Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: BK1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2,4,4-Tetrakis(3,5-dimethylpyrazol-1-yl)-$2\lambda^5,4\lambda^5,6\lambda^5$-cyclotriphosphaza-1,3,5-triene-6-spiro-2′-1′,3′-diaza-2′-phosphacyclohexane, $C_{23}H_{36}N_{13}P_3$

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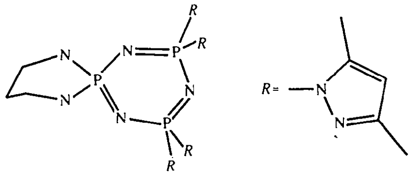
Abstract

The title phosphazene, $P_3N_3R_4XX$, where R is 3,5-dimethylpyrazole and XX is a spiro-bonded —NH—$CH_2CH_2CH_2NH$— ring, has P—N bonds of 1.554 (5)–1.614 (5) Å in the phosphazene ring with exocylic bonds of 1.609 (5) and 1.635 (5) Å to the spiro ring and 1.683 (4)–1.708 (5) Å to the pyrazole groups. The N—P—N angle within the phosphazene ring at the unique P atom is 6.9 (3)° smaller than those at the other P atoms. One of the pyrazole-substituted P atoms is displaced by 0.252 (5) Å from the best plane of the other five ring atoms, which are coplanar to within 0.087 (6) Å. The —PNCCCN— ring conformation is intermediate between a boat and a twist-boat.

Comment

The determination of the structure of the title compound, (I), was undertaken to obtain structural parameters for comparison with proposed metal complexes which utilize this molecule as a ligand (Thomas, Chandrasekhar, Scott, Hallford & Cordes, 1993).



(I)

The alternation of the P—N bond lengths in the phosphazene ring found here has been noted previously for unsymmetrically substituted rings (Cordes, Swepston, Oakley, Paddock & Ranganathan, 1981), and the long ring bonds and small ring angle in the phosphazene at P1

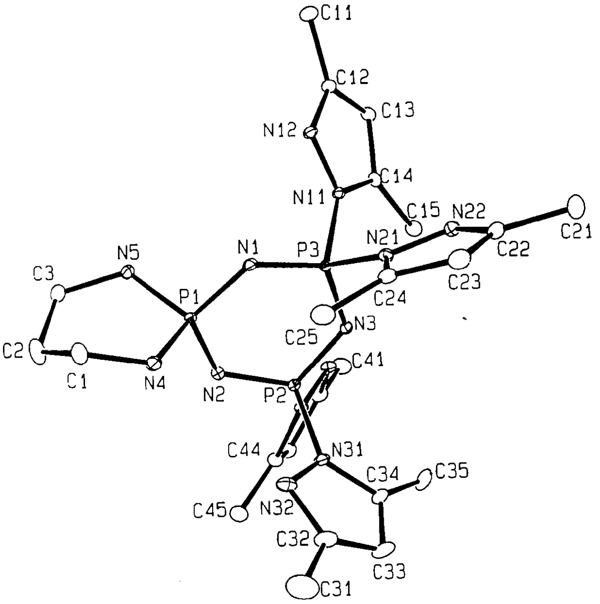


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule showing the atom-numbering scheme. Displacement ellipsoids are shown at the 5% probability level and H atoms have been omitted for clarity.

are similar to those found for the tetrachloro derivative with the same spiro ring (Guerch, Graffeuil, Labarre, Enjalbert, Lahana & Sournies, 1982). The two P—N bond distances to the N atoms of the spiro diazaphosphacyclohexane ring are both shorter than the bonds to the pyrazole rings and comparable to the bonds within the phosphazene ring, suggesting a bond order of greater than unity. This is supported by the positions found for the H atoms attached to these N atoms, which suggest sp^2 character for the N-atom bonding. Using the ring-analysis method of Cremer & Pople (1975) the —PNCCCN— ring is found to be intermediate between the twist-boat and boat conformations with θ and φ values of 81 and 13°, where values of 0 and 0° represent a chair, 90 and 0° a boat, and 90 and 30° a twist-boat.

Experimental

The title compound was prepared by the reaction of hexachlorophosphazene with propylenediamine (Chandrasekhar, Krishnamurthy, Murthy, Shaw & Woods, 1981) followed by treatment with dimethylpyrazole and triethylamine in benzene at 353 K. Crystals were obtained from methylene chloride.

