# TRANSFORMATIONS OF DIFLUOROPHOSPHINES: THE INFLUENCE OF SOLVENT ON THE REACTION PATHWAY AND RING SIZE IN CYCLOPOLYPHOSPHINES

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## PLEASE SCROLL DOWN FOR ARTICLE

# TRANSFORMATIONS OF DIFLUOROPHOSPHINES: THE INFLUENCE OF SOLVENT ON THE REACTION PATHWAY AND RING SIZE IN CYCLOPOLYPHOSPHINES

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The spontaneous transformation reactions of some difluorophosphines in chloroform as solvent are described. First, the redox disproportionation of 2,5-dimethylphenyldifluorophosphine, **1**, unexpectedly led to the formation of the cyclopolyphosphine, hexakis-(2,5-dimethylphenyl)cyclohexaphosphine, **2a** and 2,5-dimethylphenyltetrafluorophosphorane, **3**. Secondly, $CF_3PF_2$, **4**, was found to undergo a scrambling reaction with formation of $(CF_3)_2PF$, **5** and $PF_3$, **6**, rather than a redox disproportionation. In contrast, the difluorophosphines, $RPF_2$ with $R$ = 2,4,6-trimethylphenyl, 9-anthracenyl, and 9-phenanthryl were found to be stable with regard to such transformations. A single crystal X-ray diffraction study of **2** (as a 1:1 solvate with $CDCl_3$, **2a**) was conducted. **2** was found to exist in a chair conformation with a PP bond length of 222.9 pm. The previously known hexamer, $(PhP)_6$, **2b**, was formed in the redox disproportionation of a neat sample of $PhPF_2$, held at $-20°C$ for several months. Its X-ray crystal structure, first reported in 1965, was redetermined, and served to establish the nature of the product. **2b** was found to display a conformation very similar to that of **2/2a**.

Key words: Difluorophosphines; redox disproportionation; cyclopolyphosphines; X-ray crystal structure.

## INTRODUCTION

Transformations of difluorophosphines, such as their redox disproportionation, have been known since their initial discovery.[1-5] The mechanism of these disproportionations has been discussed.[2-5] Thus, for phenyldifluorophosphine, $C_6H_5PF_2$, a spontaneous redox disproportionation with formation of $C_6H_5PF_4$ and a cyclopolyphosphine, $(C_6H_5P)_n$ ($n$ = variable, usually between 4 and 6) has been reported,[2,4,6] (Equation (1)).

$$2 \text{ PhPF}_2 \longrightarrow \text{PhPF}_4 + \tfrac{1}{n}(\text{PhP})_n \quad (1)$$
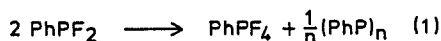
In the absence of solvent[2] the value of $n$ was 5, whereas the hexamer ($n$ = 6) was observed in acetonitrile.[4] Also, there are literature reports on a polymeric phenylcyclopolyphosphine ($n$ = ∞).[6] The ring size of the cyclopolyphosphines, i.e. the value of $n$, was found to vary with solvent and with changes in temperature.[7-9] In solution, values between 3 and 6 are known for $n$[7], and changes in the

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ring size have been reported to occur, e.g. $n = 6 \rightarrow n = 5$ in $CHCl_3$, or equilibria between species with $n = 4$ and 5.[7]

## RESULTS AND DISCUSSION

We are not aware of any cyclohexaphosphine bearing a bulky substituent group at phosphorus, e.g., an orthosubstituted phenyl group. Normally, four-membered cyclopolyphosphines are formed during the redox disproportionation of difluorophosphines. The case of $o$-methoxyphenyldifluorophosphine[12] is typical: (Equation (2)).

$$8\, ArPF_2 \xrightarrow[\text{in CHCl}_3]{80°C\,;\,2\,d} 4\, ArPF_4 + (ArP)_4 \quad (2)$$

$$(Ar = 2\text{-}MeOC_6H_4)$$
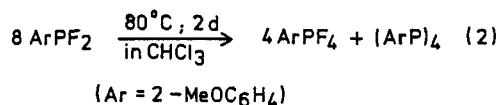
Other cyclotetraphosphines, derived from $o$-tolyl-,[8,10,11] pentafluorophenyl-,[13] and $o$-bromophenyldifluorophosphine[14] have been reported. The rate of the redox disproportionation decreases sharply when the aryl group bears two substituents in the 2,6-position, e.g. in the case of $2,6\text{-}(MeO)_2C_6H_3PF_2$[5,15] or $2,6\text{-}(PhO)_2C_6H_3PF_2$.[5]

