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Asymmetric 1,3-dipolar cycloaddition reaction of chiral 1-alkyl-1,2-diphospholes with diphenyldiazomethane†

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The 1,3-dipolar cycloaddition of chiral 1-alkyl-1,2-diphosphacyclopenta-2,4-dienes ((1-(–)-menthyl) oxymethyl-1,2-diphosphole and 1-(+)-neomenthyl-1,2-diphosphole) with diphenyldiazomethane leads to novel *P*-chiral bicyclic phosphiranes having six chiral centers. The degree of diastereoselectivity depends on the substituent at phosphorus, and dramatically increases in the case of (+)-neomenthyl group (de up to 71%). DFT calculations indicate that the cycloaddition is thermodynamically controlled.

Introduction

The addition of a 1,3-dipole to a dipolarophile is a fundamental reaction in organic chemistry, and its high utility spreads from natural product synthesis and chemical biology to materials science, drug discovery and agrochemistry, indicating its diversity.[1–3] Different substituents can be included in the 1,3-dipole and the dipolarophile resulting in a wide range of possible cycloadducts, which can serve as useful synthetic building blocks. The dipolarophile can be almost any multiple bond, such as C=C, C=O, C=N, C=S and C≡C, C≡N bonds. Organophosphorus compounds with >C=P– functionality (heterophospholes,[4,5] 1,3-diphospholes,[6] 1,2-diphospholes[7]) have also been used as dipolarophiles for construction of five-membered *P*-heterocycles with useful properties.

The asymmetric version of 1,3-dipolar cycloaddition reactions (1,3-DC) is one of the most powerful and useful tools for the construction of enantiomerically pure heterocycles.[8–10] Up to 4 stereocenters can be created in a stereoselective manner in one single step. The high regio- and stereoselectivity of 1,3-DC arouse interest to develop new types of dipolarophiles leading to novel heterocycles. Compared to a multitude of literature data on the asymmetric 1,3-DC of *C*-, *N*-, *O*-, or *S*-containing dipolarophiles, the phospha-1,3-DC reaction employing a C=P moiety as dipolarophile is still unknown, despite its potential utility to obtain *P*-chiral cyclic phosphines for use in asymmetric homogeneous catalysis.[11–14] Moreover, the principle of diastereotopic face differentiation by employing a P=C double bond of phosphaalkenes,[15] 2*H*-monophospholes,[16,17] 1,2-diphospholes[18–21] and heterophospholes[22] as prochiral motif in [4 + 2] cycloaddition reactions was successfully used in the synthesis of *P*-chiral polycyclic phosphines. Herein, we describe the first example of asymmetric 1,3-DC reaction of chiral 1-alkyl-1,2-diphospholes with diphenyldiazomethane.

Results and discussion

The reactions of heterophospholes as well as 1,2-diphospholes with diazoalkanes proceed with formation of either five-membered bicyclic diazophospholanes[23,24] or bicyclic phosphiranes formed by loss of nitrogen.[7,25,26] To the best of our knowledge there are no examples of an asymmetric 1,3-DC reaction of diazoalkanes with a >C=P– group. Chiral 1-alkyl-1,2-diphospholes **1**[27] and **4**[18,28] contain a stable P=C bond and a chiral substituent which makes them promising for different cycloaddition reactions. Indeed 1-((1*R*,2*S*,5*R*)-menthyl) oxymethyl-1,2-diphosphole (**1**) reacts with diphenyldiazomethane in toluene to form exclusively a mixture of two diastereomers, namely 2-((1*R*,2*S*,5*R*-menthyl)oxymethyl)-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0]hex-3-enes **3a** and **3b** with a ratio **3a** : **3b** = 1 : 1 (Scheme 1). The small diastereomeric excess (de) is probably caused by the far distance between (1*R*,2*S*,5*R*)-menthyl fragment and the reaction center. Decreasing the reaction temperature to −30 °C does not lead to any change in the isomer ratio.

