

99. Complexes of 2,2',2''-Nitrilotriphenol

Part IV

Cage Compounds with Phosphorus(III) and Phosphorus(V)

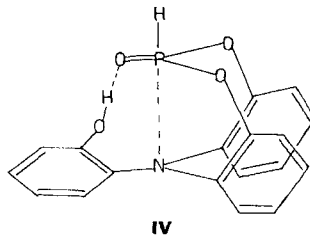
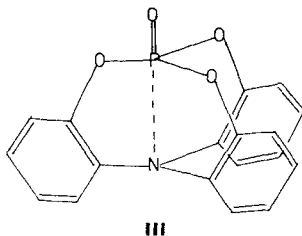
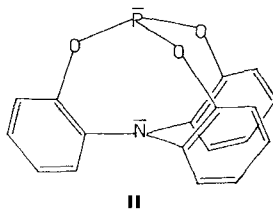
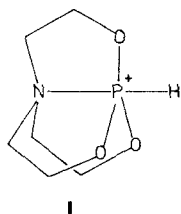
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(31. III. 87)

The ligand 2,2',2''-nitrilotriphenol reacts with P(III) and P(V) compounds to form corresponding phosphorus complexes. Syntheses and NMR data of 2,2',2''-nitrilotriphenyl phosphite (**II**), 2,2',2''-nitrilotriphenyl phosphate (**III**) and of a hydrolysis product of **II**, 2,2'-[N-(2-hydroxyphenyl)imino]diphenyl phosphonate (**IV**), are reported, as well as crystal structures of **II** and **IV**. Phosphite **II** shows a bicycloundecane framework; no N...P interaction is present. The phosphonate **IV** shows two coordinated and one dangling phenol group; the N-atom does not interact with the P-atom. Strong acids protonate **II** as well as **III** to form cations: in these, NMR evidence indicates coordination of the N-atom to the P-atom.

Introduction. – In a series of preceding papers, we reported on structure and reactivity of complexes between 2,2',2''-nitrilotriphenolate ($N(C_6H_4O^-)_3$) and B(III) or Al(III) [1] [2]. In the present paper, we describe some phosphorus compounds of 2,2',2''-nitrilotriphenolate.



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Some years ago, *Verkade* and coworkers [3] reported on a tricyclic phosphorus cage compound **I**, called phosphatrane, which can formally be regarded as a protonated complex of P(III) with 2,2',2''-nitrilotriethanol. Analogous complexes of P(V) were reported by the same research group [4–6]. The protonated phosphatrane **I** was shown to have a rather short P–H distance (1.35 Å) but a lower ^{31}P , ^1H -coupling constant (791 Hz) in the ^1H -NMR spectrum than noncyclic protonated phosphite esters (*e.g.* $(\text{CH}_3\text{O})_3\text{PH}^+$: 826 Hz [3]). These apparently controversial findings were explained as a consequence of the trigonal-bipyramidal (tbp) structure of **I**. The unprotonated precursor of (**I**) could never be crystallized, as it polymerized upon concentration of its solutions [6].

Using the more rigid 2,2',2''-nitrilotriphenolate ligand instead of the 2,2',2''-nitriloethanolate, we hoped to obtain the unprotonated phosphatrane precursor **II**, in order to elucidate its structure and to answer the question whether significant $\text{N} \cdots \text{P}$ interaction is present in an unprotonated phosphatrane or not.

The bicyclic compound **II** was synthesized straightforwardly according to *Eqn. 1*.



No high-dilution techniques were required. The corresponding phosphate **III** was obtained according to *Eqn. 2*



In CHCl_3 , $\text{N}(\text{C}_6\text{H}_4\text{OH})_3$ reacted directly with PCl_3 ; the resulting products were HCl gas and probably the protonated form of **II**, *i.e.* the analog of phosphatrane (**I**). However, during purification and crystallization, hydrolysis occurred, and compound **IV** was obtained.

