P/O Ligand Systems: Synthesis, Reactivity, and Structure of Tertiary *o*-Phosphanylphenol Derivatives

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Reactions of C,O-dilithium reagents **1** (M = M′ = Li) or C,O-lithium-sodium reagents **1** (M = Li, M′ = Na) with chlorophosphanes afford C,O-disubstitution products **2** or phosphanylphenolates **3** which are treated subsequently with $ClSiMe_3$ to give 4-methyl- and bulky 4,6-di-*tert*-butyl substituted *o*-phosphanylphenol silyl ethers **4**. These were applied for the preparation of the corresponding *o*-phosphanylphenols **5**, mainly P-asymmetric derivatives. Limitations and side reactions by use of **1** in the above synthesis are discussed. Acid-base properties, pH-dependent solubility in water/hexane, and substitution reactions at oxygen and phosphorus of selected representatives of **5** are reported. An example for the separation of enantiomers by esterification with (1*S*)-(−)-camphanic acid chloride is given. IR studies revealed intramolecular P···H−O bonds and ^2J(PC) the preferred *trans* arrangement of the phenoxy group in solution. In the solid state, inter- and intramolecular P···H−O bonds were detected by X-ray structure analysis. The *trans* arrangement of the phenoxy group is preserved. Because of steric hindrance, the O substituents are tilted towards the phosphorus atom and thus induce large through-space coupling constants. The P···Sn distance of 336.9 pm in the bulky substituted O−$SnMe_3$ moiety **8h** is however too large for the formation of genuine intramolecular coordination. The versatility of *o*-hydroxyarylphosphanes and objectives of further studies are shown by preliminary results on complex formation and applications of these phosphanes in catalysis.

o-Phosphanylphenols are bidentate molecules that are expected to undergo a variety of reactions at either or both nucleophilic sites, the hard oxygen or the soft phosphorus atom. Their electronic and steric properties may widely be varied by a suitable set of substituents at the phosphorus atom and at the aromatic ring. As recently pointed out, this should allow tuning of ligand properties in catalytical applications of the P/O^- ligands[1,2]. Furthermore, P-asymmetric, potentially chiral ligands may be constructed. Until now, however, only a few *o*-phosphanyl-phenols have been synthesized in the course of complex chemical investigations[3−7] and there are no reports on their structure and reactivity except for diphenylphosphanylphenol. The latter forms a trimethylsilyl ether and several *O*-phosphanyl and *O*-phosphonium derivatives[7,8]. The phosphonium cation contains three aryl groups with a propeller-like arrangement[7]. *o*-Di-*tert*-butylphosphanylphenyl and *o*-diphenylphosphanylphenol were first obtained by cleavage of the corresponding methyl and propyl ether, respectively, with boiling concentrated hydrobromic or hydroiodic acid[3]. Alternatively, these compounds were prepared by treatment with BBr_3 and subsequent methanolysis[6]. To avoid P−C cleavage, the methoxymethyl protecting group was introduced for the synthesis of *o*-diphenylphosphanylphenol[4]. It can be removed under milder acid conditions. Several *O*-trimethylsilyl-protected derivatives **4** were obtained by metalation of *o*-haloaryloxyphosphanes, inducing a rapid carbanionic O → C rearrangement, and subsequent silylation of the resulting *o*-phosphanylphenolates **3** (Scheme 1). This method is advantageous for the synthesis of bis(dialkylamino)- or other bulkily substituted *o*-phosphanylphenolates. It is of limited value, however, in the preparation of diaryl, arylalkyl, or less sterically protected (at OPR_2) derivatives, since the corresponding phosphinite precursors are preferentially attacked by sodium at the P−O bond and reduced to phosphides or diphosphanes[9]. Metalation with lithium prevents the reduction but the rate of this reaction is very slow.

In this paper we describe the synthesis of **4** from C,O-dilithium **1** (M = M′ = Li) or C,O-lithium-sodium reagents **1** (M = Li, M′ = Na), some limitations of this alternative method and the alcoholysis affording the title compounds **5**. Furthermore, we study the reactivity at oxygen and phosphorus, including the possibility of separating enantiomers, and structural peculiarities of *o*-phosphanylphenols with bulky substituents. Chemical investigations of the corresponding complexes will be reported separately[10].

Syntheses

C,O-Dilithium reagents are easily available from the corresponding bromophenols by reaction with two equivalents of butyllithium[11] or by treatment with LiH (2−3 d) and

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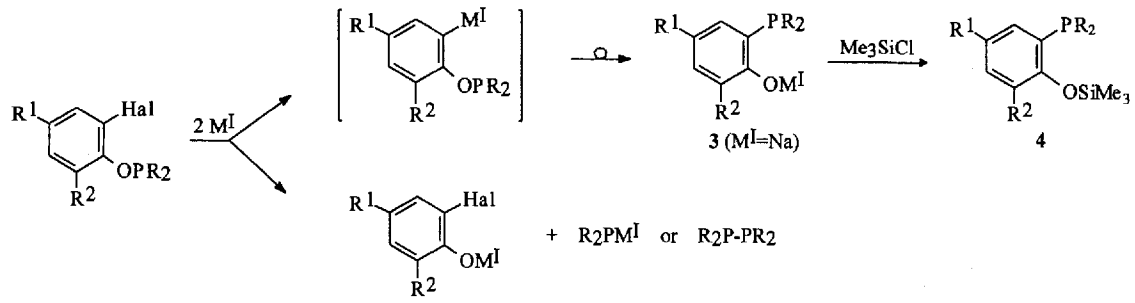
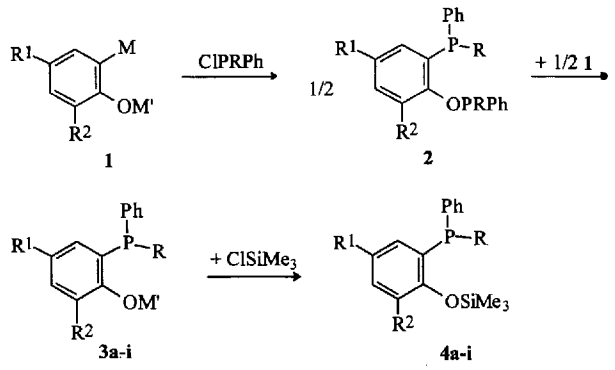
Scheme 1



subsequently with butyllithium. They are partly dissolved and partly suspended in ether and could not yet be obtained in a crystalline form for structural investigations. In the absence of any steric hindrance, **1** (M = M′ = Li) undergo regio-selective monosubstitution by treatment with equimolar amounts of halophosphanes at the carbon atom to afford the corresponding phosphanylphenolates **3** (Scheme 2). Subsequent reaction with $ClSiMe_3$ gives the silyl ethers **4** in reasonable or good yields (R = alkyl 50–70%, R = Ph up to 90%). Best results were obtained with runs of about 50–100 mmol of **1**, whereas in larger scale preparations (>0.2 mol) yields were lower.

Considerably smaller amounts of **4** were obtained with sterically hindered dilithium reagents **1** ($R^1 = R^2 = t$Bu). This is at least partly due to several side reactions, depending on the type of the chlorophosphane. Chlorodiphenylphosphane, less bulky and without α-CH, reacts with **1** ($R^1 = R^2 = t$Bu) to give some sparingly soluble C,O-disubstitution product **2h** (14–22% based on **1**), a small amount of *o*-hydrogenated 4,6-tBu$_2$C$_6$H$_3$OSiMe$_3$ and the *o*-phosphanylphenolate **3h**, the reaction of which with $ClSiMe_3$ furnishes **4h**.

Scheme 2



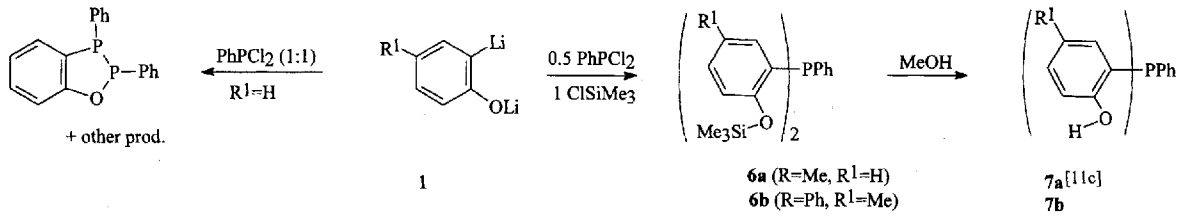
2-4	a	b	c	d	e	f	g	h	i
R	Me	iPr	tBu	tBu	Ph	iPr	tBu	Ph	NMe_2
R^1	Me	Me	H	Me	Me	tBu	tBu	tBu	Me
R^2	H	H	H	H	H	tBu	tBu	tBu	H

The phosphanylphosphinites **2** might, because of a "Schlosser-base"-like nature[12] of **1**, generally be formed preferentially as primary products in substitution reactions of C,O-dilithium species with chlorophosphanes. A similar preference for disubstitution was observed in reactions of C,N-dilithium reagents with one equivalent of chlorophosphane[11a]. The P–O bond in **2** is however easily cleaved by unreacted **1**, provided it is not sterically overcrowded and **2** sufficiently soluble. It then ensures a high regioselectivity of monosubstitution at the carbon atom (Scheme 2). Besides the C,O-disubstitution, there may also be some other side reactions favored by steric factors. Thus, the low yield of the di-*tert*-butyl-substituted isopropylphosphanyl derivatives **4f** (or **5f**) is probably caused by a competing base-induced elimination of HCl in the reaction of the sterically demanding dilithium reagent **1** ($R^1 = R^2 = t$Bu) with PhP(Cl)–$CHMe_2$, which could account for a number of by-products. The unsatisfactory results in the reaction of **1** ($R^1 = R^2 = t$Bu) with the bulky PhP(Cl)–CMe_3 affording **4g** are mainly due to accompanying metal/halogen exchange producing *meso*- and *rac*-(tBuPhP)$_2$ [$\delta(^{31}P) = -3.7$ and 2.9, intensity ≥80:20% in the crude product][9b] via intermediate PhP(Li)CMe_3.

Reaction of **1** with 0.5 equivalents of $RPCl_2$ and subsequently with 1 equivalent of chlorotrimethylsilane (Scheme 3) gave unexpectedly low yields of **6**. Attempts at ring closure by disubstitution reaction of phosphanylbis(phenolates) with Cl_2SiMe_2 failed completely, whereas similar bis(*o*-phenolato)silanes and R_nECl_2 (E = As, P, Si) undergo cyclization to eight-membered heterocycles in fair yields (30–80%)[13]. The reaction of equimolar amounts of **1** ($R^1 = R^2 = H$) with dichlorophenylphosphane furnishes a mixture of products containing considerable amounts of two diphosphanes with $\delta(^{31}P) = -57.7$ (d), 61.8 (d), J_{PP} = 233.6 Hz and $\delta = -10.0$ (d), 137.9 (d), J_{PP} = 231.6 Hz. The latter is consistent with a benzoxadiphosphole[14]. This provides evidence for lithium/chlorine exchange as an accompanying process in reactions of **1** with dichlorophosphanes.

In the search for a possibility to overcome the problems caused by bulkier substituents we also used mixed C,O-dimetalated reagents[2] instead of dilithium species **1**. Neutralization of the phenolic hydroxyl group with sodium hydride proceeds faster than with LiH. It saves one equivalent of butyllithium in the subsequent metal/halogen exchange and also increases the reactivity of the bulky 4,6-di-*tert*-butyl-substituted C,O-dimetalated species **1** (M = Li, M′ = Na) towards chlorophosphanes and improves the yield of **5h** [compared to the use of **1** (M = Li, M′ = Li)]. Formation of **2h** is not completely suppressed but metal/halogen

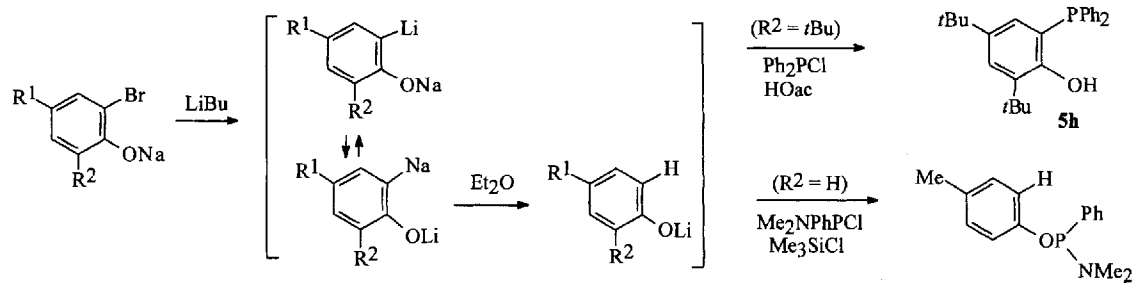
Scheme 3



exchange and ether cleavage, even after a metalation time of 20 h, were found to be unimportant in this case. Dimetalation of non-bulky bromocresol with NaH and BuLi demands, however, optimized reaction conditions since the resulting C,O-lithium-sodium reagent reacts with ether much faster than the C,O-dilithium species. Thus, after 12 h the *o*-position was completely protonated and phenylphosphonous acid *p*-cresyl ester dimethylamide obtained in high yield (66%) in place of **4f** if sodium 2-bromocresolate was treated with BuLi (for 12 h) and then with $Me_2NPhPCl$ (Scheme 4).

