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Asymmetric Diels–Alder cycloaddition of a di-*P*-stereogenic dienophile with cyclopentadiene

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Dedicated to Professor Ihsan Erden on the occasion of his 60th birthday

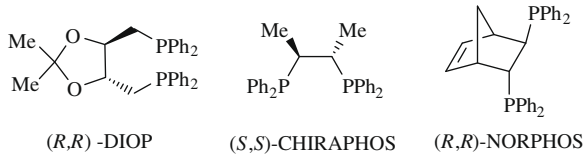
ABSTRACT

The Diels–Alder cycloaddition of the di-*P*-stereogenic dienophile (S_P,S_P)-**1** leads to novel di-*P*-stereogenic norbornene derivatives and proceeds with moderate diastereoselectivity in the absence of a catalyst. In the presence of $TiCl_4$, however, the diastereoselectivity was raised to 9:1. The major diastereoisomer has been characterized crystallographically. The separation of the diastereomeric cycloadducts was possible by fractional crystallization in the presence of (−)-*O*,*O*-dibenzoyltartaric acid monohydrate.

1. Introduction

Asymmetric hydrogenation[1] plays a vital role in fundamental research[2–4] as well as in pharmaceutical and chemical industries in providing enantiomerically pure compounds.[5–8] Chiral diphosphines,[9] which constitute the main family of ligands for catalysis, have chirality normally resident in the carbon backbone[10] or, less commonly, at the phosphorus atoms.[11–16] Although optically active diphosphines such as CHIRAPHOS, DIOP, and NORPHOS are very efficient ligands for asymmetric catalysis, ligand scaffolds, in which stereogenic phosphorus atoms are bound to a rigid 1,2-ethane backbone remain rare[17,18] (Scheme 1).

Organophosphorus compounds bearing a vinyl group are a promising class of simple alkenes due to their reactivity in many types of cycloadditions and other important transformations. For example, NORPHOS was synthesized by a Diels–Alder cycloaddition of *trans*-1,2-bis(diphenylphosphinoyl)ethene with cyclopentadiene.[19,20] Similarly, the 1,3-dipolar cycloaddition reactions of nitrones with enantiomerically pure *P*-stereogenic vinylphosphine oxides have been well established.[21–24] Recently, we have demonstrated that the homo-metathesis of (S_P)-methylphenylvinylphosphine oxide in the presence of modern olefin metathesis precatalysts allows the efficient synthesis of enantiopure *P*-stereogenic diphosphine dioxide (S_P,S_P)-**1**.[25–27] In addition, we have developed an approach to novel *C*,*P*-stereogenic diphosphines by the asymmetric 1,3-dipolar cycloaddition of (S_P,S_P)-**1** to *C*,*N*-diphenylnitrone followed by stereospecific reduction of the rigid diphosphine dioxides with Ti(O*i*Pr)$_4$/polymethylhydrosiloxane.[28] Herein



(*R*,*R*) -DIOP (*S*,*S*)-CHIRAPHOS (*R*,*R*)-NORPHOS

Scheme 1. Common optically active diphosphines.

we report on our results in using (S_P,S_P)-**1** as a dienophile in Diels–Alder cycloadditions.

2. Results and discussion

We decided to apply the Diels–Alder cycloaddition to access the rigid carbocyclic skeleton of a precursor for the novel *P*-stereogenic ligand system. Thus, the enantiomerically pure dienophile (S_P,S_P)-**1** was subjected to a Diels–Alder reaction with cyclopentadiene. The cycloaddition proceeded smoothly at 25 °C in CH_2Cl_2 to give two diastereomeric products (S_P,S_P,2*R*,3*R*)-**2** and (S_P,S_P,2*S*,3*S*)-**3** in a ratio of 1.3:1 (^{31}P NMR, ^{1}H NMR) in 92% (Scheme 2).

