Heteroatom Chemistry
Volume 9, Number 2, 1998

Phosphonous Acid Dichlorides and Tricyclic Phosphoranes from Hexafluoro- and Trifluoropentane-2,4-dione

Georgios Bekiaris and Gerd-Volker Röschenthaler*

Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Strasse, D-28334 Bremen, Federal Republic of Germany

Received 18 June 1997

ABSTRACT

1,1,1,5,5,5-Hexafluoro-2-hydroxy-2-pentene-4-one reacted diastereospecifically with phosphonous acid dichlorides, $RPCl_2$ (R = Me, Et, iPr, tBu, Me_3SiCH_2, $PhCH_2$, Ph) to give in a concerted mechanism thermally stable tricyclic $\lambda^5\sigma^5P$ phosphoranes containing two five- and one six-membered ring. In one case, hydrolysis gave 3,5-dihydroxy-2-oxo-1,2$\lambda^5\sigma^4$-oxaphosphalane, whereas methanol added to the double bond in the six-membered ring furnishing two isomeric phosphoranes. When 1,1,1-trifluro-2-hydroxy-2-pentene-4-one was reacted with $RPCl_2$ (R = Et, Me_3SiCH_2, $PhCH_2$, Ph), diastereomerically pure regioisomeric phosphoranes were obtained. The solid-state molecular structures of three $\lambda^5\sigma^5P$ species exhibited two oxygen atoms in the axial position of a slightly distorted trigonal-bipyramidal geometry at phosphorus. Surprisingly, the two CF_3 groups bonded to an sp^3-hybridized carbon were in a cisoid arrangement, having closest nonbonding F···F distances of 301.4 or 273.5 pm. These findings reflect the "through-space" F-F coupling constants of the tricyclic phosphoranes (J_{FF} = 4.0–7.0 Hz) in solution. The solid-state structure of the phospholane revealed the two hydroxy groups to be directed to one side of the five-membered ring. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:173–181, 1998

INTRODUCTION

The phosphites $(R^1O)_2POR^2$ or $(R^1O)_2PNCO$ ($R^1 = R^2$ = Me, Et; R^1–R^1 = CH_2–CH_2, CMe_2–CMe_2, R^2 = Me) have been reported to react with 1,1,1,5,5,5-hexafluoro-2-hydroxy-2-pentene-4-one to furnish either 1,2$\lambda^5\sigma^5$-oxaphospholenes [1] or bicyclic $\lambda^5\sigma^5$P phosphoranes [2], a class of compounds also obtained by reaction of the phosphites with the tautomer of 1,1,1-trifluoropentane-2,4-dione [2]. Phosphonous acid dichlorides R^3PCl_2 (R^3 = Et) underwent reaction with pentane-2,4-dione to give rise to 2-ethyl-4-methyl-6-methyl-6-methylene-1,3,2$\lambda^3\sigma^3$-dioxaphosphorin-4-ene [3]; in the case of R^3 = Ph and in reaction with dibenzoylmethane, a tricyclic $\lambda^5\sigma^5$P trioxaphosphorane was obtained, whose structure has been discussed in terms of two carbon atoms in apical and three oxygen atoms in equatorial positions of a trigonal bipyramid based on ^{1}H and ^{13}C NMR spectral data. This compound isomerized above 30°C to a phosphinic acid ester [4]. Similarly, thermally stable tricyclic phosphoranes were synthesized from 1,1,1,5,5,5-hexafluoro-2-hydroxy-2-pentene-4-one and the dichlorides R^3PCl_2 (R^3 = CH_2Ph, Ph) [5]: Here we describe the extension of this work to R^3 = Me, Et, *i*Pr, *t*Bu, Me_3SiCH_2, with hydrolysis and methanolysis of one selected phosphorane. The reaction of 1,1,1-trifluoropentane-2,4-dione, offering different regioselective reaction pathways, with R^3PCl_2 (R^3 = Et, Me_3SiCH_2, $PhCH_2$, Ph) taking into account the two tautomeric forms, is also a part of the present investigation.

---

*To whom correspondence should be addressed.