Presumably, first an unstable [3 + 2] cycloaddition product **2** is formed as intermediate, which undergoes further rearrangement and loses of N_2 with formation of **3a** and **3b**. Although we were unable to detect unstable **2** by low temperature NMR spectroscopy, a similar intermediate is proposed for

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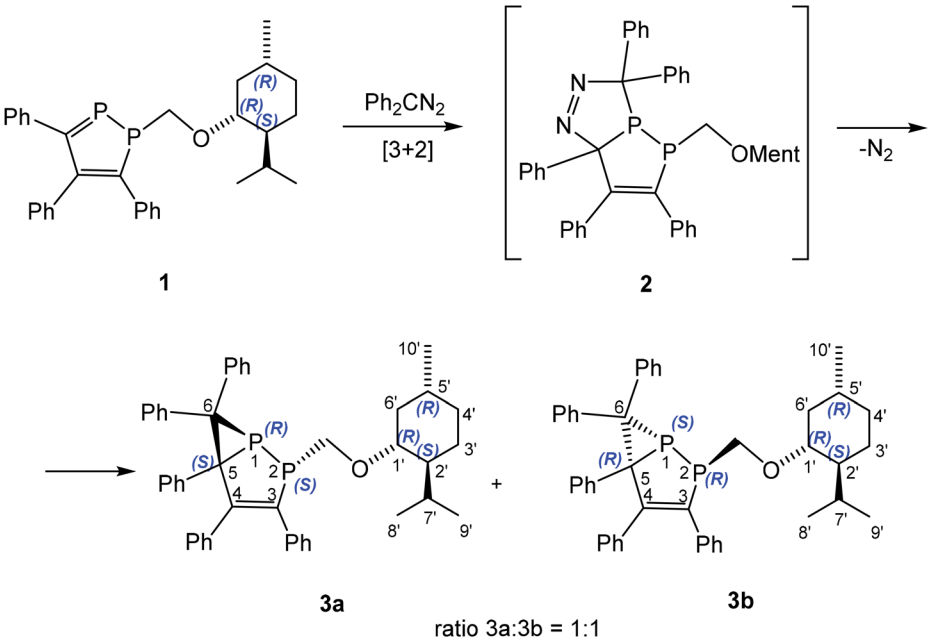


Scheme 1 Reaction of 1-((1*R*,2*S*,5*R*)-menthyl)oxymethyl-1,2-diphosphole **1** with diphenyldiazomethane.

1,3-DC reactions of heterophospholes[5] or chiral alkenes[29] with diazomethane derivatives. The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture showed only four doublets – two doublets for each diastereomer at +6.8 and −122.3 ppm with $^{1}J_{PP} = 263.8$ Hz, and at +6.4 and −119.2 ppm with $^{1}J_{PP} = 264.9$ Hz, shifted upfield in comparison to free **1** by *ca.* 50 and 300 ppm, respectively. The mixture of diastereomeric bicyclic phosphiranes **3a** and **3b** was separated by chromatography on silica gel with a petroleum ether/toluene mixture to give diastereo- and enantiopure **3a** and **3b** in 37% and 32% yield, respectively.

Most of the signals in the ^{1}H, ^{13}C and ^{31}P NMR spectra of compounds **3a** and **3b** were unequivocally assigned employing a variety of NMR correlation experiments[30,31] (see ESI† for details). The structure of the skeleton of the bicyclic phosphirane, the menthyl fragment, and their connection through the spacer were unambiguously established. From the point of view for an absolute stereochemistry determination, the *ortho*-phenyl protons at C3 (*o*-Ph3), H7′, H5′, H6′, Me-8′, Me-9′ and Me-10′ resonances are the most important. To this end, there is ^{1}H–^{13}C HMBC connectivity from the P2–CH_2O protons to C3. The exact assignment of the *o*-Ph3 protons is based on correlations from these protons to C3 (^{1}H–^{13}C HMBC) and to P2 (^{1}H–^{31}P HMBC). NOE between the *o*-Ph3 protons and the P2–CH_2O protons additionally provide support for this assignment. Good agreement between the calculated (PBE0/6-311G(2d,2p)//PBE0/6-31+G(d)) and experimental ^{13}C and ^{31}P chemical shifts[32] further supports this conclusion.

