Unusual Ring-Closure Reactions During the Oxidation of 1,1′-Bi(3-methylphosphol-2-ene) with Hexafluoroacetone – Formation of a Tricyclic Fluorine-Containing Phosphorane☆

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Reduction of the isoprene–PCl$_3$ adduct **1** with magnesium powder, or with Si$_2$Cl$_6$, furnished *P*-chloro-3-methyl-phosphol-2-ene, **2**, in satisfactory yield. Further reduction of **2** with Si$_2$Cl$_6$ gave the new trichlorosilyl-3-methylphosphol-2-ene, **3**. The reaction of **2** with magnesium powder, with **3**, or with 1/2 equivalent of Si$_2$Cl$_6$ provided the new λ^3P-λ^3P-diphosphane 1,1′-bi(3-methylphosphol-2-ene) **4**. Reduction of **4** with Si$_2$Cl$_6$ led to **3**. Oxidation of **4** with selenium gave the 1,2-diphosphane diselenide, **5**. The oxidation of **4** with hexafluoroacetone led to a mixture of products, from which a novel tricyclic phosphorane **6** was separated. The structure of **6** was determined by X-ray diffraction; the coordination geometry at phosphorus is distorted trigonal bipyramidal, with a very long equatorial P–C(CF$_3$)$_2$ bond of 193.2(2) pm.

The reactivity and stability of the λ^3P-λ^3P-phosphorus–phosphorus bond has been intensively studied[1]. An important part of these studies focussed on the reactions of PP-containing species with oxidizing agents, e.g. tetrachloroorthobenzoquinone (TOB)[2,3] and hexafluoroacetone (HFA)[4–7]. The reaction of λ^3P-λ^3P and λ^5P-λ^3P-diphosphorus compounds with *o*-quinones is, in many cases, known to proceed with oxidative addition of the *o*-quinones to λ^3P and insertion of the *o*-quinone into the P–P bond[2]. In the case of the reaction of cyclic diphosphanes with TOB it was found that oxidative addition of only one molecule of TOB at a λ^3P-atom took place[3]. The reactions of symmetrical and unsymmetrical diphosphorus compounds with HFA have not been systematically investigated.

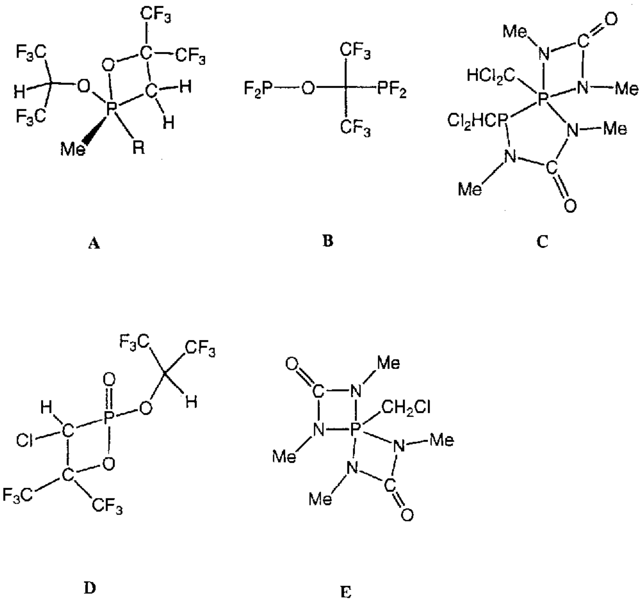
The oxidative addition of HFA to tetramethyldiphosphane led to 1,2-oxaphosphetanes, e.g. **A**[4,5] (Scheme 1).

Tetrafluorodiphosphane, however, reacted with insertion of the carbonyl function of one molecule of HFA into the P–P bond to form compound **B**[6].

The reaction of the λ^3P-λ^5P-diphosphorus compound **C** with HFA proceeded with loss of the Cl$_2$HCP-moiety, which was trapped by two equivalents of HFA, furnishing, unexpectedly, the 1,2-oxaphosphetane derivative **D**, and 2-chloromethyl-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4λ^5-phosphaspiro[3.3]heptan-2,6-dione **E**[8] (Scheme 1).

We have now investigated the reaction of the λ^3P-λ^3P-diphosphane, 1,1′-bi(3-methylphosphol-2-ene) **4** with HFA, from which a novel type of tricyclic phosphorane was isolated.