Experimental. – *General.* All chemicals were purchased from *Fluka*. The 2,2',2''-nitrilotriphenol was prepared according to [7]. ^1H -NMR spectra: δ in ppm rel. to TMS ($= 0$ ppm), J in Hz. ^{31}P -NMR spectra: δ in ppm rel. to H_3PO_4 ($= 0$ ppm), J in Hz.

2,2',2''-Nitrilotriphenyl Phosphite (II). Under N_2 , 0.60 g (3.9 mmol) of tris(dimethylamino)phosphine were added with a syringe to a stirred soln. of 1.00 g (3.4 mmol) of 2,2',2''-nitrilotriphenol in 10 ml of CHCl_3 contained in a *Schlenk* tube. The mixture was refluxed for 30 min. After evaporation, the viscous residue was dissolved in 1 ml of MeCN. After standing overnight, colourless crystals separated, which were isolated and dried *in vacuo*: 380 mg (35%) of **II**. The product is sensitive to air and moisture and has to be kept under an inert atmosphere. IR: 3070w, 3030w, 1605w, 1590w, 1580w, 1570vw (sh), 1485vs, 1450m, 1310s, 1290w, 1265m, 1255s, 1235s, 1210vw, 1180s, 1150m, 1105m (sh), 1095m, 1030m, 970w, 950w, 935w (sh), 930m, 910s, 865s, 845vs, 760s, 745vs, 725m, 695s, 620m, 570w, 540w (sh), 530w, 480m, 415m, 325w. ^1H -NMR (250 MHz, CDCl_3): 7.10 (*m*, 9H, H–C(4,4',4''), H–C(5,5',5''), H–C(6,6',6'')); 7.376 (*dd*, 3H, H–C(3,3',3'')). ^{31}P -NMR (CDCl_3): +5.20 (*br. s*). Anal. calc. for $\text{C}_{18}\text{H}_{12}\text{NO}_3\text{P}$ (321.28): C 67.29, H 3.76, N 4.36, P 9.64; found: C 66.90, H 3.88, N 4.60, P 9.27.

Protonation Experiments with II. Addition of strong acids to solns. of **II** in CDCl_3 (NMR tube) resulted in a splitting of the ^{31}P -NMR signal and in its shift to more negative δ values. ^{31}P -NMR (CDCl_3 , 1 drop of HBF_4): –14.11 (*d*, $J(\text{P},\text{H}) = 849$). An analogous splitted ^1H -NMR signal was observed ($\text{H}^+\text{–P}^+$). In a qualitative experiment, 1 drop of a strong acid was added to a soln. of 20 mg of **II** in 1 ml of CDCl_3 and the corresponding ^1H -NMR recorded (see *Table 1*).

Isolation of a crystalline salt of $\text{II} \cdot \text{H}^+$ failed in all cases, *i.e.* only oils were obtained upon evaporation of the corresponding acidified solutions.

2,2',2''-Nitrilotriphenyl Phosphate (III). A soln. of 0.52 g of POCl_3 in 10 ml of abs. THF was added under stirring to a soln. of 1.00 g (3.4 mmol) of 2,2',2''-nitrilotriphenol and 1.05 g (10.2 mmol) of Et_3N in 10 ml of abs. THF (\rightarrow white precipitate of Et_3NHCl). After completion of the addition, the precipitate was filtered and the filtrate concentrated and chromatographed over a short column of silica gel (10 g of silica gel, THF). Evaporation

Table 1. Influence of Added Acid on ¹H-NMR Data of II

Acid	ClSO ₃ H	HBF ₄	CF ₃ COOH	C ₆ H ₅ SO ₃ H	CH ₃ SO ₃ H	HCl (g)	CH ₃ COOH ^{a)}
δ (H–P ⁺) [ppm]	7.172	7.133	7.542	7.450	7.405	7.370	–
¹ J (P,H) [Hz]	853	853	794	783	779	779	–
δ (H–C(3,3',3'')) [ppm]	8.26	8.49	8.22	7.85	8.19	8.84	–

