

Short Communication

Crystal Structure of 1,1,1,3,3,3-Hexafluoro-2-propoxyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine

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Among all kinds of low-coordinated phosphorus compounds, iminophosphines $R^1-P=N-R^2$, are probably the most intensively explored species.^{1,2}

Depending on the substituents attached to the PN double bond, both the *cis* (*Z*) and *trans* (*E*) configuration, and even a nearly linear PN–R² geometry, have been observed.^{1–3} The structure of iminophosphines is strongly influenced by the electronic properties of the substituents R¹ and R². σ -Acceptors at the phosphorus atom shorten, σ -donors weaken the PN bond. A further consequence of a σ -electron acceptor bonded to the phosphorus atom is a reduction of the inversion barrier at the nitrogen atom and an increased stability of the *cis* (*Z*) configuration; for oxy-substituted iminophosphines, RO–P=N–R², so far only the *cis* (*Z*) configuration has been observed.^{2,3}

Here we report the synthesis and crystal structure of the first *trans* (*E*) oxy-substituted iminophosphine.

Experimental

Spectroscopic methods. All operations were performed under a dry argon atmosphere, with solvents dried over a Na/K alloy and distilled under argon.

³¹P-NMR. Bruker AMX 300 (121.422 MHz), external standard 85% H₃PO₄.

MS. Masslab VG 15–250 (direct insertion); the mass numbers refer to the most frequent isotope of the element.

1,1,1,3,3,3-hexafluoro-2-propoxyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine 3. One equivalent of the appropriate lithium alkoxide **2** in 100 ml diethylether was added dropwise to a solution of 3.0 g (9.2 mmol)

chloro-(2,4,6-tri-*tert*-butylphenylimino)phosphine **1** in 100 ml diethyl ether at –78 °C. The solvent was removed under vacuum and replaced by *n*-pentane. After removal of the lithium chloride precipitate, the solution was concentrated under vacuum and the target compound obtained as orange crystals.

Yield 2.4 g (57.1%); m.p. 104–105 °C. ³¹P-NMR (C₆D₆): δ = 122.4 ppm. MS: 20 eV (%), 150 °C: 457 (60) [*M*⁺], 442 (100) [*M*⁺ – CH₃], 246 (90), 57 (47) [*t*Bu⁺].

X-Ray single-crystal studies. Experimental details concerning the crystal structure determination including crystal data, data collection, structure determination and refinement for **3** are listed in Table 1. The crystals were sealed in a glass capillary because they showed a tendency to decay under atmospheric conditions. Unit cell parameters were obtained by carefully centering 25 reflections with $40 < 2\theta < 46^\circ$ using CuK α (λ = 1.541 78 Å) radiation. The data were corrected for Lorentz and polarisation factors and decay (11%). Absorption correction was made empirically using a ψ -rotation method. Structure determination and refinement were carried out using SHELXTL-Plus⁴ (structure solution), and SHELXL-93⁵ (refinement) program, respectively. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were localised by electron density determination, by using a riding model. Atomic scattering factors used were those included in the programs. Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2.

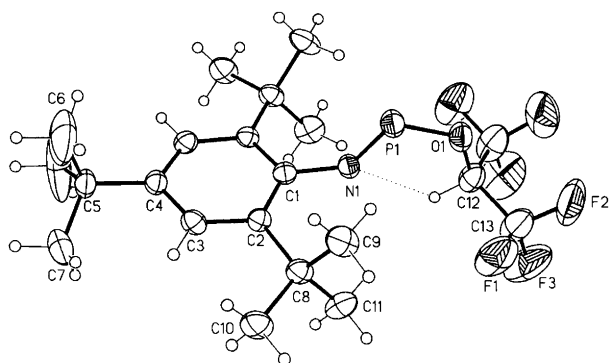
Results and discussion

The synthesis of 1,1,1,3,3,3-hexafluoro-2-propoxyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine (**3**) was performed by nucleophilic substitution at the phosphorus

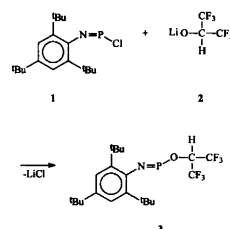
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Table 1. Structure determination summary for $C_{21}H_{30}F_6NOP$ (3).

