Stereoisomer Discrimination Through π-Stacking Interactions in Spirocyclic Phosphazenes Bearing 2,2′-Dioxybiphenyl Units

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The molecular structure of the 2,2′-dioxybiphenyl spirocyclic tetrachlorocyclotriphosphazene $[N_3P_3Cl_4(O_2C_{12}H_8)]$ (**3**) was determined by X-ray crystallography. The structure and conformation of **3** in the crystal are compared and discussed with respect to those of its analogues trispiro and dispiro derivatives, $[N_3P_3(O_2C_{12}H_8)_3]$ (**1**) and $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ (**2**), respectively. Both the (*R*) and (*S*) stereoisomers are present in the lattice of **3** as arranged in pairs (*R*)···(*S*) held together through sandwich-type π-stacking interactions of the (C7–C12)/(C7–C12)′ phenyl rings of the 2,2′-dioxybiphenyl groups. The polymer-like assembly of **2** was formed by interactions between the (*R*) and (*S*) portions of two *meso* molecules [in the sequence ···(*R*)···(*S*)···(*R*)···(*S*)···(*R*)···(*S*)···]. In this case, the pertinent phenyl rings involved in the noncovalent π-interactions assume a parallel-displaced configuration. To the best of our knowledge, no chiral discrimination in cyclic phosphazenes has been hitherto described, and the present findings provide the first evidence for the discrimination of stereoisomers in spirophosphazenes and the noncovalent forces that govern the chiral recognition in these systems. The energy of the π-stacking interaction increases with increasing number of 2,2′-dioxybiphenyl groups; i.e., on passing from **3** to **2**. In the case of molecule **1**, the discrimination of enantiomers does not take place at all because the π-stacking interaction becomes impossible because of steric hindrance.

Introduction

Many outstanding properties in materials science are expected to arise from phosphazenic macromolecules and nanosized assemblies of hexa(aryloxy)cyclotriphosphazenes acting as chiral responders and host molecules.[1−3] The spirocyclotriphosphazenes, bearing one to three dioxyaryl or other nucleophilic groups that cyclize to form rings with the phosphorus atoms,[4,5] are optimal candidates for such applications. They represent a unique class of highly tailorable host molecules,[6,7] and they have received much attention for the synthesis of new, high-molecular-weight spiropolyphosphazenes containing functionalized and optically active groups.[8,9] The basic research interest in the structural characterization of spirocyclotriphosphazenes stems from their ability to form inclusion adducts with polymers,[6] their ability, in some cases, to induce polymerization of a guest,[7] and, especially, their potential for stereoisomer discriminaton. The discrimination of enantiomers, frequently called chiral recognition,[10] is a very important concept[11] with applications in, inter alia, Langmuir−Blodgett film technology,[12] chromatographic separation of enantiomers,[13] asymmetric catalysis, and new materials.[14]

The spirocyclophosphazenes **1**, **2** and **3**, referred to as trispiro, dispiro and monospiro derivatives, respectively, have pairs of conformations that are rapidly interconverting in solution. Scheme 1 gives a schematic drawing of **1**−**3** showing the labeling of the atoms.

The molecular assembly of nanometer-sized particles in the bulk has been reported recently[15] by us for the 2,2′-dioxybinaphthyl trispirocyclic cyclotriphosphazene (+)-$[N_3P_3(O_2C_{20}H_{12})_3]$ using a combined experimental (energy-dispersive X-ray diffraction) and theoretical (molecular dynamics) approach. Previously, we reported the stereochemistry of the spirocyclophosphazenes **1**−**3** in solution.[16] Although the discrimination of enantiomers in general cannot be performed in the gas phase or in dilute solutions, it can be revealed in the solid state. A complete investigation, however, of the enantiomeric composition, and the interactions between enantiomers, in the crystal structures of **1**−**3** has not yet been undertaken.

