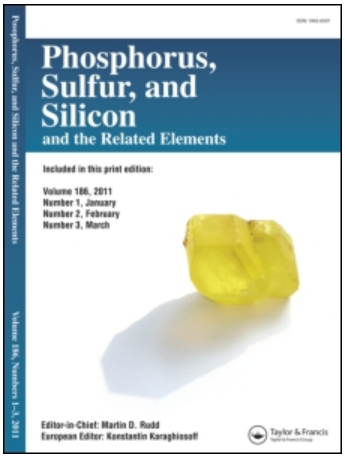

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Görg, Michaela , Lork, Enno , Kolomeitsev, Alexander A. and Röschenthaler, Gerd-Volker(1997) 'HEXAFLUOROACETONE ADDITION TO AMIDOPHOSPHITES', Phosphorus, Sulfur, and Silicon and the Related Elements, 127: 1, 15 — 25
To link to this Article: DOI: 10.1080/10426509708040492
URL: http://dx.doi.org/10.1080/10426509708040492

Phosphorus, Sulphur, and Silicon, 1997, Vol. 127, pp. 15–25
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HEXAFLUOROACETONE ADDITION TO AMIDOPHOSPHITES

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(Received 8 July 1997)

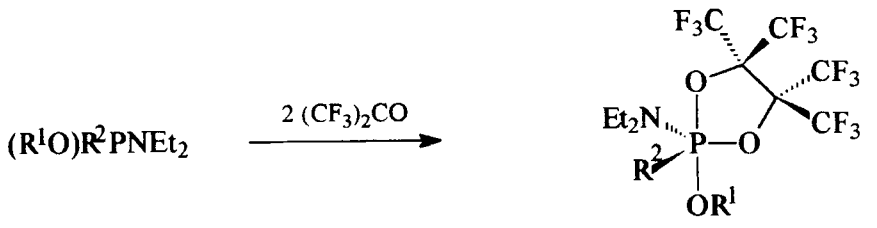
Selected mono- and bis(diethylamido) phosphites, $Et_2NP(OR^1)_2$, **1** and **2** $(Et_2N)_2POR^1$ (R^1 = OCH_2CF_3, $OCH(CF_3)_2$, OCH_2Ph; OC_6F_5) react with hexafluoroacetone to give 1,3,2$\lambda^5\sigma^5$-dioxaphospholanes **3** and **4** without any fluorine abstraction to furnish λ^5P-F bonds. Single crystal X-ray structure analysis was conducted on one phosphorane obtained from $(Et_2N)_2POC_6F_5$ and $(CF_3)_2CO$ [monoclinic, $P2_1/n$, a = 1132.5(2), b = 1633.8(3), c = 1461.8(4) pm, α = 90, β = 104.11, γ = 90°] exhibiting a slightly distorted geometry at phosphorus.

Keywords: Mono- and bis(diethylamido) phosphites; hexafluoroacetone; 1,3,2$\lambda^5\sigma^5$-dioxaphospholanes; X-ray structure analysis

INTRODUCTION

Amidophosphites are useful reagents in bioorganic chemistry.[1,2] Recently we found a convenient method for the transformation of alcohols into alkyl trifluoromethyl sulfides using bis(diethylamido) phosphites, $(Et_2N)_2POCH_2R$ (R = Ph, C(O)OEt).[3] We have taken advantage of $(Et_2N)_2POCH_2R$ (R = CH_3, CF_3, Ph) as versatile reactants in fluoroorganic chemistry.[4] There is only few information available for the reaction of hexafluoroacetone and perfluorinated α,β-diketones with mono- and bis(diethylamido) phosphites.[5–8] Since the nucleophilic hexamethylphosphorus(III) triamide abstracts fluorine from hexafluoroacetone to furnish difluorotris(dimethylamino) phosphorane, fluoro-bis(dimethylamido) phosphate and other products.[9] we here investigate the behavior of a number

*Corresponding author.



