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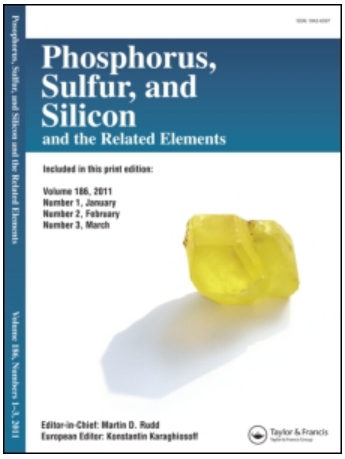

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THE REACTION OF HEXAALKYLPHOSPHOROUS TRIAMIDES WITH OLIGOPHENOLS

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THE REACTION OF HEXAALKYLPHOSPHOROUS TRIAMIDES WITH OLIGOPHENOLS

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Hexaalkylphosphorous triamides form in good yields 6-dialkylamino-*12H*-dibenzo[d,g][1,3,2]dioxaphosphocins **2a-i** in the reaction with oligophenols **1a-i.** Heating the sterical hindered compounds **2a-f** up to 315°C leads to the corresponding bicyclic phosphites **3a-d** while the non-hindered phosphocins **2g-i** react in refluxing xylene to give phosphites **3e-g.** The phosphocin **2i** formed another phosphocin **2i*** during heating to 90°C in THF by "wandering" of the phosphorus moiety. The bicyclic phosphites **3h** and **3i** were prepared starting from tetraphenol **1h** and pentaphenol **1i** by reaction with hexaethylphosphorous triamide in refluxing xylene. The diphosphorylated triphenol **4** and tetraphenol **5** are formed in the reaction of the corresponding phenols with 2 eq. of hexaalkylphosphorous triamide.

Keywords: hexaalkylphosphorous triamides; oligophenols; phosphocins; phosphites; bicycles

INTRODUCTION

Condensation products of phenols with formaldehyde are widely used in various industrial applications, for instance as precursors for duroplastics, as additives for polymers[1], as complexing agents for uranium enrichment[2] or as fungicides and bactericides[3]. During the last years oligophenols have been getting more important in the search for new flame retardants[4]. Large numbers of *12H*-dibenzo[d,g][1,3,2]dioxaphosphocins

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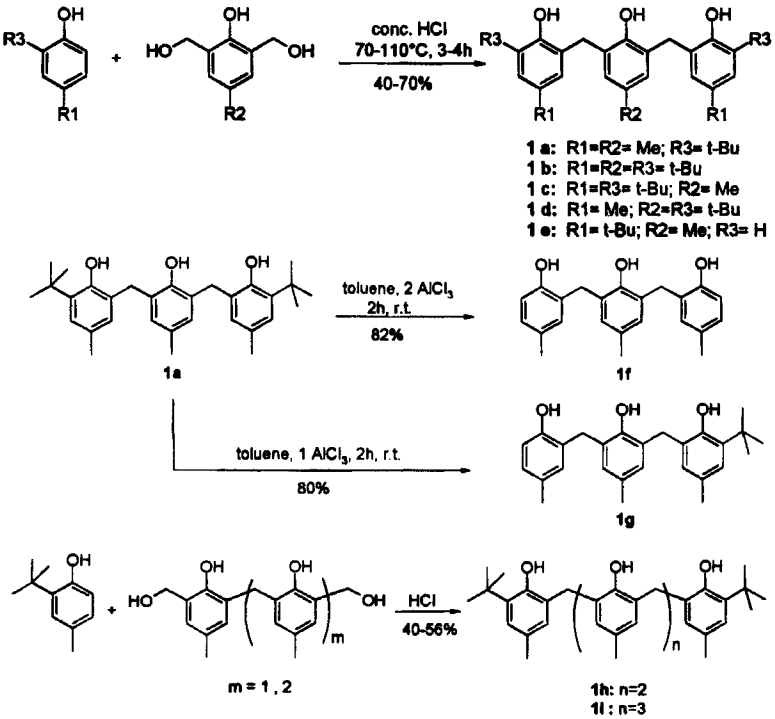
prepared by reactions of 2,2′-methylenebisphenols with different phosphorylating agents, have been reported within the last 15 years for potential use as polymer additives, as ligands for Rh(I)-catalyzed hydroformylation reactions, as pesticides, bactericides, fungicides and insecticides[5–15]. In connection with our investigations in the field of phosphorus containing additives for polymers[16] we were also interested in phosphorylation reactions of different oligophenols.

RESULTS AND DISCUSSION

The oligophenols **1a-i** used in the reaction with hexaalkylphosphorous triamides were synthesized according to ***Scheme 1***[3,15,17–21].



SCHEME 1 Syntheses of the oligophenols **1a-i**

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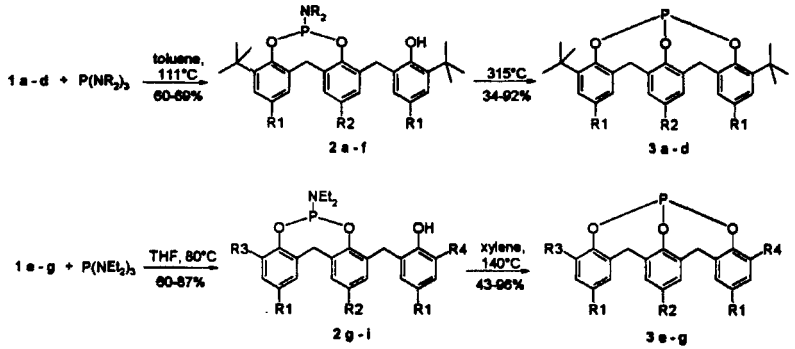
The 6-dialkylamino-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins **2a-f** were obtained by the reaction of the sterically hindered triphenols **1a-d** with equimolar ratios of hexaalkylphosphorous triamides in refluxing toluene in good yields. The corresponding 1-phosphapentacyclo[12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$]-tetracosa-3,5,7,10(24),11,13,16(21),17,19-nonaenes **3a-d** could be prepared in good yields by heating of the pure compounds **2a-f** up to 315°C (***Scheme 2***, ***Table 1***).



SCHEME 2 Syntheses of 6-dialkylaminodibenzo[*d,g*][1.3.2]dioxaphosphocins **2a-i** and 1-Phosphapentacyclo[12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$]tetracosa-3, 5, 7, 10 (24)11, 13, 16(21), 17, 19-nonaenes **3a-g**

In comparison to that, the non-hindered triphenol **1e** gave in the reaction with hexaethylphosphorous triamide in refluxing toluene a mixture of the corresponding 6-dialkylamino-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin **2g** and phosphite **3e.** Refluxing of the crude mixture of **2g** and **3e** in xylene completed the reaction to give the bicyclic phosphite **3e.** The same behavior was found for the phosphorylation of the triphenols **1f** and **1g** in the synthetic route to the phosphites **3f** and **3g.** To obtain the 6-dialkylamino-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins **2g-i,** the reaction has to be carried out at lower temperatures (***Scheme 2, Table 1***).

Sterical influences of the bulky *tert*-butyl-groups are supposed to be the reason for the different reactivities of the triphenols **1a-d** in contrast to **1g-i** in the phosphorylation reactions, and of the 6-dialkylamino-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins **2a-f** in contrast to **2g-i** in the intramolecular reactions to the corresponding bicyclic phosphites **3a-g,** too.

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TABLE I Yields and ^{31}P NMR data of compounds **2a-h** and **3a-h**

CPD.	*R*	*R1**	*R2**	*R3**	*R4**	*Yield {%}*	*^{31}P NMR δ {ppm}*
2a	Me	Me	Me	-	-	68.6	143.6
2b	Me	t-Bu	t-Bu	-	-	66.7	142.7
2c	Et	Me	Me	-	-	69.4	144.7
2d	Et	t-Bu	t-Bu	-	-	60.2	144.3
2e	Et	t-Bu	Me	-	-	87.4	144.3
2f	Et	Me	t-Bu	-	-	60.2	144.6
2g	Et	t-Bu	Me	H	H	60.2	144.1
2h	Et	Me	Me	H	H	91.7	142.1
2i	Et	Me	Me	H	t-Bu	61.8	144.5
3a	-	Me	Me	-	-	92.0	123.0
3b	-	t-Bu	t-Bu	-	-	89.5	122.4
3c	-	t-Bu	Me	-	-	34.1	122.9
3d	-	Me	t-Bu	-	-	87.0	122.6
3e	-	t-Bu	Me	H	H	43.2	101.9
3f	-	Me	Me	H	H	63.6	102.1
3g	-	Me	Me	H	t-Bu	96.3	105.7
3h	-	-	-	-	-	52.0	110.6
3i	-	-	-	-	-	54.9	101.8

In the ^{31}P NMR spectrum of the 6-dialkylaminodibenzo[*d,g*][1.3.2]dioxaphosphocin **2i** only one signal at 144.4 ppm was observed (***Figure 1a***). After heating up to 90°C, a second peak appeared at 144.8 ppm (***Figure 1b***), which belongs to a second phosphorous diester amid structure formed during the heating. It is attributed to structure **2i*** which is formed *via* a transesterification reaction leading to the "wandering" of the phosphorus moiety. The third signal at 105.6 ppm appearing after 24h is the signal of the corresponding phosphite **3g** (***Figure 1c***, ***Scheme 3***), which was obtained by further heating in xylene as the only product. The appearance of phosphites with higher molecular weight formed by intermolecular reactions could not be observed.

