Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 1159–1169

TETRAHEDRON: *ASYMMETRY*

Synthesis of enantiopure C_1 symmetric diphosphines and phosphino-phosphonites with *ortho*-phenylene backbones

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Received 19 March 2001; accepted 19 April 2001

Abstract—Reaction of 2-(diphenylphosphino)phenylphosphonous acid tetramethyldiamide **1** with (+)-menthol, (1*S*,2*S*,3*S*,5*R*)-isopinocampheol and (1*R*,2*R*)-*trans*-cyclohexanediol affords enantiopure phosphino-phosphonite ligands **3**–**5**. The X-ray structures of **1** (space group $P2_1/n$) and **3** (space group $P2_1$) have been determined. The reaction of **1** with (1*R*,2*R*,3*S*,5*R*)-(−)-pinanediol proceeds diastereoselectively to afford a novel type of enantiopure phosphino-phosphonite ligand **6** with an asymmetric substituted P atom. On reaction of (+)-cedryl alcohol with **1** the adduct **7** of the phosphonous acid 2-Ph_2P–C_6H_4–P(=O)(H)OH **9** and its dimethylammonium salt is formed through elimination of water and subsequent hydrolysis. The structure of **7** (space group $P\bar{1}$) was elucidated by X-ray structural analysis. Reduction of the chlorophosphine **8** with $LiAlH_4$ yields the novel primary–tertiary phosphine **10**, which is a valuable starting material for the synthesis of the enantiopure C_1 symmetric bidentate phospholane ligands **11** and **12**.

1. Introduction

Asymmetric catalysis using coordination complexes of transition metals is a rapidly developing research area and in its present state is known to induce high efficiencies and selectivities surpassing in some cases those of the equivalent enzyme-mediated reactions. This is mainly due to the availability of a wide range of enantiopure ligands[1] promoting highly selective catalytic reactions. Chiral diphosphines with C_2 symmetry such as DIOP,[2a] DUPHOS[2b] and BINAP[2c] have played a special role in the development of enantioselective catalysis. C_2 symmetry is not, however, a prerequisite for the selectivity and the activity of diphosphines in catalysis and C_1 symmetric bidentate diphosphine ligands also give excellent results. NORPHOS **A**,[3a] BPPFA **B**,[3b] BPPM **D**,[3c] **E**[3d] and the Takaya phosphine–phosphite ligand (*R*,*S*)-BINAPHOS **C**[2d–f] may be quoted as representative examples in this context. However, diphosphine ligands with C_1 symmetry con-

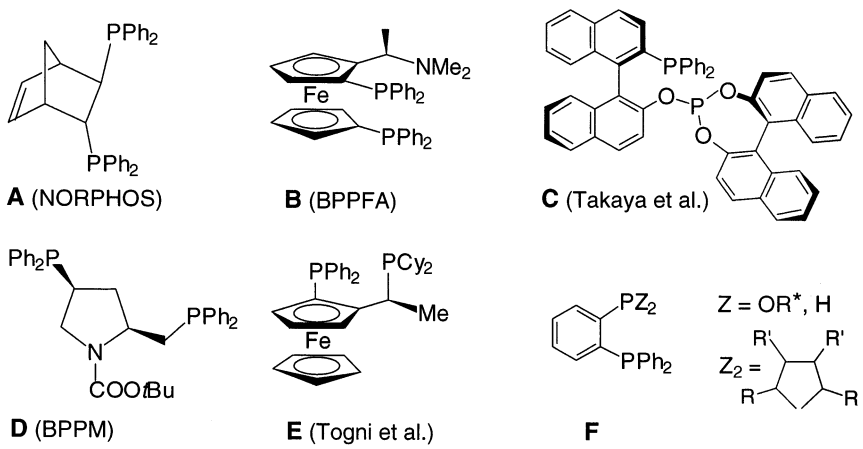

Figure 1.

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PII: S0957-4166(01)00175-6

taining *ortho*-phenylene backbones have been reported only scarcely in the literature to date (Fig. 1).[4]

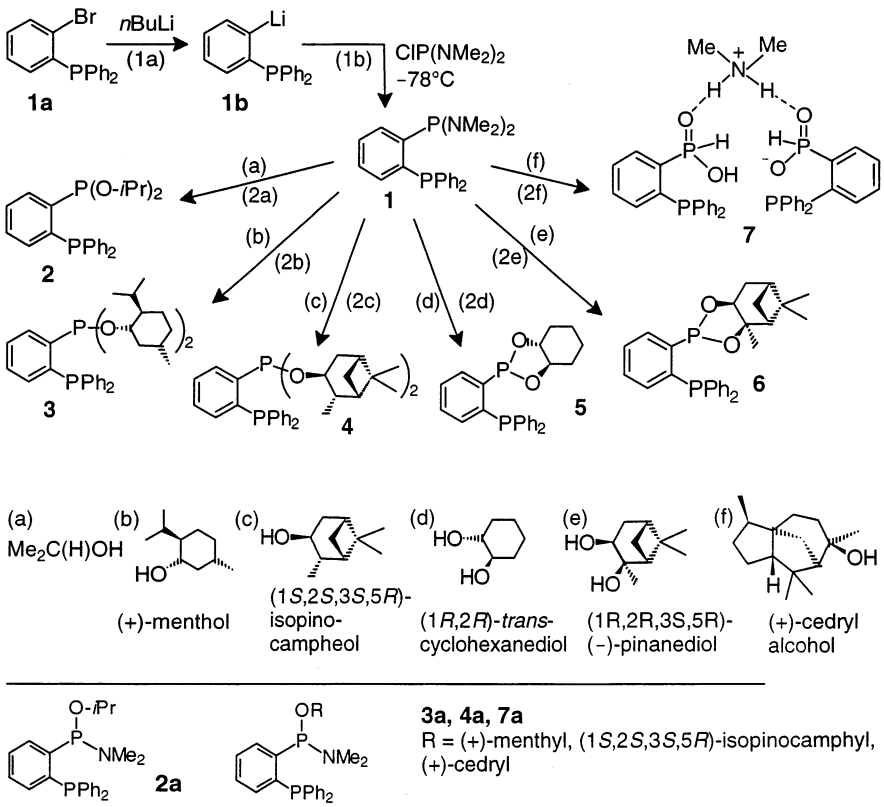
Herein, we report on the syntheses of new enantiopure C_1 symmetric bidentate phosphine ligands of type **F** (Z, Z′=OR*) containing cyclic and acyclic $P(OR^*)_2$ moieties with chiral groups R*, of which only very few examples have appeared in the recent literature.[4] Those containing an asymmetric PZZ′ group with a stereogenic phosphorus center are unreported to the best of our knowledge. The novel primary–tertiary arylphosphine **F** (Z, Z′=H) is also reported. It has great potential as synthon for the preparation of chiral tertiary diphosphine ligands with a phospholane moiety, the steric and electronic properties of which may be tuned by appropriate choice of the substituents R or R′ α or β to phosphorus.

2. Results and discussion

2.1. Synthesis of C_1 symmetric phosphino-phosphonite ligands with *ortho*-phenylene backbones

For the synthesis of C_1 symmetric phosphino-phosphonite ligands *ortho*-bromophenyl-diphenylphosphine **1a**[5] was used as the starting material. It may be obtained in large quantities and high yield by Pd-catalyzed P–C coupling[6] of diphenylphosphine and *ortho*-bromoiodobenzene, as developed by us. Halogen–metal exchange on **1a** with *n*-BuLi yields the lithio derivative **1b**,[7] which on reaction with bis(dimethylamino)chlorophosphine affords 2-(diphenylphosphino)-phenylphosphonous acid tetramethyldiamide **1**, the overall yield being 82% (Eqs. (1a, 1b)) (Scheme 1).

Reaction of **1** with excess *iso*-propanol, (+)-menthol, (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheol, (1*R*,2*R*)-*trans*-1,2-cyclohexanediol and (1*R*,2*R*,3*S*,5*R*)-(−)-pinane-2,3-diol in *n*-heptane under reflux gave **2** and the enantiopure phosphino-phosphonite ligands **3**–**6** (Eqs. (2a–2e)). These reactions proceeded stepwise, the aminophosphonites **2a**–**4a** and **7a** with unsymmetrically substituted phosphorus atoms being formed as intermediates. They have been identified by $^{31}P\{^1H\}$ NMR spectroscopy and isolated in the case of **2a**. On formation of acyclic **3** and **4** and cyclic **5** the configuration at the stereogenic carbon atoms is retained, as indicated by analysis of the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra and measurement of the optical rotation (see Section 3). The reaction of **1** with (1*R*,2*R*,3*S*,5*R*)-(−)-pinanediol proceeded with high diastereoselectivity and only one of the two possible diastereoisomers **6a** and **6b** is formed. Due to the asymmetric substitution in the organic backbone of the 1,3,2-dioxaphospholane moiety the phosphorus atom P_a was stereogenic in both diastereoisomers. Compounds **6a** and **6b** were interrelated by an interchange of the C_6H_4–2-PPh_2 substituent and the lone pair at the phosphorus atom P_a (Fig. 2). The $^{31}P\{^1H\}$ NMR spectrum showed only one pair of doublets at $\delta P = 158.2$ ppm (PO_2, P_a) and −18.7 ppm (PPh_2, P_b), $^3J(PP) = 112.3$ Hz. Accordingly a single set of ten resonances (some of them showing P–C coupling fine structure) for the ten chemically different aliphatic carbon atoms were



Scheme 1.