1a, c
2a - d

3a, c
4a - d

	R^1	R^2
1a, 3a	CF_3CH_2	CF_3CH_2O
1c, 3c	$PhCH_2$	$PhCH_2O$
2a, 4a	CF_3CH_2	Et_2N
2b, 4b	$(CF_3)_2CH$	Et_2N
2c, 4c	$PhCH_2$	Et_2N
2d, 4d	C_6F_5	Et_2N

of differently substituted, less nucleophilic bis- and mono-amidophosphites, which could render 1,3,2$\lambda^5\sigma^5$-dioxaphospholanes.

RESULTS AND DISCUSSION

The $\lambda^3\sigma^3$P derivatives $Et_2NP(OR^1)_2$, **1a–d** [R^1 = OCH_2CF_3 (**1a**),[10] $OCH(CF_3)_2$ (**1b**),[6] OCH_2Ph (**1c**),[11] OC_6F_5 (**1d**)] and $(Et_2N)_2POR^1$, **2a–d** [R^1 = OCH_2CF_3 (**2a**), $OCH(CF_3)_2$ (**2b**), OCH_2Ph (**2c**), OC_6F_5 (**2d**)] reacted with hexafluoroacetone to furnish 1,3,2$\lambda^5\sigma^5$-dioxaphospholanes **3a–c**[12] and **4a–d**, thermally stable, colorless viscous liquids in high yields, with the exception of amidophosphite **1d**, which did not give the corresponding phosphorane under the conditions applied. No fluorine abstraction has been observed to yield λ^5P-F bonds.

The structures of the new amidophosphites **1d**, **2a–d** and the new phosphoranes **3a**, **3c**, **4a–d** have been established by elemental analyses, mass spectrometry and NMR spectroscopy. The NMR data of the phosphites and the resulting

TABLE I The main geometrical parameters of **4d**

Bond lengths (pm)			
P(1)-N(1)	163.0(3)	C(15)-O(3)	135.5(5)
P(1)-N(2)	164.0(3)	C(1)-C(2)	156.0(6)
P(1)-O(1)	174.2(3)	C(1)-C(4)	161.1(6)
P(1)-O(2)	168.2(3)	N(1)-C(7)	147.9(5)
P(1)-O(3)	170.8(3)	N(1)-C(9)	149.0(5)
C(1)-O(1)	138.5(5)	C(2)-F(3)	133.3(5)
C(4)-O(2)	139.5(5)	C(16)-F(13)	135.5(4)
Bond angles (°)			
N(1)-P(1)-N(2)	111.9(2)	N(1)-P(1)-O(2)	130.9(2)
N(2)-P(1)-O(2)	117.2(2)	N(1)-P(1)-O(3)	94.6(2)
N(2)-P(1)-O(3)	90.5(2)	O(2)-P(1)-O(3)	83.82(13)
N(1)-P(1)-O(1)	89.30(14)	N(2)-P(1)-O(1)	97.7(2)
O(2)-P(1)-O(1)	85.76(13)	O(3)-P(1)-O(1)	168.89(14)
C(1)-O(1)-P(1)	118.1(2)	O(1)-C(1)-C(2)	109.0(3)
O(1)-C(1)-C(3)	107.8(3)	C(2)-C(1)-C(3)	106.8(4)
O(1)-C(1)-C(4)	101.9(3)	C(2)-C(1)-C(4)	114.8(3)
C(3)-C(1)-C(4)	116.1(4)	C(7)-N(1)-C(9)	112.2(3)
C(7)-N(1)-P(1)	118.7(2)	C(9)-N(1)-P(1)	128.4(3)
P(1)-O(3)-C(15)	129.5(3)		

phosphoranes were consistent with the constitution proposed. The δ_P and δ_F values were in the expected range.[13,14] The large coupling constants $^4J_{PF}$ = 35.2 (**1d**), 45.3 Hz (**2d**) are comparable with 30 Hz found in the case of $P(OC_6F_5)_3$.[15]

