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Sterically Stressed Amino- and PH-Functional Di-*t*-butyl-*o*-phosphinophenols—Intramolecular Interaction and Formation of Benzoxadiphospholes

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ABSTRACT

Lithium and sodium o-lithio-4,6-di-t-butyl-phenolates **1** *and* **2** *react, successively, with* $ClP(NMe_2)_2$ *and* $ClSiMe_3$ *to give* $2\text{-}(Me_2N)_2P\text{-}4,6\text{-}t\text{-}Bu_2C_6H_2OSiMe_3$ **3**. **1** *and* $ClP(NMe_2)Ph$ *furnish a small amount of the analogous compound* **4** *but mainly diastereoisomers of a C,O-diphosphinylation product* **5A/B**, *which exhibit large through-space coupling constants* ($^4J_{PP}$ = *152 and 237.5 Hz). Under certain conditions, the P–N bond is attacked, and triphosphines* **6** *and* **7** *are formed. Alcoholysis of* **3–5** *and subsequent reduction with* $LiAlH_4$ *yields the respective bulky primary and secondary phosphinophenols* **8** *and* **9**. *Both decompose partially on distillation, affording* $tBu_2C_6H_3OH$ *and the cyclic diphosphines* **10** *and* **11**. **10**, *a further dihydro-benzoxadiphosphol* **13** *and a phosphinidenephosphorane* **14** *are formed by reaction of* **8** *with* $P(NMe_2)_3$. *The molecular structure of bicyclic* **10**, *folded at the P–P bond, is reported. The uncommon features—unselective disubstitution of* **1**, *P. . .P interactions in* **5** *and* **6**, *facile P–C cleavage of* **8** *and* **9**, *and diphosphine formation—reveal a dramatic influence of the bulky substituents in the 6-position on the chemistry of 2-phosphinophenols.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:183–193, 1998

INTRODUCTION

Tertiary *o*-phosphinophenols [1–3] and *o*-phosphinophenol ethers [4] are of interest as hemi-labile or hybrid ligands in complex chemistry and catalysis; primary and secondary derivatives can serve as precursors for P-asymmetric alkylphosphinophenols [5] or as synthons for phosphorus heterocycles [5,6]. In recent studies on P-tertiary *o*-phosphinophenols and silyl-, stannyl-, and phosphinyl ethers, we observed marked effects of *t*-butyl groups in the 4,6-positions on the structure and chemistry. The 6-*t*-butyl group adjacent to the oxygen atom, shields the ether bond and causes displacement of O-substituents toward the phosphino group. The hydrolysis of the respective O-$SiMe_3$ ethers [2] or the cleavage of O–P bonds in metallation reactions are hindered [7], and intramolecular P . . . H–O hydrogen bridging

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bonds or through-space interactions are promoted, as shown by large ^4J(PP), ^4J(SnP), or ^6J(PH) coupling constants and the intramolecular distances [2]. The bending of O-substituents toward phosphorus enforces the formation of P,O-chelate complexes even with hard metal centers [3] and should generally favor ring closure reactions. This encouraged us to investigate amino- and PH-functionally substituted 4,6-di-*t*-butyl-2-phosphinophenols and the steric impact on synthesis, properties, and tendency to form heterocycles.

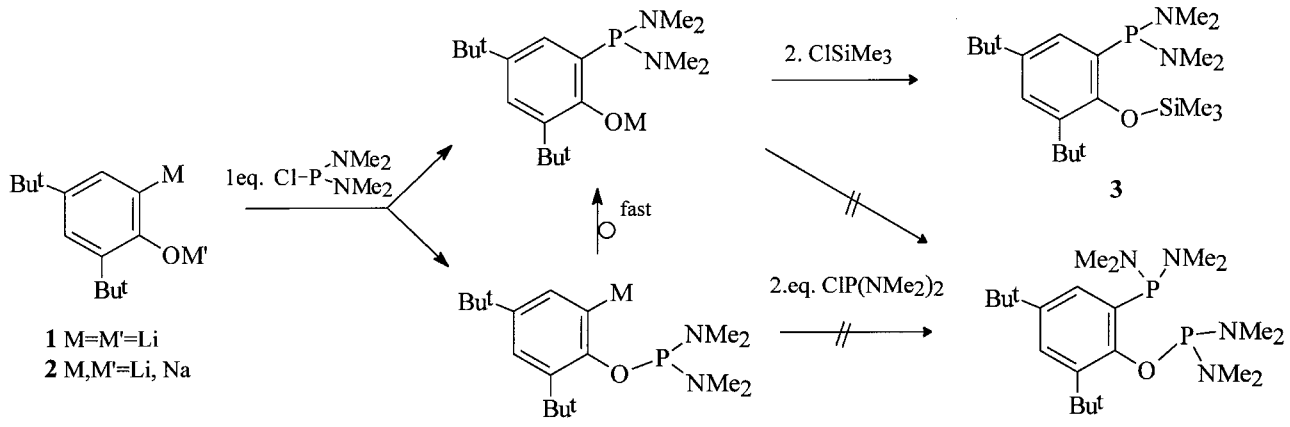
RESULTS AND DISCUSSION

Phosphinylation of Lithium and Sodium 2-Lithio-4,6-di-t-butyl-phenolate **1** *and* **2**

