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Synthesis, Complexation Chemistry and a Case of Self-Recognition of Chiral Phosphite Ligands

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Abstract

Reaction of (*R*)-(-)-1-phenyl-2,2,3-trimethylbutane-1,3-diol with PCl_3 affords *trans*-(*S*)-2-chloro-4,4,5,5-tetramethyl-6-(*R*)-phenyl-1,3,2-dioxaphosphorinane, which couples smoothly with catechol, resorcinol, 2,2-dimethyl-1,3-propanediol and fluorenedimethanol to form the corresponding diphosphites. By three different methods (oxidation to phosphates, electrospray mass spectrometry with deuterium labelled samples, and NMR spectroscopic analysis of borane adducts) it was shown that on use of racemic materials a degree, less than absolute, of self-recognition is involved in the formation of the diphosphite obtained with catechol. No self-recognition is involved in the assembly of the product with resorcinol. Determination of the degree of self-recognition was made difficult by the identity of the NMR spectra of the *meso* and *racemic* forms of the diphosphites obtained from catechol.

Phosphites assume the form of distorted tetrahedra, the phosphorus atom being surrounded by three singly bonded oxygen atoms and the lone pair at the fourth corner.[1] Although phosphites are well known to coordinate transition metals, their development as ligands has lagged considerably behind that of phosphines.[2] However, in the mid-eighties it was recognized that phosphine-based catalysts can suffer oxidative P-C bond cleavage under hydrogenation and hydroformylation conditions.[3] Interest in the use of other ligands was rekindled. Reports of the high activity of rhodium complexes of bulky (di)phosphites in hydroformylation reactions[4] underlined the potential of phosphites, also for catalytic asymmetric synthesis.[5]

Phosphite complexes have been described for almost all metals in the transition series.[6] The phosphorus-heteroatom σ^*-orbitals appear to play a greater role as acceptors than the phosphorus d-orbitals.[7,8] In general, phosphines with electron-rich phosphorus atoms are stronger σ-donors and prefer high valent, electron-poor transition metals, whereas phosphites with electron-poor phosphorus atoms are stronger π-acceptors and prefer to complex low-valent, electron-rich metals.[9] Steric effects can be used to modify properties.[10] All these aspects are

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nicely illustrated in studies of, for example, zero-valent molybdenum carbonyl complexes of phosphites,[11-14] and rhodium complexes of diphosphites.[15]

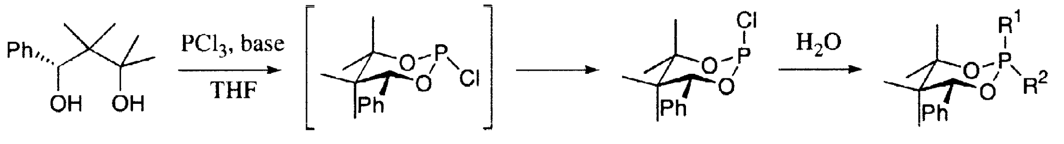
We began some time ago an investigation of novel bidentate phosphites. Cyclic phosphites have been used in which the practical aspects of the use of conformational locking and the concomitant aspect of control of stereochemistry about phosphorus have been the major points of concern. We concentrate here on 1,3,2-dioxaphosphorinanes formed from reaction of the appropriate trivalent phosphorus derivatives with 1,3-diols.[16] These ring systems have been described extensively and it is known that electronegative substitutents such as alkoxy, aryloxy and chloro at phosphorus prefer an axial disposition, apparently as an expression of an anomeric effect.[17,18] Inclusion of proper substitutents on the six-membered ring leads to conformational freezing (anancomeric molecules).[19] For illustration (Scheme 1) a monodentate borane[20] and a bidentate $Mo(CO)_4$ complex[12] are shown.

R = Me, *i*-Pr

Scheme 1

The borane complexes of tervalent phosphorus compounds deserve special mention owing to their stability, for example toleration of gaseous HCl,[21] *sec*-butyllithium,[22] aqueous work-up and column chromatography.

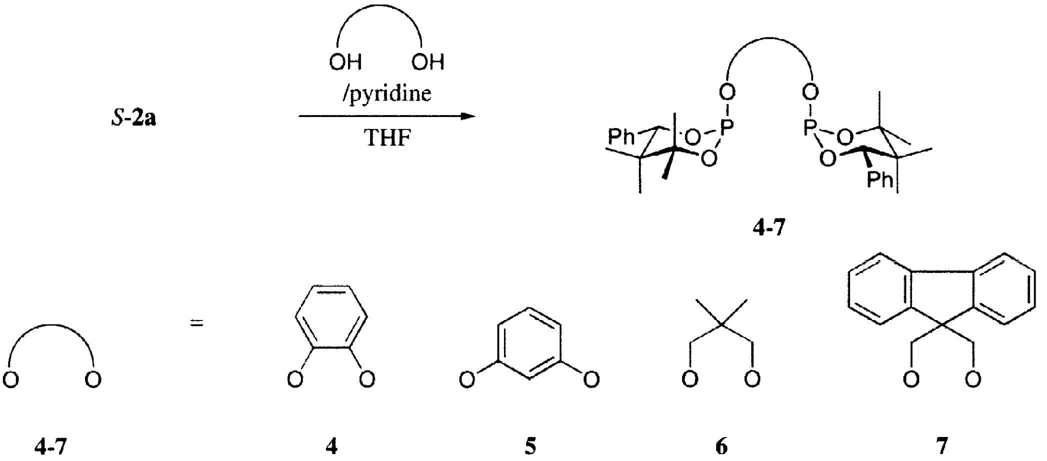
The highly substituted chiral non-racemic 1,3-diol **1**[23] was chosen because of the certainty of conformational locking and the opportunity for secondary interactions with the chiral phosphorus center. Reaction with PCl_3 should provide the 1,3,2-dioxaphosphorinanes (Scheme 2). Axially substituted[17] **2a** is obtained when pyridine is used as base. It was observed by ^{31}P NMR spectroscopy on the crude reaction mixture that if Et_3N is used as base, two epimeric phosphochloridites are obtained. The other product must be the epimer, **2b**, which, however, in solution slowly isomerizes to **2a**. If pyridine is used as base only **2a** is found; we suspect that rearrangement of **2b** to **2a** is catalyzed by a small amount of free H^+ available when the weaker base, pyridine, is used.



R-(-)-**1** **2b** **2a** **3a** $R^1 = H, R^2 = O$
3b $R^1 = O, R^2 = H$

Scheme 2

Hydrolysis gives the epimeric H-phosphonates **3a,b**, which were also prepared independently by condensation of **1** with H_3PO_3 in the presence of dicyclohexylcarbodiimide (see Experimental).[24] Because of its sensitivity, **2a** is best prepared *in situ* with avoidance of any exposure to moisture. Reaction of enantiomerically pure **2a** with catechol in THF (Scheme 3) leads to **4**, obtained as a white crystalline solid (reactions with the (*S*)-enantiomers are illustrated). Phosphites **5-7** were prepared in an analogous manner using the diols illustrated in Scheme 3. The ^{31}P NMR resonances of these compounds are found at approximately 120 ppm and the ^{1}H NMR spectra show small



Scheme 3

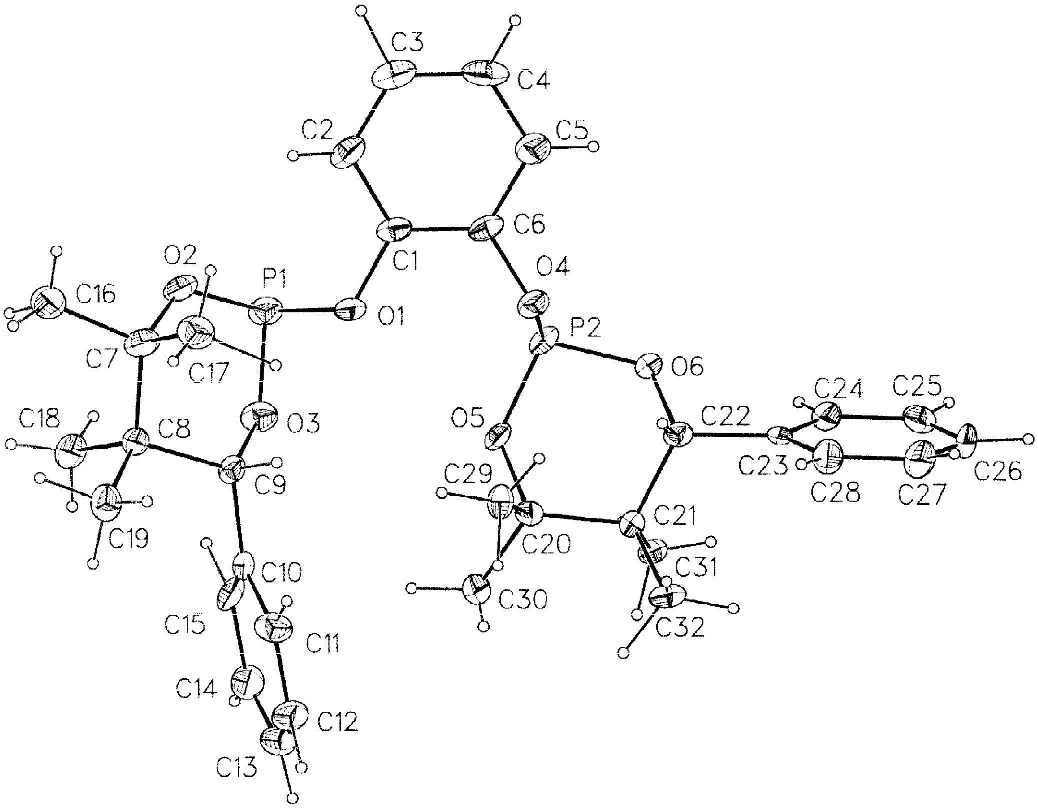
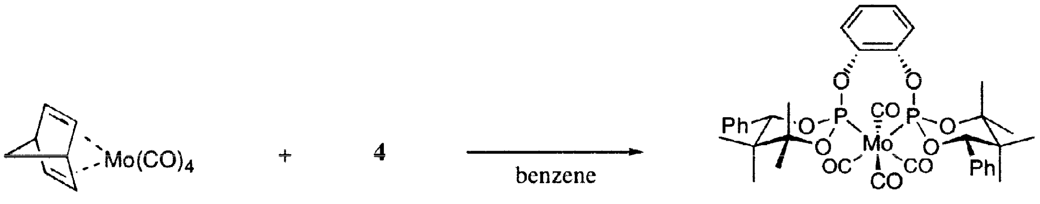