Difluorophosphines bearing still bulkier substituents, e.g. $2,4,6\text{-}Me_3C_6H_2$,[16] 9-anthracenyl[17] or 9-phenanthryl[16] were found to be stable to both redox disp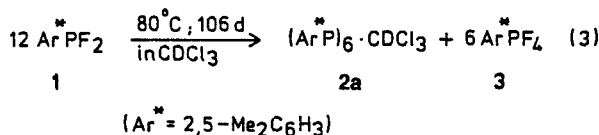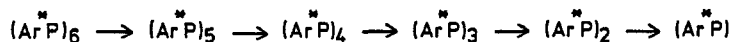roportionation and scrambling reactions. In the course of our investigations of the redox reactions of difluorophosphines we thus observed with considerable surprise that a sample of 2,5-dimethylphenyldifluorophosphine, 1,[18] when kept in a sealed glass tube for an extended period of time at elevated temperature (80°C) in deuterochloroform as solvent, underwent redox disproportionation with formation of a cyclohexaphosphine, (2a) (Equation (3)).

$$12\, Ar^{*}PF_2 \xrightarrow[\text{in CDCl}_3]{80°C\,;\,106\,d} (Ar^{*}P)_6 \cdot CDCl_3 + 6\, Ar^{*}PF_4 \quad (3)$$
$$\qquad\quad 1 \qquad\qquad\qquad\qquad 2a \qquad\qquad 3$$

$$(Ar^{*} = 2,5\text{-}Me_2C_6H_3)$$

In the mass spectrum of **2**, recorded at *ca.* 260°C, no peak higher than the parent peak was observed. Typical fragments originated from the stepwise breakdown of the cyclopolyphosphine ring, i.e.

$$(Ar^{*}P)_6 \longrightarrow (Ar^{*}P)_5 \longrightarrow (Ar^{*}P)_4 \longrightarrow (Ar^{*}P)_3 \longrightarrow (Ar^{*}P)_2 \longrightarrow (Ar^{*}P)$$

The preferred fragmentation products corresponded to one half and one third of the molecular peak. The stepwise loss of ArP fragments was found to be characteristic. Because of the poor solubility of **2** in solvents such as $CDCl_3$ or $CD_3CN$, n.m.r. spectra could not be recorded. No signals other than those of **1** and **3** were observed in the $^{31}P$ n.m.r. spectrum of the reaction mixture. The structure of **2** was established, ultimately, by a single-crystal X-ray diffraction study of its 1:1 solvate with $CDCl_3$, **2a**.

## X-Ray Diffraction Study of 2a

In the crystal, the cyclohexaphosphine rings are arranged parallel to each other. Molecules of deuterochloroform are situated between the rings. These $CDCl_3$ molecules are statistically disordered in such a way that the deuterium atoms point either up or down. The latter orientation is twisted, relative to the former, by 60°, with respect to the C—H axis (cf. Figure 1). For both orientations the three chlorine atoms are essentially coplanar. For symmetry reasons the two orientations observed result in identical interactions with neighbouring cyclophosphine molecules. This leads to a statistical distribution of the two orientations in the crystal. Specific interactions between the cyclohexaphosphine molecules and the $CDCl_3$ molecules were not observed. All intermolecular distances are longer than the sum of the appropriate van der Waals radii.
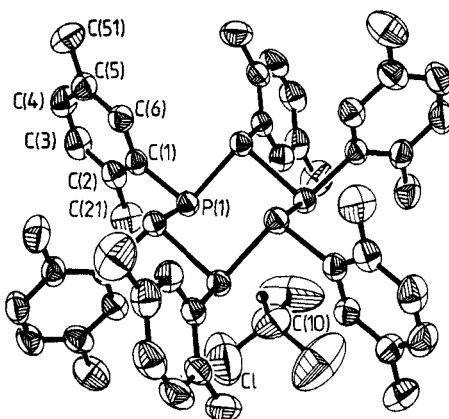


