Synthesis and Reactions of Bis(4,5-benzo-1,3-dioxa-2-phospholano)dichloromethane☆

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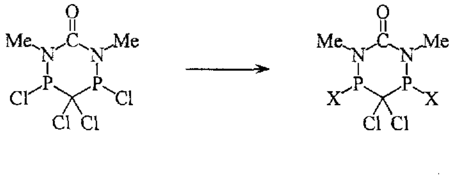
Received April 25, 1994 (revised version: May 13, 1997)

Keywords: Bisphosphane, bisdichloromethylene-bridged / Oxidation with tetrachloro-*o*-benzoquinone (TOB) / $\sigma^6\lambda^5$-phosphorate / Phosphorus Heterocycles / Structure elucidation

The title compound **3** was formed in the reaction of $Cl_2PCCl_2PCl_2$ (**2**) with catechol in the presence of triethylamine. The reaction of **3** with tetrachloro-o-benzoquinone (TOB), **4**, led to the σ^3P/σ^5P-species **5**, and the σ^5P/σ^5P-species **6a/6b**. **5** was stable only in solution, and its existence and identity are postulated on the basis of its ^{31}P-NMR spectrum. The structure of **6a/6b** could not be assigned unambiguously to one isomer. The reaction of **6a/6b** with water yielded the phosphorate **10**. The structures of **3** and **10** were determined by single crystal X-ray methods. A wide P–C–P angle (123.2°) was observed in **3**. The cation of **10** is a centrosymmetric, protonated DMF dimer with O···O 241.3 pm.

Previous investigations of derivatives of bis(dichlorophosphanyl)dichloromethane (**2**) focussed on 1,5-dimethyl-2,3,3,4-tetrachloro-1,5,2,4-diaza-diphosphorin-6-one (**1**) (Scheme 1)[1].

Scheme 1. Reactions of 1,5-dimethyl-2,3,3,4-tetrachloro-1,5,2,4-diazaphosphorinan-6-one

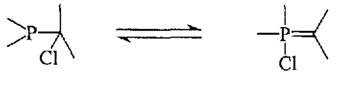


1 X = F, OMe, OEt, O^{i}Pr, OPh

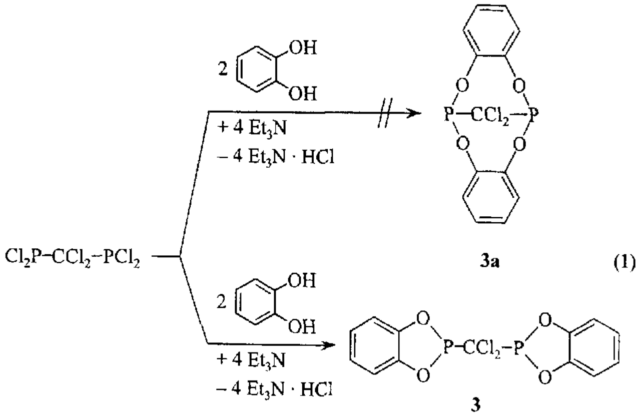
The substitution of the chlorine atoms bonded to phosphorus in **1** by fluorine, alkoxy, or phenoxy groups could be realized, with formation of the corresponding P,P′-disubstituted derivatives. A decrease of the proportion of the *cis* isomer with increasing bulk of the alkoxy substituent was noted[2].

The reaction of bis(dichlorophosphanyl)dichloromethane (**2**) with secondary amines led to mono- and disubstituted compounds of low stability that were found to change to ylidic structures via a 1,2-(C→P) migration[3] (Scheme 2). A decrease of the donor capacity of the substituents is expected to prevent this mode of migration, which has previously been described by Kolodyazhnyi[3].

