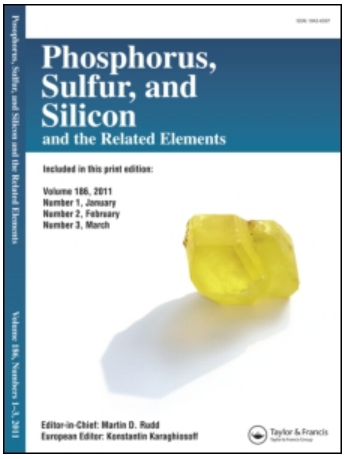

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REACTION OF SEVEN- AND EIGHT-MEMBERED CYCLIC PHOSPHOROCHLORIDITES WITH ALKANOLAMINES

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The reactions of substituted 6-chloro-12H-dibenzo[d,g][1,3,2]dioxaphosphocins and 6-chlorodibenzo[d,f][1,3,2]dioxaphosphepins with primary, secondary and tertiary alkanolamines are described. The primary and sec-aminoalkyl phosphites prepared show no IR or NMR spectroscopic evidence for formation of their tautomeric pentacoordinate form.

INTRODUCTION

The tautomeric equilibrium of tricoordinate aminoalkyl and hydroxyalkyl phosphites **1** with their corresponding pentacoordinate (phosphorane) structure **2** was first suggested by Burgada *et al.*[1] Recently the behavior of aminoalkyl phosphites prepared from *N-tert*-butyl-diethanolamine and five-membered cyclic phosphorochloridites has been described.[2] Similar studies on the behavior of aminoalkyl phosphites prepared from seven- and eight-membered cyclic phosphorochloridites have not been reported. We have described the synthesis of the 2,4,8,10-tetrasubstituted dibenzo[d,f][1,3,2]dioxaphosphepin and 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring systems.[3,4] This paper describes the reactions of the corresponding seven- and eight-membered cyclic phosphorochloridites with alkanolamines.

RESULTS AND DISCUSSION

The reaction of *N-tert*-butyl-ethanolamine (**4a**) with the eight-membered cyclic phosphorochloridite **3a**,[3] prepared *in situ*, was found to give the phosphite **5a**. Similarly, **5d** was prepared from **4a** and the phosphorochloridite **3b**.[3]

The ^{1}H, ^{13}C NMR and IR spectra of **5a** showed no evidence for the formation of **6a**. A similar result was obtained for the sterically less demanding methyl derivative **5b**, prepared from **3a** and **4b**.

The phosphite **5c** was synthesized from **3a** and the sodium salt of **4c**. In the ^{31}P spectrum of **5c** a single resonance was observed at δ 129.2, which is indicative of the tricoordinate phosphite structure.[5] The assignment of a tricoordinate structure is

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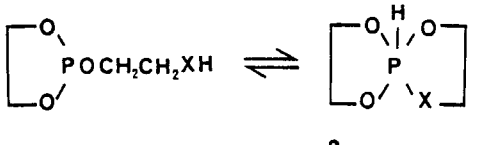
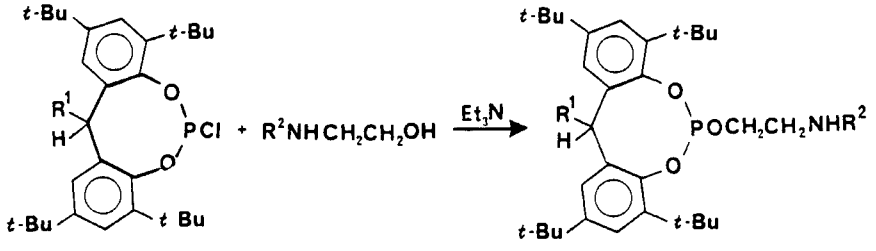