Unfortunately we did not succeed in separation of the diastereomers by column chromatography. To separate (S_P,S_P,2*R*,3*R*)-**2** and (S_P,S_P,2*S*,3*S*)-**3** a method developed by Brunner for separation of enantiomers of NORPHOS was applied.[29,30] By means of (−)-*O*,*O*-dibenzoyltartaric acid monohydrate [(−)-DBTA] in boiling methanol, the diastereomeric cycloadducts were separated affording (S_P,S_P,2*R*,3*R*)-**2** in 96% de and (S_P,S_P,2*S*,3*S*)-**3** in 90% de after hydrolysis with 2 M NaOH. This separation is based on the difference in solubility of the complexed diastereomeric cycloadducts and relies on the formation of hydrogen bridges between the carboxyl group of (−)-DBTA and the P=O groups[20,19] (Scheme 3).

It was not possible to assign the configuration to (S_P,S_P,2*R*,3*R*)-**2** and (S_P,S_P,2*S*,3*S*)-**3** by ^{1}H NMR. Fortunately, the major diastereoiso-

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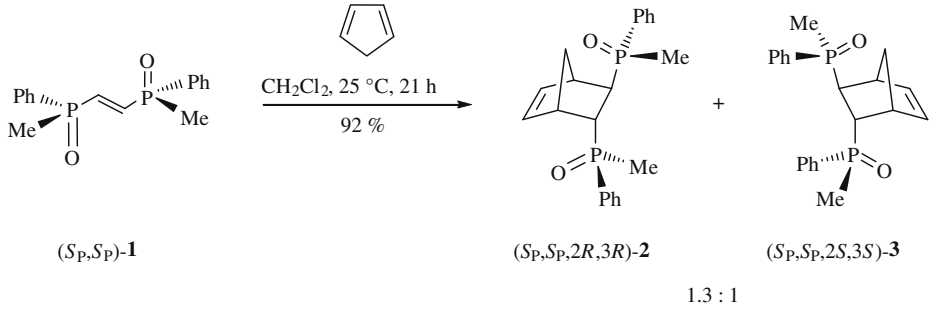
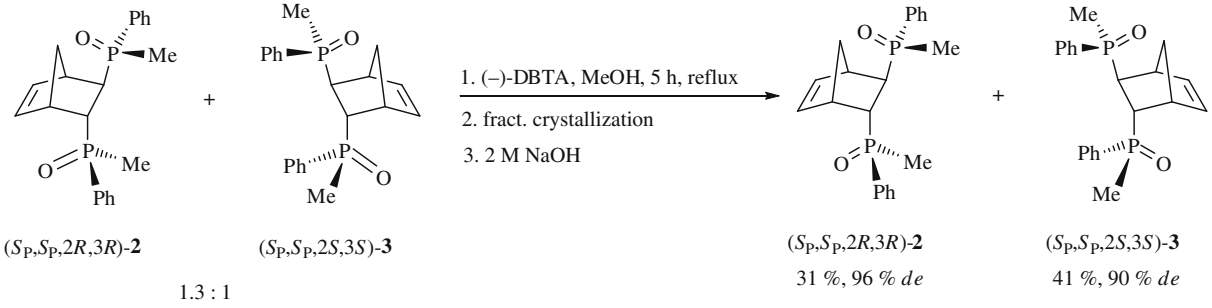


Scheme 2. Asymmetric Diels–Alder reaction of (S_P,S_P)-**1** with cyclopentadiene.



Scheme 3. Separation of diastereoisomeric cycloadducts by means of (−)-DBTA.

mer (S_P,S_P,2*R*,3*R*)-**2** crystallized from the solvent mixture ($CHCl_3$/MeOH 9:1) to give crystals suitable for an X-ray crystal structure analysis (Fig. 1). The analysis of the structure confirms that the (S_P)-methyl(phenyl)phosphinoyl groups are in *exo* and *endo* positions, *trans* to one another and that the absolute configurations at the C2, C3 carbon atoms in **2** are (*R*). The molecule adopts a conformation with the smallest substituents at the phosphorus centers, that is, phosphoryl oxygen atoms, pointing toward the sterically demanding norbornene scaffold. This results in the placement of the P═O dipoles away from one another as well as in the placement of the most bulky phenyl groups in the most distant positions. The phosphorus tetrahedron is deformed in the usual way showing increased O–P–C angles and decreased C–P–C angles with the corresponding values ranging from 114.1(5) to 109.6(4)° (Scheme 4).