In general, an absolute configuration at one chiral center of a diastereomer can be determined by correlation to another chiral center with known stereochemistry. To this end, one needs to know the geometry of the chain linking two chiral centers, and there should be experimentally observable stereoselective NMR effects (NOE or shielding) between nuclei in these two chiral fragments.[33–35]

In **3a** and **3b**, two chiral fragments are linked by the C1′–O–CH_2–P2 chain. Conformational preference around O–C1′ and CH_2–O bonds is well established: in the former the gauche (*G*) orientation of C1′–H and CH_2–O bonds is preferred,[36–38] while the trans (*T*) conformation should be favored around the later.[39] Conformational preference around the P–CH_2 bond is not obvious. Therefore, first, the conformational preference around this bond was analyzed. DFT calculations on a simpler model (methyl instead of menthyl group) for three different orientations around the P2–CH_2 bond demonstrated that a *trans* orientation of CH_2–O with respect to the lone pair of electrons at P2 should be essentially lower in energy (1.4 kcal mol^{-1}) than other orientations (Table S1†). Thus, the preferential conformation of the C1′–O–CH_2–P2 chain is expected to be *GTT* (Fig. S1a†). Taking into account these results, the structures of both diastereomers were generated and optimized (Fig. 1a and b).

Qualitative analysis of these structures demonstrates that high field shifts may be expected for H7′, Me-8′ and Me-9′ protons due to shielding effects from *o*-Ph3 protons in **3a**, while similar effects should be observed for H5′, Me-10′, H6e′ and H6a′ protons in **3b**. Thus, these effects might be used to establish an absolute stereochemistry of the diastereomers. NMR experiments are in line with these conclusions. Indeed, these protons are largely different in the ^{1}H NMR spectra of these two products, **3a** and **3b** (Fig. S2a and c†). It is important that H7′, Me-8′ and Me-9′ are observed at higher field in, as are **3a** H6e′, H6a′, H5′ and Me-10′ in **3b**. Moreover, at low temperature these NMR shielding's increase (Fig. S2b and d†) presumably due to the greater contribution of the energetically favored conformer. In addition, there are NOE's between the *o*-

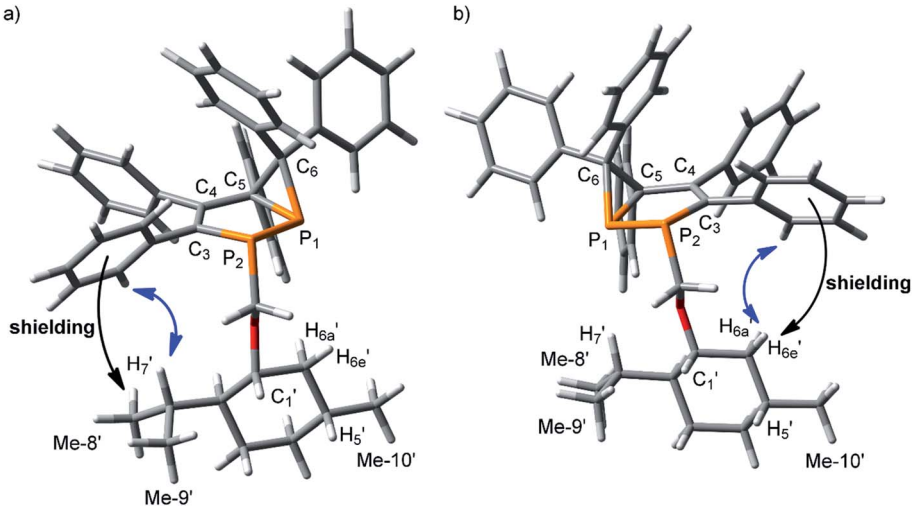


Fig. 1 (a) Optimized structures of the isomers **3a** (P1:(*R*), P2:(*S*), C5:(*S*)) and (b) **3b** (P1:(*S*), P2:(*R*), C5:(*R*)), with indicative NMR effects: aromatic shielding (black arrow) and NOE (blue arrow).

