Synthesis of (*R*,*R*)- and (*S*,*S*)-Norphos

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Dedicated to Prof. Michael P. Doyle on the occasion of his 65th birthday

Abstract: Oxidation of (*E*)-1,2-bis(diphenylphosphanyl)ethene with hydrogen peroxide gave (*E*)-1,2-bis(diphenylphosphoryl)ethene. Diels–Alder reaction of (*E*)-1,2-bis(diphenylphosphoryl)ethene with cyclopentadiene yielded 2,3-bis(diphenylphosphoryl)bicyclo[2.2.1]hept-5-ene (NorphosO). *rac*-NorphosO was resolved with *O*,*O*-dibenzoyltartaric acid. (*R*,*R*)- and (*S*,*S*)-NorphosO were reduced with trichlorosilane to give 2,3-bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene [(*R*,*R*)- and (*S*,*S*)-Norphos].

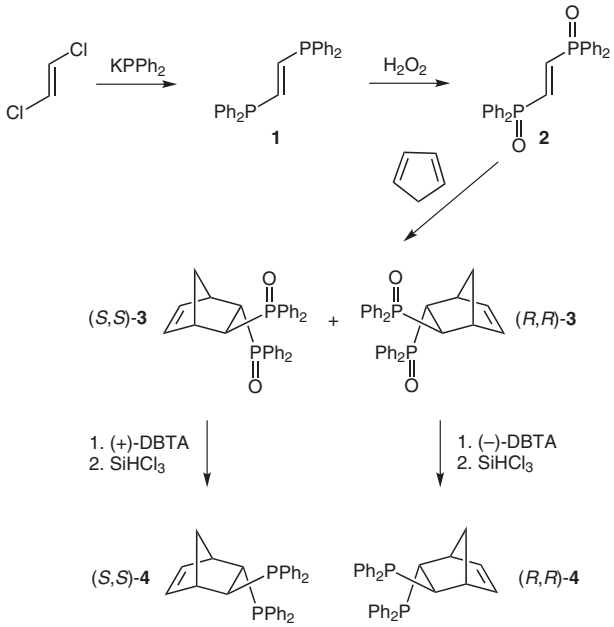
Key words: (*R*,*R*)- and (*S*,*S*)-Norphos, (*R*,*R*)- and (*S*,*S*)-2,3-bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene, enantioselective catalysis, ligand

(*R*,*R*)- and (*S*,*S*)-Norphos, (*R*,*R*)- and (*S*,*S*)-2,3-bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene, are among the optically active bisphosphane ligands most frequently used in enantioselective catalysis.[2] The ligands are commercially available from Strem Chemicals.[3] The synthesis of (*R*,*R*)- and (*S*,*S*)-Norphos was described in a preliminary communication[4] and in a patent.[5] Here, the synthesis of (*R*,*R*)- and (*S*,*S*)-Norphos is given in detail with improvements compared to the preliminary communication and patent. Norphos has been hydrogenated at the double bond of the norbornene skeleton to give 2,3-bis(diphenylphosphanyl)bicyclo[2.2.1]heptane (re-Norphos).[6,7] A chromatographic resolution of *rac*-Norphos has been described.[8]

The Norphos synthesis, shown in Scheme 1, starting from (*E*)-1,2-bis(diphenylphosphanyl)ethene (**1**),[9] which was oxidized to (*E*)-1,2-bis(diphenylphosphoryl)ethene (**2**)[9] because **1** does not function as a dienophile in the Diels–Alder reaction with cyclopentadiene. For the synthesis of Norphos, (*E*)-1,2-bis(diphenylphosphoryl)ethene (**2**) was required in large amounts, hence its preparation from the simple chemicals potassium diphenylphosphide, (*E*)-1,2-dichloroethene, and hydrogen peroxide is included here.

The Diels–Alder reaction of **2** and cyclopentadiene was carried out at 160 °C in toluene in an autoclave. Although **2** was almost insoluble in this solvent, yields of *rac*-2,3-bis(diphenylphosphoryl)bicyclo[2.2.1]hept-5-ene[10] (*rac*-**3**, *rac*-NorphosO) of 95% were achieved.

rac-NorphosO (*rac*-**3**) was resolved with *O*,*O*-dibenzoyltartaric acid (DBTA). Acids have been used several times for the resolution of phosphane oxides.[4,11–16] In the case of



Scheme 1 Synthesis of (*R*,*R*)- and (*S*,*S*)-Norphos

rac-**3**, the less soluble diastereomer (*S*,*S*)-**3**/(–)-DBTA formed polymer chains connected by strong C(O)–O–H···O=P bonds.[17]

