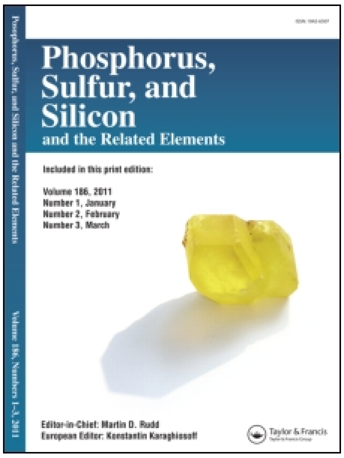

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SYNTHESIS AND STRUCTURE OF 1-METHYL-5-*t*-BUTYL-I-AZA-5-PHOSPHACYCLOOCTANE AND ITS PHOSPHINE SULFIDE

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SYNTHESIS AND STRUCTURE OF 1-METHYL-5-*t*-BUTYL-1-AZA-5-PHOSPHACYCLOOCTANE AND ITS PHOSPHINE SULFIDE

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The eight-membered phosphorus heterocycles $Bu^tP(CH_2CH_2CH_2)_2NMe$ 1 and $Bu^t(S)P(CH_2CH_2CH_2)_2NMe$ 2 have been synthesized by the reaction of Bu^tPCl_2 with the difunctional Grignard reagent $MeN(CH_2CH_2CH_2MgCl)_2$ and subsequent treatment with elemental sulfur. 2 crystallizes in the monoclinic space group $P2_1/c$ with the unit cell dimensions a 17.728(5), b 6.674(2), c 11.770(2) Å, β 98.12(2)°, Z = 4. The structure was refined to a final R value of 0.047 for 1761 observed reflections. 2 adopts a twist-boat-chair (TBC) conformation. There is no intramolecular P . . . N interaction but an unusual intermolecular P=S . . . H contact of 2.854 Å.

Key words: Eight-membered phosphorus heterocycle; phosphine sulfide; X-ray structure.

INTRODUCTION

Functional Grignard reagents of the general type $E(CH_2CH_2CH_2MgCl)_2$ (E = NMe, S, O) have been shown to be useful synthons for the synthesis of eight-membered heterocycles $E(CH_2CH_2CH_2)_2M$ (M = SnR_2, SiR_2).[1,2] Such compounds with heteroatoms in one and five positions may exhibit transannular donor-acceptor interactions. These interactions depend on the nature of the donor atom E and the acceptor atom M. Thus, for $MeN(CH_2CH_2CH_2)_2SnCl_2$ a formal Sn—N bond order of about 0.63 was found as a result of the strong Lewis acidity of the $SnCl_2$-fragment.[1] A reduction of the acceptor strength of the atom M necessarily causes a weakening of such interactions.

In a recent paper Muster *et al.*, has reported the synthesis of phosphacyclooctanes $Ph(Y)P(CH_2CH_2CH_2)_2S$ and $Ph(Y)P(CH_2CH_2CH_2)_2P(Y)Ph$ (Y = 1.p., 0) for which no transannular 1,5-interactions could be observed.[3] This paper prompts us to publish first results on the related compounds $Bu^t(Y)P(CH_2CH_2CH_2)_2NMe$ (Y = electron pair, S).[4]

RESULTS AND DISCUSSION

The reaction of the functional Grignard reagent $MeN(CH_2CH_2CH_2MgCl)_2$ with *t*-butyl dichlorophosphine in thf/toluene yields 1-methyl-5-*t*-butyl-1-aza-5-phospha-cyclooctane 1 in about 8% (Equation 1).

$$\underset{}{MeN(CH_2CH_2CH_2MgCl)_2 + Cl_2PBu^t \rightarrow} \underset{\underline{1}}{MeN(CH_2CH_2CH_2)_2PBu^t} \qquad (1)$$

1 is a distillable colourless liquid with a typical phosphine odour. Its reaction with elemental sulfur leads quantitatively to the corresponding phosphine sulfide 2 (Equation 2). 2 is a colourless crystalline solid which is well soluble in common organic solvents.

$$\underline{1} + 1/8\underline{H}S_8 \xrightarrow{C_6H_6} \underset{\underline{2}}{MeN(CH_2CH_2CH_2)_2P(S)Bu_t} \qquad (2)$$

The NMR data of 1 and 2 are summarized in Table I. The ^{31}P NMR spectrum of 1 shows a singlet at 3.3 ppm which is somewhat at low field compared with the open-chain derivative $Bu^tP(CH_2CH_2CH_2CH_2CH_3)_2$ (δ = −14.8 ppm[5]). The ^{13}C NMR spectrum displays doublets for the PCH_2-, CH_2- and *t*-butyl carbons and singlets for the NCH_2- and NCH_3-carbons. The ^1H NMR spectrum exhibits a singlet for the NCH_3-protons, a doublet for the *t*-butyl protons and complex patterns for the PCH_2-, CH_2- and NCH_2-protons.