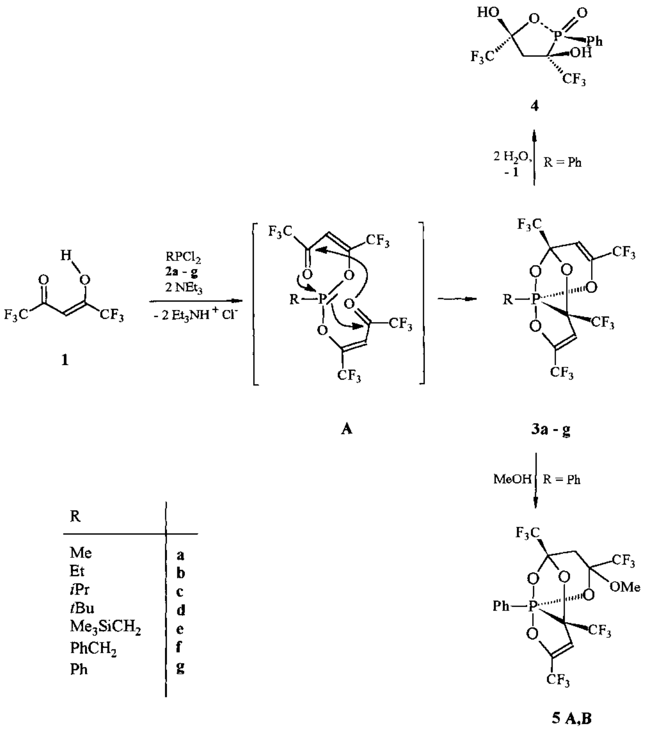
CCC 1042-7163/98/020173-09

RESULTS AND DISCUSSION

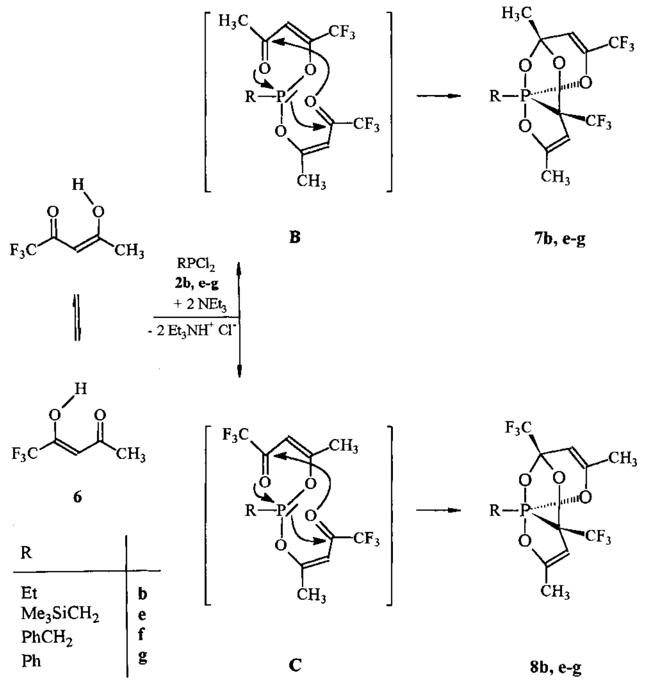
In the presence of an auxiliary base, reactions of (*Z*)-1,1,1,5,5,5-hexafluoro-2-hydroxy-2-pentene-4-one (**1**) with the phosphonous acid dichlorides, $RPCl_2$ (**2**) [R = Me (**a**), Et (**b**), *i*Pr (**c**), *t*Bu (**d**), Me_3SiCH_2 (**e**), $PhCH_2$ (**f**), Ph (**g**)], gave moisture-sensitive tricyclic trioxaphosphoranes **3** (see Scheme 1): **3a–d** as yellow liquids, crystallizing between 10–15°C, and **3e–g** as colorless solids. Nevertheless, the very fast formation of compounds **3** might have prevented us from obtaining NMR spectroscopic evidence for phosphonite **A**, proposed as a precursor for the concerted diastereospecific reaction. Trapping experiments using hexafluoroacetone failed but had been successful in a similar reaction [6]. Due to bulkier substituents, the reactions of the dichlorides **2c** and **2d** required higher reaction temperatures and longer reaction times than did **2a, b, f,** and **g.** Hydrolysis experiments were carried out in one case, namely with compound **3g** (R = Ph), resulting in the degradation of the tricyclic system with formation of **1** and the solid, nonhygroscopic 3,5-dihydroxy-2-oxo-$1,2\lambda^5\sigma^4$-oxaphospholane **4,** which could be isolated after fractional crystallization. Surprisingly, with methanol, the tricyclic system was preserved. A Markovnikov addition across the double bond in the six-membered ring from both possible sides took place, creating one more chiral center to yield the two isomeric phosphoranes, **5A** and **5B.** The other double bond in the five-membered ring was not attacked (see Scheme 1).

The reactions of the phosphonous acid dichlorides, $RPCl_2$ (**2**) [R = Et (**b**), Me_3SiCH_2 (**e**), $PhCH_2$ (**f**), Ph (**g**)], with the tautomer [7] of 1,1,1-trifluoropentane-2,4-dione **6** were conducted at 0°C and ambient temperature, respectively, due to the lower reactivity of **6.** Since two different HO functions are present in the two tautomeric (*Z*) forms of **6,** three different intermediate phosphonites might have been expected, but we found only two, namely, **B** and **C,** to give diastereoselectively two regioisomeric phosphoranes **7** and **8** in the ratio 4.2:1 (**7b**:**8b**), 6.7:1 (**7e**:**8e**), 7.2:1 (**7f**:**8f**), and 10.1:1 (**7g**:**8g**) with CF_3 in the bridge-head position in both cases (see Scheme 2). These findings account for a slight preference for the tautomer having the hydroxyl group at C(4) and a considerable influence of the substituent at phosphorus. Isomers **7** and **8** could be separated by fractional crystallization.

The X-ray diffraction investigation of the trioxaphosphorane **3e** (Figure 1 and Table 1) showed that the substituents at phosphorus are arranged in a trigonal bipyramid (two oxygen atoms in axial, one in equatorial, and two carbon atoms in equatorial positions) whose distortion originated from different bond lengths and bond angles of the apical and equatorial substituents [apical: P(1)–O(6) 170.9, P(1)–O(2) 173.4(4) pm; equatorial: P(1)–C(16) 176.5(5)



SCHEME 1



SCHEME 2

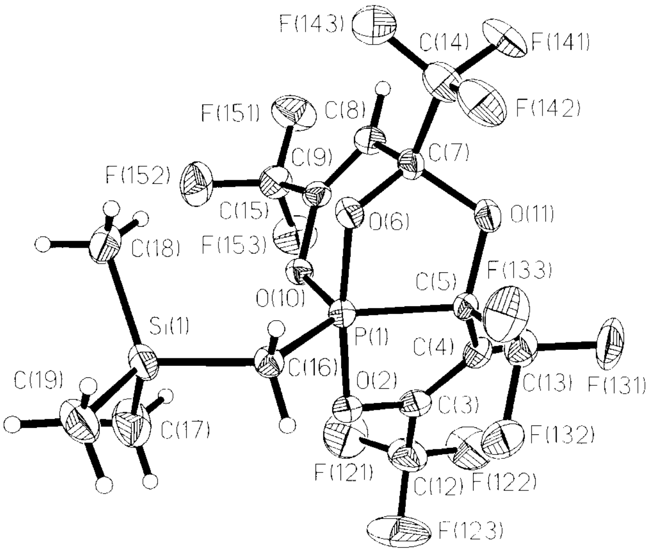


FIGURE 1 Molecular structure of compound **3e**.

TABLE 1a Selected Bond Distances (pm) of Compounds **3e, 5A,** and **7g**

	3e	*5A*	*7g*
P(1)–O(2)	173.4(4)	173.6(4)	171.8(5)
P(1)–O(6)	170.9(4)	170.5(4)	168.4(4)
P(1)–O(10)	163.2(4)	161.5(3)	163.2(5)
P(1)–C(5)	187.8(5)	188.2(3)	187.0(7)
P(1)–C(R)	176.5(5)	178.8(3)	180.1(7)
C(7)–C(8)	148.8(4)	152.9(5)	149.3(10)
C(7)–C(14)	152.0(11)	152.8(7)	151.3(10)
C(8)–C(9)	132.6(9)	151.9(5)	130.4(10)
C(9)–O(10)	135.8(8)	143.3(7)	140.1(8)
C(9)–C(15)	148.4(10)	154.8(8)	146.1(13)
O(6)–C(7)	138.9(7)	137.7(4)	141.1(9)