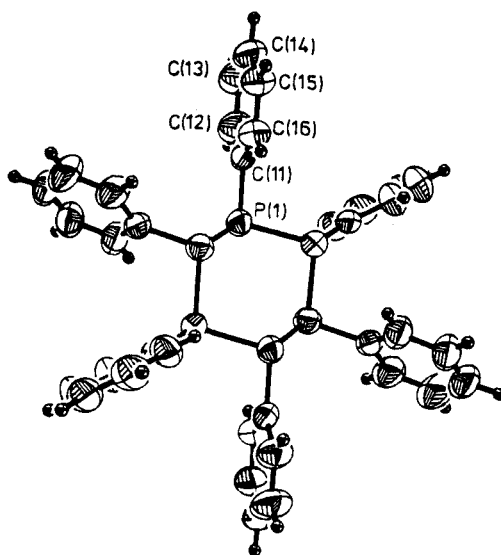FIGURE 1   The molecular structure of 2a in the crystal.



FIGURE 2   The molecular structure of 2b in the crystal.

For comparison the structure of hexaphenylcyclohexaphosphine, **2b** is of interest (Fig. 2; Tables I and II). The determination of this structure was first described in 1965.[19] Because it is almost thirty years old, we decided to repeat it. The cyclohexaphosphine ring of **2/2a** is of threefold symmetry. The PP bond lengths for both **2/2a** and **2b** are very similar to the values usually observed for PP single bonds; cf., e.g.[20] The PP bond length in hexaphenylcyclohexaphosphine was found to be 223.1 pm (compare **2/2a** 222.9 pm). Likewise, the bond angles at phosphorus in **2a** (<PPP 94.6°, <PPC 99.1° and 97.8°) and the extent of the puckering of the ring (<CPPC 76.5°; **2b**: 75.9°), as well as the orientation of the aromatic ring, relative to the cyclohexaphosphine ring (<PPCC 139.8°, −39.2°, −124.2°, and 56.9°) do not differ significantly from the values for $(PhP)_6$ (140.4, −39.2, 123.4, and 55.6°). Ortho- and meta-substituents on the aromatic ring do not apparently affect the geometry of the central ring significantly, even though the nonbonding distance

### TABLE I

Bonding parameters for **2a**.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1) | −P(1) | 1.851( 2) | | P(1) | −P(1) | 2.228( 1) | |
| P(1) | −P(1) | 2.229( 1) | | C(2) | −C(1) | 1.401( 3) | |
| C(6) | −C(1) | 1.386( 3) | | C(21) | −C(2) | 1.494( 4) | |
| C(3) | −C(2) | 1.394( 3) | | C(4) | −C(3) | 1.364( 4) | |
| C(5) | −C(4) | 1.383( 4) | | C(51) | −C(5) | 1.505( 4) | |
| C(6) | −C(5) | 1.391( 3) | | C(10) | −Cl | 1.735( 5) | |
| Cl | −Cl | 1.619( 3) | | Cl | −Cl | 1.619( 3) | |
| C(10) | −C(10) | 1.097(22) | | | | | |
| H(21) | −C(21) | 1.08( 0) | | H(22) | −C(21) | 1.08( 0) | |
| H(23) | −C(21) | 1.08( 0) | | H(3) | −C(3) | 0.93( 3) | |
| H(4) | −C(4) | 1.08( 3) | | H(51) | −C(51) | 1.08( 0) | |
| H(52) | −C(51) | 1.08( 0) | | H(53) | −C(51) | 1.08( 0) | |
| H(6) | −C(6) | 0.99( 3) | | H(10) | −C(10) | 0.99( 2) | |
| | | | | | | | |
| C(2) | −C(1) | −P(1) | 118.4( 2) | C(6) | −C(1) | −P(1) | 121.8( 2) |
| C(6) | −C(1) | −C(2) | 119.8( 2) | C(21) | −C(2) | −C(1) | 123.2( 2) |
| C(3) | −C(2) | −C(1) | 116.7( 2) | C(3) | −C(2) | −C(21) | 120.1( 2) |
| C(4) | −C(3) | −C(2) | 122.9( 2) | C(5) | −C(4) | −C(3) | 120.9( 2) |
| C(51) | −C(5) | −C(4) | 121.7( 2) | C(6) | −C(5) | −C(4) | 117.1( 2) |
| C(6) | −C(5) | −C(51) | 121.3( 3) | C(5) | −C(6) | −C(1) | 122.6( 2) |
| Cl | −C(10) | −Cl | 106.5( 4) | Cl | −C(10) | −Cl | 106.5( 4) |