^{a)} No change in the ¹H-NMR.

and crystallization from THF/hexane yielded 0.55 g (48%) of III · THF as plate-like, white crystals. IR: 3100vw (sh), 3070w, 3040vw, 1595w, 1580w, 1490vs, 1450s, 1400m, 1315s (sh), 1300vs (P=O), 1265s (sh), 1260s, 1240s, 1180s, 1150w, 1095m, 1030m, 970vs, 950s, 930m, 920s, 870w (sh), 865m, 775s, 760vs, 735m (sh), 720w (sh), 675w, 615m, 585m, 540w, 500s, 485w, 455m, 430vw, 370w, 320m, 280w. ¹H-NMR (90 MHz, CDCl₃): 7.27 (m, 9H); 7.50 (dd', 3H, H–C(3,3',3'')). ¹H-NMR (90 MHz, CDCl₃ + 1 drop of BF₃ · OEt₂): 7.27 (m, 9H); 7.75 (H–C(3,3',3'')). ¹H-NMR (90 MHz, CDCl₃ + 1 drop of ClSO₃H): 7.25 (m, 9H); 7.85 (H–C(3,3',3'')). ³¹P-NMR (CDCl₃): – 12.39 (s). ³¹P-NMR (CDCl₃ + 1 drop of BF₃ · Et₂O): – 15.10 (no splitting).

2,2'-[N-(2-Hydroxyphenyl)imino]diphenyl Phosphonate (IV). A mixture of 1.00 g (3.4 mmol) of 2,2',2''-nitrotriphenol and 0.50 g (3.6 mmol) of PCl₃ was refluxed in 10 ml of CHCl₃ until no more HCl gas was evolved. Then, 10 ml of Et₂O were added and after staying overnight, the white crystals were filtered and dried *in vacuo*: ca. 200 mg of IV. IR: 3460s, 3430s, 3060w, 3040w, 3020vw (sh), 2280w (br.), 1600m, 1590m, 1580m (sh), 1490vs, 1445m, 1405vw, 1345m, 1300s, 1270s, 1250vs (P=O), 1220s, 1165m, 1150m, 1125m, 1110s, 1090m (sh), 1030m, 1020w (sh), 975w, 940m, 925m, 895m, 870vs, 840s, 810w, 780s, 750vs (sh), 745vs, 725s, 710m, 685m, 670s, 650m, 615m, 600m, 585w (sh), 550w, 530w, 510m, 480w (sh), 470m, 450w, 415w, 350w, 310w. ¹H-NMR (250 MHz, CDCl₃): 7.41 (d, J(P,H) = 777, H–P); 7.30 (m, 8 arom. H); 7.05 (m, 3 arom. H); 6.85 (m, 1 arom. H).

X-Ray Data Collections. Preliminary investigations by precession photography (CuK_α); determination of cell parameters and data collection on an automated CAD 4 diffractometer (Enraf Nonius); integrated reflection intensities collected in bisecting geometry; first and last sixth of each scan used to correct for background scattering. Table 2 summarizes crystal data, data collection, and structure determination parameters; raw data

Table 2. Crystal Data and Parameters of II and IV Used in Data Collections and Structure Determinations

	II	IV
Formula	C ₁₈ H ₁₂ O ₃ NP	C ₁₈ H ₁₄ O ₄ NP
Space group	monoclinic	monoclinic
	C2/c	P2 ₁ /n
a [Å]	15.937 (5)	10.977 (3)
b [Å]	8.666 (5)	11.706 (2)
c [Å]	12.882 (5)	12.954 (5)
α [deg]	90.9	90.0
β [deg]	120.21 (2)	90.0
γ [deg]	90.0	112.63 (2)
V [Å ³]	1537.6	1536.2
Z	4 (disorder)	4
Crystal size [mm]	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.2
Temperature [K]	293	293
θ _{max} [deg] (λ = 0.71067 Å)	25	25
Scan type	ω	ω/2θ
Scan angle/reflection	1.5°	1.0°
Time/reflection [sec]	90	90
No of independent reflections	1356	2688
No of reflections used in refinements	925 (> σ _F)	1392 (> 2σ _F)
No of variables	181	274
Final R _w ^{a)}	0.050	0.042
Weighting, A ^{a)}	10	10