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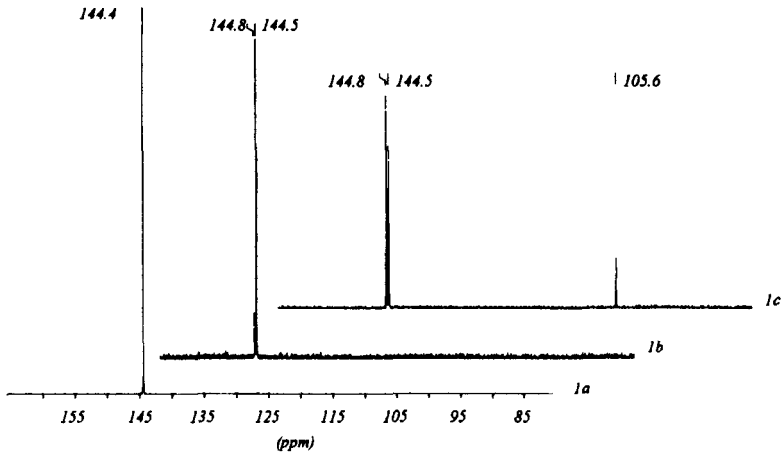
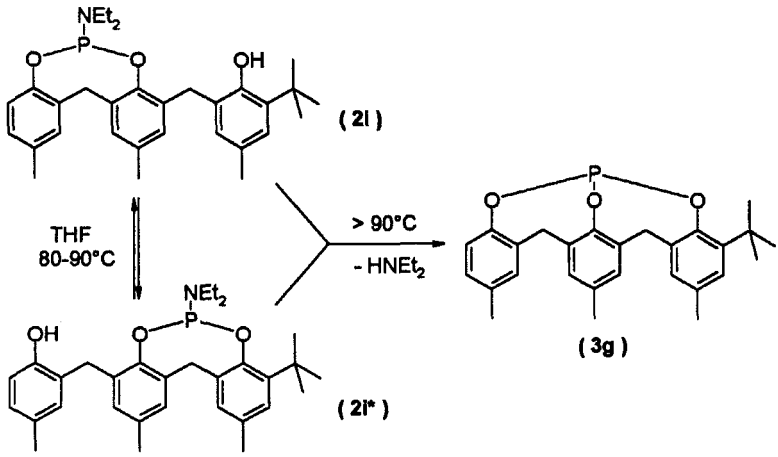


FIGURE 1 ^{31}P NMR spectra of compound **2g** in $CDCl_3$, a) starting signal, b) after 6h at 90°C, c) after 24h at 90°C



SCHEME 3

The tetraphenol **1h** and the pentaphenol **1i** reacted with hexaethylphosphorous triamide to the corresponding bicyclic phosphites **3h** and **3i** in good yields, too (***Scheme 4***). In both reactions two peaks were found in the

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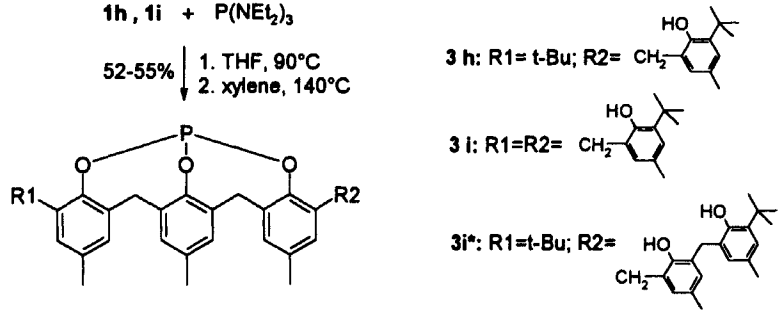
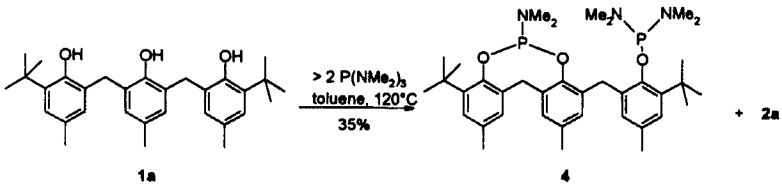
^{31}P NMR spectra for the 6-dialkylaminodibenzo[d,g][1.3.2]dioxaphosphocins which were formed in the first step. However, the reaction of the pentaphenol **1i** with $P(NEt_2)_3$ afforded only one of two possible phosphites, the symmetric compound **3i.** The other possible isomer **3i*** could not be detected in the crude product.



SCHEME 4 Reaction of tetraphenol **1h** and pentaphenol **1i** with $P(NEt_2)_3$

The phosphorylation of the oligophenol **1a** with an excess of hexamethylphosphorous triamide led to the bisphosphorylated compound **4** in moderate yield. Phosphocin **2a** was isolated as byproduct.



SCHEME 5 Synthesis of the bisphosphorylated triphenol **4**

The oligophenol **1h** containing four phenolic units reacted with excess of hexaethylphosphorous triamide to give **5** as a mixture of two diastereomeres.

Studies on the conformation of the 12*H*-dibenzo[d,g][1,3,2]dioxaphosphocin ring system have been published within the past 12 years[6–15]. The

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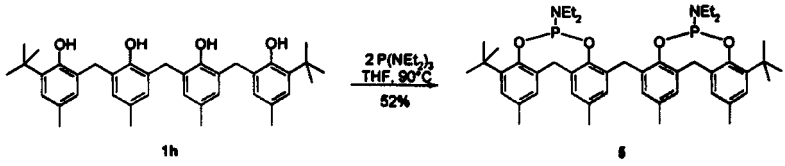

SCHEME 6 Synthesis of the bisphosphorylated tetraphenol

existence of four conformers was established, namely the boat-chair (BC), boat-boat (BB), twist-boat (TB) and the distorted twist-boat (DTB) conformation[14,15]. In ^{1}H NMR spectroscopy the nonequivalent bridging methylene protons appear as two dupletts, from which important values for the conformational analyses can be derived, the geminal coupling constant ^2J(H,H) and the long range ^5J(P,H) coupling constant[14,15]. The originally observed dependence of the coupling constants of the C(12) geminal protons in substituted 5,6,7,12-tetrahydrodibenzo[a,d]cyclooctenes upon ring conformation[22–24] was extended to probe the conformation of 12*H*-dibenzo[d,g][1,3,2]dioxaphosphocins in solution[14,15]. Trivalent phosphorus containing 12*H*-dibenzo[d,g][1,3,2]dioxaphosphocins were found to prefer two main conformations in solution, BC with ^2J(H,H) = 12–13 Hz and DTB with ^2J(H,H) = 14–16 Hz[15]. ***Table 2*** shows the coupling constants of the C(12) geminal protons of the 6-dialkylaminodibenzo[d,g][1,3,2]dioxaphosphocins in the range of 12.4–12.7 Hz, characteristic for the BC conformation of the synthesized 6-dialkylaminodibenzo[*d,g*]-[1.3.2]dioxaphosphocins **2a-2i, 4** and **5.** The observed long range ^5J(P,H) coupling of 2.8–3 Hz is consistent with an exocyclic dialkylamino substituent on phosphorus assuming an *equatorial* placement, the typical conformation found for such compounds (***Figure 2***)[14].

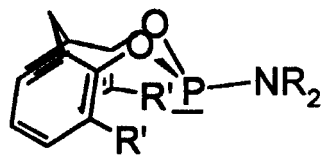

FIGURE 2 6-dialkylaminodibenzo[*d,g*][1.3.2]dioxaphosphocin with *e*-BC-conformation

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TABLE II ^2J(H,H) and ^5J(P,H) coupling constants of the synthesized phosphocins

Compound	$^2J(H,H)$ *{Hz}*	$^5J(P,H)$ *{Hz}*	*Compound*	$^2J(H,H)$ *{Hz}*
2a	12.6	3.0	**3a**	16.3
2b	12.5	2.8	**3b**	16.3
2c	12.7	3.0	**3c**	16.3
2d	12.6	2.9	**3d**	16.3
2e	12.7	2.9	**3e**	13.7
2f	12.5	3.0	**3f**	13.7
2g	12.5	3.0	**3g**	14.6, 13.5
2h	12.6	3.0	**3h**	15.1, 13.5
2i	12.5	3.0	**3i**	13.9

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The coupling constants of the ring membered geminal protons of the bicyclic phosphites **3a-i** are shown in ***Table 2***. The ^2J(H,H) coupling constants of the geminal protons of compounds **3a-d** have a value of 16.3 Hz in solution without occurrence of a long range ^5J(P,H) coupling, which is typical for the DTB conformation. The X-ray crystal structure of compound **3a** (***Figure 3***) shows a molecule with C_s-symmetry. The symmetric plain is spread by the atoms P(1)-O(2)-C(7)-C(10)-C(26). Both dioxaphosphocin rings have a DTB conformation with equatorial substituents (*e*-DTB)[15]. In the crystal structure a small deviation from the symmetry of the phosphocin rings can be observed. The reasons are the sterical strain caused by the planar aromatic rings and by the bulky *tert*-butyl groups. The exocyclic bond angles of C(7) are diminished to 118.4° and 117.6°, respectively. This is caused by a deformation of the planarity of the middle aromatic fragment and the atoms bonded to it. The deviation of the oxygen 0(2) from the theoretical plain spread by C(19)-C(8)-C(7)-C(12)-C(20) is –0.335 Å. The carbon atoms C(19) and C(20) diverge 0.051 Å and 0.019 Å from this plain. The bond angles C(1)-C(2)-C(21) and C(13)-C(18)-C(28) are extended to 124.5° and 123.1° due to the sterical strain by the *tert*-butyl groups[25].

