtCl_2(PEt_3)}]_2 \longrightarrow \mathrm{PtCl_2(PEt_3)}(\eta^1-\mathrm{ArP{=}CR^1R^2}) \quad (4)$$

In each case the platinum(II) dimer was added to a stirred solution of the phospha-alkene in a 1:2 molar ratio, in CH_2Cl_2 for **1** and in THF for **2** and **3**, at room temperature. The mixtures were stirred for 1 h (**1**), 6 h (**2**) and 30 min (**3**). The complex with **1** was isolated at −40°C as clear transparent plates with a 42% yield. Its ^{31}P NMR spectrum ($CDCl_3$) showed it to be the *cis* isomer, ^{31}P NMR: 152.1 ($^1J_{PPt}$ = 5006 Hz, $^2J_{P_AP_B}$ = 18 Hz, P_A(phospha-alkene)); 11.1 ($^1J_{PPt}$ = 3832 Hz, $^2J_{P_AP_B}$ = 18 Hz, P_B(PEt_3 group)) ppm. ^{19}F NMR ($CDCl_3$): −56.8 (6F, $^5J_{PtF}$ = 32.5 Hz); −63.0 (s, 3F) ppm. Although the mixture was stirred for a longer period the complex with **2** was present as the *trans* isomer. ^{31}P NMR (THF): 245.1 ($^1J_{PPt}$ = 3714 Hz, $^2J_{P_AP_B}$ = 788 Hz, P_A); 15.4 ($^1J_{PPt}$ = 3000 Hz, $^2J_{P_AP_B}$ = 787 Hz, P_B) ppm. When the spectrum of the solution containing the complex with **3** was recorded after stirring for 30 min, both *cis* and *trans* isomers were apparent (Fig. 1).

trans isomer ^{31}P NMR (THF): 178.6 ($^1J_{PPt}$ = 2457 Hz, $^2J_{P_AP_B}$ = 570 Hz, P_A); 15.8 ($^1J_{PPt}$ = 3253 Hz, $^2J_{P_AP_B}$ = 569 Hz, P_B) ppm.

cis isomer ^{31}P NMR (THF): 149.6 ($^1J_{PPt}$ = 4600 Hz, P_A); 9.9 ($^1J_{PPt}$ = 3219 Hz, P_B) ppm. After 2 h, only the *cis* isomer was detected.

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