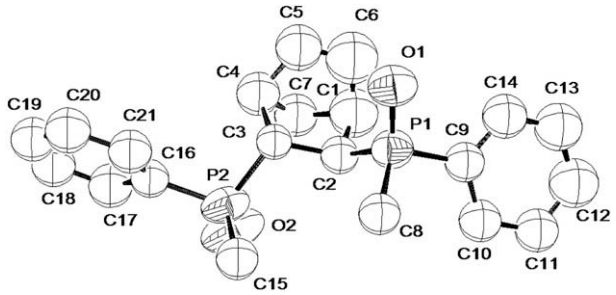
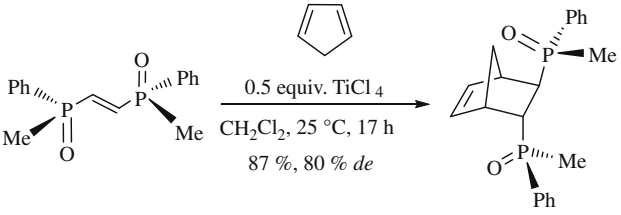


Figure 1. Structure of (S_P,S_P,2*R*,3*R*)-**2** in the crystal.[31,32] Selected bond lengths [pm], angles [°], and dihedral angles [°]: P1–O1 153.9(6), P1–C9 180.0(10), P1–C8 180.5(7), P1–C2 181.6(9), P2–O2 149.5(7), P2–C15 181.6(8), P2–C16 182.0(9), P2–C3 182.9(9), C1–C6 139.0(2), C1–C7 157.8(13), C1–C2 162.7(13), C2–C3 154.2(9), C3–C4 161.1(12), C4–C5 145.5(13), C4–C7 158.8(12), C5–C6 126.4(14), C9–C14 137.1(11), C9–C10 142.9(11), O1–P1–C9 109.6(4), O1–P1–C8 113.1(4), C9–P1–C8 105.7(5), O1–P1–C2 114.3(4), C9–P1–C2 105.9(4), C8–P1–C2 107.7(4), O2–P2–C15 113.7(4), O2–P2–C16 110.6(5), C15–P2–C16 104.7(5), O2–P2–C3 114.1(5), C15–P2–C3 106.5(4), C6–P2–C3 106.5(4), P1–C2–C3–P2 116.9(1), C15–P2–C3–C2 72.9(1), C8–P1–C2–C3 71.4(1).



Scheme 4. $TiCl_4$-assisted asymmetric Diels–Alder reaction.

In addition, (S_P,S_P,2*R*,3*R*)-**2** (96% de) was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopies. In the ^1H NMR spectrum the signals assigned to the methyl groups appeared as two doublets, with $^2J_{PH}$ = 12.7 Hz. The olefinic protons gave rise to two multiplets at δ = 5.59 and 6.02 ppm. The ^{13}C NMR spectrum showed the expected P,C spin couplings: the methyl groups gave doublets at δ = 9.2 and 13.2 ppm with $^1J_{PC}$ = 64.2 and 65.3 Hz, respectively. The carbon atoms bearing the phosphinoyl substituents gave doublets at δ = 41.9 and 42.1 ppm with coupling constants of $^1J_{PC}$ = 73.9 and 65.2 Hz, respectively. The bridgehead carbon atom next to the *endo*-phosphinoyl group gave doublet of doublets with $^2J_{PC}$ = $^3J_{PC}$ = 1.2 Hz whereas the one next to the *exo* substituent gave a doublet with $^2J_{PC}$ = 4.4 Hz. Since both stereogenic phosphorus atoms are chemically nonequivalent, there are two doublets appearing in the ^{31}P NMR spectrum at δ = +38.6 and +39.8 ppm, respectively, with a coupling constant $^3J_{PP}$ = 8.9 Hz.