Scheme 1



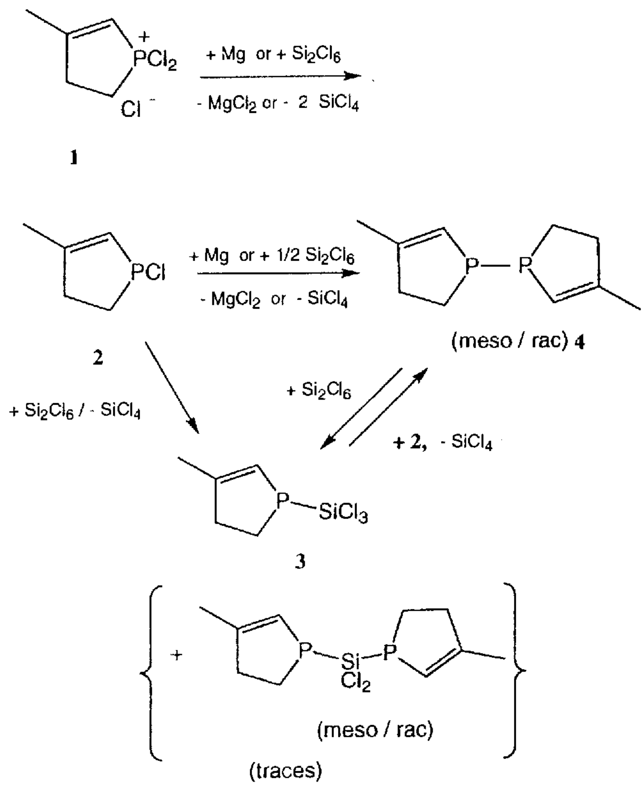
Results and Discussion

Synthesis of 1,1′-Bi(3-methylphosphol-2-ene) 4

The dehalogenation of the "isoprene–PCl$_3$ adduct" **1** with PPh$_3$ is known to furnish chloro-3-methylphosphol-2-ene (**2**) in 28% yield[9]. Reduction of **1** with magnesium powder gave **2** in 61% yield. Alternatively, the reaction of **1** with half a molar equivalent of Si$_2$Cl$_6$ led to **2** in a 45% yield (Scheme 2). In accord with literature reports[9], the identity of **2** was established by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P).

The reaction of **1** with Mg in a 1:2 molar ratio gave the new compound 1,1′-bi(3-methylphosphol-2-ene) (**4**) in good yield. The same compound was also obtained from the reaction of **2** and magnesium powder in a 1:1 molar ratio, with Si$_2$Cl$_6$ in a 2:1 molar ratio, or with 1-trichlorosilyl-3-methylphosphole-2-ene, **3**. In the case of the reaction of **2**

Scheme 2



with Si_2Cl_6 we found that the reaction, conducted in a 1:1 molar ratio, led to trichlorosilylphosphane **3** and $SiCl_4$[10,11]. Subsequently, the reaction of **2** with **3** furnished the diphosphane **4** and one equivalent of $SiCl_4$. In the presence of a slight excess of Si_2Cl_6, trichlorosilylation of **4** gave **3** in good yield[11].

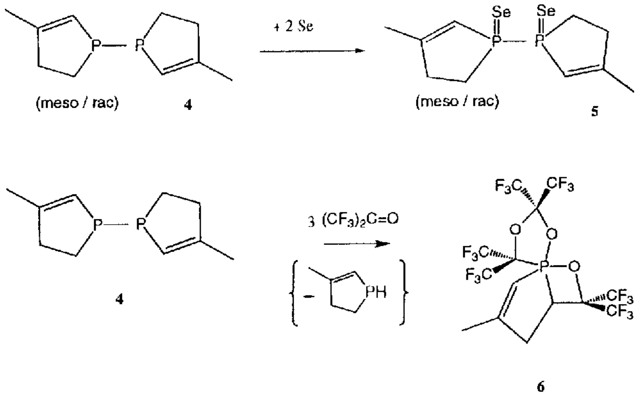
The constitution of **4** was established by elemental analysis, by ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy, and by mass spectrometry.

Like its known isomer 1,1′-bi(3-methyl-phosphol-3-ene)[12], 1,1′-bi(3-methyl-phosphol-2-ene) **4** exists as a mixture of *meso*/*rac* isomers. The ^{31}P-NMR spectrum of **4** exhibits two signals at $\delta = -1.2$ and -1.5, which indicates the presence of both diastereomers of the diphosphane in an approximate 1:1 ratio.