Scheme 2. 1,2-(C→P) chlorotropic migration

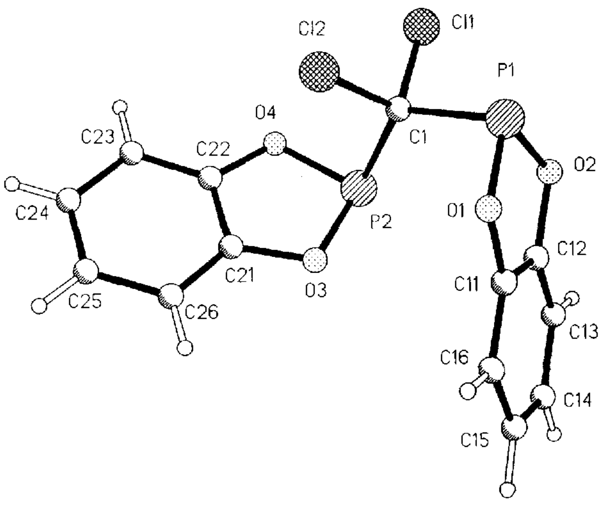


The change from the comparatively soft base, nitrogen, to the harder base, oxygen, enabled derivatives of **2** to be synthesized on a preparative scale. Diphenols were considered especially interesting in these reactions: their rearrangement by an Arbuzov mechanism is ruled out[4], the compounds are expected to be stabilized by the chelate effect, and the high reactivity, caused by the OH acidity, is desirable. The title compound **3** was obtained in the reaction of **2** with catechol in the presence of triethylamine as a base, which removed the HCl. No intermediate products were observed during this preparation; during the reaction of **2** with only one equivalent of catechol, half of **2** remained unchanged.



Two structures are conceivable for the product: (i) a bridged structure in which the two phosphorus atoms are each bonded to one catechol unit (**3a**), and (ii) a structure involving two "end-on" substituted phosphorus atoms that are part of two five-membered rings (**3**).

Figure 1. The molecule of **3** in the crystal[a]



[a] Radii are arbitrary. Selected bond distances [pm] and angles [°]: P(1)-O(1) 165.5(2), P(1)-O(2) 165.8(2), P(1)-C(1) 189.8(3), P(2)-O(3) 165.6(2), P(2)-O(4) 166.5(2), P(2)-C(1) 189.1(3), C(1)-Cl(2) 178.6(3), C(1)-Cl(1) 180.6(3); O(1)-P(1)-O(2) 94.97(11), O(1)-P(1)-C(1) 101.44(12), O(2)-P(1)-C(1) 97.16(12), O(3)-P(2)-O(4) 94.41(10), O(3)-P(2)-C(1) 102.99(12), O(4)-P(2)-C(1) 97.53(11), Cl(2)-C(1)-Cl(1) 110.1(2), Cl(2)-C(1)-P(2) 115.2(2), Cl(1)-C(1)-P(2) 100.4 (2), Cl(2)-C(1)-P(1) 105.8(2), Cl(1)-C(1)-P(1) 100.51(14), P(2)-C(1)-P(1) 123.2(2).

Because of their high symmetry, the two structures could not be distinguished by their ^{1}H-, ^{13}C- and ^{31}P-NMR spectra. Unambiguous proof for the formation of **3** was provided by a single-crystal X-ray diffraction study (see below).

The ^{31}P-NMR spectrum **3** displayed a single line at δ = 144.6. Compared to the starting compound **2** (δ = 159.04) this line is shifted to high field, and is nearly identical to the $\delta(^{31}P)$ values of the *N,N'*-dimethylurea-bridged, alkoxy-substituted bisphosphanes[2]. In the ^{13}C-NMR spectrum, the signal from the CCl_2 group (δ = 88.92) is conspicuously weak in contrast to the resonances in the aromatic region. Furthermore, this signal is split into a triplet [^1J(PC) 104.2 Hz], by coupling between ^{13}C and two ^{31}P nuclei. The unusually low intensity is probably due to the long relaxation times, as is known for quaternary carbon atoms[5].

