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Tetrahedron: *Asymmetry* 16 (2005) 4015–4021

New chiral P-ligands: *P*-amino- and *P*-cycloalkoxy dibenzo[*c.e*][1,2]oxaphosphorines

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Received 21 September 2005; revised 3 November 2005; accepted 4 November 2005

Abstract—The reaction of racemic chloro-dibenzo[*c.e*][1,2]oxaphosphorine with (*S*)-(−)-α-methyl-benzylamine and (1*R*,2*S*,5*R*)-(−)-menthol led to a mixture of optically active diastereomers of the corresponding phosphonous derivatives. The isomers were separated in a diastereomeric excess of 71–93% at the phosphonic oxide and/or at the phosphonous borane stage. The P(III) boranes are suitable precursors of the P-ligands. The absolute P-configuration in one of the menthyl phosphonates isolated was determined by single crystal X-ray analysis.

1. Introduction

P-Ligands are widely applied in transition metal complexes that are useful catalysts. The heterocyclic P-ligands including five- and six-membered P-cycles form a special class.[1] The dibenzo[*c.e*][1,2]oxaphosphorines with a P(III) function represents a group that has attracted much attention.[2–4] Previously, *P*-aryl and *P*-aryloxy derivatives were studied, which were stable in the *P*-oxide form.[5] Recently, *P*-phenyl- and 2,4,6-triisopropylphenyl dibenzooxaphosphorines, as well as their platinum complexes have been described.[6] Herein, we report the introduction of dibenzooxaphosphorines with chiral substituents on the phosphorus atom. Utilising chiral nucleophiles, we aimed at the synthesis of *P*-amino- and *P*-cycloalkoxy derivatives. The target molecules are novel chiral P-ligands that could be used in enantioselective reactions.

2. Results and discussion

Racemic chloro-dibenzooxaphosphorine **1**[2] served as the starting material in the syntheses. To find the optimum conditions for the substitution, an achiral amine was first used. The reaction of phosphonous chloride **1** with 2 equiv of diethylamine at ambient temperature in toluene gave phosphonous derivative **2a** in 94% yield. The procedure was then extended to the synthesis of another phosphonous ester-amide **2b** and phosphonous ester **2c**, using (*S*)-(−)-α-methyl-benzylamine and (1*R*,2*S*,5*R*)-(−)-menthol, respectively. Since the starting material **1** was a racemate, products **2b** and **2c** were obtained as mixtures of optically active diastereomeric pairs. The ratio of the diastereomers of **2b** and **2c** was close to unity (Scheme 1). The P-substituted dibenzooxaphosphorines **2a–c** were characterized by ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectroscopic data.

The P-ligands with tervalent phosphorus atom **2a–c** were extremely air sensitive, hence they were converted directly to the corresponding *P*-oxides **3a–c** before further manipulations. The optically active phosphonic derivatives **3b** and **3c** also consisted of diastereomers.

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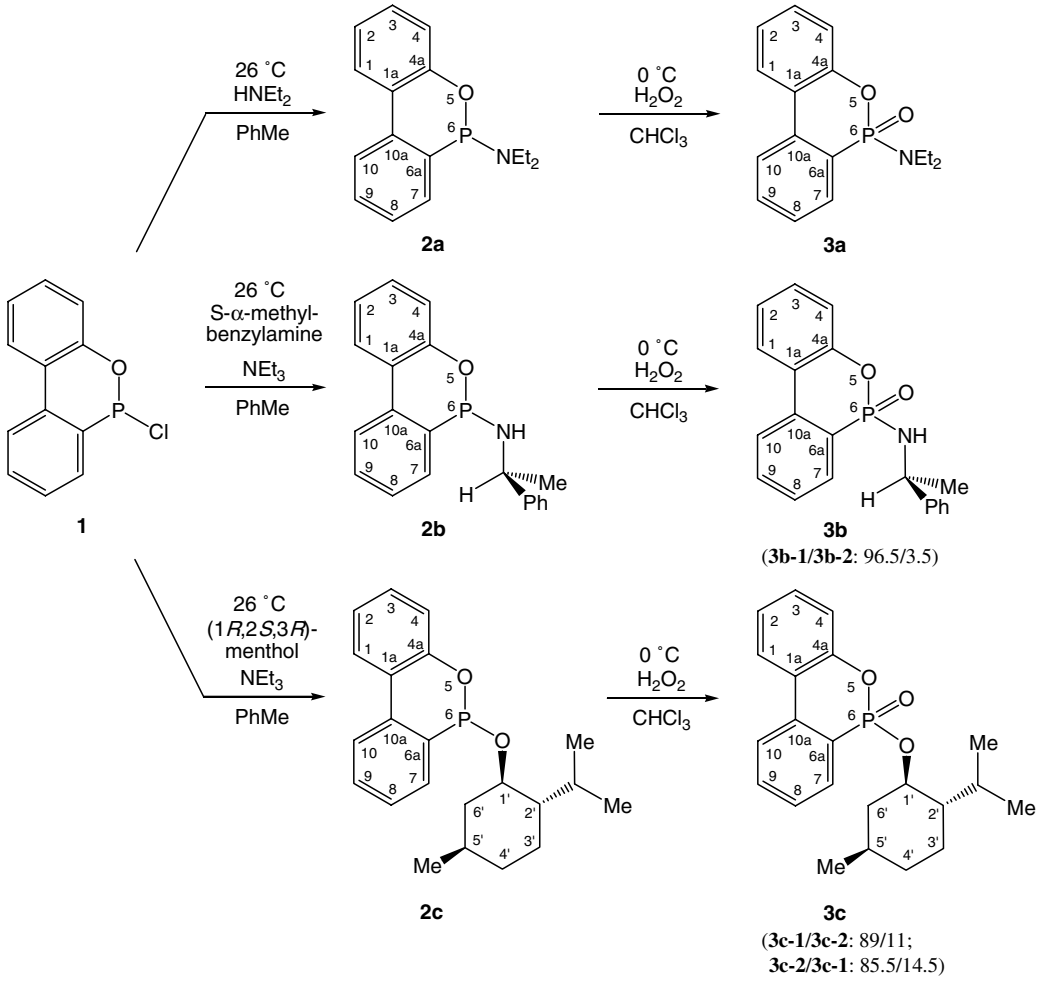
doi:10.1016/j.tetasy.2005.11.006



Scheme 1.

