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Reaction of (*E*)-Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene with Tetrachloro-*o*-benzoquinone

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ABSTRACT: *The reactions of (E)-bis(2,4,6-tri-tert-butylphenyl)diphosphene with tetrachloro-o-benzoquinone gave two products of interest, a spirophosphorane and a 1,3,2-dioxaphospholane, indicating cleavage of the P=P bond. The structures were determined by X-ray crystallographic analyses.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:300–308, 2001

INTRODUCTION

Multiple bonds containing heavier main group elements are unstable because the multiple-bond energies are not high. However, by utilizing a very bulky substituent as a protecting group, such as the 2,4,6-tri-*tert*-butylphenyl group (abbreviated Mes*) [1], we have been successful in stabilizing several kinds of low-coordinated organophosphorus compounds as stable chemical species. We isolated highly reactive but kinetically stabilized organophosphorus compounds, such as diphosphenes (R–P=P–R), phosphaethenes (R–P=CR_2), and so on. They are interesting new classes of compounds because of their unusual structures and properties [2–6]. We have reported an oxidation reaction of the diphosphene with *m*-chloroperbenzoic acid giving the corresponding diphosphene oxide [7]. We now report on the reaction of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**) with tetrachloro-*o*-benzoquinone (TOB or *o*-chloranil) [8], together with some related reactions of the catechol derivatives.

RESULTS AND DISCUSSION

A toluene solution of the diphosphene **1** was allowed to react with 4 molar equiv. of TOB to give a spirophosphorane, bis(3,4,5,6-tetrachloro-1,2-phenylenedioxa)-2,4,6-tri-*tert*-butylphenylphosphorane (**2**) in 44% yield. If the amount of TOB was reduced to half, 3,4,5,6-tetrachlorobenzo-3-(2,4,6-tri-*tert*-butylphenyl)-1,3,2-dioxaphospholane (**3**) was obtained in 16% yield (Scheme 1). It seems likely that **2** was formed via **3** in the presence of a large excess amount of TOB, since Ramirez and his coworkers have reported many examples of formation of spirophosphoranes from tervalent phosphorus compounds [9]. Indeed, reactions of the diphosphene **1** with 1, 2, 3, and 4 molar equivalents of TOB, respectively, followed by ^{31}P NMR spectroscopy, indicated that a peak due to **3** was first seen, then a small and broad

Dedicated to Prof. Naoki on the occasion of his 72nd birthday.

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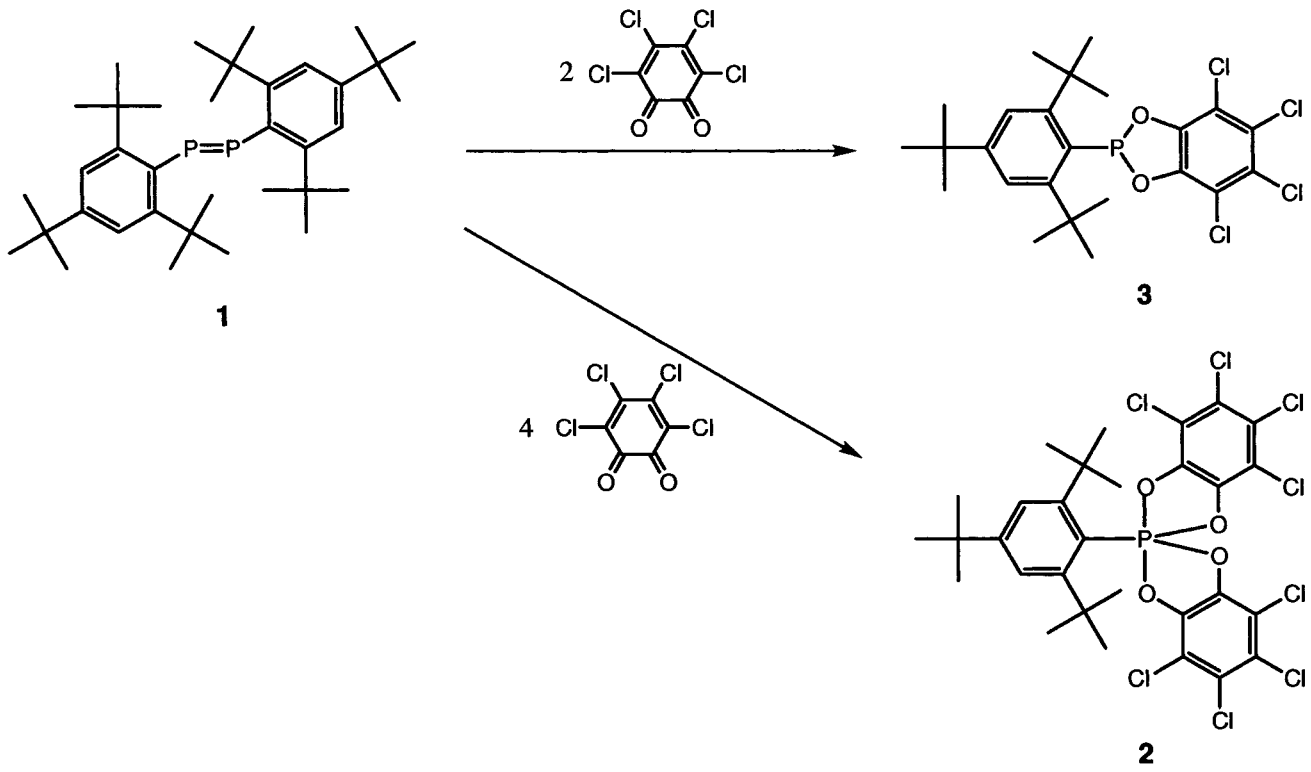