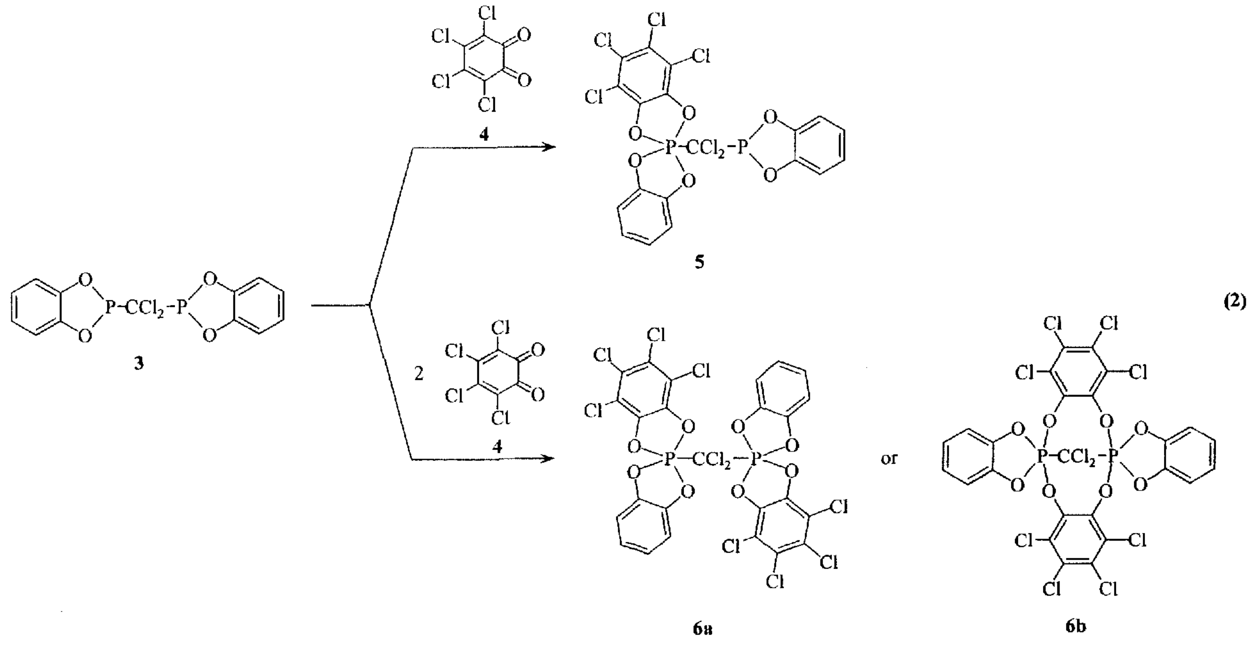
X-ray Crystal Structure of 3

The stereochemistry at the carbon atom of the dichloromethylene bridge is strongly distorted tetrahedral, conceivably due to the steric demand of two dioxaphospholane substituents. The bond angle P2–C1–P1 is widened to 123.2(2)°, and Cl1–C1–P1 and Cl1–C1–P2 are decreased to 100.51(14) and 100.4(2), respectively. An alternative rationalization would be provided by Bent's rule[6][7], according to which electronegative groups prefer hybrid orbitals of higher p-character, whereas more electropositive substituents (e.g. the phosphorus atoms bonded to carbon) prefer orbitals of pronounced s character. Few P–CCl_2–P groupings have been characterized structurally. The crystal structure of calcium dichloromethylene diphosphonate may be considered for comparison: the Cl–C–Cl angle (109.3°) is ideal tetrahedral, whereas the P–C–P angle is 114.8°[8].

The five-membered ring, made up of P2, O3, O4, C21, and C22, is nearly planar (with a maximum deviation of 2.4 pm from a plane through all the ring atoms), whereas the other heterocyclic ring was found to display a slight envelope conformation: P1 lies 25.6 pm outside the plane consisting of O1, O2, C11, and C12, the mean deviation from this plane amounting to 1.1 pm. The angle between the planes through O1, O2, C11–C16 and O3, O4, C21–C26 is 61°.

Compound **3** was allowed to react in dichloromethane with one or two equivalents of tetrachloroorthobenzoquinone (TOB) **4** [Eq. (2)].