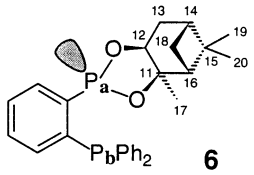


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Figure 2. One possible diastereoisomer of **6** (**6a**).

observed in the $^{13}C\{^1H\}$ NMR spectrum. Structure **6a** with the energetically favorable equatorial position of the bulky C_6H_4–2-PPh_2 group is consistent with the small coupling constant $^3J(P_aC)$ for $C(17)H_3$, which is remote from the lone pair at P_a (for indication of the carbon atoms see Fig. 2). While this coupling could not be resolved in the $^{13}C\{^1H\}$ NMR spectrum, for carbon atoms C(13) and C(16) values of 4.6 and 3.8 Hz were found for $^3J(P_aC)$. Generally, coupling constants $^3J(PC)$ between carbon and three valent phosphorus are small if the lone pair at P is remote, and large if it is in the proximity of the γ-carbon atom.[8a]

Attempts to synthesize C_1 symmetric phosphino-phosphonite ligands derived from bulky tertiary alcohols using the method applied for **2**–**6** with secondary alkoxy groups were unsuccessful. Thus, reaction of **1** with (+)-cedrol gave the salt **7** instead of the expected phosphino-phosphonite ligand of type **F** (Z = OR*). The X-ray structural analysis showed **7** to be the 1:1 adduct of the phosphonous acid **9** and its dimethylammonium salt. The formation of **7** is obviously a result of elimination of water from (+)-cedrol and subsequent hydrolysis of **1**. The reaction proceeds via the intermediate aminophosphonite **7a** with an asymmetric phosphorus atom and a chiral OR group. It is formed as a 1:1 mixture of two diastereoisomers, which in the $^{31}P\{^1H\}$ NMR spectrum show the line pattern of two AX-type spectra [isomer I: $\delta P(A) = 104.4$ ppm, $\delta P(X) = -18.7$ ppm ($^3J(PP) = 145.3$ Hz); isomer II: $\delta P(A) = 103.6$ ppm, $\delta P(B) = -18.8$ ppm ($^3J(PP) = 136.5$ Hz)].

In the $^{31}P\{^1H\}$ NMR spectra the phosphino-phosphonite ligands **2**–**6** show two resonances with ^{31}P–^{31}P coupling fine structure in the δP range of about −20 ppm and 150–160 ppm, which may be assigned to the PPh_2 groups and the phosphonite moieties, respectively. The values of $^3J(PP)$ vary in the range between 112 and 190 Hz, reflecting the differences in the mutual orientation of the lone pairs on both phosphorus atoms in the different P–C rotamers contributing to the rotamer equilibrium. As in the structurally related tetraphosphines, the coupling constants $^3J(PP)$ are large if the terminal lone pairs are close and small if they are remote.[8b,8c] For **1** a much smaller value of $^3J(PP)$ was found (91.6 Hz) than in **3** (189.6 Hz). This may, however, be due in part to the different electronic effects of the nitrogen and oxygen substituents.

The chiral substituents R* in the $P(OR^*)_2$ moieties render the Ph groups of the Ph_2P units in **3**–**5** diastereotopic, two sets of lines being observed for the aromatic carbon atoms in the $^{13}C\{^1H\}$ NMR spectra. This has been observed for the other Ph_2P units in phosphines Ph_2P–R* with a chiral group R*[9] and also applies to **6**, which according to the $^{31}P\{^1H\}$ NMR spectrum was obtained as one diastereoisomer only. One set of ten resonances was observed in the $^{13}C\{^1H\}$ NMR spectrum of **6** for the aliphatic carbon atoms C(11)–C(20) and an eight line set for the aromatic carbon atoms of the two diastereotopic Ph groups of the PPh_2 units. The assignment of the $^{13}C\{^1H\}$ NMR signals in **3**–**6** was achieved by using DEPT NMR spectra and ^1H,^1H or ^{13}C,^1H correlated spectra.[10]

2.2. X-Ray structural analysis of 1, 3 and 7

In order to obtain detailed information on the mutual orientation of the PPh_2 and the PZ_2 units (Z = NMe_2, OMen) with respect to the plane of the disubstituted aromatic ring system, a crystal structure of **1** and **3** was obtained. The results for **1** are shown in Fig. 3. Important bond lengths and angles are collected in Table 1. As expected, the phosphorus atoms P(1) and P(2) are almost coplanar with the best plane through C(11)–C(16), the dihedral angle P(1)–C(11)–C(12)–P(2) being 1.18(20)°. The PPh_2 group is not in a symmetric position with respect to this plane, as indicated by the different dihedral angles C(21)–P(1)–C(11)–C(16) (–81.95(16)°) and C(31)–P(1)–C(11)–C(16) (23.52(17)°). The same applies to the $P(NMe_2)_2$ moiety with almost planar arrangements of the substituents at N(1) and N(2), the sum of the bond angles being 355.44 and 352.34°, respectively. The C(*m*)–N(1)–P(2) and C(*n*)–N(2)–P(2) bond angles for $m = 1$, 3 and $n = 2$, 4 are rather different.

While the dihedral angle C(11)–C(12)–P(2)–N(1) is –67.73(15)°, a value of 179.76(14)° was found for C(11)–C(12)–P(2)–N(2). The bisectors of the N(1)–P(2)–N(2) and the C(21)–P(1)–C(31) moieties are rotated against each other in order to release repulsion of the lone pairs at the phosphorus atoms P(1) and P(2). The geometrical parameters of the PPh_2–C_6H_4 and the $(Me_2N)_2P$–C_6H_4 fragment in **1** may well be compared with those in PPh_3[11] or $(Me_2N)_2PPh$,[12] respectively.

The unit cell of **3** contains two crystallographically different molecules, the geometrical parameters of which differ slightly. Therefore the structure of molecule 2 (shown in Fig. 4) will only be discussed. As in **1** both phosphorus atoms P(3) and P(4) are almost coplanar with the aromatic ring system C(51)–C(56). The absolute configuration at the stereogenic carbon atoms (C(80), C(90): (*S*)-; C(81), C(91): (*R*)-; C(84), C(94): (*S*)-) of both menthyl groups is the same as in the (+)-menthol employed in the synthesis of **3**, the Flack-parameter *x*[13] being 0.022(68). In order to minimize the steric interaction between the lone pairs and the bulky groups at P(3) and P(4) the two PZ_2 units (Z = Ph, O–Men) in the *ortho*-position are not arranged in a symmetrical manner with respect to the aromatic plane C(51)–C(56), with the phosphorus lone pairs pointing towards each other. The bisectors of the O(3)–P(3)–O(4) and the C(61)–P(4)–C(71) moieties form angles of 30 and 25° with the C(51)–C(52) bond vector.

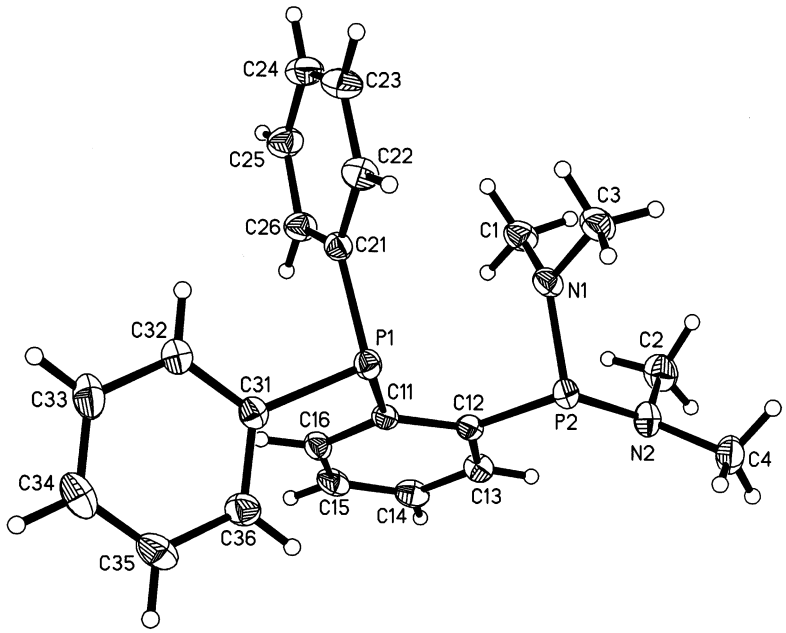


Figure 3. X-Ray structure of **1**.