Figure 1. Molecular structure of (*R*,*R*)-**4**

$^3J_{PH}$ coupling constants (2.9-4.4 Hz) for the axial benzylic hydrogen atom, consistent with a chair conformation of the 1,3,2-dioxaphosphorinane rings.[17] The chair conformations predicted from the ^1H NMR spectra as well as axial orientation of the oxygen substituent were confirmed by an X-ray molecular structure determination of **4**. Crystals of **4** suitable for X-ray diffraction were obtained by recrystallization from benzene by slow diffusion of pentane. Enantiomerically pure (*R*,*R*)-**4** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions a = 8.951 (1) Å, b = 10.515(1) Å, c = 31.850 (1) Å. Both dioxaphosphorinane rings adopt an elongated chair conformation with the phenyl groups equatorial. The bridging catechol moiety occupies the axial positions at both phosphorus atoms. The chair conformations are distorted as revealed by the fact that the methyl groups are twisted out of an "ideal" arrangement; the torsion angles between phosphorus and the axial methyl groups are 80.6 (6)° and 80.0 (5)° for the axial methyl groups and -163.1 (4)° and -164.7 (4)° for the equatorial methyl groups. The structure of **4** with adopted labelling scheme is shown in Figure 1. Selected bond lengths and angles are given in the Experimental Section.

Treatment of **4** with $Mo(CO)_4$(norbornadiene) led to **4**·$Mo(CO)_4$ as a glassy off-white solid remarkably soluble in hydrocarbons, even pentane (Scheme 4). The solid is stable in air but solutions gradually turn blue.

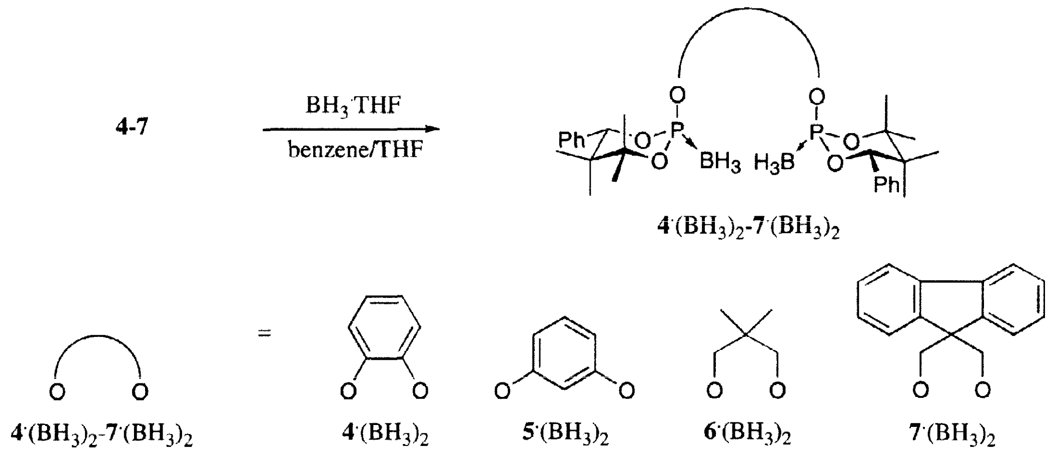


4·Mo(CO)$_4$

Scheme 4

Unfortunately the material was not suitable for an X-ray crystallographic determination. However, the observation in the infrared spectra of four CO vibrations in the 2000 cm^{-1} region attributable to two A_1 modes, a B_1 mode and a B_2 mode[20,25] is consistent with the indicated structure with the two phosphorus atoms *cis* together with two carbonyl groups to form the equatorial plane. The remaining two carbonyl groups are arranged axially. The ^{13}C NMR spectrum is also in accord with this interpretation; the *trans*-carbonyl groups give rise to a triplet at 206 ppm with a coupling constant $^2J_{PC}$ of 12.7 Hz whereas the *cis*-carbonyls are found at 213 ppm with a coupling constant of 15.0 Hz.[14] Reaction of **4** with $[Rh(CO)_2Cl]_2$ in benzene did not lead to a definable product and the reaction was not investigated further.

Borane adducts of **4**-**7** were synthesized by treatment of benzene solutions prepared *in situ* with excess BH_3·THF at ambient temperature (Scheme 5). The adducts **4**·$(BH_3)_2$, **5**·$(BH_3)_2$ and **7**·$(BH_3)_2$ were obtained crystalline, whereas **6**·$(BH_3)_2$ was an oil. Isolated yields averaged around 45%. The ^1H NMR spectra of these borane adducts show broad doublets around 0.5 ppm for the borane hydrogen atoms. Proton decoupled ^{31}P NMR spectra reveal broad doublets around 110 ppm due to coupling to ^{11}B nuclei. Broad singlets around -43 ppm are observed in the ^{11}B NMR spectra. The adducts are stable to air and can be subjected to column chromatography. Indeed the air-sensitive diphosphites, if they require purification, are best converted to their BH$_3$ adducts and purified chromatographically. The complexed BH$_3$ is readily removed by treatment with morpholine.



Scheme 5

Crystals of the resorcinol derived adduct **5**·(BH$_3$)$_2$ were subjected to X-ray crystallographic analysis. Although severe disorder hampered determination of the space group and refinement of the structure, the crude data are consistent with a C$_2$-symmetrical molecule with no unexpected features. The most electronegative substituents clearly continue to occupy the axial positions at phosphorus. The calculated structure is illustrated in Figure 2, no further refinement has been carried out.

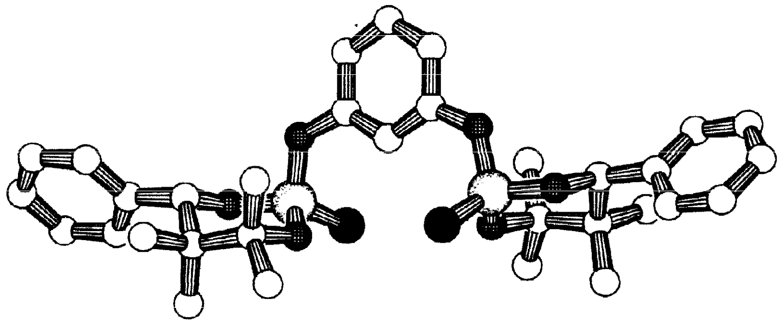
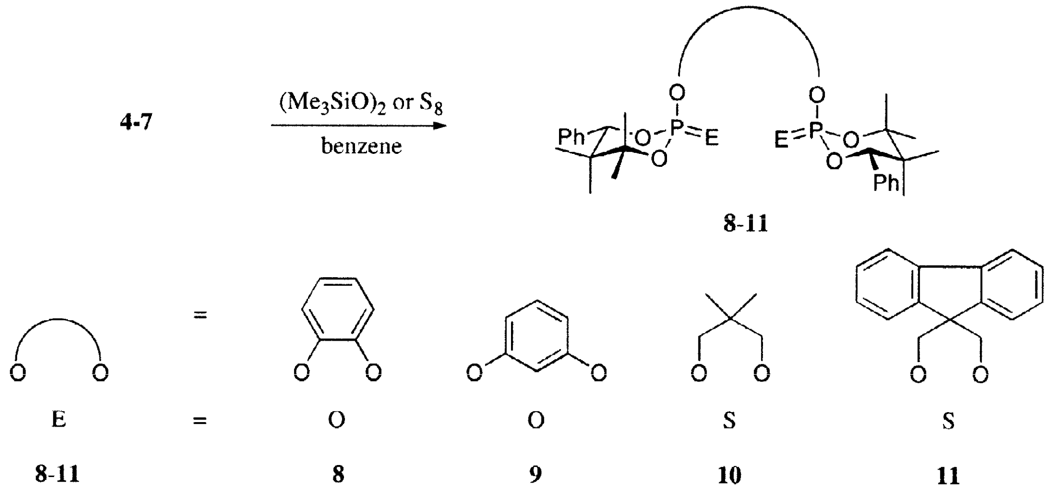


Figure 2. Preliminary molecular structure of **5**·(BH$_3$)$_2$

Oxidation to the corresponding phosphates or thiophosphates was also examined (oxidation-stable derivatives were required for purposes to be described). The aliphatic (di)phosphites **6** and **7** are smoothly converted with retention of configuration to, respectively, thiophosphates **10** and **11** on treatment with sulfur. In the ^{31}P NMR spectrum a single absorption is seen at approximately 60 ppm indicative of stereochemical homogeneity. This reaction fails with **4** and **5**. Attempted oxidation with *m*-chloroperbenzoic acid gave only hydrolysis products.