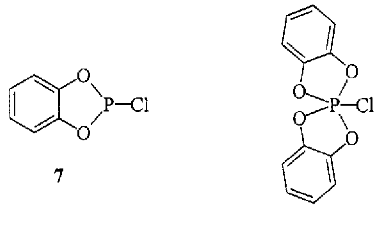
Upon addition of one mole of TOB to **3**, the formation of **5** was observed in the reaction mixture by $^{31}\{^1H\}$-NMR



spectroscopy. Because of its very limited stability, it was impossible to isolate pure **5**. Under the reaction conditions, the formation of **6a/6b** (poorly soluble in dichloromethane) was observed. **6a/6b** could be obtained in a pure state as a colourless precipitate upon reaction of **3** with two molar equivalents of TOB.

The $\delta(^{31}P)$ value of the σ^3P-atom in **5** ($\delta = 141.20$) may be compared to that of $\delta = 173$ for catechyl chlorophosphite **7**[9], synthesized in the reaction of catechol with phosphorus trichloride[10] (Scheme 3, Table 1). The $\delta(^{31}P)$ value of the TOB-substituted phosphorus atom in **5** lies in the region typical of σ^5P[11]; cf. the δ^{31}P value of the chloro-spiro-phosphorane **8** ($\delta = -9.4$)[7] (Scheme 3; Table 1), synthesized in the reaction of catechol with phosphorus pentachloride[12].

Scheme 3. Proposed formulae of compounds **7** and **8**



7

8

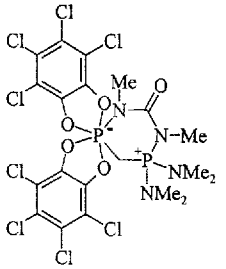
Table 1. ^{31}P{^{1}H}-NMR data of **5** and **6a/6b**, compared to those of **7** and **8**

^{31}P NMR of compound	$\sigma^3(PO_2C_6H_4)$ [δ/ppm]	$\sigma^5P(O_2C_6H_4)(O_2C_6Cl_4)$ [δ/ppm]	m[a]	^2J(PP) [Hz]
5	141.20	−12.95	d	18.3
6a/6b		−16.30	s	
7	173		s	
8		−9.4	s	

[a] m denotes the multiplicity of the signal.

For compound **6a/6b** only a singlet [$\delta(^{31}P) = -16.30$] was observed in the ^{31}{^{1}H}-NMR spectrum and, therefore, only a symmetrically substituted product is possible. A dichloromethylene species analogous to **9**[13] can therefore be excluded (Scheme 4).

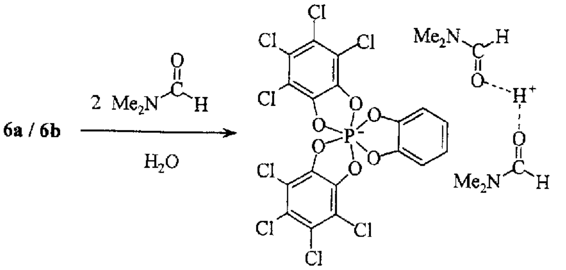
Scheme 4. Proposed formula of compound **9**



9

The isomers **6a** and **6b** [Eq. (2)] need to be distinguished. ^{13}C-NMR spectroscopy cannot accomplish this because different PC coupling constants are not to be expected. No unambiguous conclusions as to the structure can be drawn from the mass spectrum. The value of *m/z* = 383 corresponds to the fragment $\sigma^5P(O_2C_6H_4)(O_2C_6Cl_4)$, which may arise directly from **6a** or through a rearrangement of **6b**.

An attempt to prepare single crystals of the poorly soluble product **6a/6b** failed: during the attempted crystallisation from *N,N*-dimethylformamide, adventitious water led to small colourless crystals of **10** [Eq. (3)].