Phosphanylaryl silyl ethers **4** and **6** are in most cases rapidly cleaved by gentle heating with an excess of absolute methanol and somewhat less easily with ethanol affording phosphanyl phenols **5** or **7** (Scheme 5). Several products crystallize directly on cooling from the MeOH or EtOH solution. Other derivatives were isolated by evaporation of $ROSiMe_3$ and excess alcohol and recrystallization of the residue, e.g. from toluene/hexane or petroleum ether. **5e** was found to form a monoadduct with methanol. The alcoholysis of the *ortho*-substituted **4** might be assisted by weak P···H–O^{Alk}···Si interactions. Lower basicity at phosphorus (triaryl derivatives) combined with an unfavorable conformation caused by steric strain (see below) may hinder the alcoholysis. Thus, **4h** (or **2h**) can be recrystallized from ethanol and cleaved markedly only in the presence of acid catalysts such as Nafion or by glacial acetic acid. The much easier methanolysis of the more bulkily substituted **4f** and **4g** with a similar orientation of the silyl group is probably due to the increased basicity at the P atom, allowing interactions even in less favorable arrangements.

Scheme 4



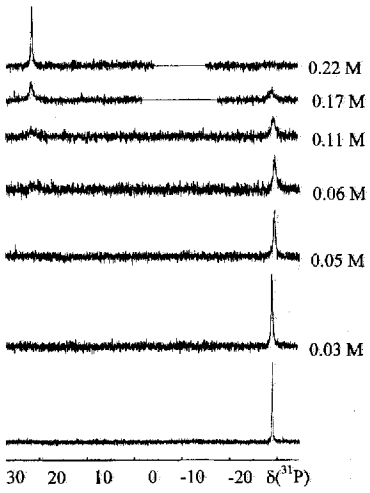
Since the silyl ethers **4** may be much more easily separated from impurities or by-products than the high-boiling tertiary *o*-phosphanylphenols, the synthesis of **5** by alcoholysis of **4** is usually more convenient than the direct work-up by acidifying phosphanylphenolates **3**. Acidification by dilute aqueous solutions of hydrochloric acid needs pH control (pH ≈ 3) to assure complete conversion of the phenolates **3** and to avoid formation of phosphonium salts. Use of excess (10–20%) of anhydrous acetic acid is more favorable; phosphonium acetates formed with the excess acid decompose on slight warming in vacuum (10^{-2} Torr). But even then the isolation may be laborious since several products, especially P-asymmetric **5**, have a low tendency to crystallize from the dried ethereal extracts in the presence of impurities.

Properties and Reactivity of *o*-Phosphanylphenols

The acidity of the phenolic OH and the basicity of the phosphanyl group are not sufficient to give rise to appreciable amounts of the tautomeric phosphonium phenolates. Sharp NMR signals are observed for dilute solutions of pure **5** in C_6D_6 or CS_2. Increasing concentration induces a slight broadening and a downfield shift of the ^{31}P signal (**5d**; 2, 10, 18% in C_6D_6: δ = −18.3, −17.9, −17.6). Addition of acids causes however much stronger broadening of the ^{31}P signals. Depending on the rate of proton exchange, we observe either averaged signals of phosphanes and the corresponding phosphonium salts, e.g. for *tert*-butylphenylphosphanylnaphthol[15], or two separate signals for the hydroxyarylphosphanes and the corresponding phosphonium salts. Thus, solution of **5d** (54 mg, 0.2 mmol) in 1.0 ml of calibrated solutions of HCl in $CDCl_3$ reveal at 25 °C two signals with line shapes indicating two-site exchange between phosphane and phosphonium species (Figure 1).

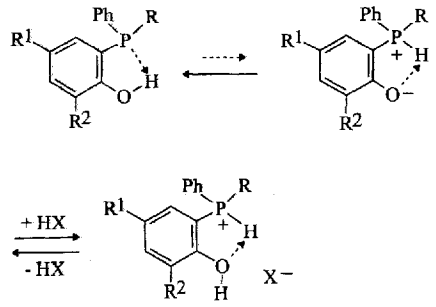
If one assumes that the line width of the latter in the absence of exchange processes is equal to that of pure **5d** ($\Delta W_o^{PH} = \Delta W_o^{P}$ = 14 Hz), the mean lifetime $\tau = \tau_P n_{PH} = \tau_{PH} n_P$ and the molar fractions n_P of the phosphane were

Figure 1. Proton exchange in phosphanylphenol phosphoniophenol solutions (**5d**/**5d** · HCl)



HCl conc. [M]	n_P	τ [s]
0.22	0.10	$0.163\pm3\times10^{-6}$
0.17	0.42	$0.169\pm7\times10^{-7}$
0.14	0.44	$0.172\pm1\times10^{-6}$
0.11	0.58	$0.110\pm7\times10^{-7}$
0.08	0.67	$0.126\pm7\times10^{-7}$
0.06	0.75	$0.118\pm3\times10^{-7}$
0.05	0.86	$0.113\pm2\times10^{-7}$
0.03	0.94	$0.7\pm2\times10^{-7}$

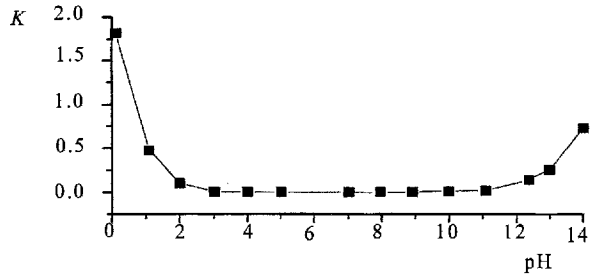
calculated from the line form by using a program for two-site exchange[16]. For simpler phosphonium salts, the kinetics of protolysis can be determined from the total exchange rate $1/\tau = R$[17]. For *o*-hydroxyarylphosphanes, a more complex behavior is anticipated involving inter- and intramolecular proton exchange reactions between the phosphane/phosphonium and the hydroxy sites. The intramolecular exchange is revealed by the strongly broadened ^{1}H-NMR signal of the OH group and a remarkable protonation not only by strong mineral acids but also by acetic acid (up to ca. 50% in *tert*-butylphenylphosphanylnaphthol[15]) suggesting a stabilization of the R_3PH^+ moiety by intramolecular hydrogen bonds.



Strong bases and even amines deprotonate phosphanylphenols. Protonation and deprotonation lead to a pH-dependent solubility of phosphanylphenols in organic solvents and water. The distribution coefficient of **5d** in a water/hexane system, determined UV spectroscopically (λ = 300 nm), shows solubility in water at $2-3 > pH > 11$ (Figure 2).

Phosphanylphenolates are soluble not only in alcohols or water ($pH > 11$) but, depending on the cation, at least partly also in ether, THF (Li) or dioxane (Na). Therefore, they are versatile starting materials for substitution reactions with hydrolytically sensitive halides. Organophosphorus, -silicon, or -tin halides and acyl chlorides undergo fast substitution reactions at the oxygen atom to give **2**, **4**, **8**, or **10**. Alkyl halides attack very slowly, methoxymethyl

Figure 2. pH dependence of the distribution coefficient $K = c_1/c_2$ of **5d** in water/hexane



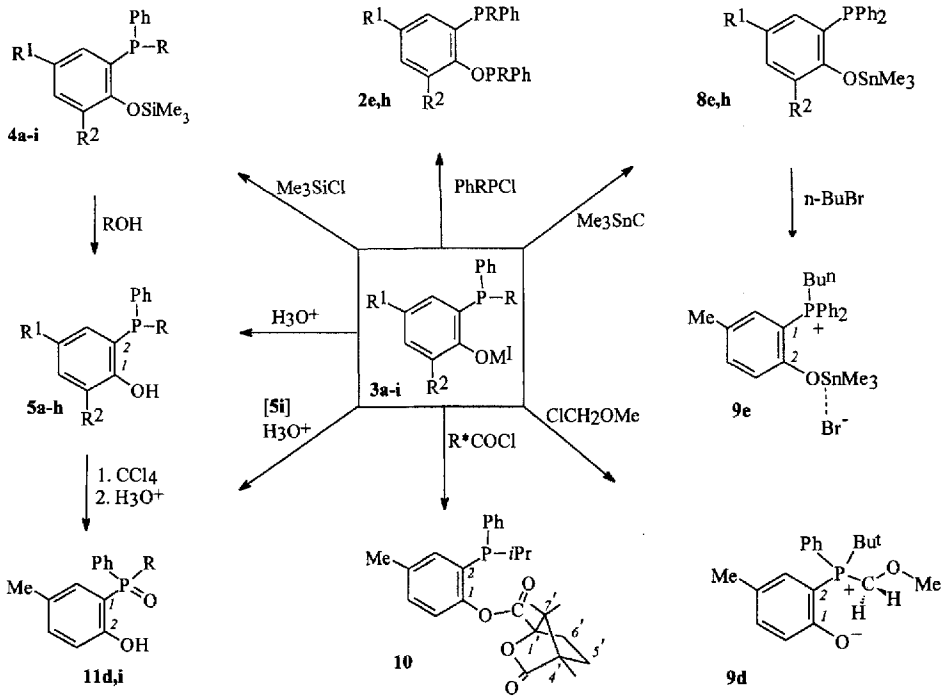
chloride rapidly at the soft phosphorus atom affording the phosphonium derivatives **9e** and **9d**. The much faster reaction of the latter may be attributed to activation by the electron-withdrawing methoxy group and also to the complexation P/O−Na···O(Me)−CH_2Cl resulting in the formation of a cyclic transition state. CCl_4, when used as a solvent, was found to form adducts at phosphorus the ^{31}P-NMR spectrum of which indicates signals at $\delta(^{31}P) = 88.9$, 91.8. In methanol these adducts liberate phosphane oxides, as exemplified by **11d**. Similarly, phosphanylphenols are oxidized by DMSO at room temperature. The secondary phosphane oxide **11i** was obtained by hydrolysis of the (dimethylamino)phenylphosphanylphenolate **3i** or the silyl ether **4i** (Scheme 5).

The derivatives **2** and **8** are of interest because of stereochemical information obtained from the magnitude of the coupling constants $^4J_{P-E}$ (E = P, Sn) (see below); **4** allows a convenient purification of **5** (see above) and **10** the separation of enantiomers. Thus, **10b** was obtained in good yield from **3d** and (*S*)-(−)-camphanic acid chloride. One of the diastereoisomers, (+)-**10b**$_A$, crystallizes much faster than the other from its solution in ether and furnishes in the first crystallization step a 85:15 ratio of diastereoisomers in the crystals, while the other diastereoisomer remains in the filtrate. Pure (+)-**10b**$_A$ was isolated from the solution of the crystalline fraction in CH_2Cl_2 by slow evaporation of the solvent. Analogous attempts with (1*R*)-(−)-camphor-10-sulfonyl chloride and **3d** failed due to oxidation of phosphorus. The phosphane oxide **11d** and two further compounds [$\delta(^{31}P) = 43.6$ and 88.9 along with the proton signals for the camphor substituent] were obtained. The latter species are split in methanol to give **11d**. All compounds are well characterized by their ^{1}H- and ^{13}C-NMR data (Tables 1−3).

Hydrogen Bonds, Conformation, and Structures

Methyl-bis(*o*-hydroxyphenyl)phosphane and tris(*o*-hydroxyphenyl)phosphane form hydrates in aqueous solution[11e], **5e** forms methanol adducts with O−H···O(H) hydrogen bonds. Indications of the presence of intramolecular hydrogen bonds $P^+-H\cdots O(H)$ in protonated phosphanylphenols (see above) prompted us to investigate whether there are also P···H−O hydrogen bonds in *o*-phosphanylphenols. Infrared spectra of diluted and concentrated solutions of the more basic *tert*-butyldiarylphosphane **5d** in CS_2