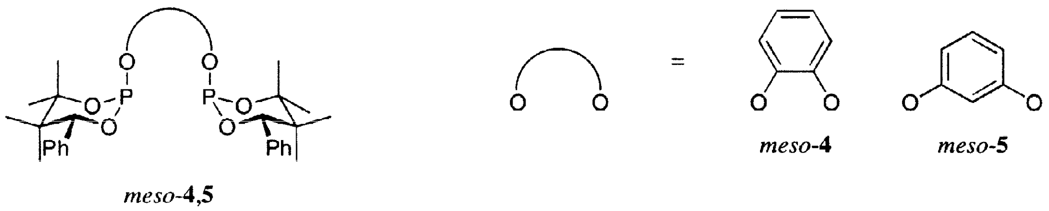
However, as followed by ^{1}H NMR spectroscopy, oxidation of **4** and **5** with anhydrous *tert*-butylperoxide or bis(trimethylsilyl)peroxides[26] provided phosphates **8** and **9**, respectively. These reactions are summarized in Scheme 6. Oxidation with these reagents is known to proceed with retention of configuration.[27]



Scheme 6

Owing to some doubts at the beginning of this work with regard to the enantiomeric purity of diol **1**, the syntheses shown in Scheme 3 were carried out with *racemic* **2a**. This is a simple way to obtain the *meso* diastereomers in solution and to establish their characteristic chemical shifts and absence (or presence) in unpurified **2a**. At the same time the enantiomeric purity of **1** can be established. This simple experiment led to some practical and stereochemical insights as described in the following paragraphs.

The *meso* diastereomers of **4** and **5** are illustrated in Scheme 7 and the *S,S*-enantiomers of the *racemates* in Scheme 3. Owing to the fact that reagents similar to **4** are used regularly for determination of enantiomeric excesses by NMR spectroscopic methods[28] and that chiral self-recognition is unusual in these reactions (a condition for success of the method) we did not anticipate much self-recognition although we realized the point would have to be checked.



Scheme 7

Two products **12a** and **12b** were obtained from resorcinol; from the NMR spectra **12a** was identified as the racemate and **12b** therefore as the *meso* stereoisomer. The ratio as determined from ^{1}H NMR spectra was 1:1 in accord with expectation.

The reaction course with catechol was significantly different. The ^{31}P NMR spectrum of crude products in benzene (a small amount of hexadeuterobenzene was added as internal lock) was identical to that of material prepared from enantiomerically pure **4**; no trace of a stereoisomer was observed. In view of the high sensitivity of NMR methods the conclusion of (unanticipated) absolute self-recognition is tempting. First, however, the possibility that the *meso* and *racemic* diastereomers have identical spectra and chromatographic behaviour had to be eliminated beyond doubt.

Deliberate attempts to prepare *meso*-**4** failed. Mono-substituted catechols - acetates, trimethylsilyl ethers, benzylated derivatives - were allowed to react with (*S*)-**2a** followed by attempted deprotection and reaction with (*R*)-**2a**. To our frustration and annoyance in no case could deprotection without destruction of the 1,3,2-dioxaphosphorinane ring already in place be achieved, and these attempts finally were abandoned.

Recourse was taken in an indirect determination of the amount of *meso*-**4** whereby use was made of the previously described chemistry of **4**. Consider the case in which two structurally identical chiral fragments are brought together in one molecule, connected through an achiral spacer. If *optically enriched* starting material is used (**2** in this case) the molar ratio q_1 of the enantiomers is defined by equation 1.

$$q_1 = \frac{[R]}{[S]} = \frac{100+\%e.e.}{100-\%e.e.} \qquad (1)$$

Limiting values are $q_1=1$ for racemic and $q_1=\infty$ for optically pure material where [*R*] and [*S*] are the molar fractions of the respective enantiomers.

The molar ratio q_2 of the *enantiomers* of the dimeric product is given by equation 2, in which Δ is the degree of self-recognition.

$$q_2 = (q_1)^{2-\Delta} \qquad (2)$$

The degree of self-recognition Δ has values between 0 (no recognition in which case the statistical result $q_1=(q_2)^2$ applies) and 1, in which case $q_1=q_2$. Note that the amount of *meso* isomer does not appear directly in the mathematics. Equation 2 can be rewritten as equation 3.

$$\Delta = 2 - \frac{({}^{10}\log q_2)}{({}^{10}\log q_1)} \qquad (3)$$

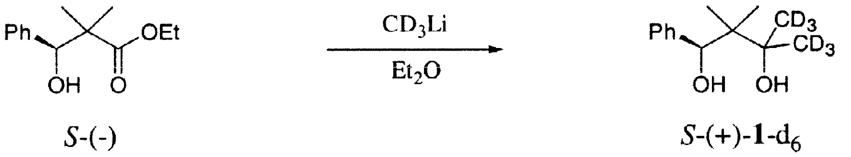
If one has an analytical method to determine q_2 (q_1 is known) then Δ can readily be calculated. The first method investigated was conversion to the phosphates, which are stable enough to withstand chiral hplc (**4** itself is not).

Compound **9** from resorcinol was used as a control since it was clear that no self-recognition had occurred in this case. Oxidation was carried out with trimethylsilyl peroxide (see Scheme 6). Unfortunately, by-products hampered accurate determination of enantiomeric excesses and recourse had to be taken in purification of the diphosphates. The crude catechol diphosphate **8** from *racemic* **1** was dissolved in ethyl acetate and precipitated with hexanes to afford pure crystalline compound; the resorcinol derived diphosphate was purified by flash column chromatography. Enantiomeric enrichment can occur during crystallization.

Starting from diol of 50% e.e. (q_1=3) catechol diphosphate **8** was obtained with 50% e.e. (q_2=3) and resorcinol diphosphate **9** with 84% e.e. (q_2=11.5). These are the averaged values of three e.e. determinations. These figures suggest complete recognition in the case of **8** ($q_1=q_2$) and no recognition in the case of **9** ($q_2>(q_1)^2$). Caution is obviously called for, however, since the e.e. of **9** should not have exceeded 80% [$q_2=(q_1)^2=9$]. Other methods were therefore investigated.

The analysis of crude, unpurified materials can often be carried out by mass spectrometry. Obviously, *meso* and *racemic* forms of one compound will not be distinguished since they have identical compositions. However, selective labelling of one enantiomer, say (*S*), of the starting material will lead to three molecular ions for the product; one without label (*R*,*R*), one with one set of labels (*meso* compound *R*,*S*) and one with two sets of labels (*S*,*S*). If one starts with a *quasi*-racemate, i.e. an equimolar mixture of (*R*) and labelled (*S*) enantiomers, the degree of recognition can be inferred from the relative intensities of the three molecular ion peaks of the products in the mass spectrum. We will assume that the degree of recognition is not affected by remote labelling.

Diol (*S*)-(+)-**1**-d_6 was prepared as shown in Scheme 8. Equimolar amounts of unlabelled diol (*R*)-**1** and labelled diol (*S*)-**1**-d_6 were allowed to react with PCl_3 and thereafter catechol in the usual manner. After exhaustive extraction with benzene, followed by oxidation to the diphosphates, the extract was evaporated to dryness. The products that can be formed are (*S*,*S*)-**8**-d_{12}, (*R*,*S*)-**8**-d_6 and (*R*,*R*)-**8**-d_0.



Scheme 8

Mass spectral analysis was carried out using electrospray (ES) techniques. Electron impact and chemical ionization mass spectrometry (NH_3 as reactant gas) were unsuitable owing to extensive fragmentation. The $(M+H)^+$ peaks for the (*R*,*R*)-**8**-d_0 enantiomer (m/z=615), the (*R*,*S*)-**8**-d_6 *meso* (m/z=621) and the (*S*,*S*)-**8**-d_{12} enantiomer (m/z=627) are separated by six mass (m/z) units. The distribution of parent peaks is 2.0:1.0:2.0 within experimental error corresponding to the presence of 20% *meso*-**8**-d_6. The diastereoselectivity D is given by equation 4, and is

$$D = \frac{[rac] - [meso]}{[rac] + [meso]} * 100\% \qquad (4)$$

equal to 60% in this experiment. There can be no enantiomeric enrichment since *quasi*-racemic diol was used ($q_1 = q_2 = 1$ by definition). In this case D is equivalent to Δ x100%. This experiment leads to the conclusion that self-recognition is present, but not complete. The observation of a d_6 peak establishes, as a cautionary note, that the ^{31}P NMR spectra of *meso* and *racemic* **8** in benzene solution, are indeed by chance exactly equivalent.