1 2

FIGURE 1

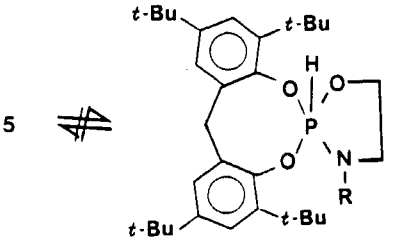


3 a. R^1 = H
b. R^1 = CH_3

4 a. R^2 = t-Butyl
b. R^2 = Methyl
c. R^2 = H

5 a. R^1 = H; R^2 = t-Butyl
b. R^1 = H; R^2 = Methyl
c. R^1 = H; R^2 = H
d. R^1 = Methyl; R^2 = t-Butyl

SCHEME 1



5 a. R = t-Butyl
b. R = Methyl
c. R = H

6 a. R = t-Butyl
b. R = Methyl
c. R = H

FIGURE 2

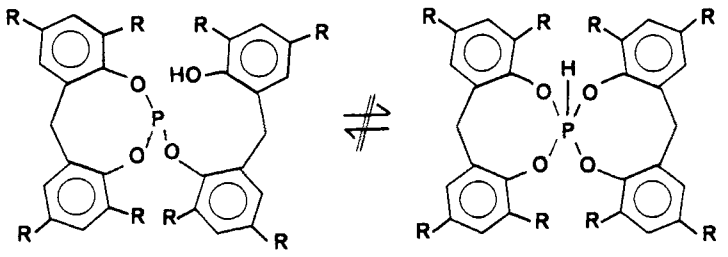


FIGURE 3

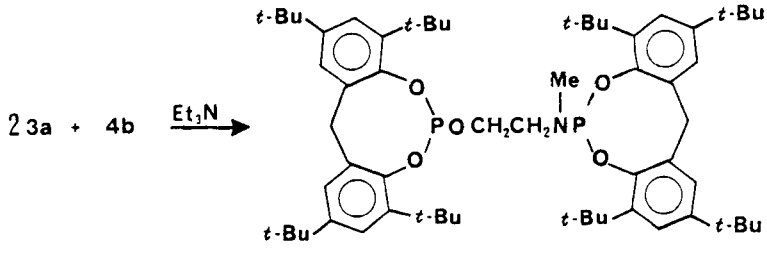
further supported by the lack of any evidence for P—H bond formation in the IR and ^{1}H NMR spectra. Compounds **5a–c** showed only one isomer by TLC.

The hydroxyaryl phosphite **7** was isolated by means of flash chromatography from the crude reaction product of **3a** and **4c**. A single resonance was observed in the ^{31}P NMR spectrum of **7** at δ 136.4, which is consistent with the tricoordinate structure. The IR spectrum of **7** had a sharp hydroxyl absorption at 3520 cm^{-1}. The ^{1}H NMR spectrum had an exchangeable resonance at δ 5.82, which integrated to a single proton, assignable to the hydroxyl proton. The ^{1}H NMR showed the presence of six non-equivalent *tert*-butyl groups (2 : 2 : 1 : 1 : 1 : 1 integrated peak areas) which is indicative of structure **7**. No spectral evidence was seen for the pentacoordinate structure **8**.

The reaction of two equivalents of **3a** with one equivalent of **4b** gave the corresponding mixed phosphite–phosphoramidite **9**.

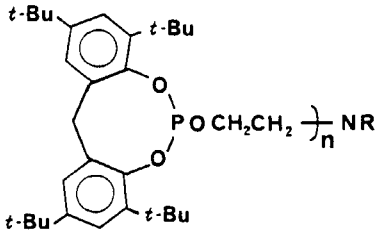
Interestingly, the analogous reaction of two equivalents of **3a** with one equivalent of **4a** gave only **5a**, presumably due to the steric effect of the *N-tert*-butyl group.

The reaction of two moles of **3a** with diethanolamine (**4d** R^2 = —CH_2CH_2OH) gave the bisphosphite **10a**. Attempts to react **10a** with an additional equivalent of **3a** were unsuccessful, again presumably due to steric crowding. However, the sterically less demanding trisphosphite **10b** was formed from triethanolamine and three equivalents of **3a** in 98 percent recrystallized yield.