The combination of *rac*-**3**, dissolved in chloroform, with one equivalent of (–)-*O*,*O*-dibenzoyltartaric acid, dissolved in ethyl acetate, gave a precipitate, in which (*R*,*R*)-**3**/(–)-DBTA was enriched to ~75–80%. The success of the resolution, here and in the following steps, was checked by measuring the optical rotations. Recrystallization of the enriched (*R*,*R*)-**3**/(–)-DBTA from methanol afforded diastereomerically pure (*R*,*R*)-**3**/(–)-DBTA, from which (–)-*O*,*O*-dibenzoyltartaric acid was removed. At this stage the enantiomeric purity of (*R*,*R*)-**3** could be checked by NMR. On addition of (+)-10-camphorsulfonic acid the ^{31}P NMR signals of the enantiomers of **3** separated in deuterochloroform solution. Precipitation of (*R*,*R*)-**3**/(–)-DBTA from chloroform–ethyl acetate and recrystallization of the enriched (*R*,*R*)-**3**/(–)-DBTA from methanol (*vide infra*), was more efficient than repeated precipitation from ethanol, as described in the preliminary communication.[4]

The enantiomerically pure (*R*,*R*)-**3** was reduced with trichlorosilane in an autoclave at 100 °C (inert atmosphere). An IR test showed that the PO bands at 1183 and 1116 cm^{-1} were absent in the product. The resulting crude

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(*R*,*R*)-**4** was dissolved in hot ethanol (N_2 atmosphere). Addition of water yielded enantiomerically pure (*R*,*R*)-**4** in crystalline form. This purification procedure was superior to a recrystallization from heptane, which gave higher yields but did not remove impurities efficiently.

Enriched material from mother liquors of recrystallizations at different stages of the synthesis can be collected and re-introduced into the resolution process.

An X-ray crystal analysis was carried out with crystals of (*S*,*S*)-Norphos [(*S*,*S*)-**4**], which established the *S*,*S*-configuration. Figure 1 shows an Ortep plot. Interestingly, two phenyl rings of the vicinal diphenylphosphanyl groups form a π-stack with a midpoint distance of 3.75 Å (dihedral angle C_{ipso}–P_{endo}–P_{exo}–C_{ipso} –32.35°). The phosphorus atoms, 4.18 Å apart from each other, bind metal atoms in five-membered chelate rings,[18–23] which are stiffened by the norbornene skeleton. This stiffening protects the chelate rings from flipping between δ- and λ-conformations,[18,24] an important point in enantioselective catalysis. The face-exposed/edge-exposed arrangement of the phenyl rings in these chelate systems leads to unexpected similarities in the CD spectra of image/mirror-image related compounds.[18,25–27]

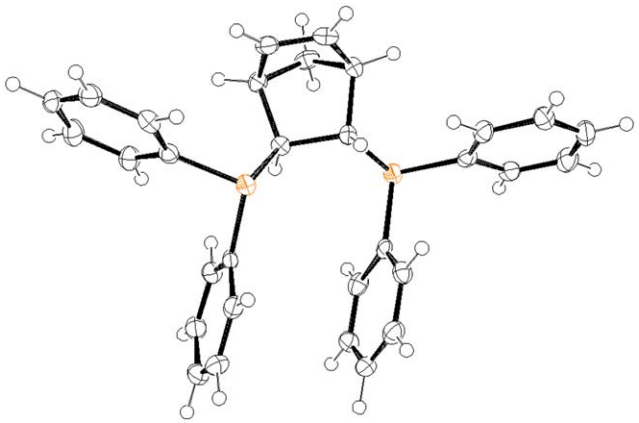

Figure 1 Ortep view of the structure of (*S*,*S*)-Norphos [(*S*,*S*)-**4**]. Ellipsoids are drawn at the 50% probability level.[28,29]

Melting points (not corrected): Büchi SMP 20. IR: Beckman IR 4240. $^1H/^{13}C/^{31}P$ NMR: Bruker Avance 400 (400/100.6/162 MHz, T = 27 °C), TMS as internal standard and H_3PO_4 as external standard. MS: Finnigan MAT 95 (EI, 70 eV). Optical rotation: Perkin-Elmer Polarimeter 241. X-ray analysis: STOE-IPDS.

(*E*)-1,2-Bis(diphenylphosphanyl)ethene (1)

$KPPh_2$ soln was formed as follows: under N_2, K (50 g, 1.28 mol) was added to anhyd dioxane (1.3 L) (pretreated with KOH, refluxed over K, and subsequently distilled under N_2). Then Ph_2PCl (125 mL, 0.7 mol) was added through a dropping funnel over 2–3 h. Similar to Grignard reactions large amounts of Ph_2PCl should only be added after the reaction had started. The mixture was stirred under reflux for 10 h.