The ^{31}P NMR spectrum of 2 shows again the expected lowfield signal. The ^{13}C NMR spectrum displays doublets for the quarternary carbon of the *t*-butyl group,

TABLE I

^1H, ^{13}C and ^{31}P NMR data of 1 and 2 in C_6D_6 $(\overset{1}{C}H_3)_3\overset{2}{C}(X)\overset{3}{P}(\overset{4}{C}H_2—\overset{5}{C}H_2—\overset{6}{C}H_2)_2N\overset{7}{C}H_3$
(1, X = l.p., 2, X = S)

compound	nucleus	chemical shifts δ (ppm) ($^nJ(^{31}P-^{13}C)$) (Hz)						
		1	2	3	4	5	6	7
1	^1H	0.99[a)]			1.44	1.67	2.14/2.45	2.21
	^{13}C	27.3 (14.3)	28.3 (13.5)		22.8 (23.8)	26.8 (9.7)	55.8	43.6
	^{31}P			3.3				
2	^1H[c)]	1.01[b)]			1.45/1.65	1.88	2.63	2.06
	^{13}C	24.9	33.5 (51.2)		23.7 (46.6)	21.3 (4.9)	52.6	44.4
	^{31}P			65.8				

a) $^3J(^{31}P-^1H)$= 10.8 Hz, b) $^3J(^{31}P-^1H)$= 15.1 Hz, c) in C_7D_8

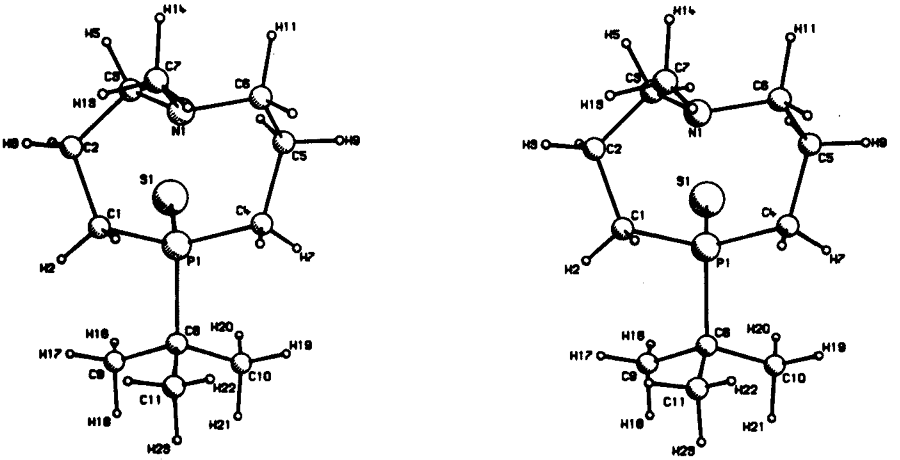

FIGURE 1 Stereoscopic view of the molecular structure of 2

the PCH_2- and the CH_2-carbons and singlets for the methyl carbons of the *t*-butyl group, the NCH_2- and the NCH_3-carbons. The ^1H NMR spectrum exhibits a doublet for the *t*-butyl group and complex patterns for the other protons. An evaluation of these NMR data with respect to a possible P . . . N interaction is difficult. To the best of our knowledge appropriate compounds for comparison as, for instance, $Bu^tP(CH_2CH_2CH_2)_2CH_2$ have not been reported yet. However, in the solid state structure 2 does not show any P . . . N contact and therefore it is very unlikely that there is one in solution.

The molecular structure of 2 is shown in Figure 1. Selected bond lengths and bond angles are listed in Tables II and III and the torsion angles are summarized in Table IV. According to the classification of Anet.[6] 2 adopts a twist-boat-chair conformation. Such conformation is relatively seldom.[7] The comparable compounds $Bu^t(S)P(2\text{-}OC_6H_4)_2P(S)Bu^t$H[8] and $Bu^t(S)P(SCH_2CH_2)_2S$H[9] show boat-chair conformations.

