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(2-Fluorophenylimino)tri(1-pyrrolyl)phosphorane

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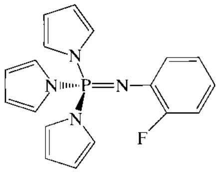
The P atom of the title compound, $C_{18}H_{16}FN_4P$, has a slightly distorted tetrahedral geometry. The P—N bond lengths range from 1.671 (3) to 1.680 (3) Å, while the P═N bond is 1.517 (3) Å. The pyrrolyl groups are arranged around the P atom in a chiral propeller-like geometry.

Comment

We have recently reported that iminophosphoranes of the type $Cl_3P{=}NAr$ (Ar is 2-fluorophenyl) are important main-group examples of well defined carbodiimide metathesis catalysts (Bell *et al.*, 2000). It is believed that these catalysts follow an addition–elimination pathway for double-bond metathesis. We produced pyrrolyl derivatives of the iminophosphoranes in an effort to rule out the possibility of HCl-mediated metathesis pathways that might arise from the decomposition of trichloroiminophosphoranes. Selection of the pyrrolyl moiety as a chloride replacement was prompted by Petersen's discussion of tripyrrolylphosphorus ligands (Moloy & Petersen, 1995). In particular, pyrrolyl is π-acidic, which allows replacement of chlorine without loss of electrophilicity at the phosphorus center, believed to be an important factor in the carbodiimide metatheses.



(I)

The structure determination of the title compound, (I), was undertaken to study the effect of substitution on significant features of the phosphorus center. We report herein the first example of a tripyrrolyl derivative of an iminophosphorane (Fig. 1). The only previous example of a pyrrolyl derivative is a dipyrrolylcyclophosphazene, namely 2,2,4,4,6,6-hexa(1-pyrrolyl)cyclotri(phosphazene) (Craig *et al.*, 1987). A notable aspect of the crystal structure reported here is the short P═N bond length [1.517 (3) Å], which is significantly shorter than in the dipyrrolylcyclophosphazene [1.583 (6) Å]. It is important to note that the P═N bond length is similar to that in chlorine-derivatized alkyl/aryliminophosphoranes, ranging from 1.505 (3) (Antipin *et al.*, 1985) to 1.557 (2) Å (Belaj, 1996).

P—N bond length has been correlated with the orbital electronegativity of the phosphorus substituents (Bullen & Tucker, 1972). The comparable P═N bond length of the trichloro- and tripyrrolyliminophosphoranes indicates a similar electronegativity of the phosphorus substituents.

The P atom is slightly distorted from tetrahedral geometry, with the bond angles around it varying from 101.93 (16) to 117.74 (17)°, the average value being 109.1 (2)°. The pyrrolyl groups make interplanar angles of 45.9 (3), 55.0 (3) and 63.4 (2)° with the 2-fluorophenyl ring. The P atom has chirality due to the propeller-like arrangement of the pyrrolyl rings, although no conclusion can be made about the absolute configuration as the Friedel pairs were not collected for this structure.

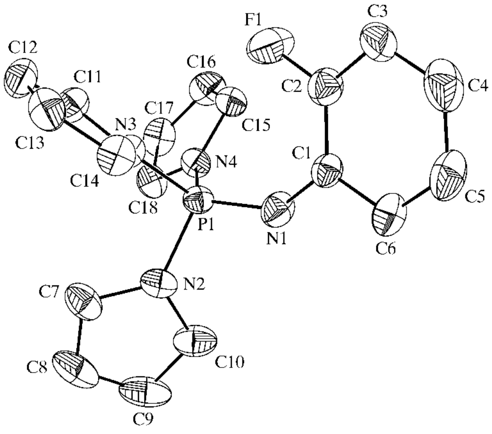


Figure 1
The structure of the title compound with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Experimental

Potassium pyrrolide (0.518 g, 4.93 mmol) was added slowly to a vigorously stirred solution of $Cl_3P{=}NAr$ (0.405 g, 1.643 mmol) in hexanes (45 ml) at 195 K. The mixture was stirred for 30 min at 195 K and then warmed to room temperature and stirred for an additional 14 h. Filtration yielded a colorless liquid that was reduced to 15 ml and cooled to 238 K. The precipitate was removed by filtration and the filtrate was again reduced in volume and cooled to yield colorless crystals (yield: 0.231 g, 41.5%). ^{1}H NMR (300 MHz, d_8-toluene, p.p.m.): δ 6.79 (*m*, 4H, aryl), 6.67 (*m*, 6H, pyrrolyl), 6.08 (*m*, 6H, pyrrolyl); ^{31}P NMR (121 MHz, d_8-toluene, p.p.m.): δ −32.4.

Crystal data

$C_{18}H_{16}FN_4P$
$M_r = 338.32$
Monoclinic, $P2_1$
$a = 7.6950\ (15)$ Å
$b = 14.828\ (3)$ Å
$c = 8.0060\ (16)$ Å
$\beta = 112.11\ (3)^\circ$
$V = 846.3\ (3)$ Å^3
$Z = 2$
$D_x = 1.328$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 9$–13°
$\mu = 0.18$ mm^{-1}
$T = 206\ (2)$ K
Plate, colorless
0.40 × 0.30 × 0.05 mm

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.932$, $T_{max} = 0.991$
2400 measured reflections
1572 independent reflections
1343 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$
$\theta_{max} = 25.0°$
$h = -3 \rightarrow 9$
$k = 0 \rightarrow 17$
$l = -9 \rightarrow 9$
3 standard reflections every 197 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.089$
$S = 1.10$
1572 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.011 (3)
Absolute structure: Flack (1983)
Flack parameter = −0.12 (16), Friedel pairs not collected

Table 1
Selected geometric parameters (Å, °).

P1—N1	1.517 (3)	P1—N2	1.680 (3)
P1—N4	1.671 (3)	F1—C2	1.361 (5)
P1—N3	1.676 (3)	N1—C1	1.394 (5)
N1—P1—N4	116.7 (2)	N4—P1—N2	101.93 (16)
N1—P1—N3	117.74 (17)	N3—P1—N2	103.22 (18)
N4—P1—N3	104.68 (16)	C1—N1—P1	137.2 (3)
N1—P1—N2	110.59 (19)		

H atoms were calculated in idealized isotropic positions [C—H = 0.94 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *P*3 *Diffractometer Control Program* (Siemens, 1990); cell refinement: *P*3 *Diffractometer Control Program*; data reduction: *P*3 *Diffractometer Control Program*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1341). Services for accessing these data are described at the back of the journal.

References

Antipin, M. Yu., Struchkov, Yu. T. & Kozlov, E. S. (1985). *Zh. Strukt. Khim.* **26**, 96–99.
Belaj, F. (1996). *Z. Naturforsch. Teil B*, **51**, 1428–1432.
Bell, S. A., Geib, S. J. & Meyer, T. Y. (2000). *J. Chem. Soc. Chem. Commun.* **15**, 1375–1376.
Bullen, G. J. & Tucker, P. J. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1651–1658.
Craig, S. L., Cordes, A. W., Stein, S. M., Chichester-Hicks, S. V. & Haddon, R. C. (1987). *Acta Cryst.* C**43**, 1978–1981.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Moloy, K. G. & Petersen, J. L. (1995). *J. Am. Chem. Soc.* **117**, 7696–7710.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997*a*). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1990). *P*3 *Diffractometer Control Program*. Version 4.01. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.