SCHEME 1

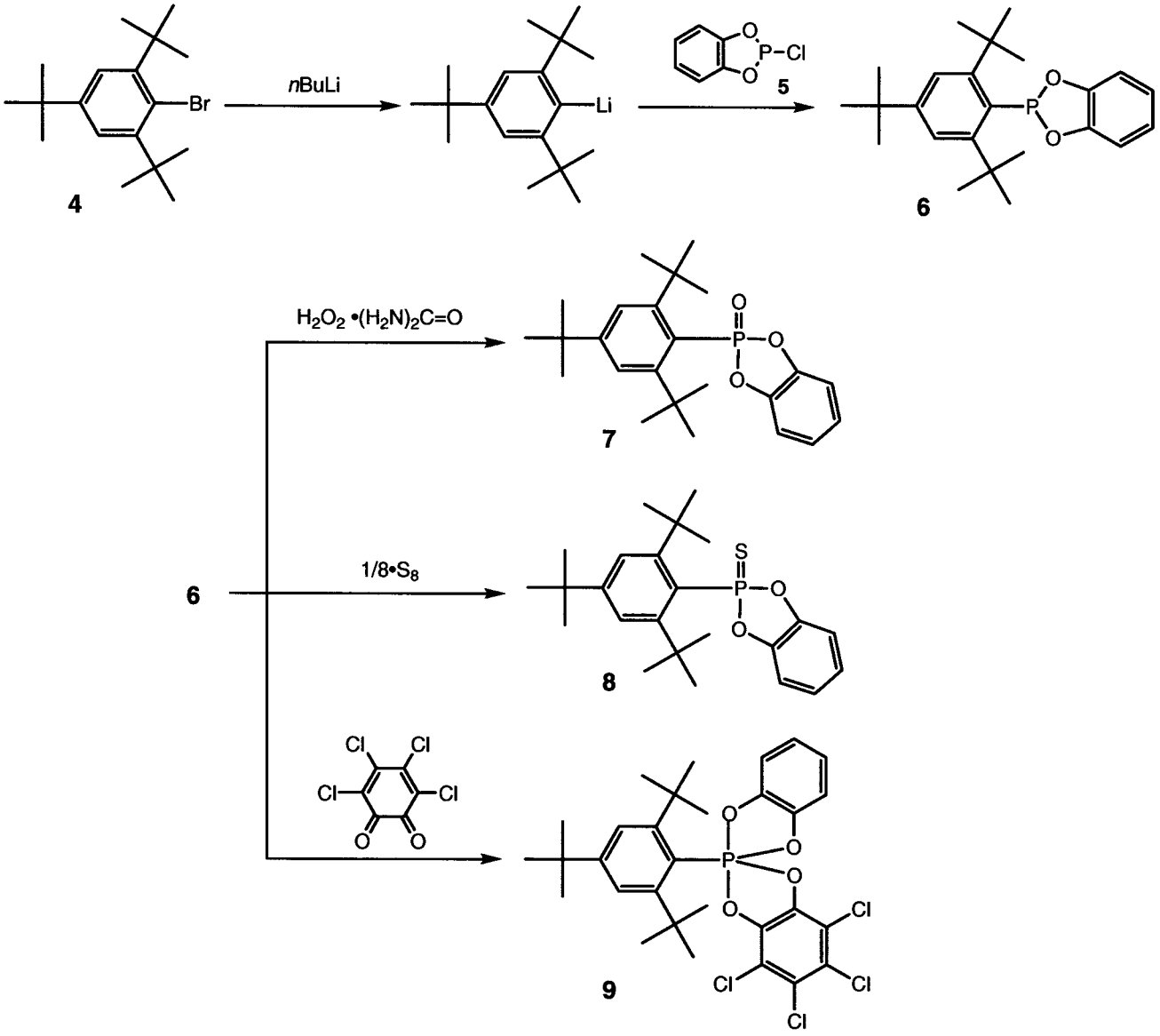
signal due to **2** appeared additionally, and finally, the signal due to **3** disappeared to show just a sharp signal of **2**.

On the other hand, as shown in Scheme 2, if a dioxaphospholane with the catechol moiety, 3-(2,4,6-tri-*tert*-butylphenyl)benzo-1,3,2-dioxaphospholane (**6**), which was prepared by reaction of 2,4,6-tri-*tert*-butylphenyllithium with 2-chlorobenzo-1,3,2-dioxaphospholane (**5**), was allowed to react with TOB, the corresponding mixed phosphorane, 2,4,6-tri-*tert*-butylphenyl (1,2-phenylenedioxa)(3,4,5,6-tetrachloro-1,2-phenylenedioxa)phosphorane (**9**) was obtained in 96% yield. The results strongly support the assumption that the product **2** from the reaction of **1** with 4 molar equiv. of TOB must have been formed via **3**. Furthermore, **6** was transferred to the corresponding oxide **7** and sulfide **8** as indicated in Scheme 2.

As for a reaction mechanism for the formation of **3** from **1** and TOB, there might be involved a radical process including electron transfer from **1** to TOB to cleave the P = P bond. Although we have not yet carried out ESR experiments of this process, we have observed significantly reduced broad signals of low intensity for the peaks in ^{31}P NMR studies during the reaction, indicating that a radical process is involved. Indeed, there have been several examples reporting such electron-transfer processes including semiquinone anion radicals and phosphinium cation radicals for the Ramirez reactions [10,11]. Furthermore, van der Knaap and Bickelhaupt have reported a reaction of TOB with 1-(2,6-dimethylphenyl)-2,2-diphenylphosphaalkene to give a spirophosphorane, discussing a mechanism for the reaction of a low-valent phosphorus compound with some *o*-quinones [12]. They concluded that their experimental results slightly favor an electron transfer mechanism compared to an ionic mechanism. As Scheme 3 shows the presumed reaction pathway, an intermediate **C** might be involved at the final stage leading to the formation of **3**, after following either route A to an intermediate **A** or route B to **B** (Scheme 3).

On the other hand, attempts were made to effect formation of a similar spirophosphorane and several other reactions of the diphosphene **1** with hexafluoroacetone (HFA) and perfluoro-4-methylpentane-2,3-dione in a [2 + 4] mode were carried out [13,14]. However, no reactions occurred, as observed from the absence of a color change as well as by ^{31}P NMR spectroscopic evidence.