The sulfur and the N-methyl group are trans to each other. The *t*-butyl group occupies an equatorial position whereas the sulfur is bonded axially. The intramolecular P . . . N distance amounts to 3.401 Å. This is exactly the sum of the van

TABLE II

Selected bond lengths of 2 (pm)

S1 - P1	1.967(1)	C2 - C1	1.530(5)
C1 - P1	1.826(3)	C3 - C2	1.522(5)
C4 - P1	1.830(4)	C5 - C4	1.524(5)
C8 - P1	1.866(4)	C6 - C5	1.523(6)
C3 - N1	1.464(5)	C9 - C8	1.522(6)
C6 - N1	1.438(5)	C10- C8	1.527(6)
C7 - N1	1.453(6)	C11- C8	1.534(6)

TABLE III
Selected bond angles of $\underline{2}$ (°)

C1 - P1 - S1	113.3(1)	C2 - C3 - N1	111.8(3)
C4 - P1 - S1	111.8(1)	C5 - C4 - P1	117.3(3)
C4 - P1 - C1	109.0(2)	C6 - C5 - C4	114.3(3)
C8 - P1 - S1	112.9(1)	C5 - C6 - N1	112.9(3)
C8 - P1 - C1	104.3(2)	C9 - C8 - P1	108.4(3)
C8 - P1 - C4	105.1(2)	C10- C8 - P1	109.4(3)
C6 - N1 - C3	114.0(3)	C10- C8 - C9	109.0(4)
C7 - N1 - C3	113.2(4)	C11- C8 - P1	110.8(3)
C7 - N1 - C6	113.1(4)	C11- C8 - C9	109.5(4)
C2 - C1 - P1	116.2(3)	C11- C8 - C10	109.7(4)
C3 - C2 - C1	112.7(3)		

TABLE IV
Selected torsion angles of $\underline{2}$ (°)

C1 - P1 - C4 - C5	-78.48
P1 - C4 - C5 - C6	91.78
C4 - C5 - C6 - N1	-47.57
C5 - C6 - N1 - C3	-61.88
C6 - N1 - C3 - C2	136.79
N1 - C3 - C2 - C1	-40.14
C3 - C2 - C1 - P1	-55.26
C2 - C1 - P1 - C4	85.77

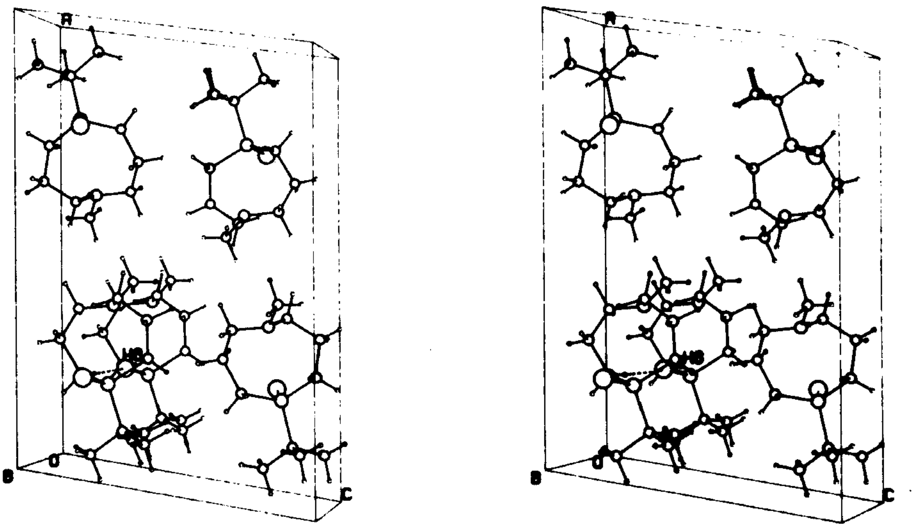

FIGURE 2 Stereoscopic view of the unit cell of $\underline{2}$

der Waals radii of these atoms.[10] In $Me(O)P(OCH_2CH_2)_2NPh$[11] and $Me(S)P(OCH_2CH_2)_2NMe$[12] these distances are shorter (3.22, 3.04 Å) and indicate a weak intramolecular P . . . N interaction. This might be a result of the enhanced Lewis acidity of the phosphorus atoms of these compounds due to the intracyclic oxygen atoms.

The P—C and P═S bond lengths don't show any particularities. They are comparable with known compounds.[3,12] An interesting feature of the molecular structure of 2 is the intermolecular C4—H8 . . . S═P contact of 2.854 Å. This contact is below the sum of the van der Waals radii of hydrogen and sulfur (3.0 Å[10]) and causes an infinite chain of the molecules (Figure 2).