As is the discrimination of any other pair of enantiomers, the types of nonbonding intermolecular forces that can be exploited are based on van der Waals, electrostatic, hydro-

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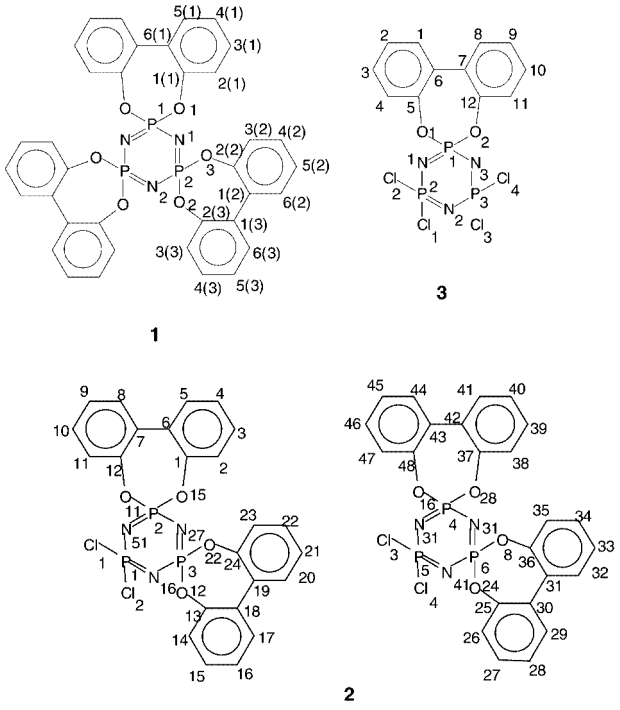


Scheme 1. Schematic drawings of **1**−**3** with atomic numbering schemes; labels of **1** are those given explicitly by Allcock in ref.[19]; labels of **2** were obtained from ref.[22], with separate labels referring to the two independent molecules

gen-bonding, and π-stacking interactions. The latter interactions are very important in systems containing aromatic rings.[17,18]

In this work, the unanswered questions concerning the occurrence, the origins, the configurations and the strengths of the interactions between the enantiomers of spirophosphazenes **1**−**3** is addressed using X-ray diffraction analyses.

Previously reported X-ray structural analyses of spirocyclophosphazenes bearing 2,2′-dioxybiphenyl groups have concerned the trispiro compound[19] $[N_3P_3(O_2C_{12}H_8)_3]$ (**1**), the transannular and spiro-substituted derivatives 1,3- and 1,1-$[N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)]$,[20] and the tetra- and difluoro-substituted analogues[21] of **1** and **2**, $[N_3P_3F_4(O_2C_{12}H_8)]$ and $[N_3P_3F_2(O_2C_{12}H_8)_2]$. Accordingly, we have compared the solid-state structure of **3** with that of **2** (as reported[22] by Dez et al.) and that of the 2,2′-dioxybiphenyl trispirocyclic cyclotriphosphazene **1** as reported[19] by Allcock et al. The goals of this paper are thus twofold: First to provide experimental information about the structure of **3** in the crystal and to compare it with those of **1** and **2**, and, secondly, to detect in **1**−**3** the factors that discriminate between stereoisomers, the operating noncovalent interactions and their relative strengths, and the resulting configurations.

Results and Discussion

X-ray Structure

An ORTEP view of compound **3** is shown in Figure 1. Bond lengths and angles of **3** are reported in Table 1. To make comparisons between structures, we consider the following aspects of the compounds in the solid state: (i) the conformation of the P_3N_3 plane, (ii) the conformation of the 2,2′-dioxybiphenyl moieties, and (iii) the intermolecular interactions. The three phosphorus and three nitrogen atoms deviate significantly from the P_3N_3 mean plane [the maximum deviation is 0.135(4) Å (N2)]. An analysis of the summary of agreement between chemically equivalent bonds and angles for **3** (Table 2) shows that: (i) the P−N distances have a noteworthy value of χ^2 because the bonds P2−N1 and P3−N3 are significantly shorter than the other four P−N bonds; (ii) the P−N−P and N−P−N angles also attain a high value of χ^2, since the angles P2−N2−P3 and N1−P1−N3 are smaller that the remaining P−N−P and N−P−N angles, respectively, which thus indicates a loss of planarity inside the P_3N_3 ring; (iii) the C−C−C angles are quite different, as is seen from the value of χ^2 for the C−C−C angle. The high value found for the angle N−P−O is due to the manner in which the biphenyl moieties are disposed with respect to the P_3N_3 ring.