After cooling, (*E*)-1,2-dichloroethene (68 mL, 0.88 mol) was added to the $KPPh_2$ soln through a dropping funnel over 1–2 h keeping the temperature between 0 and 5 °C. Stirring was continued at r.t. for 10 h. Dioxane and other volatiles were removed and the residue was extracted with Et_2O in a Soxhlet; yield: 111 g (83%).

(*E*)-1,2-Bis(diphenylphosphoryl)ethene (2)

Compound **1** (111 g, 0.295 mol) was dissolved in acetone (1.5 L) in air and oxidized with 30% H_2O_2 (133 mL) in H_2O (1.2 L), which was added while stirring in portions of 30–50 mL. The temperature was maintained between 40–50 °C; stirring at this temperature was continued for 2–3 h. The soln was concentrated to remove acetone and cooled in an ice bath for 10 h. The precipitate was filtered, washed with H_2O to remove excess H_2O_2, and dried; yield: 112 g (93%).

***rac*-2,3-Bis(diphenylphosphoryl)bicyclo[2.2.1]hept-5-ene (*rac*-3)**

The Diels–Alder reaction of **2** (10 g, 0.023 mol) and distilled cyclopentadiene (40 mL) (obtained by cracking dicyclopentadiene in hot decalin) in anhyd toluene (150 mL) was carried out in an autoclave (300 mL size) at 160 °C for 2–3 h with stirring. After cooling the volatiles (toluene, dicyclopentadiene) were removed. Then petroleum ether (~1 L) was added in which *rac*-**3** was insoluble. Filtration and washing with petroleum ether yielded almost quantitatively *rac*-**3**; yield: 11 g (95%); mp >230 °C.

IR (KBr): 1183 (s), 1116 cm^{-1} (s, P=O).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–6.95 (m, 20 H, H_{Ph}), 6.28 (m, 1 H, =CH), 5.75 (m, 1 H, =CH), 3.80–3.70 [m, 1 H, C*H*(PPh_2)], 3.28–3.20 [m, 1 H, C*H*(PPh_2)], 2.98 (m, 1 H, CH), 2.90–2.85 (m, 1 H, CH), 2.20–2.16 (m, 1 H, CH), 1.28–1.20 (m, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 38.5 (d, $^1J_{P,C}$ = 75.0 Hz, C3), 39.2 (dd, $^1J_{P,C}$ = 66.4 Hz, $^2J_{P,C}$ = 1.3 Hz, C2), 46.9 (d, $^2J_{P,C}$ = 4.0 Hz, C4), 47.2 (dd, $^2J_{P,C}$ = 2.2 Hz, $^3J_{P,C}$ = 0.9 Hz, C1), 48.1 (d, $^3J_{P,C}$ = 11.2 Hz, C7), 128.09 (d, $^3J_{P,C}$ = 11.7 Hz, *m*-C_{Ph}), 128.10 (d, $^3J_{P,C}$ = 11.7 Hz, *m*-C_{Ph}), 128.3 (d, $^3J_{P,C}$ = 11.7 Hz, *m*-C_{Ph}), 128.6 (d, $^3J_{P,C}$ = 11.2 Hz, *m*-C_{Ph}), 130.1 (d, $^2J_{P,C}$ = 8.5 Hz, *o*-C_{Ph}), 130.53 (d, $^2J_{P,C}$ = 9.0 Hz, *o*-C_{Ph}), 130.55 (d, $^2J_{P,C}$ = 8.5 Hz, *o*-C_{Ph}), 130.6 (d, $^2J_{P,C}$ = 8.5 Hz, *o*-C_{Ph}), 130.7 (d, $^4J_{P,C}$ = 2.7 Hz, *p*-C_{Ph}), 131.0 (d, $^4J_{P,C}$ = 3.1 Hz, *p*-C_{Ph}), 131.2 (d, $^4J_{P,C}$ = 2.7 Hz, 2 *p*-C_{Ph}), 130.7 (d, $^4J_{P,C}$ = 2.7 Hz, *p*-C_{Ph}), 132.2 (d, $^2J_{P,C}$ = 96.0 Hz, C_q of Ph), 133.7 (d, $^1J_{P,C}$ = 97.40 Hz, C_q of Ph), 132.2 (d, $^1J_{P,C}$ = 97.8 Hz, C_q of Ph), 134.6 (d, $^1J_{P,C}$ = 97.4 Hz, C_q of Ph), 135.3 (d, $^3J_{P,C}$ = 4.5 Hz, C6), 137.9 (d, $^3J_{P,C}$ = 12.1 Hz, C5).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 32.5, 29.3 (d, $^3J_{PP}$ = 9.5 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 494.1 (13, M), 429.0 (8), 325.1 (3), 294.1 (18), 293.1 (100), 279.1 (3), 227.1 (14), 202.1 (7), 201.1 (36), 183.0 (9).