Crystal data	
Compound	
Empirical formula	$C_{21}H_{30}F_6NOP$
Color; habit	Orange; plate
Crystal size (mm)	$0.15 \times 0.25 \times 0.45$
Crystal system	Monoclinic
Space group	P_2/m (No. 11)
Unit-cell dimensions	$a = 6.007(1) \text{ \AA}$ $b = 14.899(1) \text{ \AA}$ $c = 13.269(1) \text{ \AA}$ $\beta = 92.21(1)^\circ$ $1186.7(2) \text{ \AA}^3$
Volume	2
Z	457.4
Formula weight	1.28
Density (calc.) / $Mg \text{ m}^{-3}$	1.56
Absorption coefficient / mm^{-1}	480
F(000)	
Data collection	
Diffractometer used	Enraf-Nonius CAD4
Radiation	$CuK\alpha$ ($\lambda = 1.54178 \text{ \AA}$)
Temperature/K	293
Monochromator	Graphite
2θ range / $^\circ$	6.5–120.0
Scan type	$2\theta/\omega$
Standard reflections	2 (orientation) measured every 200 reflections 3 (intensity) measured every 120 min.
Index ranges	
	$0 \leq h \leq 6$ $-16 \leq k \leq 0$ $-14 \leq l \leq 14$
Reflections collected	
Independent reflections	2035
Reflections used in refinement	1841 ($R_{INT} = 0.048$)
Absorption correction	1840
	Empirical, ψ -scans; max. and min. transmission = 0.928/0.588
Solution and refinement	
System used	SHELXTL-Plus (solution) and SHELXL-93 (refinement)
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
No. of parameters refined	153
wR_2 (for 1840 data)	0.181
R_1	0.059 [for 1174 reflection with $I > 2\sigma(I)$]
Goodness of fit	1.02
Largest and mean Δ/σ	0.000, 0.000
Data-to-parameter ratio	12.0:1
Largest difference peak and hole / $e \text{ \AA}^{-3}$	0.30/–0.25

Fig. 1. Perspective view of 1,1,1,3,3,3-hexafluoro-2-propanoxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine (3).

atom of chloro-(2,4,6-tri-*tert*-butylphenylimino)phosphine (1)⁶ with the corresponding lithium alkoxide 2.



Compound 3 was obtained as orange crystals; its constitution was determined by X-ray structure analysis. The ^{31}P -NMR shift δ 122.4 ppm is located in the high-field range of iminophosphines bearing a σ -acceptor at the phosphorus atom as expected.^{2,3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) or $\text{C}_{21}\text{H}_{30}\text{F}_6\text{NOP}$ **3**.

Atom	x	y	z	$U(\text{eq})^a$
P(1)	4710(3)	2500	8114(1)	57(1)
O(1)	5632(7)	2500	9284(3)	63(1)
N(1)	2172(7)	2500	8142(3)	46(1)
C(1)	577(8)	2500	7326(4)	43(1)
C(2)	-240(6)	3325(2)	6942(3)	42(1)
C(3)	-1700(6)	3291(2)	6095(3)	48(1)
C(4)	-2425(9)	2500	5644(4)	46(1)
C(5)	-3891(10)	2500	4676(4)	57(2)
C(6)	-2420(17)	2500	3804(6)	173(6)
C(7)	-5352(16)	3298(5)	4599(6)	213(6)
C(8)	351(6)	4254(2)	7409(3)	51(1)
C(9)	2831(6)	4490(3)	7301(4)	71(1)
C(10)	-968(7)	5017(3)	6888(4)	70(1)
C(11)	-243(8)	4269(3)	8525(3)	73(1)
C(12)	4325(12)	2500	10138(5)	67(2)
C(13)	4807(14)	3344(4)	10722(4)	103(2)
F(1)	4435(8)	4053(2)	10151(3)	146(2)
F(2)	6922(9)	3401(3)	11040(3)	153(2)
F(3)	3655(10)	3402(3)	11525(3)	175(2)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond lengths (\AA) and angles ($^\circ$) for $\text{C}_{21}\text{H}_{30}\text{F}_6\text{NOP}$ (**3**).