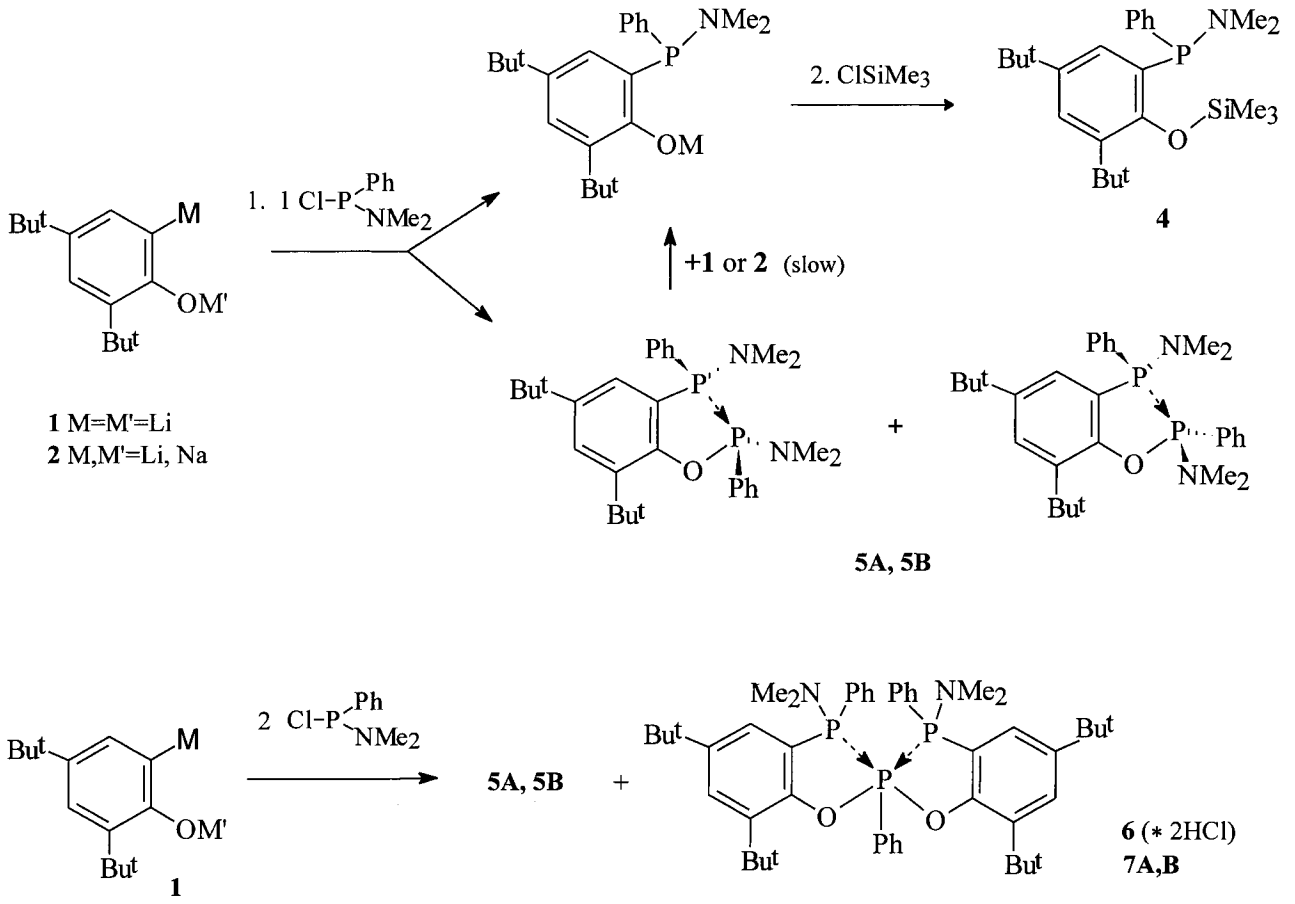
The reaction of C,O-dilithium reagents with chlorophosphines is an established route for the preparation of O-substituted *o*-hydroxy-phenylphosphonous acid amides [1c] and P-tertiary *o*-hydroxyarylphosphines [2,3]. Some limitations arise in the synthesis of 1-phosphinonaphth-2-ols from lithium-1-lithionaphth-2-olate, slightly hindered at the P-site by the rigid *peri*-CH group, and PhP(Me)Cl or PhP(*t*Bu)Cl [8]. Lithium 2-lithio-4,6-di-*t*-butyl-phenolate **1,** bearing a bulky *t*-butyl group adjacent to the oxygen atom, reacts with chlorodiphenylphosphine to give low yields (ca. 25%) of the C-monophosphinylation product; the corresponding C,O-disubstituted compound is formed preferentially. The selectivity for monosubstitution was improved (to ca. 50%) by use of the lithium-sodium reagent **2** in place of **1** [2]. The successive reaction of **1** with $ClP(NMe_2)_2$ and $ClSiMe_3$ proceeds in a more selective manner and the product of C-phosphinylation and O-silylation **3** was isolated in reasonable yields (Scheme 1). The silylation circumvents the hydrolytic workup of the aminophosphines and intermolecular condensation with the hydroxyl group. Use of **2** instead of **1** was found to be less favorable. The yield of **3** was lowered (to 22%) by metal–hydrogen exchange and other competing side reactions. Treatment of **1** or **2** with two equivalents of $ClP(NMe_2)_2$ failed to give rise to C,O-disubstitution.

In the reaction of **1** with one equivalent of $ClP(NMe_2)Ph$, followed by the addition of chlorotrimethylsilane, only a small amount of the expected *o*-trimethylsilyloxyaryl-phosphinous acid amide **4** (6%) was formed. The major reaction of **1** was C,O-diphosphinylation, yielding two pairs of diastereoisomers, mainly **5A** (46%) and some **5B.** Use of the more polar lithium-sodium reagent **2** slightly increased the amount of **4** (ca. 15%), but disubstitution remained favored, here with preference for **5B** over **5A** (ca. 30:10%). Metal–hydrogen exchange was again important (45%). The reaction of **1** with two equivalents of $ClPPhNMe_2$ provided roughly 15% of **5A** and 35% of **5B** (crude product). Additionally, ca. 40% of **6** and 10% **7A** were produced. **6** might have been formed via attack of **5A** at the P–N bond, which would explain the lower amount of **5A** compared to **5B** (Scheme 2). Treatment of the salt **6** with two equivalents of pyridine in C_6D_6 yielded a mixture of unreacted **6** (δ^{31}P: 98.7 (d), −50.7 (d), J_{PP} = 304 Hz), of **7A** (δ^{31}P: 59.3 (d), −56.9 (d), J_{PP} = 227 Hz), and of a similar compound, probably an *E*/*Z*-isomer **7B** (δ^{31}P: 63.5 (d), −53.4 (d), J_{PP} = 210 Hz). The location of the protons in **6,** at phosphorus or nitrogen, as well as the *E*/*Z*-assignment in **7A/B** cannot unambiguously be derived from the spectroscopic data.

Reaction of **2** with two equivalents of $ClP(NMe_2)_2$ or $ClP(Ph)NMe_2$ furnished neither **5** nor **6.** The ^{31}P chemical shifts are consistent with dominant metal–hydrogen exchange [$tBu_2C_6H_3OP(R)NMe_2$, R = NMe_2: $\delta(^{31}P)$ 129.8, 30%; R = Ph: $\delta(^{31}P)$ 130.1, 30% of total intensity] and formation of



SCHEME 1



SCHEME 2

2-X-4,6-tBu$_2$C$_6$H$_2$OP(R)NMe$_2$, R = NMe$_2$: δ(^{31}P) 138.8, 55%; R = Ph: δ(^{31}P) 132.5, 50%] with X = Br or Cl.

The preferred C,O-disubstitution of **1** by ClP(NMe$_2$)Ph supports our earlier assumption that the selective phosphinylation at carbon proceeded preferably via C,O-diphosphines and cleavage of the P–O bond by the second half of the dilithium reagent [1c]. The steric hindrance in **5** prevented the second step. Since the spatial demand of a dimethylamino group is larger than that of phenyl, we should expect a similar behavior toward ClP(NMe$_2$)$_2$. However, only **3** was formed. This does not contradict the above explanation, but it is an example of P-monosubstitution if the steric requirements do not allow disubstitution. We could never detect the respective C,O-diphosphine nor could it be synthesized when a molar ratio 1:2 of **1** or **2** and ClP(NMe$_2$)$_2$ was employed. An initially formed O-phosphinylated intermediate may have undergone a rapid intramolecular rearrangement to yield a less reactive, bulky phosphinophenolate. Such carbanionic rearrangements proceed rapidly and may be used to provide an alternative synthetic access to **3** and **4** via direct metallation of the respective *o*-bromoaryl esters of phosphorous (phosphonous) acid diamides with sodium [7]. This pathway was favored by the presence of the bulky 6-substituent that prevented a side reaction, the reduction at the P–O bond.

P. . .P Interactions

The compounds **5** and **6** reveal unusually large four-bond P–P coupling constants and represent a sharp contrast to 2-(Et$_2$N)$_2$PC$_6$H$_4$OP(NEt$_2$)$_2$ with $^4J_{PP} \approx 0$ Hz [1c]. The bulky *t*-butyl substituent adjacent to the oxygen atom pushes the O-phosphinyl toward the C-phosphinyl substituents. This induces large magnitudes of the P–P coupling constants, in **5A** $^4J_{PP}$ = 152 Hz, in **5B** $^4J_{PP}$ = 237 Hz, the latter being comparable to $^1J_{PP}$-values of P–P single bonds. The chemical shifts of the ^{31}P and the ^{13}C nuclei of **5A** and **5B** are very similar to each other and correspond to the ranges typical of P(C$_2$N) and P(CON) derivatives. Also, the one-bond P–C coupling constants are not increased in contrast to those in compounds of tetracoordinate phosphorus compounds. Therefore, al-