Products **3a**–**c** were characterized by ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectroscopy. One of the diastereomers of phosphonic ester-amide **3b** could be separated by crystallization in a diastereomeric excess (de) of 93% that is **3b-1**. Diastereomers **3c-1** and **3c-2** of phosphonate **3c** were separated by fractional crystallization in a de of 78% and 71%. NMR spectra of the enriched diastereomers promoted the assignments. The new P-ligands (**3b-1**, **3c-1** and **3c-2**) of 71–93% de were characterized by specific optical rotations.

Single crystal X-ray analysis of **3a** and **3c-2** revealed the structures depicted in Figures 1 and 2, respectively. It is probable that we had the major diastereomer **3c-2** of the 85.5–14.5% mixture of **3c** in hand, as X-ray analysis of three independent crystals led to the same result. On the other hand, an internal standard ^{31}P NMR measurement utilising one of the crystals used in the X-ray analysis also confirmed that it was **3c-2**. In the molecule of **3c-2**, the three condensed rings are not coplanar; the least-squares planes of the two phenyl rings have a setting angle of 13.7(4)°. The cyclohexane moiety has a chair conformation with all the substituents in the equatorial position. The absolute configuration around the P6 atom was found to be *R*. The configurations of the

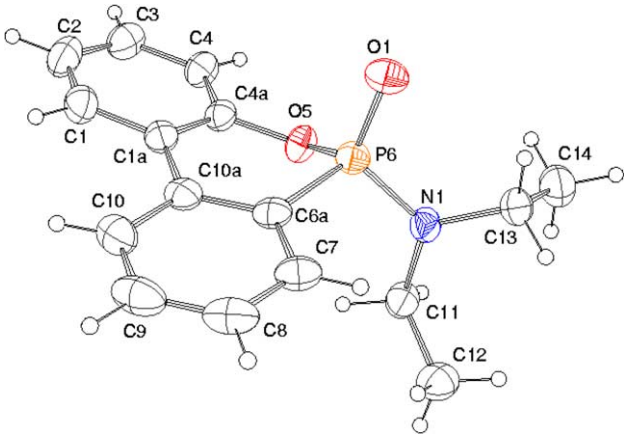


Figure 1. Perspective view of **3a** with bond distances (Å), bond angles (°) and torsion angles (°) selected [P_6–N_1 1.620(3), P_6–O_5 1.612(9), O_5–C_{4a} 1.387(4), C_{4a}–C_{1a} 1.397(13), C_{1a}–C_{10a} 1.484(5), C_{10a}–C_{6a} 1.400(7), C_{6a}–P_6 1.786(14); P_6–O_5–C_{4a} 120.9(6), O_5–C_{4a}–C_{1a} 121.6(3), C_{4a}–C_{1a}–C_{10a} 121.1(5), C_{1a}–C_{10a}–C_{6a} 120.6(7), C_{10a}–C_{6a}–P_6 119.5(2), P_6–N_1–C_{13} 120.6(3), O_1–P_6–N_1 114.3(2), O_1–P_6–O_5 113.3(6), N_1–P_6–O_5 103.5(3), O_1–P_6–C_{6a}114.3(15), N_1–P_6–C_{6a} 109.4(17), O_5–P_6–C_{6a} 100.7(7); P_6–C_{6a}–C_7–C_8 174.9(2), P_6–C_{6a}–C_{10a}–C_{10} −175.3(2), P_6–C_{6a}–C_{10a}–C_{1a} 5.5(4), C_1–C_{1a}–C_{10a}–C_{10} 13.3(5), P_6–O_5–C_{4a}–C_4 147.3(3), P_6–O_5–C_{4a}–C_{1a} −34.8(4)].

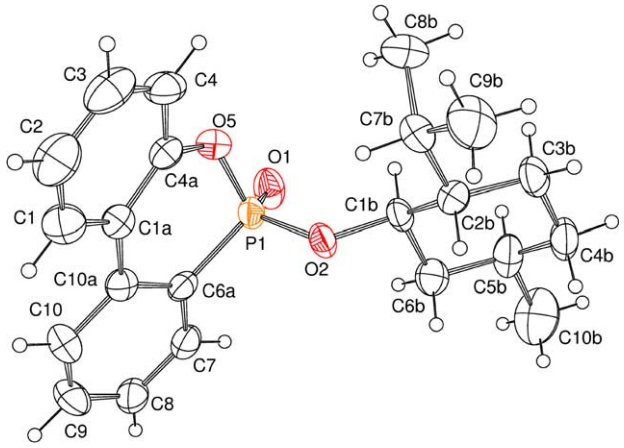


Figure 2. Perspective view of **3c-2** with bond distances (Å), bond angles (°) and torsion angles (°) selected [P_1–O_2 1.566(5), P_1–O_5 1.573(5), O_5–C_{4a} 1.388(8), C_{4a}–C_{1a} 1.393(9), C_{1a}–C_{10a} 1.459(9), C_{10a}–C_{6a} 1.406(9), C_{6a}–P_1 1.762(7); P_1–O_5–C_{4a} 123.4(4), O_5–C_{4a}–C_{1a} 120.6(7), C_{4a}–C_{1a}–C_{10a} 122.2(6), C_{1a}–C_{10a}–C_{6a} 120.1(6), C_{10a}–C_{6a}–P_1 120.6(5), P_1–O_2–C_{1b} 120.0(4), O_1–P_1–O_2 114.9(3), O_1–P_1–O_5 109.7(3), O_2–P_1–O_5 105.6(3), O_1–P_1–C_{6a} 116.6(3), O_2–P_1–C_{6a} 105.8(3), O_5–P_1–C_{6a} 103.0(3); P_1–C_{6a}–C_7–C_8 −175.6(6), P_1–C_{6a}–C_{10a}–C_{10} 175.1(5), P_1–C_{6a}–C_{10a}–C_{1a} −4.5(8), C_{10}–C_{10a}–C_{1a}–C_1 13.4(10), P_1–O_5–C_{4a}–C_4 150.7(5), P_1–O_5–C_{4a}–C_{1a} −32.1(8)].