TABLE 1b Selected Bond Angles (°) of Compounds **3e, 5A,** and **7g**

	3e	*5A*	*7g*
O(2)–P(1)–C(5)	87.8(2)	88.3(2)	87.7(3)
O(2)–P(1)–O(6)	173.2(2)	172.4(1)	174.1(3)
O(2)–P(1)–O(10)	87.4(2)	86.9(2)	87.8(2)
C(5)–P(1)–O(6)	85.5(2)	84.5(2)	86.6(3)
C(5)–P(1)–O(10)	108.9(3)	110.2(1)	109.6(3)
O(6)–P(1)–O(10)	93.3(2)	93.5(2)	95.3(2)
O(2)–P(1)–C(R)	92.3(2)	92.9(2)	92.3(3)
O(6)–P(1)–C(R)	93.4(2)	93.5(2)	90.8(3)
O(10)–P(1)–C(R)	118.6(2)	119.1(1)	115.8(3)
C(5)–P(1)–C(R)	132.4(3)	130.7(2)	134.5(3)
C(7)–C(8)–C(9)	116.7(6)	109.7(4)	118.3(6)
C(8)–C(9)–C(15)	125.1(6)	110.8(3)	126.8(7)
P(1)–C(5)–C(4)	102.6(4)	104.2(2)	103.9(5)

and P(1)–C(5) 187.8(5) pm; C(5)–P(1)–C(16) 132.4(3)°, O(10)–P(1)–C(5) 108.9(3)°, O(6)–P(1)–O(2) 173.2(2)°]. The phosphorus atom was located 2.07 pm below the C(16)–C(5)–O(10) plane toward O(2). The puckering parameters [8] indicate that the six-membered ring P(1)–O(6)–C(7)–C(8)–C(9)–O(8) shows a half-boat conformation (Q = 63.1 pm, Φ = 59.3°, θ = 57.4°), the five-membered ring P(1)–O(2)–C(3)–C(4)–C(5) an envelope (E_0, Q = 34.8 pm, Φ = 354.7°), and the anellated five-membered ring P(1)–O(6)–C(7)–O(11)–C(5) a distorted twist conformation ($^1T \rightarrow {}^1E$, Q = 48.5 pm, Φ = 195.2°) [8,9]. The C–C and C=C bond lengths were found in the expected range [10]. The two CF$_3$ groups, C(13)F$_3$ and C(14)F$_3$, are in the *cisoid* position with a closest nonbonding F(133)···F(142) distance of 301.4 pm (slightly more than twice the van der Waals radius of fluorine, 140 pm) possibly accounting for the "through-space" coupling J_{FF} = 4.2 Hz, observed in the solution ^{19}F NMR spectrum of **3e** (see discussion of the NMR data). The dihedral angle P(1)–C(5)–C(4)–H was found to be 157.4° correlating with the $^3J_{PH}$ value of 23.3 Hz measured in the ^{1}H NMR spectrum.

The oxaphospholane *4* (Figure 2 and Table 2) showed a tetrahedral coordination at phosphorus with a P(1)–O(1) double bond distance of 148.0(3)

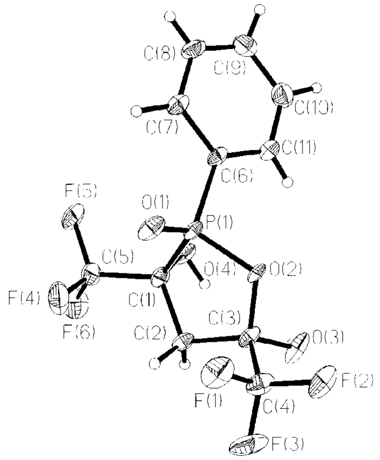


FIGURE 2 Molecular structure of compound **4**.

TABLE 2 Selected Bond Distances (pm) and Bond Angles (°) of Compound **4**

P(1)–O(1)	148.0(3)	C(1)–O(4)	141.1(5)
P(1)–O(2)	159.1(3)	C(1)–C(2)	152.5(6)
P(1)–C(1)	183.5(4)	C(3)–O(3)	135.3(5)
P(1)–C(6)	176.6(4)	O(2)–C(3)	145.8(5)
O(1)–P(1)–O(2)	114.7(2)	O(2)–P(1)–C(1)	94.1(2)
O(1)–P(1)–C(1)	113.3(2)		

pm [10]. The great difference in the P(1)–O(2) [159.1(3) pm], P(1)–C(1) [183.5(4) pm], and P(1)–C(6) [176.6(4) pm] bond lengths gave rise to the small endocyclic angle O(2)–P(1)–C(1) [94.1(2)°]. An envelope conformation (^4E, $Q = 38.9$ pm, $\Phi = 150°$) was found for the five-membered ring. The two HO groups are on *one* side of the ring, the two CF_3 groups on the other. There was observed a short intramolecular hydrogen bond between H(4) and P(1)–O(1) (179.6 pm).

The geometry of phosphorane **5A** was determined to be similar to that of compound **3e** (Table 1 and Figure 3). As expected, the main difference arose from the saturated six-membered ring, which has a boat conformation ($Q = 77.7$ pm, $\Phi = 101.4°$, $\theta = 239.2°$), with elongated C(8)–C(9) [151.9(5) pm] and C(9)–O(10) [154.8(8) pm] and smaller angles C(7)–C(8)–C(9) [116.7(6)°] and C(8)–C(9)–C(15) [110.8(3)°], respectively. The two five-membered rings were found to be in a twist-conformation [P(1)–O(2)–C(3)–C(4)–C(5), $^4E \rightarrow {}^4T_0$, $Q = 32.3$ pm, $\Phi = 177.6°$; P(1)–O(6)–C(7)–O(11)–C(5) $^0T_1$, $Q = 49.8$ pm, $\Phi = 15.5°$)]. The phosphorus atom is located 1.36 pm below the plane C(5)–O(10)–C(21) and located toward O(2). Compared to compound **3e**, the closest nonbonding F(133)···F(142) distance was considerably shorter with 273.5 pm, caused by the change in geometry of the six-membered ring. The J_{FF} value was found to be 7.1 Hz. The dihedral angle P(1)–C(5)–C(4)–H was found to be −161.3° correlating with the $^3J_{PH}$ value of 29.9 Hz observed in the ^{1}H NMR spectrum.