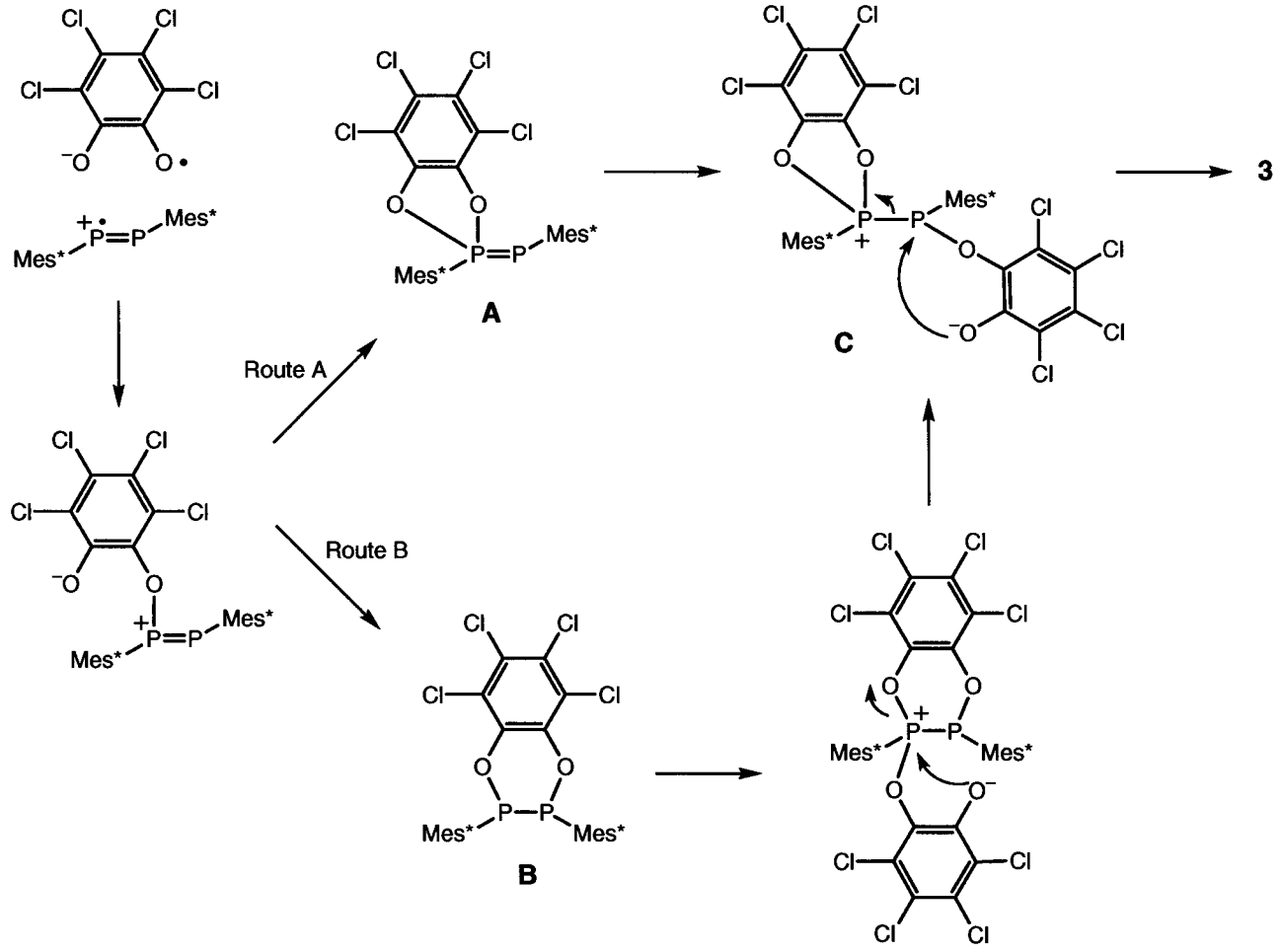
The structures of **2, 3, 6**, and **7** were unambigu-



SCHEME 2

ously determined by X-ray crystallographic analysis. Table 1 shows the crystal data for these organophosphorus compounds.

Figure 1 depicts an ORTEP drawing of **2**. The compound is the third example of a C-substituted spirophosphorane (PCO_4) with a trigonal bipyramidal geometry at phosphorus; in the presence of two chelating *O,O′*-ligands, the square pyramidal geometry is more common in such systems [15]. One reason for this may be the steric requirements of the bulky *tert*-butyl groups of the Mes* substituent in **2**, although the previously known examples [16] did not contain such bulky substituents. In **2**, the shortest distances of each oxygen towards the nearest *tert*-butyl-hydrogen atom lie between 221.8 (O3 · · · H8A) and 239.7 pm (H8A · · · 2O1). The axis O1–P–O4 is linear [179.19(10)°]; the axial-equatorial angles, including the bite angles, lie close to 90°; C1–P–O2 and C1–P–O3 are appreciably wider than ideal [128.18(11)° and 129.15(11)°]. Compared to the two other examples of trigonal bipyramidal phosphorus in this class of substances, the difference between the axial and equatorial P–O bond lengths is small (5.8 pm cf. ca. 15 pm), and the P–C bond is long [185.2(3) cf. 183.6(5) or 181.2(3) pm]. The Mes* group is approximately coplanar with the equatorial plane of the phosphorus substituents, as can be seen from the torsion angles O2–P–C1–C6 (−4.5°) and O3–P–C1–



SCHEME 3

C2 (−7.9°). In contrast to the structures of **3** and **6**, the Mes* is not distorted.

The 1,3,2-dioxaphospholane **3** crystallizes with two independent molecules and half a molecule of pentane in the asymmetric unit. Figure 2 depicts an ORTEP drawing of one molecule of **3**. The atoms of the second molecule are labeled with primes; corresponding dimensions are given here in square brackets. From a least-squares fit of P, O1, O2, and C1–C6, it can be seen that these regions of the two molecules do not differ significantly (mean deviation: 4.0 pm). Significant deviations can be found in the positions of the *tert*-butyl groups and the fold angle at phosphorus [C1–P–X (X = center of C21–C26): 99.9° or 96.3°]. The C and O atoms of the TOB units are planar (mean deviations: 1.8 and 2.1 pm) with phosphorus lying 7.8 (19.3) pm out of the best plane. The Mes* rings including their α-carbon atoms are significantly nonplanar; C1 lies 19.4 pm (16.9 pm) out of the best plane of C2 to C6 (mean deviation 1.8 pm [1.7 pm]); torsion angles P–C1–C2–C7 and P–C1–C6–C15 are 28.8° (33.9°) and −29.6° (34.1°), respectively. Compared to two other known structures of carbon-substituted 1,3,2-dioxaphospholanes, a bis-(benzo-1,3,2-dioxaphospholane)-substituted Cl_2C-compound [17] and a triphenylmethyl-substituted 3,4,5,6-tetrachlorobenzo-1,3,2-dioxaphospholane [18], the P–C1 bond lengths are significantly shorter [185.0(2) pm, cf. 189.8(3) or 191.4(2) pm] but are similar to those in compound **2** [185.6(2) pm]. The smallest angle at phosphorus is the endocyclic O1–P–O2 [91.83(7)° or 91.74(7)°], the largest is C1–P–O1 [99.51(8)°] or C1′–P′–O2′ [100.16(9)°]. The P–O bonds of **3** are longer (av. 170.0 pm) than those in the comparable structures (165.5(2)–168.4(2) pm), but correspond also to the axial P–O bond lengths in **2**. A similar distortion of the Mes* rings has been observed in several cases [19].