(3)

10

+ **other products**

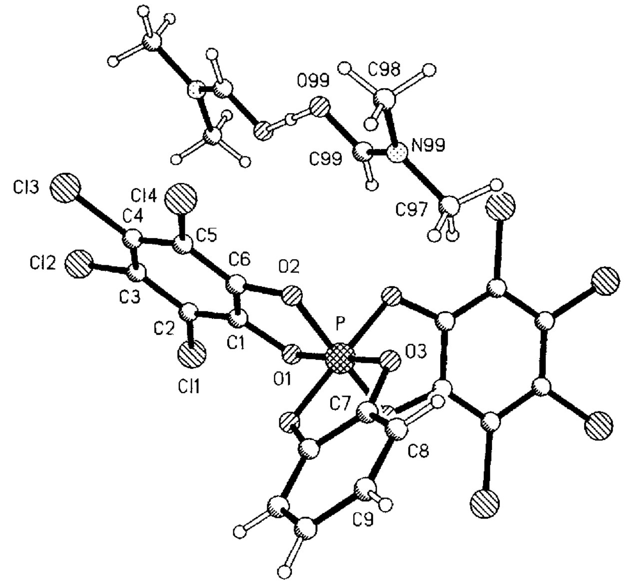
The $\delta(^{31}P)$ value of **10** ($\delta = -79.88$) is characteristic of phosphorus in coordination number six, bearing unsaturated cyclic substituents. An FAB-mass spectrum exhibited, as a molecular and base peak, the anion (*m/z* = 630). In the ^{1}H-NMR spectrum the aryl protons were observed in the appropriate ratio to the dimethylformamide protons. No resonance was observed in the ^{1}H-NMR spectrum for the proton located between two molecules of dimethylformamide. Presumably, this resonance is broadened by a dynamic process. Because of the poor solubility of **10**, even in acetonitrile, a ^{13}C-NMR spectrum could not be obtained.

X-ray Crystal Structure of 10

The structure of **10** was elucidated by X-ray structure analysis. The anion possesses twofold symmetry, with the phosphorus atom occupying the special position 0,*y*,1/4. The rest of the symmetry-independent part of the anion consists of half a catechol group and one tetrachloro-catechol group. The octahedral coordination geometry at phosphorus is only slightly distorted. The largest deviations from ideal values are O3#1−P−O2 [93.81 (13)°] and O2#1−P−O2 [176.4 (2)°].

The P−O bond distances P−O1 and P−O2 [172.9 (3) and 172.1 (3)pm] are significantly longer than P−O3 [168.8 (3) pm]. This increase in bond length of P−O1 and P−O2 is probably related to the greater steric demand of the tetrachlorocatechol system, relative to the unsubstituted catechol system. Similar P−O bond distances (170.4−173.2 pm) were observed for the compound $[Et_2NH_2]^+[\sigma^6P(O_2C_6Cl_4)_3]$[9]. The five-membered rings of the dioxaphosphole ring system display a slight envelope conformation; the phosphorus atom lies 22.8 pm outside a plane through the remaining ring atoms. The five-membered ring of the unsubstituted dioxaphosphole ring system, in contrast, is nearly planar, the mean deviation for all atoms amounting to only 0.8 pm. The protonated DMF-dimer cation, $[(DMF)_2H]^+$ exhibits inversion symmetry (the bridging proton is situated on 0, 1/2, 0). The torsion angle

Figure 2. The molecule of **10** in the crystal[a]