The X-ray structure investigation of **4d** revealed a slightly distorted trigonal bipyramid at phosphorus [bond angles N(1)-P(1)-N(2) 111.9(2), N(2)-P(1)-O(2) 117.2(2), O(2)-P(1)-O(1) 85.76(13), N(1)-P(1)-O(2) 130.9(2), O(3)-P(1)-O(1) 168.89(14)°] with 33.2% deviation along the Berry pseudorotation coordinate with O(2) as a pivot[16] (see Table I and Figure 1). The bond lengths P(1)-N(1) 163.0(3) and P(1)-N(2) 164.0(3) pm for the two equatorial diethylamino-groups are similar, the corresponding values for the axial substituents are P(1)-O(1) 174.2(3) (endocyclic) and P(1)-O(3) 170.8(3) pm (exocyclic). The five-membered ring appeared in an $E_3 \rightarrow {}^4T_3$ conformation (Puckering parameters Q = 29.9 pm, Φ = 254.1°).[17] The geometry at both nitrogen atoms, N(1) (sum of angles 360.3°) and N(2) (sum of angles 359.6°) are found to be planar. The planar C(7)-N(1)-C(9) and C(11)-N(2)-C(13) units are turned by 29.2 and 38.2° relative to the O(1)-O(3) axis. The phosphorus atom was found 1.4 pm below the O(2)-N(1)-N(2) plane.

EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. Elemental analysis: Mikroanalytisches Laboratorium Beller, Göttingen. MS: MAT 8222 (EI, electron energy 70

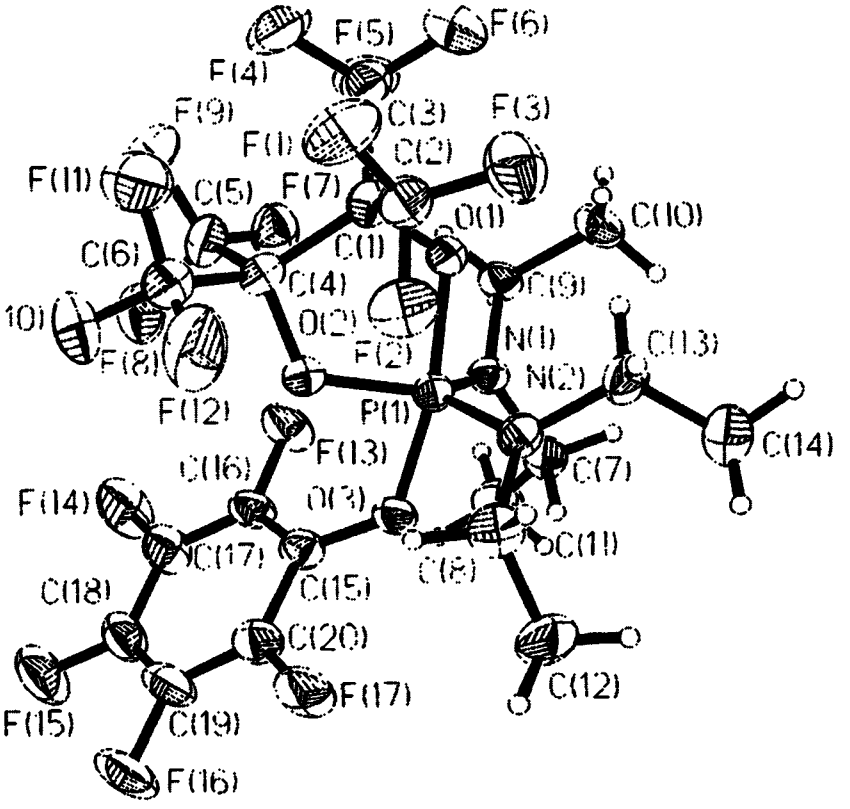


FIGURE 1 Molecular structure of **4d** (thermal ellipsoids with 50% probability)

eV). NMR: AC 80, operating at 80.13 MHz (^{1}H, internal standard TMS), 75.39 MHz (^{19}F, internal standard CCl_3F), and 32.44 MHz (^{31}P, external standard 85% H_3PO_4). High field shifts from TMS, CCl_3F and 85% H_3PO_4 were given negative signs. The amidophosphites **1a–c**, **2c** were prepared according to literature procedures[10,6,11,3]

General method for the synthesis of phosphites **1d**, **2a**, **b**, **d** (see Table II): A solution of the appropriate alcohol and triethylamine in 20 ml diethylether was added during 30 minutes to a solution of Et_2NPCl_2 (or $(Et_2N)_2PCl$ respectively) in 20 ml diethylether at -30°C, stirred for 2 h and allowed to warm to ambient temperature and filtered. The solvent was removed and the remaining substance destilled *in vacuo* to give a colorless, analytically pure liquid.

