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1,5-Dimethyl-2,3,3,4-tetrachloro-1,5,2,4-diazadiphosphorinan-6-one and Some Derivatives. Part II.

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ABSTRACT

The title compound **1** *was allowed to react with catechol, 2,3-dihydroxynaphthalene, tetrabromocatechol, resorcinol, saligenin, and 3,5-di-tert-butylcatechol in the presence of triethylamine to form compounds* **4a**–**4d** *and* **4f**. *Whereas the catechol derivative* **4a**, *the naphthol derivative* **4b**, *and the tetrabromocatechol derivative* **4c** *could be readily obtained, the saligenin derivative* **4d** *and the 3,5-di-tert-butylcatechol derivative* **4f** *were found to be stable only in solution. Contrary to expectation, compound* **4e** *was not formed in the reaction of* **1** *with resorcinol. The reaction of* **1** *with 1,2,4,5-tetrahydroxybenzene led to the pentacyclic derivative* **4g**. *Reaction of hydroquinone with* **1** *led to the formation of the polycyclic structure* **4h**. *Crystal structure analyses of* **4a** *and* **4b** *show that the nine-membered rings adopt essentially identical "tub" conformations in which the P and O atoms are coplanar. The P–C–P angles (across the CCl_2 bridge) are wide (ca. 119°).* © *1997 John Wiley & Sons, Inc.*

INTRODUCTION

Continuing our investigation of compounds containing the $PCCl_2P$ group, we recently described the reactions of heterocyclic compounds, derived from the title compound (**1**), with monofunctional alcohols and phenol [1]. The bis-OR-substituted and N,N′-dimethylurea-bridged $PCCl_2P$ compounds were found, according to their NMR spectra (^1H, ^{13}C, and ^{31}P), to exist as *cis* and *trans* isomers. The reaction of $Cl_2PCCl_2PCl_2$ **2** with catechol led to the formation of compound **3**, involving two benzodioxaphospholane rings connected via a CCl_2 group, and not to the expected isomer **3a** (Scheme 1) [2].

RESULTS AND DISCUSSION

To synthesize a catechol-bridged, seven-membered ring from **2** and catechol, a protecting group was needed to suppress the formation of the benzodioxaphospholane ring. The substitution of **2** with N,N′-dimethylurea with formation of **1** blocks one position at each λ^3-phosphorus atom, leaving the other two PCl bonds available for substitution reactions of **1** with catechol and its derivatives. The reactions were conducted in the presence of triethylamine in different solvents, depending on the solubility of the phenolic compounds. The less polar compounds, catechol, 2,3-dihydroxynaphthalene, tetrabromocatechol, 3,5-di-tert-butylcatechol, resorcinol, and saligenin reacted readily in diethyl ether or dichloromethane, whereas the reactions with 1,2,4,5-tetrahydroxybenzene and hydroquinone proceeded rapidly in tetrahydrofuran. The sequence of addition depended upon the ability of the phenols to form salts with triethylamine. If poorly soluble prod-

Dedicated to Professor Joseph Grobe on the occasion of his sixty-fifth birthday.

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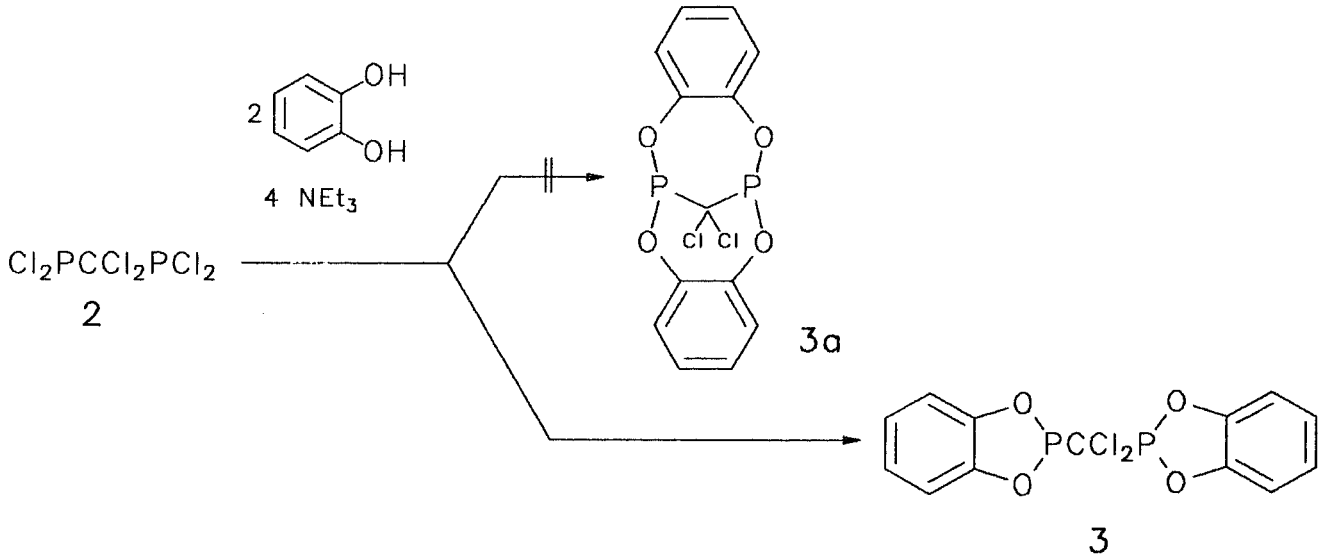


SCHEME 1 Formation of **3**.

ucts were formed, triethylamine was added first to **1**, followed by the phenol derivative. Alternatively, a neutral reaction medium was established by addition of a mixture of triethylamine and phenol to a solution of **1** in diethyl ether.

4a was formed in the reaction of **1** with catechol within 16 hours as colorless crystals in moderate yield (Scheme 2). It was identified by NMR spectroscopy and by an X-ray crystal structure determination. The naphthol derivative **4b** was obtained in very low yield and was characterized by NMR spectroscopy and X-ray crystal structure analysis only. The reaction of **1** with tetrabromocatechol took 5 days, but **4c** was formed in higher yield than **4a**.

Reaction of **1** with saligenin resulted in a mixture of products. While attempts to obtain **4d** in a crystalline state failed, the product actually produced showed two characteristic signals in the ^{31}P-NMR spectrum. In this way, the probable structure of **4d** could be established by comparison of the $\delta(^{31}P)$ values of **4d** with those of compounds **4a** and **4b**.

The reaction of **1** with resorcinol led to several oligomeric species, but the expected product **4e**, involving an eight-membered ring, was not formed. In the reaction of 3,5-di-tert-butylcatechol with **2**, the unstable compound **4f** was formed. Its identity was suggested by ^{31}P-NMR data.

1,2,4,5-Tetrahydroxybenzene and **1** reacted at -30°C with formation of **4g** as a yellow powder in moderate yield, and this product was characterized as a mixture of *cis* and *trans* isomers. The reaction mixture also contained substances similar to those observed during the reaction of resorcinol with **1** (^{31}P-NMR spectroscopic evidence). With hydroquinone, **4h** was formed at -30°C and was isolated at 0°C as a colorless oil.