For **1** and **3** bearing PZ_2 groups with rather different steric demands, the P–C bond lengths and C–P–C bond angles do not differ significantly (**1**: P(1)–C(11) = 1.842(2), P(1)–C(21) = 1.835(2), P(1)–C(31) = 1.839(2) Å, C(11)–P(1)–C(21) = 102.93(8), C(21)–P(1)–C(31) = 101.98(8), C(11)–P(1)–C(31) = 102.05(8)°; **3** (molecule 2): P(4)–C(51) = 1.837(3), P(4)–C(61) = 1.829(4), P(4)–C(71) = 1.839(4)Å,C(51)–P(4)–C(61) = 102.12(16), C(61)–P(4)–C(71) = 100.78(16),C(51)–P(4)–C(71) = 102.55(16)°) (Table 2).

Recrystallization of product **7** obtained on reaction between **1** and (+)-cedryl alcohol from *iso*-propanol gave crystals of **7** suitable for X-ray structural analysis. According to the X-ray structure determination (Fig. 5), the elemental analysis and the NMR data, it is a 1:1 mixture of the phosphonous acid **9** and its dimethylammonium salt **9a**. X-Ray structural analysis reveals that in the solid state **9** and **9a** are interconnected by N^+–H···O hydrogen bridges[14a] with the dimethylammonium cation, the distance of the hydrogen bridged N and O atoms being 2.710(6) Å (N(1)···O(2)) and 2.773(5) Å (N(1)···O(3)). These values, although short, may be compared with those in piperidinomethyl phosphonous acid.[14b] The molecules of **7** are linked by N–H···O and strong O–H···O hydrogen bridges forming endless zig-zag chains along the crystallographic *a*-axis (Table 3).

The C–C and P–C bond lengths are within the typical range.[15] Within the P(H)(=O)O groups, both with a strongly distorted geometry (O(1)–P(1)–O(2) = 118.04(16)°, C(11)–P(1)–O(2) = 111.11(14)°, C(11)–P(1)–O(1) = 106.20(15)°), the bond distances P(1)–O(2) (1.470(2) Å) and P(3)–O(3) (1.473(2) Å) are significantly shorter than P(1)–O(1) (1.514(2) Å) or P(3)–O(4) (1.511(2) Å), respectively. These P–O bond lengths, to which a higher degree of P=O double bond character may be assigned, are comparable to those found in piperidinomethyl phosphonous acid (1.469(2) Å)[14b] and phosphinic acids $R_2P(O)OH$.[16] The steric interaction of the hydrogen atoms and the P(H)(=O)O groups *ortho* to the phosphorus atoms is minimized by a propeller-type arrangement of the aromatic ring systems.

2.3. Synthesis of the primary–tertiary phosphine 10

In contrast to the well known primary diphosphine 1,2-$C_6H_4(PH_2)_2$[17] (which is commercially available) and the secondary diphosphines 1,2-$C_6H_4(PRH)_2$[18] (R = Me or *iso*-Pr) primary–tertiary 1,2-diphosphinobenzenes 1,2-$C_6H_4(PH_2)(PR_2)$ have not been reported to date. As shown above, the reactivity of the P–N bonds renders **1** a useful starting material for the preparation of C_1 symmetric phosphine–phosphonite ligands. It may also be employed for the synthesis of primary–tertiary phosphines, e.g. **10**, which turned out to be quite valuable synthons in the preparation of chiral chelating tertiary

Table 1. Selected interatomic distances (Å) and angles (°) of **1**

Bond lengths			
P(1)–C(11)	1.842(2)	P(2)–N(1)	1.684(2)
P(1)–C(21)	1.835(2)	P(2)–N(2)	1.696(2)
P(1)–C(31)	1.839(2)	P(2)–C(12)	1.841(2)
N(1)–C(1)	1.457(3)	N(2)–C(2)	1.463(3)
N(1)–C(3)	1.455(2)	N(2)–C(4)	1.451(3)
C(11)–C(12)	1.409(2)		
Bond angles			
C(11)–P(1)–C(21)	102.93(8)	C(12)–P(2)–N(1)	98.50(8)
C(11)–P(1)–C(31)	102.05(8)	C(12)–P(2)–N(2)	101.94(9)
C(21)–P(1)–C(31)	101.98(8)	N(1)–P(2)–N(2)	109.87(9)
P(1)–C(11)–C(12)	118.73(13)	P(2)–C(12)–C(11)	118.85(13)
C(1)–N(1)–C(3)	112.22(16)	C(2)–N(2)–C(4)	112.43(18)
C(1)–N(1)–P(2)	126.40(14)	C(2)–N(2)–P(2)	123.56(15)
C(3)–N(1)–P(2)	116.76(13)	C(4)–N(2)–P(2)	116.29(16)

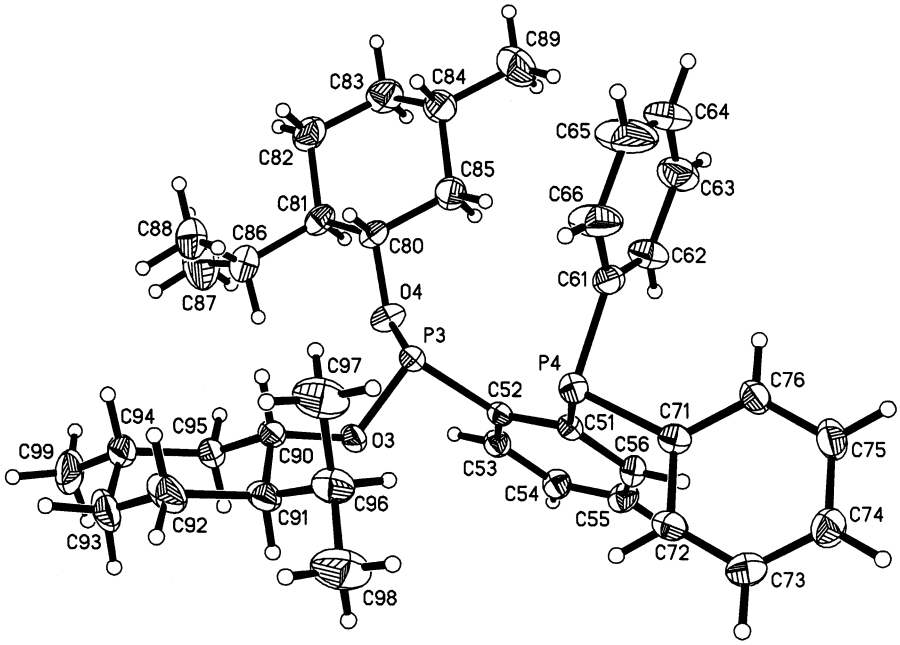


Figure 4. X-Ray structure of **3**.

diphosphines. Thus, treatment of **1** with ethereal HCl at low temperature yielded the chlorophosphine **8**[4] (Eq. (3a)), which could be reduced with $LiAlH_4$ to give the novel primary–tertiary phosphine **10** in good yield (Eq. (3c)). In the $^{31}P\{^1H\}$ NMR spectrum, **10** shows two resonances at $\delta P = -9.3$ and -125.0 ppm, each split by ^{31}P–^{31}P coupling into doublets ($^3J(PP) = 93.7$ Hz). The resonance at $\delta P = -125.0$ ppm shows additional triplet fine structure in the ^{31}P NMR spectrum ($^1J(PH) = 202.2$ Hz). The triplet lines are split further by $^nJ(PH)$ coupling ($n = 3$, 4). In solution, **10** is moderately sensitive towards oxygen, the phosphonous acid **9** being formed. It could be obtained independently by hydrolysis of the chlorophosphine **8** at 0°C (Eq. (3b)). The nitrogen analog of **10** was obtained by Cooper and Downes[19] in a laborious multistage synthesis and later by us in a single step by employing Pd-catalyzed P–C coupling reactions.[6a,6b] It may also be obtained in a straightforward manner from *N*-BOC aniline.[6c]

2.4. Synthesis of the C_1 symmetric tertiary diphosphines 11 and 12

Using the consecutive metallation–alkylation procedure, as developed by Burk et al.[2b] for the synthesis of DUPHOS-type ligands, the C_1 symmetric tertiary diphosphines **11** and **12** could be obtained from the primary–tertiary phosphine **10** in satisfactory to good yield (Scheme 2, Eqs. (3d and 3e)). The cyclic sulfate of (2*S*,5*S*)-(+)-hexane-2,5-diol **10a** was used for alkylation of the intermediate lithium phosphide. The crude **11** was purified via its dihydrochloride salt **11a**, which was prepared by treatment of **11** with excess ethereal HCl (Eq. (3f)). In contrast to the oily crude **11**, the dihydrochloride was obtained as a white crystalline material (which is stable to oxygen but hygroscopic). On treatment with aqueous $NaHCO_3$ the free phosphine was recovered quantitatively (Eq. (3g)). Using the same procedure as employed for the synthesis of **11**, ligand **12** could be obtained using (*R*,*R*)-(+)-1,4-di-*O*-*p*-toluenesulfonyl-2,3-*O*-isopropylidene-D-threitol as the alkylating agent.