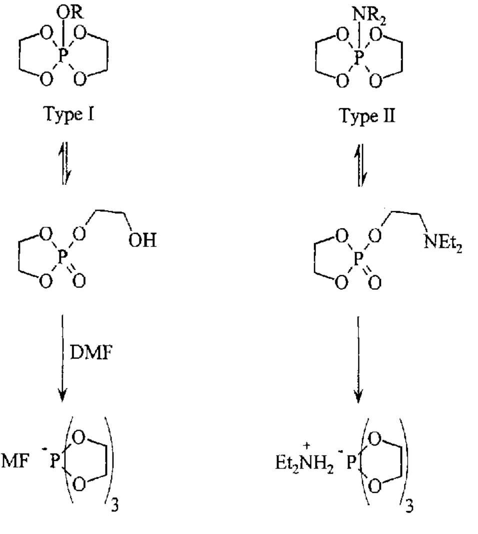
[a] Radii are arbitrary. Selected bond distances [°]: P–O(3) 168.8(3), P–O(2) 172.1(3), P–O(1) 172.9(3), O(1)–C(1) 135.1(4), O(2)–C(6) 135.1(4), O(3)–C(7) 137.1, O(99) 126.1(5), N(99)–C(99) 129.3(6), N(99)–C(98) 145.1(6), N(99)–C(97) 145.6(6); O(3)–P–O(3)#1 92.3(2), O(3)–P–O(2) 88.67(13), O(3)#1–P–O(2) 93.81(33), O(2)#1–P–O(2) 176.4(2), O(3)–P–O(1) 178.62(13), O(3)#1–P–O(1) 87.67(12), O(2)#1–P–O(1) 87.57(13), O(2)–P–O(1) 89.95(13), O(1)–P–O(1)#1 92.3(2), C(99)–N(99)–C(98) 121.6(4), C(99)–N(99)–C(97) 121.1(4), C(98)–N(99)–C(97) 117.3(4), O(99)–C(99)–N(99) 122.3(4). – Symmetry operator, #1 ≡ $-x, y, -z+1/2$

C97–N99–C99–O99 (179.8°) leads, together with the inversion symmetry, to a nearly planar nine-membered chain. The O99···O99′ distance (241.3 pm) is typical of strong hydrogen bonding. The C99–O99 bond in the carbonyl group (126.1 pm) is comparatively long. Comparable DMF-dimer cations were observed previously for $[(DMF)_2H]_2[TcBr_6]$[16]. In this compound, two molecules of the amide are coordinated by the carbonyl oxygen atoms to a proton of the complex acid. The presence of symmetrical hydrogen bridges, with the bridging proton in the center of the O···O axis, was suggested by IR spectroscopic data. Compared to **10**, the increase in the O···O distance (244 pm) is notable; it suggests somewhat weaker hydrogen bonding. The CO bond length in $[(DMF)_2H]_2[TeBr_6]$ (126.9 pm) is slightly increased.

An attempt to detect a second phosphorus-containing species by ^{31}P-NMR spectroscopy was unsuccessful. We surmise that such a species would be rapidly removed from the solution by rearrangement and elimination reactions. The formation of comparable σ^6P species has been described in the literature[13][14]. Such reactions frequently originated from spirohydroxy-phosphoranes[17] (Type I, Scheme 5) or spiroaminophosphoranes[18] (Type II, Scheme 5), both of which were in equilibrium with the isomeric σ^4-phosphate esters. The former reacted with dimethyl formamide with formation of the DMF-stabilized proton complexes and σ^6P-anions.

The latter formed ammonium salts, involving σ^6P[14] (Scheme 5).

Scheme 5. Some reaction pathways taken by σ^6P-species



I. V. S. is indebted to the *Alexander von Humboldt-Stiftung* for the award of a postdoctoral fellowship. Gifts of chemicals received from *BASF AG*, *BAYER AG* and *HOECHST AG*, used in this research, are gratefully acknowledged, as is the support of the *Fonds der Chemischen Industrie*. Thanks are due to Dipl.-Chemiker *Ralf Sonnenburg* for preparing the formula schemes.

Experimental Section

All operations were conducted with exclusion of air and moisture in carefully dried solvents[19]. Melting points are uncorrected (determined on a Büchi 530 apparatus in sealed 1mm capillaries). – NMR: Bruker AC 200. [^{1}H: 200.15 MHz, ^{13}C: 50.3 MHz, with $CDCl_3$, and ^{31}P: 81.0 MHz, using 85 % H_3PO_4 as reference]. – MS: Finnigan MAT 8430. – Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen. – The abbreviation "i. v." (in vacuo) refers to a pressure of 0.5 Torr.

The precursor **2** was synthesized in accord with the literature report[20].