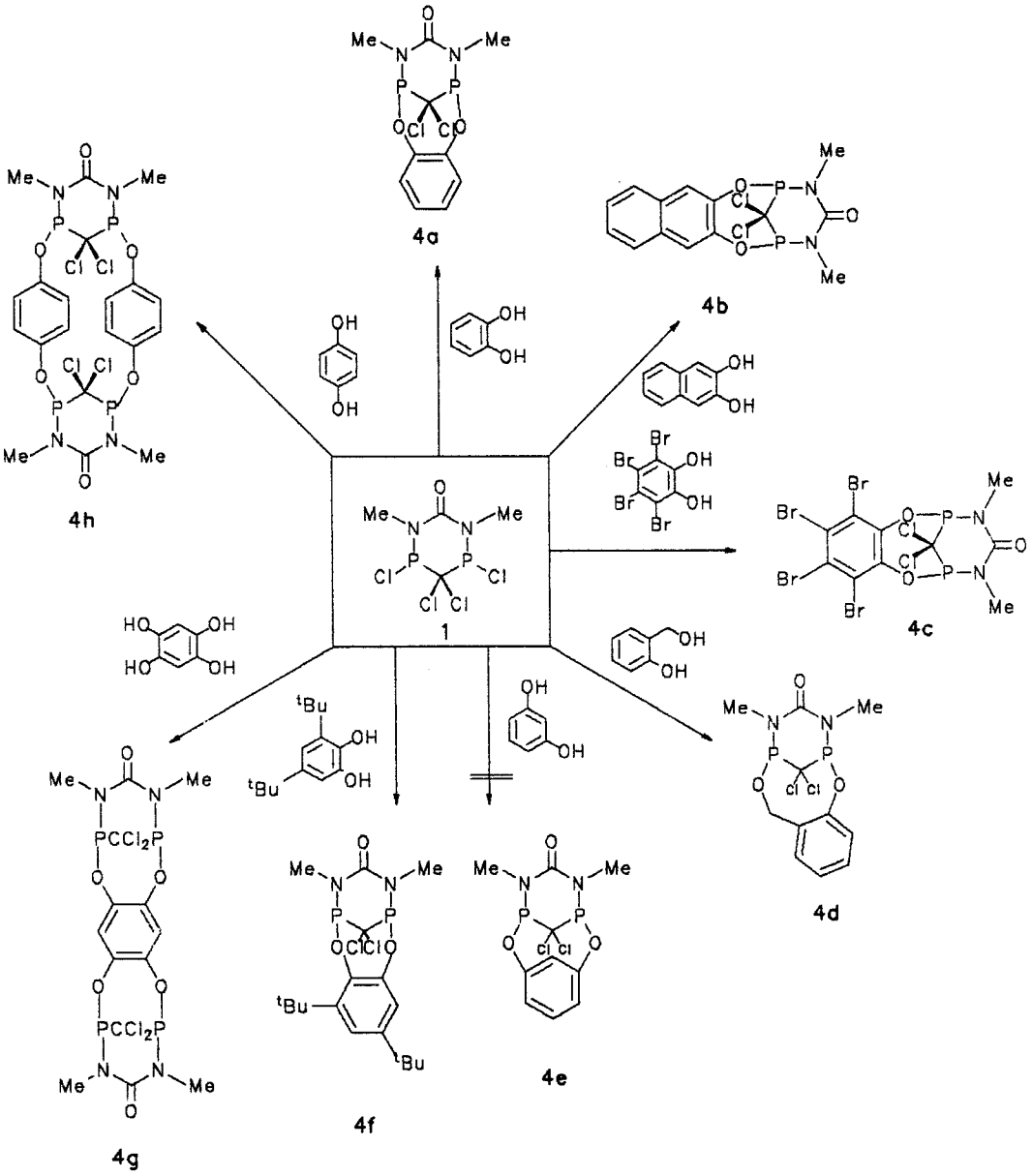
Experiments with trimethylsilylated di- and tetraphenols [e.g., bis(trimethylsilyl)catechol and 1,2,4,5-tetrakis(trimethylsiloxy)-benzene] failed; no reaction with **1** took place even on refluxing in toluene (Scheme 3). Apparently, the trimethylsiloxy group is more stable than the PO group.

DISCUSSION OF THE NMR-SPECTRA OF COMPOUNDS 4a–4h

As in the case of the bicyclic species **5** (Figure 1), there exists only one isomer of **4a**.

The ^{31}P-NMR spectrum of **4a** shows a single signal at $\delta = 96.65$ shifted to lower field (compared to **5**) because of the influence of the more electronegative oxygen atoms. The ^{1}H-NMR spectrum of **4a** reveals two groups of signals, a doublet for the two PNCH_3 groups and a multiplet for the four arylic protons. The ^{3}J(PH)-coupling constant (11.6 Hz) is similar to that of the monocyclic diphenoxy substituted derivative **6** (Figure 1). Compounds **5** and **6** have been reported earlier [1]. The ^{13}C-NMR resonances of **4a** show a triplet at $\delta = 144.51$ for the carbonyl group and two doublets of doublets caused by the presence of the two quaternary carbon atoms of the catechol ring.

The nature of compound **4b** is suggested from its $\delta(^{31}P)$ value of 101.12, 4 ppm to lower field, compared to **4a**. The ^{1}H-NMR resonances differ only as



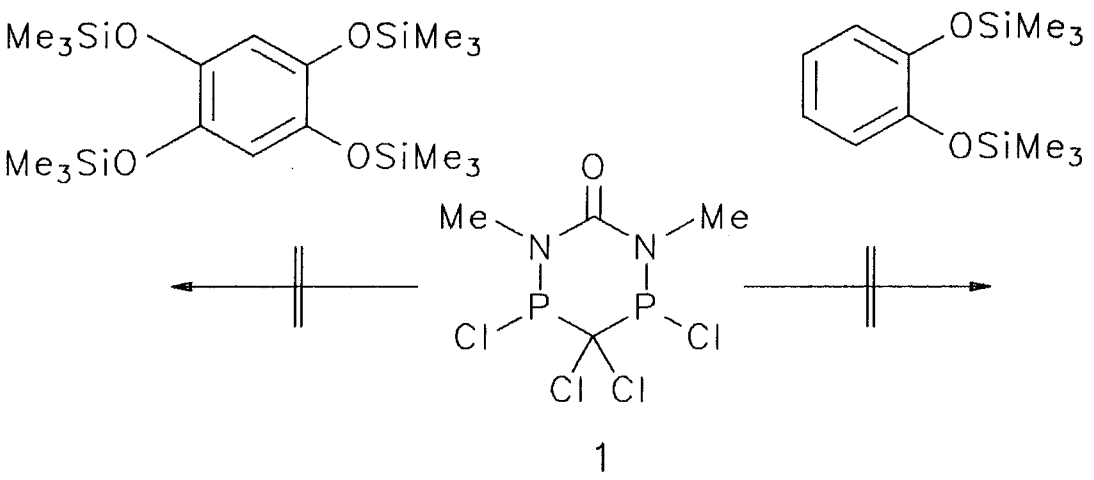
SCHEME 2 Formation of the compounds **4a**–**h**.

to the region of the aromatic rings. The $\delta(^{13}C)$ value of the carbonyl group is shifted to low field, relative to the value in **4a**, by about 6 ppm. The NMR spectra correspond to the results of the X-ray crystal structure analysis of **4b**.