The geminal protons of the compounds **3e, 3f** and **3i** show only two dupletts with coupling constants of about 13.7–13.9 Hz in the ^{1}H NMR spectrum. Either both phosphocin rings have the same fixed conformation

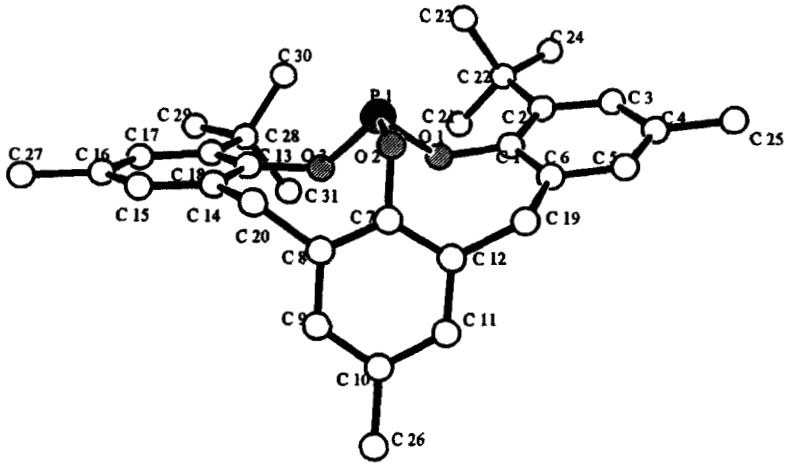

FIGURE 3 X-Ray structure of **3a**

or they have conformations which are rapidly transformed into each other. The asymmetric compounds **3g** and **3h** have two different geminal coupling constants, one with a value of 15.3 Hz and one with a value of 13.7 Hz. These results refer to a structure with one *axial*-BC (*a*-BC) and one *equatorial*-DTB (*e*-DTB) conformation for the phosphites **3e-i** (***Figure 4***), according to ARSHINOVA[14,15] and ALEKSIUK [26].

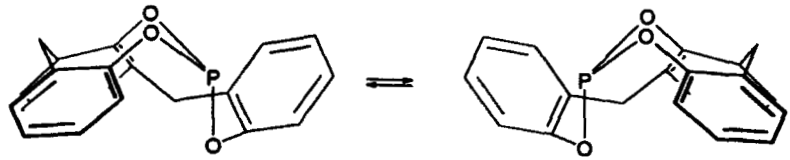

FIGURE 4 Resonance structures of 1-phosphapentacyclo [12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$] tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaenes **3e-i**

EXPERIMENTAL

All melting points were determined with a Kofler melting point apparatus and are corrected. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR

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spectra at 75 MHz in $CDCl_3$ with TMS as internal standard, ^{31}P NMR spectra were recorded at 121 MHz in $CDCl_3$ with 85% H_3PO_4 as external standard on a Bruker AC-300P. ^{13}C NMR peaks were assigned by means of DEPT (**D**istortionless **E**nhancement by **P**olarization **T**ransfer) and GD (**G**ated **D**ecoupling). Elemental analyses have been carried out with a Fa. Carlo Erba elemental analyzer. The molecular mass spectra were recorded on a Kratos Compact MALDI II mass spectrometer. Solvents were dried prior to use with appropriate drying agents. Hexamethyl and hexaethyl phosphorous triamides were synthesized according to common methods[27].

Synthesis of oligophenols by acidic condensation of 2-*tert*-butyl-4-methylphenol with bishydroxymethylphenols

4-Methyl-2,6-bis-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)phenol **1a**[17], 4-*tert*-butyl-2,6-bis-(3,5-di-*tert*-butyl-2-hydroxybenzyl)phenol **1b**[18], 4-*tert*-butyl-2,6-bis-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)phenol **1c**[18], 4-methyl-2,6-bis-(5-*tert*-butyl-2-hydroxybenzyl)phenol **1e**[19], 4- methyl-2,6-bis-(2-hydroxy-5-methylbenzyl)phenol **1f**[20], 4-methyl- 2-(3- *tert*-butyl-2-hydroxy-5-methylbenzyl)-6-(2-hydroxy-5-methylbenzyl)phenol **1g**[20] were synthesized according to the given methods. 2,6-Bishydroxymethyl-4-methylphenol was synthesized according to ULLMANN and BRITTNER[28], methylene-bis-2,2′-(6-hydroxymethyl-4-methylphenol) and 4-methyl-2,6-bis(2-hydroxy-3-hydroxymethyl-5-methylbenzyl)phenol following ref.[21].

4-Methyl-2,6-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)phenol (1d)

A mixture of 2,6-bishydroxymethyl-4-methylphenol (10.0 mmol, 16.8 g) and 2-*tert*-butyl-4-methylphenol (22.0 mmol, 45.0 g) was stirred at 80°C until all of the 2-*tert*-butyl-4-methylphenol was melted. 10 mL conc. HC were added and a strong exothermic reaction started. When the temperature had dropped to 80°C, 50 mL of *n*-heptane were added and the solution was refluxed for 1 h. After cooling to room temperature another 100 mL of *n*-heptane were added. The product crystallized after one week standing in the refrigerator and was filtered off and dried at 60°C to give 21.6 g (39.7%) of **1d** as colorless crystals, m.p. = 150°C (*n*-heptane), ^1H NMR: δ = 1.28 (s, 18H, Ar-p-C($C\underline{H}_3$)$_3$), 1.40 (s, 18H, Ar-o-C($C\underline{H}_3$)$_3$), 2.23 (s, 3H, Ar-$C\underline{H}_3$), 3.86 (s, 4H, $C\underline{H}_2$), 6.97 (s, 2H, Ar-$\underline{H}$), 7.16 (s, 4H, Ar-$\underline{H}$),

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^{13}C NMR: δ = 20.60 (Ar-$\underline{C}H_3$), 30.17, 31.59 (C($\underline{C}H_3)_3$), 31.86 ($\underline{C}H_2$), 34.26, 34.54 ($\underline{C}(CH_3)_3$), 122.52, 125.36, 126.99, 127.25, 129.57, 130.80, 135.38, 143.03, 147.76, 149.26 (C_{ar}), $C_{37}H_{52}O_3$(544.78) calcd. C 81.57 H 9.62 found C 81.65 H 9.61.

***Methylenebis-2,2′-(6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methyl)phenol* (1h)**

A mixture of methylenebis-2,2′-(6-hydroxymethyl-4-methyl)phenol (17.0 mmol, 4.90 g) and 2-*tert*-butyl-4-methylphenol (61.0 mmol, 10.0 g) was stirred at 80°C until all 2-*tert*-butyl-4-methylphenol has been melted. After adding of 5 mL conc. HCl the temperature was held for 30 min. Then the reaction mixture was stirred for additional 1.5 h at 100°C. After cooling to room temperature the crude product was recrystallized from *n*-heptane to give 5.50 g (55.8%) of **1h** as a colorless powder, m.p. = 169–171°C (*n*-heptane), ^1H NMR: δ = 1.61 (18H, C($C\underline{H}_3)_3$), 2.39, 2.43 (12H, $C\underline{H}_3$), 3.95 (2H), 3.80 (4H, $C\underline{H}_2$), 7.09–7.13 (8H, Ar-$\underline{H}$), 6.69–6.86 (br., 2H), 8.40–8.70 (br., 2H) ($O\underline{H}$), ^{13}C NMR: δ = 20.50, 20.83 ($\underline{C}H_3$), 30.11 (C($\underline{C}H_3)_3$), 34.27 ($\underline{C}(CH_3)_3$), 31.52 ($\underline{C}H_2$), 126.10, 127.37, 127.41, 127.74, 129.03, 129.54, 129.80, 130.81, 136.16, 147.46, 149.28 ($\underline{C}_{aryl}$), MS: *m/z* 582 (MH^+) 604 (MNa^+), $C_{39}H_{48}O_4$ (580.77) calcd. C 80.65 H 8.33 found C 80.53 H 8.29.

***4-Methyl-2,6-bis-(3-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-2-hydroxy-5-methylbenzyl)phenol* (1i)**

A mixture of 4-methyl-2,6-bis(2-hydroxy-3-hydroxymethyl-5-methylbenzyl)-phenol (22.5 mmol, 9.20 g) and 2-*tert*-butyl-4-methylphenol (10.0 mmol, 16.4 g) was stirred at 80°C until all 2-*tert*-butyl-4-methylphenol has been melted. After adding of 5 mL conc. HCl the temperature was held for 30 min. Then the reaction mixture was stirred for additional 3 h at 100°C. After cooling to room temperature the crude product was recrystallized from *n*-hexane to give 6.20 g (40.0%) of **1h** as a colorless powder, m.p. = 189–192°C (*n*-hexane), ^1H NMR: δ = 1.57 (18H, C($C\underline{H}_3)_3$), 2.31 (3H), 2.34 (6H), 2.37 (6H, $C\underline{H}_3$), 3.85 (4H), 3.97 (4H, $C\underline{H}_2$), 7.00–7.08 (12H, Ar-$\underline{H}$ & $O\underline{H}$), 8.93, 9.18 (3H, $O\underline{H}$), ^{13}C NMR: δ = 20.45, 20.50, 20.83 ($\underline{C}H_3$), 30.13 (C($\underline{C}H_3)_3$), 34.30 ($\underline{C}(CH_3)_3$), 31.56, 31.59 ($\underline{C}H_2$), 126.04, 127.49, 127.60, 128.18, 129.03, 129.49, 129.55, 129.97, 130.81,

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130.84, 136.51, 147.12, 147.34, 149.06 ($\underline{C}_{aryl}$), MS: *m/z* 724 (MNa^+), $C_{47}H_{56}O_5$ (700.91) calcd. C 80.53 H 8.05 found C 80.47 H 8.12.