Scheme 5

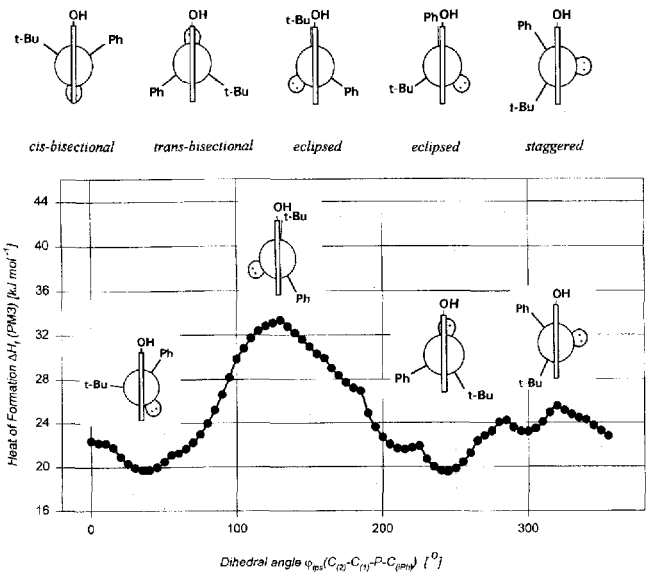


(0.3, 17.4%) and in toluene (0.4, 23.6%) are nearly identical and show, besides the weak bands at 3515 cm^{-1}, a very strong absorption at 3360 and 3361 cm^{-1}. The bulky **5f** in CS_2 (0.3, 3.8%) exhibits two weak (at 3501 and 3633 cm^{-1}) and again a very strong band at 3369 cm^{-1}. While ν_{OH} = 3501/3515 cm^{-1} and 3633 cm^{-1} correspond to the *trans* dimer and to monomer species[18], the hydroxyl stretching frequencies at 3360–3370 cm^{-1}, with $\Delta\nu_{OH} \approx 270$ cm^{-1} similar to tertiary aminophenols[19], suggest quite strong intramolecular hydrogen bonds P···H–O. This is further supported by doublets for the hydroxyl group in the proton NMR spectra of dilute (0.5%) solutions of **5d** and **5f** (J_{PH} = 11–12 Hz) in CS_2 or of **5h** (δ = 6.65 ppm, $J_{P,H}$ = 10.0 Hz) in $CDCl_3$. At higher concentration these signals turn into broad singlets since proton exchange becomes rapid within the NMR time scale. The preference of *trans*-eclipsed to *trans*-bisecting conformations, which permit formation of the intramolecular hydrogen bond, is however retained. The $^2J_{P-C}$ coupling constants, a rough measure of the dihedral angles φ(lp–P–C2–C1 or 3) in rigid molecules[20], are very different for the C1 and the opposite C3 atoms, 17 to 22 Hz for C1 and 4 to 0 Hz for C3 (Tables 2 and 3). This corresponds to small φ values for C1 (50 to 30°) and much larger φ values for C3[21], i.e. the phosphorus electron lone pair is closer to C1 and the P substituents are *trans*-directed towards C3. An average of conformations with preference of the *trans* form(s) is also consistent with the data, whereas in the case of similar amounts of *cis* and *trans* conformers the difference of ^2J(P–C1) and ^2J(P–C3) should be much smaller. As evident from ^2J(P–C3) = 40 Hz and ^2J(P–C1) = 9 Hz of the primary 4,6-di-*tert*-butyl-2-phosphanylphenol[14], the *cis* conformation implies large values for ^2J(P–C3) and small values for ^2J(P–C1). Attempts to observe two conformers of **4d**, **5d**, and **5g** in [D_8]toluene by ^{31}P- and ^{1}H-NMR spectroscopy at −75°C and −68°C failed. The ^{31}P-NMR spectra of **4d** and **5g** show sharp signals consistent with either low barriers to rotation [also at the P–C(aroxy) bond] or the existence of only one conformer in measurable amounts. The spectrum of **5d**, the least bulkily substituted of these compounds, exhibits at −68°C a broad ^{31}P absorption that becomes broader with decreasing temperature but is not split into two signals at the limit of −87°C. This indicates the presence of more than one conformer but either a relatively low barrier to rotation or small $\Delta\delta^{31}$P values. For comparison, it should be mentioned that trimesitylphosphane has a fairly high barrier to rotation of 45 kJ/mol at −45°C[22] and shows different ^{13}C signals and ^2J(P–C) values of δ = 143.0 (+37.3 Hz) and 141.6 (−2.5 Hz) for the two *o*-carbon atoms[23].

To estimate the relative energies of and energy barriers between preferred conformers of **5** we performed semiempirical calculations using PM3 (MOPAC6.0[24]) of several rotamers of *tert*-butylphenylphosphanylphenol. Since the rotation of the *tert*-butyl and the phenyl groups around the P–C axes is less hindered, the calculations were restricted to geometry-optimized structures and energies of rotamers of the P–C(phenol) bond with stepwise varied torsion angles φ_{ips}(C_{iPh}–P–C1–C2). The results are presented in Figure 3 together with the dihedral angles φ, calculated approximately for the minima and the saddle points by averaging of φ_{Ph}(C_{iPh}–P–C1–C2) and φ_{Bu}($C\alpha_{Bu}$–P–C1–C2) and addition of 180°. Although the energy profile is not monotonically increasing or decreasing (see Experimental) we find clearly two minima [$\Delta H_f(cis) - \Delta H_f(trans)$ = 0.2 kJ/mol] of similar energy near the idealized *trans*-bisecting

and *cis*-bisecting conformations with φ_{ips} = 244°, corresp. to φ = 10° and with φ_{ips} = 37°, corresp. to φ = 161°. The maximum at φ_{ipso} = 132°, corre. to φ = 291°, with $\Delta H_{spl} - \Delta H_{trans}$ = 14 kJ/mol is caused by steric repulsion of the *tert*-butyl and *o*-hydroxy groups in the eclipsed position. The second barrier, due to interactions between the phenyl and the hydroxyl group, is split and much lower ($\Delta\Delta H$ = 6 kJ/mol) and should allow population of both conformations. This is not in accordance with the observed preference for *trans* conformers. The discrepancy is probably caused by larger energy differences between the conformers than calculated, e.g. by interactions in the condensed phase, which are not properly considered in the calculations.

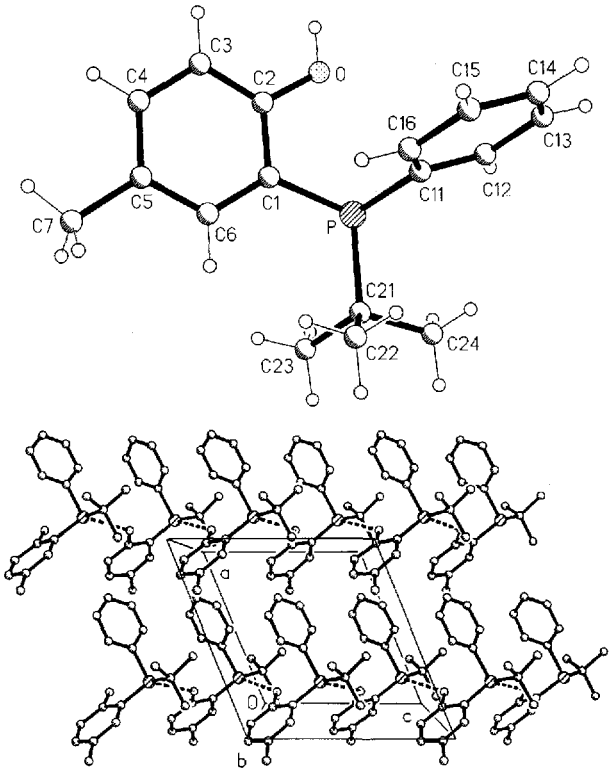
Figure 3. Idealized and preferred conformations and calculated energies (PM3) of geometry optimized rotamers of the P–C(phenol) bond



In solid **5d**, the cresol group possesses a *trans*-eclipsed (to *t*Bu) conformation with a dihedral angle of φ_X(X–P–C1–C2) = 118.6° (X = center of gravity of the P-bonded C atoms) corresponding to φ = −61.4° while the more flexible phenyl group adopts a staggered position between eclipsed and bisecting φ_X(X–P–C11–C16) = −25.8°. The intramolecular P···O distance is shortened to 278.5(1) pm by bending the P atom towards oxygen [P–C1–C2 113.9(11) and O–C2–C1 116.01(13)]. The position of the oxygen-bonded hydrogen atom shows however that intermolecular P···H–O bonds [P···O = 319.0(1), P···H = 242 pm and O–H···P 152°] are favored; thus, chains of molecules in which both enantiomers alternate are formed (Figure 4, Table 4).

The bulkier 4,6-di-*tert*-butylphenoxy group in solid **5g** is, like the naphthoxy group[15], closer to a *trans*-bisecting conformation with a dihedral angle of φ_X(X–P–C1–C2) = 156.7 corresponding to φ = −23.3; the phenyl group is arranged similarly to **5d** [φ_X(X–P–C11–C16) = −24.5°]. Surprisingly, the oxygen and also the phosphorus atom are slightly bent towards the 6-*tert*-butyl group [O–C2–C3 117.44(11)°, P–C1–C2 118.51(12)], thus increasing somewhat the intramolecular P···O distance [302.4(1) pm] compared to **5d**. The hydrogen position is consistent with an intramolecular hydrogen bond [P···H(O) 248.2 pm, P···H–O 123.6°], while the intermolecular distances (operator for P: 2 − *x*, 1 − *y*, 1 − *z*) are considerably longer [P···O 347.1(1), P···H(O) 291.5 pm, P···H–O 125.6°] (Figure 5, Table 4).

Figure 4. Crystal and molecular structure of **5d**; selected distances [pm] and angles [°]: P–C1 183.1(2), P–C11 183.2(2), P–C21 187.6(2), O–C2 136.5(2); C1–P–C11 101.80(7), C1–P–C21 110.00(7), C11–P–C21 103.57(7), P–C1–C2 113.91(11), O–C2–C1116.01(13), P–C11–C12 117.86(12), P–C11–C16 123.39(12); P···O 278.5(1); intermolecular (*x*, 1/2 − *y*, 1/2 + *z*) P···H–O see text



It should be noted for comparison that tris(*o*-tolylphosphane) similarly possesses different ^2J(P–C) coupling constants (C2 26.4 Hz, C6 0.4 Hz[25]) and torsion angles (36.7–49°[26]) with the rotation always in the same direction and the methyl groups *cis*-oriented relative to the phosphorus lone pair (*trans* conformation). From these findings it may be concluded that sterical requirements control the conformation and favor the formation of P···H–O bond interactions in **5**.

In line with this, the preference of *trans* conformation of the phenoxy substituents is observed also for *O*-substituted derivatives. The coupling constants ^2J(P–C1) = 14 to 25.6 Hz are again much larger than ^2J(P–C3) = 0 to 5 Hz, especially for sterically strained derivatives such as **2h**, **8h**, **4h**, and **4g** [^2J(P–C1) = 21–25.6 Hz]. In **2h** and **8h** additional evidence for *trans* orientation is furnished by large long-range coupling constants ^4J(P–P) = 135 Hz and ^4J(P–Sn) = 155/163 Hz with $OPPh_2$ or $OSnMe_3$, respectively, as well as in **8h**, **4h**, and **4g** by ^5J(P–C) ≈ 18 Hz and ^6J(P–H) ≈ 2–3 Hz with $OSnMe_3$ or $OSiMe_3$. These indi-

cate through-space donor-acceptor interactions between the phosphorus lone pair and the O substituents and thus *trans* arrangement of the phosphanyl and *cis* arrangement of the OR group. The interactions, and similarly the sterically forced intramolecular hydrogen bonds in **5f–h**, decrease the s-electron density at phosphorus and hence the $^1J(P-C)$ coupling constant compared to the cresyl compounds. Genuine intramolecular coordination may however be excluded. In **8h**, expected to show the strongest interactions, the ^{119}Sn-NMR signal (δ = 117.8) is found in the region of tetracoordinated tin compounds and the $^1J(Sn-P)$ coupling constants of penta- or hexacoordinated Sn–P compounds are considerably larger[27]. The structural features of **8h** in solution are preserved also in the crystalline state (Figure 6, Table 4).

Figure 5. Molecular structure of **5g**; selected distances [pm] and angles [°]: P–C1 183.7(2), P–C7 183.4(2), P–C13 188.1(2), O–C2 137.3(2); C1–P–C7 101.82(8), C1–P–C13 102.66(8), C7–P–C13 109.55(8), P–C1–C6 122.84(12), O–C2–C1 121.5(2); P···O 302.9(1), P···H(O) 248.2, P···H–O 123.6

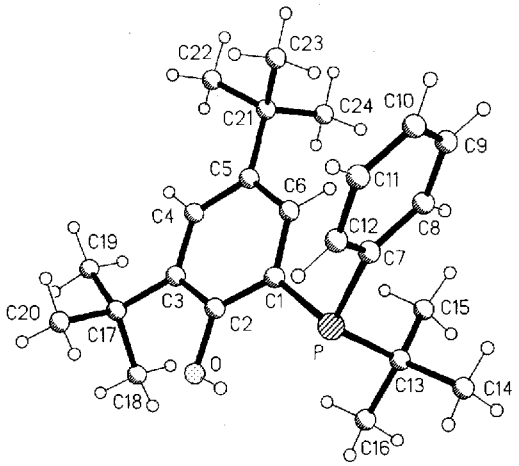
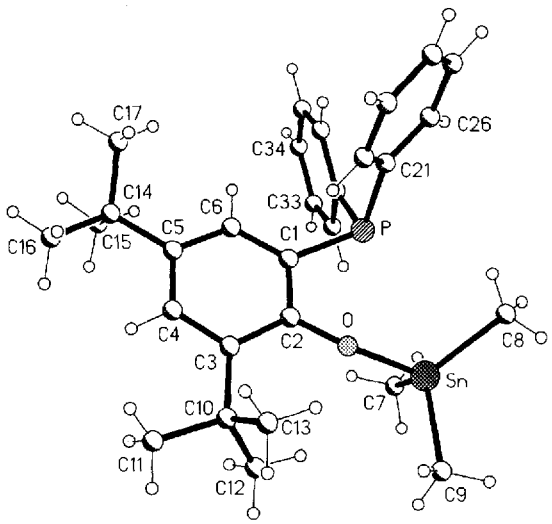


Figure 6. Molecular structure of **8h**; selected distances [pm] and angles [°]: P–C1 182.5(3), P–C21 183.1(3), P–C31 183.3(3), O–C2 134.9(4), O–Sn 201.5(2), Sn–C7 212.3(3), Sn–C8 211.4(3), Sn–C9 214.6(4); C1–P–C21 102.7, C1–P–C31 102.0, C21–P–C31 103.6, O–Sn–C9 96.2, O–Sn–C7 108.4, O–Sn–C8 110.1, C7–Sn–C8 117.5, C7–Sn–C9 113.5



The dihedral angle φ(X–P–C1–C2) = –155.4° corresponds nearly to a *trans*-bisecting conformation [φ(lp–P–C1–C2) = 24.6°], the oxygen atom is shifted out of the aryl plane by 18.7 pm [φ(C6–C1–C2–O = –172.2°] and the stannyl group arranged *cis*-eclipsed with φ(C1–C2–O–Sn) = –56.0°. The intramolecular P···Sn distance (336.9 pm) is considerably (ca. 35%) longer than the sum of standard covalent radii (250 pm) but sufficient for interactions inducing the P···Sn coupling. There is no intermolecular P···Sn (>650 pm) contact. In the absence of 6-*tert*-butyl groups, the O substituents are bent away from the phosphorus atom and no long-range couplings are observed between the phosphorus atom and the O substituents (**2e**, **4a–e**, **8e**). Broad ^{31}P-, ^{119}Sn- and ^{13}C-NMR (for C1 to C5) signals indicate however a dynamic behavior of **8e**.