A third and final approach - probably the most accurate - was used to estimate the degree of self-recognition. During the course of the work described in previous paragraphs we observed that the ^{1}H NMR spectra of the BH_3 adducts of **4** obtained from reaction of catechol with racemic **1** showed *two sets of absorptions*, arising from the *racemic* and *meso* forms of $\mathbf{4}\cdot(BH_3)_2$. This was a second indication (see previous paragraph) that **4** obtained from racemic **1** might not be diastereomerically homogeneous. The resonances of the benzylic hydrogen atoms in *rac*-$\mathbf{4}\cdot(BH_3)_2$ (major) and *meso*-$\mathbf{4}\cdot(BH_3)_2$ (minor) are particularly suitable for determination of the relative amounts; they are baseline separated and are found in an otherwise "silent" region of the spectrum (δ 5.82 and 5.76 ppm, respectively). The spectra can be determined on crude materials.

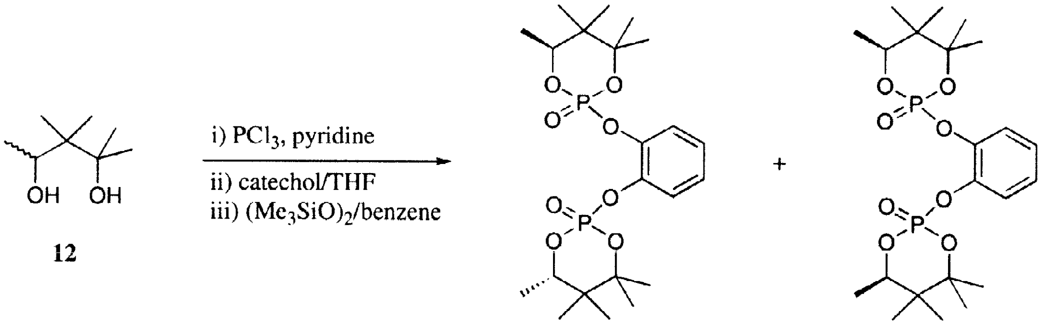
A complication was the appearance of a third benzylic resonance (δ 5.77 ppm) between the *racemic* and *meso* resonances. Separation of a crude mixture by column chromatography afforded a small amount of the compound responsible, which, as judged by ^{1}H NMR spectral data, is probably the borane adduct of the catechol mono-phosphite.

Data as a function of temperature are given in Table 1. The diastereoselectivities, indicative of the degree of self-recognition, agree well with the result of the mass spectral analysis; the loss of the capacity for self-recognition with increasing temperature is in accord with anticipation. An Arrhenius plot (not shown) of these data is linear and indicates a difference of approximately 2 kcal/mol between the activation energies for formation of *racemic* and *meso* products. A diastereoselectivity of 99% is predicted at -124°C, however, the rate of reaction at that temperature is too slow to be of practical use.

Table 1. *Meso:racemic ratios and degrees of recognition for the syntheses of borane adducts*

Temperature (°C)	*meso*-$\mathbf{4}\cdot(BH_3)_2$	*rac*-$\mathbf{4}\cdot(BH_3)_2$	diastereoselectivity (%)
-15	1	6.19	72
20	1	4.24	62
80	1	2.27	39

To investigate whether π-π-interactions might be the source of the self-recognition racemic diol **12** was prepared in which the phenyl group of **1** has been replaced by a methyl group. Synthesis of the diphosphites followed by oxidation as shown in Scheme 9 afforded *racemic*-**13** and *meso*-**13**, which were characterized by NMR spectroscopy. The ^{31}P NMR spectrum of the crude reaction mixture before any work-up revealed two signals of



12

rac-**13**
(+ enantiomer)

meso-**13**

Scheme 9

equal intensity at -15.7 and -15.9 ppm. After work-up the ^{1}H NMR spectrum of **13** was measured; the sets of signals corresponded within experimental error to a 1:1 ratio of *racemic* and *meso* diastereomers. This result is indicative of a role of the phenyl groups in **1** (and **2a**) in the self-recognition leading to **4**.

Conclusions

The need for care in drawing conclusions with regard to stereochemical homogeneity from NMR spectra is illustrated once again. The diphosphites **4** represent a rather extreme case of the potential dangers.

There certainly is a reasonable degree of self-recognition in the assembly of **4** from *racemic* **1**. Owing to the proximity of the hydroxy groups in catechol this is not entirely surprising, although the mechanism by which this occurs is unclear. The phenyl groups are likely involved in the self-recognition process.

Experimental Section

Optical rotations were measured on a Perkin-Elmer 241 polarimeter at room temperature. ^{1}H NMR spectra were recorded on Varian Gemini-200 BB, VXR-300S or Unity-500 spectrometers at 200, 300 and 500 MHz, respectively. ^{13}C and ^{1}H-decoupled ^{31}P NMR spectra were recorded at 50.3 or 75.5 MHz and 81.0 or 121.4 MHz, respectively. ^{11}B NMR spectra were recorded at 96.2 MHz. Chemical shift values are denoted in ppm and are referenced to residual protons in deuterated solvents for ^{1}H NMR ($CDCl_3$: 7.26 ppm; benzene-d_6: 7.16 ppm), to solvent resonances for ^{13}C NMR ($CDCl_3$: 77.01 ppm; benzene-d_6: 128.0 ppm) to external $(PhO)_3PO$ (-18.0 ppm) for ^{31}P NMR and external BF_3·OEt_2 (0 ppm) for ^{11}B NMR. Mass spectra were recorded on AEI-MS-902 (EI) and Ribermag R10-10C (CI) mass spectrometers operated by Mr. A. Kiewiet.# Electrospray mass spectrometry was performed with a R3010 triple-quadrupole apparatus (Delsi-Nermag, Argenteuil, France), equipped with a prototype atmospheric pressure ionization (API) source and an ionspray interface. The stainless steel capillary of the interface was kept at +3.5 kV for positive ions; the nitrogen pressure for nebulization was 3 bar. PE Sciex AP13 software was used for data acquisition and processing. Samples were dissolved in hplc grade CH_3CN. Spectra were obtained by Dr. A.P. Bruins and Mrs. M. Jeromius Stratingh of the Department of Pharmacy of this University. Elemental analyses were performed by Mr. H. Draaijer, Mr. J. Ebels, and Mr. J. Hommes. Solvents were distilled prior to use ($CHCl_3$, CH_2Cl_2, Et_2O, toluene, pentane and hexanes from P_2O_5, THF and benzene from Na/benzophenone). Both enantiomers of 1-phenyl-2,2,3-trimethylbutane-1,3-diol (**1**) and ethyl 3-hydroxy-2,2-dimethylbutanoate were prepared according to previously described procedures.[23, 29] Hplc analyses were carried out on a Waters system 600 hplc apparatus, consisting of a Waters 600 E system controller and a Waters 991 photodiode array detector, or a Waters 510 hplc pump in combination with a Waters 490E programmable multiwavelength detector. The standard operating protocol: Chiralpak® AD, hexanes/2-propanol (70:30), flow 1 ml/min, λ 210 nm.

Trans-(_S_)-2-Chloro-4,4,5,5-tetramethyl-6-(_R_)-phenyl-1,3,2-dioxaphosphorinane (2a)

Diol (*R*)-**1** (0.57 g, 2.7 mmol) and pyridine (0.5 mL, 0.49 g, 6.2 mmol) were dissolved in ether at 0 °C and PCl_3 (0.24 mL, 0.37 mg, 2.7 mmol) was added dropwise. The suspension was stirred at room temperature. After 2 hours, the volatiles were evaporated and the residue was extracted with ether (3 times 5 mL). Distillation under reduced pressure afforded **2a** (0.43 g, 1.6 mmol, 58% yield) as a colorless oil; bp 140 °C (0.02 Torr); ^1H NMR ($CDCl_3$): δ 7.37 (m, 5H, C_6H_5); 5.78 (d, $^3J_{PH} = 6.8$ Hz, 1H, CH); 1.84 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 0.76 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 136.71 (C_{qAr}); 128.11 (CH_{Ar}); 127.94 (CH_{Ar}); 127.52 (CH_{Ar}); 88.03 (d, $^2J_{PC} = 7.3$ Hz, C_q); 77.21 (d, $^2J_{PC} = 5.5$ Hz, CH); 41.89 (d, $^3J_{PC} = 3.7$ Hz, C_q); 26.31 (CH_3); 26.17 (d, $^3J_{PC} = 5.5$ Hz, CH_{3eq}); 21.89 (CH_3). ^{31}P NMR ($CDCl_3$): δ 148.9.