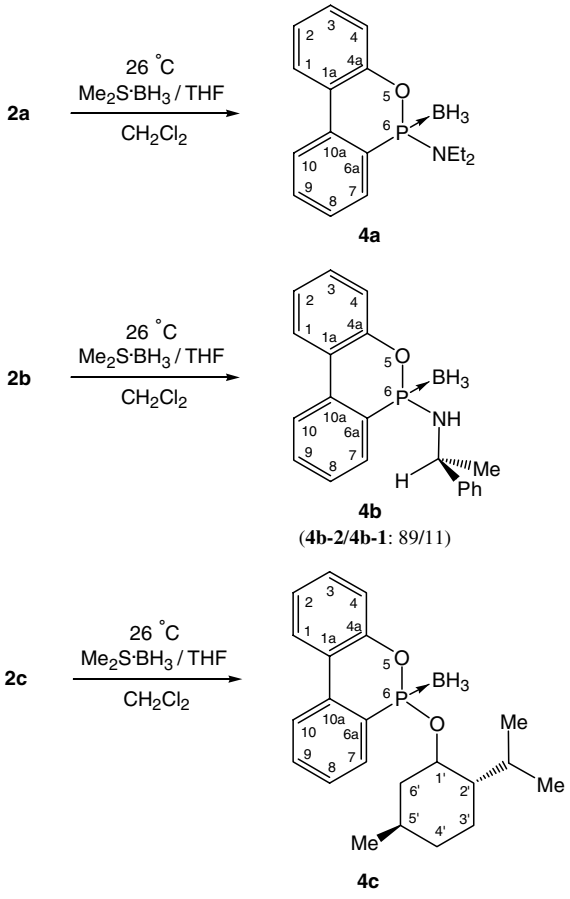
asymmetric carbon atoms in the menthyl moiety were preserved and hence were found to be *R*, *S* and *R*, around the C1b, C2b and C5b atoms, respectively. P-Heterocycle **3a** was a racemate in which the angle between the planes of the two phenyl rings was a 13.3(11)° angle. Since the sum of the bond angles is 360°, the N1 atom has a planar configuration.

Achiral dibenzooxaphosphorine **2a**, as well as the diastereomeric mixtures of the derivatives with chiral P-substituents **2b** and **2c** were converted to the corresponding boranes **4a**, **4b** and **4c**, respectively, by reaction with dimethylsulfide borane (Scheme 2).

One of the optically active diastereomers of borane complex **4b** was separated by fractional crystallization in a de of 78% and is marked as **4b-2**.

The diastereomers were characterized by ^{31}P, ^{11}B, ^{13}C and ^{1}H NMR, as well as mass spectroscopic data.

In general the unstable P-ligands are protected and stored as phosphine borane complexes.[7,8] Borane complexes of phosphonous derivatives are, however, rather rare.[8] Phosphine boranes are usually decomplexed by heating with 1 equiv of diethylamine in an aromatic solvent at ~80 °C.[9] We experienced that the decomplexation of boranes **4b** and **4c** took place only under more forcing conditions. The P–B bond in amide-ester **4b** appeared to be slightly stronger than it was in diester **4c.** Phosphonous borane **4b-2** was decomplexed by treatment with diethylamine in toluene at 80 °C for 2.5 h, while under the same conditions, decomplexation of borane **4c** was complete after 2 h. The diastereomeric excess of ca. 78% remained practically unchanged after the **4b-2**→**2b-2** conversion.



Scheme 2.

As the stereochemistry around the P atom is preserved during the decomplexation reaction, the configuration of the P6 atom in phosphonous ester-amide **2b-2** should be the same as that in phosphonous borane **4b-2**. The relative configuration of the P atom in phosphonic derivative **3b** obtained by oxidation of **2b-2**, again remains the same (marked as **3b-2**), as the oxidation involves retention at the P-centre. Diastereomer **3b-2** was definitely different from the **3b-1** form obtained by fractional crystallization of the diastereomeric mixture of **3b**.

In the next stage of our work, the optically active P(III)- and borane derivatives of chiral dibenzooxaphosphorines will be utilized in the preparation of transition metal complexes.

3. Conclusion

In conclusion, we have synthesized new optically active dibenzooxaphosphorines with an α-methyl-benzylamino- or a menthyl substituent on the phosphorus atom have been synthesized. The diastereomers were separated at the *P*-oxide and/or at the *P*-borane form. The absolute configuration of the phosphorus atom of the menthyl phosphonate isolated was determined by X-ray analysis. The phosphonous boranes, which are protected forms of the P(III) species, are suitable precursors of the corresponding P-ligands.

4. Experimental

4.1. General procedure

The ^{31}P, ^{11}B, ^{13}C and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 160.4, 125.7 and 500 MHz, respectively. Regarding ^{31}P and ^{11}B NMR, chemical shifts are downfield relative to 85% H_3PO_4 and $F_3B{\cdot}OEt_2$, respectively. The couplings are given in Hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument. The starting chloro-dibenzo[*c.e*][1,2]oxaphosphorine **1** was prepared as described earlier.[2]

4.2. General procedure for the preparation of oxaphosphorines 2a–c

To 1.0 g (4.3 mmol) of chlorooxaphosphorine **1** in 20 mL of toluene was added 0.60 mL (4.3 mmol) of triethylamine and 4.7 mmol of either (*S*)-(−)-α-methylbenzylamine (0.60 mL) or (1*R*,2*S*,5*R*)-(−)-menthol (0.73 g) at room temperature. In the case of diethylamine, 9.4 mmol (0.89 mL) of this nucleophile was used. Contents of the flask were stirred at 26 °C for 3 h under nitrogen. The reaction mixture was filtrated and the toluene phase concentrated to give **2b**, **2c** and **2a**, respectively, which were of 95–98% purity.

4.2.1. 6-Diethylamino-dibenzo[*c.e*][5,6]oxaphosphorine 2a. Yield: 1.1 g (94%); ^{31}P NMR ($CDCl_3$) δ 91.7; ^{13}C NMR ($CDCl_3$) δ 15.0 ($^3J = 3.1$, CH_3), 43.0 ($^2J = 14.8$, CH_2), 120.3 (=CH), 122.1 (=CH), 122.9 (C_{10a}), 123.0 (=CH), 124.6 (=CH), 127.1 ($^3J = 12.8$, C_8), 129.3 (=CH), 129.9 (=CH), 131.3 ($^2J = 45.6$, C_7), 132.0 ($^1J = 8.3$, C_{6a}), 134.3 ($^3J = 2.0$, C_{1a}), 152.1 ($^2J = 9.3$, C_{4a}); ^{1}H NMR ($CDCl_3$) δ 0.79 (t, $^3J_{HH} = 7.0$, 6H, $2CH_3$), 2.77–2.91 (m, 4H, $2CH_2$), 7.08–7.94 (m, 8H, Ar); $(M+H)^+_{found} = 272.1149$, $C_{16}H_{19}NOP$ requires 272.1204.