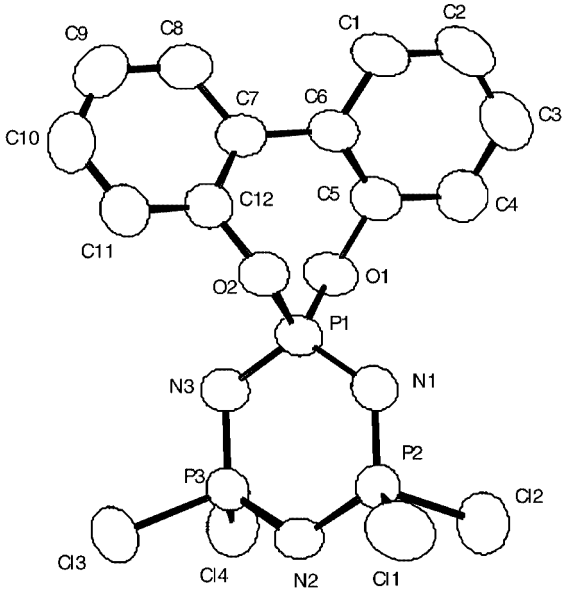


Figure 1. ORTEP view of **3**

For compound **2**, the reported[22] maximal deviations from the mean P_3N_3 planes are 0.007 and 0.054 Å for the two independent molecules **2(a)** and **2(b)**, respectively. In the case of compound **1**, the value of χ^2 found[19] for the P_3N_3 plane was 602.0, and a distortion of the P_3N_3 plane was also proposed. The analysis of the agreement between chemically equivalent bonds and angles for compound **2** attained a value of χ^2 for the C−C−C angle that is close to that found for **1** and **3**. Therefore, all the three compounds feature a significant distortion of the aromatic rings of the dioxybiphenyl moieties.

In compound **3** the dioxybiphenyl moiety is twisted by 48.19(4)° with respect to the P_3N_3 mean plane. This angle