Figure 3 depicts an ORTEP drawing of one molecule of **6** in the crystal. The compound crystallizes

TABLE 1 Crystal Data and Structure Refinement for **2, 3, 6**, and **7**

Compound	**2**	**3**	**6**	**7**
Empirical formula	$C_{30}H_{29}Cl_8O_4P$	$C_{25.25}H_{32}Cl_4O_2P$ (1/4 pentane)	$C_{24}H_{33}O_2P$	$C_{24}H_{33}O_3P$
Formula weight	768.10	540.28	384.47	400.47
Temperature (K)	143(2)	143(2)	143(2)	133(2)
Wavelength (pm)	71.073	71.073	71.073	71.073
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions	a = 1025.5(12) pm b = 2727(3) pm c = 1206.9(12) pm α = 90° β = 95.58(4)° γ = 90°	a = 931.82(10) pm b = 1576.06(16) pm c = 1866.5(2) pm α = 82.541(3)° β = 79.799(3)° γ = 83.649(3)°	a = 938.00(14) pm b = 1715.6(2) pm c = 5598.4(8) pm α = 90° β = 94.691(3)° γ = 90°	a = 1121.04(8) pm b = 1404.57(8) pm c = 1527.77(10) pm α = 74.567(3)° β = 84.129(3)° γ = 70.433(3)°
Volume (nm^3)	3.36(1)	2.6642(5)	8.98(1)	2.1847(2)
Z	4	4	16	4
Density (calculated) (Mg/m^3)	1.519	1.347	1.138	1.218
Absorption coefficient (mm^{-1})	0.753	0.525	0.137	0.147
F(000)	1568	1130	3328	864
Crystal size (mm)	0.38 × 0.20 × 0.10	0.29 × 0.24 × 0.05	0.36 × 0.29 × 0.13	0.49 × 0.27 × 0.13
θ range for data collection	1.49 to 28.34°	1.12 to 28.28°	3.77 to 26.38°	1.38 to 30.50°
Index ranges	$-13 \le h \le 13$ $-36 \le k \le 36$ $-16 \le l \le 16$	$-12 \le h \le 12$ $-20 \le k \le 21$ $-24 \le l \le 24$	$-11 \le h \le 11$ $-21 \le k \le 21$ $-69 \le l \le 69$	$-16 \le h \le 16$ $-19 \le k \le 20$ $-21 \le l \le 21$
Reflections collected	48418	38926	87844	35899
Independent reflections	8356 [R_{int} = 0.1356]	13179 [R_{int} = 0.0408]	18317 [R_{int} = 0.0820]	13192 [R_{int} = 0.0295]
Completeness	99.6% to θ = 28.34°	99.5% to θ = 28.28°	99.6% to θ = 26.38°	99.3% to θ = 30.00°
Absorption correction	Multiple scans (SADABS)	Multiple scans (SADABS)	none	none
Max. and min. transmission	0.9281 and 0.7868	0.9281 and 0.8041	—	—
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8356/0/397	13179/331/597	18317/12/1041	13192/0/523
Goodness-of-fit on F^2	1.014	0.993	0.898	1.006
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0552, $wR2$ = 0.1113	$R1$ = 0.0429, $wR2$ = 0.1079	$R1$ = 0.0452, $wR2$ = 0.0869	$R1$ = 0.0380, $wR2$ = 0.0980
R indices (all data)	$R1$ = 0.0869, $wR2$ = 0.1304	$R1$ = 0.0732, $wR2$ = 0.1215	$R1$ = 0.1017, $wR2$ = 0.0994	$R1$ = 0.0555, $wR2$ = 0.1054
Largest diff. peak and hole	1321 and −871 e nm^{-3}	832 and −499 e nm^{-3}	246 and −319 e nm^{-3}	438 and −315 e nm^{-3}

with four independent molecules (but no solvent) in the asymmetric unit and is thus not isostructural to **3**. The atoms of the second, third, and fourth molecules are labeled 1xx, 2xx, and 3xx. The *tert*-butyl groups connected to C4 and C104 are disordered over 2 positions. Because the molecules do not differ greatly, as can be seen from a least-squares fit of P, O1, O2, and C1–C6 to the corresponding atoms of the other three molecules (mean deviations: 2.7, 5.9 and 1.9 pm), averaged values are generally used in the following. Small differences can be found in the orientation of the *tert*-butyl groups, larger ones in the deviation of the phosphorus from the best plane through the catechol unit with 37.4, 36.5, 40.4, and 46.2 pm (mean deviations: 1.7, 1.7, 1.3, and 6.7 pm). As in **3**, the Mes* rings are distorted, and the best plane passes through C2 to C6 with C1 21.4 pm out of plane. The distortion is also seen in the torsion angles P1–C1–C2–C7 and P1–C1–C6–C15 with 38.1° and −37.6°, respectively. These torsion angles representing the greatest differences between the molecules can be found (absolute values: 35.8 and 34.3° in the first molecule to 40.7° and 40.7° in the third molecule). The fold angles at phosphorus [C1–P–X