9

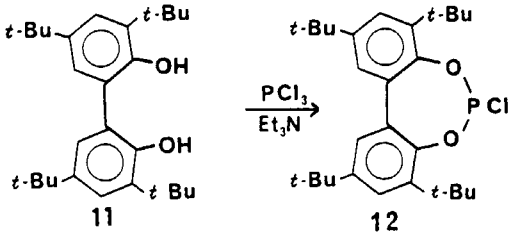
SCHEME 2



10

a n = 2; R = H
b n = 3; R = :

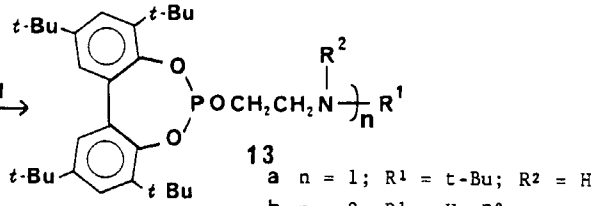
FIGURE 4



11 **12**

12 + **4**

a R = t-Bu
b R = $-CH_2CH_2OH$

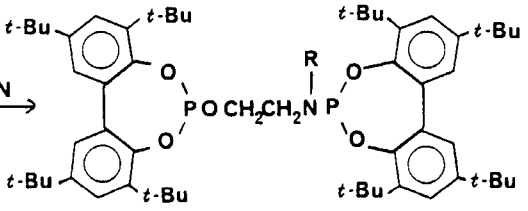


13

a n = 1; R^1 = t-Bu; R^2 = H
b n = 2; R^1 = H; R^2 = :

212 + **4**

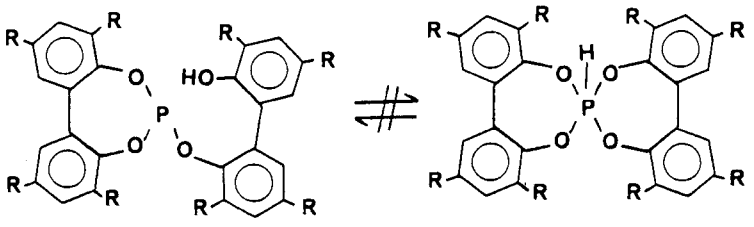
b R = Me
e R = Et
f R = n-Bu



14

a R = Me
b R = Et
c R = n-Bu

SCHEME 3



15 **16**

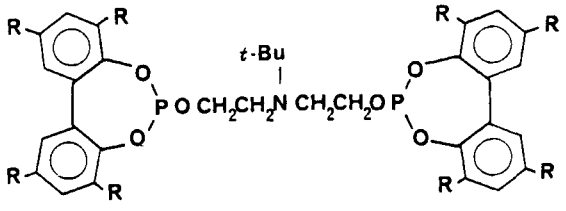
R = t-Butyl R = t-Butyl

FIGURE 5

In the ^{1}H NMR spectra of all the dioxaphosphocins prepared in this study, long-range coupling of one C12 (bridging methylene) proton to phosphorus was observed. The spectral data and TLC of the crude reaction products showed formation of only one isomer. The ^{13}C NMR spectrum of **10b** is consistent with a single conformational isomer.

Completely analogous chemistry was found for the seven-membered dibenzo-[d,f][1,3,2]dioxaphosphepin ring system. The phosphorochloridite **12** was formed *in situ* from the biphenyl-2,2′-diol **11**[6] and phosphorus trichloride using triethylamine as an acid acceptor. The aminoalkyl phosphites **13a–b** and phosphite-phosphoramidites **14a–c** were prepared from **12** and the appropriate stoichiometric amount of the corresponding alkanolamine **4**. The ^{1}H NMR and IR spectra of **13a–b** were consistent with the tricoordinate phosphite structure.

The hydroxyaryl phosphite **15** was prepared from three equivalents of **11** and one equivalent of phosphorus trichloride in 42 percent recrystallized yield. A single resonance at δ 141.1 was observed in the ^{31}P NMR spectrum of **15**. The ^{1}H NMR showed the presence of six non-equivalent *tert*-butyl groups (2 : 2 : 1 : 1 : 1 : 1 integrated peak areas). An exchangeable single resonance was observed which was assignable to the hydroxyl proton, expected for structure **15**.