Table 1. Bond lengths [Å] and angles [°] for **3**

Bond lengths		Bond angles	
P(1)−O(2)	1.576(3)	O(2)−P(1)−O(1)	104.1(2)
P(1)−O(1)	1.568(3)	O(2)−P(1)−N(3)	112.1(2)
P(1)−N(3)	1.579(4)	O(1)−P(1)−N(3)	105.2(2)
P(1)−N(1)	1.604(4)	O(2)−P(1)−N(1)	105.2(2)
P(2)−N(1)	1.544(4)	O(1)−P(1)−N(1)	113.3(2)
P(2)−N(2)	1.584(4)	N(3)−P(1)−N(1)	116.5(2)
P(3)−N(3)	1.555(4)	N(1)−P(2)−N(2)	119.9(2)
P(3)−N(2)	1.579(4)	N(1)−P(2)−Cl(1)	108.8(2)
P(2)−Cl(1)	1.977(2)	N(2)−P(2)−Cl(1)	107.5(2)
P(2)−Cl(2)	1.995(2)	N(1)−P(2)−Cl(2)	109.3(2)
P(3)−Cl(3)	1.981(2)	N(2)−P(2)−Cl(2)	108.1(2)
P(3)−Cl(4)	2.004(2)	Cl(1)−P(2)−Cl(2)	101.9(1)
O(1)−C(5)	1.411(5)	N(3)−P(3)−N(2)	118.5(2)
O(2)−C(12)	1.419(5)	N(3)−P(3)−Cl(3)	109.0(2)
C(1)−C(2)	1.383(8)	N(2)−P(3)−Cl(3)	108.3(2)
C(1)−C(6)	1.401(6)	N(3)−P(3)−Cl(4)	110.1(2)
C(2)−C(3)	1.361(9)	N(2)−P(3)−Cl(4)	108.3(2)
C(3)−C(4)	1.374(8)	Cl(3)−P(3)−Cl(4)	101.41(8)
C(4)−C(5)	1.394(7)	C(5)−O(1)−P(1)	121.3(3)
C(5)−C(6)	1.371(6)	C(12)−O(2)−P(1)	120.0(3)
C(6)−C(7)	1.494(7)	P(2)−N(1)−P(1)	121.3(2)
C(7)−C(12)	1.378(6)	P(2)−N(2)−P(3)	119.4(2)
C(7)−C(8)	1.404(7)	P(3)−N(3)−P(1)	122.9(2)
C(8)−C(9)	1.381(8)	C(2)−C(1)−C(6)	120.0(6)
C(9)−C(10)	1.374(9)	C(3)−C(2)−C(1)	121.4(6)
C(10)−C(11)	1.375(8)	C(2)−C(3)−C(4)	120.2(6)
C(11)−C(12)	1.385(7)	C(3)−C(4)−C(5)	118.2(6)
		C(6)−C(5)−O(1)	119.8(4)
		C(6)−C(5)−C(4)	123.1(5)
		O(1)−C(5)−C(4)	117.0(4)
		C(5)−C(6)−C(1)	117.1(5)
		C(5)−C(6)−C(7)	122.3(4)
		C(1)−C(6)−C(7)	120.6(4)
		C(12)−C(7)−C(8)	116.9(4)
		C(12)−C(7)−C(6)	121.5(4)
		C(8)−C(7)−C(6)	121.6(4)
		C(9)−C(8)−C(7)	120.4(5)
		C(10)−C(9)−C(8)	120.8(5)
		C(9)−C(10)−C(11)	120.1(5)
		C(10)−C(11)−C(12)	118.6(5)
		C(11)−C(12)−C(7)	123.1(5)
		C(11)−C(12)−O(2)	116.9(4)
		C(7)−C(12)−O(2)	119.7(4)

is similar to those found for **1** and for the two independent molecules **2(a)** and **2(b)**.

According to the usual convention, a positive angle [(*R*) configuration] and a negative angle [(*S*) configuration] represent a clockwise and an anticlockwise twist, respectively, of the biphenyl axis from the mean ring plane when viewed from the phosphorus atom towards the biphenyl unit. For compound **2**, we found that the C1−C12 and C37−C48 biphenyl units have positive angles with the mean P_3N_3 plane, while the C13−C24 and C25−C36 planes have negative angles. In compound **1**, two of the three dioxybiphenyl moieties have a negative angle with the P_3N_3 plane while the other has a positive one. Allcock has suggested that such conformations of these groups are due to intermolecular repulsion interactions.[19]

Retrieving molecular structures deposited at the Cambridge Structural Database[23] that contain one or two (2,2′-dioxy-1,1′-biphenyl) groups bonded to a phosphorus atom shows that the angle between the aromatic rings of the 2,2′-dioxybiphenyl unit is in the range 35.6−58.5° with a mean value of 45.5°. This finding is in agreement with the value found in molecule **3** [40.8(1)°] as well as with those previously found[19,22] in **1** and **2**.