Like the other two tricyclic phosphoranes, **3e** and **5A**, the single-crystal X-ray structure analysis of **7g** showed a distorted trigonal bipyramid (Figure 4, Table 1). The main features of the geometry were similar to those of compound **3e**, the conformation of the six- and two five-membered rings [P(1)–O(6)–C(7)–C(8)–C(9)–O(8) being half-boat, $Q = 63.9$ pm, $\Phi = 54.4°$, $\theta = 53.4°$); P(1)–O(2)–C(3)–C(4)–C(5), $^0E \rightarrow {}^0T_4$, $Q = 37.8$ pm, $\Phi = 356.4°$; P(1)–O(6)–C(7)–O(11)–C(5), ^1T, $Q = 46.7$ pm, $\Phi = 205.0°$] [8,9]: The position of the phosphorus atom was found to be 3.00 pm below the plane C(5)–C(21)–O(10) and located toward O(2). The dihedral angle P(1)–C(5)–C(4)–H was found to be 157.4° correlating with the $^3J_{PH}$ value of 31.0 Hz measured in the ^{1}H NMR spectrum.

Only *one* set of signals was observed for compounds **3**, **7**, and *8* (see Tables 3 and 4) proving the diastereospecific formation. The ^{31}P NMR shift values were found in the expected range for $\lambda^5\sigma^5$-trioxaphosphoranes [11]: The CF_3 groups at C(5) and C(7) were in a *cisoid* arrangement (including **5**), also found in the solid-state structures of **3d** and **5A.** The ^{19}F NMR spectra for compounds **3** and **5A** exhibited four signals due to four magnetically inequivalent CF_3 groups, three resonances close together in the range $-77 \parallel -79$ ppm, the fourth one having a quadruplet structure, being located 10 ppm upfield (-88 ppm), and assigned to the acetal carbon C(7). The coupling constants J_{FF} [4.2–4.9 Hz (**3a–g**) and 7.0 Hz (**5A** and **5B**)] appear again in the signals for $C(5)F_3$ where an additional $^3J_{PF}$ coupling gives rise to a dou-

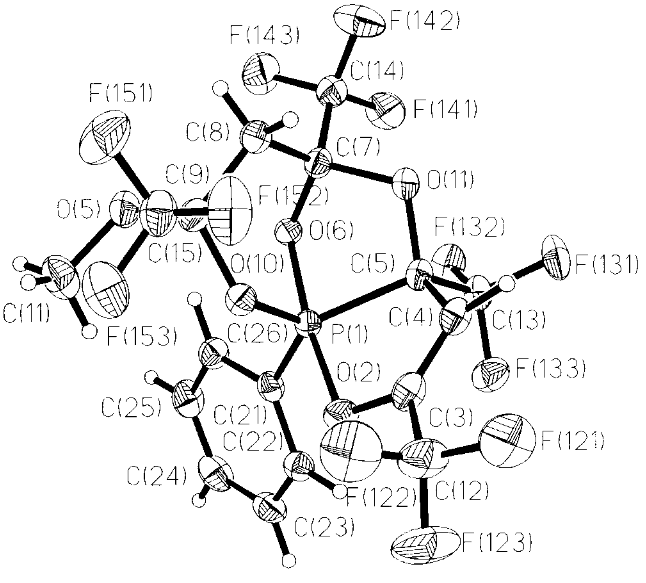


FIGURE 3 Molecular structure of compound **5A**.

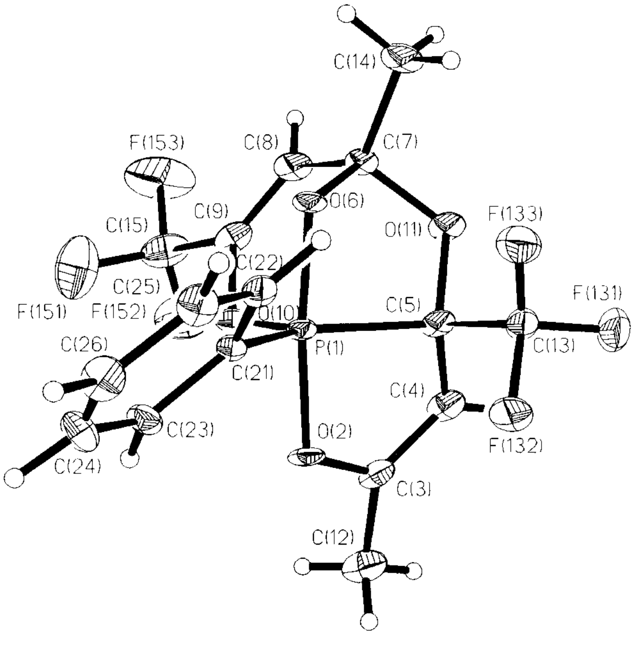


FIGURE 4 Molecular structure of compound **7g**.

TABLE 3 ^{1}H, ^{19}F, and ^{31}NMR Parameters of Compounds **3a–g** (J is given in Hz)

		$\delta_H{}^a$		$\delta_F{}^a$		
R	$C(4)H$ ($^3J_{PH}$)	$C(8)H$	$C(3,9)F_3$	$C(5)F_3$ (J_{PF}, J_{FF})	$C(7)F_3$	$\delta_P{}^a$
3a Me[b]	5.87 (29.5)	6.34	−77.54, −78.53	−78.35 (7.4, 4.5)	−88.43[c]	12.0
3b Et[d]	5.74 (29.8)	5.88	−77.06, −78.53	−78.35 (7.4, 4.5)	−88.43	13.0
3c *i*Pr[e]	5.94 (27.0)	6.10	−77.90, −78.90	−77.40 (7.2, 4.6)	−88.70	13.9
3d *t*Bu[f]	5.91 (26.2)	5.95	−78.14, −79.27	−77.64 (7.2, 4.6)	−89.04	14.6
3e CH_2SiMe_3[g]	5.82 (23.3)	5.96	−77.60, −78.41	−78.44 (8.0, 4.3)	−88.50	13.8
3f CH_2Ph[h]	5.37 (30.4)	5.93	−77.10, −78.50	−77.70 (7.4, 4.9)	−88.20[i]	5.2
3g Ph[j]	5.98 (29.9)	6.04	−77.10, −78.30	−77.80 (8.1, 4.5)	−88.10	−8.4

[a] High-field shifts from TMS, CCl_3F, and 85% H_3PO_4 were given negative signs.
[b] δ_H = *2.20 (CH₃,* $^2J_{PH}$ = 16.5).
[c] $^3J_{HF}$ = 0.9.
[d] δ_H = 1.41 (CH_3), 2.55 (CH_2, $^2J_{PH}$ = 16.5, $^3J_{HH}$ = 7.7).
[e] δ_H = 1.50 (CH_3), 3.00 (CH, $^3JH_{HH}$ = 7.0).
[f] δ_H = 1.35 (CH_3).
[g] δ_H = 0.14 (CH_3), 1.80 (CH_2).
[h] c.f. Ref. [5]; δ_H = 3.90 (CH_2, $^2J_{PH}$ = 16.7), 7.4–8.7 (C_6H_5).
[j] c.f. Ref. [5]; δ_H = 7.3–8.4 (C_6H_5).