The $\delta(^{31}P)$ value of **4c** is nearly identical to that of **4a**. The ^{1}H-NMR spectrum reveals only a doublet ($^{3}J(PH)$ = 11.3 Hz) at δ 3.13. No steric influence of the four bromine atoms at the aromatic ring is apparent (Table 1).

An attempt to expand the cyclic system to an eight-membered ring (**4d**) using saligenin led to a mixture of products. Besides two groups of signals with δ = 127.39 and 106.35, the coupling constants of which could not be resolved, further peaks in the region of δ 40 to 10 were detected in the ^{31}P-NMR spectrum of **4d**. The reaction probably involved the formation of a λ^4P=O group.

Steric overcrowding of the catechol substituent with two tert-butyl groups in positions 3 and 5 led only, in part, to a tricyclic structure **4f**. This compound proved to be unstable and could only be crystallized as a mixture of products. Thus, only the $\delta(^{31}P)$ values could be determined, which showed a



SCHEME 3 Experiments with trimethylsilylated phenol derivatives and **1**.

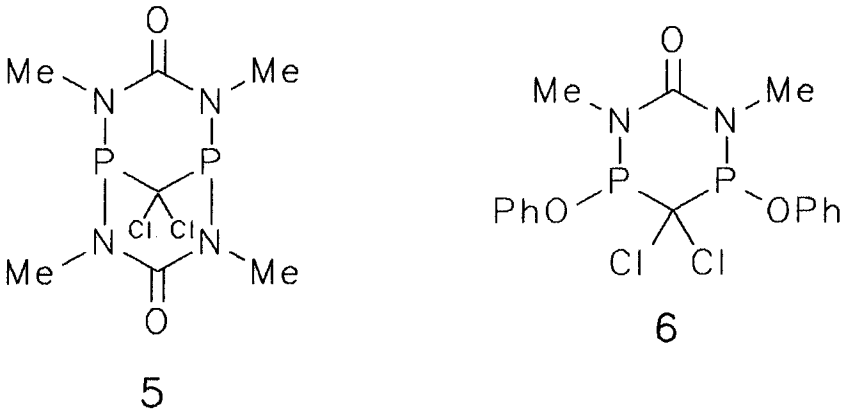


FIGURE 1 Compounds **5** and **6**.

TABLE 1 δ(^{31}P, ^{1}H, ^{13}C) Values and Coupling Constants of Compounds **4a**–**h**

Compound	*^{31}P*		*^{1}H (NCH_3)*	*^{3}J(PH)*	*^{13}C (CO)*
	δ [ppm]	δ [ppm]	δ [ppm]	[Hz]	δ [ppm]
4a	96.65		3.05	11.30	144.51
4b	101.12		3.06	11.30	150.37
4c	97.29		3.13	11.60	149.64
4d	127.39	106.35			
4f	138.40	135.28			
4g	97.11	97.62	3.06	11.60	150.09/149.87
4h	128.60	127.48	3.19/3.07	11.17/11.64	152.93/152.76

low field shift of 38 and 35 ppm, respectively, compared to **4a**. This could be interpreted by an increase of the P–O distances caused by the bulky groups on the aromatic ring. The δ(^{31}P) values differ slightly from each other because of the 3,5-substitution of the benzene ring.

4g was isolated in NMR spectroscopically pure form. The ^{31}P-NMR spectrum revealed two signals at δ 97.11 and 97.62, in a 3:1 ratio. The more intense resonance is assumed to belong to the *trans* form (Figure 2), which should be favored for steric reasons.

In the ^{1}H-NMR spectrum of **4g**, two resonances are due to the two arylic protons, and a doublet is caused by the four NCH_3 groups. The isomeric forms are not observed. The δ(^{1}H) values are similar to those of **4a**. *Cis* and *trans* isomers can also be distinguished by ^{13}C-NMR spectroscopy.

Product **4h** also exists as a mixture of *cis* and *trans* isomers as a result of the different orientation of the $PCCl_2P$ groups, relative to the aromatic rings (Figure 3). The ^{1}H-NMR spectrum shows the resonances of the NCH_3 groups as two doublets at δ 3.19 and 3.07, in a 4:1 ratio. Also, in the ^{13}C-NMR spectrum, two doublets were detected for the NCH_3

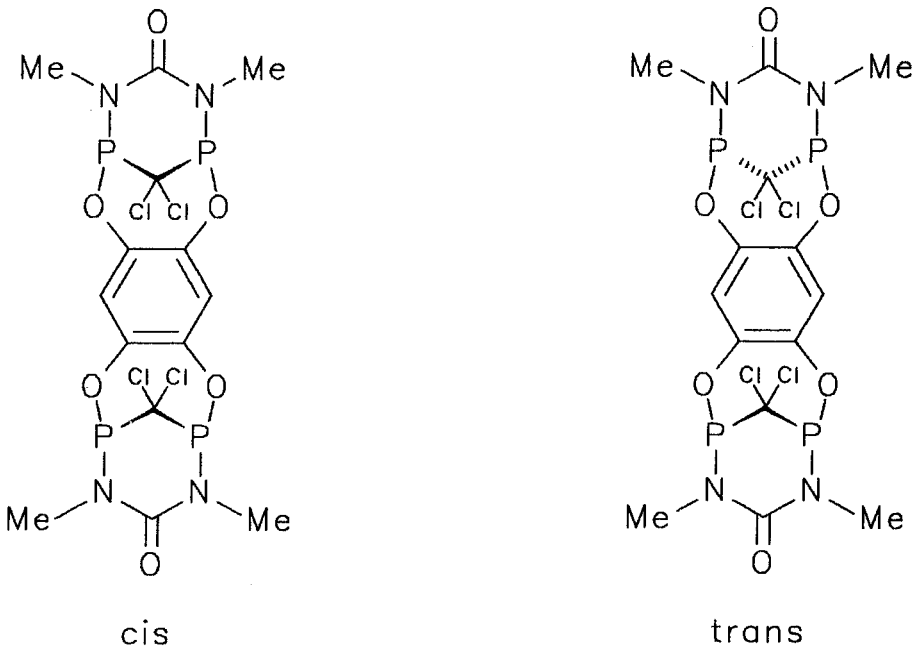


FIGURE 2 *Cis* and *trans* isomers of **4g**.

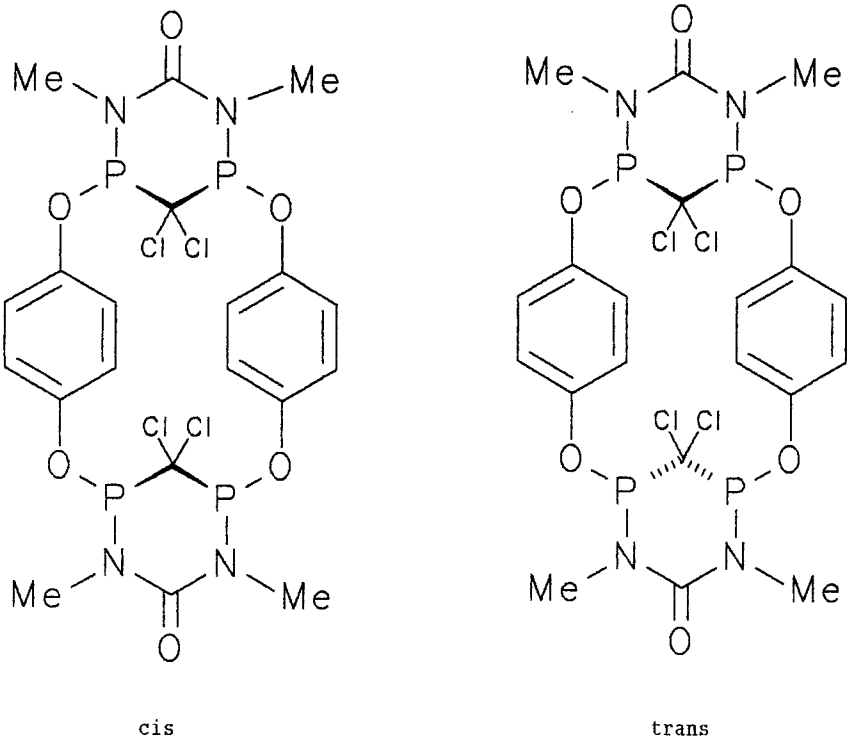


FIGURE 3 *Cis* and *trans* isomers of **4h**.