TABLE II Experimental details for the preparation of compounds **1d**, **2a**, **b**, **d**

Compound	*Reactants [g (mmol)]*	*Yield [g (%)] b.p.(°C)/Torr*
1d	C_6F_5OH: 3.7 (20)	5.0(87)
	Et_2NPCl_2: 2.1 (10)	87/0.02
2a	CF_3CH_2OH: 2.0 (20)	5.5(89)
	$(Et_2N)_2PCl$: 4.2 (20)	89/0.02
2b	$(CF_3)_2CHOH$: 3.4 (20)	6.5 (86)
	$(Et_2N)_2PCl$: 4.2 (20)	86/0.02
2d	C_6F_5OH: 3.7 (20)	6.9 (87)
	$(Et_2N)_2PCl$: 4.2 (20)	87/0.02

Diethylamido-bis(1,1,1-trifluoroethyl)phosphite (1a)[9]

MS (150°C) *m/z* (%): 301 (M^+, 50), 222 ($M^+ - NEt_2$, 100), 202 ($M^+ - OCH_2CF_3$, 70), 130 (M^+-NEt_2-OCH_2CF_3, 39), 103 (M^+-2 OCH_2CF_3, 33), 99 ($CF_3CH_2O^+$, 21), 72 (Et_2N^+, 24), 69 (CF_3^+, 27) and other fragments. NMR: ^1H: δ = 0.90 (CH_3, t, 6 H, $^3J_{HH}$ = 6.8 Hz), 2.80 (CH_2, q, 4 H), 3.60 (CH_2CF_3, q, 4 H, $^3J_{FH}$ = 8.3 Hz); ^{19}F: δ = −79.6; ^{31}P: δ = 152.4.

Diethylamido-bis(phenylmethyl) phosphite (1c)[10]

MS (150°C) *m/z* (%): 317 (M^+, 44), 245 ($M^+ - NEt_2$, 38), 210 ($M^+ - OCH_2Ph$, 67), 138 ($M^+ - NEt_2 - OCH_2Ph$, 26), 103 ($M^+ - 2\ OCH_2Ph$, 41), 72 (Et_2N^+, 100) and other fragments. NMR: ^{31}P: δ = 148.4.

Diethylamido-bis(pentafluorophenyl) phosphite (1d)

MS (190°C) *m/z* (%): 469 (M^+, 36), 397 ($M^+ - NEt_2$, 36), 286 ($M^+ - OC_6F_5$, 100), 214 ($M^+ - NEt_2 - OC_6F_5$, 36), 103 ($M^+ - 2\ OC_6F_5$, 57), 72 (Et_2N^+, 48) and other fragments. NMR: ^1H: δ = 1.00 (CH_3, t, 6 H, $^3J_{HH}$ = 6.5 Hz), 2.90 (CH_2, q, 4 H), 3.60 (CH_2CF_3, q, 4 H, $^3J_{FH}$ = 8.3 Hz); ^{19}F: δ = −159.4 ÷ −161.3 (C_6F_5, *o*-F, m, 2 F), −166.0 ÷ −167.3 (C_6F_5, *p*-F, m, 1 F), −167.9 ÷ −169.5 (C_6F_5, *m*-F, m, 2 F); ^{31}P: δ = 151.8 ($^4J_{PF}$ = 35.2 Hz).