TABLE 4 ^{1}H, ^{19}F, and ^{31}NMR Parameters of Compounds **7b, e–g** and **8b, e–g** (J is given in Hz)

		$\delta_H{}^{a,b}$			$\delta_F{}^a$		
R	$C(3,9)H$	$C(4)H$ ($^3J_{PH}$)	$C(8)H$	$C(9)F_3$	$C(5)F_3$ ($^3J_{PF}$, J_{FF})	$C(7)F_3$	$\delta_P{}^a$
7b Et[c]	1.63, 1.93	5.63 (30.6)	5.10	−78.60	−79.50 (8.1, —)		8.3
8b Et					−79.10 (8.0, 4.6)	−88.80	4.2
7e CH_2SiMe_3[d]	1.57, 1.79	5.74 (31.0)	5.00	−77.80	−79.60 (8.3, —)		9.5
8e CH_2SiMe_3					−79.10 (8.3, 4.0)	−88.50	4.9
7f CH_2Ph[e]	1.60, 1.87	5.80 (30.3)	5.10	−78.10	−78.90 (8.2, —)		1.4
8f CH_2Ph					−78.30 (8.1, 5.2)	−88.30	−2.6
7g Ph[f]	1.70, 1.95	5.90 (30.0)	5.20	−78.00	−78.90 (8.3, —)		−10.2
8g Ph					−78.40 (8.3, 5.1)	−88.30	−14.4

[a] High-field shifts from TMs, CCl_3F, and 85% H_3PO_4 were given negative signs.
[b] Signals for isomers **8** have low intensities and are partially overlapped by signals from isomers **7**.
[c] δ_H = 1.51 (CH_3), 3.40 (CH_2).
[d] δ_H = 0.21 (CH_3), 2.0–2.4 (broad, CH_2).
[e] δ_H = 3.83 (CH_2), 7.3 (C_6H_5).
[f] δ_H = 7.4–8.4 (m, C_6H_5).

blet of quadruplets. There is obviously a "through-space" interaction (see discussion of the solid-state molecular structures of **3d** and **5A**), since a through-bond mechanism would involve six or seven single bonds. No J_{FF} coupling was observed, as expected in phosphoranes **7**, the molecule having no CF_3 pairs in the necessary vicinity. Similar nonbond coupling phenomena of CF_3 groups facing each other were previously found in a tricyclic system [12] and a spirophosphorane where the ^{19}F–^{19}F homocorrelated 2D NMR spectrum could prove this assumption [13]. Characteristic for the compounds **3** and **7** were the δ_H values for the vinylic protons, C(4)H (5.4–6.0, including **5A**) and C(8)H (5.9–6.1 for **3**, 5.0–5.2 for **7**). The reason for the relatively large coupling constants $^3J_{PH}$ (23.3–31.0 Hz) may be the large P-C-C-H dihedral angle [14], found in three cases by X-ray structure analysis.

EXPERIMENTAL

The appropriate precautions for handling moisture and oxygen-sensitive compounds were observed throughout this work. Analyses: Mikroanalytisches Laboratorium Beller Göttingen. MS: Varian-MAT CH 7A spectrometer at 70 eV (EI). NMR: Bruker AC 80 instrument at 80.13 MHz (^{1}H, standard TMS), 75.39 MHz (^{19}F, standard CCl_3F), and 32.44 MHz (^{31}P, standard 85% H_3PO_4). High-field shifts from TMS, CCl_3F and 85% H_3PO_4 were given negative signs. The single-crystal X-ray structure determination was performed on a Siemens P4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) in a $\omega/2\theta$ scan. The structure was solved by direct methods and refined by full-matrix least squares using SHELXTL PLUS (VMS). Compounds **3f** and **3g** were prepared according to literature procedures [5].

General Method for the Synthesis of Phosphoranes **3a–3g, 7b,e–g,** *and* **8b,e–g** (*see Table 5*)

To a solution of stoichiometric amounts of **1** or **6** and triethylamine in 50 mL of diethyl ether, each of the compounds **2** dissolved in 20 mL of diethyl ether was added. The triethylammonium chloride formed was filtered off and the solvent removed in vacuo.

3,5,7,9-Tetrakis(trifluoromethyl)-1-methyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**3a**). MS (50°C); *m/z* (%): 460 (59) [M$^+$], 441 (10) [M − F]$^+$, 363 (56) [M − CF_3CO]$^+$, 253 (83) [M − $CF_3C(O)CHC(O)CF_3$]$^+$, 233 (28) [M − $CF_3C(O)CHC(O)CF_3$ − HF]$^+$, 139 (32) [$CF_3C(O)CH_2CO^+$], 69 (100) [CF_3^+], and other fragments. Anal. calcd for $C_{11}H_5F_{12}O_4P$ (460.11): C, 28.71; H, 1.10; F, 49.55; P, 6.73. Found: C, 28.73; H, 0.91; F, 49.60; P, 6.73.

3,5,7,9-Tetrakis(trifluoromethyl)-1-ethyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**3b**). MS (20°C); *m/z* (%): 474 (14) [M$^+$], 455 (4) [M − F]$^+$, 377 (38) [M − CF_3CO]$^+$, 267 (23) [M − $CF_3C(O)CHC(O)CF_3$]$^+$, 139 (40) [$CF_3C(O)CH_2CO^+$], 69 (100) [CF_3^+], and other fragments. Anal. calcd for $C_{12}H_7F_{12}O_4P$ (474.14): C, 30.40; H, 1.49; F, 48.08; P, 6.53. Found: C, 30.52; H, 1.47; F, 48.20; P, 6.70.

3,5,7,9-Tetrakis(trifluoromethyl)-1-[(1-methyl)ethyl]-2,6,10,11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**3c**). MS (60°C); *m/z* (%): 488 (12) [M$^+$], 469 (4) [M − F]$^+$, 69 (23) [CF_3^+], 43 (100) [$(CH_3)_2CH^+$], and other fragments. Anal. calcd for $C_{13}H_9F_{12}O_4P$ (488.17): C, 31.99; H, 1.86; F, 46.70; P, 6.34. Found: C, 32.30; H, 1.87; F, 46.20; P, 6.40.