In the *O*-stannylphosphonium salt **9e** the ^{1}H- and ^{13}C-NMR signals of $SnMe_3$ are strongly broadened and no ^{119}Sn signal can be observed, suggesting an equilibrium between the *O*-trimethylstannylcresyl-2-phosphonium bromide and a betaine-like Sn-pentacoordinated 2-phosphoniumcresyl-bromotrimethylstannate isomer, at a rate similar to the NMR time scale. The occurrence of only one set of ^{1}H- and ^{13}C-NMR signals for aryl and butyl groups is consistent with low barriers to rotation around the P–C bonds.

Perspectives

The phosphanylphenol derivatives, especially **3–5**, are useful starting materials for the preparation of chelate complexes with one or two phosphanylphenolato ligands and of homogeneous transition-metal catalysts. Only a brief overview of this field is presented here; a full description is given separately[10,24]. Reactions of **3** with a variety of nickel salts or complexes, e.g. $NiBr_2 \cdot 2\ PPh_3$, afford preferentially diamagnetic, square-planar *cis*- or *trans*-bis(phosphinophenolato)nickel(II) complexes. The stereochemistry is controlled by the spatial demand of the substituents at the phosphorus atom. Monochelate complexes are less favored, but they are available from **4** or **5** and nickelocene. The resulting phosphanylphenolato-η^5-cyclopentadienylnickel(II) is stabilized by the 18-valence-electron configuration. Less stable monochelates, anticipated to be formed from **4** or **5** and $Ni(COD)_2$ or rhodium complexes, are catalytically active. In preliminary studies with Keim and Brüll[28] we found that in the presence of catalysts obtained from $Ni(COD)_2$ (0.22 mmol) and **4b** or **5b** (0.22 mmol) ethylene polymerizes at 120 °C/4 to 3 MPa in toluene (10 ml) to give linear polymers and oligomers with high regioselectivity (TON 666, 698; PE/oligomers 88 and 85%, respectively). Tests of rhodium-catalyzed reactions in cooperation with Selke and Heller[29] showed that **5d** (0.01 mmol) and $Rh(CO)_2acac$ (0.01 mmol) enable the hydroformylation of vinyl acetate at 80 °C/5 MPa with high selectivity for the isoproduct (*i*/*n* = 99:1; 32% yield in 12 h), whereas the catalytic hydrogenation of methyl *N*-acetylcinnamate (1 mmol) in the system $[Rh(COD)_2]BF_4$ (0.01 mmol)/**4d** or **7b** (0.1 mmol)/methanol or THF under normal conditions (0.1

MPa, 25 °C) is less favorable. Yields are below 15% with **7b** (24 h) and 44–46% with **4d** (53 and 70 h). Small *ee* values were obtained with **7b** (11%) and unresolved **4d** (3%). More extensive studies of the above-mentioned catalytical applications are in progress.

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Experimental

General Considerations: All reactions are conducted under dry argon by using the Schlenk technique. Solvents are dried with sodium and freshly distilled under argon. Me_3SiCl is recondensed in vacuo, the content of *n*BuLi in *n*-hexane or *n*-pentane solution controlled prior to use. Chloro(methyl)phenylphosphane[30], *tert*-butyl(chloro)phenylphosphane[31], and $ClPhPNMe_2$[32] are prepared according to literature procedures, chloro(*iso*-propyl)phenylphosphane is prepared in analogy to *tert*-butyl(chloro)phenylphosphane from *i*PrMgCl and $PhPCl_2$ at low temperature. The NMR spectra are recorded with a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.13 (^{1}H), 121.49 (^{31}P), 75.47 (^{13}C) and 111.92 MHz (^{119}Sn). $CDCl_3$ is used as solvent unless other solvents are indicated. References are tetramethylsilane for ^{1}H, ^{13}C, and ^{29}Si data, H_3PO_4 (85%) for ^{31}P and tetramethyltin for ^{119}Sn data. Assignment is supported by DEPT or CH-COSY or CH-coupled experiments of selected compounds; numbers for H or C of the phosphanylphenol ring follow the nomenclature, phenyl or alkyl groups are indicated by *i*, *o*, *m*, *p* or α, β etc.

Phosphanylphenyl Trimethylsilyl Ethers **4a–i** *and* **6a, b** *by C/O-Dilithium Reagents. – General Procedure:* A solution of the corresponding *o*-bromophenol in dry ether (ca. 3–5 ml/mmol) is cooled to −50 °C. Two equivalents (and 0.5 ml in excess) of a 1.6 M solution of *n*BuLi in *n*-hexane are added with stirring, the first half is added dropwise and with cooling to avoid a violent reaction and partial metal/halogen exchange prior to complete metalation of the hydroxyl groups. The second half may be added rapidly and even at room temp. Stirring is continued for about 4 h to complete the metal/halogen exchange. Thus, partly dissolved and partly suspended lithium *o*-lithiophenolates **1** are obtained. After cooling to −40 to −50 °C, a solution of one equivalent of RPhPCl or half an equivalent of $RPCl_2$ in about the same volume of dry ether is added dropwise and the mixture is stirred 3–8 h at room temperature to complete the formation of **2**. Then a slight excess of Me_3SiCl (ca. 1.05–1.1 equivalents) is added at 0–10 °C and the mixture allowed to react at least 1 h at room temperature. The precipitate, mainly LiCl, is removed by filtration (three times washed with dry ether), the solvent evaporated under reduced pressure and the residue distilled in vacuo.

4-Methyl-2-[methyl(phenyl)phosphanyl]phenyl Trimethylsilyl Ether (**4a**): 2-Bromo-4-methylphenol (10.7 g, 57.4 mmol) in 200 ml of diethyl ether is dilithiated with 72 ml of 1.6 M BuLi in hexane. Chloro(methyl)phenylphosphane (9.1 g, 57.4 mmol) and later chlorotrimethylsilane (7.6 ml, 60 mmol) are added to the suspension. It is filtered and distilled at b.p. 120–125 °C/0.05 Torr to yield 9.7 g (56%) of liquid **4a**. – For ^{1}H- and ^{13}C-NMR data see Tables 1 and 2. – ^{31}P NMR: δ = −35.6. – ^{29}Si NMR (C_6D_6): δ = 18.8. – $C_{17}H_{23}OPSi$ (302.4): calcd. P 10.24; found P 9.91.

2-[Isopropyl(phenyl)phosphanyl]-4-methylphenyl Trimethylsilyl Ether (**4b**): 2-Bromo-4-methylphenol (18.7 g, 100 mmol) in 300 ml of ether is dimetalated with 134 ml of 1.6 M BuLi in hexane. The suspension is treated with chloro(isopropyl)phenylphosphane (18.7 g, 100 mmol) and later with chlorotrimethylsilane (14 ml, 110 mmol). After filtration 16.4 g (50% yield) of viscous liquid **4b** is distilled at b.p. 128–130 °C/0.2 Torr. For ^{1}H- and ^{13}C-NMR data see Tables 1 and 2. – ^{31}P NMR: δ = −10.1. – $C_{19}H_{27}OPSi$ (330.5): calcd. P 9.37; found P 9.38.

2-[tert-Butyl(phenyl)phosphanyl]phenyl Trimethylsilyl Ether (**4c**): A solution of *o*-bromophenol (3.89 g, 22.5 mmol) in ether (80 ml) is treated with 30 ml of 1.5 M BuLi in hexane, 4.5 g of *tert*-butyl(chloro)phenylphosphane (22.5 mmol) and 3.2 ml of chlorotrimethylsilane (25 mmol) to give 5.2 g (70% yield) of **4c** with b.p. 110–115 °C/0.08 Torr. – $C_{19}H_{27}OPSi$ (330.5): calcd. P 9.37; found P 8.95.

2-[tert-Butyl(phenyl)phosphanyl]-4-methylphenyl Trimethylsilyl Ether (**4d**): 32.9 g of 2-bromo-4-methylphenol (176 mmol) in 500 ml of ether is dilithiated with 222 ml of 1.6 M BuLi in hexane. *tert*-Butyl(chloro)phenylphosphane (35.3 g, 176 mmol) and, after stirring overnight at room temperature, chlorotrimethylsilane (23 ml, 182 mmol) are added to the suspension. After filtration 31.0 g (51% yield) of viscous liquid **4d** is distilled at b.p. 116–118 °C/0.06 Torr. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 2. – ^{31}P-NMR: δ = 4.5. – ^{29}Si NMR (C_6D_6): δ = 18.4. – $C_{20}H_{29}OPSi$ (344.5): calcd. C 69.73, H 8.48, P 8.99; found C 69.80, H 8.36, P 9.50.

2-(Diphenylphosphanyl)-4-methylphenyl Trimethylsilyl Ether (**4e**): A solution of 2-bromo-4-methylphenol (9.4 g, 50 mmol) in 200 ml of ether is treated with 67 ml of 1.5 M BuLi in hexane. Chlorodiphenylphosphane (11.05 g, 50 mmol) and later chlorotrimethylsilane (7.0 ml, 55.3 mmol) are added to the suspension. It is filtered and distilled at b.p. 150–155 °C/0.1 Torr to yield 15.6 g (90%) of viscous liquid **4e**. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 2. – ^{31}P NMR: δ = −15.3. – $C_{22}H_{25}OPSi$ (364.5): calcd. P 8.50; found P 8.35.

Attempt to Prepare 4,6-Di-tert-butyl-2-[isopropyl(phenyl)phosphanyl]phenyl Trimethylsilyl Ether (**4f**): A solution of 8.56 g (30 mmol) of 2-bromo-4,6-di-*tert*-butylphenol in 100 ml of ether is treated successively with 60 ml of 1.05 M BuLi in hexane (3 h), 5.62 g (30 mmol) of chloro(isopropyl)phenylphosphane (−20 to 20 °C, 15 h) and 4 ml (32 mmol) of chlorotrimethylsilane (3 h). Attempted distillation of the filtrate at 120 °C/0.01 Torr furnished 1.1 g of an ill-defined mixture; the residue was used to prepare **5f**. (The precipitate, separated by filtration, reacts vigorously with methanol, indicating unreacted lithium reagents besides LiCl.)

4,6-Di-tert-butyl-2-[tert-butyl(phenyl)phosphanyl]phenyl Trimethylsilyl Ether (**4g**): 8.6 g (30 mmol) of 2-bromo-4,6-di-*tert*-butylphenol in 20 ml of ether is treated as above with 60 ml of 1.05 M BuLi in hexane, 6.0 g (30 mmol) of *tert*-butyl(chloro)phenylphosphane and 4 ml (32 mmol) of chlorotrimethylsilane to give 3.5 g (26%) of viscous liquid **4g**, b.p. 134–136 °C/0.005 Torr. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 2. – ^{29}Si NMR: δ = 13.9. – ^{31}P NMR: δ = −0.7. – $C_{27}H_{43}OPSi$ (442.7): calcd. C 73.25, H 9.79; found C 73.35, H 10.29.