$C_{16}H_{10}F_{10}NO_2P$ (469.22)

Calcd. C 40.96 H 2.15 F 40.49 P 6.60%

Found C 41.03 H 2.13 F 40.20 P 6.64%

Bis(diethylamido)-1,1,1-trifluoroethyl phosphite (2a)

MS (150°C): *m/z* (%): 274 (M^+, 56), 245 ($M^+ - C_2H_5$, 2), 202 ($M^+ - NEt_2$, 100), 175 ($M^+ - OCF_3CH_2$), 16), 72 (Et_2N^+, 33), 69 (CF_3^+, 8) and other fragments. NMR: ^1H: δ = 1.00 (CH_3, t, 12 H, $^3J_{HH}$ = 6.7 Hz), 3.00 (CH_2, q,

8 H), 3.80 (CH_2CF_3, q, 2 H, $^3J_{FH}$ = 8.2 Hz); ^{19}F: δ = −79.4 ($^4J_{PF}$ = 5.9 Hz); ^{31}P: δ = 141.1.

$C_{10}H_{22}F_3N_2OP$ (274.17)

Calcd. C 43.70 H 8.10 F 20.80 P 11.30%

Found C 43.70 H 8.10 F 20.80 P 11.20%

Bis(diethylamido)-1,1,1,3,3,3-hexafluoroisopropyl phosphite (2b)

MS (150°C): *m/z* (%): 342 (M^+, 16), 270 (M^+ − 2 NEt_2, 100), 72 (Et_2N^+, 14), 69 (CF_3^+, 8) and other fragments. NMR: ^1H: δ = 0.90 (CH_3, t, 12 H, $^3J_{HH}$ = 7.1 Hz), 3.10 (CH_2, q, 8 H), 4.10 (CH, sep, 1 H, $^3J_{FH}$ = 6.2 Hz); ^{19}F: δ = −81.4 ($^4J_{PF}$ = 9.7 Hz); ^{31}P: δ = 153.0.

$C_{11}H_{21}F_6N_2OP$ (342.26)

Calcd. C 38.60 H 6.20 F 33.30 P 9.10%

Found C 38.60 H 6.20 F 33.60 P 8.90%

Bis(diethylamido)-phenylmethyl phosphite (2c)[3]

MS (150°C): *m/z* (%): 282 (M^+, 80), 239 (M^+ − NEt_2, 40), 224 (M^+ − C_2H_5, 14), 197 (M^+ − C_5H_5, 10), 91 ($C_6H_5CH_2^+$, 100), 77 ($C_6H_5^+$, 20), 72 (Et_2N^+, 24) and other fragments. NMR: ^{31}P: δ = 135.4.

Bis(diethylamido)-pentafluorophenyl phosphite (2d)

MS (150°C): *m/z* (%): 358 (M^+, 100), 286 (M^+ − NEt_2, 56), 251 (M^+ − OC_6F_5, 48), 179 (M^+ − OC_6F_5, − NEt_2, 56), 144 (M^+ − 2 OC_6F_5, 52), 72 (Et_2N^+, 32) and other fragments. ^1H: δ = 0.90 (CH_3, t, 12 H, $^3J_{HH}$ = 6.5 Hz), 2.80 (CH_2, q, 8 H); ^{19}F: δ = −158.0 ÷ −159.2 (C_6F_5, *o*-F, m, 2 F), −168.9 ÷ −170.0 (C_6F_5, *p*-F, m, 1 F), −170.1 ÷ −171.0 (C_6F_5, *m*-F, m, 2 F); ^{31}P: δ = 150.0 ($^4J_{PF}$ = 45.3 Hz).

$C_{14}H_{20}F_5N_2OP$ (358.29)

Calcd. C 46.93 H 5.63 F 26.51 P 8.64%

Found C 47.06 H 5.65 F 26.70 P 8.51%

General method for the synthesis of phosphoranes **3a**, **3c** *and* **4a–d** (see Table III): Hexafluoroacetone and the appropriate phosphite in 10ml diethylether were allowed to react for 1 h at ambient temperature. The volatile were removed and the remaining substances destilled *in vacuo* to give colorless liquids(solid in the case of **4d**).