General proceedings for the synthesis of the 6-dialkylaminodibenzo [d.g][1.3.2]dioxaphosphocins 2a-i

Method A

Equimolar amounts of triphenol and hexaalkylphosphorous triamide in toluene were refluxed under an inert argon atmosphere for 2.5–16 h. The solvent was removed and the residue was recrystallized from acetonitrile.

Method B

The triphenol was dissolved in THF under an inert argon atmosphere. The equimolar amount of hexaethylphosphorous triamide was added dropwise and the mixture was stirred at 60°C for 24 h. The solvent was removed and the product was purified by recrystallization from acetonitrile or by column chromatography (bas. Alox, *n*-hexane/diethylether 1: 0 → 0: 1).

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4-(3-tert-Butyl-2-hydroxy-5-methylbenzyl)-8-tert-butyl-2.10-dimethyl-6-dimethylaminodibenzo[d.g][1.3.2]dioxaphosphocin(2a)

4-Methyl-2,6-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)phenol (**1a**) (5.00 mmol, 2.30 g) and hexamethylphosphorous triamide (5.00 mmol, 0.82 g) were treated as described in *Method A* to give 1.83 g (68.6%) of **2a** as colorless crystals, m.p. = 220–226°C (acetonitrile), ^{31}P NMR: δ = 143.63, ^1H NMR: δ = 1.30, 1.32 (s, 18H, $C(C\underline{H}_3)_3$), 2.15, 2.17, 2.19 (s, 12H, $C\underline{H}_3$), 2.90, 2.95 (s, 6H, $N(C\underline{H}_3)_2$), 3.27 (d, ^2J(H,H) = 12.7 Hz, 1H, $C\underline{H}_2$), 4.21 (d, J(H,H) = 12.7 Hz, 1H) (AB_1), 3.47 ($C\underline{H}_2$, d, J(H,H) = 14.5 Hz, 1H), 3.92 (d, ^2J(H,H) = 14.5, 1H, $C\underline{H}_2$), 6.64 (1H, O$\underline{H}$), 6.86, 6.94 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 20.81, 21.90 ($\underline{C}H_3$), 29.75, 30.83 (d, *J*(P,C) = 4.5 Hz, $C(\underline{C}H_3)_3$), 31.87 (d, *J*(P,C) = 3.0 Hz, $\underline{C}H_2$), 34.40 ($\underline{C}H_2$), 34.72 (d, *J*(P,C) = 0.8 Hz, $\underline{C}(CH_3)_3$), 34.81 ($\underline{C}(CH_3)_3$), 35.32, 35.72 ($N(\underline{C}H_3)_2$), 126.17, 126.60, 126.96, 128.47, 128.81, 128.89, 129.22, 132.31 (d, *J*(P,C) = 3.0 Hz), 133.10 (d, *J*(P,C) = 1.5 Hz), 134.43 (d, *J*(P,C) = 2.0 Hz), 135.18 (d, *J*(P,C) = 3.5 Hz), 135.77 (d, *J*(P,C) = 3.0 Hz), 136.88, 141.72 (d, *J*(P,C) = 3.8 Hz), 145.55 (d, *J*(P,C) = 3.8 Hz), 148.00 (d, *J*(P,C) = 7.9 Hz), 150.79 ($\underline{C}_{aryl}$), MS: *m/z* 534 (MH^+), $C_{33}H_{44}O_3NP$ (533.66) calcd. C 74.27 H 8.31 N 2.62, found C 74.32 H 8.39 N 2.59.

4-(3-tert-Butyl-2-hydroxy-5-tert-butylbenzyl)-2.8.10-tri-tert-butyl-6-dimethylaminodibenzo[d.g][1.3.2]dioxaphosphocin (2b)

4-*tert*-Butyl-2,6-bis(3,5-di-tert-butyl-2-hydroxybenzyl)phenol **(1b)** (2.50 mmol, 1.48 g) and hexamethylphosphorous triamide (2.50 mmol, 0.41 g) were treated as described in *Method A* to give 1.10g (66.7%) of **2b** as white crystals, m.p. = 194–198°C (acetonitrile), ^{31}P NMR: δ = 142.69, ^{3}J(P,H) = 9.5 Hz, ^{1}H NMR: δ = 1.18, 1.21, 1.22 (s, 27H, p-C(C$\underline{H}_3$)$_3$), 1.32, 1.34 (s, 18H, o-C(C$\underline{H}_3$)$_3$), 4.88, 4.93 (s, 6H, N(C$\underline{H}_3$)$_2$), 3.36 (d, ^{2}J(H,H) = 12.7 Hz, 1H, C$\underline{H}_2$), 4.27 (dd, ^{2}J(H,H) = 12.7 Hz, ^{5}J(P,H) = 2.7 Hz, 1H, C$\underline{H}_2$), 3.53 (d, ^{2}J(H,H) = 14.4 Hz, 1H, C$\underline{H}_2$), 3.98 (d, ^{2}J(H,H) = 14.4 Hz, 1H, C$\underline{H}_2$), 6.78 (1H, O$\underline{H}$), 7.08, 7.10, 7.16 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 29.80 (o-C(C$\underline{H}_3$)$_3$), 30.89 (d, ^{5}J(P,C) = 4.3 Hz, o-C(C$\underline{H}_3$)$_3$), 31.39, 31.48, 31.63 (p-C(C$\underline{H}_3$)$_3$), 32.43 (d, J(P,C) = 2.5 Hz, C$\underline{H}_2$), 34.17, 34.27, 34.44, 34.99, 35.15 (C(CH$_3$)$_3$), 35.06 (C$\underline{H}_2$), 35.35, 35.62 (N(C$\underline{H}_3$)$_2$), 122.33, 122.85, 125.05, 125.13, 125.16, 125.48 ($\underline{C}_{aryl}$-H), 126.54, 132.24 (d, J(P,C) = 2.9 Hz), 134.99 (d, J(P,C) = 3.2 Hz), 135.44 (d, J(P,C) = 3.0 Hz), 136.35, 141.08 (d, J(P,C) = 3.8 Hz), 141.88, 145.39 (d, J(P,C) = 4.5 Hz), 146.22, 147.55, 147.81 (d, J(P,C) = 7.9 Hz), 150.54 ($\underline{C}_{aryl}$), MS: *m/z* 661(MH^+), 683 (MNa^+), 699 (MK^+), $C_{42}H_{62}O_3NP$ (659.89) calcd. C 76.44 H 9.47 N 2.12 found C 75.23 H 9.73 N 2.60.

4-(3-tert-Butyl-2-hydroxy-5-methylbenzyl)-8-tert-butyl-2.10-dimethyl-6-diethylaminodibenzo[d.g][1.3.2]dioxaphosphocin (2c)

4-Methyl-2,6-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)phenol **(1a)** (5.00 mmol, 2.30 g) and hexaethylphosphorous triamide (5.00 mmol, 1.24 g) were treated as described in *Method A* to give 1.96 g (69.4%) of **2c** as colorless crystals, m.p. = 186.5–191°C (acetonitrile), ^{31}P NMR: δ = 144.65, ^{1}H NMR: δ = 1.23 (t, 6H, N(CH$_2$C$\underline{H}_3$)$_2$), 1.30, 1.31 (s, 18H, C(C$\underline{H}_3$)$_3$), 2.13, 2.18, 2.19 (12H, C$\underline{H}_3$), 3.35–3.44 (m, 4H, N(C$\underline{H}_2$CH$_3$)$_2$), 3.25 (d, ^{2}J(H,H) = 12.5 Hz, 1H, C$\underline{H}_2$), 4.27 (dd, ^{2}J(H,H) = 12.7 Hz, ^{5}J(P,H) = 3.0 Hz, 1H, C$\underline{H}_2$), 3.47 (d, ^{2}J(H,H) = 14.6 Hz, 1H, C$\underline{H}_2$), 3.93 (d, ^{2}J(H,H) = 14.6 Hz, 1H, C$\underline{H}_2$), 6.59 (1H, O$\underline{H}$), 6.83–6.94 (6H, Ar-$\underline{H}$), $C_{35}H_{48}O_3NP$ (561.71) calcd. C 76.83 H 8.62 N 2.49 found C 74.90 H 8.69 N 2.56.