The enantiopure C_2 symmetric phosphine ligand **G** containing two phospholane moieties with 1,3-dioxolane groups was synthesized from 1,2-$C_6H_4(PH_2)_2$ by Lappert et al.[20]

The specific rotation values for **11** and **12** are $[\alpha]_D^{20} = -171.8$ ($c = 0.815$, $CHCl_3$) and $[\alpha]_D^{20} = +61.3$ ($c = 1.435$, $CHCl_3$), respectively. It is generally accepted that a complete inversion of configuration at the stereogenic centers of the cyclic sulfate occurs in phosphination reactions. This has been proved for the synthesis of DUPHOS,[2b] which is analogous to **11**. The conformation of the chiral carbon atoms in (+)-1,4-di-*O*-*p*-toluenesulfonyl-2,3-*O*-isopropylidene-D-threitol on formation of **12** does not change. This has been shown by us[21] and others[22,23] for similar phosphination reactions.

Table 2. Selected interatomic distances (Å) and angles (°) of **3** (molecule 2)

Bond lengths			
P(3)–O(3)	1.634(2)	P(4)–C(71)	1.839(4)
P(3)–O(4)	1.619(2)	O(3)–C(90)	1.466(3)
P(3)–C(52)	1.842(3)	O(4)–C(80)	1.455(4)
P(4)–C(51)	1.837(3)	C(51)–C(52)	1.411(4)
P(4)–C(61)	1.829(4)		
Bond angles			
O(3)–P(3)–O(4)	101.97(13)	C(51)–P(4)–C(61)	102.12(16)
O(3)–P(3)–C(52)	94.24(13)	C(51)–P(4)–C(71)	102.55(16)
O(4)–P(3)–C(52)	97.86(14)	C(61)–P(4)–C(71)	100.78(16)
P(3)–C(52)–C(51)	120.06(26)	P(3)–O(3)–C(90)	118.78(18)
P(4)–C(51)–C(52)	118.59(26)	P(3)–O(4)–C(80)	119.53(20)

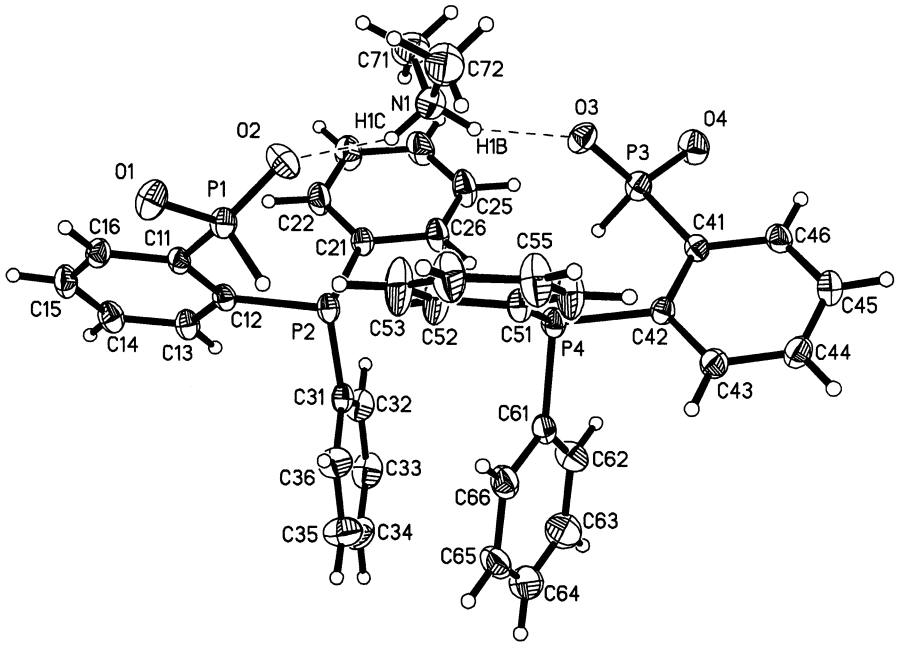


Figure 5. X-Ray structure of **7**.

The $^{31}P\{^{1}H\}$ NMR spectra of **11** and **12** show the line pattern of only one AB-type spectrum (**11**: $\delta P = 1.0$, −9.8 ppm; $^{3}J(PP) = 159.8$ Hz; **12**: $\delta P = 7.0$, −13.0 ppm; $^{3}J(PP) = 155.4$ Hz). Correspondingly only one set of lines was observed for the aliphatic carbon atoms of **11** and **12** in the $^{13}C\{^{1}H\}$ NMR spectra. Again the Ph substituents of the Ph_2P groups are diastereotopic, as indicated by the increased number of $^{13}C\{^{1}H\}$ NMR resonances.

3. Experimental

3.1. Apparatus and materials

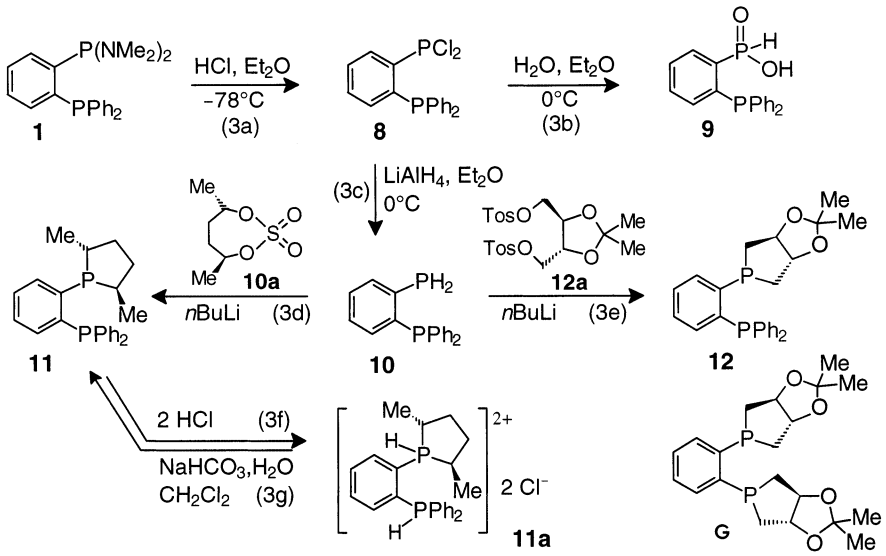
All manipulations were carried out employing standard vacuum line and inert atmosphere techniques. The ^{31}P and ^{13}C NMR spectra were obtained on JEOL FX 90Q and Bruker AC 250 and AC 400 spectrometers equipped with standard ^{1}H, ^{31}P and ^{13}C probe accessories. ^{31}P (relative to external 85% H_3PO_4) and ^{13}C, ^{1}H (relative to internal Me_4Si) chemical shifts downfield from the standard are given positive values. Mass spectra were determined on a Varian MAT 311a instrument at 70 eV. Optical rotations were recorded on a Perkin Elmer 241 polarimeter. Solvents were dried immediately before use. Compound **1a** was prepared by the method as developed by us.[5] (2*S*,5*S*)-(+)-Hexane-2,5-diol cyclic sulfate **10a** was prepared according to the literature method,[2b] (2*S*,5*S*)-(+)-hexane-2,5-diol was purchased from Jülich Fine Chemicals. (+)-Menthol, (1*S*,2*S*,3*S*,5*R*)-isopinocampheol, (1*R*,2*R*)-*trans*-cyclohexanediol, (1*R* 2*R*,3*S*,5*R*)-(−)-pinanediol, (+)-cedryl alcohol and (*R*,*R*)-(+)-1,4-di-O-*p*-toluoenesulfonyl-2,3-isopropylidene-D-threitol were obtained from Aldrich Chemicals and used without purification.

