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PECULIARITIES OF STRUCTURE AND PROPERTIES OF PHOSPHORUS-CONTAINING CATIONS WITH TWO INTRAMOLECULAR DONOR-ACCEPTOR BONDS N⟶P.

SYNTHESIS OF THE FIRST 5-COORDINATED P-CATION WITH P=N BOND.

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Abstract: cations **1a,b** display dual reactivity, and they interact both with electrophilic and nucleophilic reagents. Reaction with chloramine B or benzenesulphonylazide leads to the formation of first representative of 5-coordinated P-cations with P=N bond.

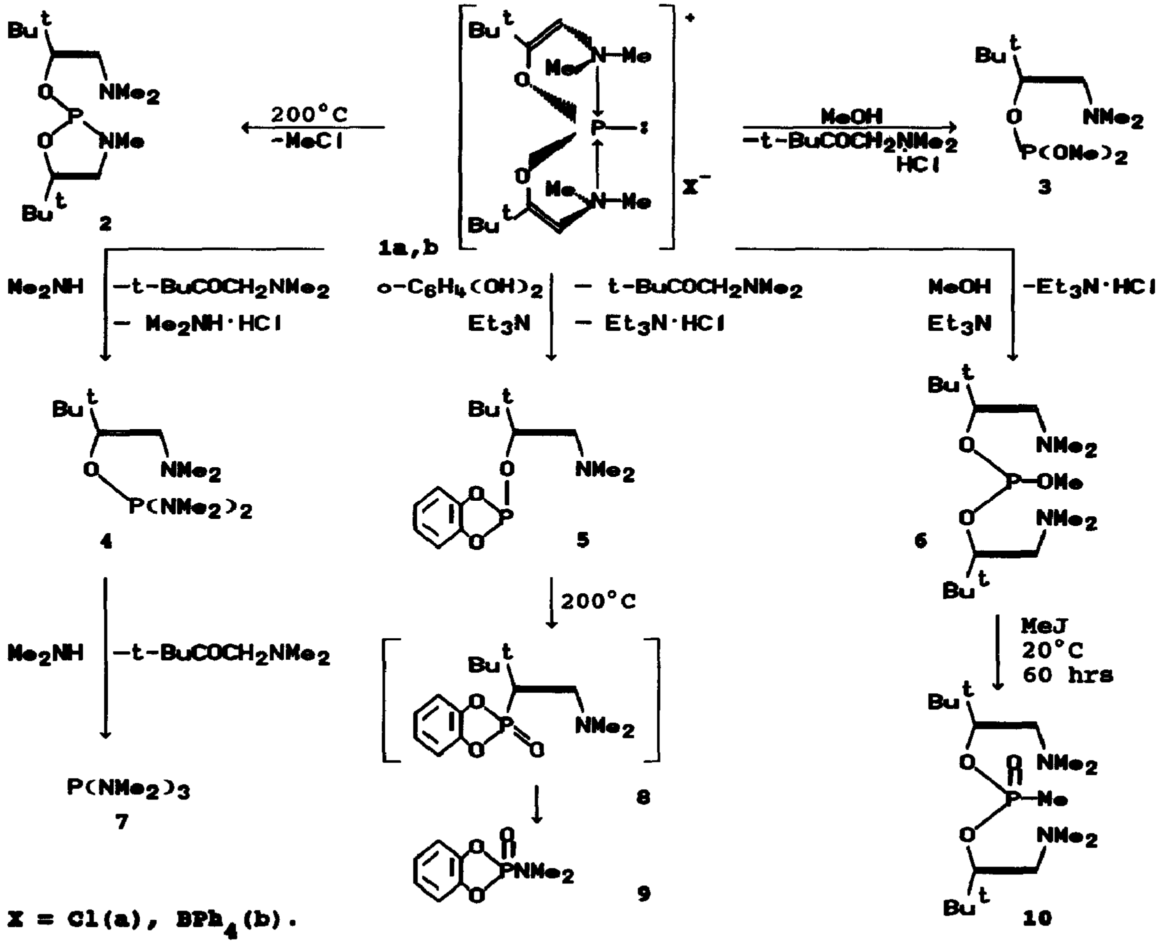
Recently we have described a synthesis of 2,2′-spirobi(3,3,3′,3′-tetramethyl-5,5′-di-tert-butyl-1,1′-dioxa-3,3′-diazonia-2-phospha-4-cyclopentene) chloride **1a** and tetraphenylborate **1b**, containing two intramolecular donor-acceptor bonds N→P[1]. Up till now the only compound of the similar type has been obtained by Schmutzler and coworkers in a series of ethylenediamine derivatives[2].