17

R = t-Butyl

FIGURE 6

In accord with the work of Osman *et al.*, the reaction of two equivalents of **12** with an equivalent of *N-tert*-butyl diethanolamine gave the bisphosphite **17**.

Neither the seven nor eight-membered aminoalkyl and hydroxyaryl phosphites prepared in this study showed any spectroscopic evidence for the formation of their tautomeric pentacoordinate form. A reasonable explanation which would account for these observations is that the pentacoordinated tautomer is disfavored by steric hindrance to cyclization by the *tert*-butyl substituents and possibly ring strain in the resultant spirophosphorane. In the hydroxyaryl phosphites **7** and **15**, there is an additional unfavorable entropy change for formation of the corresponding seven and eight-membered rings.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared Spectra (1% solution in chloroform, potassium bromide cells) were recorded on a Perkin-Elmer 710 spectrophotometer. ^{1}H NMR spectra were taken on Varian model XL-100 or FT-80 spectrometers. ^{13}C and ^{31}P NMR spectra were taken on a Varian model FT-80 spectrometer equipped with a broad band probe. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{31}P NMR spectra were acquired using a 45° flip angle, a 1 s repetition rate with no pulse delay and with full proton decoupling. ^{13}C NMR spectra were obtained using a 30° flip angle, a 2 s repetition rate with no pulse delay and with full proton decoupling. Unless otherwise indicated, all reagents were purchased from Aldrich Chemical Company. All solvents were dried prior to use. Reactions were carried out in flame-dried apparatus under a dry-nitrogen atmosphere. In general, the phosphites prepared held onto solvent tenaciously and they required heating at 100–120°C (0.1 mm) for approximately 10 hours for complete removal of solvents in order to obtain correct

TABLE I

Analytical Data

Compound	mp (°C)	Recrystallization solvent	Percent yield[c]	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
5a	153–155	Acetone/2-Butanone	52%	73.8	9.9	2.5	74.0	9.8	2.5
5b	135–140	Acetonitrile	60%	72.8	9.5	2.6	72.8	9.5	2.6
5c[a]	216–221	Acetonitrile	20%	72.5	9.4	2.7	72.7	9.8	2.9
5d	174–175	2-Butanone	56%	74.1	10.0	2.4	74.4	9.7	2.4
7[b]	246–253	Acetonitrile	42%	79.4	9.7	—	79.2	10.0	—
9	300–305	Acetonitrile/Toluene	29%	74.7	9.4	1.4	75.1	9.3	1.3
10a	226–232	2-Butanone/Toluene	16%	73.7	9.3	1.4	74.1	9.1	1.4
10b	177–181	Acetonitrile	98%	74.1	9.3	0.9	74.2	9.1	0.8
13a	135–138	Acetonitrile	64%	73.5	9.8	2.5	74.1[c]	9.7	2.5
13b	96–100	[d]	44%	73.4	9.1	1.4	73.4	9.3	1.3
14a	233–237	2-Butanone	54%	74.4	9.2	1.5	74.3	9.1	1.5
14b	238–242	2-Butanone	50%	74.6	9.2	1.4	74.6	8.8	1.5
14c	215–221	Acetone	24%	74.9	9.4	1.4	74.9	9.2	1.4
15	237–247	Acetonitrile	42%	79.2	9.6	—	79.3	9.3	—
17	160–170	Acetone	59%	74.0	9.4	1.4	74.4	9.3	1.4

[a] % P Calcd.: 6.0; Found: 5.9.
[b] % P Calcd.: 3.5; Found: 3.6.
[c] Analytically pure yields.
[c] Satisfactory elemental analysis for carbon could not be obtained.
[d] Purified by flash chromatography (silica-gel, 1 : 1 heptane : ethyl acetate eluent).