Table 2. Summary of agreement between chemically equivalent bonds [Å] and angles [°] for **3**

Bond or angle	No. of examples	Range [Å or °]	σ_{rms}	Mean	χ^2 [a]
P−N	6	1.544−1.604	0.004	1.574	144.44
P−O	2	1.568−1.576	0.003	1.572	3.56
P−Cl	4	1.977−2.004	0.002	1.989	117.25
O−C	2	1.411−1.419	0.005	1.415	1.28
C−C[b]	12	1.361−1.404	0.007	1.382	35.82
C−C[b]	1	1.494	0.007	1.494	−
N−P−N	3	116.5−119.9	0.2	118.3	146
P−N−P	3	119.4−122.9	0.2	121.2	153.5
O−P−O	1	104.1	0.2	104.1	−
N−P−O	4	105.2−113.3	0.2	108.9	1424.5
Cl−P−Cl	2	101.41−101.9	0.09	101.7	15.32
N−P−Cl	8	108.1−110.1	0.2	108.7	106.75
C−C−C	12	116.9−123.1	0.5	120.0	190

[a] The value of χ^2 is the common statistical quantity, calculated to test the significance of a deviation from the mean. It is the sum of the squares of the deviations from the mean divided by root-mean square σ^2. [b] Aromatic C−C bonds within phenyl groups. [c] Biphenoxy C−C bonds.

Crystal Packing and Discrimination of Stereoisomers

The unit cell of **3** contains four molecules assembled in two pairs, each pair being made up of the two stereoisomers [(*R*) and (*S*)] held together by π-stacking interactions between their aromatic rings (Figure 2).

The configuration attained by such a bimolecular assembly in the crystal packing of **3** evidences that the (*R*)···(*S*) discrimination from molecule to molecule features effectively eclipsed sandwich-type π-interactions between the aromatic ring (C7−C12) and the (C7−C12)′ ring of a centrosymmetrically related molecule ($' = -x + 1, -y + 1, -z + 1$) (Figures 2 and 4). In this dimer-like assembly of **3**, the distances between the carbon atoms range from 3.605(7) to 3.993(8) Å (Table 3) and the interacting phenyl planes are perfectly superimposed and parallel.

In the case of **2**, the selective crystallization of the *meso* form from a mixture of all the possible stereoisomers in solution[16] can be accounted for by the diminuation of entropy resulting from the more ordered arrangement attained in the solid (Figure 3), and thus to more effective packing forces for the polymer-like chain assembly of the molecules in the crystal. The structure of the lattice of **2** shows that such an intermolecular polymer-like assembly arises from π-stacking interactions between one enantiomeric portion of a *meso* molecule that discriminates the opposite enantiomeric portion of the adjacent *meso* molecule. In particular, two aromatic rings of **2(a)** interact through two aromatic rings of two different **2(b)** molecules: unit

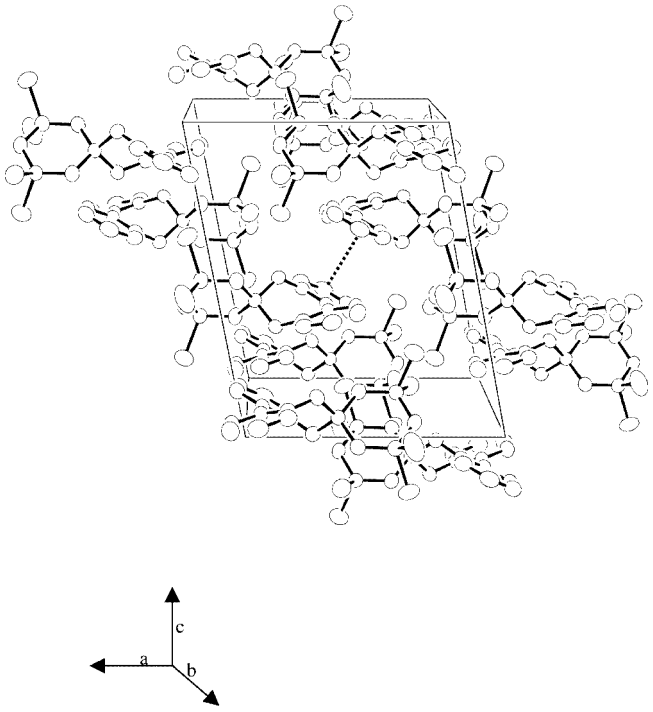


Figure 2. Crystal packing of **3**; the π-stacking interactions between the aromatic rings are denoted by dotted lines