^{a)} $W = 1/\sigma^2(F) \cdot \exp(2 \cdot A \cdot (\sin \theta/\lambda)^2)$

corrected for crystal decay, *Lorentz*, and polarization effects; solution by direct methods (MULTAN 77 [8]); weighted least-squares refinements carried out in the XRAY 72 [9] program system, weighting scheme of *Seiler* and *Dunitz* [10]. Real and imaginary scattering factors for neutral atoms [11], all non-H-atoms refined anisotropically; H-atoms refined where indicated, others in calculated positions ($d(\text{C}-\text{H}) = 1.08 \text{ \AA}$).

Some difficulties were encountered during the structure determination of **II**. Density considerations suggested the acentrosymmetric space group *Cc* with 4 molecules in the unit cell. Attempts to solve the structure using MULTAN 77 [8] failed however, and a disordered structure in the centrosymmetric space group *C2/c* was considered (8 molecules/unit cell). MULTAN solution yielded a fragment of 4 atoms which could be identified as a tertiary phosphite group. Using the position and orientation of this fragment, a trial structure for the whole cage molecule was calculated and submitted to an isotropic least-squares refinement which converged after a few cycles. Upon anisotropic refinement, C-atoms C(41), C(51), C(61), C(42), C(52), C(62), C(43), C(53), and C(63) of the benzene rings had to be constrained to form regular hexagons with $d(\text{C}-\text{C}) = 1.390 \text{ \AA}$ and $\alpha(\text{C}-\text{C}-\text{C}) = 120^\circ$. H-atoms were introduced in calculated positions with the equivalent isotropic temperature factors of the corresponding C-atoms. All atoms have population parameters of 0.5. No higher symmetry than *C2/c* could be assigned to the lattice of **II**. The crystal used was most probably a micro-twin with statistical intermixing of two primitive lattices.

Results and Discussion. – Atomic numbering is seen from the ORTEP drawings. Positional and equivalent isotropic displacement parameters are given in *Tables 3* and *4*. Anisotropic displacement parameters have been given elsewhere [1]. Molecular structures are illustrated in *Fig. 1* and *2*. Where possible, bond distances and angles are averaged over the noncrystallographic symmetry elements (3-fold axis). Values for the cage frameworks are reported in *Table 5*. Additional geometric information is given in [1].

No significant $\text{N} \cdots \text{P}$ interaction is present in **II**, as illustrated by the $\text{N}-\text{P}$ distance of 3.14 \AA . The mean $\text{P}-\text{O}$ distance (1.63 \AA) and the $\text{O}-\text{P}-\text{O}$ angles (102.7°) are typical of

Table 3. *Positional and Displacement Parameters for II*^a). E.s.d.'s in terms of the least significant digit.