3,5,7,9-Tetrakis(trifluoromethyl)-1-[(1,1-dimethyl)ethyl]-2,6,10,11-tetraoxa-1-phospha-(V) tricyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**3d**). MS (50°C); *m/z* (%): 502 (1) [M$^+$], 487 (4) [M − CH_3]$^+$, 405 (1) [M − CF_3CO]$^+$, 139 (5) [$CF_3C(O)CH_2CO^+$], 69 (8) [CF_3^+], 57 (100) [$(CH_3)_3C^+$], and other fragments. Anal. calcd for $C_{14}H_{11}F_{12}O_4P$ (502.02): C, 33.48; H, 2.21; F, 45.40; P, 6.17. Found: C, 33.72; H, 2.16; F, 45.00; P, 6.24.

3,5,7,9-Tetrakis(trifluoromethyl)-1-trimethylsilylmethyl-2,6,10,11-tetraoxa-1-phospha-(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**3e**). MS (20°C); *m/z* (%): 532 (19) [M$^+$], 517 (32) [M − CH_3]$^+$, 435 (46) [M − CF_3CO]$^+$, 265 (100) [M − $CF_3C(O)CHC(O)CF_3$ − $SiMe_3$]$^+$, 75 (83) [Me_2SiCH_2]$^+$, 69 (87) [CF_3^+], and other fragments. Anal. calcd for $C_{14}H_{13}F_{12}O_4PSi$ (532.30): C, 31.59; H, 2.46; F, 42.83; P, 5.82. Found: C, 31.67; H, 2.33; F, 43.20; P, 5.75.

The X-ray structural study of compound **3e** [15], $C_{14}H_{13}F_{12}O_4PSi$ (532.30) [single crystal 0.4 × 0.6 × 0.7 mm, orthorhombic $P2_12_12_1$ with a = 908.4(3), b = 1028.6(3), c = 2340.6(6) pm, V = 2186.3(11) Å^{-3}, Z = 4, D(calc) = 1.617 Mg/m^3, absorption coefficient 0.300 mm^{-1}, difference electron density 0.48 e·A^{-3} and −0.49 e·Å^{-3}], was carried out in a 2 θ-range 5.0–50.0° at 296 K, reflections collected 6356, independent reflections 2872 (R_{int} = 1.23%), observed reflections 1538 [F > 3.0σ(F)]; goodness of fit 0.67; final R

TABLE 5 Experimental Details for the Preparation of Compounds **3a–3e, 7b,e–g,** and **8b,e–g**

R	*Reactants [g (mmol)]*	*Reaction Time (h)/ Temperature (°C)*	*Mp (°)*	*Yield [g (%)]*
3a Me	**2a:** 3.8 (32) **1:** 13.5 (64)	3 / −30	18	6.2 (58)[a]
3b Et[b]	**2b:** 3.3 (25) **1:** 10.4 (50)	3 / −20		7.1 (60)
3c *i*Pr[b]	**2c:** 3.4 (23) **1:** 9.8 (46)	48 / 20		9.3 (81)[c]
3d *t*Bu[b]	**2d:** 4.6 (29) **1:** 12.0 (58)	36 / 20		3.6 (25)
3e CH_2SiMe_3	**2e:** 4.9 (26) **1:** 10.8 (52)	4 / 0	67	8.5 (61)[a]
7b/8b Et[b,d]	**2b:** 3.7 (28) **6:** 8.6 (56)	4 / −20		7.7 (75)
7e/8e CH_2SiMe_3[b,e]	**2e:** 3.3 (18) **6:** 5.4 (35)	12 / 20		7.0 (94)
7f/8f CH_2Ph[b,f]	**2f:** 4.8 (25) **6:** 10.5 (50)	3 / 0	55	8.7 (81)
7g/8g Ph[b,g]	**2g:** 5.1 (29) **6:** 9.2 (58)	2 / 0	61	9.1 (76)

[a] Recrystallized from *n*-hexane and chloroform.
[b] Viscous liquid, bp or mp not determined.
[c] Recrystallized from *n*-hexane / diethylether (3:5).
[d] **7b**:**8b** = 4.2:1.
[e] **7e**:**8e** = 6.7:1.
[f] Isomer **7f** could be isolated by fractionating crystallization from diethylether; **7f**:**8f** = 6.7:1.
[g] Isomer **7g** could be isolated by fractionating crystallization from diethylether; **7g**:**8g** = 10.1:1.

values **R** = 3.49%, *w***R** = 2.68%; **R** value (all reflections) 8.02%, *w***R** = 3.75%, largest difference peak 0.22 e·Å^{-3}, largest difference hole −0.26 e·Å^{-3}.

2-Oxo-2-phenyl-3,5-dihydroxy-3,5-bis(trifluoromethyl)-1,2,$\lambda^5\sigma^4$-oxaphospholane (**4**). To a solution of 5.22 g (10 mmol) of **3g** in 20 mL of diethyl ether, 0.36 g (20 mmol) of water was added at 0°C. After the mixture had been allowed to stand for 5 hours at ambient temperature, the volatile materials were removed in vacuo. The remaining colorless solid was recrystallized from acetonitrile yielding 1.10 g (30%) **4** (mp 122°C). MS (110°C); *m/z* (%): 332 (42) [M − $H_2O]^+$, 331 (32) [M − H_2O − $CF_3]^+$, 161 (55) [$C_6H_5P(O)(F)OH^+$], 141 (100) [$C_6H_5P(O)OH^+$], 77 (98) [$C_6H_5^+$], 69 (57) [CF_3^+], and other fragments. ^{1}H NMR (CD_3CN): δ = 3.00 [broad, 2H, CH_2], 4.65 [broad, 2H, OH], 7.50–8.25 [m, 5H, C_6H_5]. ^{19}F NMR (CD_3CN): δ = −73.54 [s, 3F, C(5)F_3], −84.34 [s, C(3)F_3], ^{31}P NMR (CD_3CN): δ = 55.4. Anal. calcd for $C_{11}H_9F_6O_4P$ (350.15): C, 37.73; H, 2.59; F, 32.55; P, 8.85. Found: C, 37.90; H, 2.71; F, 32.50; P, 9.00.