Reaction of Dichloromethylene Bis(dichlorophosphane) **2** *with Catechol. – Synthesis of Bis(4,5-benzo-1,3,2σ^3*-dioxaphospholano)-dichloromethane (**3**): A solution of 1.52 g (14 mmol) of catechol and 2.82 g (28 mmol) of triethylamine in 20 ml of diethyl ether was added dropwise to a solution of 2 g (7 mmol) of **2** in 10 ml of diethyl ether. The reaction mixture was cooled with ice/water during the addition. After 2 h the triethylammonium chloride formed was removed by filtration. The volume of the filtrate was reduced i. v. to 10 ml. At –30 °C 0.88 g (35 %) of **3** (mp. 104 °C) crystallized. – ^{1}H NMR ($CDCl_3$): δ = 7.15–7.01 (m, $C_{Ar}H$). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 146.40 [dd, ^2J(PC) = 5.94 Hz, ^4J(PC) = 2.97 Hz, 2 C_{ipso}]; 146.34 [dd, ^2J(PC) = 5.54 Hz, ^4J(PC) = 2.48 Hz, 2 C_{ipso}]; 123.70 (s, 4 $C_{Ar}H$); 113.08 (s, 4 $C_{Ar}H$); 88.92 [t, ^1J(PC) = 104.2 Hz, $PCCl_2P$]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 144.63 (s). – MS (EI, 70eV): *m/z* (%): 360 (4) $[M]^+$, 325 (0.3) $[M^+ - Cl]$, 248 (12) $[HP(O_2C_6H_4)_2]$, 139 (100) $[PO_2C_6H_4]$. – $C_{13}H_8Cl_2P_2O_4$ (361.04): found C 43.11, H 2.47; calc. C 43.25, H 2.23.

Reaction of **3** *with One Molar Equivalent of Tetrachloro-o-benzoquinone (TOB)* (**4**). – *Formation of (4,5-Benzo-1,3,2σ^3*-dioxaphospholano)(spiro[5.5]-(tetrachlorocatecholato)-4′,5′-benzo-1′,3′,2′σ^5-dioxaphospholano)dichloromethane (**5**): TOB (**4**) (0.14 g; 0.55

mmol) was added to a solution of 0.2 g (0.55 mmol) of **3** in 1 ml of dichloromethane. After 2 h a colourless precipitate of **6a/6b** had formed. The supernatant solution, according to the ^{31}P-NMR spectrum, besides **6a/6b**, also contained 50 % of **5**, which was stable only in solution and could not be isolated; decomposition products were not identified. – $^{31}P\{^1H\}$ NMR (CH_2Cl_2, C_6D_6 capillary); δ = 141.20 [d, $^2J(PP)$ = 18.3 Hz, $\sigma^3P(O_2C_6H_4)$]; –12.95 [d, $^2J(PP)$ = 18.3 Hz, $\sigma^5P(O_2C_6H_4)(O_2C_6Cl_4)$]. – $C_{19}H_8Cl_6O_2P_2$ (606.91).

Reaction of **3** *with Two Molar Equivalents of TOB* (**4**). – *Synthesis of* (**6a/6b**): A solution of 0.65 g (2.66 mmol) of TOB (**4**) in 10 ml of dichloromethane was added dropwise to a solution of 0.48 g (1.33 mmol) of **3** in 10 ml of dichloromethane at room temperature (20 min.). The red colour of the TOB was discharged within 2 sec after each addition. After 2 h the colourless precipitate formed was collected by filtration, and was washed with 10 ml of dichloromethane. The product was dried i. v. (0.5 Torr), 0.93 g (82 %) of **6a/6b** (m.p. 211 °C) was obtained. – ^{1}H NMR ($CDCl_3$): δ = 7.45–6.34 (m, $C_{Ar}H$). – $^{13}C\{^1H\}$ NMR ($CDCl_3$); δ = 143.95 [d, $^2J(PC)$ not resolved, 4 C_{ipso}]; 140.89 [t, $^2J(PC)$ not resolved, 4 C_{ipso}]; 126.63 (s, 4 $C_{Ar}H$), 123.37, 115,59 (s, 8 $C_{Ar}Cl$); 111.33 [t, $^3J(PC)$ = 7.53 Hz, 4 $C_{Ar}H$]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$); δ = –16.30 (s). – MS (EI, 70 eV): *m/z* (%): 848 (0.3) [M^+], 813 (0.25)[M^+ – Cl], 778 (23) [M^+ – 2 Cl], 383 (12) [$P(O_2C_6H_4)(O_2C_6Cl_4$], 139 (40) [$PO_2C_6H_4$], 121 (100). – $C_{25}H_8Cl_{10}O_8P_2$ (852.77): found, C 35.06, H 0.96; calc.: C 35.21, H 0.95.

