Preparation and Crystal Structure of a Novel Spirocyclic Derivative of Hexachlorocyclotriphosphazene†

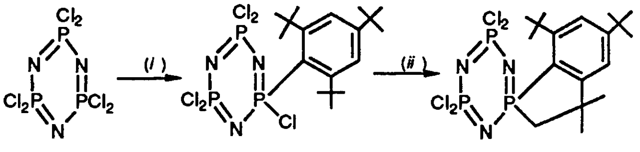
Barteld de Ruiter and Johan C. van de Grampel *
Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands
Fré van Bolhuis
Crystal Structure Center, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

The preparation and molecular structure of a novel spirocyclic derivative of $(NPCl_2)_3$ is described. The spirocyclic structure is formed by a N_3P_3 and a PC_4 ring, having one phosphorus atom in common. Two carbon atoms of the PC_4 ring are shared by an aromatic C_6 system.

Spirocyclic derivatives of $(NPCl_2)_3$ have attracted considerable attention in the past few years.[1] Examples are known of compounds with one, two, or three spirocyclic centres, but in nearly all cases the side ring is attached to the phosphazene ring through the heteroatoms oxygen and/or nitrogen. No examples are known of derivatives of $(NPCl_2)_3$ in which the side ring only consists of carbon atoms. In this note we report the preparation and molecular structure of the first example of this class of compounds.

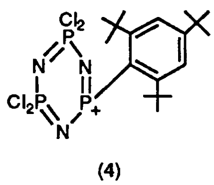
Results and Discussion

The new spirocyclic compound can be prepared by the route shown in the Scheme. The 2,4,6-tris(t-butyl)phenyl group, which has proven to be an excellent steric blocker, can be attached to the central ring with remarkable ease. This can be explained by a stabilization of the transition state in the substitution process by steric protection, thus suppressing ring degradation as a side reaction.



(1) (2) (3)

Scheme. (*i*) $MgBr(C_6H_2Bu^t\text{-}2,4,6)$ in tetrahydrofuran; (*ii*) Al_2Cl_6 in CH_2Cl_2



(4)

The reaction of compound (2) with Al_2Cl_6 probably proceeds *via* cation (4), which give rise to formation of the five-membered ring through an intramolecular C–H addition at the P^+ centre. Similar ring-closure reactions of related compounds are not uncommon.[2] The product is originally formed as an aluminium complex of unknown composition from which (3) can be liberated by a wet work-up procedure. Pure (3) gives an analogous complex (according to ^1H and ^{31}P n.m.r. spectra) upon reaction with Al_2Cl_6 in CH_2Cl_2.

Table 1. Selected bond lengths (Å) and angles (°) of compound (3) with estimated standard deviations (e.s.d.s) in parentheses

N(1)–P(1)	1.621(5)	N(1)–P(1)–N(3)	112.8(3)
N(3)–P(1)	1.633(5)	N(1)–P(2)–N(2)	120.5(3)
N(1)–P(2)	1.542(5)	N(2)–P(3)–N(3)	120.1(3)
N(3)–P(3)	1.549(5)	P(1)–N(1)–P(2)	123.3(3)
N(2)–P(2)	1.576(5)	P(2)–N(2)–P(3)	118.9(3)
N(2)–P(3)	1.584(5)	P(1)–N(3)–P(3)	122.9(3)
P–Cl (mean)	2.000(3)	Cl–P–Cl (mean)	100.1(1)
P(1)–C(1)	1.824(3)	C(1)–P(1)–C(4)	95.1(2)
C(1)–C(2)	1.533(6)	P(1)–C(1)–C(2)	104.7(3)
C(2)–C(3)	1.528(8)	C(1)–C(2)–C(3)	105.2(4)
C(3)–C(4)	1.412(8)	C(2)–C(3)–C(4)	118.0(5)
P(1)–C(4)	1.803(6)	P(1)–C(4)–C(3)	106.2(4)
C(3)–C(8)	1.386(7)	C(4)–C(3)–C(8)	120.6(5)
C(7)–C(8)	1.381(8)	C(3)–C(4)–C(5)	119.5(5)
C(6)–C(7)	1.403(8)	C(4)–C(5)–C(6)	117.1(5)
C(5)–C(6)	1.392(7)	C(5)–C(6)–C(7)	124.0(5)
C(4)–C(5)	1.420(8)	C(6)–C(7)–C(8)	117.3(5)
		C(3)–C(8)–C(7)	121.5(5)