EXPERIMENTAL

All manipulations were carried out under an atmosphere of dry argon. Solvents have been dried by standard procedures and freshly distilled before used. The ^1H (200.13 MHz), ^{13}C (50.39 MHz) and ^{31}P (81.026 MHz) NMR spectra have been recorded on a Bruker WP 200 spectrometer. The chemical shifts are related to Me_4Si (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P), respectively.

Preparation of 1-methyl-5-t-butyl-1-aza-5-phosphacyclooctane, **1**. A solution of 0.1 mol $MeN(CH_2CH_2CH_2MgCl)_2$ in 250 ml of thf and 0.1 mol *t*-butyldichlorophosphine Bu^tPCl_2 in 250 ml of toluene were dropped synchronously under vigorous stirring to 1.3 l of toluene. The reaction mixture was stirred for 4 h at room temperature. The colourless precipitate of magnesium chloride was filtered off, washed twice with 150 ml of toluene. The combined filtrates were evaporated to a volume of about 100 ml and filtered again. After removing the residual solvent the resulting viscous liquid was fractionated in vacuo to give 1.5 g (7.7%) of 1, b.p. 50–51°C (0.1 mm Hg). Anal. Calcd. for $C_{11}H_{24}NP$: C, 65.67; H, 11.94; N 6.96; Found: C, 65.31; H, 11.76; N, 6.83%.

TABLE V

Atomic coordinates (× 10^4) and equivalent temperature factors ($Å^2$). $B_{eq} = (8/3)\,\pi^2\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

	x/a	y/b	z/c	B_{eq}
P1	2198(1)	1133(1)	3329(1)	2.90(1)
S1	2349(1)	3940(1)	2904(1)	4.67(2)
N1	3834(2)	-1443(4)	3169(2)	3.77(6)
C1	2856(2)	320(6)	4577(3)	3.26(6)
C2	3675(2)	1065(7)	4652(3)	3.94(7)
C3	4039(2)	567(6)	3597(3)	4.23(8)
C4	2272(2)	-574(5)	2133(3)	3.46(6)
C5	2950(2)	-307(6)	1483(3)	4.32(8)
C6	3640(3)	-1554(7)	1930(4)	4.73(8)
C7	4378(3)	-2965(8)	3634(5)	6.06(10)
C8	1235(2)	662(5)	3733(3)	3.70(6)
C9	1106(3)	2155(8)	4667(5)	5.76(10)
C10	631(3)	999(8)	2694(4)	5.82(10)
C11	1173(3)	-1480(7)	4170(4)	5.37(9)

TABLE VI
Crystallographic data of 2

Formula	$C_{11}H_{24}NSP$
M	233.36
System	monoclinic
Space group	$P2_1/c$
a	17.728(5) Å
b	6.674(2) Å
c	11.770(2) Å
β	98.12(2) °
Z	4
F(000)	512
D_c	1.12 g/cm^3
$\lambda(MoK_\alpha)$	0.71069 Å
μ	2.76 cm^{-1}
Independent reflections ($\sin\theta/\lambda \leq 0.628$ Å^{-1})	2863
Observed reflections ($I \geq 2.5\sigma(I)$)	1761
Crystal size	0.1 x 0.15 x 0.30 mm
Diffractometer	Syntex $P2_1$

Preparation of 1-Methyl-5-t-butyl-1-aza-5-phosphacyclooctane-5-sulfide, **2**. 1 g (0.005 mol) of 1 was solved in 10 ml of benzene. To the stirred solution 160 mg (0.005 mol) of sulfur were added and the resulting mixture was refluxed for 20 minutes. Evaporation of the solvent yielded 1.1 g (94.4%) colourless crystals of 2, m.p. 90–92°C. Anal. Calcd. for $C_{11}H_{24}NSP$: C, 56.65; H, 10.30; N, 6.01; Found: C, 56.59; H, 10.21; N, 5.89%.

Crystal structure determination. The fractional atomic coordination of 2 are listed in Table V. Crystallographic data are summarized in Table VI. The structure was solved by the Patterson method.[13] The H atoms were obtained from difference Fourier synthesis. The refinement of the non-hydrogen atoms was performed anisotropically[14] whereas the H atoms were refined isotropically with common refined temperature factor (B = 4.0 Å^2). The atomic scattering factors were taken from International Tables for X-ray Crystallography.[15]

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