TABLE II

IR and NMR spectral data

Compound	IR (cm^{-1})	^{31}P NMR (benzene-d_6)	^{1}H NMR (deuteriochloroform)
5a	3300 (NH), 1020 (POC aliphatic stretch)	δ 130.0	δ 1.14 (s, $NC(CH_3)_3$, 9 H), 1.28 (s, $C(CH_3)_3$, 18 H), 1.42 (s, $C(CH_3)_3$, 18 H), 2.96 (t, $—NCH_2—$, 2 H), 3.40 (d, C12—H, 1 H), 4.36 (d of d, C12—H, 1 H), 4.54, d of t, $—OCH_2—$, 2 H), 7.24 (c, ArH, 4 H)
5b	3350 (NH), 1020 (POC aliphatic stretch)	δ 129.5	δ 1.28 (s, $C(CH_3)_3$, 18 H), 1.42 (s, $C(CH_3)_3$, 18 H), 2.54 (s, NCH_3, 3 H), 3.00 (t, NCH_2, 2 H), 3.42 (d, C12—H, 1 H), 4.34 (d of d, C12—H, 1 H), 4.55 (d of t, $—OCH_2$, 2 H), 7.26 (c, ArH, 4 H)
5c	3400, 3350 (NH_2), 1010 (POC aliphatic stretch)	δ 129.2	δ 1.34 (s, $C(CH_3)_3$, 18 H), 1.42 (s, $C(CH_3)_3$, 18 H), 3.10 (t, $—NCH_2—$, 2 H), 3.42 (d, C12—H, 1 H), 4.36 (d of d, C12—H, 1 H), 4.48 (d of t, $—OCH_2—$, 2 H), 7.26 (c, ArH, 4 H)
5d	3300 (NH), 1020 (POC aliphatic stretch)	δ 129.5	δ 1.14 (s, $NC(CH_3)_3$, 9 H), 1.32 (s, $C(CH_3)_3$, 18 H), 1.44 (s, $C(CH_3)_3$, 18 H), 1.82 (d, CH_3, 3 H), 2.98 (t, $—NCH_2$, 2 H), 4.46 (c, $—OCH_2—$ and C12—H, 3 H), 7.20–7.38 (c, ArH, 4 H)
7	—	δ 136.1	δ 1.16 (s, $C(CH_3)_3$, 9 H), 1.20 (s, $C(CH_3)_3$, 18 H), 1.24 (s, $C(CH_3)_3$, 9 H), 1.26 (s, $C(CH_3)_3$, 18 H), 1.32 (s, $C(CH_3)_3$, 9 H), 1.50 (s, $C(CH_3)_3$, 9 H), 3.46 (d, C12—H, 1 H), 4.34 (s, CH_2, 2 H), 4.50 (d of d, C12—H, 1 H), 5.82 (s, OH, 1 H), 6.82–7.52 (c, ArH, 8 H)
9	1020 (POC aliphatic stretch)	—	δ 1.30 (s, $C(CH_3)_3$, 36 H), 1.44 (s, $C(CH_3)_3$, 36 H), 3.11 (d, NCH_3, $^3J_{HCNP}$ = 10 Hz, 3 H), 3.36 (d, C12—H, 1 H), 3.44 (d, C12′—H, 1 H), 3.76 (d of t, $—NCH_2—$, $^3J_{HCCH} = {}^3J_{HCNP}$ = 6 Hz, 2 H), 4.40 (2 overlapping d of d, C12—H and C12′—H, 2 H), 4.74 (d of t, $^3J_{HCCH} = {}^3J_{HCOP}$ = 6 Hz), 7.24 (c, ArH, 8 H)
10a	3300 (NH), 1020 (POC aliphatic stretch)	—	δ 1.27 (s, $C(CH_3)_3$, 36 H), 1.44 (s, $C(CH_3)_3$, 36 H), 3.17 (t, $—NCH_2—$, 4 H), 3.41 (d, C12—H, 2 H), 4.37 (d of d, C12—H, 2 H), 4.62 (d of t, $—OCH_2—$, 4 H), 7.25 (c, ArH, 8 H)
10b	1010 (POC aliphatic stretch)	δ 129.1[a]	δ 1.38 (s, $C(CH_3)_3$, 54 H), 1.50 (s, $C(CH_3)_3$, 54 H), 3.38 (partially obscured t, $—NCH_2—$, 6 H), 3.41 (d, C12—H, $^2J_{HCH}$ = 12.7 Hz, 3 H), 4.43 (d of d, C12—H, $^2J_{HCH}$ = 12.7 Hz, $^5J_{HP}$ = 3.0 Hz, 3 H), 4.71 (d of t, $—OCH_2$, $^3J_{HCCH} = {}^3J_{HCOP}$ = 6 Hz, 6 H), 7.35 (c, ArH, 12 H)
13a	3350 (NH), 1020 (POC aliphatic stretch)	—	δ 1.04 (s, $NC(CH_3)_3$, 9 H), 1.35 (s, $C(CH_3)_3$, 18 H), 1.50 (s, $C(CH_3)_3$, 18 H), 2.70 (t, $—NCH_2—$, 2 H), 3.90 (d of t, $—OCH_2—$, 2 H), 7.12 (meta d, $^4J_{HCCCH}$ = 2 Hz, 2 H), 7.38 (meta d, $^4J_{HCCCH}$ = 2 Hz, 2 H)
13b	1020 (POC aliphatic stretch)	—	δ 1.32 (s, $C(CH_3)_3$, 36 H), 1.46 (s, $C(CH_3)_3$, 36 H), 2.70 (t, $—NCH_2—$, 4 H), 3.82 (d of t, $—OCH_2—$, 4 H), 7.12 (meta d, 4 H), 73.8 (meta d, 4 H)