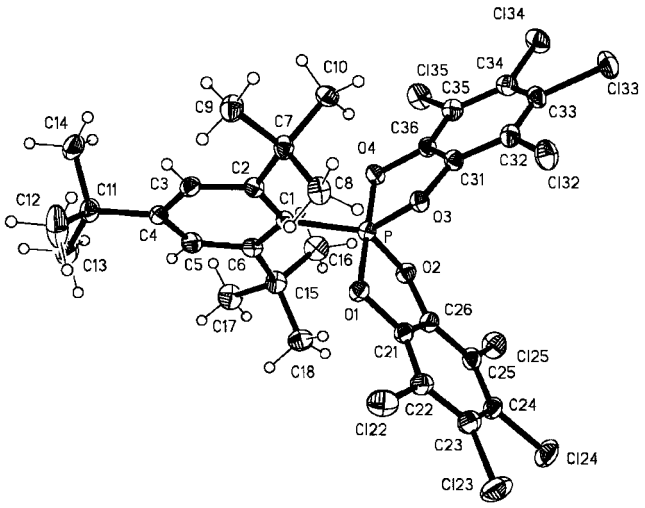


FIGURE 1 An ORTEP drawing of **2** with 50% probability ellipsoids. Selected bond lengths (pm) and angles (°): P–O1, 170.9(2); P–O2, 165.1(2); P–O3, 164.8(2); P–O4, 179.6(2); P–C1, 185.2(3); O1–P–O2, 90.81(11); O1–P–O3, 88.62(11); O1–P–O4, 179.19(10); O2–P–O3, 102.65(10); O2–P–O4, 89.24(11); O3–P–O4, 90.58(11); C1–P–O1, 89.25(11); C1–P–O2, 128.18(11); C1–P–O3, 129.15(12); C1–P–O4, 91.36(11).

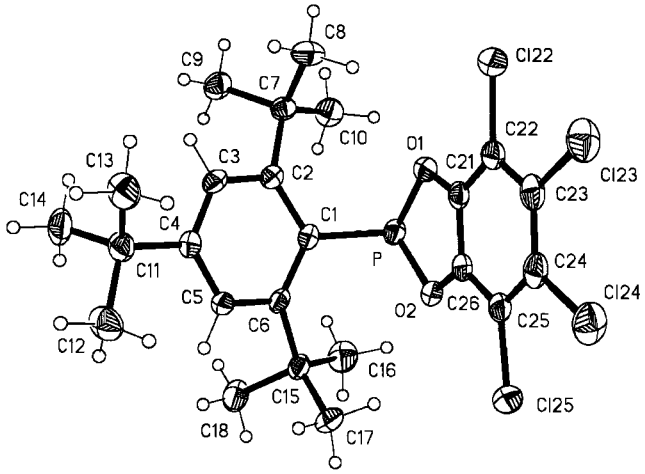


FIGURE 2 An ORTEP drawing of **3** with 50% probability ellipsoids. Selected bond lengths (pm) and angles (°): P–O2, 170.05 (15); P–O1, 170.20(16); P–C1, 185.0(2); O2–P–O1, 91.83(7); O2–P–C1, 99.45(8); O1–P–C1, 99.51(8).

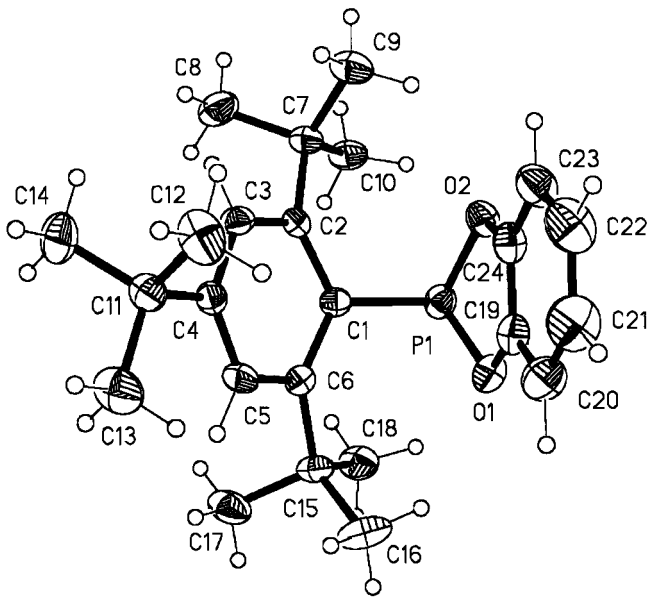


FIGURE 3 An ORTEP drawing of **6** with 50% probability ellipsoids. The second position of the *p-tert*-butyl group is omitted for clarity. Selected bond lengths (pm) and angles (°): P–O2, 167.81 (15); P–O1, 168.16(14); P–C1, 186.02(19); O2–P–O1, 92.03(7); O2–P–C1, 97.82(8); O1–P–C1, 97.47(8).

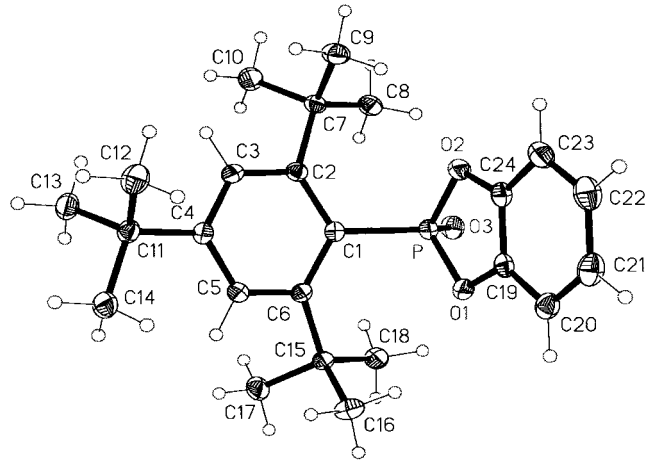


FIGURE 4 A thermal ellipsoid drawing of **7** with 50% levels. Selected bond lengths (pm) and angles (°): P–O3, 145.52 (8); P–O2, 163.72(8); P–O1, 162.66(9); P–C1, 180.71(10); O3–P–O1, 114.25(5); O3–P–O2, 114.24(4); O1–P–O2, 95.08(4); O3–P–C1, 121.25(5); O1–P–C1, 104.57(5); O2–P–C1, 103.81(4).