A classical method to enhance the diastereoselectivity of Diels–Alder cycloadditions is based on Lewis acid catalysis.[33–36] Also, it has been shown that the *endo*/*exo* ratio of cycloadducts can be influenced by the addition of various Lewis acids.[37]

To increase the diastereoselectivity of the Diels–Alder cycloaddition studied, we tested several Lewis acids such as $AlCl_3$, $Sc(OTf)_3$, $SnCl_4$, and $TiCl_4$. After some screening it was found that

Table 1
The asymmetric Diels–Alder cycloaddition of (S_P,S_P)-**1** with cyclopentadiene

$TiCl_4$ (equiv)	Solvent/T (°C)	t (h)	(S_P,S_P,2*R*,3*R*)-**2**:(S_P,S_P,2*S*,3*S*)-**3**[a]	Yield (%)
–	Toluene/110	18	1.3:1	95
–	CH_2Cl_2/20	21	1.3:1	90
0.5	CH_2Cl_2/20	17	9:1	87
1.0	CH_2Cl_2/20	19	7:1	85
1.5	CH_2Cl_2/20	24	5:1	82
2.0	CH_2Cl_2/20	48	3:1	70

[a] The diastereomeric ratio was determined by ^{31}P NMR.

$TiCl_4$ can be successfully used to improve the diastereomeric ratio of the cycloadducts (S_P,S_P,2*R*,3*R*)-**2** and (S_P,S_P,2*S*,3*S*)-**3** (Table 1). The best results were obtained by addition of only 0.5 equiv of $TiCl_4$, which resulted in a significant increase of the ratio of diastereoisomers to 9:1 whereas the addition of larger amounts of Lewis acid resulted in lower diastereoselectivities.

The formation of the two diastereomeric adducts in unequal amounts indicates asymmetric induction by the chiral dienophile (S_P,S_P)-**1**. Stereochemical studies concerning asymmetric cycloaddition reactions involving vinylphosphine oxides and related dienophiles revealed that under thermal reaction conditions the reactive conformations of the dienophiles reflect their ground state conformations, which are *s*-cis for the majority of the systems studied.[21,38,23,39] However, recently (S_P)-methylphenylvinylphosphine oxide was used for the thermal Diels–Alder reaction with cyclopentadiene, and the structure of the major *endo* adduct was analyzed by single-crystal X-ray diffraction showing the (2*S*)-configuration at the carbon atom bearing the phosphine oxide substituent. This led to the conclusion that the *P*-stereogenic vinyl phosphine oxide adopted an *s*-trans conformation during the Diels–Alder reaction,[40] thus contrasting with its ground state conformation.[41] As (S_P,S_P)-**1** differs from the vinylphosphine oxides studied so far in the presence of two polar phosphine oxide units instead of only one, we recently carried out an X-ray crystallographic analysis of the structure of (S_P,S_P)-**1** in the solid state, which clearly established the di-*s*-cis conformation of the dienophile.[42]

For the stereochemical analysis of the studied cycloaddition both di-*s*-cis and di-*s*-trans conformations of (S_P,S_P)-**1** as the reactive conformations were considered. If the cycloaddition took place with di-*s*-cis-(S_P,S_P)-**1** one would expect a situation as shown in Figure 2 (left). The analysis clearly shows that the major (2*R*,3*R*)-configured product results from a transition state in which cyclopentadiene faces steric interactions with the phenyl substituents rather than the methyl groups of the incoming dienophile. In contrast, the respective cycloaddition of di-*s*-trans-(S_P,S_P)-**1** leads to the major (2*R*,3*R*) diastereomer via a transition state involving steric interactions of cyclopentadiene with the methyl substituents of the dienophile. As the steric bulk of the phenyl group is considered to be more dominant than that of the methyl group we conclude that the dienophile reacts preferentially in its di-*s*-trans conformation.