### TABLE II

Bonding parameters for **2b**.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(11) | −P(1) | 1.834( 2) | | P(1) | −P(1) | 2.231( 1) | |
| P(1) | −P(1) | 2.231( 1) | | C(12) | −C(11) | 1.384( 3) | |
| C(16) | −C(11) | 1.376( 3) | | C(13) | −C(12) | 1.395( 5) | |
| C(14) | −C(13) | 1.333( 5) | | C(15) | −C(14) | 1.360( 5) | |
| C(16) | −C(15) | 1.390( 3) | | | | | |
| H(12) | −C(12) | 1.03( 3) | | H(13) | −C(13) | 0.85( 4) | |
| H(14) | −C(14) | 0.98( 3) | | H(15) | −C(15) | 0.98( 3) | |
| H(16) | −C(16) | 0.87( 2) | | | | | |
| | | | | | | | |
| C(12) | −C(11) | −P(1) | 117.0( 2) | C(16) | −C(11) | −P(1) | 124.8( 2) |
| C(16) | −C(11) | −C(12) | 118.2( 2) | C(13) | −C(12) | −C(11) | 119.4( 3) |
| C(14) | −C(13) | −C(12) | 121.5( 3) | C(15) | −C(14) | −C(13) | 120.1( 3) |
| C(16) | −C(15) | −C(14) | 119.8( 3) | C(15) | −C(16) | −C(11) | 120.9( 3) |

between the ortho-substituents, C(21) and P = 312 pm (P . . . H(21) 290 pm) is significantly shorter than the sum of the van der Waals radii (P + C, 350 pm).[22]

## Transformation of Trifluoromethyldifluorophosphine, $CF_3PF_2$, 4

Neat $CF_3PF_2$, 4 was reported[2] to undergo a redox disproportionation reaction on heating (e.g., Equation (4)),

$$CF_3PF_2 \xrightarrow[\text{heat}]{115°C\,;\,40h} CF_3PF_4 + (CF_3P)_{4.5} \quad (4)$$

4
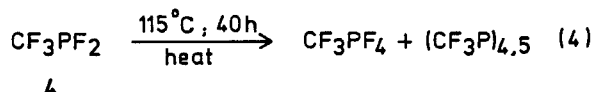
It was observed that the course of this transformation was entirely different when 4 was kept in a solvent, e.g. $CDCl_3$, at elevated temperature for extended periods of time: Bis(trifluoromethyl)fluorophosphine, 5 and phosphorus trifluoride, 6 were identified by n.m.r. spectroscopy[2] as the sole products of a scrambling reaction (e.g., Equation(5)).

$$2\,CF_3PF_2 \xrightarrow[\text{in CDCl}_3]{80°C\,;\,80d} (CF_3)_2PF + PF_3 \quad (5)$$

4                       5      6
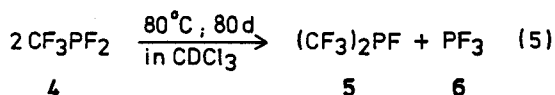
## Conclusion and Prospect

In the case of both 1 and 4 the course of the transformation reaction of $RPF_2$ is different in solution in $CDCl_3$, compared to the neat compounds. In the case of 2, reaction pathway and ring size of the cyclopolyphosphine produced depend, apparently, on the interaction between the reactive species and solvent molecules. It would seem that the chemistry of cyclopolyphosphines merits further study, e.g. with regard to some disagreement concerning the ring size of cyclopolyphosphines,[2,6-8] and the influence of electronic,[2,11] steric,[8] solvent,[4,7] and possible catalytic[3,5] effects on the ring size.

## EXPERIMENTAL

All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen, using standard techniques.

N.m.r. spectra were recorded on a BRUKER AM 200 instrument, using the following standards and conditions: [13]C (50 Mz, in $CDCl_3$; $\delta(C)$ = 77.05 ppm); [19]F (188 Hz, in $CDCl_3$; ext. $CCl_3F$ Reference; [31]P (81 Hz, in $CDCl_3$; ext. 85% $H_3PO_4$ Reference). Low field shifts were given positive, high field shifts negative signs.