Reaction of **6a/6b** *with Water in Dimethylformamide (DMF). – Formation of the Phosphorate* **10**: A few crystals of **6a/6b** (0.5 g; 0.6 mmol), were dissolved in 2 ml of wet DMF. After 1 h stirring at room temperature 20 ml of acetonitrile was added. Stirring at room temperature was then continued for 24 h. Subsequently, the acetonitrile and DMF were removed by pumping i. v. (0.5 Torr) over 8 h. The oily residue was dissolved in 10 ml of dichloromethane. At –30 °C 0.22 g (47 %) of crystalline **10** was formed. – ^{1}H NMR ($CDCl_3$): δ = 8.05 [s, $HC(:O)N(CH_3)_2$], 6.75 (s, 4 $C_{Ar}H$), 3.08 (s, 2 NCH_3), 2.95 (s, 2 NCH_3). – ^{13}C NMR: because of the poor solubility of **10** in all common organic solvents, no ^{13}C-NMR spectrum could be obtained. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –79.88 (s, σ^6P). – MS (FAB neg., glycerol matrix), *m/z* (%): 630 (100) [anion]. – $C_{24}H_{19}Cl_8N_2O_8P$ (777.98).

X-ray Crystal Structure Analysis of Compounds **3** *and* **10**. – *Compound* **3**: $C_{13}H_8Cl_2O_4P_2$, M = 361.03, monoclinic, $P2_1/n$, a = 998.3(3), b = 958.8(3), c = 1546.0(4) pm, β = 101.97(2) °, V = 1.4476(7) nm^3, Z = 4, D_x = 1.657 Mg/m^3, μ = 0.68 mm^{-1}, T = 178 K, $F(000)$ = 728, $2\Theta_{max}$ = 55 °, 3621 reflections (3326 independent), R_{int} = 0.042, R (F, > $4\sigma F$) = 0.040, wR (F^2, all reflections) = 0.113, 190 parameters, S = 1.0, max. Δ/σ = 0.001, max. $\Delta\rho$ = 299 e nm^{-3}; colourless crystal, 0.84 × 0.18 × 0.16 mm^3.

Compound **10**: $C_{24}H_{19}Cl_8N_2O_8P$, M = 777.98, monoclinic, $C2/c$, a = 1970.5(5) pm, b = 953.6 (3) pm, c = 1667.0(4) pm, β = 103.54(2) °, V = 3.0453(14) nm^3, Z = 4, 3046 reflections (2689 independent), R_{int} = 0.039, R (F, >$4\sigma F$) = 0.048, wR(F^2, all reflections) = 0.118, 197 parameters, S = 1.1, Max. Δ/σ < 0.001, Max. $\Delta\rho$ = 363 e nm^{-3}; colourless crystal, 0.60 × 0.35 × 0.20 mm^3.

Data Collection and Reduction: The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer [Siemens R3 (**3**) and Stoe STADI-4 (**10**), each with a Siemens LT-2 low temperature attachment]. Monochromated Mo-K_α radiation was employed. The orientation matrix for **3** was refined from diffractometer angles of 50 reflections in the 2Θ region 20–23 °. For **10**, the lattice constants were refined from ± ω values of 60 reflections in the 2Θ region 20–23 °.

Structure Solution and Refinement: The structures were solved using direct methods, and were refined anisotropically on F^2 (Program SHELXL-92[21]). Hydrogen atoms were refined with a riding model. Full details of the structure determinations have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, from where this material may be requested, quoting the full literature citation, and the reference numbers CSD 400 869 (**3**), and CSD 400 870 (**10**).

☆ Dedicated to Professor *Hans-Georg Maier* on the occasion of his 65th birthday.

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