This conclusion is further corroborated by the observed increase in selectivity of the cycloadditions carried out in the presence of $TiCl_4$. In these cycloadditions, the preferred di-*s*-trans conformation, in which the phosphoryl oxygen atoms are pointed outside the dienophile core should be favored over the di-*s*-cis conformation to an even larger extent because of the added steric bulk of the complexed Lewis acid.

3. Conclusion

A new bicyclic enantiopure *P*-stereogenic diphosphine dioxide is now accessible by an asymmetric Diels–Alder reaction of cyclopentadiene with a homochiral *P*-stereogenic dienophile. It has been shown, that a high diastereoselectivity (9:1) can be conveniently achieved by using 0.5 equiv of $TiCl_4$ as a Lewis acid catalyst. The absolute configuration of the major diastereomer has been established crystallographically. The diastereomeric cycloadducts could be separated with the help of (−)-*O*,*O*-dibenzoyltartaric acid monohydrate by fractional crystallization providing high de of both cycloadducts.

4. Experimental

4.1. General

All glassware was flame-dried at reduced pressure and filled with N_2. Dichloromethane was distilled from calcium hydride. ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured at 25 °C with Bruker AM 400 (^1H: 400.1, ^{13}C: 100.1, ^{31}P NMR: 162 MHz), 500 (^1H: 500, ^{13}C: 125 MHz) or WP 200 SY (^1H: 200.1, ^{13}C: 50.3 MHz) spectrometers. The chemical shifts refer to δ_{TMS} = 0 ppm or to residual

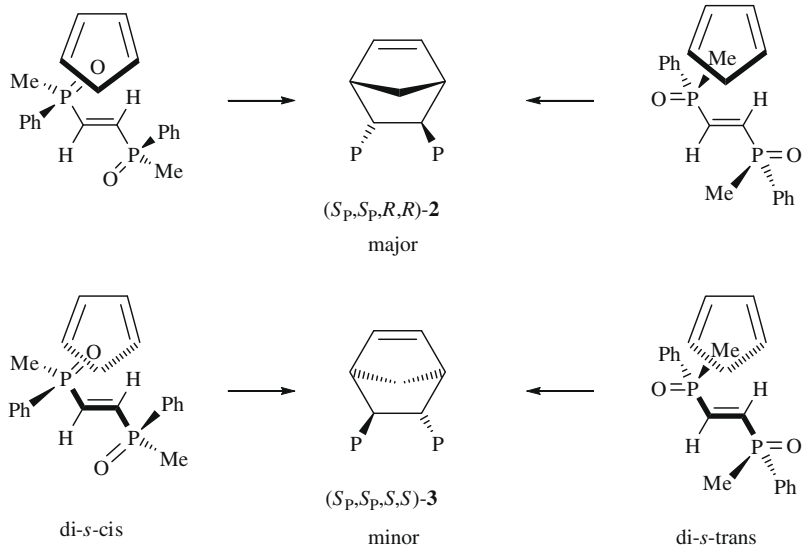


Figure 2. Stereochemistry of the Diels–Alder cycloaddition of cyclopentadiene with di-*s*-cis-(S_P,S_P)-**1** (left) and with di-*s*-trans-(S_P,S_P)-**1** (right). *P* Substituents in the cycloadducts are omitted for clarity.

solvent signals as internal standard. For ^{31}P NMR a solution of H_3PO_4 30% in water is used as an external reference. The multiplicity of the peaks is abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared spectra (IR) were recorded on a Perkin–Elmer FT-IR 580 and 1710 spectrometers. Signal intensities are abbreviated s (strong), m (medium) or w (weak). Mass spectra (MS) were measured on a Micromass LCT with Lock-Spray-unit (ESI). The injection was made in Loop-Modes in a HPLC-Alliance 2695 (Waters). All values are given in atomic units of mass per elemental charge (*m/z*). The intensity is given as a percentage of the base peak. High resolution mass spectra (HRMS) were recorded with the peak-matching method in Micromass LCT with Lock-Spray-unit (ESI). All values are given in atomic units of mass per elemental charge (*m/z*). Optical rotations were determined with a Perkin–Elmer PE-241 instrument at 20 °C with the light frequency of 589 nm (D-line of a sodium vapor lamp) in a cuvette (length d = 1 dm or d = 0.1 dm; concentration (c) is given in g/100 mL). Melting points were determined with the Electrothermal IA 9200. Microanalyses were conducted with a Elementar Vario EL instrument with acetamide as standard.