Atom	x	y	z	$U_{\text{eq}} \cdot 100$
P	0.0331(1)	0.1847(2)	0.5755(1)	5.1(1)
N	0.0008(3)	0.2005(4)	0.7961(3)	3.8(2)
O(1)	0.0798(3)	0.1992(5)	0.5422(3)	5.2(2)
O(2)	0.0714(3)	0.0355(4)	0.6648(4)	5.0(2)
O(3)	0.0849(3)	0.3297(5)	0.6677(4)	5.4(2)
C(11)	-0.1234(9)	0.1202(16)	0.5965(12)	4.5(7)
C(21)	-0.0860(4)	0.1189(10)	0.7181(8)	4.3(4)
C(31)	-0.1318(5)	0.0356(10)	0.7652(10)	5.4(5)
C(41)	-0.2140(-)	-0.0480(-)	0.6925(-)	7.4(6)
C(51)	-0.2523(-)	-0.0484(-)	0.5688(-)	6.8(5)
C(61)	-0.2056(-)	0.0369(-)	0.5214(-)	6.5(4)
C(12)	0.1235(6)	0.0377(9)	0.7895(7)	4.1(4)
C(22)	0.0914(7)	0.1187(15)	0.8532(13)	3.9(6)
C(32)	0.1452(6)	0.1190(9)	0.9764(9)	5.0(4)
C(42)	0.2315(-)	0.0376(-)	1.0357(-)	5.7(4)
C(52)	0.2644(-)	-0.0456(-)	0.9709(-)	7.6(6)
C(62)	0.2088(-)	-0.0447(-)	0.8462(-)	5.6(4)
C(13)	0.0448(8)	0.4228(12)	0.7196(8)	4.6(5)
C(23)	0.0030(6)	0.3626(6)	0.7802(5)	4.1(4)
C(33)	-0.0368(8)	0.4615(12)	0.8276(8)	5.3(5)
C(43)	-0.0350(-)	0.6196(-)	0.8157(-)	7.9(6)
C(53)	0.0082(-)	0.6808(-)	0.7542(-)	8.0(5)
C(63)	0.0488(-)	0.5827(-)	0.7060(-)	6.4(5)

^a) H-atoms in calculated positions with isotropic temperature factors of the corresponding C-atoms.

Table 4. *Positional and Displacement Parameters for IV*. E.s.d.'s in terms of the least significant digit.

Atom	x	y	z	$U_{eq} \cdot 100$
P	0.4514(1)	0.1509(1)	0.1114(1)	3.9(1)
O(4)	0.5798(3)	0.2145(3)	0.0640(3)	4.7(2)
C(11)	0.2562(4)	-0.0365(4)	0.0309(4)	3.8(3)
C(21)	0.2380(4)	0.0175(4)	-0.0581(3)	3.2(2)
C(31)	0.1136(4)	-0.0272(4)	-0.1039(4)	3.9(3)
C(41)	0.0133(5)	-0.1293(5)	-0.0605(4)	4.8(3)
C(51)	0.0361(5)	-0.1852(5)	0.0263(4)	5.0(3)
C(61)	0.1567(5)	-0.1386(5)	0.0737(4)	4.6(3)
O(1)	0.3779(3)	0.0100(3)	0.0817(3)	4.6(2)
C(12)	0.3403(4)	0.2843(4)	0.0129(4)	3.4(3)
C(22)	0.3385(4)	0.2385(4)	-0.0868(3)	3.1(2)
C(32)	0.3294(5)	0.3108(5)	-0.1690(4)	4.3(3)
C(42)	0.3217(6)	0.4246(5)	-0.1505(5)	5.3(3)
C(52)	0.3205(5)	0.4664(5)	-0.0518(5)	5.5(4)
C(62)	0.3309(5)	0.3968(5)	0.0301(4)	4.6(3)
O(2)	0.3467(3)	0.2136(3)	0.0986(2)	4.0(2)
C(13)	0.5457(4)	0.1791(4)	-0.2068(3)	3.4(3)
C(23)	0.4133(4)	0.1017(4)	-0.1894(3)	2.8(2)
C(33)	0.3520(4)	0.0050(4)	-0.2580(3)	3.5(3)
C(43)	0.4183(5)	-0.0130(5)	-0.3434(4)	4.1(3)
C(53)	0.5461(5)	0.0681(5)	-0.3609(4)	4.2(3)
C(63)	0.6092(4)	0.1624(5)	-0.2935(4)	4.2(3)
O(3)	0.6134(3)	0.2719(3)	-0.1402(3)	4.9(2)
N	0.3475(3)	0.1212(3)	-0.0993(3)	3.0(2)
H(1)	0.464(5)	0.156(4)	0.219(4)	5.7(14)
H(3)	0.591(8)	0.257(8)	-0.073(7)	17.9(39)
H(31)	0.099(4)	0.011(4)	-0.164(3)	3.4(12)
H(41)	-0.071(5)	-0.165(5)	-0.094(4)	6.8(15)
H(51)	-0.036(5)	-0.253(4)	0.058(4)	6.1(15)
H(61)	0.178(4)	-0.169(4)	0.128(3)	4.4(14)
H(32)	0.327(4)	0.276(4)	-0.240(4)	5.8(14)
H(42)	0.326(5)	0.475(5)	-0.206(4)	4.7(16)
H(52)	0.311(5)	0.535(5)	-0.038(4)	9.1(20)
H(62)	0.330(5)	0.418(4)	0.100(4)	7.1(15)
H(33)	0.265(4)	-0.052(4)	-0.248(3)	4.4(13)
H(43)	0.370(5)	-0.083(5)	-0.388(4)	7.3(17)
H(53)	0.592(4)	0.060(4)	-0.418(3)	5.1(13)
H(63)	0.690(4)	0.217(4)	-0.309(3)	4.0(12)