4.2.2. 6-(*S*)-(−)-α-Methyl-benzylamino-dibenzo[*c.e*][5,6]-oxaphosphorine 2b. Yield: 1.3 g (95%); obtained as a 55:45 mixture of two diastereomers **2b-1** and **2b-2**; FAB-MS, 320 (M+H); $(M+H)^+_{found} = 320.1154$, $C_{20}H_{19}NOP$ requires 320.1204.

Compound **2b-1**: ^{31}P NMR ($CDCl_3$) δ 76.3; ^{13}C NMR ($CDCl_3$) δ 25.4 ($^3J = 8.7$, CH_3)[a], 55.5 ($^2J = 16.8$, NH*CH*)[b], 121.4 (CH=)[c], 122.5 (CH=)[d], 123.5 ($^2J = 5.8$, C_{10a})[e], 123.6 (CH=), 124.6 (CH=)[f], 125.8 ($C_{2'}$), 126.6 ($C_{4'}$)[g], 127.2 ($^3J = 13.3$, C_8)[h], 128.3 ($C_{3'}$)[i], 129.4 (CH=)[j], 130.4 (CH=), 130.8 ($^2J = 44.8$, C_7)[k], 132.9 (C_{1a}), 133.7 ($^1J = 4.5$, C_{6a})[l], 145.9 ($^3J = 2.0$, $C_{1'}$), 149.7 ($^2J = 7.6$, C_{4a}); ^{1}H NMR ($CDCl_3$) δ 1.25 (d, $^3J_{HH} = 6.7$, 3H, CH_3), 3.16–3.21 (m, 1H, NH), 4.26 (q, $^3J_{HH} = 7.5$, 1H, NH*CH*), 6.97–7.88 (m, 13H, Ar).

Compound **2b-2**: ^{31}P NMR ($CDCl_3$) δ 76.0; ^{13}C NMR ($CDCl_3$) δ 25.8 ($^3J = 4.7$, CH_3)[a], 55.1 ($^2J = 16.0$, NH*CH*)[b], 121.2 (CH=)[c], 122.6 (CH=)[d], 123.4 ($^2J = 6.2$, C_{10a})[e], 123.6 (CH=), 124.7 (CH=)[f], 125.8 ($C_{2'}$), 126.7 ($C_{4'}$)[g], 127.3 ($^3J = 13.3$, C_8)[h], 128.2 ($C_{3'}$)[i], 129.5 (CH=)[j], 130.4 (CH=), 130.9 ($^2J = 44.6$, C_7)[k], 132.9 (C_{1a}), 133.4 ($^1J = 4.5$, C_{6a})[l], 145.9 ($^3J = 2.0$, $C_{1'}$), 149.7 ($^2J = 7.6$, C_{4a}), [a–l]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, $^3J_{HH} = 6.8$, 3H, CH_3), 3.16–3.21 (m, 1H, NH), 4.26 (q, $^3J_{HH} = 7.5$, 1H, CH), 6.97–7.88 (m, 13H, Ar).

4.2.3. 6-(1*R*,2*S*,5*R*)-(−)-Menthyl-dibenzo[*c.e*][5,6]oxaphosphorine 2c. Yield: 1.5 g (97%); obtained as a 1:1 mixture of two diastereomers **2c-1** and **2c-2**; FAB-MS, 355 (M+H); $(M+H)^+_{found} = 355.1758$, $C_{22}H_{28}O_2P$ requires 355.1827.

Compound **2c-1**: ^{31}P NMR ($CDCl_3$) δ 124.8; ^{13}C NMR ($CDCl_3$) δ 15.6 (CH_3), 20.9 (CH_3), 22.1 ($C_{5'}$)[a], 22.9 ($C_{3'}$)[b], 24.8 ($C_{5'}$–*CH*$_3$)[c], 31.8 ($C_{2'}$–*CH*), 34.1 ($C_{4'}$)[d], 43.7 ($^3J = 1.8$, $C_{6'}$)[e], 48.4 ($C_{2'}$)[f], 79.6 ($^2J = 13.4$, $C_{1'}$)[g], 120.6 (=CH)[h], 122.7 ($^2J = 6.2$, C_{10a})[i], 123.1 (=CH)[j], 123.5 (=CH)[k], 124.8 (=CH)[l], 127.4 ($^3J = 13.5$, C_8)[m], 129.3 (=CH)[n], 131.1 ($^2J = 49.0$, C_7), 131.4 (=CH), 131.8 ($^3J = 3.0$, C_{1a})[o], 133.0 ($^1J = 7.8$, C_{6a})[p], 149.5 ($^2J = 8.5$, C_{4a})[q]; ^{1}H NMR ($CDCl_3$) δ 0.63 (d, $^3J_{HH} = 6.5$, 3H, CH_3)[r], 0.78 (d, $^3J_{HH} = 6.5$, 3H, CH_3)[s], 0.87 (d, $^3J_{HH} = 6.0$, 3H, $C_{5'}$–CH_3)[t], 1.96 (dsep, $^3J_{HH} = 2.5$, $^3J_{HH} = 7.0$, 1H, $C_{2'}$–*CH*)[u], 1.95–2.02 (m, 1H, *CH*Me)[v], 3.94 (dq, $^3J_{HH} = 4.5$, $^3J_{PH} = 9.5$, 1H, OCH), 7.15–7.98 (m, 8H, Ar).

Compound **2c-2**: ^{31}P NMR ($CDCl_3$) δ 130.7; ^{13}C NMR ($CDCl_3$) δ 15.6 (CH_3), 20.9 (CH_3), 22.2 ($C_{5'}$)[a], 23.0 ($C_{3'}$)[b], 25.5 ($C_{5'}$–*CH*$_3$)[c], 31.8 ($C_{2'}$–*CH*), 34.2 ($C_{4'}$)[d], 44.0 ($^3J = 3.6$, $C_{6'}$)[e], 48.5 ($C_{2'}$)[f], 81.0 ($^2J = 16.1$, $C_{1'}$)[g], 120.7 (=CH)[h], 122.8 ($^2J = 6.4$, C_{10a})[i], 123.2 (=CH)[j], 123.6 (=CH)[k], 124.9 (=CH)[l], 127.5 ($^3J = 13.6$, C_8)[m], 129.5 (=CH)[n], 131.1 ($^2J = 49.0$, C_7), 131.4 (=CH), 132.1 ($^3J = 2.9$, C_{1a})[o], 133.2 ($^1J = 9.6$, C_{6a})[p], 149.8 ($^2J = 9.1$, C_{4a})[q], [a–q]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 0.65 (d, $^3J_{HH} = 7.5$, 3H, CH_3)[r], 0.82 (d, $^3J_{HH} = 7.0$, 3H, CH_3)[s], 0.86 (d, $^3J_{HH} = 6.5$, 3H, $C_{5'}$–CH_3)[t], 1.99 (dsep, $^3J_{HH} = 2.5$, $^3J_{HH} = 7.5$, 1H, $C_{2'} - CH$)[u], 2.04–2.10 (m, 1H, *CH*Me)[v], 3.75 (dq, $^3J_{HH} = 4.5$, $^3J_{PH} = 10.5$, 1H, OCH), 7.15–7.98 (m, 8H, Ar), [r–v]tentative assignment.