though superimposed Lewis-base Lewis-acid (empty d orbital of the phosphonite P-atom) and repulsive interactions of the lone-electron pairs cannot be excluded, the large ^4J(PP) coupling constants are most likely due to strong through-space dipolar interactions. The situation is changed in **6** [δ^{31}P($CDCl_3$) = 97.8 (σ^4 − P), −54.2 (σ^5 − P), $^4J_{PP}$ = 283 Hz] and **7A** [δ^{31}P($CDCl_3$) = 62.3 (σ^4 − P), −58.8 (σ^5 − P), J_{PP} = 233 Hz] with ^{31}P-signals and $^1J_{PC}$-coupling constants (*ipso*-C of 2-Ph) of a pentacoordinate phosphorus P-atom (spiro-bridging). The two phosphinophenol groups reveal slightly different ^{13}C signals for most of the carbon atoms while phosphorus gives an averaged signal, with small changes of the chemical shift and magnitude of $^1J_{PC1}$, compared to those of **4.** It should be mentioned that the resonance of the diphenylphosphino group in similar cyclic *o*-phosphinophenol-phosphenium salts (J_{PP} = 382 Hz) [9] also appears in the "normal" region (δ^{31}P −0.9), while the phosphenium nucleus absorbs in the region of three-coordinate phosphorus atoms. Repeated attempts to collect single crystals of **5, 6,** or **7** in order to obtain further structural information failed, unfortunately. However, the steric situation in **5** may roughly be compared to that in 2-Ph_2P-4,6-t-$Bu_2C_6H_3OSnMe_3$ ($^4J_{SnP}$ = 155/163 Hz) [2].

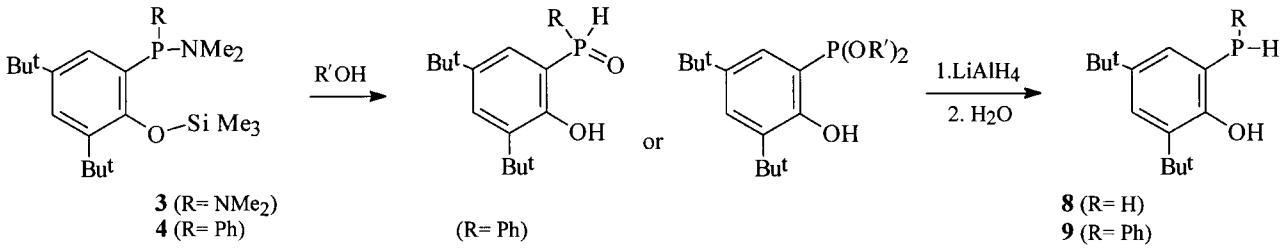
Primary and Secondary Di-t-butyl-o-phosphinophenols

4,6-Di-*t*-butyl-2-phosphino-phenol **8** and the secondary 4,6-di-*t*-butyl-2-phenylphosphinophenol **9** were obtained by alcoholysis of **3** or **4** and subsequent reduction with $LiAlH_4$ of the respective phosphonous and phosphinic acid ester (Scheme 3). The latter was isolated in one case and fully characterized.

Usually, *o*-substituted phenols, including phosphinophenols, are known to form inter- or intramolecular hydrogen bonds. The *t*-butyl group in 6-position hinders association via O. . .H–O or P. . .H–O bridging bonds, even in the solid state, and promotes intramolecular P. . .H–O interactions. Evidence is provided for the solid state by the molecular structure of 2-*t*-BuPhP-4,6-t-$Bu_2C_6H_2OH$, and for solutions by larger coupling constants $^2J_{PC}$ = 20–26 Hz involving the O-substituted C1-atom [2]. This corresponds to relatively small dihedral angles between this atom and the position ascribed to the lone electron pair at phosphorus [10]. The $^2J_{PC}$ value of the C3-atom is about 0 Hz [2]. The PH-functional di-*t*-butyl-phosphinophenols **8** and **9** unexpectedly exhibit the opposite *cis*-conformation with the lone electron pair close to C3 (**8**: $^2J_{PC3}$ = 40 Hz; **9**: $^2J_{PC3}$ = 39 Hz) and *trans* to the C1-hydroxyl group (**8**: $^2J_{PC1}$ = 2.5 Hz; **9**: $^2J_{PC1}$ = 9 Hz). A similar tendency, but strongly diminished by averaged conformations, is observed for unsubstituted 2-phosphinophenol ($^2J_{PC3}$ = 20, $^2J_{PC1}$ = 6 Hz) and 2-H_2P-4-MeC_6H_3OH ($^2J_{PC3}$ = 21, $^2J_{PC1}$ = 5 Hz) [5]. The *cis*-arrangement was found to be the lowest energy conformer in ab initio calculations at the HF/3-21 G(d) level of theory. There are no stabilizing π interactions between the lone pair of phosphorus and the aryl-π-system, as indicated also by the photoelectron spectra [11].

P–P Heterocycles

The externally directed, "open" position of the lone pair of phosphorus might be responsible for the substantially lower thermal stability of **8** and **9** compared to that of P-tertiary di-*t*-butylphosphinophenols. **8** and **9** are partially decomposed during distillation. We assume that the reaction is facilitated by traces of acids and P-protonation, which is favored by sterically forced P^+–H. . .O bridging bonds. Thus, the amount of decomposition of **8** is larger during workup with hydrochloric acid than with acetic acid. The decomposition products of **8** are di-*t*-butylphenol, the less volatile bicyclic dihydro-1,2,3-benzoxadiphosphole **10** and, probably, PH_3. Similarly, repeated distillation of **9** produced di-*t*-butylphenol, some 2,3-diphenyl-2,3-dihydro-1,2,3-benzoxadiphosphole **11,** and phenylphosphine. The mechanism is not clear; formally, it may be regarded as a phosphinidene extrusion–insertion reaction (Scheme 4).