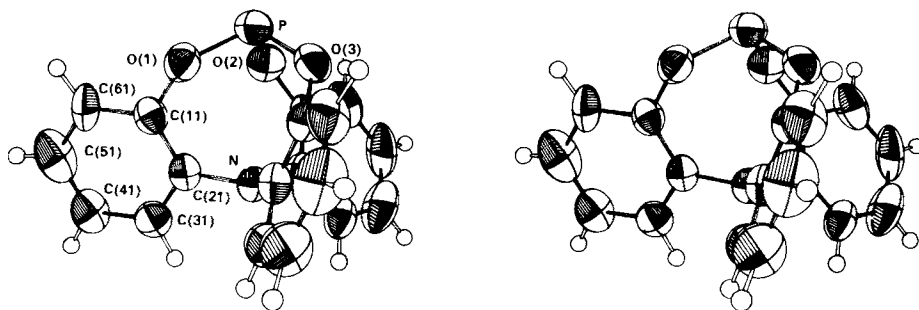


Fig. 1. ORTEP [15] drawing of molecule II, viewed perpendicular to the 3-fold axis. Atomic numbering is shown for benzene ring 1; numbering of rings 2 and 3 is analogous.

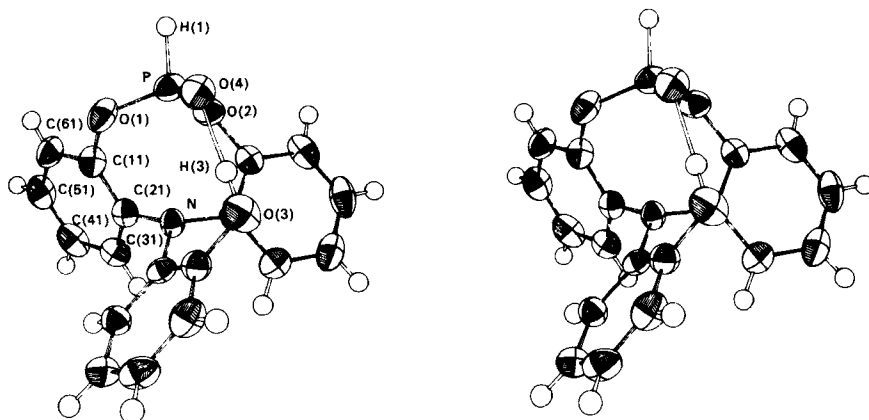


Fig. 2. ORTEP [15] drawing of molecule IV, viewed perpendicular to the $N \cdots P$ vector. Atomic numbering is shown for benzene ring 1; numbering of rings 2 and 3 is analogous; ring 3 is the dangling one.

a tertiary phosphite ester [14]. The geometry around the N-atom is slightly pyramidalized towards the outside of the cage. The structure of II resembles thus the structures of the $N(C_6H_4O)_3B$ fragment in the exocyclic pyridine and quinuclidine adducts of the 2,2',2''-nitrilotriphenolboron complexes [2].