3.2. Procedures

3.2.1. Synthesis of 1. To a solution of **1a** (30.0 g, 88.1 mmol) in diethyl ether (500 mL) a solution of *n*-BuLi in *n*-hexane (1.6 M, 55.1 mL, 88.1 mmol) was added over a period of 20 min at ambient temperature. The solvents were separated by decantation from the precipitate formed, which was washed with diethyl ether (40 mL) and dissolved in toluene (400 mL). To this residue was added a solution of bis(diethylamino)chlorophosphine (11.6 g, 74.8 mmol) at −78°C and the reaction mixture was stirred for 10 min. The coolant was removed and the reaction mixture was stirred for a further 50 min. After addition of a solution of dimethylamine in THF (2.0 M, 10 mL) to

Table 3. Selected interatomic distances (Å) and angles (°) of **7**

Bond lengths			
P(1)–O(1)	1.514(2)	P(3)–O(3)	1.473(2)
P(1)–O(2)	1.470(2)	P(3)–O(4)	1.511(2)
P(1)–C(11)	1.799(3)	P(3)–C(41)	1.800(3)
P(2)–C(12)	1.845(3)	P(4)–C(42)	1.844(3)
P(2)–C(21)	1.833(3)	P(4)–C(51)	1.827(3)
P(2)–C(31)	1.829(4)	P(4)–C(61)	1.825(4)
C(11)–C(12)	1.409(4)	C(41)–C(42)	1.403(4)
N(1)–C(71)	1.458(5)	N(1)–O(2)	2.710(6)
N(1)–C(72)	1.483(6)	N(1)–O(3)	2.773(5)
Bond angles			
O(1)–P(1)–O(2)	118.04(16)	O(4)–P(3)–O(3)	118.31(15)
C(11)–P(1)–O(2)	111.11(14)	C(41)–P(3)–O(3)	113.04(14)
C(11)–P(1)–O(1)	106.20(15)	C(41)–P(3)–O(4)	105.94(15)
C(12)–P(2)–C(21)	102.33(15)	C(42)–P(4)–C(51)	102.99(15)
C(12)–P(2)–C(31)	100.82(14)	C(42)–P(4)–C(61)	101.49(15)
C(21)–P(2)–C(31)	102.97(15)	C(51)–P(4)–C(61)	103.18(16)
C(71)–N(1)–C(72)	114.25(39)		



Scheme 2.

bind unreacted bis(diethylamino)chlorophosphine, the reaction mixture was filtered through a suction funnel and the solvent was removed in vacuo (50°C, 0.01 mBar) to afford **1** (27.4 g, 96%). ^{1}H NMR (C_6D_6): δ 6.99–6.67 (m, 14H), 2.50 (d, 12H, J=8.9 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 148.0 (dd, J=7.1, 27.2 Hz), 141.1 (dd, J=17.8, 24.7 Hz), 139.0 (dd, J=14.5, 2.8 Hz), 136.2 (dd, J=3.3, 1.0 Hz), 134.2 (d, J=20.6 Hz), 131.1 (t, J=7.4 Hz), 128.5 (d, J=6.6 Hz), 128.4, 128.3, 128.1 (d, J=1.5 Hz), 41.7 (dd, J=17.3, 1.5 Hz); ^{31}P{^{1}H} NMR (C_6D_6): δ 99.9 (d, J=91.6 Hz), −11.5 (d, J=91.6 Hz); MS: m/z (%) 380 (58, M^+), 337 (37, $[M-CH_2NCH_3]^+$), 336 (100, $[M-NMe_2]^+$), 183 (99, [9-phosphafluorenyl]$^+$). Anal. calcd for $C_{22}H_{26}N_2P_2$: C, 69.46; H, 6.89; N, 7.36; P, 16.28. Found: C, 69.47; H, 7.14; N, 7.32; P, 16.08%.

3.2.2. Synthesis of 2 and 2a. A solution of **1** (1.5 g, 4.0 mmol) in *iso*-propanol (15 mL) was heated under reflux for 24 h. The solvent was removed in vacuo (40°C, 0.01 mBar) and the residue obtained was washed with two aliquots of *iso*-propanol (3 mL each). An oily residue was obtained, which crystallized on standing. For the analogous synthesis of **2a**, a solution of **1** (1.0 g, 2.7 mmol) in *iso*-propanol (20 mL) was heated for 3.5 h at 85°C. The work-up procedure was as for **2**. Yields: **2** (0.90 g, 55%); **2a** (1.02 g, 96%).

Analytical data for **2**: ^{1}H NMR (C_6D_6): δ 6.9–8.3 (m, 14H), 4.23 (m, 2H, J=8.2, 6.2, 6.1 Hz), 1.14 (d, 6H, J=6.1 Hz), 1.09 (d, 6H, J=6.2 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 149.7 (dd, J=17.3, 29.0 Hz), 140.8 (dd, J=15.3, 32.3 Hz), 138.3 (dd, J=12.7, 5.8 Hz), 134.3 (d, J=1.5 Hz), 134.2 (d, J=19.3 Hz), 130.1, 129.7 (dd, J=9.9, 4.8 Hz), 129.0, 128.6 (d, J=6.6 Hz), 128.5, 71.1 (d, J=18.3 Hz), 24.70 (d, J=4.6 Hz), 24.65 (d, J=3.8 Hz); ^{31}P{^{1}H} NMR (C_6D_6): δ 150.6 (d, J=164.6 Hz), −14.4 (d, J=164.6 Hz); MS: m/z (%) 410 (57, M^+), 367 (17, $[M-CH_3CHCH_3]^+$), 326 (39, $[M-2CH_2CHCH_3]^+$), 183 (100, [9-phosphafluorenyl]$^+$). Anal. calcd for $C_{24}H_{28}O_2P_2$: C, 70.23; H, 6.89; Found: C, 70.57; H, 7.08%.

Analytical data for **2a**: ^{1}H NMR (C_6D_6): δ 6.9–8.2 (m, 14H), 4.14 (dsp, 1H, J=8.1, 6.1, 6.3 Hz), 2.40 (d, 3H, J=8.6 Hz), 1.22 (d, 3H, J=6.1 Hz), 1.20 (d, 3H, J=6.3 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 149.5 (dd, J=6.6, 27.5 Hz), 140.6 (dd, J=15.5, 27.7 Hz), 140.0 (dd, J=10.9, 1.3 Hz), 137.3 (dd, J=15.0, 6.9 Hz), 135.5 (dd, J=4.1, 1.5 Hz), 134.2 (d, J=20.3 Hz), 133.7 (d, J=18.8 Hz), 130.8 (dd, J=9.2, 6.1 Hz), 128.8, 128.54 (d, J=6.1 Hz), 128.52 (d, J=6.1 Hz), 128.4 (d, J=7.1 Hz), 128.1, 70.5 (d, J=23.9 Hz), 38.6 (d, J=15.8 Hz), 24.9 (d, J=4.1 Hz), 24.4 (d, J=6.6 Hz); ^{31}P{^{1}H} NMR (C_6D_6): δ 122.8 (d, J=129.2 Hz), −16.2 (d, J=129.2 Hz); MS: m/z (%) 396 (17, $[M+H]^+$), 395 (65, M^+), 352 (100, $[M-H_3CCHCH_3]^+$). Anal. calcd for $C_{23}H_{27}NOP_2$: C, 69.86; H, 6.88; P, 15.67; N, 3.54. Found: C, 69.67; H, 6.93; P, 15.70; N, 3.67%.

3.2.3. Synthesis of 3. To a solution of **1** (0.50 g, 1.3 mmol) in *n*-heptane (20 mL) was added (+)-menthol (0.40 g, 2.6 mmol). The resultant mixture was heated under reflux for 24 h. The solvent was removed in vacuo and the remaining residue was washed with *iso*-propanol (5 mL). Evaporation of all volatiles in vacuo gave **3** as a colorless powder (0.68 g, 87%). For further purification **3** was recrystallized from *iso*-propanol at −18°C. Compound **3**: ^{1}H NMR (C_6D_6): δ 8.3–6.9 (m, 14H), 3.95–3.75 (m, 2H), 2.64 (m, 1H, J=7.0, 2.5 Hz), 2.43–2.34 (m, 2H), 2.25 (m, 1H, J=7.0, 2.6 Hz), 2.18–2.10 (m, 2H), 1.6–0.6 (m, 12H), 0.97 (d, 3H, J=7.1 Hz), 0.91 (d, 3H, J=6.1 Hz), 0.88 (d, 3H, J=6.9 Hz), 0.82 (d, 3H, J=7.1 Hz), 0.80 (d, 3H, J=7.1 Hz), 0.77 (d, 3H, J=6.6 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 150.5 (dd, J=17.0, 27.7 Hz), 140.5 (dd, J=15.0, 34.3 Hz), 138.5 (dd, J=13.0, 6.4 Hz), 138.4 (dd, J=13.5, 7.9 Hz), 134.4 (d, J=18.8 Hz), 134.3 (d, J=19.3 Hz), 133.2 (dd, J=6.1, 1.0 Hz), 130.3, 130.0 (dd, J=9.2, 4.1 Hz), 129.0 (d, J=1.0 Hz), 128.72 (d, J=6.1 Hz), 128.71 (d, J=7.1 Hz), 128.62, 128.58, 79.0 (d, J=18.3 Hz), 77.6 (d, J=15.3 Hz), 49.7 (d, J=5.1 Hz), 49.6 (d, J=5.1 Hz), 44.9 (d, J=3.6 Hz), 44.5 (dd, J=5.6, 1.5 Hz), 34.7, 34.6, 32.1, 31.8, 25.7, 25.5, 23.4,