groups. The ^2J(PC) values (37.0 and 38.9 Hz) are very similar to those of **4a**, **4b** (38.8 Hz), **4c** (40.4 Hz), and **4g** (39.9 Hz). It is impossible to decide if the *cis* or the *trans* isomer is the preferred conformer, because of the large distance between the two N,N′-dimethylurea bridges.

Furthermore, the formation of species **7** (rather than **4h**) also has to be considered, according to the NMR-spectroscopic data and the elemental analysis (Figure 4).

The mass spectrum of **4h** was ambiguous. Species **7** has to be excluded because of the extreme strain that the nearly planar hydroquinone group would impose on the molecule. Also, the existence of two isomers could not be explained by structure **7**.

DISCUSSION OF THE MASS SPECTRA OF COMPOUNDS 4a, 4c, 4g, and 4h

The EI mass spectra of **4a** and **4c** showed a peak caused by the molecular ion. **4g** and **4h** revealed only uncharacteristic fragments in their EI, CI, and FAB mass spectra. Compound **4a** gives rise to the molecular ion (m/z = 338) and shows the fragments characteristic of derivatives of **1** ($[M–Cl]^+$ and $[M–Cl–CH_3NCO]^+$) (Scheme 4). The base peak m/z = 139 is caused by the fragment ion **8**.

The mass spectrum of **4c** results from a similar kind of fragmentation. Initially, the extrusion of methyl isocyanate takes place. An important fragment is the ion m/z = 455, which corresponds to the formula $PO_2C_6Br_4$. This was proved by the bromine isotopic pattern.

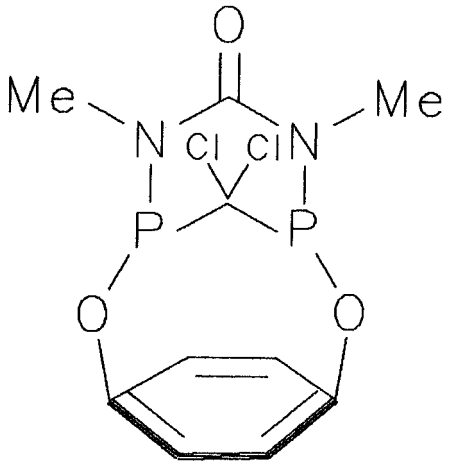


FIGURE 4 Structure of the hypothetical species **7**.

DISCUSSION OF THE X-RAY CRYSTAL STRUCTURES OF 4a and 4b

4b crystallizes as a 1:1 dichloromethane solvate. Both **4a** and **4b** (Figures 5 and 6) show no significant differences in related bond lengths and angles and display very similar ring conformations. The phosphorus atoms lie at the apical positions of trigonal pyramids. In **4a**, P1 and P2 lie 78 and 79 pm out of a plane defined by their α-substituents (O2, N1, C1 for P1, and O3, N2, C1 for P2). In **4b**, the corresponding distances are 77 pm for P1 and 79 pm for P2. Whereas the ring members P1, P2, N1, N2, and C2 are essentially coplanar (mean deviation from the best plane 3 pm for **4a**, 2 pm for **4b**), C1 lies 69 pm (**4a**), 70 pm (**4b**) out of the plane so defined. The dihedral angles between these planes and the aromatic rings (O2, O3, C5–C10 for **4a**; O2, O3, C5–C14 for **4b**) are 51.1° (**4a**) and 54.1° (**4b**). The nine-membered rings display a "tub" conformation, whereby the four atoms P1, P2, O2, and O3 are almost coplanar. N1 and C5, N2 and C10 (**4a**), N1 and C5, and N2 and C14 (**4b**) are approximately synperiplanar [mean deviation from the best plane 0.6 pm (**4a**), 0.2 pm (**4b**), torsion angles N1–P1–O2–C5 18.1, N2–P2–O3–C10 18.3° (**4a**); N1–P1–O2–C5 17.9, N2–P2–O3–C14 17.9° (**4b**)]. The transannular P1 . . . P2 distances are 317.8 (**4a**) and 318.0 (**4b**) pm, and are associated with wide P–C–P angles of 119.0° (**4a**) and 118.66° (**4b**).

CONCLUSIONS

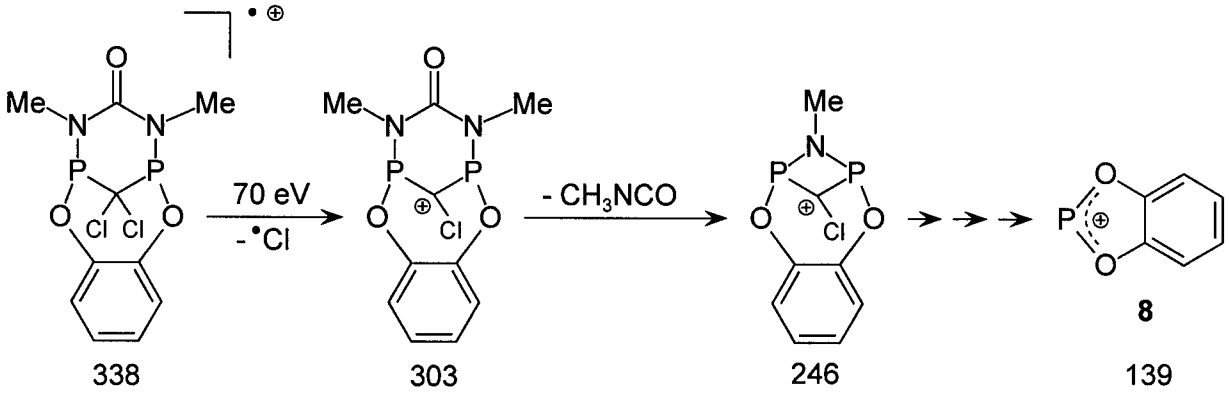
The heterocycle **1** reacts with 1,2-diphenols to form polycyclic species, consisting of an N,N′-dimethylurea-group connected to a seven-membered ring with an annelated aromatic system (**4a**, **4b**, and **4c**). Steric hindrance by the large tert-butyl groups at the aromatic ring does not completely prevent the formation of the bicyclic species.

The expansion of the cyclic system from seven- (**4a–4c**, **4g**) to eight-membered (**4d**, **4e**) resulted in the formation of a mixture of products, including oligomeric compounds.

The change to a 1,4-diphenolic system resulted in the predominance of the dimeric form as in **4h**.