The X-ray structural study of compound **4** [15], $C_{11}H_9F_6O_4P$ (350.15) [single crystal 0.35 × 0.6 × 0.4 mm, monoclinic $P2_1/n$ with a = 1450.2(5), b = 589.9(5), c = 1583.0(5) pm, β = 96.57(3)°, V = 1345.3(7) Å^{-3}, Z = 4, D (calc) = 1.729 Mg/m^3, absorption coefficient 0.292 mm^{-1}, difference electron density 0.30 e·Å^{-3} and −0.20 e·Å^{-3}], was carried out in a 2 θ-range 5.0–50.0° at 153 K, reflections collected 2794, independent reflections 2347 (R_{int} = 1.48%), observed reflections 1629 [F > 4.0σ(F)]; goodness of fit 0.67; final R values **R** = 3.49%, *w***R** = 2.68%; **R** value (all reflections) 8.02%, *w***R** = 3.75%, largest difference peak 0.51 e·Å^{-3}, largest difference hole −0.55 e·Å^{-3}.

3,5,7,9-Tetrakis(trifluoromethyl)-9-methoxy-1-phenyl-2,6,10,11-tetraoxa-1-phospha(V)-tricyclo-[5.3.1.0^{1,5}]-undeca-3-ene (**5**). To a solution of 3.6 g (0.007 mmol) of the phosphorane in 30 mL of diethyl ether, 0.5 g (0.014 mmol) of methanol was added at 0°C. After 2 hours, the solution was allowed to warm to ambient temperature and was then stirred for 12 hours. The volatile materials were removed in vacuo. The remaining yellow solid containing the two isomers **5A** and **5B** (**A**:**B** = 1:1) underwent a fractional crystallization from diethyl ether/hexane (1:1) solution; 1.3 g (32%) **5A** was obtained as a colorless solid (mp 86°C). MS (**5A**) (20°C); *m/z* (%): 554 (28) [M^+], 539 (9) [M − F]$^+$, 523 (3) [$CH_3CO]^+$, 457 (17) [M − $CF_3CO]^+$, 443 (19) [M − $CF_3C(O)CH_2]^+$, 331 (43) [M − $CF_3C(O)CH_2C(OCH_3)CF_3]^+$, 263 (25) [M − $CF_3C(O)CH_2C(OCH_3)CF_3$ − $CF_3]^+$, 77 (100) [$C_6H_5^+$], and other fragments. ^{1}H NMR (**5A**) ($CDCl_3$): δ = 2.70 [s, 2H, CH_2], 3.00 [q, 3H, CH_3], 6.00 [d, 1H, C(4)H,

$^3J_{\mathrm{PH}}$ = 29.9 Hz), 7.40–8.60 [m, 5H, C$_6$H$_5$]. ^{19}F NMR (CDCl$_3$) (**5A**): δ = −77.37 [s, 3F, C(3)F$_3$], −77.42 [dq, 3F, C(5)F$_3$, $^3J_{\mathrm{PF}}$ = 7.5, J_{FF} = 7.0 Hz], −85.10 [s, C(9)F$_3$], −89.00 [q, 3F, C(7)F$_3$, J_{FF} = 7.0 Hz]; (**5B**) (CDCl$_3$): δ = −76.62 [s, 3F, C(3)F$_3$], −77.20 [dq, 3F, C(5)F$_3$, $^3J_{\mathrm{PF}}$ = 7.8, J_{FF} = 6.9 Hz], −85.50 [s, C(9)F$_3$], −88.50 [q, 3F, C(7)F$_3$, J_{FF} = 6.9 Hz]; ^{31}P NMR (CDCl$_3$) (**5A**): δ = −14.9 (q); (**5B**) −13.0. Anal. calcd for C$_{17}$H$_{11}$F$_{12}$O$_5$P (554.23): C, 36.84; H, 2.00; F, 41.14; P, 5.59. Found: C, 36.98; H, 2.35; F, 40.50; P, 5.74.

The X-ray structural study of compound **5A** [15], C$_{17}$H$_{11}$F$_{12}$O$_5$P (554.23) [single crystal 0.5 × 0.45 × 0.7 mm, triclinic P $\bar{1}$ with a = 981.8(2), b = 1003.4(3), c = 1243.7(4) pm, α = 70.59(2), β = 78.54(2), γ = 61.04(2)°, V = 1009.8(5) Å^{-3}, Z = 2, D (calc) = 1.823 Mg/m^3, absorption coefficient 0.276 mm^{-1}], was carried out in a 2 θ-range 5.0–55.0° at 153 K, reflections collected 10150, independent reflections 4655 (R_{int} = 1.02%), observed reflections 3156 [F > 6.0σ(F)]; goodness of fit 2.49; final R values **R** = 5.91%, w**R** = 6.85%; **R** value (all reflections) 9.42%, w**R** = 10.35%, largest difference peak 0.61 e·Å^{-3}, largest difference hole −0.52 e·Å^{-3}.

Attempted Thermolysis of Compound **3g.** Compound **3g** (3.5 g, 6.8 mmol) was heated for 20 hours at 50°C. No decomposition was observed.

Attempted Trapping of Intermediate **A** (*R = Me*). The reaction mixture (see Table 5) was cooled to 60°C 20 minutes after the start of the reaction, and 10.6 g (64 mmol) of hexafluoroacetone was added. After the mixture had been warmed to ambient temperature for 2 hours and the volatile materials removed in vacuo, only compound **3a** was found.

3,7-Dimethyl-5,9-bis(trifluoromethyl)-1-ethyl-2,6,10,11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**7b**) *and 3,9-Dimethyl-5,7-bis(trifluoromethyl)-1-ethyl-2,6,10,11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene* (**8b**). MS (**7b, 8b**) (60°C); m/z (%): 366 (45) [M$^+$], 347 (5) [M − F]$^+$, 323 (5) [M − CH$_3$CO]$^+$, 154 (22) [CF$_3$C(O)CH$_2$C(O)CH$_3^+$], 69 (87) [CF$_3^+$], 43 (100) [CH$_3$CO$^+$], and other fragments. Anal. calcd for C$_{12}$H$_{13}$F$_6$O$_4$P (366.20): C, 39.36; H, 3.58; F, 31.13; P, 8.46. Found: C, 39.71; H, 3.60; F, 31.00; P, 8.52.