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4-(3,5-di-tert-Butyl-2-hydroxybenzyl)-2.8.10-tri-tert-butyl-6-diethylaminodibenzo-[d.g][1.3.2]dioxaphosphocin (**2d**)

4-*tert*-Butyl-2,6-bis(3.5-di-tert-butyl-2-hydroxybenzyl)phenol (**1b**) (7.00 mmol, 4.10 g) and hexaethylphosphorous triamide (1.73 g, 7.00 mmol) were treated as described in *Method A* to give 2.90 g (60.2%) of **2d** as a colorless solid, m.p. = 156–158°C (acetonitrile), ^{31}P NMR: δ = 144.26, ^{1}H NMR: δ = 1.16, 1.21, (s, 27H, p-C(C$\underline{H}_3$)$_3$), 1.33, 1.34 (s, 18H, o-C(C$\underline{H}_3$)$_3$), 1.26 (t, ^{3}J(H,H) = 7.1 Hz, 6H, N(CH$_2$CH$_3$)$_2$), 3.37–3.48 (m, 4H, N(CH$_2$CH$_3$)$_2$), 3.34 (d, ^{2}J(H,H) = 12.5 Hz, 1H, C$\underline{H}_2$), 4.32 (d, ^{2}J(H,H) = 12.5 Hz, ^{5}J(P,H) = 2.9 Hz, 1H C$\underline{H}_2$), 3.53 (d, ^{2}J(H,H) = 14.6 Hz, 1H, C$\underline{H}_2$), 4.01 (d, ^{2}J(H,H) = 14.6 Hz, 1H, C$\underline{H}_2$), 6.66 (1H, O$\underline{H}$), 7.06–7.17 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 14.73, 14.79 (N(CH$_2$$\underline{C}H_3$)$_2$), 29.77 (o-C($\underline{C}H_3$)$_3$), 31.11 (d, ^{5}J(P,C) = 4.9 Hz, o-C($\underline{C}$H$_3$)$_3$), 31.37, 31.48, 31.66 (p-C($\underline{C}$H$_3$)$_3$), 32.50 (d, J(P,C) = 2.7 Hz, $\underline{C}$H$_2$), 34.19, 34.27, 34.44, 35.07, 35.11 ($\underline{C}$(CH$_3$)$_3$), 34.93 ($\underline{C}$H$_2$), 38.99, 39.28 (N($\underline{C}$H$_2$CH$_3$)$_2$), 122.34, 122.81, 124.90, 125.04, 125.12, 125.32 ($\underline{C}_{aryl}$-H), 126.30, 131.94 (d, J(P,C) = 2.4 Hz), 135.45 (d, J(P,C) = 2.4 Hz), 135.85 (d, J(P,C) = 2.4 Hz), 136.04, 141.15 (d, J(P,C) = 3.5 Hz), 141.76, 145.40 (d, J(P,C) = 3.6 Hz), 146.14, 147.49, 147.77 (d, J(P,C) = 7.3 Hz), 150.71 ($\underline{C}_{aryl}$), $C_{44}H_{65}O_3NP$ (686.93) calcd. C 76.81 H 9.67 N 2.04 found C 76.77 H 9.64 N 2.10.

4-(3,5-di-tert-Butyl-2-hydroxybenzyl)-8.10-di-tert-butyl-6-diethylamino-2-methyl dibenzo[d.g][1.3.2]dioxaphosphocin (**2e**)

4-Methyl-2,6-bis(3.5-di-*tert*-butyl-2-hydroxybenzyl)phenol (**1c**) (10.00 mmol, 5.44 g) and hexaethylphosphorous triamide (10.10 mmol, 2.50 g) were treated as described in *Method A* to give 5.64 g (87.4%) of **2e** as colorless crystals, m.p. = 165°C (acetonitrile), ^{31}P NMR: δ = 144.27, ^{1}H NMR: δ = 1.22, 1.23, (s, 18H, p-(C(C$\underline{H}_3$)$_3$), 1.32, 1.33 (s, 18H, o-(C(C$\underline{H}_3$)$_3$), 1.24 (t, ^{3}J(H,H) = 7.2 Hz, 6H, N(CH$_2$C$\underline{H}_3$)$_2$), 3.36–3.46 (m, 4H, N(C$\underline{H}_2$CH$_3$)$_2$,), 3.32 (d, ^{2}J(H,H) = 12.6 Hz, 1H, C$\underline{H}_2$), 4.29 (dd, ^{2}J(H,H) = 12.6 Hz, ^{5}J(P,H) = 2.9 Hz, 1H, C$\underline{H}_2$), 3.50 (d, ^{2}J(H,H) = 14.5 Hz, 1H, C$\underline{H}_2$), 3.99 (d, ^{2}J(H,H) = 14.5 Hz, 1H, C$\underline{H}_2$), 6.74 (1H, O$\underline{H}$), 6.86–7.17 (6H, C$\underline{H}_{aryl}$), ^{13}C NMR: δ = 14.70, 14.76 (N(CH$_2$$\underline{C}H_3$)$_2$), 20.91 ($\underline{C}H_3$), 29.74 (o-C($\underline{C}H_3$)$_3$), 31.10 (d, ^{5}J(P,C) = 4.7 Hz, o-C($\underline{C}$H$_3$)$_3$), 31.52, 31.71 (p-C($\underline{C}$H$_3$)$_3$), 32.36 (d,

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J(P,C) = 3.2 Hz, $\underline{C}H_2$), 34.21, 34.46, 35.08, 35.10 ($\underline{C}(CH_3)_3$), 34.76 ($\underline{C}H_2$), 38.92, 39.20 ($N(C\underline{H}_2CH_3)_2$), 122.70, 123.01, 125.04, 125.10, 128.64, 129.20 ($\underline{C}_{aryl}$-H), 126.05, 132.19 (d, J(P,C) = 3.0 Hz), 134.46 (d, J(P,C) = 1.5 Hz), 135.50 (d, J(P,C) = 2.6 Hz), 135.77 (d, J(P,C) = 3.1 Hz), 135.93, 141.19 (d, J(P,C) = 3.7 Hz), 141.60, 145.40 (d, J(P,C) = 3.7 Hz), 146.15 (d, J(P,C) = 1.2 Hz), 147.90 (d, J(P,C) = 7.8 Hz), 150.96 ($\underline{C}_{aryl}$), $C_{41}H_{60}O_3NP$ (645.86) calcd. C 76.24 H 9.36 N 2.17 found C 76.17 H 9.36 N 2.22.

4-(3-tert-Butyl-2-hydroxy-5-methylbenzyl)-2.8-di-tert-butyl-6-diethylamino-10-methyldibenzo[d.g][1.3.2]dioxaphosphocin (2f)

4-*tert*-Butyl-2,6-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)phenol (**1d**) (10.00 mmol, 5.02 g) and hexaethyl phosphorous triamide (10.10 mmol, 2.50 g) were treated as described in *Method A* to give 4.20 g (60.2%) of **2f** as colorless crystals, m.p. = 137–141°C (acetonitrile), ^{31}P NMR: δ = 144.55, ^{1}H NMR: δ = 1.16, (s, 9H, p-C($C\underline{H}_3$)$_3$), 1.31, 1.32 (s, 18H, O-C($C\underline{H}_3$)$_3$), 1.23 (t, ^3J(H,H) = 7.1 Hz, 6H, $N(CH_2C\underline{H}_3)_2$), 3.34–3.45 (m, 4H, $N(C\underline{H}_2CH_3)_2$), 3.31 (d, ^2J(H,H) = 12.6 Hz, 1H, C$\underline{H}_2$), 4.30 (dd, ^2J(H,H) = 12.6 Hz, ^5J(P,H) = 3.0 Hz, 1H, C$\underline{H}_2$), 3.53 (d, ^2J(H,H) = 14.8 Hz, 1H, C$\underline{H}_2$), 3.96 (d, ^2J(H,H) = 14.8 Hz, 1H, C$\underline{H}_2$), 6.43 (1H, O$\underline{H}$), 6.85–7.15 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 14.68, 14.74 ($N(CH_2\underline{C}H_3)_2$), 20.82, 21.03 ($\underline{C}H_3$), 29.72 (o-C($\underline{C}H_3$)$_3$), 31.02 (d, ^5J(P,C) = 4.7 Hz, o-C($\underline{C}H_3$)$_3$), 31.42, (p-C($\underline{C}H_3$)$_3$), 32.31 (d, J(P,C) = 2.7 Hz, $\underline{C}H_2$), 34.72, 34.77, ($\underline{C}(CH_3)_3$), 34.30 ($\underline{C}H_2$), 38.89, 39.18 ($N(\underline{C}H_2CH_3)_2$), 125.00, 125.38, 126.06, 126.54, 128.80, 128.95 ($\underline{C}_{aryl}$-H), 126.66, 128.38, 131.38 (d, J(P,C) = 2.9 Hz), 133.02, 135.06 (d, J(P,C) = 3.2 Hz), 136.32 (d, J(P,C) = 3.0 Hz), 136.53, 141.85 (d, J(P,C) = 3.7 Hz), 145.78 (d, J(P,C) = 4.0 Hz), 147.42 (d, J(P,C) = 1.6 Hz), 148.08 (d, J(P,C) = 8.0 Hz), 150.90 ($\underline{C}_{aryl}$), $C_{38}H_{54}O_3NP$ (603.79) calcd. C 75.59 H 9.02 N 2.32 found C 75.54 H 9.14 N 2.27.