4.3. General procedure for the preparation of oxaphosphorine oxides 3a–c

The corresponding phosphine **2a**–**c** (4.1 mmol) was taken up in 20 mL of chloroform and treated with 0.46 mL (4.3 mmol) of 30% hydrogen peroxide at 0 °C. After stirring for 1 h, the organic phase was washed with 3×10 mL of water, dried over Na_2SO_4 and finally concentrated. Column chromatography (silica gel, 3% methanol in chloroform) of the residue afforded the product **3a**–**c**, which was recrystallized from ethanol.

4.3.1. 6-Diethylamino-dibenzo[*c.e*][5,6]oxaphosphorine 6-oxide 3a. Yield: 1.1 g (93%); mp 114–115 °C (ethanol); ^{31}P NMR ($CDCl_3$) δ 17.0; ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3); 38.5 ($^2J = 4.2$, CH_2); 119.7 ($^3J = 6.2$, C_4), 121.1 ($^2J = 11.2$, C_{10a}), 123.0 ($^3J = 11.1$, C_{10}), 123.5 (C_2), 124.0 ($^1J = 165.5$, C_{6a}), 124.3 (C_1), 127.5

($^3J = 14.5$, C_8), 129.1 ($^2J = 9.1$, C_7), 129.5 (C_3), 132.0 (C_9), 136.6 ($^3J = 7.0$, C_{1a}), 149.6 ($^2J = 8.0$, C_{4a}); ^{1}H NMR ($CDCl_3$) δ 1.15 (t, $^3J_{HH} = 7.0$, 6H, $2CH_3$), 3.13–3.20 (m, 4H, $2CH_2$), 7.00–8.01 (m, 8H, Ar); FAB-MS, 288 (M+H); $M^+_{found} = 288.1100$, $C_{16}H_{19}NO_2P$ requires 288.1153.

4.3.2. 6-(*S*)-(−)-α-Methyl-benzylamino-dibenzo[*c.e*][5,6]-oxaphosphorine 6-oxide 3b. Yield: 0.81 g (59%) obtained as a 52:48 mixture of two diastereomers (**3b-1** and **3b-2**, respectively); FAB-MS, 336 (M+H); $(M+H)^+_{found} = 336.1103$, $C_{20}H_{19}NO_2P$ requires 336.1153; $[\alpha]^{25}_D = -32.3$ (*c* 1.0, $CHCl_3$); fractional crystallization (ethanol) afforded 10.7 mg (16%) of **3b-1** {de 93%; mp 156–157 °C; $[\alpha]^{25}_D = -72.1$ (*c* 0.6, $CHCl_3$)}.

Compound **3b-1**: ^{31}P NMR ($CDCl_3$) δ 14.0; ^{13}C NMR ($CDCl_3$) δ 25.1 ($^3J = 7.8$, CH_3), 51.2 (NH*CH*), 120.1 ($^3J = 6.5$, C_4), 121.4 ($^2J = 11.9$, C_{10a}), 123.0 ($^3J = 12.1$, C_{10}), 123.7 (C_2)*, 124.1 ($^1J = 163.8$, C_{6a}), 124.4 (C_1)*, 125.6 ($C_{2'}$), 126.5 ($C_{4'}$), 127.8 ($^3J = 14.6$, C_8), 128.0 ($C_{3'}$), 129.8 (C_3), 130.0 ($^2J = 9.4$, C_7), 132.4 (C_9), 136.6 ($^3J = 7.2$, C_{1a}), 144.1 ($^3J = 4.7$, $C_{1'}$), 149.5 ($^2J = 7.6$, C_{4a}), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.42 (d, $^3J_{HH} = 6.5$, 3H, CH_3), 3.96 (t, $^3J_{HH} = {}^2J_{PH} = 9.5$, 1H, NH), 4.25 (dq, $^3J_{HH} = 7.0$, $^3J_{PH} = 2.0$, 1H, NH*CH*), 7.00–7.97 (m, 13H, Ar).

Compound **3b-2**: ^{31}P NMR ($CDCl_3$) δ 14.5; ^{13}C NMR ($CDCl_3$) δ 25.4, ($^3J = 5.2$, CH_3), 51.4 (NH*CH*), 120.2 ($^3J = 6.3$, C_4), 121.8 ($^2J = 11.9$, C_{10a}), 123.1 ($^3J = 12.0$, C_{10}), 123.8 (C_2)*, 124.1 ($^1J = 163.8$, C_{6a}), 124.6 (C_1)*, 125.6 ($C_{2'}$), 126.4 ($C_{4'}$), 127.5 ($^3J = 14.5$, C_8), 127.9 ($C_{3'}$), 129.7 (C_3), 130.2 ($^2J = 9.5$, C_7), 132.2 (C_9), 136.4 ($^3J = 7.2$, C_{1a}), 144.6 ($C_{1'}$), 149.7 ($^2J = 7.6$, C_{4a}), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.50 (d, $^3J_{HH} = 7.0$, 3H, CH_3), 4.03 (t, $^3J_{HH} = {}^2J_{PH} = 9.5$, 1H, NH), 4.25 (dq, $^3J_{HH} = 7.0$, $^3J_{PH} = 2.0$, 1H, NH*CH*), 7.00–7.97 (m, 13H, Ar).

4.3.3. (6*S*)- and (6*R*)-6-(1*R*,2*S*,5*R*)-(−)-Menthyl-dibenzo[*c.e*][5,6]oxaphosphorine oxides 3c-1 and 3c-2. Yield: 0.96 g (91%); a 1:1 mixture of the two diastereomers **3c-1** and **3c-2**; FAB-MS, 371 (M+H); $(M+H)^+_{found} = 371.1712$, $C_{22}H_{28}O_3P$ requires 371.1776; $[\alpha]^{25}_D = -62.2$ (*c* 1.0, $CHCl_3$); the two diastereomers **3c-1** and **3c-2** were separated by fractional crystallization.