Trans-2H-2-Oxo-4,4,5,5-tetramethyl-6-(_S_)-phenyl-1,3,2-dioxaphosphorinane (3a)

A solution of H_3PO_3 (0.39 g, 4.76 mmol) in THF (5 mL) was added to an ice-cooled solution of (*S*)-**1** (1.0 g, 4.80 mmol) and dicyclohexylcarbodiimide (1.98 g, 9.60 mmol) in THF (15 mL). The resulting white suspension was stirred for 15 minutes and sonicated for 45 minutes. The solids were filtered off and washed with small portions of ether. The combined filtrates were evaporated to give a white solid. ^1H NMR showed the presence of two epimeric H-phosphonates. Crystallization from EtOAc/hexanes afforded 0.36 g (1.42 mmol, 30%) of the *S,S*-epimer as colorless crystals. Concentration of the mother liquor afforded a second crop of crystals, total yield 0.79 g (3.1 mmol, 65%); $[\alpha]_{578}$ +25.3 (c 1.03, $CHCl_3$), $[\alpha]_{365}$ + 91.7 (c 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.37 (s, 5H, C_6H_5); 7.16 (d, $^1J_{PH} = 677$ Hz, 1H, PH); 5.54 (d, $^3J_{PH} = 3.6$ Hz, 1H, CH); 1.71 (s, 3H, CH_3); 1.45 (d, $^4J_{PH} = 2.6$ Hz, 3H, CH_3); 1.13 (s, 3H, CH_3), 0.79 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 135.73 (C_{qAr}); 128.49 (CH_{Ar}); 128.05 (CH_{Ar}); 127.76 (CH_{Ar}); 90.05 (d, $^2J_{PC} = 8.0$ Hz, C_q); 83.03 (d, $^2J_{PC} = 4.8$ Hz, CH); 41.81 (d, $^3J_{PC} = 4.8$ Hz, C_q); 25.99 (d, $^3J_{PC} = 5.5$ Hz, CH_{3eq}); 24.25 (CH_3); 21.55 (CH_3); 15.52 (CH_3). ^{31}P NMR ($CDCl_3$): δ -3.2. Anal. calcd for $C_{13}H_{19}O_3P$: C, 61.41; H, 7.53; P, 12.18. Found: C, 61.39; H, 7.69; P, 12.07.

Catechol diphosphite 4

To an ice-cooled stirred solution of (*S*)-**1** (251.8 mg, 1.21 mmol) and pyridine (0.35 mL, 0.34 g, 4.3 mmol) in THF (10 mL) was added dropwise PCl_3 (0.106 mL, 166 mg, 1.21 mmol). A white precipitate formed and the suspension was stirred at room temperature for 20 minutes. Catechol (67.0 mg, 6.08 mmol) was added and the reaction mixture was stirred overnight. The volatiles were evaporated and the resulting white solid was stripped twice with 5 mL of benzene. After five extractions with benzene (10 mL) the extracts were concentrated and the product crystallized by slow diffusion of pentane, yield 0.223 g (0.38 mmol, 63%) of **4** as white crystalline material; ^{1}H NMR (C_6D_6): δ 7.29-7.14 (m, 12H, Ar); 6.69-6.65 (m, 2H, C_6H_4); 5.91 (d, $^3J_{PH}$ = 2.9 Hz, 2H, CHPh); 1.77 (s, 6H, CH_3); 1.20 (s, 6H, CH_3); 1.05 (s, 6H, CH_3); 0.47 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 145.03 (m, C_{qAr}); 138.81 (C_{qAr}); 128.85 (CH_{Ar}); 127.56 (CH_{Ar}); 123.80 (CH_{Ar}); 121.54 (CH_{Ar}); 121.39 (CH_{Ar}); 83.89 (d, J_{PC} = 3.7 Hz, C_q); 75.23 (CHPh); 41.76 (C_q); 26.86 (CH_3); 26.47 (CH_3); 21.95 (CH_3); 15.95 (CH_3); ^{31}P NMR (C_6D_6): δ 121. Anal. calcd for $C_{32}H_{40}O_6P_2$: C, 65.97; H, 6.92; P, 10.63. Found: C, 66.02; H, 7.07; P, 10.55. HRMS calcd 582.230, found 582.230.

Diphosphites 5-7. General Procedure.

To an ice-cooled solution of **1** (1 eq.) and pyridine (3.5 eq.) in THF was added dropwise PCl_3 (1 eq.). The white suspension was stirred at room temperature for 15 minutes. Diol (0.5 eq.) was added and the suspension was stirred overnight at room temperature. The volatiles were evaporated and the resulting solid was stripped with benzene. Three extractions with benzene afforded, after evaporation of the solvent, the crude products as white foams in essentially quantitative yields. The diphosphites were contaminated with, *inter alia*, phosphonates **3** (^{1}H NMR, ^{31}P NMR).

Resorcinol diphosphite 5

^{1}H NMR (C_6D_6): δ 7.24-7.21 (m, 4H, C_6H_5); 7.14-7.10 (m, 6H, C_6H_5); 6.96 (m, 1H, C_6H_4); 6.88 (m, 3H, C_6H_4); 5.76 (d, $^3J_{PH}$ = 4.4 Hz, 2H, CH); 1.58 (s, 6H, CH_3); 1.10 (s, 6H, CH_3); 1.01 (s, 6H, CH_3); 0.39 (s, 6H, CH_3). ^{31}P NMR (C_6D_6): δ 122.

Dimethyl propanediol diphosphite 6

^{1}H NMR (C_6D_6): δ 7.34-7.29 (m, 4H, C_6H_5); 7.14-7.08 (m, 6H, C_6H_5); 5.68 (d, $^3J_{PH}$ = 3.9 Hz, 2H, CH); 1.67 (s, 6H, CH_3); 1.16 (s, 6H, CH_3); 1.07 (s, 6H, CH_3); 0.78 (s, 6H, CH_3); 0.47 (s, 6H, CH_3). ^{31}P NMR (C_6D_6): δ 130.0.

Fluorenedimethanol diphosphite 7

^{1}H NMR (C_6D_6): δ 7.59-7.48 (m, 8H, C_6H_4); 7.34-7.29 (m, 4H, C_6H_5); 7.28-7.07 (m, 6H, C_6H_5); 5.58 (d, $^3J_{PH}$ = 3.4 Hz, 2H, CH); 4.21-3.91 (dAB, 4H, CH_2); 1.47 (s, 6H, CH_3); 1.09 (s, 6H, CH_3); 1.01 (s, 6H, CH_3); 0.42 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 146.08 (C_{qAr}); 141.44 (C_{qAr}); 139.06 (C_{qAr}); 128.87 (CH_{Ar}); 128.22 (CH_{Ar}); 127.82 (CH_{Ar}); 127.54 (CH_{Ar}); 127.26 (CH_{Ar}); 125.61 (CH_{Ar}); 120.12 (CH_{Ar}); 82.77 (d, J_{PC} = 7.6 Hz, C_q); 74.30 (CHPh); 64.94 (d,

J_{PC} = 21.4 Hz, CH_2); 56.16 (t, C_q); 41.48 (C_q); 26.67 (CH_3); 26.37 (CH_3); 21.81 (CH_3); 15.77 (CH_3). ^{31}P NMR (C_6D_6): δ 128.9.

Molybdenum complex 4·Mo(CO)$_4$

(NBD)Mo(CO)$_4$ (50.2 mg, 0.167 mmol) and **4** (97.5 mg, 0.167 mmol) were dissolved in benzene (5 mL). After stirring overnight, the volatiles were removed under reduced pressure and the yellowish foam was purified by column chromatography (Al_2O_3 neutral, Act I; EtOAc/hexanes 1:5). The resulting colorless oil was dissolved in pentane. Slow evaporation of the solvent afforded **4**·Mo(CO)$_4$ as a glassy solid (105.3 mg, 0.133 mmol, 80% yield); ^{1}H NMR ($CDCl_3$); δ 7.46-7.34 (m, 10H, C_6H_5); 7.05-7.03 (m, 2H, C_6H_4); 6.99-6.97 (m, 2H, C_6H_4); 5.79 (s, 2H, CH); 1.75 (s, 6H, CH_3); 1.36 (s, 6H, CH_3); 1.14 (s, 6H, CH_3); 0.75 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$): δ 212.75 (dd, $^2J_{PC}$ = 15.0 Hz, CO); 206.12 (t, $^2J_{PC}$ = 12.7 Hz, CO); 143.68 (C_{qAr}); 137.47 (C_{qAr}); 128.26 (CH_{Ar}); 127.79 (CH_{Ar}); 127.50 (CH_{Ar}); 125.87 (CH_{Ar}); 124.89 (CH_{Ar}); 87.43 (C_q); 78.37 (CH); 41.34 (C_q); 25.96 (CH_3); 21.90 (CH_3); 15.85 (CH_3); ^{31}P NMR ($CDCl_3$): δ 151.8; IR (nujol): 2043 cm^{-1}, 1958 cm^{-1} (CO, A_1); 1941 cm^{-1} (CO, B_1); 1915 cm^{-1} (CO, B_2).

Attempted synthesis of 4·Rh(CO)Cl

Benzene-d_6 (0.6 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (8.1 mg, 20.8 μmol) and **4** (24.7 mg, 42.4 μmol). A yellow precipitate (19.5 mg) formed. The solid was dried and dissolved in $CDCl_3$. No definable products could be identified by NMR spectroscopy.

Borane complexes 4·(BH$_3$)$_2$-7·(BH$_3$)$_2$. General procedure

Diphosphites were prepared from (*S*)-**1** (0.25 g, 1.2 mmol) as described above. To the crude diphosphite in benzene a twofold excess of BH_3·THF (0.7 M in THF) was added. After stirring for 1-3 h at room temperature, the excess BH_3 was decomposed by addition of 1 mL of methanol. The solution was evaporated to dryness and the air-stable residue purified by column chromatography (silica, EtOAc/hexanes 1:1).