EXPERIMENTAL

All experiments were conducted with exclusion of air and moisture in sealed systems in an atmosphere of dried nitrogen (BASF BTS catalyst). Reaction mixtures were stirred magnetically. "I.v." refers to a pressure of 0.5 mm Hg, unless stated otherwise. The addition of one solution to another solution of a reactant to form the reaction mixtures was conducted



SCHEME 4 Fragmentation pattern in the mass spectrum of **4a**.

within 10 minutes, unless stated otherwise. Solvents were purified and dried according to the usual methods [3,4]. NMR spectra: Bruker AC 200 (^{1}H at 200.15 MHz; ^{13}C at 50.3 MHz; ^{31}P at 81.3 MHz); reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). High field shifts were given positive signs. Mass spectrometry: low-resolution electron impact (EI) mass spectra were obtained with the double-focusing instrument Finnigan MAT 8430 in combination with the data system SS 300. The electron energy was 70 eV. Dichloromethylenebis(dichlorophosphine) [6], N,N′-dimethyl-N,N′-bis(trimethylsilyl)urea [6], and 1,5-Dimethyl-2,3,3,4-tetrachloro-1,5,2,4-diazadiphosphorinan-6-one **1** [1] were synthesized according to the procedures described in the literature.

Synthesis of **4a**

A mixture of 0.73 g (13.2 mmol) of catechol and 1.34 g (13.2 mmol) of triethylamine in 20 mL of ether was added at 0°C with stirring to a solution of 2 g (6.6 mmol) of **1** in 10 mL of ether. After the mixture had been stirred for 16 hours at ambient temperature, the precipitate that had formed was filtered off and was washed three times with a total of 20 mL of ether. The ether was removed i.v. from the combined organic extracts. **4a** was crystallized as a colorless substance at −30°C from 10 mL of ether, yield 0.64 g (30%), mp. 168°C.

^{1}H NMR ($CDCl_3$) δ: 7.18–7.04 (m, 4x C(Ar) *H*)), 3.05 (d, ^3J(PH) = 11.3 Hz, 2x PNCH_3). ^{13}C–{^{1}H}–NMR ($CDCl_3$) δ: 144.51 (*t*, ^2J(PC) = 11.35 Hz, PN*C*(:O)), 144.70 (dd, ^2J(PC) = 14.5 Hz, ^3J(PC) = 2.7 Hz, 2x *COP*), 126.35 (s, 2x 3-*C*(Ar)H), 123.44 (d, ^3J(PC) = 1.75 Hz, 2x 2-*C*(Ar)H), 39.92 (d, ^2J(PC) = 38.5 Hz, 2x PN*C*H_3) (the *C*Cl_2 resonance could not be observed). ^{31}P–{^{1}H}–NMR ($CDCl_3$) δ: 96.7 (s). Mass spectrum (EI, 70 eV) *m/z* (%): 338 ([M]$^+$, 18%), 303 ([M–Cl]$^+$, 32%), 281 ([M–CH_3NCO]$^+$, 60%) 139 ([$PO_2C_6H_4$]$^+$, 100%). Anal. calcd. for $C_{10}H_{10}Cl_2N_2O_3P_2$ (339.04): C 35.43, H 2.97, N 8.26; found: C 34.79, H 3.47, N 8.49.

Synthesis of **4b**

A solution of 1.06 g (6.6 mmol) 2,3-dihydroxynaphthalene and 1.34 g (13.2 mmol) of triethylamine in 10 mL of dichloromethane was added to a solution of 2 g (6.6 mmol) of **1** at 0°C. After the mixture had been stirred for 16 hours at room temperature, the solvent was removed i.v. The residue was dissolved in ether, and the resulting colorless precipitate of triethylamine hydrochloride was filtered off. **4b** was crystallized at −20°C from 5 mL of dichloromethane and petroleum ether (bp. 30–40°C) (1:1), yield 0.25 g (10%).

^{1}H NMR ($CDCl_3$) δ: 7.74–7.69 (m, 2x C(Ar)*H*), 7.50–7.41 (m, 4x C(Ar)*H*), 3.06 (d, ^3J(PH) = 11.3 Hz, 2x PNCH_3). ^{13}C–{^{1}H}–NMR ($CDCl_3$) δ: 150.37 (*t*, ^2J(PC) = 11.0 Hz, PN*C*(:O)), 143.54 (d, ^2J(PC) = 14.5 Hz) and 143.48 (d, ^2J(PC) = 14.8 Hz, 2x COP), 131.39 (s, 2x *C*(q)), 127.02 (s, 2x *C*(Ar)H), 126.41 (s, 2x *C*(Ar)H), 120.40 (d, ^3J(PC) = 2.23 Hz, 2x 2-*C*(Ar)H), 74.91 (*t*, ^1J(PC) = 50.2 Hz, *C*Cl_2), 40.08 (d, ^2J(PC) = 38.8 Hz, 2x PN*C*H_3). ^{31}P–{^{1}H}–NMR ($CDCl_3$) δ: 101.1 (s). $C_{15}H_{14}Cl_4N_2O_3P_2$ **4b**. CH_2Cl_2 (474.0). Because of the evaporation of CH_2Cl_2 from the crystals, no melting point could be determined.

Synthesis of **4c**

A solution of 1.41 g (3.3 mmol) of tetrabromocatechol and 0.67 g (6.6 mmol) of triethylamine in 20 mL of dichloromethane was added to a solution of 1 g (3.3 mmol) of **1** in 10 mL of diethyl ether at

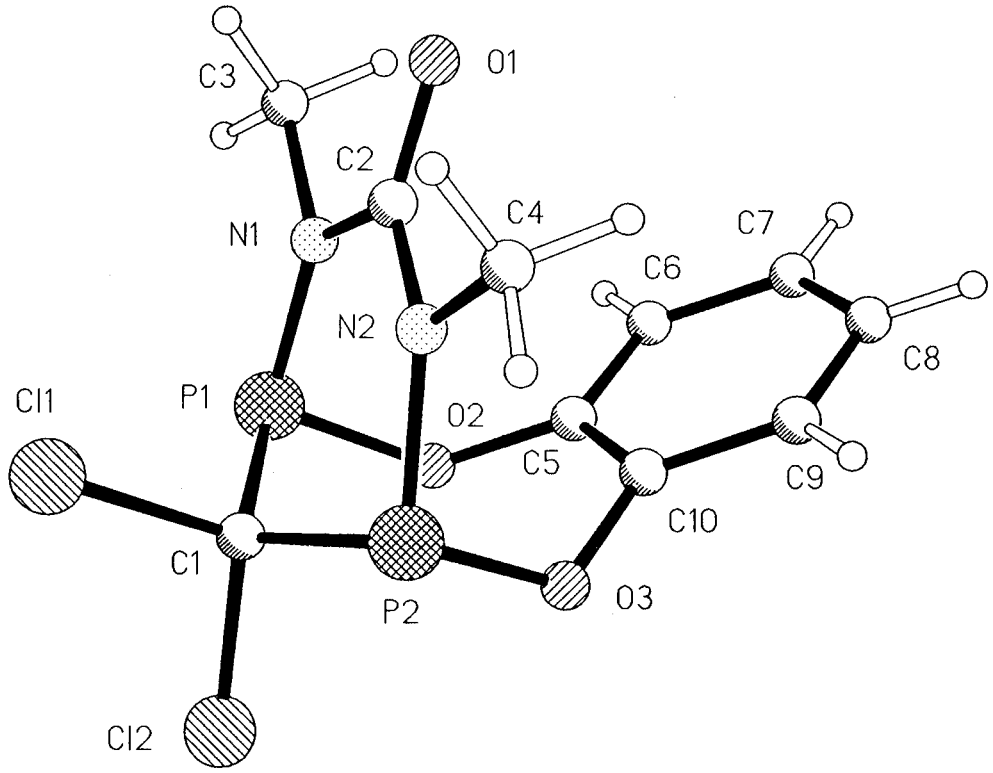


FIGURE 5 Molecular structure of **4a** in the crystal; radii are arbitrary.