Reaction of 1,1′-Bi(3-methylphosphol-2-ene) 4 with Selenium and with Hexafluoroacetone

With elemental selenium as oxidizing agent, **4** reacts under mild conditions without cleavage of the P–P bond, to form the stable 1,2-diselenide **5**, which was isolated in over a 80% yield as a green solid. Like **4**, the diphosphane diselenide **5** exists in solution as a diastereomeric *meso*/*rac* mixture. Thus **4** behaves like other non-strained diphosphanes with respect to selenium as an oxidizing agent.

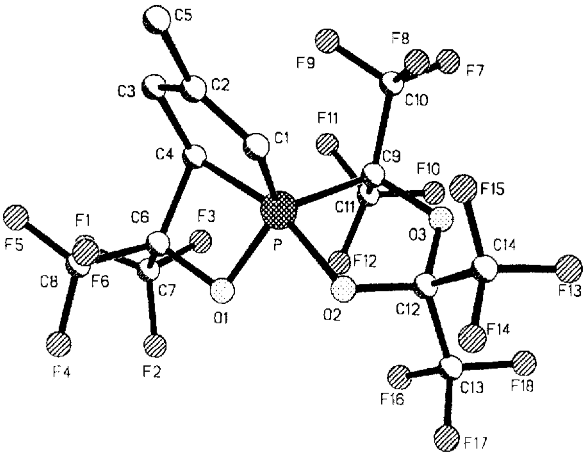
The behaviour of **4** towards HFA, however, is different from that of all compounds with P–P bonds as yet studied. Within four days at room temperature in dichloromethane, the reaction of **4** with HFA led to a mixture of at least seven products (major ^{31}P-NMR signals at $\delta = +83.4, +80.9, +52.7, +23.7, +9.0$ and -5.6, small peaks at $\delta = +82.5$ and -12.3). Crystallisation from diethyl ether provided the pure compound **6** ($\delta^{31}P = +8.6$) as a colourless solid in 15% yield.



6 was characterised by elemental analysis, by ^{1}H-, ^{13}C-, ^{19}F-, and ^{31}P-NMR spectroscopy and by mass spectrometry, and its solid state structure was established by a single crystal X-ray diffraction study.

Like its precursor molecule **4**, **6** is a derivative of 3-methylphosphol-2-ene. However, the 3-methylphosphol-2-ene function in **6** is now part of a unique tricyclic phosphorane system, linking a 1,3-dioxaphospholane and a 1,2-oxaphosphetane ring system (Figure 1). Oxidation reactions of a number of phosphorus compounds with HFA are known to produce compounds with 1,3-dioxaphospholane moieties, and 1,2-oxaphosphetanes have also been isolated in several cases, but the combination of both functions in one molecule (as in **6**) is unique. The tricyclic phosphorane **6** can be derived, formally, from **4** by a sequence of radical P–P bond cleavage, loss of a hydrogen atom at the 5-position (from the saturated carbon atom adjacent to phosphorus), "unsymmetric 2 + 2 + 1 addition" of two C(:O) moieties to the phosphorus atom (leading to a *spiro*-bicyclic system) and "2 + 2 addition" of an endocyclic formal P=C double bond to the carbonyl group of a third HFA molecule, forming the oxaphosphetane ring system. Retrosynthetically, a spirocyclic ylide and HFA would be the precursors of the tricyclic 1,2-oxaphosphetane **6**. The actual reaction pathway leading to **6** is not known. Invoking individual steps that have been proposed in the course of investigations of various P^{III}–HFA systems[4,5,12,13], a sequence as proposed in Scheme 3 would conceivably lead to **6**: in the first step of the reaction nucleophilic P → C attack would lead to a zwitterionic intermediate (**a**). The negatively charged oxygen atom of the zwitterion could then abstract a proton from the acidic methylene group adjacent to four-coordinate phosphorus, giving rise to a P^{+}–C^{-} ylide (**b**). The next two steps required would be oxaphosphetane formation from the cycloaddition of the ylidic P=C moiety to the C=O group of HFA and 1,3-dioxaphospholane formation with another molecule of HFA, with cleavage of the P–P bond. We do not know which of these steps is the final one: the number of unidentified products, besides **6**, suggests