(X = center of C19–C24)] is 88.7°. The P–C bond lengths lie in the same range as in **2** and **3** (186.1 pm), whereas the P–O bonds are shorter (168.1 pm). The endocyclic angle O1–P–O2 (92.1°) does not differ from those in **3**.

Figure 4 depicts a thermal ellipsoid drawing of one molecule of **7** in the crystal. The compound crystallizes with two independent molecules in the asymmetric unit. The second molecule is labeled with primes, and the corresponding dimensions are given in square brackets. The C and O atoms of the catechol units are planar (mean deviation, 0.9° [1.8°]) with phosphorus lying 2.8 pm [1.5 pm] outside the best plane. As in the unoxidized form, the Mes*-rings with their α-carbon atoms are significantly distorted, as can be seen from the torsion angles P1–C1–C2–C7

[28.9° (−33.3°)] and P1–C1–C6–C15 [32.6° (−31.3°)]. The deviation of C1 from the best plane through C2 to C6 [mean deviation, 2.1 pm (2.1 pm)] is 17.1 pm (20.8 pm). The P–O and P–C bonds (163.1 or 180.4 pm av.) are shorter than those for the corresponding unoxidized compound **6** by 5 and 6 pm, respectively. The fold angle at phosphorus is, at 111.4° (110.2°), much wider than in **6** (88.7° av.). The smallest angle at phosphorus is still the endocyclic angle, and the largest is now C1–P–O3 at 121.25(5) pm [121.01(5) pm].

In summary, the diphosphene **1** reacted with TOB to give the spirophosphorane **2** via the 1,3,2-phospholane **3**, probably due to an electron-transfer process. The structures of **2, 3, 6**, and **7** were determined by X-ray analysis.

EXPERIMENTAL

All operations were carried out in standard Schlenk glassware in an atmosphere of dry nitrogen. Solvents were dried, purified, and stored according to the common procedures [20]. (*E*)-1,2-Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**) [1,21], 2,4,6-tri-*tert*-butylbromobenzene (**4**) [21], and 2-chlorobenzo-1,3,2-dioxaphospholane (**5**) [22] were prepared by the literature methods. Other compounds were commercially available. We thank Dr. A. Kadyrov for a sample of perfluoro-4-methylpentan-2,3-dione. Melting points were determined on a Büchi 530 melting point apparatus using sealed 0.1 mm capillary tubes and are uncorrected. NMR: Bruker DPX 200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81.0 MHz) and DRX 400 (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{31}P: 162.0 MHz). NMR experiments were made in C_6D_6 (2) or $CDCl_3$; atoms are named as in the structures or corresponding to **6** (for **7–9**). MS: Finnigan MAT 8430; EI at 70 eV. Elemental analyses were carried out by Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie, and Analytisches Laboratorium des Instituts für Pharmazeutische Chemie der Technischen Universität Braunschweig. In vacuo refers to a pressure of 0.05 Torr at 25°C. Yields have not been optimized.

*Preparation of Bis(3,4,5,6-tetrachloro-1,2-phenylenedioxa) (2,4,6-tri-tert-butylphenyl)phosphorane (**2**)*

To a solution of 300 mg (0.54 mmol) **1** in 5 mL toluene a solution of 536 mg (2.16 mmol) tetrachloro-*o*-benzoquinone (TOB) in 5 mL toluene was added dropwise. After half an hour the dark red solution became lighter, and then dark red-brown. After 4 hours, the solution volume was reduced by half in vacuo. After 18 hours at −10°C, the colorless precipitate was filtered off and washed with cold toluene. A suitable single crystal for X-ray analysis was obtained by evaporation from a $CDCl_3$ solution in an NMR tube. Yield: 180 mg (43.5%); m.p. 106°C. Analysis: C, 45.45; H, 3.60; Cl, 37.74%. Calcd for $C_{30}H_{29}CI_8O_4P$: C, 46.91; H, 3.81; Cl, 36.92%. ^{1}H NMR: δ = 1.17 (s, 9H, C4-*t*-Bu); 1.55 (s, 18H, C2,6-*t*-Bu); 7.68 (d, 2H, ^4J(PH) = 9.73 Hz, C5-H, C6-H. ^{13}C {^{1}H} NMR: δ = 30.95 (s, 3C, C12–C14); 34.01 (s, 6C, C8–C10, C16–C18); 35.10 (s, 1C, C11); 38.89 (d, ^3J(PC) = 4.9 Hz, 2C, C7, C15); 125.03 (d, ^3J(PC) = 23.2 Hz, 2C, C3, C5); 148.70 (d, ^4J(PC) = 14.1 Hz, 1C, C4); 151.77 (d, ^2J(PC) = 5.5 Hz, 2C, C2, C6); other signals could not be observed. ^{31}P {^{1}H} NMR: δ = 6.77 (s). EI-MS: *m/z* (%): 768 ($C_{30}H_{29}{}^{35}Cl_6{}^{37}Cl_2O_4P$) (4) [M]$^+$, the experimental isotopic pattern corresponds to the calculated: 711 (30) [M$^+$ ($C_{30}H_{29}{}^{35}Cl_6{}^{37}Cl_2O_4P$) − *t*-Bu]; 248 (100) [$C_6H_2O_2{}^{35}Cl_3{}^{37}Cl$]; 231 (49) [$C_6H_2tBu_2CMe_2$ + H]; 57 (32) [*t*-Bu]. $C_{30}H_{29}Cl_8O_4P$ (766.14).