TABLE II (*Continued*)

Compound	IR (cm^{-1})	^{31}P NMR (benzene-d_6)	^{1}H NMR (deuteriochloroform)
14a	1010 (POC aliphatic stretch)	δ 146.9 133.2[a]	δ 1.45 (s, $C(CH_3)_3$, 36 H), 1.55 (s, $C(CH_3)_3$, 18 H), 1.57 (s, $C(CH_3)_3$, 18 H), 2.34 (m, NCH_3, 3 H), 2.88 (m, $-NCH_2-$, 2 H), 3.64 (d of t, $-OCH_2-$, 2 H), 7.28–7.53 (c, ArH, 8 H)
14b	1010 (POC aliphatic stretch)	δ 147.8, 132.0[a]	—
14c	1020 (POC aliphatic stretch)	δ 146.7 132.5[a]	δ 1.28 (c, $C(CH_3)_3$ and $CH_3(CH_2)_2-$, 79 H), 2.90 (c, $-CH_2NCH_2-$, 4 H), 3.70 (d of t, $-OCH_2-$, 2 H), 7.07 (c, ArH, 4 H), 7.35 (c, ArH, 4 H)
15	3530 (OH)	δ 141.1	δ 1.22 (s, $C(CH_3)_3$, 9 H), 1.41 (s, $C(CH_3)_3$, 9 H), 1.45 (s, $C(CH_3)_3$, 18 H), 1.41 (s, $C(CH_3)_3$, 18 H), 1.56 (s, $C(CH_3)_3$, 9 H), 1.61 (s, $C(CH_3)_3$, 9 H), 5.59 (exchangeable s, OH, 1 H), 7.23–7.58 (c, ArH, 8 H)
17	1010 (POC aliphatic stretch)	δ 136.0[a]	δ 0.80 (s, $-N(CH_3)_3$, 9 H), 1.34 (s, $C(CH_3)_3$, 36 H), 1.48 (s, $-C(CH_3)_3$, 36 H), 2.60 (t, $-NCH_2-$, 4 H), 3.62 (d of t, $-OCH_2-$, 4 H), 7.12 (meta d, 4 H), 7.38 (meta d, 4 H)