4-(5-tert-butyl-2-hydroxybenzyl)-10-tert-butyl-6-diethylamino-2-methyldibenzo[d.g][1.3.2]dioxaphosphocin (2g)

4-Methyl-bis(2-hydroxy-5-*tert*-butylbenzyl)phenol (2.50 mmol, 1.08 g) (**1e**) and hexaethylphosphorous triamide (2.50 mmol, 0.62 g) were treated as described in *Method B*. The crude product was recrystallized from ace-

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tonitrile to give 0.80 g (60.2%) of **2g** as a colorless solid, m.p. = 90–100°C (gradual decomp.) (acetonitrile), ^{31}P NMR: δ = 144.13, ^{1}H NMR: δ = 1.19 (t, 6H, $N(CH_2\underline{C}H_3)_2$), 1.22 (s, 18H, $C(\underline{C}H_3)_3$), 2.12 (s, 3H, Ar-$\underline{C}H_3$), 3.24–3.45 (m, 5H, $N(\underline{C}H_2CH_3)_2$, Ar-$\underline{C}H_2$-Ar), 4.30 (dd, ^{2}J(H,H) = 12.6 Hz, ^{5}J(P,H) = 3.0 Hz, 1H, Ar-$\underline{C}H_2$-Ar), 3.55 (d, ^{2}J(H,H) = 14.8 Hz, 1H), 3.99 (d, ^{2}J(H,H) = 14.8 Hz, 1H, $\underline{C}H_2$), 6.68–7.22 (8H, Ar-$\underline{H}$), ^{13}C NMR: δ = 15.09, 15.12 ($N(CH_2\underline{C}H_3)_2$), 20.83 (Ar-$\underline{C}H_3$), 31.45, 31.58 ($C(\underline{C}H_3)_3$), 32.06 (d, ^{4}J(P,C) = 3.25 Hz, $\underline{C}H_2$), 33.98 ($\underline{C}H_2$), 24.30, 34.36 ($\underline{C}(CH_3)_3$), 38.89, 39.17 ($N(\underline{C}H_2CH_3)_2$), 115.72, 122.11 (d, J(P,C) = 2.6 Hz), 124.90 (d, J(P,C) = 2.5 Hz), 125.58, 126.55, 127.43, 128.79, 129.02, 132.22 (d, J(P,C) = 2.4 Hz), 134.24, 134.6 (d, J(P,C) = 2.64 Hz), 135.48 (d, J(P,C) = 3.2 Hz), 142.92, 145.70 (d, J(P,C) = 3.7 Hz), 147.37, 148.69 (d, J(P,C) = 5.2 Hz), 152.11 ($\underline{C}_{aryl}$).

4-(2-hydroxy-5-methylbenzyl)-6-diethylamino-2.10-dimethyldibenzo[d.g][1.3.2]-dioxaphosphocin (2h)

4-Methyl-bis(2-hydroxy-5-methylbenzyl)phenol (**1f**) (3.00 mmol, 1.05 g) and hexaethylphosphorous triamide (3.00 mmol, 0.75 g) were treated as described in *Method B*. The product was purified by column chromatography (Alox, *n*-hexane/diethylether 1: 0 → 0: 1) to give 1.24 g (91.7%) of **2h** as a colorless oil, ^{31}P NMR: δ = 142.05, ^{1}H NMR: δ = 1.18 (t, 6H, $N(CH_2\underline{C}H_3)_2$), 2.11, 2.17, 2.19 (s, 9H, $\underline{C}H_3$), 3.24–3.45 (m, 5H, $N(\underline{C}H_2CH_3)_2$, $\underline{C}H_2$), 4.27 (dd, ^{2}J(H,H) = 12.6 Hz, ^{5}J(P,H) = 3.0 Hz, 1H, $\underline{C}H_2$), 3.52 (d, ^{2}J(H,H) = 14.8 Hz, 1H), 3.93 (d, ^{2}J(H,H) = 14.8 Hz, 1H, $\underline{C}H_2$), 6.64–7.02 (8H, Ar-$\underline{H}$).

4-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-6-diethylamino-2.10-dimethyl dibenzo[d.g][1.3.2]dioxaphosphocin (2i)

4-Methyl-(2-hydroxy-5-methylbenzyl)(3-*tert*-butyl-5-methylbenzyl)phenol (**1g**) (4.90 mmol, 1.99 g) and hexaethyl phosphorous triamide (5.00 mmol, 1.24 g) were treated as described in *Method B*. The residue was purified by column chromatography (Alox, *n*-hexane/diethylether 1:0 → 0:1) to give 1.54 g (61.8%) of **2i** as colorless crystals, m.p. = 178–180°C (acetonitrile), ^{31}P NMR: δ = 143.57 ^{1}H NMR: δ = 1.29 (t, 6H, $N(CH_2\underline{C}H_3)_2$), 1.37 (s, 9H, $C(\underline{C}H_3)_3$), 2.21, 2.26, 2.28 (s, 9H, $\underline{C}H_3$), 3.39–3.51 (m, 5H, $N(\underline{C}H_2CH_3)_2$, $\underline{C}H_2$), 4.37 (dd, ^{2}J(H,H) = 12.4 Hz,

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^5J(P,H) = 3.0 Hz, 1H, C$\underline{H}_2$), 3.55 (d, ^2J(H,H) = 14.8 Hz, 1H), 3.99 (d, ^2J(H,H) = 14.8 Hz, 1H, C$\underline{H}_2$), 6.46 (s, 1H, O$\underline{H}$), 6.68–7.22 (7H, Ar-$\underline{H}$), ^{13}C NMR: δ = 14.99, 15.05 (N($CH_2\underline{C}H_3)_2$), 20.73, 20.78 ($\underline{C}H_3$), 29.72 ($C(\underline{C}H_3)_3$), 32.00 (d, ^4J(P,C) = 3.32 Hz, $\underline{C}H_2$), 34.02 ($\underline{C}H_2$), 34.71 ($\underline{C}(CH_3)_3$), 38.87, 39.15 (N($\underline{C}H_2CH_3)_2$), 122.54 (d, J(P,C) = 3.3 Hz), 126.22, 126.55, 128.28, 128.50, 128.83, 128.95, 129.11, 130.27, 132.11 (d, J(P,C) = 2.94 Hz), 134.05, 134.21, 135.26 (d, J(P,C) = 3.02 Hz), 135.41 (d, J(P,C) = 2.9 Hz), 136.51, 145.85 (d, J(P,C) = 3.7 Hz), 148.81 (d, J(P,C) = 5.51 Hz), 151.00 ($\underline{C}_{aryl}$).

General proceedings for the synthesis of 1-phosphapentacyclo [12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$]tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaenes 3a-3i

Method A

The given amount of the 6-diethylamino-2.10-dimethyldibenzo [d.g][1.3.2]dioxaphosphocin was heated in a metal bath under a weak flow of argon until a homogenous melting had been formed. The temperature was graded up to 315°C and held at this temperature for 10 min, while all diethylamine was removed destillatively. After cooling to room temperature the resinous crude product was recrystallized from acetonitrile.

Method B

A solution of the 6-diethylamino-2.10-dimethyldibenzo[d.g][1.3.2]dioxaphosphocin in xylene was refluxed for 24 h under an inert argon atmosphere. The solvent was removed and the residue was purified by recrystallization or by column chromatography.

4, 20-di(tert-butyl)-6, 12, 18-trimethyl-1-phosphapentacyclo [12.8.2. $0^{3,8}$.$0^{10,24}$.$0^{16,21}$]-tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaene (3a)

The compound was prepared according to *Method A* with 1.00 g (1.78 mmol) of compound **2c** to give 0.80 g (92.0%) of **3a** as colourless crystals, m.p. = 198–200°C, ^{31}P NMR: δ = 123.02, ^{1}H NMR: δ = 1.37 (s, 18H, $C(C\underline{H}_3)_3$), 2.18 (s, 3H), 2.23 (s, 6H, $C\underline{H}_3$), 3.63 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 4.30 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 6.88–7.01 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 20.86, 20.81 ($\underline{C}H_3$), 31.42 (d,

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J(P,C) = 4.5 Hz, C($\underline{C}H_3)_3$), 35.38 ($\underline{C}(CH_3)_3$), 37.10 ($\underline{C}H_2$), 126.78, 128.69, 130.43 ($\underline{C}_{aryl}$-H), 130.35 (d, J(P,C) = 3.0 Hz), 133.06, 133.38 (d, J(P,C) = 2.3 Hz), 134.12, 142.65 (d, J(P,C) = 3.9 Hz), 144.48 (d, J(P,C) = 3.0 Hz), 146.34 ($\underline{C}_{aryl}$), MS: *m/z* 490 (MH^+), $C_{31}H_{37}O_3P$ (488.57) calcd. C 76.20 H 7.63 found C 76.08 H 7.68.

4, 6, 12, 18, 20-penta(tert-butyl)-1-phosphapentacyclo[12.8.2.0^{3,8}.0^{10,24}.0^{16,21}]tetracosa-3, 5, 7,10(24), 11, 13, 16(21), 17, 19-nonaene (3b)

The compound was prepared according to *Method A* with 1.00 g (1.46 mmol) **2d.** After recrystallization from 5 mL acetonitrile 0.80 g (89.5%) of **3b** were yielded, m.p. = 234–236°C, ^{31}P NMR: δ = 122.39, ^{1}H NMR: δ = 1.22 (s, 9H, C$\underline{H}_3$), 1.26 (s, 18H, p-C(C$\underline{H}_3)_3$), 1.40 (s, 18H, o-C(C$\underline{H}_3)_3$), 3.71 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 4.40 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 7.13, 7.25 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 31.41, 31.46, 31.60 (C($\underline{C}H_3)_3$), 34.41, 35.76 ($\underline{C}(CH_3)_3$), 37.94 ($\underline{C}H_2$), 123.14, 125.32, 126.86 ($\underline{C}_{aryl}$-H), 129.73 (d, J(P,C) = 2.8 Hz), 132.85 (d, J(P,C) = 2.3 Hz), 142.06 (d, J(P,C) = 4.0 Hz), 144.48 (d, J(P,C) = 3.2 Hz), 145.96, 146.33 (d, J(P,C) = 1.9 Hz), 147.31 ($\underline{C}_{aryl}$), $C_{40}H_{55}O_3P$ (614.8) calcd. C 78.14 H 9.02 found C 77.15 H 9.04 N 0.30 (*2/15 CH_3CN).