TABLE III Experimental details for the preparation of compounds **3a**, **3c** and **4a–d** (HFA ≡ $(CF_3)_2CO$)

Compound	*Reactants [g (mmol)]*	*Yield [g (%)] b.p.(°C)/Torr; m.p.(°C)*
3a	**1a**: 1.8 (6)	3.8 (100)
	HFA: 2.0 (12)	37/0.001
3c	**1c**: 1.9 (6)	3.9 (100)
	HFA: 2.0 (12)	36/0.001
4a	**2a**: 1.6 (6)	3.6 (100)
	HFA: 2.0 (12)	38/0.001
4b	**2b**: 2.1 (6)	4.1 (100)
	HFA: 2.0 (12)	37/0.001
4c	**2c**: 1.7 (6)	3.7 (100)
	HFA: 2.0 (12)	39/0.001
4d	**2d**: 2.1 (6)	4.1 (100)
	HFA: 2.0 (12)	*46*

2-Diethylamino-2-bis(trifluoroethoxy)-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^{5}σ^5-dioxaphospholane (3a)

MS (200°C): *m/z* (%): 467 (M^+, 48), 395 ($M^+ - NEt_2$, 44), 368 ($M^+ - OCF_3CH_2$, 56), 295 ($M^+ - NEt_2, - OCF_3CH_2$, 100), 269 ($M^+ - 2\,OCF_3CH_2$, 48), 197 ($M^+ - 2\,OCF_3CH_2 - NEt_2$, 40), 72 ($Et_2N^+$, 48) and other fragments. ^{1}H: δ = 1.00 (CH_3, t, 6 H, $^3J_{HH}$ = 6.7 Hz), 2.80 (CH_2, q, 4 H), 3.70 (CH_2CF_3, q, 4 H, $^3J_{FH}$ = 7.9 Hz); ^{19}F: δ = −72.6 (CF_3, 12 F), −79.8 (CF_3, 3 F); ^{31}P: δ = −47.6.

$C_{11}H_{14}F_{12}NO_2P$ (467.19)
Calcd. C 26.56 H 2.23 F 54.01 P 4.80%
Found C 26.43 H 2.38 F 54.60 P 5.05%

2-Diethylamino-2,2-bis(phenylmethyloxy)-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^{5}σ^5-dioxaphospholane (3c)

MS (200°C): *m/z* (%): 483 (M^+, 60), 411 ($M^+ - NEt_2$, 42), 376 ($M^+ - OC_7H_7$, 63), 304 ($M^+ - OC_7H_7 - NEt_2$, 57), 269 ($M^+ - 2\,C_7H_7$, 100), 197 ($M^+ - 2\,OC_7H_7, - NEt_2$, 30), 72 ($Et_2N^+$, 36) and other fragments. ^{1}H: δ = 0.90 (CH_3, t, 6 H, $^3J_{HH}$ = 6.6 Hz), 2.70 (CH_2, q, 4 H), 4.50 (CH_2Ph, q, 4 H, $^3J_{PH}$ = 7.3 Hz), 6.9–7.8 (Ph, m, 10 H); ^{19}F: δ = −72.0 (CF_3, 12 F); ^{31}P: δ = −42.8.

$C_{18}H_{24}NO_2P$ (483.39)
Calcd. C 44.39 H 3.72 F 35.10 P 4.77%
Found C 45.63 H 3.87 F 32.50 P 4.62%

2,2-Bis(diethylamino)-2-(1,1,1,-trifluoroethoxy)-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ⁵σ⁵-dioxaphospholane (4a)

MS (200°C): *m/z* (%): 440 (M^+, 47), 368 ($M^+ - NEt_2$, 46), 341 ($M^+ - OCH_2CF_3$, 100), 296 ($M^+ - 2\ NEt_2$, 65), 197 ($M^+ - OCH_2CF_3 - 2\ NEt_2$, 40), 72 ($Et_2N^+$, 34) and other fragments. ^1H: δ = 1.00 (CH_3, t, 12 H, $^3J_{HH}$ = 6.6 Hz), 2.70 (CH_2, q, 8 H), 3.60 (CH_2CF_3, q, 2 H, $^3J_{FH}$ = 7.8 Hz); ^{19}F: δ = −72.0 (CF_3, 12 F), −78.3 (CF_3, 3 F); ^{31}P: δ = −36.4.