4.2. Asymmetric Diels–Alder cycloaddition of (S_P,S_P)-1 with cyclopentadiene

A solution of freshly distilled cyclopentadiene (10 equiv, 108.3 mg, 1.6 mmol) and (S_P,S_P)-**1**[25–27,43] (50 mg, 0.2 mmol) in dichloromethane (3 mL) was stirred at 20 °C for 24 h under TLC control (benzene/EtOH 4:1). The solvent was removed at reduced pressure, and the yellow residue was purified by flash chromatography (SiO_2, 20 × 2 cm, $CHCl_3$/MeOH 9:1) to afford 58.0 mg (0.19 mmol, 95%) of (S_P,S_P,2*R*,3*R*)-**2** and (S_P,S_P,2*S*,3*S*)-**3** as a mixture of diastereoisomers (1.3:1) as a colorless powder.[31]

4.3. Separation of diastereoisomers (S_P,S_P,2*R*,3*R*)-2 and (S_P,S_P,2*S*,3*S*)-3 with (−)-*O*,*O*-dibenzoyl-L-tartaric acid monohydrate

(−)-*O*,*O*-Dibenzoyl-L-tartaric acid monohydrate (101.6 mg, 0.27 mmol) was added as a powder to a solution of (S_P,S_P,2*R*,3*R*)-**2** and (S_P,S_P,2*S*,3*S*)-**3** (1.3:1, 100 mg, 0.27 mmol) in methanol (4 mL). The resulting suspension was stirred at reflux for 5 h and cooled to 25 °C. After addition of ethyl acetate (2 mL) the mixture was heated at reflux for 2 h and cooled to 25 °C. The white precipitate formed was filtered off and washed with ethyl acetate (10 mL). The precipitate was then treated with 2 M aq NaOH solution (3 mL) and extracted with CH_2Cl_2 (3 × 10 mL) and dried with anhydrous $MgSO_4$. After solvent removal at reduced pressure (S_P,S_P,2*R*,3*R*)-**2** was obtained as a colorless solid 31 mg (0.10 mmol, 31%, 96% de). $[\alpha]_D^{20} = -83.5$ (c 0.69, $CHCl_3$), mp = 207–208 °C.

The filtrate was also treated with 2 M aq NaOH (5 mL), extracted with CH_2Cl_2 (3 × 10 mL), and dried over $MgSO_4$ to give (S_P,S_P,2*S*,3*S*)-**3** as a colorless solid after solvent removal at reduced pressure (41 mg, 0.11 mmol, 41%, 90% de). $[\alpha]_D^{20} = +15.4$ (c 0.72, $CHCl_3$), mp = 211.5–212 °C. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 38.3, (d, ^3J = 9.5 Hz), 39.5, (d, ^3J = 9.5 Hz) ppm. ^1H NMR ($CDCl_3$, 400.1 MHz): δ = 1.42 (m, 1H, CH_2), 1.49 (d, $^2J_{PH}$ = 12.6 Hz, *endo*-PCH_3), 1.68 (d, $^2J_{PH}$ = 12.6 Hz, *exo*-PCH_3), 1.79 (d, J_{HH} = 7.8 Hz, 1H, CH_2), 2.26 (dd, 1H, $^2J_{PH}$ = 16.3 Hz; $^2J_{HH}$ = 6.0 Hz CH_{endo}), 2.90 (m, 1H, CH_{exo}), 3.30 (br s, 1H, CH_2CHCH_{exo}), 3.34 (m, 1H, CH_2CHCH_{endo}), 6.31 (m, 2H, =$CHCH_{endo}$, =$CHCH_{exo}$), 7.15–7.42 (m, 10H, H_{Ph}) ppm.