The molecular structure of compound (3) together with the adopted numbering scheme is shown in the Figure. Selected bond lengths and angles are listed in Table 1. As expected, the N–P bond lengths in the heterogeneously substituted N_3P_3 ring are not equal, but can be divided into three sets, 1.627(6), 1.546(4), and 1.580(4) Å (mean values). This phenomenon arises from the difference in electronegativity of the phosphorus centres.[3] The all-carbon spiro ring is not planar, the largest deviations from planarity being C(1) -0.271 and C(2) 0.203 Å, whereas the sum of the endocyclic angles amounts to 529.2°. In the aromatic moiety [C(3)–C(8)] slightly different bond lengths [variation 1.381(8)—1.420(8) Å] and angles [variation 117.1(5)—124.0(5)°] are observed.

Experimental

All experiments were carried out in an atmosphere of dry

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 2. Positional parameters for the non-hydrogen atoms with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cl(1)	0.766 1(2)	0.266 4(2)	0.464 9(2)	C(5)	0.266 1(6)	0.604 2(5)	0.265 5(4)
Cl(2)	0.509 3(3)	0.161 9(2)	0.437 7(2)	C(6)	0.161 3(6)	0.708 6(5)	0.268 8(5)
Cl(3)	0.934 0(2)	0.346 3(2)	0.043 1(2)	C(7)	0.187 5(6)	0.837 6(5)	0.251 9(4)
Cl(4)	0.668 5(2)	0.241 6(2)	0.033 3(1)	C(8)	0.326 7(6)	0.861 2(5)	0.225 4(5)
P(1)	0.572 9(2)	0.535 2(2)	0.247 9(1)	C(9)	0.603 9(7)	0.907 3(6)	0.241 3(6)
P(2)	0.643 0(2)	0.292 8(2)	0.359 7(1)	C(10)	0.653 7(7)	0.803 4(7)	0.067 9(6)
P(3)	0.731 5(2)	0.336 6(2)	0.130 6(1)	C(11)	0.064 9(6)	0.943 9(5)	0.257 4(5)
N(1)	0.561 4(6)	0.429 0(5)	0.360 0(4)	C(12)	0.107 6(8)	1.075 0(6)	0.261 1(7)
N(2)	0.734 3(6)	0.245 8(5)	0.245 5(4)	C(13)	0.012 5(7)	0.955 7(7)	0.150 6(6)
N(3)	0.649 5(6)	0.473 5(5)	0.131 8(4)	C(14)	−0.056 9(8)	0.914 5(7)	0.362 0(6)
C(1)	0.663 2(2)	0.668 9(2)	0.254 8(1)	C(15)	0.220 4(7)	0.467 3(5)	0.287 5(5)
C(2)	0.589 3(6)	0.787 7(5)	0.196 0(5)	C(16)	0.075 5(8)	0.468 7(7)	0.266 1(7)
C(3)	0.435 6(6)	0.761 5(5)	0.222 6(4)	C(17)	0.207 2(8)	0.415 2(7)	0.413 7(6)
C(4)	0.407 1(6)	0.631 9(5)	0.244 8(4)	C(18)	0.327 3(8)	0.379 2(6)	0.213 0(6)