23.3, 22.4, 22.3, 21.5, 21.3, 16.5, 16.2 (dd, $J=3.3$, 1.8 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 154.9 (d, $J=189.6$ Hz), −11.9 (d, $J=189.6$ Hz); MS: m/z (%) 603 (3, $[M+H]^+$), 602 (4, M^+), 326 (100, $[M-2C_{10}H_{18}]^+$), 183 (24, [9-phosphafluorenyl]$^+$); $[\alpha]_D^{20}=+61.5$ ($c=2$, toluene). Anal. calcd for $C_{38}H_{52}O_2P_2$: C, 75.72; H, 8.70; P, 10.27. Found: C, 75.66; H, 8.32; P, 9.78%.

3.2.4. Synthesis of 4. Compound **4** was synthesized according to the same procedure as for **3**. Thus, from **1** (0.99 g, 2.6 mmol) and (1*S*,2S,3*S*,5*R*)-(+)-isopinocampheol (0.80 g, 5.2 mmol), dissolved in *n*-heptane (40 mL), **4** was formed after heating for 72 h under reflux. The product obtained after evaporation of the solvent was washed with *iso*-propanol (10 mL) and dried in vacuo affording **4** as a colorless solid (1.25 g, 80%). Compound **4**: ^1H NMR (C_6D_6): δ 8.35–6.95 (14H), 4.57 (sp, 1H, $J=4.8$ Hz), 4.53 (sp, 1H, $J=4.7$ Hz), 2.58–2.01 (m, 6H), 1.83 (sp, 1H, $J=3.1$ Hz), 1.79 (sp, 1H, $J=3.0$ Hz), 1.72 (td, 1H, $J=5.8$, 1.9 Hz), 1.66 (td, 1H, $J=5.8$, 1.8 Hz), 1.22–1.08 (m, 4H), 1.20 (d, 3H, $J=7.6$ Hz), 1.13 (d, 3H, $J=7.4$ Hz), 1.10 (6H), 0.82 (3H), 0.81 (3H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 150.1 (dd, $J=19.1$, 28.7 Hz), 140.9 (dd, $J=15.0$, 32.3 Hz), 138.34 (dd, $J=12.7$, 6.1 Hz), 138.30 (dd, $J=12.7$, 6.1 Hz), 134.3 (d, $J=19.3$ Hz), 134.2 (d, $J=19.3$ Hz), 134.0 (dd, $J=5.1$, 1.5 Hz), 130.3, 129.8 (dd, $J=9.9$, 4.8 Hz), 129.0, 128.7 (d, $J=6.6$ Hz), 128.6 (d, $J=6.6$ Hz), 128.54, 128.53, 78.9 (d, $J=16.8$ Hz), 78.0 (d, $J=15.8$ Hz), 48.2, 46.8 (d, $J=4.1$ Hz), 46.5 (d, $J=3.6$ Hz), 42.1, 38.5 (d, $J=2.8$ Hz), 38.4, 38.3 (dd, $J=4.5$, 0.9 Hz), 34.2, 34.0, 27.7, 23.91, 23.87, 20.7, 20.6 (t, $J=1.9$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 156.8 (d, $J=168.4$ Hz), −13.3 (d, $J=168.4$ Hz); MS: m/z (%) 598 (7, M^+), 462 (3, $[M-C_{10}H_{16}]^+$), 325 (100, $M-2C_{10}H_{16}-H]^+$), 183 (27, [9-phosphafluorenyl]$^+$); $[\alpha]_D^{20}=+43.5$ ($c=1$, toluene). Anal. calcd for $C_{38}H_{48}O_2P_2$: C, 76.23; H, 8.08; P, 10.34. Found: C, 76.13; H, 8.21; P, 10.83%.

3.2.5. Synthesis of 5. Using the same procedure as outlined above, **1** (1.5 g, 3.9 mmol) and (1*R*,2*R*)-*trans*-1,2-cyclohexanediol (0.45 g, 3.9 mmol) in *n*-heptane (60 mL) afforded **5** after heating for 20 h under reflux. The crude material was washed with *iso*-propanol (1×5 mL and 1×2 mL) and dried in vacuo to afford **5** (1.34 g, 85%). ^1H NMR (C_6D_6): δ 7.9–6.9 (14H), 3.19–3.10 (1H), 2.96–2.87 (1H), 2.04–1.93 (1H), 1.53–1.44 (1H), 1.29–0.98 (4H), 0.79–0.64 (1H), 0.61–0.46 (1H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.0 (dd, $J=30.0$, 55.9 Hz), 140.5 (dd, $J=14.8$, 21.9 Hz), 138.2 (dd, $J=11.2$, 4.6 Hz), 137.8 (dd, $J=9.7$, 2.5 Hz), 135.0 (d, $J=1.5$ Hz), 134.2 (d, $J=18.8$ Hz), 134.0 (d, $J=18.3$ Hz), 130.0, 129.2 (dd, $J=12.5$, 8.4 Hz), 128.65, 128.59 (d, $J=6.1$ Hz), 128.47 (d, $J=7.1$ Hz), 128.46, 82.5 (dd, $J=5.6$, 2.0 Hz), 78.8 (d, $J=7.1$ Hz), 30.7, 29.8 (d, $J=4.6$ Hz), 24.0, 23.8; $^{31}P\{^1H\}$ NMR (C_6D_6): δ 163.3 (d, $J=111.5$ Hz), −17.6 (d, $J=115.5$ Hz); MS: m/z (%) 406 (43, M^+), 325 (17, $[M^+-C_6H_8-H]^+$), 183 (100, [9-phosphafluorenyl]$^+$); $[\alpha]_D^{20}=+8.6$ ($c=5$, toluene). Anal calcd for $C_{24}H_{24}O_2P_2$: C, 70.93; H, 5.95; P, 15.24. Found: C, 70.32; H, 6.04; P, 14.74%.

3.2.6. Synthesis of 6. The compound was synthesized by the same procedure as for **5**. Heating **1** (4.79 g, 12.6 mmol) and (1*R*,2*R*,3*S*,5*R*)-(−)-pinanediol (2.15 g, 12.6 mmol) in *n*-heptane (100 mL) for 24 h at 95°C gave **6** as a white pasty material. It was recrystallised methanol. After drying in vacuo **6** was obtained as a white powder (3.70 g, 64%). ^1H NMR (C_6D_6): δ 7.74–6.98 (m, 14H), 4.15 (d, 1H, $J=7.6$ Hz), 2.19 (dd, 1H, $J=14.6$, 3.2 Hz), 2.09–1.92 (m, 2H), 1.89 (t, 1H, $J=5.7$ Hz), 1.67–1.58 (m, 2H), 0.97 (3H), 0.58 (3H), 0.42 (3H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.6 (dd, $J=31.3$, 58.0 Hz), 140.6 (dd, $J=14.2$, 20.9 Hz), 138.9 (dd, $J=10.9$, 5.3 Hz), 136.3 (dd, $J=10.3$, 1.4 Hz), 135.5 (d, $J=1.8$ Hz), 135.4 (d, $J=20.1$ Hz), 133.4 (d, $J=17.8$ Hz), 129.6, 129.1, 129.0, 128.54 (d, $J=6.1$ Hz), 128.49 (d, $J=7.4$ Hz), 128.2, 127.8 (dd, $J=13.0$, 7.6 Hz), 88.3 (d, $J=10.7$ Hz), 78.4 (dd, $J=8.1$, 2.0 Hz), 52.5 (d, $J=3.8$ Hz), 40.1, 37.6, 34.8 (d, $J=4.6$ Hz), 27.7, 27.0, 25.8, 23.8; $^{31}P\{^1H\}$ NMR (C_6D_6): δ 158.2 (d, $J=112.3$ Hz), −18.7 (d, $J=112.3$ Hz); MS: m/z (%) 461 (17, $[M+H]^+$), 460 (58, M^+), 326 (75, $[M^+-C_{10}H_{14}]^+$), 325 (100, $M-C_{10}H_{14}-H]^+$), 183 (77, [9-phosphafluorenyl]$^+$); $[\alpha]_D^{20}=+26.4$ ($c=5$, toluene). Anal. calcd for $C_{28}H_{30}O_2P_2$: C, 73.03; H, 6.57; P, 13.45. Found: C, 73.16; H, 6.60; P, 13.43%.