4, 12, 20-tri(tert-butyl)-6, 18-dimethyl-1-phosphapentacyclo-[12.8.2.0^{3,8}.0^{10,24}.0^{16,21}]-tetracosa-3, 5, 7,10(24), 11, 13, 16(21), 17, 19-nonaene (3c)

The compound was prepared according to *Method A* with 1.00 g (1.55 mmol) **2e.** After recrystallization from 5 mL acetonitrile 0.30 g (34.1%) of **3c** were yielded, m.p = 217–218°C, ^{31}P NMR: δ = 122.92, ^{1}H NMR: δ = 1.21 (s, 9H, p-C(C$\underline{H}_3)_3$), 1.38 (s, 18H, O-C(C$\underline{H}_3)_3$), 2.24 (s, 6H, C$\underline{H}_3$), 3.68 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 4.33 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 6.94–7.08 (6H, Ar-$\underline{H}$), ^{13}C NMR: δ = 20.84 ($\underline{C}H_3$), 31.40, 31.47, 31.58 (C($\underline{C}H_3)_3$), 34.38, 35.40 ($\underline{C}(CH_3)_3$), 37.58 ($\underline{C}H_2$), 125.14, 126.77, 130.56 ($\underline{C}_{aryl}$-H), 129.82 (d, J(P,C) = 2.6 Hz), 133.06, 133.59 (d, J(P,C) = 2.5 Hz), 142.69 (d, J(P,C) = 4.0 Hz), 144.58 (d, J(P,C) = 3.7 Hz), 146.40 (d, J(P,C) = 2.4 Hz), 147.41 ($\underline{C}_{aryl}$), $C_{34}H_{43}O_3P$ (530.65) calcd. C 76.95 H 8.17 found C 76.91 H 8.23.

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4, 6, 18, 20-tetra(tert-butyl)-12-methyl-1-phosphapentacyclo-[12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$]tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaene (**3d**)

The compound was prepared according to *Method A* with 1.00 g (1.66 mmol) **2f**. After recrystallization from 5 mL acetonitrile 0.86 g (97.0%) of **3d** were obtained, m.p = 184°C, ^{31}P NMR: δ = 122.6, ^{1}H NMR: δ = 1.26 (s, 18H, p-C(C<u>H</u>$_3$)$_3$), 1.39 (s, 18H, o-C(C<u>H</u>$_3$)$_3$), 2.20 (s, 3H, C<u>H</u>$_3$), 3.67 (d, ^{2}J(H,H) = 16.2 Hz, 2H, C<u>H</u>$_2$), 4.37 (d, ^{2}J(H,H) = 16.2 Hz, 2H, C<u>H</u>$_2$), 6.93–7.25 (6H, Ar-<u>H</u>), ^{13}C NMR: δ = 20.87 (<u>C</u>H$_3$), 31.42, 31.45, 31.48 (C(<u>C</u>H$_3$)$_3$), 34.40, 35.74 (<u>C</u>(CH$_3$)$_3$), 37.49 (<u>C</u>H$_2$), 123.15, 126.72, 128.77 (<u>C</u>$_{aryl}$-H), 130.39 (d, J(P,C) = 2.9 Hz), 132.71 (d, J(P,C) = 2.3 Hz), 134.09, 142.05 (d, J(P,C) = 3.8 Hz), 144.58 (d, J(P,C) = 3.7 Hz), 146.00, 146.29 (d, J(P,C) = 1.9 Hz) (<u>C</u>$_{aryl}$), $C_{37}H_{49}O_3P$ (572.73) * 1/2.3 CH_3CN calcd. C 77.01 H 8.59 N 1.03 found C 76.40 H 8.62 N 1.05.

6, 18-di(tert-butyl)-12-methyl-1-phosphapentacyclo[12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$]tetracosa-3, 5, 7, 10(24), 11, 13, 16,(21), 17, 19-nonaene (**3e**)

The compound was prepared according to *Method B* with compound **2g** (2.81 mmol, 0.80 g). After recrystallization from acetonitrile 0.56 g (43.2%) of **3e** were obtained as colorless crystals, m.p. = 190–191°C, ^{31}P NMR: δ = 101.96, ^{1}H NMR: δ = 1.19 (s, 18H, C(C<u>H</u>$_3$)$_3$), 2.11 (s, 3H, C<u>H</u>$_3$), 3.40 (d, ^{2}J(H,H) =13.7 Hz, 2H, C<u>H</u>$_2$), 4.40 (d, ^{2}J(H,H) = 13.7 Hz, 2H, C<u>H</u>$_2$), 6.80 (d, ^{3}J(H,H) = 8.4 Hz, 2H,), 6.83 (s, 2H), 7.00 (d, ^{3}J(H,H) = 8.4 Hz, 2H,), 7.11 (s, 2H, Ar-<u>H</u>), ^{13}C NMR: δ = 20.83 (<u>C</u>H$_3$), 31.39 (C(<u>C</u>H$_3$)$_3$), 34.21 (<u>C</u>(CH$_3$)$_3$), 35.30 (<u>C</u>H$_2$), 122.82 (d, J(P,C) = 2.5 Hz), 124.67, 127.31, 128.38 (<u>C</u>$_{aryl}$), 131.73 (d, J(P,C) = 1.8 Hz), 132.07 (d, J(P,C) = 2.2 Hz), 134.74 (d, J(P,C) = 1.0 Hz), 145.14 (d, J(P,C) = 9.2 Hz), 147.50 (d, J(P,C) = 6.2 Hz), 147.62 (<u>C</u>$_{aryl}$), $C_{29}H_{33}O_3P$ (460.52) * 1/4 CH_3CN calcd. C 75.26 H 7.23 N 0.75 found C 75.06 H 7.28 N 0.80.

6, 12, 18-trimethyl-1-phosphapentacyclo[12.8.2.$0^{3,8}$.$0^{10,24}$.$0^{16,21}$] tetracosa-3, 5, 7, 10 (24), 11, 13, 16(21), 17, 19-nonaene (**3f**)

The compound was prepared according to *Method A* with 0.20 g (0.45 mmol) of compound **2h.** The crude product was purified by column

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chromatography (silicagel, $CHCl_3$) to give 0.13 g (76.8%) of **3f** as colorless crystals, m.p. = 185–192°C, ^{31}P NMR: 102.14, ^{1}H NMR: 2.12 (s, 3H), 2.18 (s, 6H, Ar-C$\underline{H}_3$), 3.35 (2H, d, ^{2}J(H,H) = 13.7 Hz), 4.38 (2H, d, ^{2}J(H,H) = 13.7 Hz, C$\underline{H}_2$), 6.75–6.94 (8H, C$\underline{H}_{aryl}$), ^{13}C NMR: 20.58, 20.81 (C$\underline{H}_3$), 34.93 (C$\underline{H}_2$), 123.78 (d, J(P,C) = 2.8 Hz), 128.28, 128.49 (d, J(P,C) = 0.8 Hz), 131.06, 131.61 (d, J(P,C) = 1.8 Hz), 132.52 (d, J(P,C) = 2 Hz), 134.27, 134.73, 145.15 (d, J(P,C) = 9. 1 Hz), 147.64 (d, J(P,C) = 6 Hz) (C$\underline{_{aryl}}$), $C_{23}H_{21}O_3P$ (376.4) calcd. C 73.40 H 5.62 found C 73.48 H 5.65.

4-tert-butyl-6, 12, 18-trimethyl-1-phosphapentacyclo [12.8.2.2^{3,8}.0^{10,24}.0^{16,21}]-tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaene (3g)

The compound was prepared according to *Method A* with 0.40 g (0.80 mmol) of compound **2i.** The crude product was purified by column chromatography (silicagel, $CHCl_3$) to give 0.33 g (96.3%) of **3g** as colouless crystals, m.p. = 190–191°C, ^{31}P NMR: δ = 105.6, ^{1}H NMR: δ = 1.29 (s, 9H, C(C$\underline{H}_3$)$_3$), 2.14 (s, 3H), 2.19 (s, 6H, C$\underline{H}_3$), 3.37 (d, ^{2}J(H,H) = 13.5 Hz, 1H, C$\underline{H}_2$), 4.37 (d, ^{2}J(H,H) = 13.5 Hz, 1H, C$\underline{H}_2$), 3.38 (d, ^{2}J(H,H) = 14.4 Hz, 1H, C$\underline{H}_2$), 4.43 (d, ^{2}J(H,H) = 14.6 Hz, 1H, C$\underline{H}_2$), 6.80–6.94 (7H, Ar-$\underline{H}$), $C_{27}H_{29}O_3P$ (432.47) calcd. C 74.98 H 6.76 found C 74.81 H 6.90.