P(1)–N(1)	1.526(4)	C(2) ⁱ –C(1)–N(1)	119.4(2)
P(1)–O(1)	1.628(4)	C(3)–C(2)–C(1)	117.1(3)
O(1)–C(12)	1.403(7)	C(3)–C(2)–C(8)	118.7(3)
N(1)–C(1)	1.419(6)	C(1)–C(2)–C(8)	124.2(3)
C(1)–C(2)	1.412(4)	C(4)–C(3)–C(2)	123.7(4)
C(1)–C(2) ⁱ	1.412(4)	C(3) ⁱ –C(4)–C(3)	116.6(5)
C(2)–C(3)	1.399(5)	C(3) ⁱ –C(4)–C(5)	121.7(2)
C(2)–C(8)	1.552(5)	C(3)–C(4)–C(5)	121.7(2)
C(3)–C(4)	1.386(4)	C(7) ⁱ –C(5)–C(7)	107.0(9)
C(4)–C(3) ⁱ	1.386(4)	C(7) ⁱ –C(5)–C(6)	108.4(6)
C(4)–C(5)	1.528(7)	C(7)–C(5)–C(6)	108.4(6)
C(5)–C(7) ⁱ	1.480(7)	C(7) ⁱ –C(5)–C(4)	112.3(4)
C(5)–C(7)	1.480(7)	C(7)–C(5)–C(4)	112.3(4)
C(5)–C(6)	1.483(10)	C(6)–C(5)–C(4)	108.3(6)
C(8)–C(10)	1.534(5)	C(10)–C(8)–C(11)	106.8(3)
C(8)–C(11)	1.537(5)	C(10)–C(8)–C(9)	105.9(3)
C(8)–C(9)	1.543(5)	C(11)–C(8)–C(9)	110.3(3)
C(12)–C(13)	1.499(6)	C(10)–C(8)–C(2)	111.9(3)
C(12)–C(13) ⁱ	1.499(6)	C(11)–C(8)–C(2)	109.9(3)
C(13)–F(3)	1.296(7)	C(9)–C(8)–C(2)	111.9(3)
C(13)–F(1)	1.314(6)	O(1)–C(12)–C(13)	108.3(4)
C(13)–F(2)	1.326(8)	O(1)–C(12)–C(13) ⁱ	108.3(4)
		C(13)–C(12)–C(13) ⁱ	114.0(6)
N(1)–P(1)–O(1)	106.3(2)	F(3)–C(13)–F(1)	109.6(6)
C(12)–O(1)–P(1)	126.1(4)	F(3)–C(13)–F(2)	105.6(5)
C(1)–N(1)–P(1)	128.8(4)	F(1)–C(13)–F(2)	105.8(6)
C(2)–C(1)–C(2) ⁱ	121.2(4)	F(3)–C(13)–C(12)	112.5(6)
C(2)–C(1)–N(1)	119.4(2)	F(1)–C(13)–C(12)	110.6(4)
		F(2)–C(13)–C(12)	112.5(6)

Symmetry transformations used to generate equivalent atoms: ⁱ $x - y + 1/2, z$.

Figure 1 shows the X-ray structure of **3** with numbering of the atoms; bond lengths and bond angles are collected in Table 3.

1,1,1,3,3,3-Hexafluoro-2-propanyloxy-(2,4,6-tri-*tert*-butylphenylimino)phosphine (**3**) has C_s -symmetry and is the first example of a *trans* (*E*) oxy-substituted iminophosphine. This special constitution can be explained by an intramolecular hydrogen bridge between the nitrogen atom and the alkoxy hydrogen atom [$\text{N1-H(C12)} = 2.37 \text{ \AA}$]. Furthermore, **3** possesses the shortest P–N bond [$1.526(4) \text{ \AA}$] ever observed in *trans* (*E*) iminophosphines. Other essential structural parameters are the P–O bond length [$1.628(4) \text{ \AA}$], the N1–C12 distance (2.90 \AA), the C12–H(C12)–N1 angle (114°), the C1–N1–P1 bond angle [$128.8(4)^\circ$] and the N1–P1–O1 bond angle [$106.3(2)^\circ$].^{2,3}

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