Compound **3c-1** (S_P): 95 mg (18%); mp 164–166 °C (ethanol) de 78%; $[\alpha]^{25}_D = -19.8$ (*c* 1.0, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 9.9; ^{13}C NMR ($CDCl_3$) δ 15.4 (CH_3), 20.5 (CH_3), 21.8 ($C_{5'}$), 22.7 ($C_{3'}$), 25.5 ($C_{5'}$–*CH*$_3$), 31.4 ($C_{2'}$–*CH*), 33.8 ($C_{4'}$), 42.8 ($C_{6'}$), 47.9 ($^3J = 7.5$, $C_{2'}$), 78.6 ($^2J = 7.5$, $C_{1'}$), 119.9 ($^3J = 2.1$, C_4), 122.4 ($^2J = 12.4$, C_{10a}), 123.0 ($^1J = 182.7$, C_{6a}), 123.8 ($^3J = 12.0$, C_{10}), 125.0 (C_2), 127.9 ($^3J = 15.3$, C_8), 129.7 ($^2J = 9.0$, C_7), 130.1 (C_1), 133.0 (C_3)*, 133.1 (C_9)*, 136.5 ($^3J = 6.9$, C_{1a}), 149.7 ($^2J = 8.3$, C_{4a}), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 0.71 (d, $^3J_{HH} = 6.9$, 3H, $CH(CH_3)_2$), 0.78 (d, $^3J_{HH} = 7.2$, 3H, $CH(CH_3)_2$), 0.93 (d, $^3J_{HH} = 6.6$, 3H, $C_{5'}$–CH_3), 0.75–1.27 (overlapping, 4H, $2CH_2$), 1.45–1.52 (m, 1H, $C_{2'}H$), 1.58–1.67 (m, 2H, $C_{6'}H_2$), 1.81 (dsep, $^3J_{HH} = 2.5$, $^3J_{HH} = 6.9$, 1H, *CH*Me$_2$), 2.19–2.44 (m, 1H, $C_{5'}H$), 4.49 (dq, $^3J_{HH} = 4.5$, $^3J_{PH} = 9.2$, 1H, OCH), 7.22–7.98 (m, 8H, Ar).

Compound **3c-2** (R_P): 80 mg (15%); mp 113–115 °C (ethanol) de 71%; $[\alpha]^{25}_D = -41.7$ (*c* 1.0, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 9.3; ^{13}C NMR ($CDCl_3$) δ 15.5 (CH_3), 20.6 (CH_3), 21.7 ($C_{5'}$), 22.6 ($C_{3'}$), 25.2 ($C_{5'}$–CH_3), 31.3 ($C_{2'}$–CH), 33.7 ($C_{4'}$), 43.1 ($C_{6'}$), 48.0 ($^3J = 6.2$, $C_{2'}$), 79.1 ($^2J = 7.8$, $C_{1'}$), 120.0 ($^3J = 2.2$, C_4), 122.3 ($^2J = 12.4$, C_{10a}), 123.2 ($^1J = 182.6$, C_{6a}), 123.7 ($^3J = 12.1$, C_{10}), 124.9 (C_2), 128.0 ($^3J = 15.5$, C_8), 129.8 ($^2J = 9.1$, C_7), 130.0 (C_1), 132.9 (C_9)*, 133.0 (C_3)*, 136.6 ($^3J = 6.9$, C_{1a}), 149.9 ($^2J = 9.0$, C_{4a}), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 0.72 (d, $^3J_{HH} = 7.0$, 3H, $CH(CH_3)_2$), 0.74 (d, $^3J_{HH} = 7.0$, 3H, $CH(CH_3)_2$), 0.90 (d, $^3J_{HH} = 6.5$, 3H, $C_{5'}$–CH_3), 0.76–1.26 (overlapping, 4H, $2CH_2$), 1.44–1.48 (m, 1H, $C_{2'}H$), 1.59–1.65 (m, 2H, $C_{6'}H_2$), 1.79 (dsep, $^3J_{HH} = 2.5$, $^3J_{HH} = 7.0$, 1H, $CHMe_2$), 2.12–2.38 (m, 1H, $C_{5'}H$), 4.46 (dq, $^3J_{HH} = 4.5$, $^3J_{PH} = 8.5$, 1H, OCH), 7.13–7.98 (m, 8H, Ar).

4.4. General procedure for the preparation of phosphine boranes 4a–c

To 20 mL dichloromethane solution of 4.1 mmol of the corresponding phosphine **2a**–**c** were added 2.6 mL (5.1 mmol) of 2 M tetrahydrofuran solution of dimethylsulfide borane at 26 °C under nitrogen and the mixture stirred for 24 h. Evaporation of the volatile components led to **4** as a white solid.

4.4.1. 6-Diethylamino-dibenzo[*c.e*][5,6]oxaphosphorine 6-borane 4a. Column chromatography (silica gel, 2% methanol in chloroform) of the white solid yielded 0.94 g (94%) product **4a**; mp 68–70 °C (ethanol); ^{31}P NMR ($CDCl_3$) δ 94.2 (broad); ^{11}B NMR ($CDCl_3$) δ −36.2 (broad); ^{13}C NMR ($CDCl_3$) δ 14.3 ($^3J = 2.4$, CH_3); 40.9 ($^2J = 2.4$, CH_2); 120.5 ($^3J = 4.3$, C_4), 122.2 ($^2J = 9.6$, C_{10a}), 123.4 ($^3J = 6.4$, C_{10}), 123.9 ($^1J = 79.7$, C_{6a}), 124.0 (C_2)[a], 125.1 (C_1)[a], 128.5 ($^3J = 13.6$, C_8)[b], 130.4 (C_3), 131.3 ($^2J = 18.8$, C_7)[b], 132.5 (C_9), 135.8 ($^3J = 2.5$, C_{1a}), 150.2 ($^2J = 12.4$, C_{4a}), [a,b]may be reversed; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, $^3J_{HH} = 7.0$, 6H, $2CH_3$), 2.93–3.08 (m, 4H, $2CH_2$), 7.17–7.99 (m, 8H, Ar); FAB-MS, 272 (M–BH_3+H).