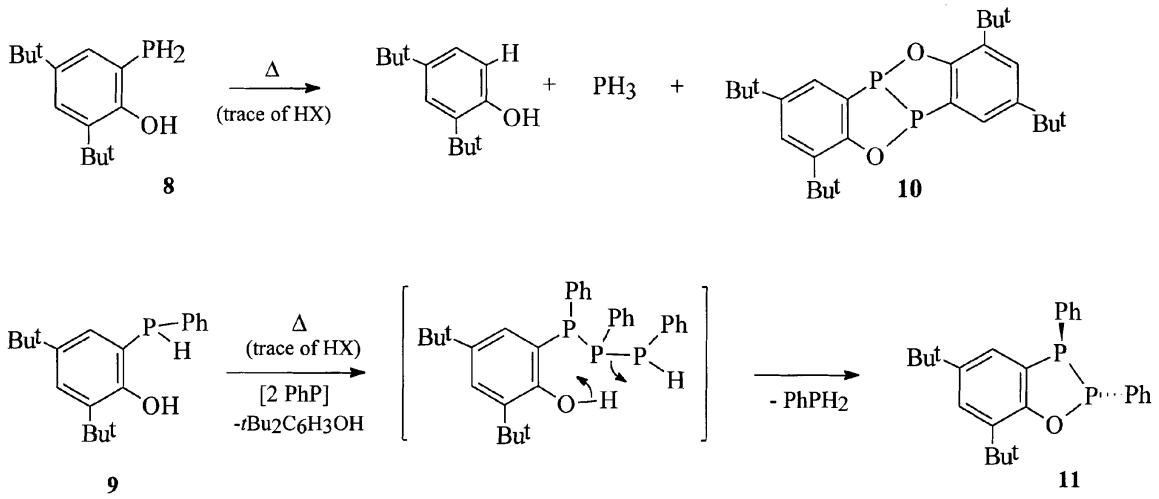


SCHEME 3

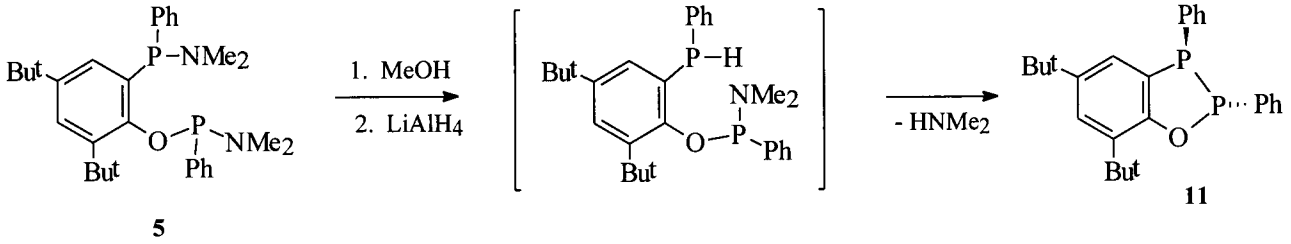
The heterocycle **11** is also formed, together with **9,** if **5A/B** is treated with two equivalents of methanol and reduced with $LiAlH_4$. The *o*-substituent preferentially methanolyzed was reduced and underwent ring closure with elimination of dimethylamine (Scheme 5). This reaction is thus related to the O-substitution and cyclization of 2-phenylphosphinocresol with $RP(NMe_2)_2$, which furnishes diastereoselectively one pair of the respective dihydrobenzoxadiphospholes with the 2- and 3-substituents in the *trans*-arrangement [5].

The analogous reaction of the primary *o*-phosphinophenol **8** with $P(NMe_2)_3$ proceeded less selectively than that of the secondary *o*-phosphinocresols. The initially formed O-substituted product **12** (J_{PP} = 155.4 Hz) underwent rapid ring closure, forced by the steric impact of the bulky 6-*t*-butyl group. The resulting dihydro-benzoxadiphosphole **13,** bearing a hydrogen atom at one P atom and an amino group at the other, is rather unstable and could not be detected if the reaction was carried out at a higher temperature (50°C). The phosphorus signals appear between the typical ranges of primary and secondary phosphines (P3, δ −94.1) or OPN_2- and OP(N)P-species (P2, δ 148.4), and the PP-coupling constant $^1J_{PP}$ = 194 Hz is much lower than in **11.** Formation of a 1,2,3-benzoxadiphosphole by elimination of Me_2NH was not observed, although this should be 10π stabilized, as are the electronically related 1,3-benzoxaphospholes [6] or 1,2,3-benzazadiphospholes [12]. We obtained evidence, however, of formation of a cyclic phosphinidene-phosphorane **14,** and the decomposition products **15** and **10** (Scheme 6). **15** (identified by NMR spectroscopy) was isolated by vacuum distillation, **10** having crystallized on addition of hexane; **14** has not yet been isolated in a pure state.

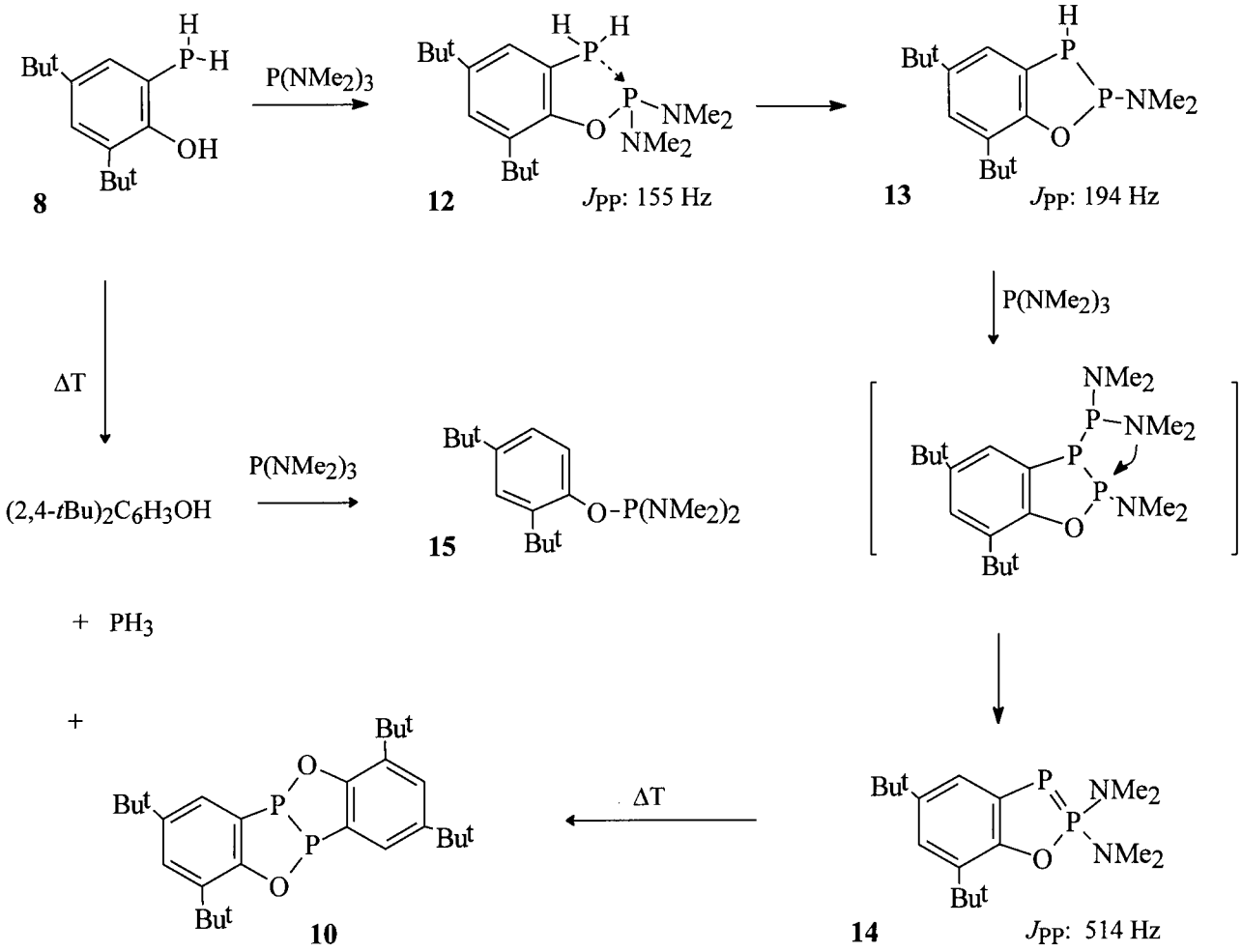
Compound **10** was identified by X-ray diffraction (Figure 1, Table 1). It is a fully eclipsed heterosubstituted diphosphine folded by 85° along the P–P axis. The two asymmetric phosphorus atoms possess the same configuration. The crystals are racemic with each two R,R- and S,S-diastereoisomers in the centrosymmetric unit cell (space group $P2_1/c$). The coordination at phosphorus is, as expected, pyramidal, with bond lengths P–P 224.73 (13), P–O 168.0, 167.7 (2), P–C 182.8, 183.0 (3) ppm. The origins of **10** and **15** are not clear. The compounds could have



SCHEME 4



SCHEME 5



SCHEME 6

been formed by decomposition of **8** (see above, **15** after reaction of di-*t*-butylphenol with $P(NMe_2)_3$), but possibly also by decomposition of **12, 13,** or **14.**

Evidence for the nature of **14** is given by the typically large PP coupling constant $^1J_{PP}$ = 525 Hz, chemical shifts for bi- and tetracoordinate phosphorus, $\delta(^{31}P)$ − 191.4 (d) and 130.4 (d) [13] and the splitting of the signals by coupling with protons. The formation of **14** can be explained by reaction of **13** with unreacted $P(NMe_2)_3$ and decomposition of the resulting amino-substituted triphosphine by migration of a dimethylamino group and extrusion of an aminophosphinidene. The assumed low stability of triaminotriphosphines is plausible in view of the slow unsymmetrical decomposition of $Ph(Me_2N)P–P(NMe_2)Ph$ at room temperature [7].