*Preparation of 3,4,5,6-Tetrachlorobenzo-3-(2,4,6-tri-tert-butylphenyl)-1,3,2-dioxaphospholane (**3**)*

To a solution of 300 mg (0.54 mmol) **1** in 5 mL toluene, a solution of 268 mg (1.08 mmol) TOB in 5 mL toluene was added dropwise. The dark-red solution became lighter during the reaction. After 1 hour, the solvent was evaporated in vacuo, and the residue, extracted with 6 mL pentane, showed ^{31}P NMR signals of **1** and **3** (1:2) and a small signal of **2**. After 18 hours at −10°C, orange crystals of **1** and colorless crystals of **3** grew. The solvent was decanted, and the colorless crystals were separated mechanically for analysis. Yield: 45 mg (15.9%); m.p. 132°C. The yield was insufficient for elemental analysis. ^{1}H NMR: δ = 1.20 (s, 9H, C4-*t*-Bu); 1.53 (d, 18H, ^5J(PH) = 1.42 Hz, C2,6-*t*-Bu); 7.11 (d, 2H, ^4J(PH) = 1.71 Hz, C5-H, C6-H). ^{13}C {^{1}H} NMR: δ = 31.07 (s, 3C, C12–C14); 34.07 (d, ^4J(PC) = 9.3 Hz, 6C, C8–C10, C16–C18); 34.60 (s, 1C, C11); 39.46 (s, 2C, C7, C15); 122.54 (s, 2C, C3, C5); 150.88 (s, 1C, C4); 157.55 (d, ^2J(PC) = 6.7 Hz, 2C, C2, C6); other signals could not be observed. ^{31}P {^{1}H} NMR: δ = 218.07 (s). EI-MS: *m/z* (%): 523 ($C_{24}H_{30}{}^{35}Cl_2{}^{37}Cl_2O_2P$) (11) [M$^+$ + 1], the experimental isotopic pattern corresponds to the calculated; 277 (33) [$C_6{}^{35}Cl_3{}^{37}ClO_2P$]; 231 (39) [$C_6H_2$-*t*-$Bu_2CMe_2$ + H]; 57 (100) [t-Bu]. $C_{24}H_{29}Cl_4O_2P$ (522.3).

*Preparation of 3-(2,4,6-Tri-tert-butylphenyl)benzo-1,3,2-dioxaphospholane (**6**)*

1-Bromo-2,4,6-tri-*tert*-butylbenzene (10 g, 30.8 mmol) was dissolved in 100 mL THF and at −78°C 23.2 mL (37 mmol) of a solution of *n*-butyllithium

in hexane was added dropwise over 5 minutes from a syringe. The solution was stirred for 10 minutes at −78°C, and then 7.33 g (42 mmol) **5** were slowly added via a syringe. The solution was allowed to warm to room temperature and finally heated under reflux for 1 hour with stirring. After the mixture had cooled to room temperature, the solvent was evaporated in vacuo. The residue was extracted with 30 mL pentane, and the LiCl was filtered off three times over Celite, then the solvent was evaporated in vacuo. Single crystals for X-ray analysis were obtained from a solution in pentane after 1 day at −10°C. Yield: 4.2 g (35.4%); m.p. 95°C. Analysis: C, 75.16; H, 8.77%. Calcd for $C_{24}H_{33}O_2P$: C, 74.97; H, 8.65%. ^{1}H NMR: δ = 1.00 (s, 9H, C4-*t*-Bu); 1.51 (s, 18H, C2, 6-*t*-Bu); 6.53–6.63 (m, 4H, C_6H_4); 6.94 (d, 2H, ^4J(PH) = 1.52 Hz, C5-H, C6-H). ^{13}C {^{1}H} NMR: δ = 30.87 (s, 3C, C12-C14); 33.39 (d, ^4J(PC) = 8.8 Hz, 6C, C8–C10, C16–C18); 34.28 (s, 1C, C11); 39.12 (d, 2C, ^3J(PC) = 2.7 Hz, 2C, C7, C15); 112.52 (s, 2C, C20, C23); 119.47 (s, 2C, C3, C5); 121.49 (d, ^4J(PC) = 0.1 Hz, 2C, C21, C22); 140.20 (d, ^1J(PC) = 78.0 Hz, 1C, C1); 146.83 (d, ^4J(PC) = 7.8 Hz, 1C, C4); 149.73 (d, ^2J(PC) = 39.0 Hz, 2C, C19, C24); 157.77 (d, ^2J(PC) = 6.3 Hz, 2C, C2, C6). ^{31}P {^{1}H} NMR: δ = 188.69 (s). EI-MS: *m/z* (%): 384 (19) [M]$^+$; 275 (100) [$M^+ - C_6H_4O_2 - H$]; 231 (40) [C_6H_2-*t*-Bu_2CMe_2 + H]; 57 (22) [*t*-Bu]. $C_{24}H_{33}O_2P$ (384.54).

*Preparation of 2-(2,4,6-Tri-tert-butylphenyl) benzo-1,3,2-dioxaphospholane 2-Oxide (**7**)*

To a solution of 400 mg (1.04 mmol) **6** in 7 mL toluene, 1.4 g (14.9 mmol) $(H_2N)_2CO \cdot H_2O_2$ was added. After 4 hours of stirring at room temperature, the reaction mixture was filtered, and the filtrate was washed twice with 3 mL water, dried over $MgSO_4$, and evaporated in vacuo. Single crystals suitable for X-ray analysis were grown by evaporation from pentane. Yield: 260 mg (62.4%); m.p. 148°C. Analysis: C, 71.96; H, 8.78%. Calcd for $C_{24}H_{33}O_3P$: C, 71.98; H, 8.31%. ^{1}H NMR: δ = 1.23 (s, 9H, C4-*t*-Bu); 1.63 (s, 18H, C2,6-*t*-Bu); 6.87–6.95 (m, 4H, C_6H_4; 7.36 (d, 2H, ^4J(PH) = 6.21 Hz, C5-H, C6-H). ^{13}C {^{1}H} NMR: δ = 30.82 (s, 3C, C12–C14); 33.22 (s, 6C, C8–C10, C16–C18); 34.73 (s, 1C, C11); 39.45 (s, 2C, C7, C15); 112.05 (d, ^3J(PC) = 10.5 Hz, 2C, C20, C23); 123.01 (s, 2C, C21, C22); 124.26 (d, ^3J(PC) = 16.7 Hz, 2C, C3, C5); 144.31 (s, 1C, C4); 152.53 (d, ^2J(PC) = 4.2 Hz, 2C, C19, C24); 156.10 (d, ^2J(PC) = 11.7 Hz, 2C, C2, C6); C1 could not be observed. ^{31}P {^{1}H} NMR: δ = 44.43 (s). EI-MS: *m/z* (%): 400 (76) [M]$^+$; 385 (100) [M^+ − Me]; 291 (55) [$M^+ - C_6H_4O_2$]; 244 (73) [C_6H_2-*t*-Bu_3 − H]; 229 (28) [C_6H_2-*t*-Bu_2CMe_2 − H]; 57 (43) [*t*-Bu]. $C_{24}H_{33}O_3P$ (400.54).