4,6-Di-tert-butyl-2-(diphenylphosphanyl)phenyl Trimethylsilyl Ether (**4h**) *and [4,6-Di-tert-butyl-2-(diphenylphosphanyl)phenoxy]-diphenylphosphane* (**2h**): A solution of 2.3 g (8.1 mmol) of 2-bromo-4,6-di-*tert*-butylphenol in 20 ml of ether is treated successively with 11.5 ml of 1.5 M BuLi (−30 to 20 °C, 5 h), 1.5 ml (1.8 g, 8.1 mmol) of chlorodiphenylphosphane (−15 to 20 °C, 1 d) and 1.2 ml (9.5 mmol) of $ClSiMe_3$ (20 °C, 1 d). After filtration ca. 50% of the sol-

vent are removed, the precipitate is collected and washed with hexane to give 1.0 g (22% based on **1**) of **2h**. 2.7 g of crude semisolid **4h**, easily soluble even in pentane, is isolated from the filtrate and 1.2 g (32%) of **4h** is obtained by distillation, b.p. 150–160°C/10^{-4} Torr, m.p. 118–119°C (EtOH). – **4h**: ^{1}H- and ^{13}C-NMR data: Tables 1 and 2. – ^{29}Si NMR (C_6D_6): δ = 15.5. – ^{31}P NMR (C_6D_6): δ = −14.1. – $C_{29}H_{39}OPSi$ (462.7): calcd. C 75.28, H 8.50; found C 74.70, H 8.25. – **2h**: ^{13}C NMR: δ = 30.4 and 31.3 (s, CMe_3), 34.4 (s) and 35.1 (d, J_{PC} = 1.4 Hz, CMe_3), 125.9 (dd, $^1J_{PC}$ = 2.4, $^3J_{PC}$ = 12.8 Hz, C-2), 125.6 (C-5), 127.8 (d, J_{PC} = 7.3 Hz, 2 C-*m*), 128.0 (d, J_{PC} = 6.4 Hz, 2 C-*m*), 127.8 (2 C-*p*), 129.1 (2 C-*p*), 131.9 (dd, J_{PC} = 23.3, 2.9 Hz, 4 C-*o*), 132.6 (C-3), 133.4 (dd, J_{PC} = 18.8, 1.5 Hz, 4 C-*o*), 139.2 (dd, $^1J_{PC}$ = 7.1, J_{PC} = 13.6 Hz, 2 C-*i*), 139.9 (dd, J_{PC} = 2.5, 3.6 Hz, C_q-6), 142.7 (dd, $^1J_{PC}$ = 10.8, J_{PC} = 18.2 Hz, 2 C-*i*), 144.1 (C_q-4), 158.5 (dd, $^2J_{PC}$ = 21.1, $^2J_{POC}$ = 8.0 Hz, C-1). – ^{31}P NMR: δ = −20.5, 116.1 (2 d, $^4J_{PP}$ = 135 Hz). – $C_{38}H_{40}OP_2$ (574.7): calcd. C 79.42, H 7.02; found C 78.65, H 6.85.

2-[Dimethylamino(phenyl)phosphanyl]-4-methylphenyl Trimethylsilyl Ether (**4i**): 9.4 g of 2-bromo-4-methylphenol (50 mmol) in 150 ml of ether is dimetalated with 63 ml of 1.6 M BuLi in hexane. To the suspension chloro(dimethylamino)phenylphosphane (9.4 g, 50 mmol) and then chlorotrimethylsilane (6.5 ml, 51.4 mmol) are added. After filtration and evaporation of the solvents 8.5 g (51% yield) of viscous liquid **4i** is distilled, b.p. 130–133°C/0.3 Torr. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 2. – ^{31}P NMR: δ = 56.7. – $C_{18}H_{26}NOPSi$ (331.5): calcd. C 65.22, H 7.91; found C 65.61, H 8.22.

Methylbis[2-(trimethylsilyloxy)phenyl]phosphane (**6a**): 5.05 g of 2-bromophenol (29.2 mmol) in 50 ml of ether is dilithiated with 37 ml of 1.6 M BuLi in hexane. Dichloromethylphosphane (1.7 g, 14.5 mmol) and, after the reaction is complete, chlorotrimethylsilane (3.8 ml, 30 mmol) are added. The suspension is filtered, the solvent evaporated and the residue distilled to yield 2.1 g (38% yield) of liquid **6a**, b.p. 120–123°C/0.01 Torr. ^{1}H-NMR data: Table 1. – ^{31}P NMR: δ = −43.9. – $C_{19}H_{29}O_2PSi_2$ (376.6): calcd. P 8.22; found P 8.40.

Bis[4-methyl-2-(trimethylsilyloxy)phenyl]phenylphosphane (**6b**): 2-Bromo-4-methylphenol (13.7 g, 73.4 mmol) in 200 ml of ether is dilithiated with 95 ml of 1.55 M BuLi in hexane. The suspension is treated with dichlorophenylphosphane (6.6 g, 36.7 mmol) and later with chlorotrimethylsilane (9.5 ml, 75 mmol). After filtration and removal of the solvent 6.0 g (35% yield) of highly viscous liquid **6b** is distilled in the temperature range 155–170°C/0.05 Torr. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 2. – ^{31}P NMR: δ = −24.7. – $C_{26}H_{35}O_2PSi_2$ (466.7): calcd. P 6.64; found P 6.93.

o-Phosphanylphenols **5a–e** *by Alcoholysis. – General Procedure:* The corresponding *o*-phosphanylphenyl trimethylsilyl ether is dissolved in an excess of anhydrous methanol or ethanol (ca. 10 ml per 10 mmol) and the solution is heated at reflux for 1 h. On slow cooling to room temp. some phosphanylphenol crystallizes; otherwise, pentane is slowly added (condensed to the cooled solution) to precipitate **5**. The crude yields are >90%.

4-Methyl-2-[methyl(phenyl)phosphanyl]phenol (**5a**): 3.2 g (10.6 mmol) of **4a** is heated with 10 ml of methanol and the larger part of the solvent evaporated in vacuo. Crystals deposit on cooling which are washed with little ether/pentane (ca. 1:1) to give 1.7 g (70% yield) of colorless crystals, m.p. 96–97°C. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR (C_6D_6): δ = −0.9. – $C_{14}H_{15}OP$ (230.2): calcd. P 13.46; found P 13.25.

2-[Isopropyl(phenyl)phosphanyl]-4-methylphenol (**5b**): 7.0 g (21.2 mmol) of **4b** and 15 ml of methanol give 3.4 g (62% yield) of a viscous oil, b.p. 130–135°C/0.8 Torr. – ^{1}H- and ^{13}C-NMR: Tables 1 and 3. – ^{31}P NMR: δ = −29.8; (C_6D_6): δ = −28.8. – $C_{16}H_{19}OP$ (258.3): calcd. P 11.99; found P 11.73.

2-[tert-Butyl(phenyl)phosphanyl]phenol (**5c**): Heating of 5.2 g (16.0 mmol) of **4c** with 25 ml of methanol affords >90% of crude **5c** as a viscous oil. Distillation at 137–142°C/0.8 Torr furnishes 2.5 g (60% yield) of pure **5c**. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −17.5. – $C_{16}H_{19}OP$ (258.3): calcd. P 11.99; found P 12.51.

2-[tert-Butyl(phenyl)phosphanyl]-4-methylphenol (**5d**): 13.0 g (37.7 mmol) of **4d** and 30 ml of alcohol are refluxed and the main part of the solvent is evaporated in vacuo. On cooling 9.2 g (90% yield) of crystalline **5d** is obtained, m.p. 97–98°C. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −18.7. – X-ray data in Table 4. – $C_{17}H_{21}OP$ (272.3): calcd. P 11.37; found P 11.05.

2-(Diphenylphosphanyl)-4-methylphenol (**5e**): 7.7 g (21.1 mmol) of **4e** is heated with 20 ml of alcohol. About half of the solvent is removed in vacuo. On cooling, 5.2 g (84% yield) of colorless crystals of **5e** is isolated, m.p. 96–98°C. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −27.2. – $C_{19}H_{17}OP$ (292.3): calcd. P 10.60; found P 10.90. – In methanol a monoadduct **5e-MeOH** crystallizes.

4,6-Di-tert-butyl-2-[isopropyl(phenyl)phosphanyl]phenol (**5f**): Crude **4f** from above is heated in 50 ml of MeOH and the mixture is allowed to stand for 1 d. 1.4 g (13%) of **5f**, m.p. 64–67°C, crystallizes slowly from the solution. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −30.0. – $C_{23}H_{33}OP$ (356.5): calcd. C 77.49, H 9.33; found C 76.56, H 9.50.

4,6-Di-tert-butyl-2-[tert-butyl(phenyl)phosphanyl]phenol (**5g**): 1.3 g (3 mmol) of **4g** is heated with 10 ml MeOH and **5g** is precipitated with pentane; yield 0.47 g (43%), m.p. 119–122°C. – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −18.9. – X-ray data in Table 4. – $C_{24}H_{35}OP$ (370.5): calcd. C 77.80, H 9.52; found C 76.72, H 10.19.

4,6-Di-tert-butyl-2-(diphenylphosphanyl)phenol (**5h**): 0.6 g (1.3 mmol) of **4h** is refluxed for 10 min with 2 ml of EtOH. On cooling unchanged **4h** (^{31}P: δ = −14.0, m.p. 118–119°C) precipitates. In the presence of a strongly acidic ion exchanger (Nafion) **4h** is alcoholyzed affording impure **5h**, ^{31}P NMR: δ = −29.7 (broad); pure **5h** see below).

o-Phosphanylphenols by Direct Work-up of Phosphanylphenolates **3**. – *2-[tert-Butyl(phenyl)phosphanyl]-4-methylphenol* (**5d**): As described above for phosphanylphenyl trimethylsilyl ethers, 2-bromo-4-methylphenol (6.0 g, 32 mmol) was dilithiated with 43 ml of 1.5 M BuLi in hexane and treated with *tert*-butyl(chloro)phenylphosphane (6.4 g, 32 mmol). The mixture is then acidified with dilute sulfuric acid (1 M), the phosphanylphenol extracted with ether, the ether phase dried with sodium sulfate, 50 ml of toluene added (azeotropical drying) and the solvent removed. The residue is distilled in vacuo at 121–123°C/0.08 Torr to give 3.3 g (38%) of a viscous liquid, solidifying after cooling (m.p. 93–95°C). – ^{31}P NMR: δ = −18.7.

Phenylphosphanediyl-2,2'-bis(4-methylphenol) (**7b**) *and Bis(2-hydroxy-5-methylphenyl)phenylphosphane Oxide* [**7b(O)**]: A solution of 18.7 g (100 mmol) of 2-bromo-4-methylphenol in 250 ml of ether is treated as described above with 125 ml of 1.6 M BuLi in hexane and dropwise at −40°C with dichlorophenylphosphane (9.0 g, 50 mmol). After stirring overnight, water is added, the organic phase (leaving little viscous material) removed and the aqueous solution acidified with a NaH_2PO_4 solution. Since **7b** does not pre-

cipitate, water is evaporated in vacuo and the residue extracted with alcohol to give 8.0 g (47% yield) of crude viscous **7b**. Repeated attempts at crystallization from alcohol yield 2.5 g of high-melting phosphane oxide **7b(O)**, m.p. 239°C (EtOH). – **7b**: ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −29.3. – **7b(O)** [numbering of atoms see Scheme 5]: ^{1}H NMR: δ = 6.89 (dd, $^4J_{HH}$ = 1.9, $^3J_{HP}$ = 14.5 Hz, 6-H), 2.23 (s, 3H, 5-Me), 7.49 (m, J_{HH} = 8.4, 1.9, J_{HP} = 1 Hz, 4-H), 6.98 (dd, $^3J_{HH}$ = 8.4, $^4J_{HP}$ = 5.9 Hz, 3-H), 7.6–7.7 (m, 4H, Ph), 7.75–7.82 (m, 1H, Ph). – ^{13}C NMR: δ = 20.4 (Me-5), 104.9 (d, J = 90.9 Hz, C-1), 117.7 (d, J = 7.4 Hz, C-3), 122.0 (d, J = 95 Hz, C-*i*), 131.5 (d, J = 11.9 Hz, C-5), 135.1 (s, C-*p*), 130.8 (d, J = 12.7 Hz, C-6), 138.9 (s, C-4), 160.2 (d, J = 2.9 Hz, C-2), 135.4 (d, J = 8.1 Hz, C-*o*), 133.9 (d, J = 9.9 Hz, C-*m*). – ^{31}P NMR: δ = 28.4. – $C_{20}H_{19}O_3P$ (338.3): calcd. P 9.16; found P 8.63.

Reactions With ClO-Lithium-Sodium Reagents. – 4,6-Di-tert-butyl-2-(diphenylphosphanyl)phenol (**5h**): A solution of 9.5 g (33.3 mmol) of 2-bromo-4,6-di-*tert*-butylphenol in 250 ml of ether is treated with 0.8 g (33.3 mmol) of NaH (2 d 20°C, 1 h reflux) and to the resulting suspension 24 ml of 1.4 M BuLi in hexane is added. The suspension is stirred for 12 h and chlorodiphenylphosphane (6.0 ml, 33.3 mmol) is added. Stirring is continued for 2–3 d, 2.0 ml (33.3 mmol) of glacial acetic acid is added and after 1 h the precipitate is filtered off and thoroughly washed with ether. The solvent is removed at 10^{-2} Torr leaving a viscous oil mixed with a little solid (ca. 14 g) consisting mainly of **5h** (68%) and smaller amounts of **2h** (13%), 2-Br-4,6-(tBu)$_2$C$_6$H$_2$OPPh$_2$ (^{31}P: δ = 112.0, 13%) and the *o*-protonated 2,4-(tBu)$_2$C$_6$H$_3$OPPh$_2$ (^{31}P: δ = 108.1, 6%), based on ^{31}P signal intensities. The solid **5h** was separated by dissolution of the oil in ether (840 ml). Ether was replaced by methanol (25 ml) from which pure crystalline **5h**, m.p. 87–88°C, separated after some hours. A second portion was obtained from the mother liquor to give 6.3 g (50%). – ^{1}H- and ^{13}C-NMR data: Tables 1 and 3. – ^{31}P NMR: δ = −29.7. – MS (70 eV); *m/z* (%): 391 (68) [M$^+$ + 1], 390 (100) [M$^+$], 375 (62), 348 (57), 333 (35), 201 (52). – $C_{26}H_{31}OP$ (390.51): calcd. P 7.93; found P 7.75.