EXPERIMENTAL

All operations were performed under an argon atmosphere using the Schlenk technique and employing freshly distilled dry solvents. Me_3SiCl was recondensed before use, $ClP(NMe_2)_2$ and $ClP(Ph)NMe_2$ were prepared according to the literature [14,15]. NMR data were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 MHz (^{31}P). References are TMS for ^1H and ^{13}C, H_3PO_4 (85%) for ^{31}P spectra. $CDCl_3$ was used as solvent unless otherwise stated. Assignment numbers within the aroxy group follow the nomenclature, if not given in the formula. Mass spectra (EI, 70eV) were recorded on a single-focusing sector-field mass spectrometer AMD40 (Intectra), IR spectra on a Model System 2000 of Perkin Elmer.

3,5-Di-t-butyl-2-trimethylsilyloxy-benzenephosphonous Acid Dimethylamide **3**. A 22.0 mL solution of butyllithium (1.6 M in hexane, 35.8 mmol) was added dropwise at −30°C to a solution of 2-bromo-4,6-di-*t*-butylphenol (4.9 g, 17.2 mmol) in 30 mL of diethyl ether. Formation of **1** was completed by stirring 4 hours at 20°C; then $ClP(NMe_2)_2$ (2.7 g, 17.4

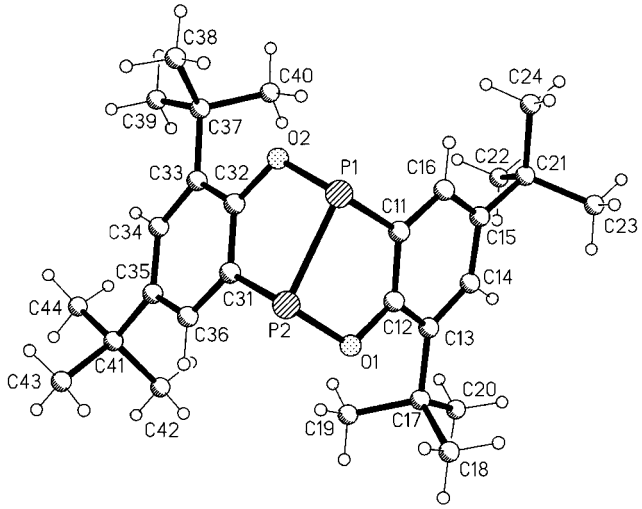


FIGURE 1 Crystal and molecular structure of **10**; selected distances [pm] and angles [°]: P1–O2 168.0(2), P2–O1 167.7(2), P1–P2 224.73(13), P1–C11 182.8(3), P2–C31 183.0(3); C11–P1–P2 87.46(10), C31–P2–P1 87.80(10), O1–P2–P1 96.39(8), O2–P1–P2 95.79(8), O2–P1–C11 100.49(12), O1–P2–C31 101.08(12).

mmol), dissolved in diethyl ether (10 mL), was added dropwise. $ClSiMe_3$ (1.9 g, 17.2 mmol) was added to the suspension after stirring overnight. The mixture was filtered, the solvent removed, and 3.6 g (53%) of colorless liquid **3** was distilled at 116°C/0.001 Torr. **3** solidified after a few days, mp 35–40°C. ^{1}H NMR: δ 0.33 (d, $^6J_{PH}$ = 1.3 Hz, 9H, $SiMe_3$), 1.30 and 1.38 (2s, 2 × 9H, 5,3-*t*Bu), 2.59 (d, J = 8.8 Hz, 12H, NMe_2), 7.22 (dd, J = 2.5, 3.8 Hz, 6-H), 7.29 (dd, J = 2.5, 1.2 Hz, 4-H). ^{13}C NMR (J_{PC} in Hz): δ 2.4 (d, J = 10.2, $SiMe_3$), 30.8 and 31.62 (C*Me*$_3$-3,5), 34.2 and 35.0 (*C*Me_3-3,5), 40.8 (d, J = 15.2, NMe_2), 124.7 (C-4), 126.5 (d, J = 6.2, C-1), 130.9 (d, J = 12.8, C-6), 139.4 (C-3), 142.2 (C-5), 153.0 (d, J = 17.6, C-2). ^{31}P NMR: δ 99.1. Anal. calcd for $C_{21}H_{41}N_2OPSi$ (396.6): C, 63.59; H, 10.42. Found: C, 63.75; H, 10.22.

Reaction of 2-Li-4,6-t$Bu_2C_6H_2OLi$ (**1**) *with Cl*P(*Ph*)*NMe_2 and Cl$SiMe_3$ Affording* **4**, **5A**. A 39.0 g (137 mmol) amount of 2-Br-4,6-*t*$Bu_2C_6H_2OH$ in 300 mL of diethyl ether was dilithiated with BuLi (180 mL 1.55 M in hexane, 279 mmol) at −50°C and stirred overnight. ClP(Ph)NMe_2 (25.7g, 137 mmol) was added dropwise at −30°C, and stirring was continued for 1 day. Then 20 mL (158 mmol) of $ClSiMe_3$ was added to the suspension at 10°C. The precipitate was filtered off, washed with ether, and the solvent removed. Crystals were deposited within 1 day and were washed with pentane (3 × 20 mL). 15.8 g (46% rel. to $ClPPhNMe_2$) of **5A** was obtained, mp 76–78°C. ^{1}H NMR: δ 1.39 (s, 9H, 5-*t*Bu), 1.67 (s, 9H, 3-*t*Bu), 2.81 (d, J_{PH} = 9.1 Hz, 6H, $CPNMe_2$), 2.84 (d, J_{PH} = 8.6, 6H, $OPNMe_2$), 7.15–7.37 (m, 9H, aryl), 7.55–7.60 (m, 3H, aryl). ^{13}C NMR: δ (J_{PC} in Hz) 31.6 and 31.7 (C*Me*$_3$-3,5), 34.4 and 35.6 (*C*Me_3-3,5), 41.4 (broad d, J = 16.6, $OPNMe_{AB}$), 42.35 (d, J = 13.4, NMe_C), 42.42 (d, J = 13.4, $CPNMe_D$), 125.1 (C-4), 127.0 (C-*p*), 127.5 (d, J = 4.2, C-*m*), 127.7 (d, J = 5.7, C-*m*), 128.2 (C-*p*), 129.0 (d, J = 22.6, C-1), 130.6 (dd, J = 18.1, 3.2, C-*o*), 130.8 (C-6), 130.9 (d, J = 17.9, C-*o*), 139.4 (dd, J = 2.4, 2.4, C-3), 141.7 (C-5), 142.2 (d, J = 10.5, C-*i*), 142.4 (d, J = 9.7, C-*i*), 157.8 (dd, J = 22.7, 7.7, C-2). ^{31}P NMR: δ 52.8 (d), 130.8 (d), $^4J_{PP}$ = 151.1 Hz. Anal. calcd for $C_{30}H_{42}N_2OP_2$ (508.6): C, 70.84; H, 8.32%. Found: C, 69.91; H, 8.51.

The ^{31}P spectra of the filtrate indicated the presence of **4** [7] and **5B** (see below). Distillative workup gave 7.1 g of 4,6-*t*$Bu_2C_6H_3OSiMe_3$ and 3.6 g (6%) of **4**, δ(^{31}P) 57.4 [7].