Crystal data

$C_{23}H_{36}N_{13}P_3$
$M_r = 587.54$
Monoclinic
$C2/c$
$a = 31.998\ (8)$ Å
$b = 10.1595\ (11)$ Å
$c = 20.373\ (3)$ Å
$\beta = 111.557\ (17)°$
$V = 6159.7\ (19)$ Å^3
$Z = 8$
$D_x = 1.267$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.00–9.50°$
$\mu = 0.22$ mm^{-1}
$T = 293$ K
Block
0.34 × 0.40 × 0.30 mm
Colorless

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans [speed 4–16° min^{-1}, width $(1.0 + 0.35\tan\theta)°$]
Absorption correction: ψ scans (3 reflections)
$T_{min} = 0.820$, $T_{max} = 1.000$
5507 measured reflections
5404 independent reflections

2506 observed reflections [$I > 3.0\sigma(I)$]
$R_{int} = 0.045$
$\theta_{max} = 24.91°$
$h = -38 \rightarrow 35$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 24$
3 standard reflections frequency: 60 min intensity variation: 1.8% in 44.4 h

Refinement

Refinement on F
$R = 0.052$
$wR = 0.073$
$S = 1.15$
2506 reflections
352 parameters
H atoms treated using a riding model
$w = 1/[\sigma^2(F) + 0.0025F^2]$

$(\Delta/\sigma)_{max} = 0.019$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
P1	0.44355 (5)	0.40306 (16)	0.12028 (8)	0.0535 (9)
P2	0.37788 (5)	0.23918 (16)	0.03000 (7)	0.0486 (9)
P3	0.39574 (5)	0.22557 (14)	0.17005 (7)	0.0418 (8)
N1	0.42840 (15)	0.3452 (4)	0.1809 (2)	0.053 (3)
N2	0.41949 (16)	0.3301 (5)	0.0454 (2)	0.057 (3)
N3	0.36946 (15)	0.1703 (5)	0.0931 (2)	0.049 (3)
N4	0.43328 (18)	0.5605 (5)	0.1070 (3)	0.076 (4)
N5	0.49759 (16)	0.3998 (5)	0.1504 (3)	0.075 (4)
N11	0.42237 (14)	0.0981 (4)	0.2211 (2)	0.044 (3)
N12	0.45407 (14)	0.1326 (4)	0.2862 (2)	0.051 (3)
N21	0.35819 (15)	0.2656 (4)	0.2079 (2)	0.049 (3)
N22	0.33736 (17)	0.1642 (5)	0.2279 (3)	0.059 (3)
N31	0.33020 (16)	0.3232 (6)	−0.0181 (2)	0.062 (4)
N32	0.3316 (2)	0.4594 (6)	−0.0125 (3)	0.080 (4)
N41	0.37748 (15)	0.1240 (5)	−0.0298 (2)	0.056 (3)
N42	0.38509 (17)	−0.0058 (5)	−0.0103 (3)	0.064 (4)
C1	0.4688 (3)	0.6547 (6)	0.1227 (4)	0.087 (6)
C2	0.5034 (3)	0.6122 (8)	0.0963 (5)	0.108 (8)
C3	0.5262 (2)	0.4827 (9)	0.1280 (4)	0.094 (6)
C11	0.5036 (2)	0.0192 (7)	0.3909 (4)	0.081 (5)
C12	0.46933 (19)	0.0208 (6)	0.3180 (3)	0.056 (4)
C13	0.4474 (2)	−0.0860 (6)	0.2761 (3)	0.058 (4)
C14	0.4177 (2)	−0.0360 (5)	0.2157 (3)	0.051 (4)
C15	0.3840 (2)	−0.1065 (6)	0.1554 (3)	0.070 (5)
C21	0.2773 (3)	0.1370 (10)	0.2736 (5)	0.113 (8)
C22	0.3077 (2)	0.2202 (8)	0.2498 (3)	0.071 (5)
C23	0.3090 (3)	0.3559 (9)	0.2444 (4)	0.087 (6)
C24	0.3403 (2)	0.3852 (7)	0.2167 (3)	0.063 (4)
C25	0.3534 (3)	0.5146 (7)	0.1952 (4)	0.093 (6)
C31	0.2779 (4)	0.6399 (11)	−0.0510 (7)	0.177 (11)
C32	0.2899 (4)	0.4929 (10)	−0.0462 (5)	0.102 (7)
C33	0.2612 (3)	0.3893 (13)	−0.0739 (4)	0.113 (8)
C34	0.2874 (2)	0.2765 (9)	−0.0542 (3)	0.074 (5)
C35	0.2764 (3)	0.1345 (11)	−0.0660 (4)	0.111 (7)
C41	0.3958 (3)	−0.2106 (9)	−0.0655 (4)	0.113 (7)
C42	0.3872 (2)	−0.0646 (7)	−0.0663 (4)	0.073 (5)
C43	0.3816 (2)	0.0226 (8)	−0.1213 (3)	0.072 (5)
C44	0.3760 (2)	0.1424 (8)	−0.0978 (3)	0.069 (5)
C45	0.3690 (3)	0.2754 (9)	−0.1328 (4)	0.094 (6)