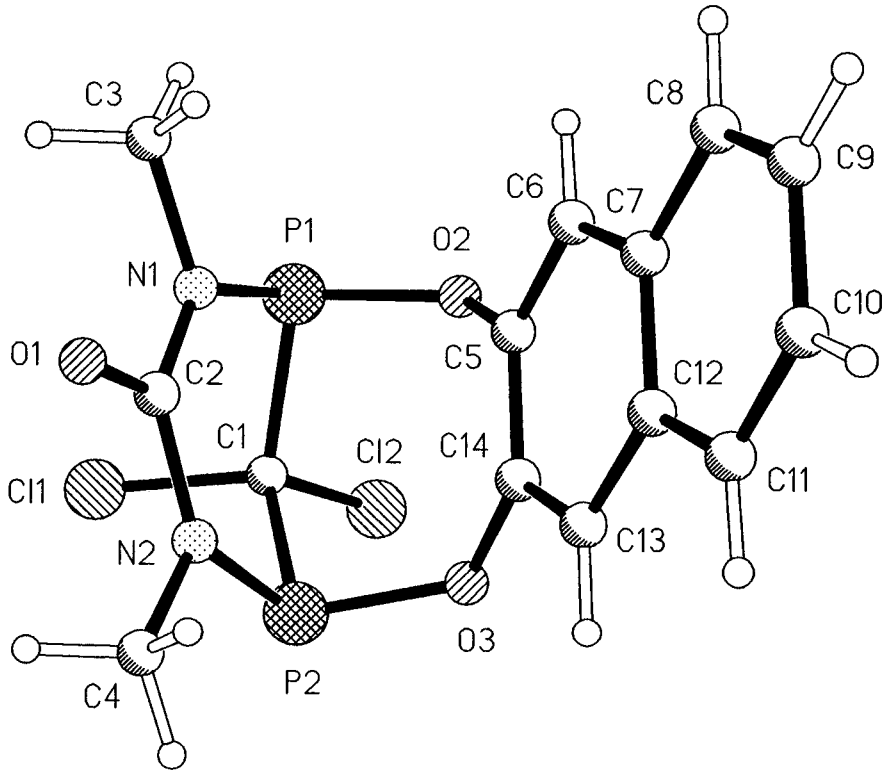


FIGURE 6 Molecular structure of **4b** in the crystal; radii are arbitrary.

0°C within 10 minutes. The mixture was stirred for 5 days at room temperature. Subsequently, the solvent was removed i.v. An amount of 50 mL of ether was added to the residue, and the precipitated triethylamine hydrochloride was filtered off. The volume of the solvent was reduced i.v. to 10 mL. Colorless **4c** crystallized at −20°C, yield 1.58 g (73%). Mp. 121°C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 3.13 (d, ^3J(PH) = 11.6 Hz, 2x PNCH_3). ^{13}C–{^{1}H}–NMR ($CDCl_3$) δ: 149.64 (*t*, ^2J(PC) = 11.2 Hz, PN*C*(:O)), 142.73 (d, ^2J(PC) = 12.8 Hz, 2x *C*OP), 124.88, 121.04 (s, 4x *C*Br), 73.72 (*t*, ^1J(PC) = 49.7 Hz, *C*Cl_2), 41.04 (d, ^2J(PC) = 40.4 Hz, 2x PN*C*H_3). ^{31}P–{^{1}H}–NMR ($CDCl_3$) δ: 97.3 (s). Mass spectrum (EI, 70 eV) *m/z* (%): 654 ([M]$^+$, 10%), 597 ([M–CH_3NCO]$^+$, 38%), 455 ([$PO_2C_6Br_4$]$^+$, 24%), 60 ([$PNCH_3$]$^+$, 100%). Anal. calcd. for $C_{10}H_6Br_4Cl_2N_2O_3P_2$ (654.65): C 18.34, H 0.92, P 9.46; found: C 20.47, H 2.35, P 10.14.

Reaction of **1** *with Saligenin. Formation of the Bicyclic Species* **4d**

A solution of 1 g (3.3 mmol) of **1** in 10 mL of ether was added to a solution of 0.41 g (3.3 mmol) of saligenin and 0.67 g (6.6 mmol) of triethylamine in 20 mL of ether at 0°C within 30 minutes. After the mixture had been stirred for 16 hours at room temperature, 0.95 g of solid was filtered off. The ether solution contained mostly oligomeric substances, and only a small amount of a substance was believed to be **4d**. Attempts to isolate **4d** by crystallization from dichloromethane, diethyl ether, and petroleum ether (30/40) were unsuccessful.

^{31}P–{^{1}H}–NMR ($CDCl_3$) δ: 127.4, 106.4 (d, ^2J(PP) not resolved, CO*P*, CH_2O*P*). $C_{11}H_{12}Cl_2N_2O_3P_2$ (353.07).

Reaction of **1** *with Resorcinol*

As described in the preceding experiment, 2 g (6.6 mmol) of **1** were allowed to react with a mixture of 0.73 g (6.6 mmol) of resorcinol and 1.34 g (13.3 mmol) of triethylamine. The ^{31}P–{^{1}H}–NMR spectrum indicated a mixture of products; there was no indication of the formation of **4e**.

Reaction of **1** *with 3,5-Di-tert-butylcatechol: Formation of* **4f**

A solution of 1.47 g (6.6 mmol) 3,5-di-tert-butylcatechol and 1.34 g (13.2 mmol) of triethylamine in 20 mL of ether was added dropwise to a solution of 2 g (6.6 mmol) of **1** in 10 mL of ether at 0°C. After the mixture had been stirred for 16 hours at room temperature, the triethylamine hydrochloride formed was filtered off. After removal of the ether i.v., an oily residue was left, consisting of a mixture of **4f** and **1**. Decomposition occurred within 24 hours.

^{31}P–{^{1}H}–NMR ($CDCl_3$, reaction mixture) δ: 138.4 (m, ^2J(PP) not resolved, COP), 135.3 (m, ^2J(PP) not resolved, COP). $C_{18}H_{26}Cl_2N_2O_3P_2$ (451.26).