Remarks on the Reaction Conditions: The reaction of di-*tert*-butylphenol with commercial NaH proceeds slowly (ca. 1–2 d). If BuLi is added too early, it is consumed by OH and the metal/halogen exchange is incomplete, thus forming 2-Br-4,6-(tBu)$_2$C$_6$H$_2$OPPh$_2$ by reaction with ClPPh$_2$. If boiling dioxane is used, the reaction with NaH proceeds rapidly, but the Li-Na reagent formed in the subsequent metal/halogen exchange with BuLi reacts with the solvent to afford after 1 h exchange and subsequent reaction with ClPPh$_2$ mainly the *o*-hydrogenated 2,4-(tBu)$_2$C$_6$H$_3$OPPh$_2$ (^{31}P: δ = 108.1, ca. 50%) besides the *o*-brominated phosphinite (18%) a small amount of **5h** (ca. 5%) and some other products. The reaction of sodium di-*tert*-butylphenolate with butyllithium in ether is complete after 1–2 h. After stirring overnight only a small part (ca. 13%, see above) of the bulky lithium-sodium reagent undergoes metal/hydrogen exchange with ether.

Phenylphosphonous Acid p-Cresyl Ester Dimethylamide: Sodium hydride (5.4 g, 225 mmol) is added to a solution of 2-bromo-4-methylphenol (38.2 g, 205 mmol) in 250 ml of ether and the mixture is stirred until the evolution of hydrogen ceases (ca. 1 h). After cooling to 0°C, 130 ml of BuLi in hexane (1.6 M) is added. The mixture is stirred for 8 h and ClPhPNMe$_2$, freshly prepared from 20.1 g (102.5 mmol) of PhP(NMe$_2$)$_2$ and 18.4 g (102.8 mmol) of PhPCl$_2$ (3 h at 60–65°C), is added dropwise at −30°C. The mixture is stirred for 8 h and 28 ml (221 mmol) of chlorotrimethylsilane is added, the suspension is filtered, the solvent removed and the residue distilled at 110–116°C/0.01 Torr to yield 35.3 g (66%) of colorless liquid phenylphosphonous acid *p*-cresyl ester dimethylamide (in place of the expected **4i**). – ^{1}H NMR: δ = 2.28 (s, 3H, 4-Me), 2.71 (d, $^3J_{PH}$ = 9.4 Hz, 6H, NMe), 7.08 (m, AA'BB'X, J_{PH} = 1.4 Hz, 2H, 2/6-H), 7.08 (m, AA'BB', 2H, 3/5-H), 7.3–7.45 (m, 3H, Ph), 7.58–7.65 (m, 2H, Ph). – ^{31}P NMR: δ = 133.6.

O-Phosphanyl and O-Stannyl Derivatives. – (2-Diphenylphosphanyl-4-methylphenoxy)diphenylphosphane (**2e**): 2.4 g (12.8 mmol) of 2-bromo-4-methylphenol is dilithiated as described above and 4.7 ml (5.7 g = 24.5 mmol) of chlorodiphenylphosphane added dropwise at 10°C to the mixture. After stirring for 5 h, it is filtered, the solvent removed and the viscous oil dissolved in a small amount of ether or benzene/hexane or CH_2Cl_2. Since it does not crystallize (within weeks at different temperatures), hexane is added and the precipitated oil dried to give 4.2 g (ca. 69%) of viscous **2e**. – ^{31}P NMR: δ = −15.1 (s, PC$_3$), 111.6 (s, POC$_2$). [The oil contains about 15% impurities. Preparative column chromatography on silica gel causes cleavage of the P–O bond, use of surface-modified (PhMeSi(OEt)$_2$ in boiling toluene) silica gel and elution with mixtures of di(isopropyl) ether/hexane or acetonitrile/hexane do not improve the purity.]

2-(Diphenylphosphanyl)-4-methylphenyl Trimethylstannyl Ether (**8e**): 3.75 g (20 mmol) of 2-bromo-4-methylphenol is dilithiated with butyllithium as described above. A solution of 3.7 ml (20 mmol) of chlorodiphenylphosphane in 5 ml of pentane is added dropwise at −30°C. After stirring for 3 h a solution of 4.0 g (20 mmol) of chlorotrimethyltin in 10 ml of pentane is added. The mixture is stirred for 6 h, filtered, washed with ether, and the solvent removed. The highly viscous residue is dissolved in a little ether and hexane added dropwise to the solution until an oil starts to precipitate. No crystallization occurs in the cold (over several days). Some more hexane is added and the precipitated oil dried in vacuo to afford 3.2 g (35%) of solid **8e**, m.p. 84–86°C. – ^{1}H NMR: δ = 0.42 (s, $^2J_{SnH}$ = 57.4 Hz, 9H, SnMe), 2.12 (s, 3H, 4-Me), 6.40 (br. d, J = 2 Hz, 1H, 3-H), 6.48 (dd, J_{HH} = 7.9, J_{PH} = 4.9 Hz, 1H, 6-H), 6.97 (br. d, J = 7.9 Hz, 1H, 5-H), 7.2–7.6 (m, 10H, Ph). – ^{13}C NMR: δ = −1.9 ($^1J_{SnC}$ = 387.8/403.9 Hz, SnMe), 20.5 (Me-4), 117.8 (s, C-6), 128.0 (s, 2 C-*p*), 128.1 (br. s, 4 C-*m*), 128.6 (br. d, 12.2 Hz, C$_q$-2), 133.7 (d, J = 19.8 Hz, 4 C-*o*), 137.3 (d, J = 9.9 Hz, 2 C-*i*), 161.2 (br. d, J = 14.6 Hz, C-1); strongly broadened signals: 127.6, 130.6 (130.7 sh.), 133.2, (C-3 to C-5). – ^{31}P NMR: δ = −16.4 (br). – ^{119}Sn NMR: δ = 144 (very broad). – MS (FAB, 70 eV); *m/z* (%): 456 (8) [M$^+$], 451 (60) [M$^+$ − Me], 292 [M$^+$ − SnMe$_2$CH$_2$], 165 (100) [SnMe$_3^+$]. – $C_{22}H_{25}OP^{120}Sn$ (456.1).

4,6-Di-tert-butyl-2-(diphenylphosphanyl)phenyl Trimethylstannyl Ether (**8h**) *and (4,6-Di-tert-butyl-2-diphenylphosphanylphenoxy)diphenylphosphane* (**2h**): 4.9 g (17.2 mmol) of 2-bromo-4,6-di-*tert*-butylphenol is dissolved in ether (20 ml) and dilithiated with 34.5 ml of BuLi (1.05 M in hexane) at 10°C. After 14 h a solution of 3.3 ml (3.80 g, 17.2 mmol) of chlorodiphenylphosphane in 3 ml of hexane is added dropwise. A yellow color is observed when the drops mix with the suspension of **1**, but rapidly a colorless precipitate is formed. After 3 h a solution of 3.45 g of chlorotrimethyltin in 10 ml of ether is added dropwise to the suspension and the mixture is stirred for 5 h. It is then filtered. While ether is recondensed for washing (in the closed apparatus), a precipitate is formed in the filtrate which does not redissolve in ether. 1.4 g (28% yield based on ClPPh$_2$) of fine colorless crystals of **2h**, m.p. 185–187°C, is collected and washed with pentane/ether. Further crystals, larger and of another shape, precipitate when the filtrate is concentrated by evaporation of a part of the solvent in vacuo. After cooling, they are separated and washed with little cold pentane/ether (ca. 5:1). 4.0 g (42% yield) of **8h**, m.p. 165–167°C, is obtained. X-ray

diffraction data in Table 4. – **8h**: ^{1}H NMR ($CDCl_3$, CH_2Cl_2): δ = 0.59 (d, $^6J_{PH}$ = 3.1, $^2J_{SnH}$ = 54/56.5 Hz, $SnMe_3$), 1.08 (s, 9H, 4-*t*Bu), 1.41 (s, 9H, 6-*t*Bu), 6.49 (dd, J_{HH} = 2.6, J_{PH} = 4.9 Hz, 1H, H-3), 7.15–7.36 (m, 6H, H-5, Ph). – ^{13}C NMR and CH-COSY: δ = 1.2 (d, $^5J_{PC}$ = 18.2, $^1J_{SnC}$ = 404.7/386.4 Hz, SnMe), 30.3, 31.5, 34.2, 35.2 (4,6-*t*Bu), 124.3 (d, $^1J_{PC}$ = 3.7, $^3J_{SnC}$ = 12 Hz, C-2), 125.3 (C-5), 128.2 (d, J_{PC} = 2 Hz, 4 C-*m*), 128.3 (2 C-*p*), 128.8 (C-3), 133.5 (d, J_{PC} = 17.8 Hz, 4 C-*o*), 137.2 (d, J_{PC} = 7.1, $^3J_{SnC}$ = 55 Hz, C-*i*), 139.2 (d, J_{PC} = 1.9, $^3J_{SnC}$ = 13 Hz, C-6), 140.1 (C-4), 161.2 (d, J_{PC} = 21.1, $^2J_{SnC}$ = 36.6 Hz, C-1). – ^{31}P NMR: δ = −22.8 (s, sat. $^4J_{PSn}$ = 155.5/163 Hz). – ^{119}Sn NMR: δ = 117.8 (d, $^4J_{PSn}$ = 163 Hz). – $C_{29}H_{39}OPSn$ (553.3): calcd. C 62.95, H 7.10; found C 61.70, H 7.35. – **2h**: ^{1}H NMR: δ = 1.12, 1.13 (2 s, 4,6-*t*Bu), 7.04 (dd, J_{HH} = 2.5, J_{PH} = 4.0 Hz, 1H, H-3), 7.2–7.5 (m, 21H, H-5, Ph). – ^{13}C NMR: See above. – ^{31}P NMR: δ = −20.6, 116.0 (2 d, $^4J_{PP}$ = 135 Hz).

P-Alkylation. – n-Butyl(diphenyl)[5-methyl-2-(trimethylstannyloxy)phenyl]phosphonium Bromide (**9e**): The crude filtrate of **8e**, prepared from 10 mmol of bromocresol, is allowed to stand for 2 months. Crystals of **9e** deposit. 0.5 ml of *n*-butyl bromide is added to improve the yield and compensate for loss of BuBr (formed by metal/halogen exchange). After further 2 months 1.9 g (32%) of **9e**, m.p. 177–179°C, is collected. – ^{1}H NMR: δ = 0.53 (br, 3H, SnMe), 0.95 (t, *J* = 7.5 Hz, 3H, δ-Me), 1.53 (m, 2H, γ-CH_2), 1.64 (m, 2H, β-CH_2), 2.97 (m, 2H, α-CH_2), 2.12 (s, 3H, 5-Me), 6.43 (dd, *J* = 1.8, 1.4 Hz, 1H, H-6), 6.50 (dd, *J* = 6.8, 8.4 Hz, 1H, H-3), 7.27 (dd, *J* = 8.5, 1.9 Hz, 1H, H-4), 7.50–7.73 (m, 10H, 2 Ph). – ^{13}C NMR: δ = 3.4 (strongly broadened, SnMe), 13.3 (Me-δ), 20.2 (Me-5), 23.6 (d, *J* = 74.7 Hz, C-α), 23.8 (br., C-γ), 25.2 (d, *J* = 4.4 Hz, C-β), 100.9 (d, *J* = 95.8 Hz, C-1), 121.6 (d, *J* = 86.9 Hz, 2 C-*i*), 118.9 (d, *J* = 7.7 Hz, C-3), 123.9 (d, *J* = 13.8 Hz, C_q-5), 129.6 (d, *J* = 12.1 Hz, 4 C-*m*), 132.4 (d, *J* = 9.4 Hz, 4 C-*o*), 133.5 (d, *J* = 5 Hz, C-6), 133.6 (d, *J* = 2.8 Hz, 2 C-*p*), 138.4 (d, *J* = 1.6 Hz, C-4), 168.4 (d, *J* = 3.6 Hz, C-2) [assignment checked by CH-coupled spectrum]. – ^{31}P NMR: δ = 22.2. – $C_{26}H_{34}BrOPSn$ (592.14): calcd. Br 13.49; found Br 13.2.

2-[tert-Butyl(methoxymethyl)phenylphosphonio]-4-methylphenolate (**9d**): 1.6 g (5.9 mmol) of **5d** is refluxed for 1 h with 0.2 g (0.83 mmol) of NaH in ether (40 ml). 0.44 ml (0.59 mmol) of $ClCH_2OMe$ is added dropwise (20°C) to this suspension. After stirring for 12 h, the powdery precipitate is separated, dissolved in CH_2Cl_2 to remove sodium chloride and the solvent evaporated to give 1.25 g (67%) of viscous, partly solidifying **9d** with 3 sets of NMR signals in a ratio of ca. 2:1:1; ^{31}P NMR: δ = 32.8, 32.5, 31.4. Slow, stepwise precipitation with ether from the concentrated CH_2Cl_2 solution gives a high-melting solid, m.p. 195–200°C with an intensity ratio of ca. 90:5:5 of ^{31}P signals. – Major species: ^{1}H NMR (CD_3OD): δ = 1.57 (d, J_{PH} = 17.2 Hz, *t*Bu), 2.31 (s, 4-Me), 3.50 (s, OMe), 5.01 and 5.03 (m, J_{AB} = 13, J_{PH} = 4.6, 4.4 Hz, P^+CH_2) [in $CDCl_3$ 4.77, 5.09 (J_{AB} = 13, J_{PH} = 5.4, 4.0 Hz)], 7.01 (dd, *J* = 8.4, 5.8 Hz, H-6), 7.35 (dd, J_{PH} = 13 Hz, J_{HH} = 1–2 Hz, H-3), 7.51 (m, *J* = 8.3, 1–2, H-5), 7.6–7.7 (2H, Ph), 7.8–7.9 (3H, Ph). – ^{13}C (CD_3OD): δ (J_{PC} [Hz]) = 20.42 (Me-4), 27.59 (CMe_3), 35.09 (41.1, CMe_3), 62.23 (13.0, OMe), 65.31 (64.8, P^+CH_2O), 102.58 (79.5, C-2), 118.06 (7.5, C-6), 119.09 (78.6, C-*i*), 130.86 (11.6, C-*m*), 131.68 (9.8, C-4), 134.55 (8.4, C-*o*), 135.36 (3.7, C-*p*), 135.93 (7.0, C-3), 139.13 (2, C-5), 160.45 (2.3, C-1). – $C_{19}H_{25}O_2P$ (316.4): calcd. P 9.79; found P 9.45.