Alcoholysis of 3,5-Di-t-butyl-2-hydroxyphenyl-(phenyl)phosphinous Acid. The residue of the distillation described earlier (**5B**) was refluxed for 10 hours in ethanol (95%). Then EtOH was removed in vacuo, the residue extracted with toluene, the solution dried over sodium sulfate, and 2.7 g of the phosphinous acid was precipitated by addition of hexane, mp 230–232°C. ^{1}H NMR (CD_3OD): δ 1.17, 1.41 (2s, 2 × 9H, 2CMe_3), 6.92 (dd, J_{PH} = 14.7, J_{HH} = 2.6 Hz, 6-H), 7.36 (d, J_{HH} = 2.6 Hz, 4-H), 7.48–7.52 (m, 3H, *m*, *p*-Ph), 7.71–7.78 (m, 2H, *o*-Ph). ^{31}P NMR (CD_3OD): δ 23.71 (t, $^1J_{PD}$ = 76.5 Hz by proton-deuterium exchange). Anal. calcd for $C_{20}H_{27}O_2P$ (330.4): C, 72.70; H, 8.24. Found: C, 73.34; H, 9.47. MS (70 eV): m/z = 330 (29%, M^+), 315 (33%), 191 (61%), 57 (68%, Bu^+), 44 (100%).

Reaction of 2-Li-4,6-t$Bu_2C_6H_2OLi$ (**1**) *with Cl*P(*Ph*)*NMe_2 and Cl$SiMe_3$ Affording* **4** *and* **6**. **1**, obtained from 5.5 g (19.2 mmol) of 2-Br-4,6-*t*Bu_2-C_6H_2OH and BuLi (24 mL 1.6M in hexane, 38.4 mmol), was reacted at −35°C with $ClPPhNMe_2$, freshly prepared from $PhPCl_2$ (1.35 mL, 10.0 mmol) and $PhP(NMe_2)_2$ (2.05 mL, 10.1 mmol) at 60°C/2.5 hours and used without distillation. Excess $ClSiMe_3$ (4.0 mL, 31.6 mmol) was added, and the mixture was allowed to stand for a week. The solid precipitate was filtered off, leaving a heavy, viscous oil and an ethereal solution. Within 4 months, 1.6 g (20%) of cubic crystals of **6** was formed from the oil and deposited from the solution. The crystals became turbid on removing the supernatand solution, mp 177–178°C. Distillation of the solution furnished 2.3 g (28%) of slightly contamined **4**, bp 140–150°C/0.01 Torr. ^{31}P (δ 57.4) and ^{13}C NMR data of **4** are identical with a sample obtained according to Ref. [7]. **6**: ^{1}H

TABLE 1 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **10**

	x	*y*	*z*	*U*(*eq*)[a]
P(1)	4622.6 (8)	4127.0 (3)	4403.6 (7)	22.3 (2)
P(2)	6849.5 (8)	4050.8 (3)	5137.5 (7)	21.7 (2)
O(1)	7255 (2)	4689.2 (8)	4598 (2)	21.6 (5)
O(2)	4507 (2)	3575.1 (8)	3436 (2)	21.8 (5)
C(11)	4969 (3)	4745.7 (12)	3532 (3)	20.6 (6)
C(12)	6285 (3)	4934.0 (12)	3677 (2)	18.0 (6)
C(13)	6658 (3)	5358.9 (12)	2961 (2)	20.0 (6)
C(14)	5594 (3)	5600.7 (12)	2123 (3)	21.6 (7)
C(15)	4246 (3)	5443.8 (12)	1968 (3)	23.0 (7)
C(16)	3957 (3)	5011.0 (12)	2681 (3)	23.4 (7)
C(17)	8122 (3)	5545.7 (13)	3088 (3)	23.0 (7)
C(18)	8641 (3)	5857.6 (14)	4261 (3)	37.5 (9)
C(19)	9004 (3)	5008.6 (14)	3018 (3)	33.2 (8)
C(20)	8266 (3)	5974.0 (14)	2125 (3)	32.4 (8)
C(21)	3169 (3)	5745.2 (14)	1002 (3)	28.6 (7)
C(22)	3455 (4)	5633 (2)	−179 (3)	41.9 (9)
C(23)	3200 (4)	6411 (2)	1237 (4)	49.5 (11)
C(24)	1768 (4)	5520 (2)	981 (4)	55.4 (12)
C(31)	6887 (3)	3547.0 (12)	3936 (2)	19.5 (6)
C(32)	5682 (3)	3374.1 (11)	3195 (2)	17.5 (6)
C(33)	5640 (3)	2997.1 (12)	2247 (2)	18.0 (6)
C(34)	6874 (3)	2820.2 (12)	2081 (2)	20.9 (7)
C(35)	8111 (3)	2989.6 (12)	2796 (2)	18.9 (6)
C(36)	8083 (3)	3350.5 (12)	3742 (3)	21.5 (7)
C(37)	4308 (3)	2787.4 (12)	1440 (3)	22.1 (7)
C(38)	3491 (3)	2456.1 (13)	2158 (3)	29.2 (8)
C(39)	4540 (3)	2366 (2)	500 (3)	36.0 (9)
C(40)	3509 (3)	3317.7 (14)	826 (3)	32.5 (8)
C(41)	9448 (3)	2804.9 (13)	2558 (3)	23.2 (7)
C(42)	10153 (3)	3352.2 (15)	2227 (3)	41.2 (9)
C(43)	10355 (3)	2519 (2)	3648 (3)	33.1 (8)
C(44)	9275 (3)	2361 (2)	1558 (3)	37.6 (9)

[a]Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

NMR (CH-COSY): δ 1.39, 1.52 (2s, 2 × 9H, 5,3-*t*Bu), 2.68 (s, br, 3H, NMe_2-*a*), 3.00 (d, J_{PH} = 10.3 Hz, 3H, NMe_2-*b*), 3.18 (d, J_{PH} = 12.0 Hz, 6H, NMe_2'), 7.08 (m, 8 *o,m*-HH′, Ph-P^{III}), 7.20 (m, 2 *p*-HH′, Ph-P^{III}), 7.44 (m, $J_{PH} \approx 5$, J_{HH} = 7–8 Hz, 2 *m*-H, Ph-P^{V}), 7.63 (m, 1 *p*-H, Ph-P^{V}), 7.63 (d, *J* = 2.1 Hz, 1H, 6-H), 7.66 (d, *J* = 2.1 Hz, 1H, 6′-H), 7.70 (d, J_{HH} = 2.1 Hz, 2H, 4-H, 4′-H), 7.87 (m, J_{PH} = 13.4, J_{HH} = 7–7.5, 1 Hz, 2 *o*-H, Ph-P^{V}). ^{13}C NMR: δ 29.6 (*C*Me_3-3), 31.3 (*C*Me_3-5), 35.04 and 35.30 (C*Me*$_3$), 34.8 (*a*-NMe_2), 38.3 (br, *b*-NMe_2), 40.1 (d, *J* = 6.2 Hz, NMe_2'); 1Ph(P^{V}): 115.3 (dd, *J* = 124.9, 2.8 Hz, C-*i*), 129.7 (d, *J* = 14.9 Hz, C-*m*), 134.4 (d, *J* = 11.4 Hz, C-*o*), 135.8 (d, *J* = 3.4 Hz, C-*p*); 2Ph(P^{III}): 137.5 (d, *J* = 8.2 Hz, 2C-*i*), 129.3 (d, *J* = 6.4 Hz, C-*m*), 129.35 (d, *J* = 6.3 Hz, C-*m*′), 130.86 (C-*p*), 130.93 (C-*p*′), 133.46 (d, *J* = 18.6 Hz, C-*o*), 133.54 (d, *J* = 18.6 Hz, C-*o*′), 2aryl: 118.9 (dd, *J* = 21.7, 7.1 Hz, C_q-1), 124.6 (dd, *J* = 26.6, 3.0 Hz, C_q-1′), 128.2 (d, *J* = 15.4 Hz, C-6), 128.6 (d, *J* = 15.7 Hz, C-6′), 129.1 (s, 2C-4), 149.4 (dd, *J* = 8.9, 1.9 Hz, C-2), and 152.9 (dd, *J* = 5.2, 1.9 Hz, C-2′), 135.0 (br) and ca. 139.3 (uncertain because of low intens.) (C_q3, C_q5); assignment supported by CH-COSY and DEPT135. ^{31}P NMR: δ 97.8 (d), −54.2 (d), intensity ratio 2:1, J_{PP} = 283.1 Hz. Anal. calcd for $C_{50}H_{67}N_2O_2P_3$2HCl (893.94): C, 67.18; H, 7.67; Cl, 7.93; N, 3.13. Found: C, 60.8 (incomplete combustion); H, 7.65; Cl, 7.40; N, 3.15.