Figure 1. Structure of **6**[a] in the crystal



[a] Hydrogen atoms are omitted for clarity, selected bond lengths [pm] and angles [°]: P–O(1) 165.5(2), P–O(2) 172.0(2), P–C(1) 176.9(2), P–C(4) 189.9(2), P–C(9) 193.2(2), C(1)–C(2) 132.7(3); C(1)–P–C(4) 91.05(11), O(1)–P–C(4) 78.12(10), O(2)–P–C(9) 85.71(9), O(1)–P–O(2) 85.35(8), O(1)–P–C(9) 113.24(10), C(4)–P–O(2) 163.33(9), C(1)–P–O2 95.98(10).

that, in fact, several reaction pathways, including radical reaction steps, are in competition when **4** reacts with HFA.

X-Ray Crystal Structure Determination of 6

The geometry at the phosphorus atom is distorted trigonal bipyramidal, whereby the atoms C1 (an sp^2-hybridized carbon atom of the 2-phospholene), O1 (belonging to the oxaphosphetane ring), and C9 (part of the 1,3-dioxaphospholane ring system) occupy the equatorial positions (they and the P atom are coplanar within 1 pm). The oxaphosphetane shares the apical P–C4 bond with the adjacent phospholene ring system; this mode of condensation of the unique bicyclic substituent at pentacoordinated phosphorus does not allow the O1 atom to adopt the usually preferred apical position. A major distortion of the trigonal bipyramid around P is necessarily caused by the very small bite of the four-membered ring [O1–P–C4 78.1(1)°; other "bite" angles at phosphorus are C1–P–C4 91.1(1) and O2–P–C9 85.71(9)°]. All rings are essentially planar, with mean deviations of 4 pm for P, C4, C6, O1; 3 pm for P, C1–C4 (interplanar angle 59°), and 3 pm for P, O2, O3, C9, C12.

The bond lengths at phosphorus do not without exception follow the usual trend that axial bonds are longer than equatorial bonds at trigonal-bipyramidal phosphorus. The equatorial bond P–O1 is indeed shorter [165.5(2) pm] than the apical P–O2 [172.0(2) pm]; however, compared to the apical P–C4 bond length, [189.9(2) pm], the equatorial P–C9 bond at 193.2(2) pm is remarkably long. Similarly long equatorial P–C(CF$_3$)$_2$ bonds have been observed in other five-membered rings [190.3(3) pm[7], 194.9(6) pm[16]].

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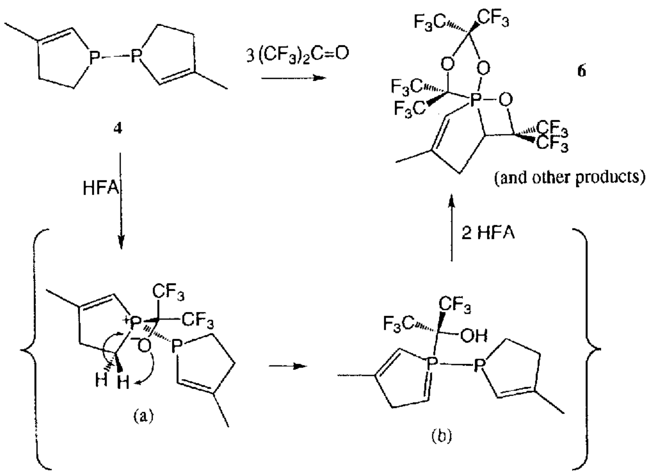
Scheme 3



Experimental Section

All experiments were carried out with 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 0.05 Torr at 25°C, unless otherwise stated. – 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), CFCl$_3$ ext. (^{19}F), and 85% H$_3$PO$_4$ ext. (^{31}P). – MS: Finnigan MAT 8430. – Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen, and Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig.

1-Chloro-3-methylphosphole-2-ene (**2**): a) From **1** with Ph$_3$P see ref.[9]. – b) From **1** with Mg powder: To a suspension of 5.7 g (28 mmol) of **1** in 50 ml of THF 0.55 g (23 mmol) of Mg powder was added. An exothermic reaction took place; the mixture was temporarily cooled with ice and stirred for 2 h. The suspension was extracted with four 25-ml portions of pentane. Distillation furnished 2.3 g (61%) **2**.