According to X-ray analysis data[3], the structure of compound **1b** is close to a trigonal-bipyramidal one with nitrogen atoms in the axial positions and with oxygen and lone pair in the equatorial ones. The main geometrical parameters: P-N 2.053 and 2.056 Å, P-O 1.638 and 1.641 Å, ∠NPN 166.9°, ∠OPO 102.2°, ∠OPN_{endo} 84.5° and 84.3°. An unusual elongation of the N→P bonds is in the accord with their donor-acceptor character.

Cations **1a,b**, as well as the related phosphenium cations[4], display dual reactivity interacting both with electrophilic and nucleophilic reagents.

Compound **1a** has two electrophilic centers - phosphorus and carbon of the N-CH_3 groups. Regioselectivity of the reactions is controlled by the reagent's nature. Such nucleophiles as alcohols, phenols, amines easily attack phosphorus atom to form a formal product of substitution of the chloride anion and the aminovinyl group as well. For example, methanol forms phosphite **6**[6] in the presence of Et_3N. Dissolving of **1a** in methanol without a base affords simultaneous substitution of both chloride and aminovinyloxy group and formation of phosphite **3**[6]. Pyrocatechol, which tends to form cyclic derivatives, reacts with **1a** substituting aminovinyloxy group even in the presence of a base. The reaction product is phosphite **5**[6].

Interaction of **1a** with dimethylamine at any reagents' ratio leads to diamidophosphite **4**.[6] Even with an excess of **1a**, a ^{31}P NMR spectrum of a reaction mixture reveals only two signals: δ 103 ppm (**1a**) and δ 139 ppm (amidophosphite **4**). A prolonged storing of compound **1a** in an excess of the amine leads to full substitution of aminovinyloxy groups.



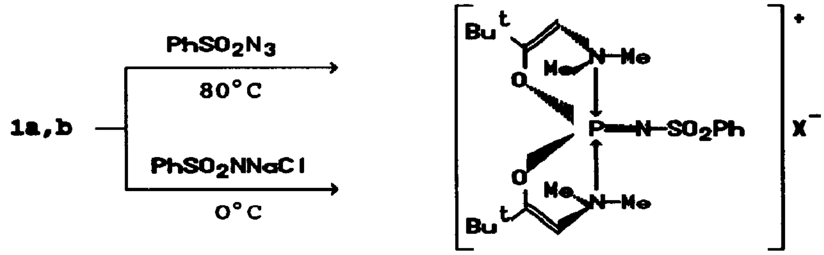
X = Cl(**a**), BPh$_4$(**b**).

An electrophilic character of carbon in the NCH_3 group is displayed in reactions with nucleophiles, which reversibly interact with the phosphorus atom. Thus, abstraction of methyl chloride from **1a** proceeds under conditions of vacuum pyrolysis at 200°C and leads to formation of 1-dimethylamino-2(3-methyl-5-tert-butyl-Δ^4-1,3,2-oxazaphospholine-2-yloxy)-3,3-dimethyl-1-butene **2**.[1] More nucleophilic pyridine, compared to chloride anion, causes dealkylation even at 115°C.

The obtained compounds are typical derivatives of trivalent phosphorus, and this is confirmed by their reactions. Phosphite **6** easily undergoes the Arbusov reaction with MeI and it forms phosphonate **10**.[6] Phosphite **5** smoothly transforms into o-phenylenedioxy(dimethylamino)phosphate **9**. This unusual transformation includes, probably, the vinylphosphite-vinylphosphonate rearrangement followed by a β-decomposition by the scheme, which has been established in a series of C-phosphorylated enamines.[5] The intermediate vinylphosphonate **8** was detected in the course of the reaction by ^{31}P (δ_P 12.5 ppm) and ^1H NMR (d 5.94 ppm, 1H, C=CH, $^3J_{PH}$ 26.4 Hz) spectra. Tert.-butylacetylene, which evidently is the second reaction product, polymerizes and after distillation it is present in the residue as a tar.

A general feature of the reactions between chelate of the type **1a** and nucleophiles is cleavage of the donor-acceptor bonds N→P, which is evidently controlled by a decrease in nucleophilicity of phosphorus in compounds **2-6** due to loss of the cationic character by the phosphorus-containing particle. Vice versa, interaction of compounds **1a,b** with electrophiles proceeds with the retention of donor-acceptor bonds N→P.