*Preparation of 2-(2,4,6-Tri-tert-butylphenyl-benzo-1,3,2-dioxaphospholane 2-sulfide (**8**)*

To a solution of 400 mg (1.04 mmol) **6** in 7 mL toluene, 33 mg (1.04 mmol) S were added. After 6 hours of refluxing, the solvent was evaporated in vacuo. Yield: 390 mg (90%); m.p. 125°C. Analysis: C, 67.66; H, 7.93; S, 8.60%. Calcd for $C_{24}H_{33}O_2PS$: C, 69.20; H, 7.98; S, 7.70%. ^{1}H NMR: δ = 1.16 (s, 9H, C4-*t*-Bu); 1.65 (s, 18H, C2,6-*t*-Bu); 6.78–6.86 (m, 4H, C_6H_4); 7.26 (d, 2H, ^4J(PH) = 6.07 Hz, C5-H, C6-H). ^{13}C {^{1}H} NMR: δ = 30.70 (s, 3C, C12–C14); 34.44 (s, 6C, C8–C10, C16–C18); 34.55 (s, 1C, C11); 40.49 (d, ^3J(PC) = 0.03 Hz, 2C, C7, C15); 112.13 (d, ^3J(PC) = 0.1 Hz, 2C, C20, C23); 122.81 (s, 2C, C21, C22); 124.38 (d, ^3J(PC) = 15.0 Hz, 2C, C3, C5); 144.90 (s, 1C, C4); 151.83 (d, ^2J(PC) = 4.0 Hz, 2C, C19, C24); 157.10 (d, ^2J(PC) = 10.0 Hz, 2C, C2, C6); a resonance due to C1 could not be observed. ^{31}P {^{1}H} NMR: δ = 115.23 (s). EI-MS: *m/z* (%): 416 (4) [M]$^+$; 384 (1.5) [M^+ − S]; 359 (100) [M^+ − *t*-Bu]; 231 (20) [$C_6H_2tBu_2CMe_2$ + H]; 57 (16) [*t*-Bu]. $C_{24}H_{33}O_2PS$ (416.60).

*Preparation of 2,4,6-Tri-tert-butylphenyl(1,2-phenylenedioxa)(3,4,5,6-tetrachloro-1,2-phenylenedioxa)phosphorane (**9**)*

To a solution of 400 mg (1.04 mmol) **6** in 7 mL toluene, 256 mg (1.04 mmol) TOB were added. During 4 hours of stirring, the solution became lighter. The solvent was then evaporated in vacuo to give a light-red powder, which is a hint for contamination with unreacted TOB. Yield: 633 mg (96%); m.p. 135°C. Analysis: C, 55.30; H, 5.52%. Calcd for $C_{30}H_{33}Cl_4O_4P$ + 8% TOB: C, 55.32; H, 5.12%. ^{1}H NMR: δ = 1.16 (s, 9H, C4-*t*-Bu); 1.59 (s, 18H, C2, 6-*t*-Bu); 6.53–6.76 (m, 4H, C_6H_4; 7.76 (d, 2H, ^4J(PH) = 9.31 Hz, C5-H, C6-H). ^{13}C {^{1}H} NMR: δ = 31.04 (s, 3C, C12–C14); 33.98 (s, 6C, C8–C10, C16–C18); 35.08 (s, 1C, C11); 38.79 (d, ^3J(PC) = 4.6 Hz, 2C, C7, C15); 123.32 (s, 2C, C21, C22 (catechol)), 124.48 (d, ^3J(PC) = 22.5 Hz, 2C, C3, C5); 148.01 (d, ^2J(PC) = 14.1 Hz, 2C, C2, C6); other carbon resonances could not be observed or assigned. ^{31}P {^{1}H} NMR: δ = 5.48 (s). EI-MS: *m/z* (%): 630 ($C_{30}H_{33}{}^{35}Cl_3{}^{37}ClO_4P$) (11) [M]$^+$, the experimental isotopic pattern corresponds to the calculated; 573 (100) [M − *t*-Bu]; 385 (13) [M − C_6H_2-*t*-Bu_3]; 231 (7) [$C_6H_2tBu_2CMe_2$ + H]; 57 (25) [*t*-Bu]. $C_{30}H_{33}Cl_4O_4P$ (630.43).

Some Attempted Reactions of **1** *with Anhydrous Hexafluoroacetone or Perfluoro-4-methylpentane-2,3-dione*

A solution of 80 mg (0.21 mmol) diphosphene **1** was allowed to react with several drops of perfluoro-4-

methylpentane-2,3-dione (excess molar amount) in 3 mL refluxing toluene for 2 hours, but no reaction was observed from color change as well as in the ^{31}P NMR spectrum. No reaction was observed in the following reactions under the conditions listed: 400 mg (1.04 mmol) diphosphene **1** was allowed to react with 800 mg (4.8 mmol) hexafluoroacetone (HFA) in 20 mL toluene with stirring for 18 hours at room temperature, then for 3 hours at 80°C; 400 mg (1.04 mmol) diphosphene **1** was allowed to react with 1.2 g (7.2 mmol) HFA in 15 mL CH_2Cl_2, with stirring for 18 hours at room temperature, then 3 hours at 50°C; 500 mg (1.30 mmol) diphosphene **1** was allowed to react with 5.1 g (30.7 mmol) HFA without solvent for 24 hours at room temperature. No change of color and no new ^{31}P NMR signals were observed under the aforementioned conditions.

X-Ray Crystal Structure Determination of **2,3,6***, and* **7**

Data Collection and Reduction. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (Bruker Smart 1000 CCD with a LT-3 low-temperature attachment; monochromated MoKα radiation).

Structure Solution and Refinement. The structures were solved by direct methods and refined anisotropically on F^2 [23]. H atoms were included using a riding model or rigid methyl groups. The weighting schemes were of the form $w_{-1} = [\sigma^2(\mathrm{Fo}^2) + (aP)^2 + bP]$, with $P = (Fo^2 + 2Fc^2)/3$. The pentane in **3** is disordered over an inversion center.

Full details of the crystal structure determinations (except structure factors) have been deposited under the numbers 156380, 156381, 156382, and 157203 at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Telefax: Int. + 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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