4.4. $TiCl_4$-assisted asymmetric Diels–Alder cycloadditon

At first, $TiCl_4$ (0.5 equiv, 15.6 mg, 0.1 mmol,1 M in CH_2Cl_2) was carefully added dropwise over 3 min at −78 °C to a stirred solution of (S_P,S_P)-**1** (50 mg, 0.2 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at −78 °C for 10 min, and freshly distilled cyclopentadiene (10 equiv, 108.3 mg, 1.6 mmol) was added as a −50 to −60 °C cold solution in dichloromethane (5 mL) over 15 min. After addition was completed the reaction mixture was allowed to warm to 20 °C and was stirred for 17 h under TLC control (benzene/EtOH 4:1). The reaction was quenched by addition of water (5 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with brine (30 mL) and dried with anhydrous $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 25 × 2 cm, $CHCl_3$/MeOH 9:1) to afford (S_P,S_P,2*R*,3*R*)-**2** (major product) and (S_P,S_P,2*S*,3*S*)-**3** (minor product) as a white powder (55.6 mg, 0.15 mmol, 91%, 80% de). $[\alpha]_D^{20} = -119$ (c 0.5, $CHCl_3$), mp = 191–192 °C. IR (ATR): $\tilde{\nu}$ = 3050 (w) cm^{-1}, 2973 (w), 1483 (w), 1335 (w), 1299 (w), 1173 (s, P=O), 1112 (s), 1070 (w), 891 (s), 857 (w), 792 (w), 729 (s), 685 (s), 643 (w). ^1H NMR ($CDCl_3$, 400.1 MHz): δ = 1.06 (m, 1H, CH_2), 1.46 (d, J_{HH} = −8.7 Hz, 1H, CH_2), 1.86 (d, $^2J_{PH}$ = 12.7 Hz, *endo*-PCH_3), 1.87 (d, $^2J_{PH}$ = 12.7 Hz, *exo*-PCH_3), 2.34 (m, 1H, CH_{endo}), 2.76 (m, 1H, CH_2CHCH_{endo}), 2.80 (br s, 1H, CH_2CHCH_{exo}), 2.93 (m, 1H, CH_{exo}), 5.59 (m, 1H, =$CHCH_{exo}$), 6.02 (m, 1H, =$CHCH_{endo}$), 7.48 (m, 6H, H_{Ph}), 7.70 (m, 4H, H_{Ph}) ppm. ^{13}C NMR (100.6 MHz BB, DEPT, HMQC, HMBC, HH-COSY, NOE, $CDCl_3$): δ = 9.2 (d, $^1J_{PC}$ = 64.2 Hz, *endo*-PCH_3), 13.2 (d, $^1J_{PC}$ = 65.3 Hz, *exo*-PCH_3), 41.9 (d, $^1J_{PC}$ = 73.9 Hz, CHP_{exo}), 42.1 (dd, $^1J_{PC}$ = 65.2 Hz, $^1J_{PC}$ = 1.2 Hz, CHP_{endo}), 45.8 (dd, $^2J_{PC}$ = $^3J_{PC}$ = 1.2 Hz, $CHCHP_{exo}$), 45.9 (d, $^2J_{PC}$ = 4.4 Hz, $CHCHP_{endo}$), 48.1 (d, $^3J_{PC}$ = 11.3 Hz, CH_2), 128.5 (d, $^3J_{PC}$ = 11.3 Hz, *m*-$CH_{Ph}P_{endo}$), 128.6 (d, $^3J_{PC}$ = 11.3 Hz, *m*-$CH_{Ph}P_{exo}$), 130.4 (d, $^4J_{PC}$ = 1.3 Hz, *p*-$CH_{Ph}P_{endo}$), 130.5 (d, $^4J_{PC}$ = 1.3 Hz, *p*-$CH_{Ph}P_{exo}$), 131.6 (d, $^2J_{PC}$ = 2.7 Hz, *o*-$CH_{Ph}P_{endo}$), 131.7 (d, $^2J_{PC}$ = 2.7 Hz, *o*-$CH_{Ph}P_{exo}$), 132.5 (d, $^1J_{PC}$ = 90.1 Hz, $P_{endo}C_q$), 133.5 (d, $^1J_{PC}$ = 90.1 Hz, $P_{exo}C_q$), 135.1 (d, $^3J_{PC}$ = 4.0 Hz, =$CHCHCP_{endo}$), 137.1 (d, $^3J_{PC}$ = 11.9 Hz, =$CHCHCP_{exo}$) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = +38.6, (d, $^3J_{P,P}$ = 8.9 Hz), +39.8, (d, $^3J_{P,P}$ = 8.9 Hz) ppm. MS (EI) *m/z* (%): 370 (11) [M^+], 305 (17) [$M^+-C_5H_5$], 231 (100) [M^+−P(O)MePh], 165 (28), 139 (37), 91 (18), 77 (20) [Ph^+]. HRMS (ESI) calcd for: [M+H]$^+$ ($C_{21}H_{24}O_2P_2Na$): calcd 393.1149, found 393.1152. Anal. Calcd for $C_{21}H_{24}O_2P_2$: C, 68.10; H, 6.53. Found: C, 67.46; H, 6.61.