3.2.7. Reaction of 1 with (+)-cedrol. To a solution of **1** (0.99 g, 2.6 mmol) in toluene (40 mL) was added (+)-cedrol (1.16 g, 5.2 mmol) and the reaction mixture was heated at reflux. After 100 h, the mono-substitution product **7a** was formed, as indicated by two sets of doublets for the two diastereoisomers in the $^{31}P\{^1H\}$ NMR spectrum (isomer I: $\delta P(A)=104.4$ ppm, $\delta P(X)=-18.7$ ppm ($^3J(PP)=145.3$ Hz); isomer II: $\delta P(A)=103.6$ ppm, $\delta P(B)=-18.8$ ppm ($^3J(PP)=136.5$ Hz)). Further heating of the reaction mixture for 3 days afforded the hydrolysis product **7** exclusively. Evaporation of the solvent in vacuo afforded **7** as a colorless solid (0.73 g, 80%). On repeated recrystallization from *iso*-propanol, **7** could be obtained as colorless crystals, which were identified by X-ray structural analysis.

3.2.8. Synthesis of 9. A solution of **1** (0.99 g, 2.6 mmol) in toluene (20 mL) was cooled to −78°C and a solution of HCl in diethyl ether (1 M, 11 mL) was added. After stirring for 15 min the coolant was removed and the reaction mixture was stirred for 90 min at ambient temperature. The precipitate formed was removed by filtration and water (0.2 mL) was added at 0°C to the filtrate. After stirring for 2 h the solvent was removed in vacuo. The evaporation residue was recrystallized from benzene to afford **9** (0.76, 90%). ^1H NMR ($CDCl_3$): δ 12.37 (broad, 1H), 8.13 (d, 1H, $J=585.2$ Hz), 8.1–7.1 (m, 14H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.8 (dd, $J=14.7$, 20.3 Hz), 136.9 (dd, $J=135.8$, 29.5 Hz), 136.0 (d, $J=9.7$ Hz), 134.7 (dd, $J=12.2$, 1.3 Hz), 133.7 (d, $J=19.3$ Hz), 132.3 (d, $J=2.5$ Hz), 131.8 (t, $J=9.7$ Hz), 128.9 (d, $J=12.2$ Hz), 128.7, 128.5 (d, $J=12.2$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.6 (d, $J=61.2$ Hz), −15.3 (d, $J=61.2$ Hz); MS: m/z (%) 326 (4, M^+), 325 (9, $[M-H]^+$), 183 (100, [9-phosphafluorenyl]$^+$). Anal. calcd

for $C_{18}H_{16}O_2P_2$: C, 66.26; H, 4.94. Found: C, 66.39; H, 5.19%.

3.2.9. Synthesis of 10. To a solution of **1** (60.0 g, 157.7 mmol) in toluene (800 mL) was added an ethereal solution of HCl in diethyl ether (2 M, 320 mL, 4.06 equiv.) at −78°C over 1 h. After stirring the mixture for 10 min the cooling bath was removed and the reaction mixture was stirred at ambient temperature for a further 45 min. Most of the ether was evaporated in vacuo (20°C, 0.01 mbar) and the mixture was filtered through a glass fritted suction funnel with exclusion of air and moisture. The solvents were completely evaporated in vacuo. The residue **8** was dissolved in THF (400 mL) and this solution was added over 2 h at 0°C to a solution of $LiAlH_4$ in THF (1 M, 100 mL, 2.54 g, 100 mmol) diluted with THF (400 mL). After 45 min the reaction mixture was quenched with conc. HCl (10 mL) and the solvents were removed in vacuo. The residue was partitioned between dichloromethane (1 L) and dilute aqueous HCl (1 L water+15 mL conc. HCl). The organic phase was separated and dried over magnesium sulfate. After filtration the solvents were evaporated and the residue was recrystallized from *iso*-propanol to afford **10** (34.4 g, 74%). ^{1}H NMR (C_6D_6): δ 7.38–6.87 (m, 14H), 4.03 (dd, 2H, J=202.2, 11.7 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 142.2 (dd, J=14.5, 10.9 Hz), 137.5 (dd, J=35.9, 10.4 Hz), 136.8 (dd, J=11.4, 2.8 Hz), 136.1 (dd, J=9.7, 6.6 Hz), 134.3 (d, J=19.3 Hz), 133.8 (d, J=3.1 Hz), 129.0, 128.9 (d, J=7.1 Hz), 128.8 (d, J=3.6 Hz), 128.6; ^{31}P{^{1}H} NMR (C_6D_6): δ −9.3 (d, J=93.7 Hz), −125.0 (d, J=93.7 Hz); ^{31}P NMR (C_6D_6): δ −9.3 (d, J=93.7), −125.0 (m, J=202.2, 93.5, 6.3, 2.6 Hz); MS: m/z (%) 295 (41, $[M+H]^+$), 294 (100, M^+), 293 (64, $[M-H]^+$), 292 (23, $[M-2H]^+$), 186 (43, $[M-PPh]^+$), 185 (49, $[M-PPh-H]^+$), 183 (97, [9-phosphafluorenyl]$^+$). Anal. calcd for $C_{18}H_{16}P_2$: C, 73.47; H, 5.48; P, 21.05. Found: C, 73.38; H, 5.28; P, 20.87%.

3.2.10. Synthesis of 11 and 11a. To a solution of **10** (4.0 g, 13.6 mmol) in THF (250 mL) at 0°C was added a solution of *n*-BuLi in *n*-hexane (1.6 M, 8.5 mL, 13.6 mmol). After stirring the mixture for 30 min a solution of the cyclic sulfate of (2*S*,5*S*)-hexane-2,5-diol (2.45 g, 13.6 mmol) in THF (20 mL) was added at 0°C. After removal of the coolant, the reaction mixture was stirred for 2 h at ambient temperature and treated with a solution of *n*-BuLi in *n*-hexane (10.2 mL, 16.3 mmol) at 0°C. The reaction mixture was stirred at ambient temperature for 2 h and the excess *n*-BuLi was quenched by addition of methanol (1 mL). The waxy solid left after all volatiles had been removed in vacuo was extracted at 60°C with *n*-hexane (2×200 mL). After evaporation of the solvent in vacuo **11** was obtained as a pale yellow oil (3.93 g, 77%).

For the preparation of **11a**, a solution of **11** (3.84 g, 10.2 mmol) in *n*-hexane (60 mL) was treated with a solution of HCl in diethyl ether (2 M, 15 mL). An oily product separated from the reaction mixture. After removal of the solvent in vacuo a second equivalent of HCl in diethyl ether was added. The colorless solid of **11a** that precipitated on addition of *n*-hexane was collected by filtration, washed with three aliquots of *n*-hexane (15 mL) and dried in vacuo to afford **11a** (4.40 g, 96%). Compound **11** could be retained from the dihydrochloride **11a** quantitatively by treatment with $NaHCO_3$ in a two-phase H_2O/CH_2Cl_2 system.

Analytical data for **11**: ^{1}H NMR (C_6D_6): δ 7.50–6.93 (m, 14H), 2.51–2.39 (m, 1H), 2.39–2.22 (m, 1H), 2.04–1.91 (m, 1H), 1.89–1.76 (m, 1H), 1.49–1.28 (m, 1H), 1.21–1.1 (m, 1H), 1.09 (dd, 3H, J=18.3, 7.1 Hz), 0.99 (dd, J=9.2, 7.1 Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 146.4 (dd, J=32.6, 11.2 Hz), 143.7 (dd, J=29.5, 28.5 Hz), 139.2 (dd, J=16.3, 10.7 Hz), 138.4 (dd, J=11.7, 4.1 Hz), 134.8 (dd, J=19.8, 1.0 Hz), 134.3 (dd, J=18.8, 1.0 Hz), 133.8 (d, J=7.1 Hz), 133.1 (dd, J=6.1, 2.5 Hz), 129.0 (d, J=0.9 Hz), 128.7 (d, J=6.1 Hz), 128.57 (d, J=7.1 Hz), 128.56, 128.5, 128.4, 37.1 (d, J=2.0 Hz), 36.4 (J=3.1 Hz), 35.6 (dd, J=13.0, 9.4 Hz), 35.0 (dd, J=14.8, 1.0 Hz), 20.6 (d, J=36.1 Hz), 17.2 (dd, J=5.1, 2.0 Hz); ^{31}P{^{1}H} NMR (C_6D_6): δ 1.0 (d, J=159.8 Hz), −9.8 (d, J=159.8 Hz); MS: m/z (%) 377 (27, $[M+H]^+$), 376 (99, M^+), 375 (44, $[M-H]^+$), 299 (65, $[M-Ph]^+$), 183 (100, [9-phosphafluorenyl]$^+$); $[\alpha]_D^{20}$=−171.8 (c=0.815, $CHCl_3$). Anal. calcd for $C_{24}H_{26}P_2$: C, 76.58; H, 6.96; P, 16.46. Found: C, 76.69; H, 6.86; P, 15.88%.