Reaction of **1** *with 1,2,4,5-Tetrahydroxybenzene. Synthesis of the Pentacyclic Species* **4g**

A solution of 0.23 g (1.65 mmol) of 1,2,4,5-tetrahydroxybenzene in 30 mL of tetrahydrofuran was added dropwise at −30°C (30 minutes) to a solution of 1 g (3.3 mmol) of **1** and 0.66 g (6.6 mmol) of triethylamine in 20 mL of the same solvent. After 24 hours of stirring at room temperature, the colorless precipitate was filtered off, and the tetrahydrofuran was removed i.v. The residue was extracted three times with 15 mL portions of ether, and **4g** was obtained as a yellow powder (0.46 g; 46%) of **4g**. Mp. 171°C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 6.81 (s, 2x C(Ar)*H*), 3.06 (d, ^3J(PH) = 11.6 Hz), 3.07 (d, ^3J(PH) = 11.5 Hz, 4x PNCH_3, *cis/trans* 1:3) [for a discussion of the *cis/trans* ratio, cf. the section on discussion of

TABLE 2 Crystal Data for Compounds **4a** and **4b**

Compound	**4a**	**4b** · CH_2Cl_2
Formula	$C_{10}H_{10}Cl_2N_2O_3P_2$	$C_{15}H_{14}Cl_4N_2O_3P_2$
M_r	339.0	474.0
Temperature (K)	173	143
Crystal habit	colorless prism	colorless block
Crystal size (mm)	0.75 × 0.65 × 0.60	0.75 × 0.50 × 0.40
Space group	Pbca	$P2_1/n$
Cell constants:		
a(pm)	1444.7(6)	1267.2(3)
b(pm)	824.4(4)	1137.3(2)
c(pm)	2389.2(11)	1355.5(3)
β(°)	—	95.45(3)
V(nm^3)	2.8456	1.9447
Z	8	4
D_x (Mg m^{-3})	1.583	1.619
F(000)	1376	960
μ (mm^{-1})	0.68	0.79
$2\theta_{max}$ (°)	50	55
No. of reflections:		
measured	3525	9089
independent	2516	4478
R_{int}	0.053	0.040
$R(F > 4\sigma)$	0.043	0.036
$wR(F^2$, all data)	0.125	0.098
Number of parameters	174	233
S	1.1	1.1
Max. Δ/σ	<0.001	<0.001
Max. $\Delta\rho$(e pm^{-3} × 10^6)	0.97	0.42

TABLE 3 Selected Bond Lengths (pm) and Angles (°) for Compound **4a**

P(1)–O(2)	164.9(3)	P(1)–N(1)	168.7(3)
P(1)–C(1)	184.3(4)	P(2)–O(3)	165.3(2)
P(2)–N(2)	169.1(3)	P(2)–C(1)	184.5(4)
C1(1)–C(1)	178.5(3)	C1(2)–C(1)	178.8(3)
O(1)–C(2)	120.8(4)	O(2)–C(5)	139.5(4)
O(3)–C(10)	139.4(4)	N(1)–C(2)	139.5(4)
N(1)–C(3)	148.4(5)	N(2)–C(2)	138.8(4)
N(2)–C(4)	148.6(4)		
O(2)–P(1)–N(1)	104.54(13)	O(2)–P(1)–C(1)	101.04(15)
N(1)–P(1)–C(1)	96.98(14)	O(3)–P(2)–N(2)	103.84(13)
O(3)–P(2)–C(1)	101.00(14)	N(2)–P(2)–C(1)	96.80(14)
C(5)–O(2)–P(1)	123.2(2)	C(10)–O(3)–P(2)	123.5(2)
C(2)–N(1)–C(3)	113.1(3)	C(2)–N(1)–P(1)	132.5(2)
C(3)–N(1)–P(1)	114.1(2)	C(2)–N(2)–C(4)	113.4(3)
C(2)–N(2)–P(2)	132.6(2)	C(4)–N(2)–P(2)	113.5(3)
Cl(1)–C(1)–C1(2)	109.4(2)	C1(1)–C(1)–P(1)	106.5(2)
Cl(2)–C(1)–P(1)	107.0(2)	C1(1)–C(1)–P(2)	106.4(2)
Cl(2)–C(1)–P(2)	108.3(2)	P(1)–C(1)–P(2)	119.0(2)
O(1)–C(2)–N(2)	120.3(3)	O(1)–C(2)–N(1)	119.6(3)
N(2)–C(2)–N(1)	120.0(3)		

TABLE 4 Selected Bond Lengths (pm) and Angles (°) for Compound **4b**

P(1)–O(2)	165.03(14)	P(1)–N(1)	169.5(2)
P(1)–C(1)	184.6(2)	P(2)–O(3)	165.31(14)
P(2)–N(2)	169.6(2)	P(2)–C(1)	185.2(2)
Cl(1)–C(1)	178.3(2)	Cl(2)–C(1)	178.4(2)
O(1)–C(2)	121.5(2)	O(2)–C(5)	139.1(2)
O(3)–C(14)	139.2(2)	N(1)–C(2)	139.2(3)
N(1)–C(3)	147.7(2)	N(2)–C(2)	139.3(3)
O(2)–P(1)–N(1)	103.97(8)	O(2)–P(1)–C(1)	100.56(8)
N(1)–P(1)–C(1)	97.50(9)	O(3)–P(2)–N(2)	104.29(8)
O(3)–P(2)–C(1)	100.72(8)	N(2)–P(2)–C(1)	97.32(9)
C(5)–O(2)–P(1)	124.86(12)	C(14)–O(3)–P(2)	124.60(12)
C(2)–N(1)–C(3)	113.6(2)	C(2)–N(1)–P(1)	132.79(14)
C(3)–N(1)–P(1)	113.28(12)	C(2)–N(2)–C(4)	113.6(2)
C(2)–N(2)–P(2)	132.86(14)	C(4)–N(2)–P(2)	113.32(12)
Cl(1)–C(1)–Cl(2)	110.39(10)	Cl(1)–C(1)–P(1)	106.50(10)
Cl(2)–C(1)–P(1)	107.35(10)	Cl(1)–C(1)–P(2)	106.97(10)
Cl(2)–C(1)–P(2)	106.89(10)	P(1)–C(1)–P(2)	118.66(10)
O(1)–C(2)–N(1)	120.2(2)	O(1)–C(2)–N(2)	119.6(2)
N(1)–C(2)–N(2)	120.1(2)	C(6)–C(5)–O(2)	118.9(2)

the NMR Spectra of compounds **4a**–**4h**.] ^{13}C–{^{1}H}–NMR ($CDCl_3$) *cis*-isomer: δ: 149.87 (*t*, ^{2}J(PC) = 11.3 Hz, 2x PN*C*(:O)), 141.65 (d, ^{2}J(PC) = 14.8 Hz, 4x *COP*), 117.33 (s, 2x *C*(Ar)H), 39.90 (d, ^{2}J(PC) = 38.91 Hz, 4x PN*C*H_3); *trans*-isomer: δ: 150.09 (*t*, ^{2}J(PC) = 11.1 Hz, 2x PN*C*(:O)), 141.60 (d, ^{2}J(PC) = 14.5 Hz, 4x COP), 117.33 (s, 2x *C*(Ar)H), 74.46 (*t*, ^{1}J(PC) = 49.8 Hz, 2x *C*Cl_2), 40.01 (d, ^{2}J(PC) = 38.9 Hz, 4x PN*C*H_3). ^{31}P–{^{1}H}–NMR ($CDCl_3$) δ: 97.6 (s), 97.1 (s); *cis*/*trans* ratio 1:3. Mass spectrum (EI, 70 eV), CI, FAB): no molecular ion, no characteristic fragments. Anal. calcd. for $C_{14}H_{14}Cl_4N_4O_6P_4$ (599.97): C 28.03, H 2.35, N 9.34; found: C 29.58, H 2.98, N 9.63.