Table 5. Average Geometries of the Bicycloundecane Framework of II and of the Open Structure IV

	II	IV	
P–H(1)	–	1.40(5)	
P–N	3.136(5)	2.926(8)	
P–O	1.634(4)	1.586(6) ^{a)}	1.453(7) ^{c)}
O–C	1.390(14)	1.400(10) ^{a)}	1.362(14) ^{b)}
C–C	1.362(18)	1.381(13) ^{a)}	1.404(6) ^{b)}
C–N	1.427(9)	1.433(9) ^{a)}	1.436(7) ^{b)}
H-bridge O(3)–H(3) \cdots O(4)		2.721(8)	
P–O–C	126.9(5)	123.8(4) ^{a)}	
O–C–C	122.0(8)	120.2(4) ^{a)}	121.6(4) ^{b)}
C–C–N	121.4(10)	118.7(4) ^{a)}	119.2(3) ^{b)}
O–P–H(1)		103.0(22) ^{a)}	109.9(18) ^{c)}
O–P–O	102.7(2)	116.3(2) ^{c)} ^{d)}	106.7(2) ^{c)}
C–N–C	118.5(6)	118.3(3) ^{a)} ^{d)}	115.2(4) ^{c)}
P–O–C–C	52.5	50.8 ^{a)}	
O–C–C–N	1.6	–0.3 ^{a)}	0.0 ^{b)}
C–C–N–P	–20.7	–20.3 ^{a)}	–48.8 ^{b)}
C–N–P–O	33.9	34.7 ^{a)}	35.0 ^{b)}
N–P–O–C	–43.6	–43.4 ^{a)}	
N–P–O(4)–O(3)			7.1 ^{b)}
P–O(4)–O(3)–C(13)			–47.7 ^{b)}
O(4)–O(3)–C(13)–C(23)			43.8 ^{b)}
^{a)} Mean values of the 2 coordinated phenoxy groups.		^{d)} Mean of two similar angles.	
^{b)} Dangling phenol group.		^{c)} Unique angle.	
^{c)} P–O(4), O(4)–P–H(1), and O(4)–P–O, resp.			

Strong acids protonate the cage of **II** at the P-atom, as seen from the splitting of the ^{31}P -NMR signal into a *d* and from the appearance of a *d* in the ^1H -NMR spectrum with the same coupling constant (see *Experimental*). The observed ^{31}P , ^1H -coupling constants as well as the ^1H -NMR chemical shifts depend to some extent on the nature of the added acid; because of the qualitative nature of these experiments, no definitive conclusions on this dependence seems warranted. AcOH does not protonate **II**. The **II**·H⁺ cation is, therefore, much more acidic than the aliphatic phosphatrane (**I**), which has been reported not to be deprotonated even by as strong bases as methoxide anions [3].

There is evidence for coordination of the nitrilotriphenolat-ligand N-atom to the P-atom upon protonation of the latter to form a tricyclic compound analogous to phosphatrane (**I**): The low-field shift of the NMR signals of the aromatic protons *o* to the N-atom (H–C(3,3',3'')) by ca. 1 ppm is an indicator for coordination of this N-atom, as shown in the case of the corresponding boron complexes [2]. The rest of the aromatic multiplet remains more or less at its original place (7.1 ppm). The protonated adduct could not be isolated in a crystalline form in any of the cases.

The phosphate **III** has probably a structure very similar to **II** with no or very little N···P interaction, as judged on the chemical shift of the protons *o* to the N-atom of the nitrilotriphenol ligand. Addition of Lewis- or proton acids results in a pronounced shift of the H–C(3,3',3'') ^1H -NMR signals towards lower field, indicating a coordination of the acid with the P=O group with a concomitant coordination of the N-atom to the now positively charged P-atom.

The phosphonate **IV** is a hydrolysis product of **II**; its structure is characterized by a H-bond from the dangling phenol group towards the P=O O-atom. The geometry around the P-atom is within the range of values normally found for phosphonates [14], and the N-atom of the ligand does not participate in the coordination sphere of the P-atom.

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