Catechol diphosphite borane adduct 4·(BH$_3$)$_2$

White crystalline solid; R_f 0.69; yield 45%; $[\alpha]_{578}$ - 18.2 (c 0.516; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 10H, Ph); 7.17 (m, 2H, C_6H_4); 7.01 (m, 2H, C_6H_4); 5.76 (d, $^3J_{PH}$ = 3.3 Hz, 2H, CHPh); 1.79 (s, 6H, CH_3); 1.48 (s, 6H, CH_3); 1.12 (s, 6H, CH_3); 0.75 (s, 6H, CH_3); 0.55 (br. d, 6H, BH_3). ^{13}C NMR ($CDCl_3$): δ 142.11 (m, C_{qAr}); 135.85 (d, J_{PC} = 7.3 Hz, C_{qAr}); 128.35 (CH_{Ar}); 128.16 (CH_{Ar}); 127.71 (CH_{Ar}); 125.42 (CH_{Ar}); 121.81 (d, J_{PC} = 2.4 Hz, CH_{Ar}); 90.05 (d, J_{PC} = 11.0 Hz, C_q); 80.58 (d, J_{PC} = 8.5 Hz, CHPh); 41.89 (d, J_{PC} = 3.6 Hz, C_q); 26.08 (d, J_{PC} = 8.5 Hz, CH_3); 25.44 (CH_3); 21.72 (CH_3); 15.49 (CH_3). ^{31}P NMR ($CDCl_3$): δ 103.7 (d, J_{PB} = 106 Hz). ^{11}B NMR ($CDCl_3$): δ -43.3. Anal. calcd for $C_{32}H_{46}B_2O_6P_2$: C, 62.98; H, 7.60; P, 10.15. Found: C, 63.03; H, 7.64; P, 10.01.

Resorcinol diphosphite borane adduct $5{\cdot}(BH_3)_2$

White crystalline solid; R_f 0.58; yield 43%; $[\alpha]_{578}$ +20.6 (c 0.50; $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.38-7.35 (m, 10H, Ph); 7.20 (m, 1H, C_6H_4); 7.00 (m, 1H, C_6H_4); 6.90 (m, 2H, C_6H_4); 5.72 (d, $^3J_{PH}$ = 3.6 Hz, 2H, CHPh); 1.72 (s, 6H, CH_3); 1.47 (d, $^4J_{PH}$ = 0.8 Hz, 6H, CH_3); 1.13 (s, 6H, CH_3); 0.77 (s, 6H, CH_3); 0.57 (br. d, $^4J_{HP}$ = 122 Hz, 6H, BH_3). ^{13}C NMR ($CDCl_3$): δ 151.40 (m, C_{qAr}); 135.74 (d, J_{PC} = 8.2 Hz, C_{qAr}); 130.25 (CH_{Ar}); 128.43 (CH_{Ar}); 128.17 (CH_{Ar}); 127.75 (CH_{Ar}); 116.75 (d, J_{PC} = 4.1 Hz, CH_{Ar}); 112.91 (CH_{Ar}); 89.79 (d, J_{PC} = 10.7 Hz, C_q); 80.68 (d, J_{PC} = 8.2 Hz, CHPh); 41.98 (d, J_{PC} = 4.1 Hz, C_q); 25.99 (d, J_{PC} = 8.2 Hz, CH_3); 25.07 (CH_3); 21.78 (CH_3); 15.47 (CH_3). ^{31}P NMR ($CDCl_3$): δ 103.1 (d, J_{PB} = 113 Hz). ^{11}B NMR ($CDCl_3$): δ -42.0. Anal. calcd for $C_{32}H_{46}B_2O_6P_2$: C, 62.98; H, 7.60; P, 10.15. Found: C, 62.94; H, 7.58; P, 10.05.

Dimethylpropanediol diphosphite borane adduct $6{\cdot}(BH_3)_2$

Colorless oil characterised spectroscopically and not purified further; ^1H NMR ($CDCl_3$): δ 7.36-7.33 (m, 10H, Ph); 5.56 (d, 2H, $^3J_{PH}$ = 3.6 Hz, 2H, CHPh); 5.72 (d, $^3J_{PH}$ = 2.9 Hz, 2H, CHPh); 3.86-3.71 (m, 4H, CH_2); 1.71 (s, 6H, CH_3); 1.40 (s, 6H, CH_3); 1.06 (s, 6H, CH_3); 0.95 (s, 6H, CH_3); 0.73 (s, 6H, CH_3); 0.6 (br. d, 6H, BH_3); ^{13}C NMR ($CDCl_3$): δ 136.20 (d, J_{PC} = 8.6 Hz, C_{qAr}); 128.21 (CH_{Ar}); 128.16 (CH_{Ar}); 127.63 (CH_{Ar}); 88.23 (d, J_{PC} = 9.76 Hz, C_q); 79.71 (d, J_{PC} = 8.5 Hz, CHPh); 71.35 (CH_2); 41.67 (d, J_{PC} = 4.9 Hz, C_q); 36.35 (m, C_q); 25.95 (d, J_{PC} = 8.6 Hz, CH_3); 25.54 (CH_3); 21.65 (CH_3); 21.15 (CH_3); 15.37 (CH_3). ^{31}P NMR ($CDCl_3$): δ 107.5 (d, J_{PB} = 123 Hz). ^{11}B NMR ($CDCl_3$): δ -43.1.

Fluorenedimethanol diphosphite borane adduct $7{\cdot}(BH_3)_2$

White crystalline solid; R_f 0.65; yield 47%; $[\alpha]_{578}$ -54.4 (c 0.502; $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.67-7.21 (m, 18H, Ar); 5.16 (d, $^3J_{PH}$ = 3.3 Hz, 2H, CHPh); 4.32 (d, $^3J_{PH}$ = 4.4 Hz, 4H, CH_2); 1.27 (s, 12H, CH_3); 0.96 (s, 6H, CH_3); 0.60 (s, 6H, CH_3); 0.5 (br. d, 6H, BH_3). ^{13}C NMR ($CDCl_3$): δ 143.94 (C_{qAr}); 141.17 (C_{qAr}); 136.03 (d, J_{PC} = 8.6 Hz, C_{qAr}); 128.56 (CH_{Ar}); 128.19 (CH_{Ar}); 127.53 (CH_{Ar}); 127.43 (CH_{Ar}); 124.52 (CH_{Ar}); 120.07 (CH_{Ar}); 88.54 (d, J_{PC} = 11.0 Hz, C_q); 79.51 (d, J_{PC} = 8.5 Hz, CHPh); 68.71 (CH_2); 55.22 (C_q); 41.56 (d, J_{PC} = 4.9 Hz, C_q); 25.79 (d, J_{PC} = 8.5 Hz, CH_3); 24.83 (CH_3); 21.57 (CH_3); 15.28 (CH_3). ^{31}P NMR ($CDCl_3$): δ 107.4 (d, J_{PB} = 120 Hz). ^{11}B NMR ($CDCl_3$): δ -43.4.

Deprotection of $7{\cdot}(BH_3)_2$

A solution of $7{\cdot}(BH_3)_2$ (143 mg, 0.20 mmol) in morpholine (3 mL) was heated at 100 °C overnight. The solvent was evaporated and the resulting oil was stripped twice with benzene (2 mL). Extraction with benzene (5 mL) afforded an impure oily substance. Diphosphite **7** was the only phosphorus compound detectable by NMR spectroscopy.

Diphosphates and di(thiophosphates). General procedure.

Diphosphites were prepared as described above. To the crude benzene extract of the diphosphite was added a slight excess of oxidant (*t*-BuOOH, $(Me_3SiO)_2$ or S_8). After standing overnight, the solution was evaporated to dryness and the product was purified by column chromatography and/or crystallization.

Catechol diphosphate 8

Obtained from (*S*)-**1** (0.25 g, 1.20 mmol) by oxidation with $(Me_3SiO)_2$, followed by crystallization from ethanol; yield 191 mg (0.31 mmol, 52%) of **8** as a white solid; ^{1}H NMR ($CDCl_3$): δ 7.37-7.27 (m, 12H, Ar); 7.04-7.00 (m, 2H, C_6H_4); 5.72 (d, $^3J_{PH}$ = 2.0 Hz, 2H, CHPh); 1.70 (s, 6H, CH_3); 1.46 (d, J_{PH} = 3.2 Hz, 6H, CH_3); 1.09 (s, 6H, CH_3); 0.70 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 141.33 (m, C_{qAr}); 135.74 (d, J_{PC} = 11.0 Hz, C_{qAr}); 128.28 (CH_{Ar}); 127.99 (CH_{Ar}); 127.63 (CH_{Ar}); 125.21 (CH_{Ar}); 120.82 (d, J_{PC} = 2.4 Hz, CH_{Ar}); 91.81 (d, J_{PC} = 8.5 Hz, C_q); 84.12 (d, J_{PC} = 6.1 Hz, CHPh); 41.38 (d, J_{PC} = 3.6 Hz, C_q); 25.97 (d, J_{PC} = 10.9 Hz, CH_3); 24.15 (CH_3); 21.50 (CH_3); 15.19 (CH_3). ^{31}P NMR ($CDCl_3$): δ -15. Anal. calcd for $C_{32}H_{40}O_8P_2$: C, 62.54; H, 6.56; P, 10.08. Found: C, 62.29; H, 6.59; P, 9.95. Hplc: R_f 8.4 minutes [(*S*,*S*)-enantiomer)], R_f 9.7 minutes [(*R*,*R*)-enantiomer)].