4.4.2. 6-(*S*)-(−)-α-Methyl-benzylamino-dibenzo[*c.e*][5,6]-oxaphosphorine 6-borane 4b. Column chromatography (silica gel, 2% methanol in chloroform) of the white solid yielded 1.3 g (95%) product **4b** consisting of a 53:47 mixture of the two diastereomers (**4b-1** and **4b-2**); FAB-MS, 320 (M–BH_3+H); $[\alpha]^{25}_D = -30.4$ (*c* 1.0, $CHCl_3$); fractional crystallization (ethanol) afforded 0.26 g (38%) of **4b-2** {de 78%; mp 132–134 °C; $[\alpha]^{25}_D = -71.3$ (*c* 1.1, $CHCl_3$)}.

Compound **4b-1**: ^{31}P NMR ($CDCl_3$) δ 84.5 (broad); ^{11}B NMR ($CDCl_3$) δ −37.1 (broad); ^{13}C NMR ($CDCl_3$) δ 25.0, ($^3J = 6.1$, CH_3), 52.6 ($^2J = 3.3$, NH*CH*), 120.8

($^3J = 4.3$, C_4), 122.3 ($^2J = 10.6$, C_{10a}), 123.5 ($^1J = 77.8$, C_{6a}), 123.6 ($^3J = 6.1$, C_{10}), 124.2 (C_2)*, 124.9 (C_1)*, 125.6 ($C_{2'}$), 127.1 ($C_{4'}$), 128.2 ($^3J = 9.4$, C_8), 128.3 ($C_{3'}$), 130.2 (C_3), 131.0 ($^2J = 19.5$, C_7), 132.7 (C_9), 135.0 (C_{1a}), 143.8 ($^3J = 4.1$, $C_{1'}$), 148.9 ($^2J = 12.7$, C_{4a}); ^{1}H NMR ($CDCl_3$) δ 1.28 (d, $^3J_{HH} = 8.0$, 3H, CH_3), 3.44–3.49 (m, 1H, NH), 4.29 (broad q, $^3J_{HH} = 7.0$, 1H, NH*CH*), 6.90–8.01 (m, 13H, Ar).

Compound **4b-2**: ^{31}P NMR ($CDCl_3$) δ 83.2 (broad); ^{11}B NMR ($CDCl_3$) δ −37.1 (broad); ^{13}C NMR ($CDCl_3$) δ 25.4, ($^3J = 4.6$, CH_3), 52.7 ($^2J = 5.4$, NH*CH*), 120.6 ($^3J = 4.4$, C_4), 121.9 ($^2J = 10.0$, C_{10a}), 122.9 ($^1J = 75.8$, C_{6a}), 123.5 ($^3J = 5.9$, C_{10}), 124.0 (C_2)*, 124.7 (C_1)*, 125.4 ($C_{2'}$), 127.0 ($C_{4'}$), 128.4 ($C_{3'}$), 128.5 ($^3J = 9.0$, C_8), 130.3 (C_3), 131.1 ($^2J = 20.1$, C_7), 132.8 (C_9), 135.4 (C_{1a}), 144.0 ($^3J = 2.6$, $C_{1'}$), 149.1 ($^2J = 13.3$, C_{4a}), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.27 (d, $^3J_{HH} = 7.0$, 3H, CH_3), 3.60 (broad t, $^3J_{HH} = {}^2J_{PH} = 9.5$, 1H, NH), 4.089 (q, $^3J_{HH} = 7.5$, $^3J_{PH} = 3.0$, 1H, NH*CH*), 6.90–8.01 (m, 13H, Ar).

4.4.3. 6-(1*R*,2*S*,5*R*)-(−)-Menthyl-dibenzo[*c.e*][5,6]oxaphosphorine 6-borane 4c. Yield: ~100%; crystalline compound (acetone) as a 51:49 mixture of two diastereomers (**4c-1** and **4c-2**); mp 137–139 °C (ethanol) FAB-MS, 355 (M–BH_3+H); $[\alpha]_D^{25} = -26.2$ (*c* 1.0, $CHCl_3$).

Compound **4c-1**: ^{31}P NMR ($CDCl_3$) δ 115.4 (broad); ^{11}B NMR ($CDCl_3$) δ −38.9 (broad); ^{13}C NMR ($CDCl_3$) δ 15.7 (CH_3)[a], 20.9 (CH_3)[b], 22.1 ($C_{5'}$)[c], 22.8 ($C_{3'}$)[d], 25.1 ($C_{5'}$–*CH*$_3$)[e], 31.5 ($C_{2'}$–*CH*)[f], 34.0 ($C_{4'}$), 43.1 ($C_{6'}$)[g], 48.6 ($^3J = 4.1$, $C_{2'}$), 81.0 ($^2J = 5.0$, $C_{1'}$)[h], 120.4 ($^3J = 4.3$, C_4)[i], 122.1 ($^2J = 10.3$, C_{10a})[j], 123.8 ($^3J = 5.9$, C_{10})[k], 124.6 ($^1J = 78.2$, C_{6a})[l], 124.7 (C_2), 125.2 (C_1)[m], 128.4 ($^2J = 10.4$, C_7)[n], 130.3 (C_3)[o], 130.9 ($^3J = 17.5$, C_8)[p], 133.4 (C_9), 133.6 ($^3J = 4.5$, C_{1a})[q], 148.5 ($^2J = 12.7$, C_{4a})[r]; ^{1}H NMR ($CDCl_3$) δ 0.67 (d, $^3J_{HH} = 7.0$, 3H, CH(*CH*$_3$)$_2$)[s], 0.78 (d, $^3J_{HH} = 7.0$, 3H, CH(*CH*$_3$)$_2$)[t], 0.90 (d, $^3J_{HH} = 6.5$, 3H, $C_{5'}$–CH_3)[u], 0.94–1.17 (overlapping, 4H, $2CH_2$), 1.27–1.36 (m, 1H, $C_{2'}H$)[v], 1.53–1.62 (m, 2H, $C_{6'}H_2$), 1.63 (dm, $^3J_{HH} = 2.0$, $^3J_{HH} = 7.0$, 1H, *CH*Me$_2$)[w], 2.09–2.13 (m, 1H, $C_{5'}H$)[x], 4.40 (dq, $^3J_{HH} = 5.5$, $^3J_{PH} = 6.3$, 1H, OCH), 7.22–8.02 (m, 8H, Ar).