Ph3 and H7′ protons in **3a**, while in **3b**, such effects are observed between the *o*-Ph3 and H6e′ protons. Based on these findings, the absolute configuration of **3a** can be ascribed as P1:(*R*), P2:(*S*), C5:(*S*) and of **3b** as P1:(*S*), P2:(*R*), C5:(*R*).

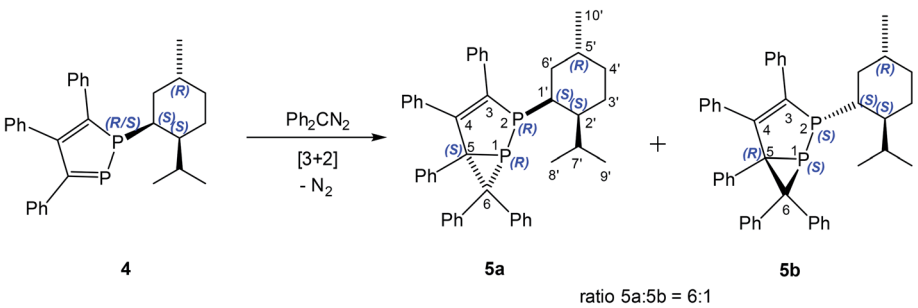
Similarly, 3,4,5-triphenyl-1-(+)-neomenthyl-1,2-diphosphole (**4**) reacts with diphenyldiazomethane at 25 °C to form a mixture of two diastereomers, namely 2-(+)-neomenthyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0]hex-3-enes **5a** (major) and **5b** (minor) with higher diastereoselectivity de = 71% (ratio **5a** : **5b** = 6 : 1) than observed for **1** (Scheme 2).

An analysis of the structure of **4**[18] shows that two different reactions pathways may be considered for the 1,3-DC reaction (Fig. 2). Steric shielding of one side by the bulky isopropyl group causes a preferential approach of the diphenyldiazomethane from the opposite side resulting in one attractive and one repulsive pathway for the 1,3-dipolar cycloaddition reaction.

Bicyclic chiral phosphirane **5a** was isolated by crystallization and fully characterized by ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR spectroscopy and X-ray structure analysis. In the ^{31}P{^{1}H} NMR spectrum two doublets are observed at +16.0 and −103.3 ppm with $^{1}J_{PP}$ = 298.1 Hz. Only one set of signals was observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of the bicyclic phosphine **5a** indicating an enantiomerically pure compound.

Most of the signals in the NMR spectra of the major isomer **5a** were unequivocally assigned employing NMR correlation experiments. For the minor isomer **5b**, the ^{31}P and only some ^{1}H and ^{13}C NMR signals can be assigned with confidence. In the major isomer, the key signals that can be used to establish the absolute configuration are due to the *ortho*-phenyl protons at C3 (*o*-Ph3), H5′, and Me-8′ protons. Namely, there is a strong NOE between the *o*-Ph3 and Me-8′ protons, and a large downfield shift of H5′ (*ca.* 3.05 ppm) relative to its "normal" position (1.4–1.2 ppm) and an upfield shift of the Me-8′ protons (see ESI† for details).