O-Acylation. – 2-[Isopropyl(phenyl)phosphanyl]-4-methylphenyl (1S)-Camphanoate (**10b**): 684 mg (2.65 mmol) of **4b** in ether (10 ml) is lithiated at −50°C with 1.77 ml of 1.5 M butyllithium in hexane and the mixture is treated with a cooled solution of 574 mg (2.65 mmol) of (1*S*)-(−)-camphanic acid chloride. After 4 h at room temp. the suspension is filtered and about half of the solvent evaporated. Colorless crystals precipitate on cooling, which are washed with hexane and dried in vacuo to yield 650 mg (56%) of **10b**, m.p. 173.5–174.5°C, $[\alpha]_D^{20}$ = +9.3 (*c* = 9.0) in CH_2Cl_2. Removal of the solvent of the filtrate leaves ca. 700 mg of a viscous substance. According to ^{31}P NMR (C_6D_6, δ = -16.24_A, -16.08_B), the crystals consist of a mixture of the diastereoisomers $\mathbf{10b_A}$ and $\mathbf{10b_B}$ in a 85:15 ratio, the viscous material in the opposite ratio of 15:85. Recrystallization by dissolution in methylene chloride and slow evaporation of the solvent through a septum give the pure enantiomer (+)-$\mathbf{10b_A}$. – ^{13}C NMR (C_6D_6): δ = 9.8 (Me-4′), 16.7 (Me_a-7′), 17.1 (d, J_{PC} = 2.4 Hz, Me_b-7′), 19.7 (d, J_{PC} = 17.1 Hz, $CHMe_a$), 20.0 (d, J_{PC} = 20.3 Hz, $CHMe_b$), 20.8 (Me-4), 25.0 (d, J_{PC} = 9.1 Hz, $CHMe_2$), 28.9 (CH_2-5′), 31.5 (CH_2-6′), 54.3 and 54.9 (C_q-4′ and C_q-7′), 90.9 (C_q-1′), 122.4 (d, J_{PC} = 2.4 Hz, C-6), 128.6 (d, J_{PC} = 6.5 Hz, C-*m*), 128.8 (C-*p*), 131.07 (C-5), 131.07 (d, J_{PC} = 20.6 Hz, C_q-2), 133.6 (d, J_{PC} = 18.9 Hz, C-*o*), 133.9 (C-3), 136.2 (C_q-4), 137.5 (d, J_{PC} = 14.8 Hz, C-*i*), 152.4 (d, J_{PC} = 20.4 Hz, C_q-1), 166.7 (CO-3′), 177.2 (CO-1′). – MS (70 eV); *m/z* (%): 438 (20) [M^+], 396 (11), 395 (16) [M^+ − *i*Pr], 394 (14), 380 (28), 379 (100) [M^+ − OPr], 286 (16), 285 (87) [$MeC_6H_3(PPhPr)OCO^+$], 259 (31) [$MeC_6H_3(PHPhPr)OH^+$]. – $C_{26}H_{31}O_4P$ (438.5).

Reaction of Camphor-10-sulfonyl Chloride with **2d** *to Give* **11d** *and Other Products:* To a solution of 0.70 g of **4d** in 10 ml of ether, 1.8 ml of BuLi (1.5 M in hexane) is added. At −50°C a solution of 0.644 g (1*R*)-(−)-camphor-10-sulfonyl chloride in ether is added. A precipitate forms rapidly which is separated, washed three times with ether and dried to give 1.7 g of a mixture of LiCl and the phosphane oxide **11d**, δ(^{31}P, [D_6]acetone) = 50.5, and two substituted derivatives, δ(^{31}P) = 88.9 and 43.6, in a ratio of ca. 54:20:26. The latter are cleaved by methanol to give **11d**.

Phosphane Oxides. – tert-Butyl(2-hydroxy-5-methylphenyl)phenylphosphane Oxide (**11d**): 160.5 mg (0.6 mmol) of **5d** is dissolved in 1 ml of CCl_4. A white precipitate forms rapidly (^{31}P-NMR signals at δ = 89.0 and 91.8). The mixture is dissolved in little methanol and the solution allowed to stand overnight. 110 mg (65% yield) of the phosphane oxide **11d**, m.p. 167–169°C, precipitates. – ^{1}H NMR: δ = 1.30 (d, $^3J_{HP}$ = 15.4 Hz, 9H, *t*Bu), 2.27 (s, 3H, 5-Me), 6.84 (dd, J_{HH} = 8.8, J_{HP} = 4.4 Hz, 3-H), 7.15–7.20 (m, 2H, 4,6-H), 7.50–7.54 (m, 3H, Ph), 7.93–8.00 (m, 2 *o*-H, Ph). – ^{13}C NMR: δ = 20.7 (Me), 24.7 (CMe_3), 35.2 (d, *J* = 69.3 Hz, CMe_3), 109.3 (d, *J* = 91.6 Hz, C-1), 118.6 (d, *J* = 7.4 Hz, C-3), 128.5 (d, *J* = 10.6 Hz, C-5), 128.6 (d, *J* = 11.3 Hz, C-*m*), 130.5 (d, *J* = 90.2 Hz, C-*i*), 130.8 (d, *J* = 9.2 Hz, C-6), 131.7 (d, *J* = 8.3 Hz, C-*o*), 132.0 (d, *J* = 3.2 Hz, C-*p*), 134.9 (d, *J* = 2.2 Hz, C-4), 162.5 (d, *J* = 2.1 Hz, C-2). – ^{31}P NMR: δ = 51.05. – MS (70 eV); *m/z* (%): 288 (59) [M^+], 232 (100) [$M^+ - C_4H_8$], 213 (66), 199 (20), 154 (20). – $C_{17}H_{21}O_2P$ (288.3).

(2-Hydroxy-5-methylphenyl)phenylphosphinous Acid (**11i**): 7.1 g (21.4 mmol) of **4i** and 20 ml of methanol are refluxed (3 h) and then the mixture is allowed to cool slowly. 4.5 g (91% yield) of **11i** precipitates which is recrystallized from ethanol/benzene, m.p. 138–141°C. – ^{1}H NMR: δ = 2.19 (s, 5-Me), 6.91 (m, J_{HH} = 8.4–9.0, J_{PH} = 5.5–6.2 Hz, 3-H), 7.12 (br. s, 1H, 6-H), 7.49 (m, $^3J_{HH}$ = 8.4, 4-H), 7.5–7.7 (m, 3H, Ph), 7.73–7.80 (m, 2H, Ph), 8.19 (d, J_{PH} = 500.3 Hz, PH); (in $CDCl_3$, acetone): significant data δ = 6.84 (dd, $^4J_{HH}$ = 1.8, $^3J_{PH}$ = 16.2 Hz, 6-H), 6.88 (dd, $^3J_{HH}$ = 8.4, $^4J_{PH}$ = 5.3 Hz, 3-H), 8.23 (d, J_{PH} = 492.5 Hz, PH). – ^{13}C NMR: δ = 20.31 (Me-5), 112.83 (d, J_{PC} = 103.4 Hz, C_q-1), 116.96 (d, J_{PC} = 7.1 Hz, C-3), 128.76 (d, J_{PC} = 12.9 Hz, C-*m*), 128.79 (d, J_{PC} = 12.9 Hz, C_q-5), 130.61 (d, J_{PC} = 11.8 Hz, C-*o*), 130.97 (d,

Table 1. ^{1}H-NMR data of phosphanylphenyl trimethylsilyl ethers **4** and phosphanylphenols **5**; in $CDCl_3$ unless otherwise indicated (δ; *J* in Hz)

No.	3-H	4-H / 1-R	5-H	6-H	Ph[b] *OSiMe$_3$ or OH*	2-R
4a	6.97 (dd) (2.3/5.0)	2.28 (s)	7.03 (ddd) (8.1/2.3/0.4)	6.68 (dd) (8.1/4.2)	7.3-7.45 (m, 3H) *0.15 (s)*	1.55 (d) ($^2J_{PH}$ = 4.2)
4b	7.24 (dd) (1.9/3.7)	2.34 (s)	7.05 (dd) (8.1/1.9)	6.69 (dd) (8.1/4.1)	7.2-7.5 (m) *0.11 (s)*	2.40 (hept) (6.8) 1.01; 1.20 (dd) (7/14; 7/16)
4d	7.36 (dd) (ca.2.2/2.5)	2.30 (s)	7.02 (dd) (8.2/2.2)	6.66 (dd) (8.2/4.5)	7.2-7.4 (m) *0.07 (s)*	1.21 (d) (J_{PH}= 12.2)
4g	7.3-7.4[b]	1.30 (s)	7.45 (d) (2.6)	1.51 (s)	7.3-7.6 (6H) *0.53 (d) (2.2)*	1.22 (d) (J_{PH}= 12.2)
4h	7.02 (dd) (2.6/4.2)	1.19 (s)	7.65 (d) (2.6)	1.59 (s)	= R^2 *0.58 (d) (2.2)*	7.1-7.16 (6H) 7.4-7.5 (4H)
4i	7.08 (m)[b] (2.3/3.5)	2.30 (s)	7.04 (m)[b] (8.1/1.4/1)	6.66 (dd) (8.1/4.7)	7.3-7.4 (m, 5H) *0.07 (s)*	2.634 / 2.631 (d, 9.3 / d, 9.3)
6a[c]	6.6-7.3[b]	[b]	[b]	[b]	0.20 (s)	1.51 (d, 4.5)
6b	6.48 (dd) (2.4/4.2)	2.14 (s)	7.01 (dd) (8.1/2.3)	6.67 (dd) (8.1/4.8)	7.2- 7.8 (m) *0.10 (s)*	=Ar
5a (C_6D_6)	6.82-6.87[b] (m)	1.98 (d)	6.98-7.07[b] (m)	6.92-6.87 (m)	6.98-7.07 (4H) 7.24-7.31 (2H)	1.33 (d) (J_{PH} = 2.8)
5b (C_6D_6)	7.12 (m) (1.6/4.6/0.6)	2.01 (s)	6.83 (dd) (8.3/2.1)	6.91 (dd) (8.3/5.4)	7.0-7.1 (3H) 7.4-7.5 (2H)	2.32 (6.9/1.6) 1.04; 0.95 (dd) (7/17.3; 7/16)
5c	7.55 (m) (7.6/1.7/3.7)	6.95 (m) (7.5/6/1.3)	ca. 7.34 (m) [b]	7.03 (m) (8.2/6.0/1.2)	7.3-7.4 (3.7H) 7.55-7.65 (2H)	1.26 (d) (13.7)
5d	7.28 (-dd) (2.2/4-5)	2.27 (s)	7.12 (dd) (8.2/2.2)	6.86 (dd) (8.2/6.3)	7.3-7.4 (3H) 7.5-7.6 (2H)	1.21 (d) (13.8)
5d (C_6D_6)	7.35 (m) (2/4/0.5)	2.09 (s)	6.90 (m) (8.3/2.1/0.4)	7.03 (dd) (8.3/6.1)	7.05-7.1 (3H) 7.5-7.6 (2H)	1.12 (d) (13.5)
5e[d]	6.80 (dd) (2/ 6.1)	2.19 (s)	7.12 (dd) (8.2/2)	6.85 (dd) (8.2/5.5)	7.2-7.35 (m)	= R^1
5f (C_6D_6)	7.32 (dd) (2.3, 4.2)	1.26 (s)	7.52 (d) (2.2)	1.58 (s)	7.0-7.05 (3H) 7.40-7.46 (2H) *7.55 (d) (11.9)*	2.32 (7/8.3) 0.95; 1.05 (dd) (7/15.5; 17.6)
5g	7.10 (dd) (2.0, 3.7)	1.27 (s)	6.97 (d) (2.0)	1.41 (s)	7.3-7.6 (5H) *7.9 (d) (12.6)*	1.18 (d) (13.7)
5h	6.88 (dd) (2.5/5.8)	1.15 (s)	[b]	1.41 (s)	7.3-7.4 (m) *6.65 (d) (10.0)*	= R^1
7b (CD_3OD)	6.48 (dd) (2.2/4.9)	2.06 (s)	6.98 (m) (8.1/2.2/0.5)	6.70 (dd) (8.1/5.2)	7.2-7.35 (5H)	=Ar

[a] Reference is δ(CH_2Cl_2) = 5.30 for **4** and TMS for **5**; assignments are supported by CH-COSY experiments (**4i**, **5a**), coupling constants are based on a first-order analysis of spread signals. – [b] Superimposed or unresolved signals. – [c] **4h** was measured at 100 MHz with HA100 (Bruker). – [d] Solid **5e** forms a monoadduct with methanol, ^{1}H NMR ($CDCl_3$): δ = 3.50 (s, 3H, OMe), 1.12 (br, 1H, MeOH), 6.12 (d 5.9 Hz, 1H, OH_{ar}).