Reaction of 2-Li-4,6-t$Bu_2C_6H_2$OLi with 2 ClP(Ph)NMe_2 and Isolation of **5B**. **1** was prepared from 5.2 g (18.3 mmol) of 2-Br-4,6-*t*$Bu_2C_6H_2$OH and BuLi (23 mL 1.6M in hexane, 36.6 mmol), with $ClPPhNMe_2$ (7.5 g, 40 mmol) being added at −35°C. The suspension was stirred for 1 day, filtered, and the solvent removed from the filtrate to leave a viscous yellow oil with roughly 36% **5B,** 38% **6,** 18% **5A,** and 8% **7A** (based on ^{31}P intensities of C*P*N signals). **5B** is extracted with pentane and crystallizes at −20°C (1.0 g, 10%, mp 118–120°C). The residue is

dissolved in toluene. 1.8 g of **6** [$\delta(^{31}P)$: 98.1 (d), −53.1 (d), J_{PP} = 286.7 Hz)], slightly contaminated by **7A** [$\delta(^{31}P)$: 62.3 (d), −58.8 (d), J_{PP} = 233.3 Hz)], crystallizes at −20°C. **5A** [$\delta(^{31}P)$: 52.7 (d), 130.5 (d), J_{PP} = 151.5 Hz)] remains in the mother liquor: **5B** ^{31}P NMR: δ 49.2 (d), 132.5 (d), J_{PP} = 237.9 Hz. ^{1}H NMR: δ 1.23 (s, 9H, 5-*t*Bu), 1.50 (s, 9H, 3-*t*Bu), 2.43 (d, J_{PH} = 9.2 Hz, 6H, $CPNMe_2$), 2.63 (br.d, J_{PH} = 8.4 Hz, 6H, $OPNMe_2$), 7.09 ("t", $|J + J'|$ = 5.3 Hz, 1H, 6-H), 7.2–7.38 (m, 8H, Ph), 7.41 (d, J_{HH} = 2.5 Hz, 1H, 4-H), 7.61 (m, 2H, *m*-H). ^{13}C NMR: δ (J_{PC} in Hz) 30.3 and 31.5 (CMe_3–), 34.3 and 35.5 (CMe_3), 41.3 (very broad, $OPNMe_{AB}$), 41.79 (d, J = 15.3, NMe_C), 41.83 (d, J = 15.3, $CPNMe_D$), 125.2 (C-4), 126.9 (d, 1.4, C-*p*), 127.4 (d, J = 3.5, C-*m*), 127.5 (d, J = 5.7, C-*m*), 128.2 (C-*p*), 128.7 (dd, J = 27.9, 1.3, C_q-1), 130.0 (C-6), 131.1 (dd, J = 17.2, J = 3.2, C-*o*), 131.5 (dd, J = 14.7, 2.6, C-*o*), 139.1 (dd, J = 3.3, 1.5, C_q-3), 141.1 (dd, J = 5.5, 1.0, C_q-*i*), 142.0 (d, J = 4.3, 0.9, C_q-*i*), 142.7 (C-5), 158.3 (dd, J = 24.0, 6.8, C_q-2). Anal. calcd for $C_{30}H_{42}N_2OP_2$ (508.6): C, 70.84; H, 8.32. Found: C, 70.25; H, 8.15.

Reactions of 2-M-4,6-t$Bu_2C_6H_2OM'$ (**2**) (*M,M' = NaLi*) *with ClP* (*Ph*)NMe_2 *and* $ClSiMe_3$ *Affording* **4,5**. A 5.50 g (19.3 mmol) amount of 2-Br-4,6-*t*-$Bu_2C_6H_2OH$ was dissolved in ether (150 mL) and stirred with 0.45 g of NaH (19 mmol) 2d to complete the reaction. A 12 mL amount of BuLi (1.6 M in hexane, 19.7 mmol) was added. The suspension was stirred for 24 hours, then a solution of 3.70 g (19.7 mmol) $ClP(Ph)NMe_2$ in ether (15 mL) was added at −40°C. After the mixture had been stirred for 4 hours, $ClSiMe_3$ (2.10 g, 19.3 mmol) was added. The suspension was filtered after 1 hour, the solvent removed, and the ^{31}P and ^{1}H spectra of the residual orange viscous oil were recorded. Observed intensity ratio [based on the P(ONC) signals]: **4** (15%), **5A** (10%), **5B** (30%), 2,4-t$BuC_6H_3OP(Ph)NMe_2$ (45%). The reactions with $ClP(NMe_2)_2$ and $ClSiMe_3$ or with two equivalents of $ClP(NMe_2)_2$ were carried out analogously; for results, see text.

4,6-Di-t-butyl-2-phosphinophenol **8** *and Dibenzo[c,g]-2,6-dioxa-1,5-diphospha-bicyclo-[3,3,0]-octane* **10**. A 32.2 g (81 mmol) amount of **3** was heated with excess methanol (11 mL) to 50°C, for 3 hours at 760 Torr and then for 1 hour at 10^{-2} Torr. The residue was dissolved in ether (100 mL) and added dropwise to 4 g (105 mmol) of $LiAlH_4$ in ether (50 mL). The suspension was stirred for 2 days and hydrolyzed with dilute sulfuric acid, and the organic extracts were washed with water and dried over Na_2SO_4. Benzene was added, and the solvent was distilled off at 760 Torr and the residue at 74–76°C/0.005 Torr to give 13.5 g of a mixture of **8** and 2,4-di-*t*-butylphenol (ca. 3:1). Repeated distillation improved the ratio to 85:15%. **8** was found to decompose slowly, and more rapidly on heating. The solid residue of the distillation was crystallized from benzene to give 1.5 g of **10,** $\delta(^{31}P)$ 126.9, slightly soluble in acetone, $CHCl_3$ or MeOH, well soluble in toluene. For the molecular structure of **10,** see Figure 1 and Table 1, for NMR data *vida infra*. **8** ^{1}H NMR: δ 1.27 (s, 4-*t*Bu), 1.42 (s, 6-*t*Bu), 3.67 (d, J_{PH} = 204.5 Hz, PH_2), 7.38 (m, J_{HH} = 2.5, J_{PH} = 2.1 Hz, 5-H), 7.21 (m, J_{HH} = 2.1, J_{PH} = 11.5 Hz, 3-H). ^{13}C NMR: $\delta(J_{PC}$ in Hz) 29.8, 31.5 (CMe_3-4,6), 34.2, 35.0 (CMe_3-4,6), 111.4 (d, 8.4, C-2), 123.8 (d, 40, C-3), 132.3 (d, 31, C-5), 135.2 (C-6), 142.5 (d, 10.6, C-4), 154.5 (d, 2.5, C-1). ^{31}P NMR: δ-159.6. Mol. mass calcd for $C_{14}H_{23}OP$: 238.15. Found: MS (70 eV): *m/z* = 239 (40%, M + H^+).