Compound	^{13}C NMR (dichloromethane-d_2)
5a[a]	29.5 (s, $(\underline{C}H_3)_3CN-$), 31.4 (d, $(\underline{C}H_3)_3C-$, $^5J_{CP}$ = 4.0 Hz),[b] 31.9 (s, $(\underline{C}H_3)_3C-$), 34.9 and 35.5 (two s, $(CH_3)_3\underline{C}-$), 35.8 (s, $ArCH_2Ar$), 43.8 (d, $-NCH_2-$, $^3J_{CCOP}$ = 3.5 Hz), 50.7 (s, $(CH_3)_3\underline{C}N-$), 64.5 (d, $-CH_2O-$, $^2J_{COP}$ = 4.5 Hz), 123.4 (s), 125.4 (s), 136.3 (d, J = 3.8 Hz), 141.7 (d, J = 3.8 Hz), 146.1 (d, J = 8.1 Hz), 147.0 (d, J = 1.3 Hz)
10b	31.1 (d, $(\underline{C}H_3)_3C-$, $^5J_{CP}$ = 4.2 Hz),[b] 31.6 (s, $(\underline{C}H_3)_3C$), 34.8 (s, $(CH_3)_3\underline{C}-$), 35.3 (s, $(CH_3)_3\underline{C}-$ and $ArCH_2Ar$), 56.0 (d, $-NCH_2-$, $^3J_{CCOP}$ = 3.2 Hz), 62.2 (d, $-OCH_2-$, $^2J_{COP}$ = 4.8 Hz), 123.3 (s), 125.2 (s), 136.4 (d, J = 3.2 Hz), 141.8 (d, J = 3.7 Hz), 146.0 (d, J = 7.5 Hz), 147.1 (d, J = 1.2 Hz)
17	27.3 (s, $(\underline{C}H_3)_3C$), 31.2 (d, $(\underline{C}H_3)_3C$), $^5J_{CP}$ = 2.7 Hz)[b] and 31.6 (s, $(\underline{C}H_3)_3C$), 34.9 and 35.6 (two s, $(CH_3)_3\underline{C}-$), 54.7 (s, $N-\underline{C}(CH_3)_3$), 52.0 (d, $-NCH_2-$, $^3J_{CCOP}$ = 3.3 Hz), 65.7 (d, $-OCH_2-$, $^2J_{COP}$ = 4.0 Hz), 124.6 (s), 126.6 (s), 133.0 (d, J = 3.6 Hz), 140.3 (s), 146.3 (d, J = 5.8 Hz), 146.9 (s)

[a] Solvent is deuteriochloroform.

[b] 5-bond P—C coupling has been demonstrated on 6-(2,2,2-trifluoroethoxy)-substituted 2,4,8,10-tetra(*tert*-butyl)dibenzodioxaphosphocins and phosphepins at 80 and 200 MHz.[7]

elemental analysis. All spectral data were obtained on analytical samples. Elemental analysis were performed by Analytical Research Services, CIBA-GEIGY Corporation. The synthesis of compounds **5a–c**, **9**, **10b**, and **15** are illustrative of the methods employed for compound preparation. Analytical and spectral data are collected in Tables I and II.

2,4,8,10-Tetra-tert-butyl-6-[2-(N-tert-butylamino)ethoxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin (**5a**). To a solution of 27.47 g (0.2 mol) of phosphorus trichloride in 200 mL of toluene at 5°C was added a

solution of 84.93 g (0.2 mol) of 2,2′-methylenebis (4,6-di-*tert*-butylphenol)[8] and 40.48 mL of toluene. The reaction mixture was stirred at rt until disappearance of the phenolic OH absorption in the IR spectrum occurred (approximately 2–4 hours). The reaction mixture was then cooled to 5°C and to it was added a solution of 23.44 g (0.2 mol) of *N*-*tert*-butyl ethanolamine and 20.24 g (0.2 mol) of triethylamine in 125 mL of toluene. The reaction mixture was stirred at rt for 15 hours and the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from an acetone : 2-butanone mixture to give 59.48 g (52%) of a white solid, mp 153–156°C.