c) From **1** with Si$_2$Cl$_6$: A suspension of 6.5 g (31 mmol) of **1** in 25 ml of dichloromethane was cooled to 0°C and 7.5 g (4.8 ml, 28 mmol) of hexachlorodisilane was added dropwise. The reaction mixture was allowed to attain room temperature and was stirred for 1 h. Distillation furnished 1.9 g (45%) of **2**, bp. 56°C (5 Torr). – ^{1}H NMR (C$_6$D$_6$): δ = 1.41 (d, 3H, $^4J_{PH}$ = 2.5 Hz, CH$_3$), 1.48–2.47 (m, 4H, CH$_2$), 5.78 (d, $^2J_{PH}$ = 46.9 Hz, α-CH). – ^{13}C NMR (C$_6$D$_6$): δ = 19.40 (d, $^3J_{PC}$ = 2.21 Hz, CH$_3$), 32.84 (d, $^1J_{PC}$ = 25.23 Hz, α-CH$_2$), 39.00 (d, $^2J_{PC}$ = 8.10 Hz, β-CH$_2$), 126.50 (d, $^1J_{PC}$ = 38.60 Hz, α-CH), 164.39 [s, *C*(Me)]. – ^{31}P NMR (CDCl$_3$): δ = 127.8 (s). – EI-MS, *m/z* (%): 134 (97) [M$^+$], 119 (9) [M – CH$_3$]$^+$, 99 (100) [M – Cl]$^+$. – C$_5$H$_8$P (134.55): calcd. C 44.64, H 5.99; found C 44.54, H 6.25.

Diphosphane **4**: a) From **1** with Mg: To a suspension of 4.0 g (19.5 mmol) of **1** in 50 ml of THF 0.9 g (37.5 mmol) of Mg was added. The reaction mixture was cooled temporarily with ice and stirred for 2 h. The suspension was extracted with four 25-ml portions of pentane. Distillation furnished 1.55 g (86%) **4**.

b) from **2** with Mg: A solution of 3.7 g (12.7 mmol) of **2** in 25 ml of THF was cooled to 0°C and 0.34 g (14.2 mmol) of Mg was added. The reaction mixture was allowed to reach room temperature, and was stirred for 2 h. The solvent was removed i.V. The residue was extracted with three 15-ml portions of pentane (separation of **4** from triethylammonium choride) and distilled. The diphosphane **4** was obtained as a colourless liquid. Yield 2.3 g (85%).

c) From **2** with Si_2Cl_6: A solution of 1.4 g (10.4 mmol) of **2** in 25 ml of dichloromethane was cooled to 0°C and 2.8 g (10.4 mmol) Si_2Cl_6 was added dropwise. The reaction mixture was allowed to reach room temperature and was stirred for 30 min. Distillation furnished 0.6 g (58%) of **4**, bp. 70°C (0.1 Torr). – ^1H NMR (C_6D_6): δ = 1.84 (4 lines, 6H, CH_3), 1.97 (3 lines, 4H, α-CH_2), 2.52 (3 lines, 4H, β-CH_2), 5.44 (d, 2H, $^2J_{PH}$ = 39.4 Hz, α-CH). – ^{13}C NMR (C_6D_6): δ = 19.45 (s, CH_3), 21.70 (3 lines, α-CH_2), 39.73 (4 lines, β-CH_2), 121.25 (5 lines, α-CH), 153.02 [s, *C*(Me)]. – ^{31}P NMR (C_6D_6): δ = −1.21 (s, *meso*), −1.54 (s, *rac.*)[12,17]. – EI-MS, *m/z* (%): 198 (32) $[M]^+$, 100 (62) $[C_5H_9P]^+$, 99 (100) $[C_5H_8P]^+$, 85 (32) $[C_5H_9P - CH_3]^+$. – $C_{10}H_{16}P_2$ (198.18): calcd. C 60.61, H 8.14; found C 60.42, H 8.46.

Diphosphane Diselenide **5**: To a solution of 0.5 g (2.5 mmol) of **4** in 15 ml of dichloromethane an excess (6.0 mmol) of selenium powder was added. The reaction mixture was stirred overnight and was filtered to remove unreacted selenium. The suspension was extracted twice with 10 ml of dichloromethane. The solvent was removed i.V. and **5** was obtained as a green solid. Yield: 0.75 g (83%), m.p. 134°C. – ^1H NMR ($CDCl_3$): δ = 2.00 (7 lines, 6H, CH_3), 2.2–3.5 (m, 8H, α,β-CH_2), 5.8 (6 lines, 2H, α-CH). – ^{13}C NMR (C_6D_6): δ = 20.1 (m, CH_3), 30.36 (m, α-CH_2), 38.98 (m, β-CH_2), 116.2 (m, α-CH), 165.6 (m, β-C). – ^{31}P NMR ($CDCl_3$): δ = 51.98 (s, *meso*), 52.70 (s, *rac.*)[17]. – EI-MS, *m/z* (%): 358 (6) $[M^+]$, 179 (12) $[C_5H_8PSe]^+$, 99 (16) $[C_5H_8P]^+$ (356.10). – $C_{10}H_{16}P_2Se_2$ (356.10): calcd. C 33.52, H 4.53; found C 33.08, H 4.53.