4-(3-tert.butyl-2-hydroxy-5-methylbenzyl)-20-tert-butyl-6, 12, 18-trimethyl-1-phosphapentacyclo[12.8.2.2^{3,8}.0^{10,24}.0^{16,21}]-tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaene (3h)

Phenol **1h** (1.16 g, 2.00 mmol) was dissolved in 30 mL xylene under an inert argon atmosphere. Hexaethyl phosphorous triamide (0.50 g, 2.02 mmol) was added and the mixture was refluxed for 16h. After cooling to room temperature the liquids were removed under reduced pressure and the crude product was purified by column chromatography (Silicagel 60, $MeCl_2$/*n*-hexane 2:1) to give 0.63 g (52.0%) of **3h** as a colorless solid, ^{31}P NMR: δ = 110.63, ^{1}H NMR: δ = 1.25, 1.30 (s, 18H, C(C$\underline{H}_3$)$_3$), 2.10 (s, 3H), 2.17 (s, 3H), 2.20 (s, 6H, C$\underline{H}_3$), 3.42 (d, ^{2}J(H,H) = 13.6 Hz, 1H, C$\underline{H}_2$), 4.42 (d, ^{2}J(H,H) = 13.6 Hz, 1H, C$\underline{H}_2$), 3.45 (d, ^{2}J(H,H) = 15.2 Hz, 1H, C$\underline{H}_2$), 4.39 (d, ^{2}J(H,H) = 15.2 Hz, 1H, C$\underline{H}_2$), 3.65 (d,

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^2J(H,H) = 15.4 Hz, 1H, C$\underline{H}_2$), 4.20 (d, ^2J(H,H) = 15.4 Hz, 1H, C$\underline{H}_2$), 6.71–6.94 (8H, Ar-$\underline{H}$), ^{13}C NMR: δ = 20.63, 20.78, 20.84, 20.92 ($\underline{C}H_3$), 29.74, 31.04 (d, J(P,C) = 3.5 Hz, C($\underline{C}H_3)_3$), 34.62, 35.25 ($\underline{C}(CH_3)_3$), 32.56, 35.21, 36.42 ($\underline{C}H_2$), 126.32–150.78 (24C, $\underline{C}_{aryl}$), MS: *m/z* 610 (MH^+), $C_{39}H_{45}O_4P$ (608.72) calcd. C 76.95 H 7.45 found C 76.50 H 7.31.

4, 20-di(3-tert-butyl-2-hydroxy-5-methylbenzyl)-6, 12, 18-trimethyl-1-phosphapentacyclo[12.8.2.0^{3,8}.0^{10,24}.0^{16,21}]-tetracosa-3, 5, 7, 10(24), 11, 13, 16(21), 17, 19-nonaene (3i)

Phenol **1i** (1.40 g, 2.00 mmol) was dissolved in 30 mL xylene under an inert argon atmosphere. Hexaethyl phosphorous triamide (0.50 g, 2.02 mmol) was added and the mixture was refluxed for 16 h. After cooling to room temperature the liquids were removed under reduced pressure and the crude product was purified by column chromatography (Silicagel 60, $MeCl_2$/*n*-hexane 1:2) to give 0.80 g (54.9%) of **3i** as a colourless solid, m.p. = 260°C, ^{31}P NMR: 101.83, ^{1}H NMR: 1.28 (s, 18H, C($\underline{C}H_3)_3$), 1.99, (s, 6H), 2.1 (s, 6H), 2.18 (s, 3H, C$\underline{H}_3$), 3.48 (d, ^2J(H,H) = 13.8 Hz, 2H, C$\underline{H}_2$), 3.73 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 3.97 (d, ^2J(H,H) = 16.3 Hz, 2H, C$\underline{H}_2$), 4.36 (d, ^2J(H,H) = 13.8 Hz, 2H, C$\underline{H}_2$), 6.35, 6.45, 6.78, 6.91, 6.94, 7.23 (s, 12H, Ar-$\underline{H}$and O-$\underline{H}$), ^{13}C NMR: 19.02, 19.10 ($\underline{C}H_3$), 28.28 (C($\underline{C}H_3)_3$), 32.17 ($\underline{C}(CH_3)_3$), 29.94, 33.15, (Ar-$\underline{C}H_2$-Ar), 123.98, 125.05, 126.303, 126.62, 127.13, 127.35, 127.74, 129.88 (d, J(P,C) = 1.7 Hz), 130.55 (d, J(P,C) = 1.96 Hz), 131.47 (d, J(P,C) = 2.64 Hz), 132.06, 133.02, 135.35, 143.48 (d, J(P,C) = 7.8 Hz), 144.55 (d, J(P,C) = 7.5 Hz), 149.57 ($\underline{C}_{aryl}$), MS: *m/z* 729 (MH^+), $C_{47}H_{53}O_5P$ (728.86) calcd. C 77.44 H 7.33 found C 77.27 H 7.50.

4-(3-tert-butyl-2-oxy- (bisdimethylaminophosphino)-5-methylbenzyl)-8-tert-butyl- 2.10-dimethyl-6-dimethylaminodibenzo [d.g][1.3.2]dioxaphosphocin (4)

To a solution of 4-methyl-2,6-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)phenol (2.30 g, 5.00 mmol) in 50 mL toluene hexamethylphosphorous triamide (4.90 g, 30.0 mmol) was added and the mixture was refluxed for 12h. After evaporation of the liquids *in vacuo* the oily residue was crystallized from acetonitrile to give 1.30 g (32.6%) of **4** as a colourless solid, m.p. = 140–142°C, ^{31}P-NMR: δ = 132.42, 141.85, ^{1}H-NMR: δ = 1.27,

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1.33 (s, 18H, $C(C\underline{H}_3)_3$), 2.06, 2.11, 2.20 (s, 12H, $C\underline{H}_3$), 2.48, 2.51, 2.52, 2.54, 2.68, 2.71 (s, 18H, $N(C\underline{H}_3)_2$), 3.33 (d, ^2J(H,H) = 12.6 Hz, 1H, $C\underline{H}_2$), 4.23 (d, ^2J(H,H) = 12.6 Hz, 1H, $C\underline{H}_2$), 3.93 (d, ^2J(H,H) = 16.6 Hz, 1H, $C\underline{H}_2$), 4.10 (d, ^2J(H,H) = 16.6, 1H, $C\underline{H}_2$), 6.50–6.98 (6H, Ar-$\underline{H}$), ^{13}C-NMR: δ = 20.86, 21.01 ($\underline{C}H_3$), 30.48, 30.76 (d, J(P,C) = 4.0 Hz, $C(\underline{C}H_3)_3$), 32.05 (d, J(P,C) = 15.6 Hz, $\underline{C}H_2$), 34.71 ($\underline{C}H_2$), 34.91 ($\underline{C}(CH_3)_3$), 35.17, 35.54, 36.79 (d, J(P,C) = 3.0 Hz), 37.18 (d, J(P,C) = 3.0 Hz, $N(\underline{C}H_3)_2$), 125.90, 126.35, 127.80, 128.84, 129.84, 130.20, 130.71, 131.89, 132.55, 133.05, 133.95, 134.61, 136.05, 140.61, 141.73 (d, J(P,C) = 3.3 Hz), 147.19, 148.60 (d, J(P,C) = 7.9 Hz), 151.20 (d, J(P,C) = 9.6 Hz) ($\underline{C}_{aryl}$), MS: *m/z* 652 (MH^+), $C_{37}H_{55}O_3N_3P_2$ (651.77) calcd. C 69.24 H 8.52 N 6.45 found C 69.65 H 8.55 N 6.39.

4,4′-Methylenebis-(8-tert-butyl-2.10-dimethyl-6-dimethylaminodibenzo [d.g][1.3.2]dioxaphosphocin(**5**)

To a solution of methylenebis-2,2′-(6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methyl)phenol (**1h**) (1.00 g, 1.72 mmol) in 30 mL toluene hexaethylphosphorous triamide was added and the mixture was stirred at 80°C for 16h. After evaporation of the liquids *in vacuo* the crude product was purified by column chromatography (bas. Alox, Et_2O/*n*-hexane 1:1) to give 0.70 g (51.9%) of 5 as an yellowish solid, m.p. = 145–155°C, P-NMR: δ = 142.92, 143.16, ^{1}H-NMR: δ = 0.98 (t, ^3J(H,H) = 7.1 Hz, 6H, $N(CH_2C\underline{H}_3)_2$), 1.09 (t, ^3J(H,H) = 7.1 Hz, 6H, $N(CH_2C\underline{H}_3)_2$), 1.29 (s, 18H, $C(C\underline{H}_3)_3$), 2.09 (s, 3H), 2.10 (s, 3H), 2.20 (s, 6H, $C\underline{H}_3$), 3.02–3.30 (m, 10H, $C\underline{H}_2$ & $N(C\underline{H}_2CH_3)_2$,), 3.76 (d, ^2J(H,H) = 11.4 Hz), 3.90 (d, ^2J(H,H)= 11.4 Hz, 1.1H, $C\underline{H}_2$), 3.83 (s, 0.9H, $C\underline{H}_2$,), 4.28 (dd, ^2J(H,H) = 12.4 Hz, ^5J(P,H) = 3.0 Hz, 2H, $C\underline{H}_2$), 6.54, 6.67, 6.91–6.97 (8H, Ar-$\underline{H}$), ^{13}C-NMR: δ = 14.59, 14.66, 14.79 ($N(CH_2\underline{C}H_3)_2$), 20.78, 21.00 ($\underline{C}H_3$), 30.91 (d, J(P,C) = 4.7 Hz, $C(\underline{C}H_3)_3$), 34.75 ($\underline{C}(CH_3)_3$), 31.40, 34.52 ($\underline{C}H_2$), 126.33–148.54 (12C, $\underline{C}_{aryl}$), MS: *m/z* 783 (MH^+), $C_{47}H_{64}N_2O_4P_2$ (782.93) calcd. C 72.09 H 8.24 N 3.58 found C 69.54 H 8.27 N 3.72.

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