Table 3. Selected intermolecular distances [Å] for molecules of **3** in the crystal

C7···C10′[a]	3.614(7)
C7···C11′	3.947(6)
C8···C10′	3.786(7)
C8···C11′	3.605(7)
C9···C11′	3.645(7)
C9···C12′	3.626(7)
C10···C11′	3.993(8)
C10···C12′	3.718(7)

[a] ′: $-x + 1, -y + 1, -z + 1$.

C7−C12 of **2(a)** interacts with unit C31−C36 of **2(b)**, and unit C13−C18 of **2(a)** interacts with unit C37′−C42′ of **2(b)** of a symmetry-related [$x + 0.5, y + 0.5, z$] molecule (Figure 3). The aromatic rings involved in these π-interactions assume a parallelly displaced configuration in which the (C7−C12)/(C31−C36), and (C13−C18)/(C37−C42)′ ring planes make angles of 4.6(3)° and 8.5(4)°, respectively (Figure 4). The distances of 3.78(2) and 3.85(3) Å between the planes (C7−C12)/(C31−C36) and (C13−C18)/(C37−C42)′, respectively, are similar to the value of 3.723(7) Å found for (C7−C12)/(C7−C12)′ in spirocyclophosphazene **3**.

In compound **3**, where only one 2,2′-dioxybiphenyl group is present, the sandwich-type π-stacking interaction between the rings responsible of the discrimination of enantiomers is stronger with respect to that in **2**. In compound **2**, the presence of two 2,2′-dioxybiphenyl moieties leads to the formation of a polymer-like structure through a parallelly displaced π-stacking interaction of the aromatic units of the dioxybiphenyl groups (Figure 4).

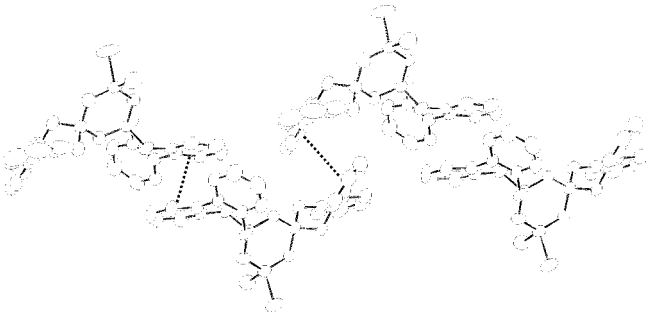
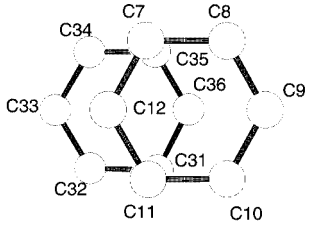


Figure 3. Molecular assembly of **2** (as obtained using the crystal coordinates available from ref.[22]); the chiral recognition (*R*)···(*S*) from molecule to molecule in the *meso* form is denoted by a dotted line



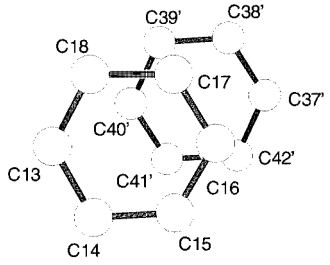


Figure 4. Sandwiched (**3**) and parallelly displaced (**2**) π-stacks of the aromatic units

In the case of compound **1**, in which the P_3N_3 ring bears three 2,2′-dioxybiphenyl groups, the intermolecular enantiomer discrimination does not operate. In fact, the molecules of **1** [(*SSR*) enantiomer] in the lattice[19] are not assembled with respect to each other in configurations that attain some π-stacking interactions, probably because of steric hindrance.