Resorcinol diphosphate 9

From (*S*)-**1** (0.25 g, 1.20 mmol). Oxidation with $(Me_3SiO)_2$, crystallization from ethanol; yield 185 mg (0.30 mmol, 50%) of **9** as a white solid; ^{1}H NMR ($CDCl_3$): δ 7.36 (s, 10H, Ph); 7.21-7.02 (m, 4H, C_6H_4); 5.64 (d, $^3J_{PH}$ = 2.0 Hz, 2H, CHPh); 1.65 (s, 6H, CH_3); 1.46 (d, $^4J_{PH}$ = 3.2 Hz, 6H, CH_3); 1.10 (s, 6H, CH_3); 0.75 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 151.36 (d, J_{PC} = 6 Hz, C_{qAr}); 135.60 (d, J_{PC} = 11 Hz, C_{qAr}); 130.43 (CH_{Ar}); 128.42 (CH_{Ar}); 128.03 (CH_{Ar}); 127.71 (CH_{Ar}); 115.73 (d, J_{PC} = 5 Hz, CH_{Ar}); 111.57 (t, J_{PC} = 7 Hz, CH_{ar}); 91.44 (d, P_{PC} = 9 Hz, C_q); 84.17 (d, J_{PC} = 6 Hz, CH); 41.33 (d, J_{PC} = 4 Hz, C_q); 25.90 (d, J_{PC} = 11 Hz, CH_3); 24.03 (CH_3); 21.51 (CH_3); 15.11 (CH_3). ^{31}P NMR ($CDCl_3$): δ -15. Hplc: R_f 8.4 minutes [(*R*,*R*)-enantiomer)], R_f 10.4 minutes [(*S*,*S*)-enantiomer)], R_f 14.8 minutes (*meso*).

2,2-Dimethylpropanediol di(thiophosphate) 10

From (*S*)-**1** (269 mg, 1.29 mmol). Oxidation with sulfur, purification by column chromatography (silica, EtOAc/hexanes 1:5) and crystallization from EtOAc/hexanes; yield 111.3 mg, (0.174 mmol, 27%) of **10** as white crystals; R_f 0.37; ^{1}H NMR ($CDCl_3$): δ 7.37-7.30 (m, 10H, Ph); 5.60 (d, J_{PH} = 2.9 Hz, 2H, CH); 3.87 (m, 4H, CH_2); 1.71 (s, 6H, CH_3); 1.43 (d, J_{PH} = 2.6 Hz, 6H, CH_3); 1.09 (s, 6H, CH_3); 0.96 (s, 6H, CH_3); 0.72 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 136.07 (d, J_{PC} = 11 Hz, C_{qAr}); 128.22 (CH_{Ar}); 127.61 (CH_{Ar}); 91.25 (d, J_{PC} = 10 Hz, C_q); 83.14 (d, J_{PC} = 7 Hz, CHPh); 72.36 (d, J_{PC} = 5 Hz, CH_2); 41.20 (d, J_{PC} = 4 Hz, C_q); 35.99 (t, J_{PC} = 9 Hz, C_q); 26.23 (d, J_{PC} = 11 Hz, CH_3); 25.12 (CH_3); 21.56 (CH_3); 21.56 (CH_3); 21.46 (CH_3); 15.55 (CH_3). ^{31}P NMR ($CDCl_3$): δ 60.2.

Fluorenedimethanol di(thiophosphate) 11

From (*S*)-**1** (255 mg, 1.22 mmol). Oxidation with sulfur, purification by column chromatography (silica, EtOAc/hexanes 1:4) and crystallization from EtOAc/hexanes, yield 179.9 mg (0.234 mmol, 39%) of **11** as a white solid; R_f 0.38; ^{1}H NMR ($CDCl_3$): δ 7.66 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C_6H_4); 7.50 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C_6H_4); 7.40-7.23 (m, 14H, Ph); 5.19 (d, J_{PH} = 2.9 Hz, 2H, CH); 4.46-4.11 (m, 4H, CH_2); 1.30 (d, $^4J_{PH}$ = 2.9 Hz, 6H, CH_3); 1.24 (s, 6H, CH_3); 0.99 (s, 6H, CH_3); 0.59 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 144.17 (C_{qAr}); 141.14 (C_{qAr}); 135.91 (d, J_{PC} = 9.8 Hz, C_{qAr}); 128.52 (CH_{Ar}); 128.24 (CH_{Ar}); 128.18 (CH_{Ar}); 127.51 (CH_{Ar}); 127.43 (CH_{Ar}); 124.58 (CH_{Ar}); 120.05 (CH_{Ar}); 91.50 (d, J_{PC} = 9.8 Hz, C_q); 82.91 (d, J_{PC} = 8.6 Hz, CH); 69.66 (d, J_{PC} = 4.9 Hz, C_q); 54.85 (t, J_{PC} = 9.8 Hz, C_q); 41.07 (d, J_{PC} = 3.7 Hz, C_q); 26.03 (d, J_{PC} = 17.0 Hz, CH_3); 24.36 (CH_3); 21.46 (CH_3); 15.44 (CH_3). ^{31}P NMR ($CDCl_3$): δ 59.4.

Enantiomericaly enriched diphosphates 8 and 9

Two 0.10 g samples of (*S*)-**1** (50% e.e.; Hplc: Chiralpak OD, 3% 2-propanol in hexanes) were converted to the diphosphates **8** and **9** as previously described. Diphosphate **8** was purified by column chromatography (silica, ethyl acetate/hexanes 1:1) and diphosphate **9** was purified by crystallization from ethyl acetate/hexanes. Enantiomeric compositions of the diphosphates were determined by chiral Hplc. The values given are the averages of three determinations. Diphosphate **8**: 84% e.e., diphosphate **9**: 50% e.e.

(*S*)-1-Phenyl-2,2-dimethyl-3,3-bis(trideuteromethyl)propane-1,3-diol (1-d_6)

This diol was prepared analogously to diol **1** from (*S*)-(-)-ethyl 3-phenyl-3-hydroxy-2,2-dimethyl propionate (1.87 g, 8.4 mmol) and 0.36 M methyllithium-d_3 (65 mL, 23.4 mmol) to give 0.65 g (3.03 mmol, 36% yield) of **1**-d_6 as white crystals; ^{1}H NMR ($CDCl_3$): δ 7.35-7.26 (m, 5H, Ph); 4.97 (s, 1H, CH); 3.87 (s, 1H, OH); 3.26 (s, 1H, OH); 0.95 (s, 3H, CH_3); 0.64 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 141.7 (C_{qAr}); 128.55 (CH_{Ar}); 127.50 (CH_{Ar}); 127.54 (CH_{Ar}); 79.96 (CH); 43.08 (C_q); 22.77 (CH_3); 14.46 (CH_3).

Labelled diphosphates 8

A mixture of (*R*)-**1** (49.8 mg, 0.239 mmol) and (*S*)-**1**-d_6 (51.2 mg, 0.239 mmol) was converted to the diphosphates as described previously. The crude products were analyzed using electrospray mass spectrometry (ES-MS).

Borane adducts 4·$(BH_3)_2$ from racemic 1.

The borane complexes were prepared by means of a standard procedure: 0.10 g of *rac*-**1** (0.48 mmol) was dissolved in THF (5 mL). Pyridine (0.15 mL, 0.15 g, 1.85 mmol) was added and the solution was cooled to 0 °C. PCl_3 (43 μL, 67.5 mg, 0.49 mmol) was added dropwise and the white suspension was stirred at room temperature for 30 minutes. Catechol (55 mg, 0.50 mmol) was added and the mixture was stirred at -15 °C (5 days), room temperature (overnight), or 80 °C (5 hours). After the indicated periods, the products were extracted with benzene (5 times with 10 mL). Excess BH_3·THF was added and the solution was stirred for 1 hour at room temperature. Excess borane was decomposed with methanol. Evaporation of the solution gave the crude products as white solids. ^{1}H NMR spectra were recorded to establish the *meso:rac* ratios. Column chromatography (silica, ethyl acetate/hexanes 1:3) of the crude sample from the reaction run at 80 °C afforded pure *rac*-**4**·(BH$_3$)$_2$, *meso*-**4**·(BH$_3$)$_2$, and catechol monophosphite borane adduct. NMR spectral data for the *rac*-diphosphite borane adduct are identical to those for the enantiomerically pure adduct.

meso-Borane adduct (*meso*-4·(BH$_3$)$_2$)

^{1}H NMR (CDCl$_3$): δ 7.38-7.33 (m, 10H, C$_6$H$_5$); 7.21-7.18 (m 2H, C$_6$H$_4$); 7.07-7.04 (m 2H, C$_6$H$_4$); 5.82 (d, ^{3}J$_{PH}$ = 3.7 Hz, CH); 1.65 (s, 6H, CH$_3$); 1.11 (s, 6H, CH$_3$); 1.06 (s, 6H, CH$_3$); 0.69 (s, 6H, CH$_3$); 0.6 (br. d, 6H, BH$_3$). ^{13}C NMR (CDCl$_3$): δ 142.17 (dd, ^{2}J$_{PC}$ = 3.7 Hz, ^{3}J$_{PC}$ = 3.7 Hz, C$_{qAr}$); 136.11 (d, ^{3}J$_{PC}$ = 7.3 Hz, C$_{qAr}$); 128.39 (CH$_{Ar}$); 128.31 (CH$_{Ar}$); 127.64 (CH$_{Ar}$); 125.25 (CH$_{Ar}$); 121.55 (d, J$_{PC}$ = 3.7 Hz, CH$_{AR}$); 89.87 (d, ^{2}J$_{PC}$ = 11.0 Hz, C$_q$); 80.60 (d, ^{2}J$_{PC}$ = 8.6 Hz, CH); 41.89 (d, ^{3}J$_{PC}$ = 4.9 Hz, C$_q$); 25.45 (d, ^{3}J$_{PC}$ = 8.6 Hz, CH$_3$); 24.95 (CH$_3$); 21.65 (CH$_3$); 15.40 (CH$_3$). ^{31}P NMR (CDCl$_3$): δ 104.3.