$C_{13}H_{22}F_9N_2O_2P$ (440.29)

Calcd. C 31.70 H 3.66 F 47.00 P 5.11%

Found C 31.86 H 3.83 F 46.96 P 5.36%

2,2-Bis(diethylamino)-2-(1,1,1,3,3,3-hexafluoro)isopropoxy-4,4,5,5-tetrakis-(trifluoromethyl)-1,3,2-λ⁵σ⁵-dioxaphospholane (4b)

MS (200°C): *m/z* (%): 508 (M^+, 100), 436 ($M^+ - NEt_2$, 36), 341 ($M^+ -$; $OCH(CF_3)_2$, 63), 364 ($M^+ - 2\ NEt_2$, 54), 269 ($M^+ - OCH(CF_3)_2O - NEt_2$, 72), 197 ($M^+ - OCH(CF_3)_2 - 2\ NEt_2$, 34), 72 ($Et_2N^+$, 32) and other fragments. ^1H: δ = 1.00 (CH_3, t, 12 H, $^3J_{HH}$ = 6.5 Hz), 2.60 (CH_2, q, 8 H), 4.20 (CH, sep, 1 H, $^3J_{FH}$ = 6.2 Hz); ^{19}F: δ = −72.5 (CF_3, 12 F), −77.1 (CF_3, 6 F); ^{31}P: δ = −30.9.

$C_{14}H_{21}F_{12}N_2O_2P$ (508.29)

Calcd. C 31.02 H 3.22 F 51.95 P 4.71%

Found C 30.84 H 3.37 F 51.20 P 4.97%

2,2-Bis(diethylamino)-2-phenylmethyloxy-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-λ⁵σ⁵-dioxaphospholane (4c)

MS (200°C): *m/z* (%): 448 (M^+, 100), 376 ($M^+ - NEt_2$, 44), 341 ($M^+ - OC_7H_7$, 48), 304 ($M^+ - 2\ NEt_2$, 42), 269 ($M^+ - OC_7H_7, - NEt_2$, 81), 197 ($M^+ - OC_7H_7 - NEt_2$, 80), 72 (Et_2N^+, 36) and other fragments. ^1H: δ = 0.90 (CH_3, t, 12 H, $^3J_{HH}$ = 6.6 Hz), 2.70 (CH_2, q, 8 H), 4.40 (CH_2Ph, q, 2 H, $^3J_{PH}$ = 7.2 Hz), 6.8–7.8 (Ph, m, 5 H); ^{19}F: δ = −72.2 (CF_3, 12 F); ^{31}P: δ = −33.5.

$C_{18}H_{27}F_6N_2O_2P$ (448.39)

Calcd. C 41.05 H 4.43 F 37.10 P 5.04%

Found C 42.53 H 4.94 F 33.50 P 6.10%

TABLE IV Coordinates ($\times 10^{-4}$) for non-hydrogen atoms and their equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$)