Compound **4c-2**: ^{31}P NMR ($CDCl_3$) δ 112.8 (broad); ^{11}B NMR ($CDCl_3$) δ −38.9 (broad); ^{13}C NMR ($CDCl_3$) δ 16.2 (CH_3)[a], 21.0 (CH_3)[b], 22.2 ($C_{5'}$)[c], 23.1 ($C_{3'}$)[d], 25.8 ($C_{5'}$–*CH*$_3$)[e], 31.6 ($C_{2'}$–*CH*)[f], 34.0 ($C_{4'}$), 43.2

Table 1. Crystal data and structure refinement parameters

Identification code	**3a**	**3c-2**
Empirical formula	$C_{16}H_{18}NO_2P$	$C_{22}H_{27}O_3P$
Formula weight	287.28	370.41
Temperature (K)	293	293
Wavelength (Å)	1.54178	1.54178
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	$P2_12_12_1$
Unit cell dimensions		
a (Å)	17.927(3)	14.729(11)
b (Å)	8.669(3)	14.939(19)
c (Å)	18.672(3)	9.23(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	2901.9(13)	2031(6)
Z	8	4
D_{calc} (g cm^{-3})	1.315	1.212
Absorption coefficient, μ (mm^{-1})	1.685	1.337
F(000)	1216	792
Crystal colour	White	Colourless
Crystal size (mm)	$0.75 \times 0.75 \times 0.30$	$0.75 \times 0.15 \times 0.13$
Theta range for data collection (°)	$4.74 \leqslant \theta \leqslant 75.16$	$4.21 \leqslant \theta \leqslant 75.14$
Index ranges	$-22 \leqslant h \leqslant 22$, $-10 \leqslant k \leqslant 10$, $-23 \leqslant l \leqslant 23$	$0 \leqslant h \leqslant 18$, $-18 \leqslant k \leqslant 18$, $-11 \leqslant l \leqslant 11$
Reflections collected	5750	8330
Independent reflections	2875 [$R_{int} = 0.0701$]	4054 [$R_{int} = 0.1853$]
Reflections [$I > 2\sigma(I)$]	1737	1712
Completeness to θ	$\theta = 75.17°$ 96.1%	$\theta = 75.14°$ 98.6%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.987, 0.677	0.998, 0.927
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2875/0/182	4054/0/235
Goodness-of-fit on F^2	1.036	0.984
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0531$, $R_w = 0.1332$	$R_1 = 0.0788$, $R_w = 0.1694$
R indices (all data)	$R_1 = 0.1008$, $R_w = 0.1568$	$R_1 = 0.2008$, $R_w = 0.2283$
Extinction coefficient	0.0092(6)	—
Absolute structure parameter	—	–0.01(6)
Largest difference peak and hole (e Å^{-3})	0.384 and −0.662	0.233 and −0.330

($C_{6'}$)[g], 48.3 ($^3J = 7.5$, $C_{2'}$), 81.1 ($^2J = 6.5$, $C_{1'}$)[h], 120.5 ($^3J = 4.6$, C_4)[i], 122.4 ($^2J = 10.5$, C_{10a})[j], 123.9 ($^3J = 6.1$, C_{10})[k], 124.7 ($^1J = 76.2$, C_{6a})[l], 124.7 (C_2), 125.3 (C_1)[m], 128.6 ($^2J = 10.4$, C_7)[n], 130.4 (C_3)[o], 131.2 ($^3J = 17.6$, C_8)[p], 133.4 (C_9), 133.7 ($^3J = 4.6$, C_{1a})[q], 148.8 ($^2J = 13.3$, C_{4a})[r], [a–r]tentative assignment; ^{1}H NMR ($CDCl_3$) δ 0.68 (d, $^3J_{HH} = 7.0$, 3H, $CH(CH_3)_2$)[s], 0.75 (d, $^3J_{HH} = 7.0$, 3H, $CH(CH_3)_2$)[t], 0.85 (d, $^3J_{HH} = 6.5$, 3H, $C_{5'}$–CH_3)[u], 0.94–1.17 (overlapping, 4H, $2CH_2$), 1.43–1.52 (m, 1H, $C_{2'}H$)[v], 1.53–1.62 (m, 2H, $C_{6'}H_2$), 1.63 (dsep, $^3J_{HH} = 2.0$, $^3J_{HH} = 7.0$, 1H, $CHMe_2$)[w], 2.22–2.28 (m, 1H, $C_{5'}H$)[x], 4.19 (dq, $^3J_{HH} = 4.5$, $^3J_{PH} = 10.5$, 1H, OCH), 7.22–8.02 (m, 8H, Ar), [s–x]tentative assignment.

4.5. General procedure for the decomplexation of phosphine boranes 4b and 4c

To a 5 mL toluene solution of 0.45 mmol of the corresponding phosphonous borane **4b** or **4c** was added 0.094 mL (0.9 mmol) of diethylamine and the mixture stirred at 80 °C under nitrogen for 2.5 h. Evaporation of the volatile components afforded phosphonous derivatives **2b** and **2c**, respectively, in ca. 90% yield.

4.6. X-ray analysis for compounds 3a and 3c-2

A summary of the crystallographic data for **3a** and **3c-2** is shown in Table 1.

The crystals were mounted on a glass fibre. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Cu-K_α radiation ($\lambda = 1.54178$ Å). Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of carefully centred reflections. The data were collected at a temperature of 293 K using the $\omega/2\theta$ scan technique. Backgrounds were measured in half the total time of peak scans. The intensities of three representative reflections were monitored after every 150 reflections. No decay correction was applied. The data were corrected for Lorentz and polarization effects.

For **3a**, a total of 5750 reflections were collected, of which 2875 were unique [$R_{int} = 0.0701$]. For **3c-2**, of the 8330 reflections, which were collected, 4054 were unique [$R_{int} = 0.1853$]. The linear absorption coefficient, μ, for Cu-K_α radiation is 1.685 and 1.337 for **3a** and **3c-2**, respectively. An empirical absorption correction was applied to the data.[10]

Data processing was carried out using the software supplied with the diffractometer. The initial structure model was obtained from direct methods[11] for **3a** and heavy atom Patterson methods[12] for **3c**. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated based upon geometric evidence and their positions were refined by the riding model. All calculations were performed using the teXsan[13] crystallographic software package of Molecular Structure Corporation except for refinement, which was performed using SHELXL-97[14] with full-matrix least-squares method on F^2.

Crystallographic data of the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, for phosphinic derivative **3a** (CCDC No. 264671) and for phosphonate **3c-2** (CCDC No. 285360). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk).

Acknowledgements

The above project was supported by the joint funds from the European Union and the Hungarian State (GVOP-3.2.2.-2004-07-0006/3.0) and by the Hungarian Scientific and Research Fund (OTKA T042479).

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