    Mass spectra: FINNIGAN MAT 8430 instrument, using E.I. conditions.

    The following starting materials were prepared by literature procedures: Phenyldifluorophosphine,[21] 2,5-dimethylphenyldifluorophosphine, 1,[16] 9-anthracenyldifluorophosphine,[17] 9-phenanthryldifluorophosphine,[18] 2,4,6-trimethylphenyldifluorophosphine,[18] and trifluoromethyldifluorophosphine.[2]

*Redox Disproportionation of 2,5-Dimethylphenyldifluorophosphine, 1: Formation of Hexakis(2,5-dimethylphenyl)cyclohexaphosphine, 2, and of 2,5-Dimethylphenyltetrafluorophosphorane, 3.*

A solution of *ca*. 0.25 g (0.14 mmol) of 1 in *ca*. 1 mL of $CDCl_3$ was sealed into a 5 mm n.m.r. tube, and was maintained at 80°C for 106 d. Colourless needles were formed. The [31]P n.m.r. spectrum of the liquid revealed the presence only of the tetrafluorophosphorane, 3 ($\delta(P)$ − 42.2 ppm, quintet,

$^1$J(PF) 982 Hz) whereas, due to its poor solubility in organic solvents, no $^{31}$P n.m.r. signal for **2** could be observed. The needles precipitated were collected by filtration; yield: *ca.* 0.09 g (*ca.* 80%); m.r. 230–250°C (with loss of CDCl$_3$); dec. >280°C. One of these needles, the 1:1 CDCl$_3$ solvate of (2,5-Me$_2$C$_6$H$_3$P)$_6$, **2·CDCl$_3$**, **2a**, was used in the X-ray crystal structure determination.

### Disproportionation of PhPF$_2$: Formation of (PhP)$_6$, **2b**.

A small sample of neat PhPF$_2$ was sealed in an n.m.r. tube, and was stored at −20°C for a period of 4 months. According to the $^{31}$P n.m.r. spectrum *ca.* 20% of the PhPF$_2$ had undergone disproportionation with formation of PhPF$_4$ and (PhP)$_6$. The latter was precipitated as fine needles which were collected by filtration, and dried *in vacuo* (10$^{-1}$ mm; 25°C). Their identity as the hexamer, (PhP)$_6$, was confirmed by a subsequent X-ray diffraction study.

### X-Ray Crystal Structure Determinations—Experimental

The product, **2·CDCl$_3$** = **2a**, was found to crystallize in the trigonal space group, R$\overline{3}$, with the following lattice constants, determined diffractometrically from 15 reflections (±hkl): *a* = 2116.10(18); *c* = 947.63(19) pm; *Z* = 6; *d*$_{calc.}$ = 1.269 gcm$^{-3}$. The diffraction intensities were measured at 293K on a Siemens four circle diffractometer of type P2$_1$, using monochromated Cu-K$_\alpha$ radiation (λ = 154.184 pm) in the θ − 2θ-mode (3° ≤ 2θ ≤ 135°). The rate of this measurement varied, depending on the intensity of the reflection, between 2.93 and 29.30°/min.

During the data reduction, Lorentz polarization and an empirical absorption corrections (μ = 3.649 mm$^{-1}$) were applied. In the refinement, 1210 of the 1446 measured reflections with *I* ≥ 2.0σ(I) were used. The structure was solved with direct methods and difference Fourier syntheses. Hydrogen atom positions, except for those of the methyl groups, were determined from difference Fourier syntheses, and were arbitrarily refined, using isotropic temperature factors. The refinement converged at *R* = 0.038 (*R*$_W$ = 0.040). In the final refinement cycle the ratio of change in parameter versus estimated standard deviation was smaller than 1.0% for all parameters. A final difference Fourier synthesis led to values of 0.18 × 10$^{-6}$ e/pm$^3$ for the highest maxima of the electron density. Besides our own programs SHELX-76$^{23}$ and complex atom scattering factors$^{24}$ were employed.