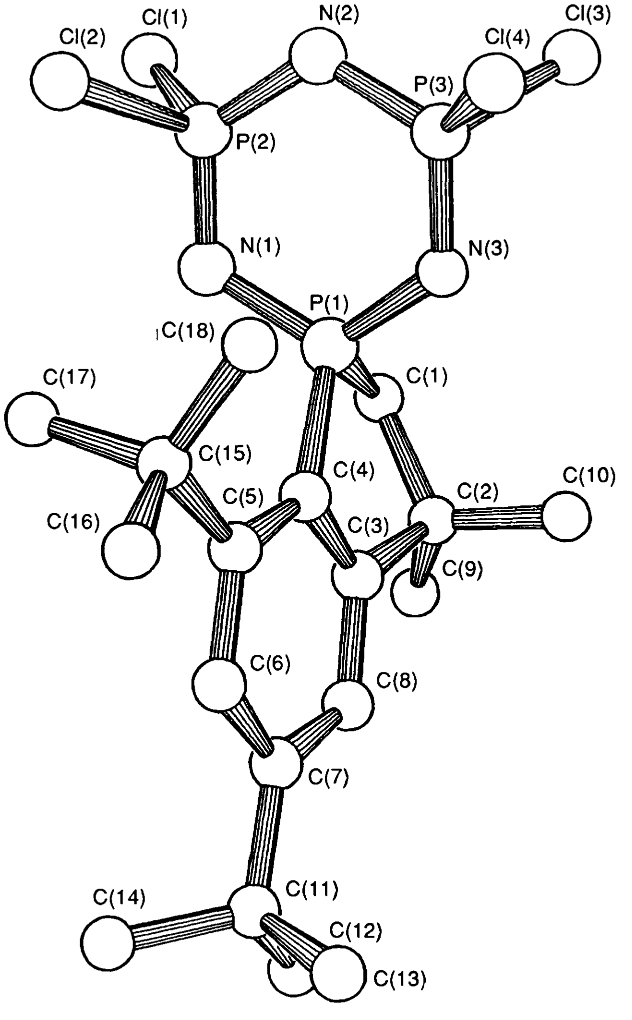


Figure. Molecular structure of compound (**3**) showing the atomic numbering scheme

nitrogen. Reagents and solvents were purified and dried by standard methods. The compound 2,4,6-tris(t-butyl)phenyl bromide and its corresponding Grignard reagent were prepared according to published procedures.[4–6] The compound $(NPCl_2)_3$ (**1**) was obtained from Shin Nisso Kaku.

Preparation of Compound (**2**).—A Grignard solution, resulting from magnesium turnings (0.36 g, 17.0 mmol) and 2,4,6-tris(t-butyl)phenyl bromide (4.89 g, 15.0 mmol) in tetrahydrofuran (50 cm^3) was added in 1 h to an ice-cooled solution of compound (**1**) (5.10 g, 14.7 mmol) in tetrahydrofuran (100 cm^3). After warming to room temperature the mixture was heated under reflux for 42 h. After cooling to room temperature, propan-2-ol (5.6 cm^3) was added, the mixture stirred for 3 h, and then evaporated *in vacuo*. The residue was extracted three times with boiling pentane (150 cm^3), and the combined fractions evaporated to give 8.1 g of a white solid. After sublimation at 0.2 mmHg (*ca.* 27 Pa) (70 °C) for 8 h the sublimation residue was recrystallized from n-pentane, yielding 4.79 g (8.59 mmol, 58%) of white crystals of compound (**2**), m.p. 140—141.5 °C (Found: C, 38.85; H, 5.25; Cl, 31.65; N, 7.55%; M^+ 555 for ^{35}Cl. $C_{18}H_{29}Cl_5N_3P_3$ requires C, 38.75; H, 5.25; Cl, 31.80; N, 7.55%; *M* 555); $\delta_H(CDCl_3$, 90 MHz) 1.31 (9 H, s, *p*-CMe_3), 1.56 (18 H, s, *o*-CMe_3), and 7.35 [2 H, d, ^4J(PH) 7.5, aryl CH]; $\delta_P(CDCl_3$, 81.0 MHz) 17.3 [d, ^2J(PP) 15.8, PCl_2] and 24.0 p.p.m. [t, ^2J(PP) 15.8 Hz, PClC].

Preparation of Compound (**3**).—To an ice-cooled solution of compound (**2**) (0.777 g, 1.39 mmol) in dry (molecular sieves) CH_2Cl_2 (20 cm^3) was added at once freshly sublimed Al_2Cl_6 (0.230 g, 0.862 mmol). The homogeneous solution was stirred at room temperature for 4 h, evaporated to dryness *in vacuo*, and the residue treated with water (25 cm^3). The resulting mixture was extracted three times with diethyl ether (50 cm^3). The combined fractions were dried over $MgSO_4$ and evaporated to give 0.633 g of a white solid, which was recrystallized from hot acetonitrile to yield 0.525 g (1.00 mmol, 72%) of white crystals of compound (**3**), m.p. 162—163.5 °C (Found: C, 41.45; H, 5.50; Cl, 27.20; N, 8.20%; M^+ 519 for ^{35}Cl. $C_{18}H_{28}Cl_4N_3P_3$ requires C, 41.50; H, 5.40; Cl, 27.20; N, 8.05%; *M* 519); $\delta_H(CDCl_3$, 90 MHz) 1.33 (9 H, s, *p*-CMe_3), 1.49 (6 H, s, CMe_2), 1.55 (9 H, s, *o*-CMe_3), 2.27 [2 H, d of t, ^2J(PH) 13.0, ^4J(PH) 1.2 Hz, CH_2], and 7.25—7.52 (2 H, m, aryl CH); $\delta_P(CDCl_3$, 81.0 MHz) 16.8 (br s, PCl_2) and 44.8 (br s, PC_2).