4,6-Di-t-butyl-2-phenylphosphino-phenol **9**. A 20.0 g (46.5 mmol) amount of **4** [7] was treated with excess methanol (10 mL) and, after removal of volatile components, reduced as described earlier with 3.0 g of $LiAlH_4$ in ethereal solution. Distillation furnished 9 g of a fraction at 125–130°C/0.005 Torr consisting of ca. 2/3 of **9** (40% yield) and 1/3 of 2,4-di-*t*-butylphenol. $PhPH_2$ [$\delta(^{31}P)$ − 122] was detected in the cold trap, **11** [$\delta(^{31}P)$ − 11.3 (d), 139.8 (d), J_{PP} = 229 Hz)] in the residue. **9** ^{1}H NMR: δ 1.27 (s, 4-*t*Bu), 1.40 (s, 6-*t*Bu), 5.13 (d, J_{PH} = 228 Hz, PH), 7.07 (m, J_{HH} = 8.2, 2.1, 0.6 Hz, 5-H), 7.21 (dd, J_{HH} = 2.1, J_{PH} = 8.5 Hz, 3-H) 7.0–7.3 (m, 3H, Ph), 7.33–7.4 (m, 2H, Ph). ^{13}C NMR: $\delta(J_{PC}$ in Hz) 29.4, 31.5 (CMe_3-4,6), 34.4, 35.1 (CMe_3-4,6), 116.8 (d, 7, C-2), 123.7 (d, 39, C-3), 128.4 (C-*p*), 128.8 (d, 5, C-*m*), 131.7 (d, 20, C-5), 132.4 (d, 15, C-*o*), 133.0 (d, 6, C-*i*), 135.7 (C-6), 142.5 (d, 8, C-4), 155.2 (d, 9, C-1). ^{31}P NMR: δ −67.2. Mol. mass calcd for $C_{20}H_{27}OP$ (314.18). MS (70 eV): *m/z* = 314 (66%, M^+), 299 (40%, M^+ − 15), 224 (45%), 212 (65%), 200 (100%), 57 (98%).

4,6-Di-t-butyl-2-phenylphosphino-phenol **9** *and 5,7-Di- t-butyl-2,3-diphenyl-2,3-dihydro-1,2,3-benzoxadiphosphole* **11**. A 9.7 g (19 mmol) amount of **5** was treated with 2 mL of absolute methanol, reduced with $LiAlH_4$ and worked up as described earlier. A 4.3 g (54%) amount of a viscous liquid was obtained at bp 180–184°C/0.01 Torr, consisting of **9** (1/3) and **11** (2/3). ^{1}H NMR: δ 1.29 (s, 4-*t*Bu), 1.50 (s, 6-*t*Bu), 7.0–7.5 (m, aryl). ^{31}P NMR: δ −11.5 (d), 139.9 (d), J_{PP} = 229 Hz. Mol. mass calcd for $C_{26}H_{30}OP_2$ (420.47). MS (70 eV): *m/z* = 420 (70%, M^+), 73 (100%).

Reaction of 4,6-di-t-butyl-2-phosphinophenol **8** *with* $P(NMe_2)_3$. A solution of 2.2 g (9.2 mmol) of **8**

and 1.65 g (10.1 mmol) of $P(NMe_2)_3$ in 20 mL of toluene was stirred at 20°C. After 1 day and 3 days NMR spectral data were recorded by $^{31}P\{^1H\}$ and proton-coupled ^{31}P NMR. The condensation products **12, 13, 14,** and **10** and the decomposition product **15** could be identified. The content of **12** and **13** decreased, and that of **14** and **10** increased, from the first to the third day. (**12** and **13** could not be detected if the reaction was performed with heating.) Finally, the mixture was distilled affording ca. 0.20 g of **15** (120–122°C/0.01 Torr) and 0.85 g of a mixture of mainly **10** and some **14** at 150–180°C/0.01 Torr. Pure bicyclic diphosphine **10** (0.2 g) crystallized on addition of hexane, mp 212–214°C. **10**: ^1H NMR: δ 1.259, 1.262 (2s, 18H, 2*t*Bu), 7.26 (d, J_{HH} = 2.2 Hz, 6-H), 7.78 (d″t″, J_{HH} = 2.2, $|J_{PH} + J_P''H|$ = 6.8 Hz, 4-H). ^{13}C NMR (CD_2Cl_2): δ (AA′X, $|J_{PC} + J_P'C|$ in Hz) = 29.4 (CMe_3), 31.6 (CMe_3), 34.7 (CMe_3), 35.3 (CMe_3), 127.7 (C-6), 128.1 ("t," 31.6, C-4), 128.7 ("t," 42.3, C-3a), 137.2 (C-5), 145.3 ("t," 7.0, C-7), 158.9 ("t," 12.8, C-7a). ^{31}P NMR: δ 126.2 ("t," $|J_{PH} + J_P''H|$ = 6.8 Hz). Anal. calcd for $C_{28}H_{40}O_2P_2$ (470.57): C, 71.47; H, 8.57. Found: C, 70.0; H, 8.82. MS (70 eV): *m/z* = 470 (50%, M^+), 455 (100%), 399 (18%), 220 (24%), 57 (43%). **12.** ^{31}P NMR: δ −120.2 (dtd, J_{PP} = 155.4, J_{PH} = 204, J_{HH} = 5.7 Hz), 135.4 (d, m, J_{PP} = 155.4, J_{HH} not determ.). ^1H NMR: δ 2.65 (d, J_{PH} = 8.6 Hz, NMe_2), 4.03 (dd, J_{PH} = 206, $^5J_{PH}$ = 24.3 Hz). **13.** ^{31}P NMR: δ −94.1 (ddd, J_{PP} = 194, J_{HH} = 200, J_{HH4} = 7.5 Hz), 148.4 (dsept, J_{PP} = 194 Hz, J_{PH} = 9–10 Hz). **14.** ^{31}P NMR (C_6D_6): δ − 191.4 (dd, J_{PP} = 525, J_{PH} = 6 Hz), 130.4 (dsept, J_{PP} = 525, J_{PH} = 12 Hz). ^1H NMR: δ 2.34 (d, J_{PH} = 12 Hz, $PNMe_2$). **15.** ^{31}P NMR (C_6D_6): δ 129.9 (J_{PH} = 9 Hz, $PNMe_2$). ^1H NMR: δ = 2.58 (d, J_{PH} = 9.3 Hz).

X-ray Structure Determination of Compound **10**

Crystal Data. $C_{28}H_{40}O_2P_2$, M_r = 470.54, monoclinic, space group $P2_1/c$, a = 1027.9 (2), b = 2271.3 (4), c = 1180.4 (2) pm, β = 104.15 (2) °, V = 2.6721 nm^3, Z = 4, D_x = 1.170 Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 0.18 mm^{-1}, T = −100°C.

Data Collection and Reduction. A colorless prism 0.9 × 0.3 × 0.2 mm was mounted in inert oil. Data were collected to $2\theta_{max}$ 50° on a Siemens P4 diffractometer. Of 4733 measured data, 4669 were unique.

Structure Solution and Refinement. The structure was solved by direct methods and refined anisotropically on F^2 using all reflections (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or rigid methyl groups. The final *wR* (F^2) was 0.130 for 301 parameters, conventional *R*(*F*) 0.049. S = 0.97; max. $\Delta/\sigma < 0.001$; max. $\Delta\rho$ 432 e nm^{-3}.

Complete data of the X-ray structure analyses were deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. This material can be ordered on quoting the deposition number CSD-407302 (**10**) and the complete literature reference.

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