The X-ray crystal structure of **2b** was redetermined in the trigonal space group P3c1. Lattice constants were determined diffractometrically from 15 reflections (+hkl), *a* = 1302.5(3), *c* = 1152.8(3) pm; *Z* = 2; *d*$_{calc.}$ = 2.271 gcm$^{-3}$. Intensities were measured and corrected under the same conditions as described for **2a**. In the refinement 885 of 1017 measured reflections with *I* ≥ 2.0σ(I) were used. Hydrogen atom positions were determined from difference Fourier syntheses, and were refined, using isotropic temperature factors. The refinement converged at *R* = 0.034 (*R*$_W$ = 0.035). In the final refinement cycle the relation of change in parameter versus estimated standard deviation for all parameters was less than 1%. A final difference Fourier synthesis gave values of 0.16 × 10$^{-6}$ e/pm$^3$ for the highest electron density maxima.

For compound **2a** atomic coordinates are listed in Table III, bonding parameters in Table I, with the numbering scheme as employed in Figures 1 and 2. The corresponding values for **2b** are listed in Tables II and IV.

Further details of both X-ray structure analyses (thermal parameters, H atom coordinates, structure factors) have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen 2, Germany. This material may be requested, quoting the literature reference, the names of the authors, and the deposition number CSD 57651.

### Preparation of Trifluoromethyldifluorophosphine, CF$_3$PF$_2$, **4**.

The fluorination of CF$_3$PCl$_2$, using SbF$_3$, was conducted in a 200 mL heavy-wall glass tube, fitted with a TEFLON® stopcock. A mixture of 30.0 g (0.168 mol) of SbF$_3$ (dried for 2 h at 200°C) and 15.0 g (0.088 mol) of CF$_3$PCl$_2$ was placed into this tube, which was evacuated to 10$^{-2}$ mm and heated to 200°C for 15 min. in an oil bath. The reaction mixture was allowed to stand for 12 h at room temperature. Volatile products were then removed via a vacuum line.

According to the n.m.r. spectra **4** was the sole product.

Yield 11.2 g (92%).

N.m.r. spectra:

$^{13}$C: δ(C) = 123.3 ppm. (qdt; $^1$J(CF) = 322.5 Hz; $^1$J(CP) = 45.2 Hz; $^2$J(CF) = 22.5 Hz);

$^{19}$F: δ(F)(PF) = −104.7 p.p.m. (dq; $^1$J(PF) = 1249.5 Hz; $^3$J(FF) = 5.6 Hz); δ(F)(CF) = −81.3 p.p.m. (dt; $^2$J(PF) = 85.5 Hz; $^3$J(FF) = 5.6 Hz)

### Scrambling reaction of **4**: Formation of Bis(trifluoromethyl) monofluorophosphine, **5** and Phosphorus Trifluoride, **6**.

TABLE III

Atomic coordinates and isotropic temperature factors for **2a**.

Positional Parameters

|       | X/A        | Y/B        | Z/C          | UEQ         |
|-------|------------|------------|--------------|-------------|
| P(1)  | 0.2587( 0) | 0.5676( 0) | 0.1045( 1)   | 0.041( 0)   |
| C(1)  | 0.1944( 1) | 0.4802( 1) | 0.1908( 2)   | 0.043( 1)   |
| C(2)  | 0.1562( 1) | 0.4180( 1) | 0.1062( 3)   | 0.052( 1)   |
| C(21) | 0.1663( 2) | 0.4185( 1) | -0.0499( 3)  | 0.071( 1)   |
| C(3)  | 0.1075( 1) | 0.3535( 1) | 0.1748( 3)   | 0.066( 1)   |
| C(4)  | 0.0956( 1) | 0.3496( 1) | 0.3168( 3)   | 0.067( 1)   |
| C(5)  | 0.1331( 1) | 0.4105( 1) | 0.4016( 3)   | 0.060( 1)   |
| C(51) | 0.1213( 2) | 0.4071( 2) | 0.5586( 3)   | 0.090( 1)   |
| C(6)  | 0.1824( 1) | 0.4753( 1) | 0.3353( 3)   | 0.051( 1)   |
| Cl    | 0.3517( 7) | 0.6017( 5) | -0.3449( 4)  | 0.199( 3)   |
| C(10) | 0.3333( 0) | 0.6667( 0) | -0.2754(12)  | 0.100( 3)   |