Tricyclic Phosphorane **6**: A solution of 1.5 g (7.6 mmol) of **4** in 10 ml of dichloromethane was placed into a heavy-walled glass tube, equipped with a Teflon® stopcock. The solution was cooled to −196°C, and 8.9 g (53 mmol) of hexafluoroacetone was condensed into the tube. The reaction mixture was allowed to warm up to room temperature. After stirring for 4 days the solvent and all volatile components were removed i.V., and the residue was crystallized from diethyl ether. Product **6** was obtained as colourless crystals. Yield 1.3 g (15%), m.p. 102°C. – ^1H NMR ($CDCl_3$): δ = 2.08 (s, 3H, CH_3), 2.72 (m, 2H), 4.27 (t, $^3J_{HH}$ = 9.4 Hz), 5.68 (d, $^2J_{PH}$ = 28.7 Hz). – ^{13}C NMR ($CDCl_3$): δ = 20.50 (d, $^1J_{PC}$ = 10.1 Hz), 35.39 (d, $^1J_{PC}$ = 25.3 Hz), 56.40 (d, $^1J_{PC}$ = 37.8 Hz), 76.48 (s), δ = 113.52 (s), 115.91 (d, $^2J_{PC}$ = 16.7 Hz), 117.28, 117.79, 121.48 (s, 6 C, CF_3), 123.26 $^1J_{PC}$ = 24.8 Hz), 173.57 (d, $^1J_{PC}$ = 36.3 Hz). – ^{19}F NMR ($CDCl_3$): δ = −67.54 (sept, 3 F), −68.82 (sept, 3 F), −71.12 (q, 3 F), −75.19 (sept, 3 F), −79.05 (sept, 3 F), −80.43 (sept, 3 F). – ^{31}P NMR ($CDCl_3$): δ = 8.64 (s). – EI-MS: *m/z* (%): 596 (32) $[M]^+$, 577 (52) $[M - F]^+$, 527 (98) $[M - CF_3]^+$, 430 (54) $[M - HFA]^+$, 196 (90) $[C_7H_7F_3PO - CH_3]^+$, 127 (38) $[C_6H_7PO - CH_3]^+$, 115 (100) $[C_5H_7PO - CH_3]^+$. – $C_{14}H_7F_{18}O_3P$ (596.17): calcd. C 28.19, H 1.18; found C 28.34, H 1.29.

Crystal Structure Analysis of **6**: Crystal data: $C_{14}H_7F_{18}O_3P$, M_r = 596.17, triclinic, $P\bar{1}$, a = 794.6(4), b = 1030.1(5), c = 1275.0(8) pm, α = 102.68(3), β = 91.12(3), γ = 108.35(3)°, V = 0.9619 nm³, Z = 2, D_x = 2.058 Mg m^{-3}, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, μ = 0.3 mm^{-1}, $F(000)$ = 584, T = −130°C. Data collection and reduction: A colourless prism was cut to ca. 0.8 × 0.8 × 0.4 mm, mounted in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low temperature attachment). A total of 3729 intensities were determined to 2Θ 50° (3394 unique, R_{int} 0.024). Cell constants were refined from $\pm\omega$ angles of 54 reflections with 2Θ 20–23°. Structure solution and refinement: The structure was solved by direct methods and refined on F^2 using the program SHELXL-93. Hydrogen atoms were refined as rigid methyls or with a riding model. The final $wR(F^2)$ for all reflections was 0.105, with a conventional $R(F)$ of 0.039, for 326 parameters; S. = 1.01, max. Δ/σ = 0.002, max. $\Delta\rho$ = 363 e nm^{-3}. Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD-406001.

☆ Dedicated to Professor *Rudolf Taube* on the occasion of his 65th birthday.

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