Anal. Calcd for $C_{31}H_{28}O_2P_2$ (494.5): C, 75.30; H, 5.60. Found: C, 75.25; H, 5.85.

Resolution of *rac*-3 with *O*,*O*-Dibenzoyltartaric Acid Enrichment of (*R*,*R*)-3/(–)-DBTA and (*S*,*S*)-3

Two solns were made: *rac*-**3** (50 g, 0.10 mol) was dissolved in $CHCl_3$ (650 mL) and (–)-*O*,*O*-dibenzoyltartaric acid monohydrate [(–)-DBTA, 38 g, 0.10 mol] was dissolved in EtOAc (1.7 L). Both solns were combined at r.t. and stirred; precipitation began after 5–10 min. The mixture was stirred for 1 h, the slightly brown precipitate was filtered and washed with petroleum ether (bp 40–60 °C); yield: 40 g. This contained (*R*,*R*)-**3**/(–)-DBTA enriched to ~75–80%; $[\alpha]_D$ –77 to –79.5 (*c* 1, 99% EtOH).

The mother liquor and the petroleum ether washings of the precipitate were combined; evaporation of the volatiles gave a residue enriched in (*S*,*S*)-**3**/(–)-DBTA to ~80% (48 g). The residue was dissolved in $CHCl_3$ (400 mL) and shaken with aq KOH [300 mL, containing KOH (15 g)] to remove (–)-DBTA. The $CHCl_3$ soln was washed with aq KOH [200 mL, containing KOH (5 g)] and then with H_2O (200 mL). The soln was dried (Na_2SO_4) and thus the

cloudy $CHCl_3$ soln became clear. Evaporation of the solvent and drying gave **3** enriched with (*S*,*S*)-**3**; yield: 27.5 g (99%). This sample was saved for resolution with (+)-*O*,*O*-dibenzoyltartaric acid.

Diastereomerically Pure (*R*,*R*)-3/(–)-DBTA

Enriched (*R*,*R*)-**3**/(–)-DBTA (40 g) {$[\alpha]_D$ –77 to –79.5 (*c* 1, 99% EtOH)} was dissolved in hot MeOH (350 mL); if the resulting soln was cloudy, it was filtered. Cooling to r.t. and then cooling in an ice bath for 15 min gave diastereomerically pure (*R*,*R*)-**3**/(–)-DBTA, which was washed with petroleum ether (bp 40–60 °C) and dried; yield 26 g; $[\alpha]_D$ –88 (*c* 1, 99% EtOH).

Enantiomerically Pure (*R*,*R*)-3

Diastereomerically pure (*R*,*R*)-**3**/(–)-DBTA (26 g) {$[\alpha]_D$ –88 (*c* 1, 99% EtOH)} was dissolved in $CHCl_3$ (200 mL) and shaken with aq KOH [150 mL, containing KOH (9 g)] to remove (–)-DBTA . The $CHCl_3$ soln was washed with aq KOH [100 mL, containing KOH (3 g)], with H_2O (100 mL), and dried (Na_2SO_4). Evaporation of the solvent gave of enantiomerically pure (*R*,*R*)-**3**; yield: 14.5 g (99%); $[\alpha]_D$ –59 (*c* 1, $CHCl_3$).

The enantiomeric purity of (*R*,*R*)-**3** [or (*S*,*S*)-**3**] can be checked by ^{31}P NMR. In a soln of *rac*-**3** (5 mg) and D-(+)-10-camphorsulfonic acid (13 mg) in $CDCl_3$ (0.8 mL), the ^{31}P NMR signals of the enantiomers of **3** separate.

Enrichment of (*S*,*S*)-3/(+)-DBTA

Two solns were made: enriched (*S*,*S*)-**3** (27.5 g, 0.56 mol) was dissolved in $CHCl_3$ (400 mL) and (+)-*O*,*O*-dibenzoyltartaric acid monohydrate [(+)-DBTA, 21 g, 0.055 mol] was dissolved in EtOAc (940 mL). Both solns were combined at r.t. and stirred; precipitation began immediately. The mixture was stirred for 1 h, the precipitate was filtered and washed with petroleum ether (bp 40–60 °C); yield: 33 g; $[\alpha]_D$ +80 to +81.5 (*c* 1, 99% EtOH).