Hydrogen atoms,
Positional parameters and isotropic temperature factors

|       | X/A        | Y/B        | Z/C          | U          |
|-------|------------|------------|--------------|------------|
| H(21) | 0.162( 0)  | 0.462( 0)  | -0.100( 0)   | 0.141( 0)  |
| H(22) | 0.125( 0)  | 0.367( 0)  | -0.091( 0)   | 0.141( 0)  |
| H(23) | 0.220( 0)  | 0.425( 0)  | -0.071( 0)   | 0.141( 0)  |
| H(51) | 0.150( 0)  | 0.460( 0)  | 0.608( 0)    | 0.282( 0)  |
| H(52) | 0.131( 0)  | 0.369( 0)  | 0.618( 0)    | 0.282( 0)  |
| H(53) | 0.064( 0)  | 0.389( 0)  | 0.557( 0)    | 0.282( 0)  |
| H(10) | 0.333( 0)  | 0.667( 0)  | -0.171( 2)   | 0.101(34)  |
| H(3)  | 0.079( 2)  | 0.311( 2)  | 0.122( 3)    | 0.086( 9)  |
| H(4)  | 0.056( 1)  | 0.301( 2)  | 0.372( 3)    | 0.086( 9)  |
| H(6)  | 0.212( 1)  | 0.518( 1)  | 0.396( 3)    | 0.060( 7)  |

TABLE IV

Atomic coordinates and isotropic temperature factors for **2b**.

Positional Parameters

|       | X/A       | Y/B       | Z/C       | UEQ      |
|-------|-----------|-----------|-----------|----------|
| P(1)  | 9484( 0)  | 1127( 0)  | 4489( 1)  | 57( 0)   |
| C(11) | 9069( 2)  | 2135( 2)  | 5183( 2)  | 62( 1)   |
| C(12) | 8935( 2)  | 2913( 2)  | 4467( 3)  | 94( 1)   |
| C(13) | 8643( 3)  | 3715( 3)  | 4951( 5)  | 124( 2)  |
| C(14) | 8489( 3)  | 3751( 3)  | 6090( 5)  | 116( 1)  |
| C(15) | 8614( 3)  | 2994( 3)  | 6811( 3)  | 99( 1)   |
| C(16) | 8901( 2)  | 2182( 2)  | 6356( 2)  | 78( 1)   |

Hydrogen atoms,
Positional parameters and isotropic temperature factors

|       | X/A      | Y/B      | Z/C      | U        |
|-------|----------|----------|----------|----------|
| H(12) | 909( 2)  | 286( 2)  | 360( 2)  | 102( 9)  |
| H(13) | 856( 3)  | 415( 3)  | 447( 3)  | 142(13)  |
| H(14) | 829( 2)  | 429( 3)  | 651( 3)  | 121(10)  |
| H(15) | 848( 3)  | 296( 2)  | 765( 3)  | 123(11)  |
| H(16) | 899( 2)  | 173( 2)  | 685( 2)  | 83( 8)   |

A mixture of *ca.* 0.3 g of **4** and 0.6 mL of $CDCl_3$ was sealed into a heavy-wall n.m.r. tube. The mixture was held at 80°C for 11 weeks. N.m.r. spectra recorded at this stage revealed the presence of **5** and **6**.

N.m.r. spectra:

**5:** $^{19}$F: $\delta(F)(PF) = -217.8$ ppm (d of septets; $^1J(PF) = 1012$ Hz; $^3J(FF) = 3.2$ Hz); $\delta(F)(CF) = -66.5$ ppm (dd; $^2J(PF) = 87.3$ Hz; $^3J(FF) = 3.2$ Hz).

$^{13}$C: $\delta(C) = 125.3$ ppm (qdd; $^1J(CF) = 320.5$ Hz; $^2J(CF) = 18.6$ Hz; $^1J(CP) = 31.1$ Hz; $^3J(CF) = 6.3$ Hz).

$^{31}$P: $\delta(P) = 123.7$ ppm (d septets; $^1J(PF) = 1012$ Hz; $^2J(PF) = 87.3$ Hz).

**6:** $^{19}$F: $\delta(F) = -34.0$ ppm (d, $^1J(PF) = 1402$ Hz); $^{31}$P, $\delta(P) = 105.6$ ppm (q, $^1J(PF) = 1402$ Hz).

## ACKNOWLEDGEMENTS

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