2,4,8,10-Tetra-tert-butyl-6-[2-(N-methylamino)ethoxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin (**5b**). By the procedure used to prepare compound **5a**, compound **5b** was prepared from 32.3 g (0.24 mol) of phosphorus trichloride, 100 g (0.24 mol) of 2,2′-methylenebis(4,6-di-*tert*-butyl-phenol), 87.8 g (1.17 mol) of *N*-methyl ethanolamine,[9] and 71.3 (0.71 mol) of triethylamine. The reaction was heated to 90°C until the reaction was complete as indicated by TLC. After removal of triethylamine hydrochloride by filtration, the solvent was removed *in vacuo* and the residue was purified by flash chromatography (silica gel, dichloromethane–methyl alcohol eluent). The product was recrystallized from acetonitrile to give 74.4 g (60%) of a white solid. mp 135–140°C.

6-[2-(amino)ethoxy]-2,4,8,10-Tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin (**5c**). To a suspension of 0.98 g (41 mmole) of sodium hydride in 100 mL of tetrahydrofuran was added 2.5 g (41 mmole) of 2-aminoethanol. The reaction mixture was stirred until the evolution of hydrogen was complete. To the resultant homogeneous solution was added a solution of 20 g (41 mmole) of **3a** in 50 mL of tetrahydrofuran. The reaction mixture was stirred at rt until disappearance of **3a** as indicated by TLC. The solvent was removed *in vacuo* and the residue was triturated with 200 mL of toluene. The sodium chloride suspension was removed by filtration and the solvent was removed *in vacuo*. The residue was flash chromatographed (silica gel; dichloromethane–methyl alcohol eluent) and the product was recrystallized from acetonitrile to give 2.4 (20%) of a white solid, mp 216–221°C.

N-(2,4,8,10-Tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl)-2-(2,4,8,10-Tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl-6-oxy)-N-methyl-ethylamine (**9**). To a solution of 27.24 g (0.2 mol) of phosphorus trichloride in 200 mL of toluene at 5–10°C was added a solution of 84.93 g (0.2 mol) of 2,2′-methylenebis(2,4-*tert*-Butylphenol) and 40.48 g (0.4 mol) of triethylamine in 250 mL of toluene. The reaction mixture was stirred at rt until disappearance of the phenolic OH absorption in the IR spectrum. The reaction mixture was cooled to 10°C and to it was added a mixture of 7.51 g (0.1 mol) of 2-(methylamino)ethanol and 20.24 g (0.2 mol) of triethylamine. The reaction was stirred for 15 hours at 60°C and the resultant suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized twice from a acetonitrile–toluene mixture to give 26.7 (29%) of a white solid, mp 300–305°C.

2,2′2″-Tri-(2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl-6-oxy)-triethylamine (**10b**). To a solution of 8.24 g (60 mmol) of phosphorus trichloride in 150 mL of toluene at 10°C was added with stirring a solution of 25.48 g (60 mmol) of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) and 18.21 g (180 mmol) of triethylamine in 100 mL of toluene over a one hour period. The reaction mixture was stirred at rt until disappearance of the phenolic OH absorption in the IR spectrum. The reaction mixture was cooled to 10°C and to it was added 2.98 g (20 mmol) of triethanolamine. The reaction was stirred for 15 hours at rt and the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 29.40 g (98%) of a white solid, mp 177–181°C.

2-(2,4,8,10-Tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl-6-oxy)-2′-hydroxy-biphenyl (**15**). To a solution of 24.6 g (60 mmol) of biphenyl-2,2′-diol and 9.09 g (90 mmol) of triethylamine in 400 mL of toluene at 10–12°C was added dropwise 4.11 g (30 mmol) of phosphorus trichloride. The reaction was stirred for 15 hours at rt and then the suspension of triethylamine hydrochloride was removed by filtration. The filtrate was washed with water until the pH of the wash water was near seven. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 10.8 g (42%) of a white solid, mp 237–247°C.

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