The phosphorus atom in compounds **1a,b** posesses a lone pair of electrons, and therefore, it is potentially able to interact with electrophiles. But nucleophilicity of phosphorus is reduced due to the cationic charge, and so compounds **1a,b** are able to interact only with strong electrophiles. For example, compound **1a** does not react with MeI at 20°C during a month and with PhCOCOPh at 100°C during 5 hours. But anhydrous chloramine B at 0°C or benzenesulphonylazide at reflux in CH_3CN react with **1a,b** to form 2,2'-spirobi(3,3,3',3'-tetramethyl-5,5'-di-tert-butyl-2-phenylsulfonylimino-1,1'-dioxa-3,3'-diazonia-2-phospha-4-cyclopentene) chloride **11a** and -tetraphenylborate **11b**.[6]



11a, X = Cl
11b, X = BPh_4

Imines **11a,b** are the first representatives of a new type of organophosphorus compounds. Their structure is confirmed by NMR spectra and X-ray analysis data.[3] The obtained parameters of **11b** (P-N 1.96 and 2.02 Å; P-O 1.61 and 1.60 Å, P=N 1.54 Å, ∠NPN 160.2°, ∠PNS 134.7°, ∠OPN$_{endo}$ 88.0 and 86.8°) give evidence about a distorted trigonal-bipyramidal environment of P atom and some shortening of the bonds N→P and O-P compared to the cation **1b**.

The electronic structure of the cations **1** and **11**, which have 10- and 12-electron shell, correspondingly, is rather unusual. Usually 10- or 12-electron shells are considered in connection with the structure of neutral 4- and 5-coordinated phosphorus compounds, or with the structure of 6-coordinated P-anions having an octahedral configuration, correspondingly. In connection with an unusual structure of cations **1**, **11**, their quantum chemical investigation is being carried out.

Table 1. Spectral characteristics of compounds **1-6**,**10**,**11** [a].

	δ_P	$\delta_H(J_{PH})$: NMe$_2$	t-Bu	C=CH-	other groups
1a	103.5	d 2.79(7.8), s 2.98	s 1.11	d 5.90(2.0)	
1b	103.5	d 2.14(7.8), s 2.35	s 1.04	d 5.22(2.0)	BPh$_4$ m 6.9-7.5
2	135.6	s 2.27	s 1.10	d 4.84(2.0)	cycle: t-Bu s 0.94 C=CH d 5.56(5.4) NMe d 2.97(10.0)
3	123	s 2.24	s 1.09	d 4.90(1.4)	OMe$_3$ d 3.52(8.5)
4	139	s 2.28	s 1.05	d 4.84(1.4)	P(NMe$_2$)$_2$ m 2.59
5	120	s 2.27	s 0.90	d 5.13(1.7)	H$_{arom}$ m 6.9-7.0
6	124.6	s 2.28	s 1.09	s 4.89	OMe d 3.56(8.6)
10	24.5	s 2.44	s 1.14	d 5.15(2.8)	PMe d 1.87(18.8)
11a	-32	s 3.22, d 3.27(4.7)	s 1.25	d 6.43(14.4)	H$_{arom}$ m 7.4-7.9
11b	-32	s 2.96, d 3.00(4.8)	s 1.20	d 6.06(14.4)	H$_{arom}$ m 6.8-7.9

[a] NMR: Bruker Jeminy 200, ^{1}H (200.13 MHz), ^{31}P (81.02 MHz). Reference substances: ^{1}H, TMS int., ^{31}P, 85% H_3PO_4 ext. All NMR spectra were recorded in $CDCl_3$ as a solvent. All chemical shift values are listed in p.p.m. The integration of all ^{1}H NMR spectra are consistent with the structure. s-singlet, d-dublet, m-multiplet.

REFERENCES AND NOTES

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6. **3** b.p. 69-70°C/0.1 mm Hg; $C_{10}H_{22}NO_3P$ (235.26); anal. found: N, 5.93, P, 13.10; calc.: N, 5.95, P, 13.16. **4** b.p. 49-50°C/0.05 mm Hg; $C_{12}H_{28}N_3OP$ (261.35); anal. found: N 16.02, P 11.92, calc.: N 16.08, P 11.85. **5** b.p. 95-97°C/0.05 mm Hg; $C_{14}H_{20}NO_3P$ (281.29); anal. found: N, 4.91, P, 11.07, calc.: N 4.98, P 11.01. **6** b.p. 102-103°C/0.05 mm Hg; $C_{17}H_{35}N_2O_3P$ (346.44); anal. found: N 8.01, P 8.99, calc.: N 8.09, P 8.94. **10** $C_{17}H_{35}N_2O_3P$ (346.44); anal. found: N 8.13, P 8.89, calc.: N 8.09, P 8.94. **11a** $C_{22}H_{37}ClN_3O_4PS$ (506.05); anal. found: Cl 7.08, N 8.37, P 6.19, S 6.28, calc.: Cl 7.01, N 8.30, P 6.12, S 6.34. **11b** $C_{48}H_{57}BN_3O_4PS$ (789.84), anal. found: N 5.38, P 3.98, S 4.01, calc.: N 5.32, P 3.92, S 4.06.

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