Catechol monophosphite borane adduct

^{1}H NMR (CDCl$_3$): δ 7.41-7.35 (m, 5H, C$_6$H$_5$); 7.11-7.06 (m, 1H, C$_6$H$_4$); 7.05-7.03 (m, 1H, C$_6$H$_4$); 6.99-6.97 (m, 1H, C$_6$H$_4$); 6.81-6.78 (m, 1H, C$_6$H$_4$); 5.77 (d, ^{3}J$_{PH}$ = 3.4 Hz, 1H, CH); 5.40 (s, 1H, OH); 1.75 (s, 3H, CH$_3$); 1.50 (d, ^{4}J$_{PH}$ = 1.0 Hz, 3H, CH$_3$); 1.15 (2, 3H, CH$_3$); 0.79 (s, 3H, CH$_3$); 0.6 (br. m, 3H, BH$_3$). ^{13}C NMR (CDCl$_3$): δ 146.91 (C$_{qAr}$); 135.50 (d, J$_{PC}$ = 7.5 Hz,C$_{qAr}$); 128.60 (CH$_{PH}$); 128.10 (CH$_{PH}$); 127.85 (CH$_{PH}$); 125.99 (CH$_{Ar}$); 120.66 (CH$_{Ar}$); 120.25 (CH$_{Ar}$); 116.96 (CH$_{Ar}$); 90.20 (d, J$_{PC}$ = 11.2 Hz, CH); 81.11 (d, J$_{PC}$ = 7.5 Hz, C$_q$); 41.96 (d, J$_{PC}$ = 3.7 Hz, C$_q$); 26.00 (d, J$_{PC}$ = 9.3 Hz, CH$_3$); 25.12 (CH$_3$); 21.80 (CH$_3$); 15.49 (CH$_3$).

rac-2,3,3-Trimethyl-2,4-pentanediol (12)

A 1.85 M solution of MeMgI (70 mL, 0.13 mol) in ether was added dropwise to a stirred solution of ethyl 3-hydroxy-2,2-dimethylbutanoate (5.35 g, 33.4 mmol) in THF (30 mL). The resulting white suspension was stirred overnight. Saturated aqueous NH$_4$Cl was added carefully and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic layers were washed with aqueous Na$_2$S$_2$O$_5$ and brine and were dried over Na$_2$SO$_4$. Evaporation of the solvent gave **12** as a white solid; yield 2.95 g (20.2 mmol, 60%); ^{1}H NMR (CDCl$_3$): δ 4.09 (q, ^{3}J$_{HH}$ = 6.2 Hz, 1H, CH); 3.89 (br. s, 2H, OH); 1.28 (s, 3H, CH$_3$); 1.18 (s, 3H, CH$_3$); 1.11 (d, ^{3}J$_{HH}$ = 6.2 Hz, 3H, CH$_3$); 0.96 (s, 3H, CH$_3$); 0.71 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 77.50 (C$_q$); 72.32 (CH); 42.36 (C$_q$); 26.20 (CH$_3$); 25.21 (CH$_3$); 22.40 (CH$_3$); 18.38 (CH$_3$); 14.03 (CH$_3$). Anal. calcd for C$_8$H$_{18}$O$_2$: C, 65.71; H, 12.41. Found: C, 65.86; H, 12.47.

rac- and *meso*-Diphosphates 13

To a stirred solution of **12** (110.2 mg, 0.75 mmol) and pyridine (0.2 mL, 0.2 g, 2.5 mmol) in THF (5mL) was added PCl$_3$ (70 μL, 0.11 g, 0.8 mmol) at 0 °C. The white suspension was stirred at room temperature for 15 minutes and catechol (45.9 mg, 0.42 mmol) was added. The mixture was stirred overnight. The solvent was evaporated and the residue was stripped twice with 5 mL of benzene. The products were extracted five times with benzene (10 mL). To the extract $(Me_3SiO)_2$ was added (0.2 mL, excess) and stirring continued overnight. A sample from the reaction mixture revealed the presence of two equally intense signals attributable to the diphosphates. Evaporation of the volatiles and column chromatography (Al_2O_3/ethyl acetate) afforded a mixture of *meso*- and *rac*-**13** as a white foam (77 mg, 0.16 mmol, 42% yield); ^1H NMR ($CDCl_3$): δ 7.46-7.37 (m, 2H, C_6H_4); 7.10-7.05 (m, 2H, C_6H_4); 4.91-4.85 (m, 2H, CH); 1.55/1.54 (s, 3+3H, 6_{ax}-CH_3); 1.41/1.39 (s, 3+3H, 6_{eq}-CH_3); 1.35-1.29 (dd, 3+3H, 4_{eq}-CH_3); 1.14 (s, 6H, 5_{ax}-CH_3); 0.82 (s, 6H, 5_{eq}-CH_3). ^{31}P NMR ($CDCl_3$): δ -15.03, -15.14.

Molecular structure of (*R,R*)-4

Suitable transparent white block-shaped crystals of (*R*,*R*)-**4** were obtained by recrystallization from benzene/pentane. Crystal data for $C_{32}H_{40}O_6P_2$, M_r=582.61, orthorhombic $P2_12_12_1$, cell dimensions: a=8.951 (1) Å, b=10.515 (1) Å, c=31.851 (2) Å, V=2997.7 (5) Å^3, Z=4, D=1.291 g/cm^3, T=130 K, R=0.052 for 2789 unique observed reflections.

Table 2. *Selected bond angles (deg) for diphosphite (R,R)-4*[a]

O(1)-P(1)-O(2) 103.1(2)	O(4)-P(2)-O(6) 97.99(18)	P(1)-O(3)-C(9) 120.1(3)
O(1)-P(1)-O(3) 96.3(2)	O(5)-P(2)-O(6) 101.7(2)	P(2)-O(4)-C(6) 120.4(3)
O(2)-P(1)-O(3) 102.3(2)	P(1)-O(1)-C(1) 119.9(3)	P(2)-O(5)-C(20) 126.2(3)
O(4)-P(2)-O(5) 102.4(2)	P(1)-O(2)-C(7) 127.0(3)	P(2)-O(6)-C(22) 119.1(3)

[a] Standard deviations in the last decimal are given in parentheses

Table 3. *Selected bond lengths (Å) for diphosphite (R,R)-4*[a]

P(1)-O(1) 1.668(4)	C(8)-C(18) 1.535(8)	O(6)-C(22) 1.457(6)	C(20)-C(30) 1.527(8)
P(1)-O(2) 1.604(4)	C(8)-C(19) 1.529(8)	C(1)-C(2) 1.402(8)	C(21)-C(22) 1.555(7)
P(1)-O(3) 1.600(4)	C(9)-C(10) 1.504(8)	C(1)-C(6) 1.380(7)	C(21)-C(31) 1.522(7)
P(2)-O(4) 1.663(4)	C(10)-C(11) 1.395(8)	C(2)-C(3) 1.375(9)	C(21)-C(32) 1.541(8)
P(2)-O(5) 1.603(4)	C(10)-C(15) 1.391(8)	C(3)-C(4) 1.372(9)	C(22)-C(23) 1.514 (7)
P(2)-O(6) 1.617(4)	C(11)-C(12) 1.403(9)	C(4)-C(5) 1.392(9)	C(23)-C(24) 1.377(8)
O(1)-C(1) 1.388(7)	C(12)-C(13) 1.381(9)	C(5)-C(6) 1.403(8)	C(23)-C(28) 1.382(8)
O(2)-C(7) 1.455(7)	C(13)-C(14) 1.376(9)	C(7)-C(8) 1.575(8)	C(24)-C(25) 1.389(9)
O(3)-C(9) 1.452(6)	C(14)-C(15) 1.406(8)	C(7)-C(16) 1.540(9)	C(25)-C(26) 1.395(9)
O(4)-C(6) 1.368(6)	C(20)-C(21) 1.564(7)	C(7)-C(17) 1.512(8)	C(26)-C(27) 1.377(10)
O(5)-C(20) 1.477(6)	C(20)-C(29) 1.517(8)	C(8)-C(9) 1.565(7)	C(27)-C(28) 1.371(9)

[a] Standard deviations in the last decimal are given in parentheses

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No HRMS data are available for compounds **4-11** and borane adducts **4**$\cdot(BH_3)_2$-**7**$\cdot(BH_3)_2$ due to extensive fragmentation of the molecular ions under EI conditions.