Table 2. *Selected geometric parameters* (Å, °)

P1—N1	1.596 (5)	P2—N31	1.708 (5)
P1—N2	1.614 (5)	P2—N41	1.686 (5)
P1—N4	1.635 (5)	P3—N1	1.565 (4)
P1—N5	1.609 (5)	P3—N3	1.585 (4)
P2—N2	1.554 (5)	P3—N11	1.683 (4)
P2—N3	1.571 (4)	P3—N21	1.698 (5)
N1—P1—N2	112.8 (2)	N1—P3—N3	120.0 (2)
N1—P1—N4	112.8 (3)	N1—P3—N11	110.5 (2)
N1—P1—N5	106.7 (3)	N1—P3—N21	107.3 (3)
N2—P1—N4	107.2 (3)	N3—P3—N11	107.6 (2)
N2—P1—N5	115.1 (3)	N3—P3—N21	109.1 (2)
N4—P1—N5	101.9 (3)	N11—P3—N21	100.7 (2)
N2—P2—N3	119.4 (2)	P1—N1—P3	123.6 (3)
N2—P2—N31	109.7 (3)	P1—N2—P2	122.7 (3)
N2—P2—N41	109.7 (3)	P2—N3—P3	117.6 (3)
N3—P2—N31	107.8 (2)	P1—N4—C1	121.6 (5)
N3—P2—N41	108.9 (2)	P1—N5—C3	126.0 (4)
N31—P2—N41	99.4 (2)		

The crystal used for data collection was mounted on a glass fiber with epoxy glue. The structure was solved by direct methods. In the final least-squares refinement the H atoms were constrained to idealized (C—H = 0.95, N—H = 0.90 Å) positions, where the orientation of the methyl groups and the direction of the N—H vector were determined from difference Fourier maps. All H atoms were assigned isotropic U values of 0.01 Å^2 plus U of the attached N or C atom.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1993). Data reduction, structure solution, structure refinement, molecular graphics and preparation of material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: BK1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(+)-*N*-Trichloroacetyl-7,8-dimethoxy-1-vinyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine at 153 K

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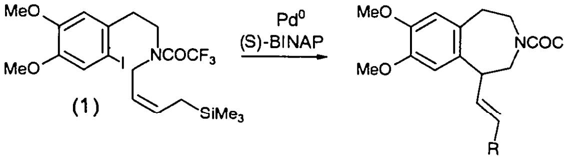
Abstract

The crystal structure analysis of the title compound, $C_{16}H_{18}Cl_3NO_3$, has been carried out at low temperature in order to determine the absolute configuration of the compound.

Comment

The Pd^0-catalyzed reaction of aryl or vinyl halides with alkenes, known as the Heck reaction, is an important method of C—C bond formation. A major drawback, however, is the low regioselectivity in constructing tertiary C_{sp^3} centres. The Si-terminated asymmetric Heck reaction now constitutes a new methodology for the regio- and enantioselective formation of such a centre (Tietze & Schimpf, 1994; Schimpf, 1994). With a catalyst system based on $Pd_2(dba)_3$ [tris(dibenzylideneacetone)dipalladium(0)] and (*S*)-BINAP [(*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] a mixture of compounds (2*a*) and (2*b*) (7 and 72%, respectively) was obtained, the latter in an enantiomeric excess of 64%. Recrystallization of (2*b*) gave an enantiomerically pure sample, which was converted to (2*c*) for elucidation of the absolute configuration by X-ray crystallography.



(2*a*) *R* = $SiMe_3$, *X* = F
(2*b*) *R* = H, *X* = F
(2*c*) *R* = H, *X* = Cl

Knowledge of the absolute configuration is required for the explanation of the mechanism of this enantioselective Heck reaction. Comparison of the optical rotation was not feasible because of the lack of reference compounds. All bond lengths and angles are within the expected range and comparable to values found for other 3-benzazepines (Eggleston, 1987; Berger, Chang, Clader, Hou, Chipkin & McPhail, 1989).

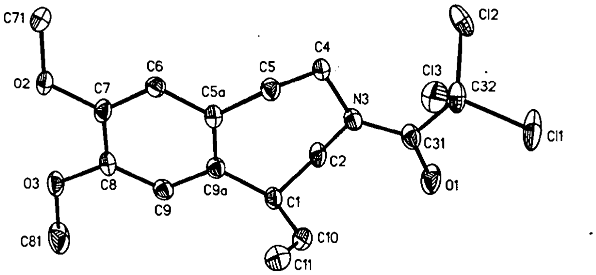


Fig. 1. Structure of the compound showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

Crystal data

$C_{16}H_{18}Cl_3NO_3$
$M_r = 378.66$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å