Conclusions

The 2,2′-dioxybiphenyl spirocyclic tetrachlorocyclotriphosphazene **3** was characterized crystallographically by X-ray analysis, and its structure is compared to that of the analogous derivatives **1** and **2**. Both the (*R*) and (*S*) stereoisomers are present in the unit cell of **3**. A twisting angle of ca. 48° between the dioxybiphenyl moiety and the P_3N_3 mean plane, and a significant distortion of the aromatic rings of the dioxybiphenyl moieties, are common features in the crystals of **1**−**3**.

The molecules of **3** in the crystal are assembled in pairs. Each pair is self-assembled in stacks of (*R*) and (*S*) stereoisomers. This structure results from attractive noncovalent π-stacking interactions (eclipsed sandwich configurations of the interacting aromatic units) between the dioxybiphenyl groups of two centrosymmetrically related molecules. A noncovalent π-stacking interaction (parallelly displaced configuration of the interacting aromatic units) between dioxybiphenyl groups was found to be effective also for molecules of **2** in its crystal. The ordered polymer-like assembly (Figure 3) in the solid state is determined by enantiomeric discrimination between the (*R*) and (*S*) molecular portions of the *meso* molecules of **2** in a sequential fashion [···(*R*)···(*S*)···(*R*)···(*S*)···(*R*)···(*S*)···]. The binding energy between the enantiomers on passing from the eclipsed sandwich configuration of the π-stacks in **3** to the parallelly displaced configuration of the π-stacks in **2** should be the same, and have a value of ca. 3 kcal·mol^{-1} suggested by recent findings for the benzene dimmer.[17] An analogous recognition of the stereoisomers is not present in the case of **1** because the nonbonded π-interactions between the possible stereoisomers (*RRR*/*SRR*/*RSS*/*RSR*/*SSR*/*SSS*) cannot take place because of steric hindrance.

Experimental Section

Sample Preparation: Compound **3** (m.p. 193 °C) was prepared as reported in the literature.[24] Crystals of **3** were obtained by slow diffusion of hexane into a dichloromethane solution and successive recrystallization from dichloromethane.

Crystal Structure Determination: The cell parameters and intensity data for **3** were obtained with a Siemens P4 diffractometer, using graphite-monochromated Cu-K_α radiation (λ = 1.54184 Å). Cell parameters were determined by least-squares fitting of 25 centered reflections. The intensities of three standard reflections were measured every 60 min to check the stability of the diffractometer and the decay of the crystal. Intensity data were corrected for Lorentz and polarization effects, and an absorption correction was applied once the structure was solved by using the Walker and Stuart method.[25] The structure was solved using the SIR-97 program[26] and subsequently refined by the full-matrix least-squares SHELX-97 program.[27] The hydrogen atoms were found in difference syntheses and their positions were refined as well as their isotropic displacement parameters. All the non-hydrogen atoms were refined anisotropically. Atomic scattering factors and anomalous dispersion corrections for all the atoms were taken from literature data.[28] Geometrical calculations were performed by the PARST97 routine.[29] The molecular plot was produced by the ORTEP program.[30] Crystal and structure refinement data are reported in Table 4. CCDC-197311 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data and structure refinement for **3**

Empirical formula	$C_{12}H_8Cl_4N_3O_2P_3$
Formula mass	460.92
Temperature [K]	293
λ [Å]	1.5418
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions [Å, °]	a = 11.085(5) b = 12.168(9), β = 100.92(4) c = 13.705(4)
V [Å]	1815(2)
Z	4
$D_{calcd.}$ [g/cm^3]	1.687
μ [mm^{-1}]	8.553
Crystal size [mm]	0.35 × 0.50 × 0.60
2θ range for data collection [°]	9 to 130
Reflections collected	2945
Data/restraints/parameters	2945/0/251
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0545, $wR2$ = 0.1372
R indices (all data)	$R1$ = 0.0606, $wR2$ = 0.1495

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