Diastereomerically Pure (*S*,*S*)-3/(+)-DBTA

Enriched (*S*,*S*)-**3**/(+)-DBTA (33 g) {$[\alpha]_D$ +80 to +81.5 (*c* 1, 99% EtOH)} was dissolved in hot MeOH (300 mL). Cooling to r.t. and then cooling in an ice bath for 15 min gave diastereomerically pure (*S*,*S*)-**3**/(+)-DBTA, which was washed with petroleum ether (bp 40–60 °C) and dried; yield: 26 g; $[\alpha]_D$ +89 (*c* 1, 99% EtOH).

Enantiomerically Pure (*S*,*S*)-3

Diastereomerically pure (*S*,*S*)-**3**/(+)-DBTA (26 g) {$[\alpha]_D$ +89 (*c* 1, 99% EtOH)} was dissolved in $CHCl_3$ (200 mL) and shaken with aq KOH [150 mL, containing KOH (9 g)] to remove (+)-DBTA . The $CHCl_3$ soln was washed with aq KOH [100 mL, containing KOH (3 g)] and H_2O (100 mL) and dried (Na_2SO_4). Evaporation of the solvent gave enantiomerically pure (*S*,*S*)-**3**; yield: 16 g (99%); $[\alpha]_D$ +60 (*c* 1, $CHCl_3$).

(*S*,*S*)- and (*R*,*R*)-2,3-Bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene [(+)- and (–)-Norphos, (*S*,*S*)- and (*R*,*R*)-4]

Under N_2, (*S*,*S*)- or (*R*,*R*)-**3** (9 g, 0.018 mol), $SiHCl_3$ (15 g, 0.11 mol), and anhyd toluene (150 mL) were placed in a 300-mL autoclave. The autoclave was heated to 100 °C. After cooling the volatiles were removed including excess $SiHCl_3$. The residue was dissolved in toluene (50 mL). At 0 °C a soln of NaOH (25 g) in N_2-saturated H_2O (75 mL) was added in portions. After shaking the toluene phase was passed through basic alumina (3–4 cm). The extraction process was repeated. Removal of the toluene gave a residue which was suspended in petroleum ether (bp 40–60 °C) (30 mL), filtered, washed with petroleum ether, and dried to give crude (*S*,*S*)- or (*R*,*R*)-**4** (5.5 g, 65%).

Under N_2, (*S*,*S*)- or (*R*,*R*)-**4** (5.5 g) was dissolved in hot 99% EtOH (310 mL), then H_2O (50 mL) was added. After cooling to r.t. and then cooling in an ice bath for 15 min, filtration, washing with petroleum ether (bp 40–60 °C), and drying gave crystallized (*S*,*S*)- or (*R*,*R*)-**4**; yield: 3.8 g (75%); mp 120 °C.

(*S*,*S*)-**4**: $[\alpha]_D$ +47 to +48 (*c* 1, $CHCl_3$).

(*R*,*R*)-**4**: $[\alpha]_D$ –46 to –47 (*c* 1, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.10 (m, 20 H, H_{Ph}), 6.29 (m, 1 H, =CH), 6.08 (m, 1 H, =CH), 2.96–2.88 [m, 1 H, C*H*(PPh_2)], 2.79 (m, 2 H, CH), 2.29–2.25 [m, 1 H, CH(PPh_2)], 1.10–1.08 (m, 1 H, CH_2), 0.94–0.92 (m, 1 H, CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 0.1, –2.0 ($^3J_{PP}$ = 2.9 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 462.3 (2, M), 396.2 (5), 319.1 (1), 287.2 (4), 278.2 (21), 277.2 (100), 262.2 (8), 231.3 (3), 186.1 (3), 185.1 (18), 184.1 (9), 183.1 (66).

Anal. Calcd for $C_{31}H_{28}P_2$ (462.5): C, 80.50; H, 6.06. Found: C, 80.52; H, 6.30.

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(28) The CCDC deposition number for (+)-(*S*,*S*)-Norphos is 659276. Unit cell parameters: a = 5.91520 (10), b = 14.2274 (2), c = 28.3338 (4), space group $P2_12_12_1$.
(29) Crystallographic data (excluding structure factors) for the structure of (+)-(*S*,*S*)-Norphos have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2, UK [fax: +44 (1223)336033 or e-mail: deposit@ccdc.cam.ac.uk].