Crystal Structure Determination of Compound (**3**).—A colourless crystal of compound (**3**), recrystallized from a pentane–hexane mixture and with dimensions 0.40 × 0.20 × 0.35 mm, was used for data collection (CAD-F diffractometer).

Crystal data. $C_{18}H_{28}Cl_4N_3P_3$, $M = 521.18$, triclinic, $a = 9.939(5)$, $b = 10.625(1)$, $c = 12.500(2)$ Å, $\alpha = 79.59(1)$, $\beta = 73.39(3)$, $\gamma = 80.78(30)°$, $U = 1\,235.8$ Å^3 (by least-squares refinement on 25 setting angles in the range $9.2 < \theta < 16.9°$,

$\lambda = 0.710\,73$ Å), space group $P\bar{1}$, (no. 2), $Z = 2$, $D_c = 1.40$ g cm^{-3}, μ(Mo-K_α) = 6.83 cm^{-1}, $F(000) = 540$.

Data collection. Intensity data for 4 597 reflections were collected at room temperature in the range $1.00 < \theta < 25.00°$ (h 0—11, k −12 to 12, l −14 to 14), using the ω—2θ technique with ω scan width = $(0.85 + 0.35 \tan\theta)°$ and graphite-monochromated Mo-$K_{\bar{\alpha}}$ radiation. Three reference reflections (02$\bar{4}$, 13$\bar{1}$, and 23$\bar{1}$) measured every 3 h showed no indication of crystal decomposition. Intensities were corrected for scale variation and for Lorentz and polarization effects, but not for absorption. The data set consisted of 4 319 unique reflections, of which 3 146 satisfied the $I \geqslant 3\sigma(I)$ criterion of observability.

Structure analysis and refinement. The structure was solved by direct methods[7] and refined on F by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were refined in a riding mode with a fixed C–H distance (0.95 Å) and an overall isotropic thermal parameter ($B_{iso} = 5.0$ Å^2). Final $R (= \Sigma||F_o| - |F_c|| / \Sigma|F_o|)$ and $R' \{= [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{\frac{1}{2}}, w = 1\}$ are 0.060 and 0.069, respectively. All computations were performed using CAD4-SDP/PDP programs (Enraf-Nonius and B. A. Frenz and Associates). Scattering factors and anomalous dispersion corrections were taken from refs. 8 and 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

The authors are indebted to Shin Nisso Kaku Co. Ltd., Tokyo, for their generous gift of $(NPCl_2)_3$.

References

1 For a recent review see, R. A. Shaw, *Phosphorus, Sulfur, Silicon*, 1989, **45**, 103.

2 See, for example, A. H. Cowley, J. E. Kilduff, N. C. Norman, M. Pakulski, J. L. Atwood, and W. E. Hunter, *J. Am. Chem. Soc.*, 1983, **105**, 4845; A. Baceiredo, G. Bertrand, P. Mazerolles, and J-P. Majoral, *J. Chem. Soc., Chem. Commun.*, 1981, 1197; M. Yoshifuji, I. Shima, K. Ando, and N. Inamoto, *Tetrahedron Lett.*, 1983, **24**, 933; A. H. Cowley and M. Pakulski, *ibid.*, 1984, **25**, 2125; H. H. Karsch, F. H. Köhler, and H-U. Reisacher, *ibid.*, p. 3687.

3 J. C. van de Grampel, *Rev. Inorg. Chem.*, 1981, **3**, 1.

4 D. E. Pearson, M. G. Frazer, V. S. Frazer, and L. C. Washburn, *Synthesis*, 1976, 621.

5 F. A. Davis, R. H. Jenkins, jun., S. Q. A. Rizvi, and S. G. Yocklovich, *J. Org. Chem.*, 1981, **46**, 3467.

6 W. Rundel, *Chem. Ber.*, 1968, **101**, 2956.

7 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN 82, A System of Computer Programs for Automatic Solution of Crystal Structures from *X*-Ray Data, Universities of York and Louvain, 1982.

8 D. T. Cromer and J. T. Weber, in 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, table 2.2B.

9 D. T. Cromer, in ref. 8, table 2.3.1.

Received 10*th November* 1989; *Paper* 9/04832D