Analytical data for **11a**: ^{1}H NMR ($CDCl_3$): δ 9.24 (broad, 2H), 8.35–7.15 (m, 14H), 3.72–3.58 (m, 1H), 3.45–3.27 (m, 1H), 2.66–2.38 (m, 2H) 2.18–2.00 (m, 2H), 1.37 (dd, 3H, J=19.8, 6.6 Hz), 1.18 (dd, 3H, J=19.8, 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.9 (dd, J=14.8, 9.7 Hz), 137.6 (dd, J=12.5, 9.4 Hz), 136.3 (d, J=10.7 Hz), 135.0 (d, J=3.1 Hz), 133.6 (d, J=18.8 Hz), 133.5 (d, J=18.8 Hz), 133.3 (d, J=5.6 Hz), 133.1 (d, J=5.6 Hz), 131.2 (d, J=12.2 Hz), 130.0 (d, J=1.5 Hz), 129.3 (d, J=7.1 Hz), 129.2 (d, J=7.6 Hz), 121.1 (d, J=38.1 Hz), 120.3 (d, J=37.6 Hz), 35.0 (dd, J=6.6, 3.6 Hz), 34.1 (dd, J=44.8, 11.2 Hz), 33.8 (d, J=9.7 Hz), 31.1 (dd, J=45.8, 2.0 Hz), 14.5, 14.4 (d, J=2.5 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) 33.5 (d, J=42.5 Hz), −10.0 (d, J=43.0 Hz). Anal. calcd for $C_{24}H_{28}Cl_2P_2$: C, 64.15; H, 6.28. Found: C, 64.11; H, 6.93%.

3.2.11. Synthesis of 12. To a solution of **10** (2.0 g, 6.8 mmol) in THF (120 mL) was added a solution of *n*BuLi in *n*-hexane (1.6 M, 4.3 mL) at 0°C and the reaction mixture was stirred for 30 min. Thereafter a solution of (*R*,*R*)-(+)-1,4-di-O-*p*-toluenesulfonyl-2,3-*O*-isopropylidene-D-threitol (3.20 g, 6.8 mmol) in THF (20 mL) was added over 5 min and the reaction mixture was stirred for 2 h at ambient temperature. After cooling to 0°C a *n*BuLi solution in *n*-hexane (1.6 M, 5.5 mL, 8.8 mmol) was added. The reaction mixture was then stirred for 2 h at room temperature and excess *n*BuLi was quenched by addition of methanol (1 mL). The residue obtained after evaporation of all volatiles in vacuo was dissolved in dichloromethane (120 mL) and washed with saturated aqueous $NaHCO_3$ solution (3×100 mL) and saturated solution of NaCl (50 mL). The organic phase was separated and dried over $MgSO_4$. The oily residue left after removal of the solvent was recrystallized from methanol to afford **12**

Table 4. Crystal and refinement data for **1**, **3** and **7**

Compound	**1**	**3**	**7**
Chemical formula	$C_{22}H_{26}N_2P_2$	$C_{38}H_{52}O_2P_2$	$C_{38}H_{39}NO_4P_4$
Formula weight	380.39	602.74	697.58
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1$	$P\bar{1}$
a (Å)	9.0861(14)	11.1787(12)	10.9756(14)
b (Å)	19.7870(37)	26.8194(37)	12.1468(16)
c (Å)	11.5829(22)	12.7123(19)	16.2695(23)
α (°)	90	90	94.499(11)
β (°)	93.266(14)	107.206(10)	108.935(11)
γ (°)	90	90	114.149(10)
V (Å^3)	2079.1(6)	3640.7(8)	1815.2(4)
Z	4	4	2
Temperature (K)	295(2)	294(2)	297(2)
D_{calcd} (g cm^{-3})	1.215	1.100	1.276
Radiation	Mo K_α	Mo K_α	Mo K_α
Wave length (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.217	0.149	0.248
$F(000)$	808	1304	732
Crystal size (mm)	$0.74\times0.42\times0.35$	$0.80\times0.36\times0.27$	$0.59\times0.52\times0.23$
2θ Range (°)	4.08–50.00	4.10–44.98	4.10–40.00
Index range	$0\le h\le10,\ 0\le k\le23,\ -11\le l\le13$	$-12\le h\le12,\ -28\le k\le28,\ -13\le l\le13$	$0\le h\le10,\ -11\le k\le10,\ -15\le l\le14$
Reflections collected	3788	10328	3622
Independent reflections	3568	9494	3387
R_{int}	0.0211	0.0165	0.0212
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
Max./min. transmission	0.26937–0.24833	0.34374–0.32906	0.99124–0.91677
Data/restraints/parameters	3563/0/243	9494/1/769	3387/0/435
Goodness-of-fit	0.880	0.909	1.073
Final indices [$I>2\sigma(I)$]	$R_1=0.0340,\ wR_2=0.0827$	$R_1=0.0357,\ wR_2=0.0797$	$R_1=0.0372,\ wR_2=0.1026$
R indices (all data)	$R_1=0.0531,\ wR_2=0.0895$	$R_1=0.0511,\ wR_2=0.0840$	$R_1=0.0427,\ wR_2=0.1057$
ΔF (e Å^{-3})	0.153 to −0.260	0.155 to −0.177	0.605 to −0.175
Flack parameter x	None	0.02(7)	None

(0.89 g, 31%). ^{1}H NMR (C_6D_6): δ 7.39–6.88 (m, 14H), 4.25 (ddd, 1H, J=12.1, 9.3, 6.2 Hz), 3.80 (dddd, 1H, J=12.4, 9.2, 6.0, 1.3 Hz), 2.23 (ddd, 1H, J=29.0, 11.0, 6.1 Hz), 1.92 (dd, 1H, J=13.1, 6.2 Hz), 1.85–1.66 (m, 2H), 1.42 (3H), 1.40 (3H); ^{13}C{^{1}H} NMR (C_6D_6): δ 146.4 (dd, J=31.7, 27.2 Hz), 142.7 (dd, J=29.8, 11.6 Hz), 137.7 (dd, J=12.4, 1.0 Hz), 137.6 (d, J=12.3 Hz), 134.7 (d, J=5.7 Hz), 134.4 (d, J=19.7 Hz), 134.2 (d, J=19.5 Hz), 129.5, 129.3 (d, J=7.8 Hz), 128.83, 128.80 (d, J=6.4 Hz), 128.77 (d, J=6.7 Hz), 128.77, 128.70, 118.6 (d, J=1.3 Hz), 84.7 (dd, J=2.0, 1.8 Hz), 83.9 (dd, J=7.4, 1.6 Hz), 27.73, 27.67, 24.8 (dd, J=19.5, 7.4 Hz), 20.9 (dd, J=20.9, 11.4 Hz); ^{31}P{^{1}H} NMR (C_6D_6): δ 7.0 (d, J=155.4 Hz), −13.0 (d, J=155.5 Hz); MS: m/z (%): 422 (70, [M+2H]$^+$), 421 (30, [M+H]$^+$), 420 (60, M$^+$), 362 (20, [M$^+$−Me_2CO]$^+$), 305 (21, [M−2Me_2CO+H]$^+$), 294 (81, [M−$C_7H_{10}O_2$]$^+$), 183 (100, [9-phosphafluorenyl]$^+$); $[\alpha]_D^{20}=+61.3$ (c=1.435, $CHCl_3$). Anal. calcd for $C_{25}H_{26}O_2P_2$: 71.42; H, 6.23; P, 14.73. Found: C, 70.77; H, 6.40; P, 13.75%.

3.3. X-Ray crystallography

A crystal of **1** was mounted in a glass capillary, while crystals of **3** and **7** were glued on a glass fiber. The data were collected on a Siemens P 3 four-circle diffractometer employing graphite monochromated Mo K_α radiation (λ=0.71073 Å).

The structures were solved by direct methods and refined against F^2 on all data by full-matrix least-squares with SHELXTL-93 programs.[24,25] H atoms of the organic groups were included at geometrically calculated positions using the riding model (C–H=0.95 Å). Experimental data for the X-ray structure determination and refinement details for **1**, **3** and **7** are collected in Table 4.

Acknowledgements

This work was supported by Symyx Technologies Inc., Santa Clara, USA, and the Fonds der Chemischen Industrie.

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25. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-157403 (**1**), CCDC-157402 (**3**) and CCDC-159178 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].