4.4.1. Crystal structure analysis of (S_P,S_P,2*R*,3*R*)-2[31,32]

Single crystals of (S_P,S_P,2*R*,3*R*)-**2** were obtained by slow evaporation from chloroform/MeOH (9:1) at 20 °C. Empirical formula $C_{21}H_{24}O_2P_2$, formula weight 370.34 g/mol, crystal system orthorhombic, space group $P2_12_12_1$, unit cell dimensions a = 11.857(3), b = 16.383(13), c = 20.093(8) Å, α = 90°, β = 90°, γ = 90°, V = 3903(4) Å^3, Z = 8, d_{calcd} = 1.260 g/cm^3, μ = 0.234 mm^{-1}, crystal size 0.15 × 0.15 × 0.18 mm, F(000) = 1568, refinement method full-matrix least-squares on F^2, STOE IPDS one-axis diffractometer with imaging plate detector, T = 300(2) K, Mo Kα radiation (λ = 0.71073 Å), θ-range 1.99–24.32°, reflections collected/unique 12,481/6266 [R_{int} = 0.1301], completeness of data θ = 24.3° (99.7%), index ranges $-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 23$, direct methods, full-matrix least-squares refinement on F^2, goodness-of-fit on F^2 = 0.729, R_1 = 0.0623 ($I > 2\sigma_I$), wR_2 = 0.0879, R-indices [all data] R_1 = 0.2372 , wR_2 = 0.1144, final difference electron density map 0.347 and −0.229 e Å^{-3}.

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31. According to the IUPAC atomic numbering scheme based on the norbornene base system the olefinic carbon atoms are C-2 and C-3, those bearing the P substituents are C-5 (*endo*) and C-6 (*exo*); thus the IUPAC name for **2** is (S_P,S_P,5*R*,6*R*)-*endo*-5-*exo*-6-di(methylphenylphosphanoyl)bicyclo[2.2.1]hept-2-ene and that of **3** is (S_P,S_P,5*S*,6*S*)-*endo*-5-*exo*-6-di(methylphenylphosphanoyl) bicyclo[2.2.1]hept-2-ene. However, a literature (SciFinder) search revealed that the closely related NORPHOS system is commonly numbered as C-2 and C-3 being the P substituted carbon atoms, the olefinic carbon atoms being C-5 and C-6. In order to correspond to the current literature practise, this numbering scheme is also applied here.
32. CCDC 716060 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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