J_{PC} = 9.1 Hz, C-6), 131.20 (d, J_{PC} = 103 Hz, C-*i*), 132.55 (d, J_{PC} = 2.3 Hz, C-*p* or C-4), 135.39 (d, J_{PC} = 1.9 Hz, C-4 or C-*p*), 158.93 (d, J_{PC} = 4.3 Hz, C_q-2). – ^{31}P NMR: δ = 22.2. – $C_{13}H_{13}O_2P$ (232.2): calcd. P 13.34; found P 13.15.

Extraction Experiments: A 0.002 M bulk solution of **5d** in hexane was prepared. Each 10 ml of this was stirred for 1 h with 10 ml of an appropriate acid, base or buffer solution, the organic phase separated and the extinction $E = \varepsilon \cdot c \cdot d$ measured at λ = 300 nm (d = 0.1 cm) to calculate the distribution coefficient $K = c_1/c_2 = (E_0 - E)/E$ (E_0 = extinction of bulk solution); pH calibration: pH = 0.1 (1 N HCl), pH = 1.1 (0.1 N HCl), pH = 2–5 (buffer standards), pH = 7.94 (4.5 ml 0.1 N HCl + 5.5 ml 0.1 N Na_3BO_3), pH = 8.9 (2 ml 0.1 N HCl + 8 ml 0.1 N Na_3BO_3), pH = 9.97 (4 ml 0.1 N NaOH + 6 ml 0.1 N Na_3BO_3), pH = 11.07 (5 ml 0.1 N NaOH + 5 ml 0.1 N Na_3BO_3), pH = 12.37 (6 ml 0.1 N NaOH + 4 ml 0.1 N Na_3BO_3), pH = 13 (0.1 N NaOH), pH = 14 (1 N NaOH).

Crystal-Structure Analyses: Crystal data are presented in Table 4. – *Data collection:* Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (**5d**, **8h**: Stoe STADI-4; **5g**: Siemens P4). Data were collected with monochromated Mo-K_α radiation. Cell constants were refined from ±ω angles (Stoe) or setting angles (Siemens) of ca. 50 reflections to $2\Theta_{max}$ 25°. Scan type: ω/Θ (Stoe), ω (Siemens). An absorp-

Table 2. ^{13}C-NMR data of phosphanylphenol trimethylsilyl ethers **4**; in $CDCl_3$ unless otherwise indicated (δ; *J* in Hz)[a]

	C-1	C-2	C-3	C-4	C-5	C-6	Ph *i/o*	Ph *m/p*	R *α/β*	R^1 *α/β*
4a	*155.1*	*130.0*	132.1	*130.3*	130.0	117.6	*140.2 (11.4)*	128.1 (5.8)	11.5	20.7
	(14.1)	*(11.4)*	(4.7)	*(2.2)*	(-)	(ca.1)	132.3 (19.5)	128.2 (-)	(13.2)	0.25
4b	*155.7*	*128.1*	132.7	*130.1*	130.1	117.9	*138.1 (15)*	127.8 (8)	23.9 (8.4)	20.77
	(14.3)	*(14)* [a,b]	(4)	*(2)* [a,b]	(-)	(-)	133.7 (20)	128.2 (-)	19.5 (16.8)	0.19
									20.3 (20.3)	
4d	*157.4*	*129.6*	135.9	*130.8*	131.1	119.8	*139.6 (20.1)*	128.7 (6.4)	*31.2 (16.5)*	21.6
(C_6D_6)	*(17.7)*	*(20.6)*	(-)	*(-)*	(-)	(1.5)	135.3 (19.8)	128.8 (-)	29.7 (14.9)	1.19 (2.2) [c]
4g	*157.3*	*126.4*	132.0	*142.3*	126.0	*139.9*	*139.7 (21.7)*	128.2 (4.6)	*32.1 (18.2)*	*34.5, 35.4 (1.8)*
(C_6D_6)	*(25.6)*	*(14.0)*	(1.8)	*(-)*	(-)	*(3.1)*	133.1 (15.9)	127.3 (-)	28.9 (14.4)	30.7, 31.6
										3.5 (13.3)
4h	*155.1*	*126.6*	129.9	*142.9*	125.3	*139.1*	*137.5 (11.5)*	127.9 (9.3)	= Ph	*34.5, 35.4 (br.)*
(C_6D_6)	*(22.6)*	*(8.4)*	(-)	*(-)*	(-)	*(2.2)*	133.3 (19.6)	127.9 (-)		30.19, 30.8
										2.4 (11.8)
4i	*154.4*	*129.1*	132.4	*130.0*	129.9	117.4	*138.4 (13.6)*	127.7 (6.0)	42.2	20.8
	(18.1)	*(13.6)*	(3.0)	*(-)*	(-)	(-)	131.7 (20.4)	127.9 (-)	(15.9)	0.1
6b	*155.3*	*127.6*	134.1	*130.0*	130.0	117.3	*136.6 (10.5)*	128.1 (7.4)	-	20.7
	(17.8)	*(10.3)*	(br)	*(2)*	(-)	(-)	134.5 (21.5)	128.4 (-)		0.2

[a] Assignments are supported by DEPT 90 (**4b**, **4d**, **5d**) and CH-COSY (**4i**, **5a**) studies of selected compounds; C_q atoms in italics. – [b] Superimposed signals. – [c] J_{SiC} = 59.5 Hz (satellites).

Table 3. ^{13}C-NMR data of phosphanylphenols **5**; in $CDCl_3$ unless otherwise indicated (δ; *J* in Hz)[a]

	C-1	C-2	C-3	C-4	C-5	C-6	Ph *i/o*	Ph *m/p*	R *α/β*	R^1 *α/β*
5a	*158.7*	*124.0*	133.6	*130.7*	133.0	116.4	*140.4 (7.1)*	129.4 (5.9)	11.5	21.1
(C_6D_6)	*(18.7)*	*(7.2)*	(3.5)	*(2.3)*	(-)	(2.0)	133.2 (17.4)	128.9 (-)	(11.6)	
5b	*159.6*	*120.8*	133.9	*130.3*	133.1	115.7	*137.1 (8.0)*	129.5 (8.2)	25.5 (3.7)	21.2
(C_6D_6)	*(18.9)*	*(7.0)*	(br)	*(2.2)*	(-)	(1.7)	134.0 (18.5)	129.4 (-)	19.9 (15.8)	
									20.7 (20.1)	
5d	*160.6*	*119.9*	135.7	*129.6*	133.6	116.5	*136.2 (10.8)*	129.1 (6.8)	*32.0 (8.8)*	21.3
(C_6D_6)	*(21.1)*	*(6.5)*	(br)	*(1.3)*	(-)	(2.0)	134.5 (17.1)	129.1 (-)	29.3 (13.9)	
5e	*156.9*	*121.1*	134.2	*129.3*	131.6	115.1	*135.7 (7.2)*	128.3 (6.7)	= Ph	20.4
	(17.1)		(3.6)	*(1.9)*	(-)	(2.2)	133.4 (19.0)	128.5 (-)		
5f	*156.5*	*119.5*	128.7	*141.6*	125.7	*134.9*	*135.7 (6.0)*	128.4 (7.0)	25.3 (2.9)	*34.4, 35.0*
	(19.8)	*(br)*	(or 127)	*(-)*	(-)	*(br)*	133.0 (17.6)	127.0 (or128.7)	19.0 (14.8)	29.6, 31.5
									19.9 (19.8)	
5g	*158.0*	*119.1*	129.7	*141.3*	126.2	*135.4*	*135.4 (9.1)*	[128.3 (7.3)	*31.4 (8.2)*	*34.4, 35.4 (2.3)*
(C_6D_6)	*(21.2)*	*(2.3)*	(0.9)	*(1.1)*	(-)	*(-)*	*133.8 (16.6)*	128.4 $CDCl_3$]	28.6 (13.6)	29.84 31.8
5h	*155.9*	*119.9*	129.2	*142.2*	126.2	*135.3*	*135.4 (3.5)*	128.6 (7.4)	= Ph	*34.4, 35.1 (2.0)*
	(19.3)	*(-)*	(3.9)	*(2.9)*	(-)	*(1.3)*	*133.3 (18.3)*	128.8 (-)		29.6, 31.4
7b	*159.5*	*124.2*	136.2	*130.9*	132.8	116.7	*138.9 (8)*	130.3 (7)	= Ar	21.8
	(16)	*(10)*	(-)	*(-)*	(-)	(2.4)	136.2 (15)	130.4 (-)		

[a] Assignments are based on DEPT 90 (**5a**, **b**, **d**, **7b**) and CH-COSY (**5a**) studies; C_q atoms in italics. – [b] Superimposed signals.

tion correction based on ψ scans was performed for **8h**. – *Solution and Refinement:* Structures were solved by direct methods and refined anisotropically on F^2[33]. Hydrogen atoms were included by using a riding model (exception: OH and methyls as rigid group). For compound **5g**, the butyl carbon atoms C22 to C24 are disordered over two positions.

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-405659 (**5d**), CSD-405660 (**5g**), CSD-405661 (**8h**) and the complete literature reference.

Semiempirical Calculations: Calculations of energies of conformations of [(2-*tert*-butylphenyl)phosphanyl]phenol were carried out by using PM3 (standard parametrization), program package MOPAC6.0[24]. Geometry optimization was performed with given torsion angles φ_{ips} of C(iPh)–P–C(1)–C(2) (numbering see Figure 4) in steps of 5°. The resulting energy profile is not monotonic since in some cases there are two or more acceptable geometries with the same dihedral angle, i.e. the calculated energy profile is only a section of a multidimensional potential energy surface with the lowest energy calculated for every dihedral angle. Such uncertainties were discussed by Clark[34]. Minima in the plot of ΔH_f versus φ_{ips} are controlled by the keyword FORCE, the maxima were determined

Table 4. Crystallographic data for **5d**, **5g** and **8h**

	5d	**5g**	**8h**
Empirical formula	$C_{17}H_{21}OP$	$C_{24}H_{35}OP$	$C_{29}H_{39}OPSn$
Molecular mass	272.31	370.49	553.26
Crystal size [mm]	0.70 x 0.60 x 0.50	0.90 x 0.40 x 0.35	0.80 x 0.25 x 0.15
Temperature [K]	143 (2)	173 (2)	143 (2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a [pm] ; α [°]	862.8 (2) ; 90	942.2 (2) ; 90	891.0 (2) ; 90
b [pm]; β [°]	2235.2 (4) ; 112.143 (12)	2131.7 (2) ; 100.527 (10)	1271.6 (2) ; 91.50 (2)
c [pm]; γ [°]	844.4 (2) ; 90	1145.18 (12) ; 90	2421.5 (4) ; 90
V [nm^3] ; Z	1.5083 (5) ; 4	2.2614 (6) ; 4	2.7426 (9) ; 4
Density (calculated) [Mg/m^3]	1.199	1.088	1.340
Absorption coefficient [mm^{-1}]	0.173	0.131	1.008
F(000)	584	808	1144
θ range for data collection [°]	3.02 to 27.52	3.21 to 24.99	3.20 to 25.04
Limiting indices	$-10 \le h \le 11$, $-29 \le k \le 0$, $-10 \le l \le 2$	$-11 \le h \le 0$, $-25 \le k \le 2$, $-13 \le l \le 13$	$0 \le h \le 10$, $0 \le k \le 15$, $-28 \le l \le 28$
Reflexions collected	4173	4593	5165
Independent reflexions	3473 (R_{int} = 0.0114)	3962 (R_{int} = 0.0159)	4836 (R_{int} = 0.0163)
Absorption correction	none	none	Psi-scans
Max.& min.transmission			0.891 and 0.832
Data / restraints / parameters	3467 / 0 / 177	3962 / 78 / 270	4825 / 0 / 298
Goodness-of-fit on F^2	1.083	0.959	1.055
Final R indices [$I>2\sigma$ (I)]	$R1$ = 0.0376, $wR2$ = 0.0890	$R1$ = 0.0382, $wR2$ = 0.0948	$R1$ = 0.0332, $wR2$ = 0.0762
R indices (all data)	$R1$ = 0.0470, $wR2$ = 0.0988	$R1$ = 0.0557, $wR2$ = 0.0989	$R1$ = 0.0414, $wR2$ = 0.0859
Largest diff. peak and hole	291 and -215 e.nm^{-3}	265 and -180 e.nm^{-3}	441 and -1122 e.nm^{-3}

by SADDLE. Two energetically similar minima were calculated for φ_{ips} = 244.1° (ΔH_f = 19.6 kJmol^{-1}, ΔH_{rel} = 0 kJmol^{-1}) and for φ_{ips} = 37.1 (ΔH_f = 19.8 kJmol^{-1}, ΔH_{rel} = 0.2 kJmol^{-1}), a maximum and barrier to rotation for φ_{ips} = 132.0° (ΔH_f = 33.5 kJmol^{-1}, ΔH_{rel} = 13.9 kJmol^{-1}); Figure 3.

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