3,7-Dimethyl-5,9-bis(trifluoromethyl)-1-trimethylsilylmethyl-2,6,10,11-tetraoxa-1-phospha(V) tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**7e**) *and 3,9-Dimethyl-5,7-bis(trifluoro-methyl)-1-trimethylsilylmethyl-2,6,10,11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene* (**8e**). MS (**7e, 8e**) (60°C);m/z (%): 424 (1) [M$^+$], 409 (1) [M − CH$_3$]$^+$, 405 (1) [M − F]$^+$, 352 (18) [M − Me$_3$SiCH$_2$]$^+$, 139 (22) [CF$_3$C(O)CH$_2$CO$^+$], 69 (28) [CF$_3^+$], 43 (100) [CH$_3$CO$^+$], and other fragments. Anal. calcd for C$_{14}$H$_{19}$F$_6$O$_4$PSi (424.35): C, 39.63; H, 4.51; F, 26.86; P, 7.30. Found: C, 39.71; H, 4.70; F, 27.00; P, 7.22.

3,7-Dimethyl-5,9-bis(trifluoromethyl)-1-phenylmethyl-2,6,10,11-tetraoxa-1-phospha(V)tricyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**7f**) *and 3,9-Dimethyl-5,7-bis(trifluoromethyl)-1-phenylmethyl-2,6,10, 11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene* (**8f**). MS (**7f, 8f**) (40°C); m/z (%): 428 (3) [M$^+$], 409 (1) [M − F]$^+$, 385 (1) [M − CH$_3$CO]$^+$, 231 (8) [M − CF$_3$C(O)CH$_2$C(O)CH$_3$ − CH$_3$CO]$^+$, 91 (100) [C$_6$H$_5$CH$_2^+$], 43 (33) [CH$_3$CO$^+$], and other fragments. Anal. calcd for C$_{17}$H$_{15}$F$_6$O$_4$P (428.27): C, 47.68; H, 3.53; F, 26.62; P, 7.23. Found: C, 47.46; H, 3.65; F, 26.30; P, 7.38.

3,7-Dimethyl-5,9-bis(trifluoromethyl)-1-phenyl-2,6,10,11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene (**7g**) *and 3,9-Dimethyl-5,7-bis(trifluoromethyl)-1-phenyl-2,6,10,11-tetraoxa-1-phospha(V)tri-cyclo-[5.3.1.0^{1,5}]-undeca-3,8-diene* (**8g**). MS (**7g, 8g**) (30°C); m/z (%): 414 (93) [M$^+$], 395 (11) [M − F]$^+$, 371 (52) [M − CH$_3$CO]$^+$, 329 (23) [M − CF$_3$O]$^+$, 317 (13) [M − CF$_3$CO]$^+$, 261 (17) [M − CF$_3$C(O)CHC(O)CH$_3$]$^+$, 231 (20) [M − CF$_3$C(O)CHC(O)CH$_3$ − CH$_2$O]$^+$, 154 (42) [CF$_3$C(O)CH$_2$C(O)CH$_3^+$], 77 (24) [C$_6$H$_5^+$], 69 (79) [CF$_3$], 43 (100) [CH$_3$CO$^+$], and other fragments. Anal. calcd for C$_{16}$H$_{13}$F$_6$O$_4$P (414.24): C, 46.39; H, 3.16; F, 27.52; P, 7.48. Found: C, 46.25; H, 3.18; F, 27.50; P, 7.37.

The X-ray structural study of compound **7g** [15], C$_{16}$H$_{13}$F$_6$O$_4$P (414.24) (single crystal 0.4 × 0.5 × 0.7 mm, monoclinic P2$_1$/n with a = 803.6(3), b = 783.5(3), c = 2814.4(9) pm, β = 97.15(3)°, V = 1758.3(11) Å^{-3}, Z = 4, D (calc) = 1.565 Mg/m^3, absorption coefficient 0.237 mm^{-1}, was carried out in a 2 θ-range 5.0–50.0° at 296 K, reflections collected 3787, independent reflections 3116 (R_{int} = 1.27%), observed reflections 1450 [F > 4.0σ(F)]; goodness of fit 1.47; final R values **R** = 6.62%, w**R** = 6.59%; **R** value (all reflections) 15.00%, w**R** = 10.01%, largest difference peak 0.38 e·Å^{-3}, largest difference hole −0.40 e·Å^3.

ACKNOWLEDGMENTS

We thank the Hoechst AG and the Solvay Fluor and Derivate GmbH for donation of precious starting materials, Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and Dipl.-Chem. Jan Przyborowski for helping with the X-ray structural data.

REFERENCES

[1] R. Francke, G.-V. Röschenthaler, *Chemiker-Ztg., 113,* 1989, 183–186.

[2] R. Francke, W. S. Sheldrick, G.-V. Röschenthaler, *Chem. Ber., 122,* 1989, 301–306.

[3] E. S. Mukhametov, L. V. Stepashkina, E. E. Korshin, R. R. Shagidullin, N. I. Rizpolozhenskii, *Zh. Obshch. Khim., 53,* 1983, 1274–1281.

[4] W. V. Dahlhoff, K. M. Taba, R. Mynott, *Z. Naturforsch., 44b,* 1989, 41–46.

[5] G. Bekiaris, G.-V. Röschenthaler, *Z. Naturforsch., 45b,* 1990, 1460–1462.

[6] V. G. Ratner, E. Lork, K. I. Pashkevich, G.-V. Röschenthaler, *J. Fluorine Chem., 85,* (1997), 129–133.

[7] M. Basetti, G. Cerichelli, B. Floris, *Tetrahedron, 44,* 1988, 2997–3004.

[8] J. B. Hendrickson, *J. Am. Chem. Soc., 89,* 1967, 7036–7043.

[9] D. Cremer, J. A. Pople, *J. Am. Chem. Soc., 97,* 1975, 1354–1358.

[10] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor: in A. J. C. Wilson (ed); *International Tables for Crystallography* Dordrecht, vol. C, pp. 691–706 (1995).

[11] S. Berger, S. Braun, H.-O. Kalinowski: in NMR-Spektroskopie von Nichtmetallen, *^{31}P-NMR-Spektroskopie,* Thieme, Stuttgart, pp. 48–50, 59–62 (1993).

[12] R. D. Hund, U. Behrens, G.-V. Röschenthaler, *Phosphorus Sulfur Silicon, 69,* 1992, 119–127.

[13] R. Bohlen, J. Heine, W. Kuhn, W. Offermann, J. Stelten, W. G. Bentrude, G.-V. Röschenthaler, *Phosphorus Sulfur, 27,* 1986, 313–320.

[14] H. Günter: *NMR-Spektroskopie,* Thieme, Stuttgart, p. 113 (1983).

[15] Further details of the crystal structure investigations are available from Fachinformationsdienst Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-59428 and the journal citation.