	x	*y*	*z*	*U(eq)*
P(1)	2510(1)	3092(1)	5137(1)	27(1)
O(1)	1073(2)	3206(2)	5352(1)	29(1)
C(1)	690(4)	2623(3)	5904(3)	35(1)
C(2)	1087(4)	2894(3)	6959(3)	44(1)
F(1)	591(3)	2457(2)	7526(2)	65(1)
F(2)	2292(2)	2867(2)	7298(2)	52(1)
F(3)	781(3)	3673(2)	7045(2)	61(1)
C(3)	−743(4)	2612(3)	5626(4)	42(1)
F(4)	−1171(2)	1977(2)	6000(2)	62(1)
F(5)	−1197(2)	2602(2)	4715(2)	59(1)
F(6)	−1175(2)	3284(2)	5948(2)	68(1)
C(4)	1352(4)	1809(3)	5655(3)	35(1)
C(5)	651(5)	1338(3)	4759(4)	47(1)
F(7)	298(2)	1845(2)	4030(2)	51(1)
F(8)	1379(2)	798(2)	4488(2)	59(1)
F(9)	−313(2)	940(2)	4881(2)	65(1)
C(6)	1727(4)	1158(3)	6460(4)	49(1)
F(10)	2071(3)	459(2)	6151(2)	69(1)
F(11)	793(3)	980(2)	6821(2)	86(1)
F(12)	2624(3)	1397(2)	7143(2)	78(1)
O(2)	2413(2)	2109(2)	5451(2)	32(1)
N(1)	2019(3)	3549(2)	4124(2)	28(1)
C(7)	2895(4)	4014(3)	3725(3)	34(1)
C(8)	3210(4)	3652(3)	2860(3)	45(1)
C(9)	737(3)	3672(3)	3578(3)	32(1)
C(10)	177(4)	4467(3)	3793(3)	44(1)
N(2)	3246(3)	3723(2)	5952(2)	31(1)
C(11)	4431(4)	3517(3)	6604(3)	41(1)
C(12)	5536(4)	3885(3)	6345(4)	59(2)
C(13)	2687(4)	4491(3)	6155(3)	39(1)
C(14)	3232(5)	5264(3)	5858(4)	55(1)
O(3)	3851(2)	2784(2)	4908(2)	31(1)
C(15)	4157(4)	2049(3)	4605(3)	31(1)
C(16)	3502(4)	1626(3)	3841(3)	36(1)
F(13)	2398(2)	1905(2)	3361(2)	49(1)
C(17)	3898(4)	906(3)	3529(3)	43(1)
F(14)	3219(3)	504(2)	2794(2)	64(1)
C(18)	5021(4)	590(3)	3986(3)	44(1)
F(15)	5407(3)	−115(2)	3689(2)	68(1)
C(19)	5707(4)	1000(3)	4738(4)	48(1)
F(16)	6791(2)	698(2)	5205(2)	72(1)
C(20)	5291(4)	1713(3)	5049(3)	41(1)
F(17)	5980(2)	2094(2)	5810(2)	57(1)

2-Bis(diethylamino)-2-pentafluorophenoxy-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-λ⁵σ⁵-dioxaphospholane (4d)

MS (200°C): *m/z* (%): 524 (M^+, 68), 452 ($M^+ - NEt_2$, 30), 341 ($M^+ - OC_6F_5$, 100), 269 ($M^+ - OC_6F_5 - NEt_2$, 24), 380 ($M^+ - 2\ NEt_2$, 42), 197 ($M^+ - OC_6F_5 - 2\ NEt_2$, 18), 72 (Et_2N^+, 15) and other fragments. ^1H: δ =

1.00 (CH_3, t, 12 H, $^3J_{HH}$ = 6.5 Hz), 2.70 (CH_2, q, 8 H); ^{19}F: δ = −72.2 (CF_3, 12 F), −158.1 ÷ −160.1 (C_6F_5, *o*-F, m, 2 F), −168.9 ÷ −170.7 (C_6F_5, *p*-F, m, 1 F), −171.1 ÷ −172.2 (C_6F_5, *m*-F, m, 2 F); ^{31}P: δ = −31.1.

$C_{17}H_{20}F_{11}N_2O_2P$ (524.31)

Calcd. C 34.80 H 2.92 F 46.78 P 4.49%

Found C 34.82 H 2.91 F 46.30 P 4.53%

Crystal structure analysis of **4d**: $C_{20}H_{20}F_{17}N_2O_3P$ (the main crystallographic data are listed in Table IV), single crystal 0.3 × 0.4 × 0.5 mm, monoclinic $P2_1/n$, a = 1132.5(2), b = 1633.8(3), c = 1461.8(4) pm, α = 90, β = 104.11, γ = 90°, Z = 4, D = 1.748 Mg/m^3, absorption coefficient 0.254 mm^{-1}, difference electron density 320 and −346 e.nm^{-3}, θ-range 2.61 to 22.50°, reflections collected 4444, independent reflections 3428 (R_{int} = 0.0575), goodness of fit at F^2 0.921; final R values [$I > 2\sigma(I)$], R1 = 0.0497, wR2 = 0.1090; R value (all reflections) R1 = 0.0863, wR2 = 0.1207.

Acknowledgements

The Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is thanked for financial support, Hoechst AG, Frankfurt for precious chemicals.

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