TABLE 5 Atomic Coordinates ($\times$ 10^4) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Compound **4a**

	x	*y*	*z*	*U(eq)*
P(1)	4148.0(5)	6047.9(12)	1429.3(3)	36.9(4)
P(2)	5113.9(6)	8948.2(10)	776.5(3)	36.3(5)
Cl(1)	3758.4(6)	6806.6(12)	264.8(3)	45.1(4)
Cl(2)	3168.7(7)	9032(2)	1144.3(4)	68.8(6)
O(1)	6559(2)	4981(3)	819.1(10)	48.4(12)
O(2)	4489.6(14)	7038(3)	1992.2(8)	37.6(10)
O(3)	5362(2)	9605(3)	1413.1(9)	38.2(14)
N(1)	5121(2)	5189(3)	1176.1(10)	30.2(13)
N(2)	5854(2)	7385(3)	679.0(10)	31.0(12)
C(1)	4075(2)	7711(5)	916.0(13)	38(2)
C(2)	5886(2)	5823(4)	894.0(12)	28.5(14)
C(3)	5234(3)	3455(5)	1329(2)	58(3)
C(4)	6693(3)	7834(6)	355(2)	56(2)
C(5)	5412(2)	7443(4)	2094.4(11)	28.9(15)
C(6)	5890(2)	6588(4)	2499.3(12)	34(2)
C(7)	6801(2)	6979(4)	2614.1(13)	38(2)
C(8)	7232(2)	8209(4)	2321.9(13)	41(2)
C(9)	6758(2)	9057(4)	1916.8(13)	38(2)
C(10)	5844(2)	8689(4)	1807.2(11)	29(2)

TABLE 6 Atomic Coordinates ($\times$ 10^4) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Compound **4b**

	x	*y*	*z*	*U(eq)*
P(1)	3280.6(4)	3880.3(5)	1778.0(4)	24.2(1)
P(2)	3314.5(4)	1089.6(5)	1633.0(4)	23.7(1)
Cl(1)	1862.5(4)	2383.9(5)	2784.9(4)	30.7(1)
Cl(2)	1637.3(4)	2527.9(5)	618.2(4)	34.9(1)
O(1)	5399.6(12)	2381.1(14)	3640.1(12)	34.5(4)
O(2)	3897.8(11)	3807.8(12)	761.1(10)	26.6(3)
O(3)	3925.1(10)	1332.6(13)	627.6(10)	25.6(3)
N(1)	4222.4(12)	3495.4(15)	2692.6(12)	24.3(3)
N(2)	4247.4(13)	1377.2(15)	2583.4(12)	24.6(3)
C(1)	2553.0(14)	2472(2)	1701.0(14)	23.8(4)
C(2)	4665.4(15)	2419(2)	2996.1(14)	24.4(4)
C(3)	4751(2)	4515.0(14)	3201.2(15)	36.8(5)
C(4)	4780(2)	315.9(14)	3001(2)	38.2(5)
C(5)	4843.9(15)	3211(2)	679.0(13)	23.4(4)
C(6)	5752(2)	3845(2)	624.4(14)	26.1(4)
C(7)	6714(2)	3271(2)	481.4(14)	25.4(4)
C(8)	7674(2)	3907(2)	425(2)	31.7(5)
C(9)	8596(2)	3323(2)	323(2)	35.7(5)
C(10)	8613(2)	2090(2)	264(2)	35.5(5)
C(11)	7702(2)	1450(2)	295.7(15)	30.8(4)
C(12)	6730(2)	2032(2)	409.7(14)	25.6(4)
C(13)	5775.5(15)	1396(2)	478.4(14)	25.5(4)
C(14)	4857.1(15)	1977(2)	608.2(14)	23.2(4)
Cl(98)	5888.4(6)	7064.6(9)	1901.1(6)	69.0(2)
Cl(99)	7281.7(6)	9085.9(7)	1917.1(5)	55.3(2)
C(99)	7196(2)	7562(3)	1946(2)	52.7(7)

Reaction of **1** *with Hydroquinone; Synthesis of* **4h**

A solution of 1 g (3.3 mmol) of **1** and 0.67 g (6.6 mmol) of triethylamine in 15 mL of tetrahydrofuran was added dropwise to a solution of 0.36 g (3.3 mmol) of hydroquinone in 30 mL of tetrahydrofuran at −30°C (30 minutes). After 16 hours of stirring at room temperature, the reaction mixture was filtered. The solvent was removed from the filtrate i.v., and the oily residue was dissolved in 10 mL of ether. **4h** precipitated as a colorless oil at −30°C, yield 0.75 g (67%).

^{1}H NMR ($CDCl_3$) δ: 7.04 (s, 8x C(Ar)*H*), 3.19 (d, ^3J(PH) = 11.17 Hz), and 3.07 (d, ^3J(PH) = 11.64 Hz, 4x PNCH_3, ratio *trans*/*cis* 4:1). ^{13}C–{^{1}H}–NMR ($CDCl_3$) δ: 152.93 (*t*, ^2J(PC) = 8.85 Hz) and 152.76 (*t*, ^2J(PC) = 8.67 Hz, 2x PN*C*(:O), ratio 4:1) [for a discussion of the *cis*/*trans* ratio, cf. the section on the discussion of the NMR Spectra of Compounds **4a**–**4h**], 121.77 (m, 4x *COP*), 120.93 (d, ^3J(PC) = 8.34 Hz), and 120.69 (d, ^3J(PC) = 8.47 Hz, 8x *C*(Ar)H, ratio 1:4), 75.96 (*t*, ^1J(PC) = 39.5 Hz, 2x *C*Cl_2), 39.13 (d, ^2J(PC) = 37.0 Hz) and 38.95 (d, ^2J(PC) = 38.95 Hz, 4x PN*C*H_3, ratio 1:4). ^{31}P–{^{1}H}–NMR ($CDCl_3$) δ: 128.6 (s) and 127.5 (s, ratio 4:1). Mass spectrum (EI, 70 eV), CI, FAB): no molecular ion, no characteristic fragments were observed. Anal. calcd. for $C_{20}H_{20}Cl_4N_4O_6P_4$ (678.09): C 38.28, H 3.59, N 7.61; found C 35.43, H 2.97, N 8.26.

X-ray Structure Determinations

Data Collection and Reduction: Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 for **4a**, Stoe STADI-4 for **4b**, both with LT-2 low-temperature attachment). The orientation matrix for **4a** was refined from setting angles of 50 reflections in the 2θ range 20–23°; the cell constants for **4b** were refined from $\pm\omega$ angles of 48 reflections in the same 2θ range (monochromated MoK_α radiation).

Structure Solution and Refinement: The structures were solved by direct methods. Both structures were refined anisotropically on $\underline{F}^2$ (program system: SHELXL-93, pre-release version, G. M. Sheldrick, Universität Göttingen). H atoms were included using a riding model. Weighting schemes of the form $w^{-1} = [\sigma^2 (\underline{F}_0^2) + (a\underline{P})^2 + b\underline{P}]$ were employed, with $\underline{P} = (\underline{F}_0^2 + 2\underline{F}_c^2)/3$ [7] (see Tables 2–6).

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[7] Further details of the X-ray crystal structure analyses (H-atom coordinates, complete bond lengths and angles, structure factors, and temperature factors) have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. Any request for this material should quote a full literature citation and the reference numbers CSD 400871 (**4a**) and CSD 400872 (**4b**).