If low energy structures for these two isomers are considered (Fig. S3†), only the structure **5a** can explain these NMR effects. Thus, the close proximity and orientation of *o*-Ph3 with respect to the Me-8′ group explains the observed NOE and upfield shift of the Me-8′ due to its aromatic shielding effect; the opposite is observed for H5′, which is observed in the deshielding region of the lone pair of electrons at P1. Thus, the major product **5a** can be ascribed as the P1:(*R*), P2:(*R*), C5:(*S*) isomer. Given the similarity in changes in the calculated and experimental ^{31}P NMR chemical shifts for these two isomers, the minor product **5b** can be assigned to the structure with configuration P1:(*S*), P2:(*S*), C5:(*R*). It is also interesting that in this case the major



Scheme 2 Reaction of 3,4,5-triphenyl-1-(+)-neomenthyl-1,2-diphosphole (**4**) with diphenyldiazomethane.

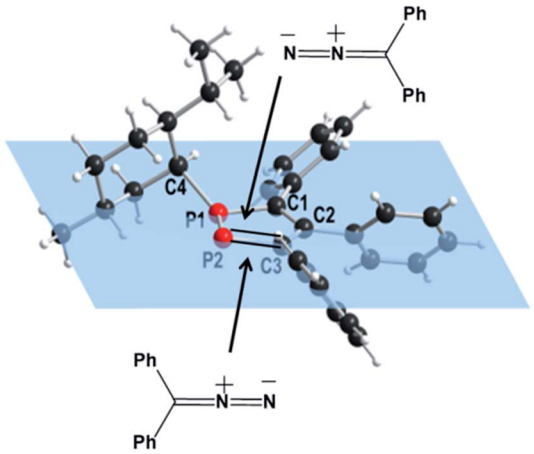


Fig. 2 Possible routes for the reaction of 3,4,5-triphenyl-1-(+)-neomenthyl-1,2-diphosphole (**4**) with diphenyldiazomethane.

isomer **5a** is lower in energy than **5b** (Table S3†). Thus, the observed stereoselectivity of the cycloaddition reaction may be due to the relative thermodynamic stability of the two possible isomers.

A crystal structure analysis of **5a** (Fig. 3) confirmed the identity and stereochemistry and showed that only one diastereomer was presented with the neomenthyl group in an *anti* orientation to the 3-membered P2–C3–C4(Ph_2) fragment. Compound **5a** crystallizes in the monoclinic space group C_2 with a Flack parameter of −0.01(3). There are 6 chiral centers in **5a**, each phosphorus-atom has a typical pyramidal environment, the menthyl fragment has the configuration of (+)-neomenthol or (1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol.

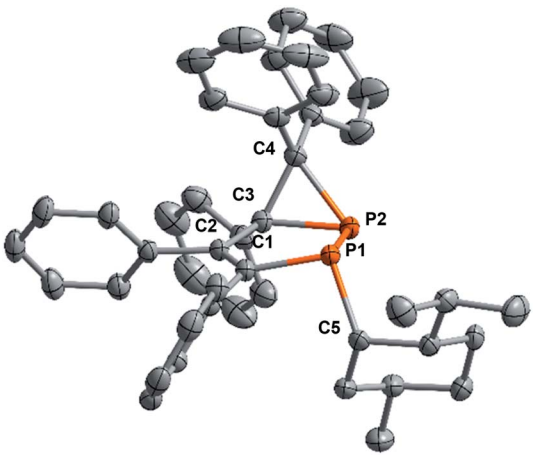


Fig. 3 Molecular structure of 2-((+)-neomenthyl)-3,4,5,6,6-pentaphenyl-1,2-($P1_RP2_RC3_S$)-diphosphabicyclo[3.1.0]hex-3-ene (**5a**). Hydrogen atoms are omitted for clarity. Configuration of chiral atoms in the five-membered ring: P1:(*R*), P2:(*R*), C3:(*S*). Selected bond lengths [Å] and angles [°]: P1–C1 1.818(3); P1–C5 1.888(3); P1–P2 2.194(1); P2–C4 1.877(3); P2–C3 1.879(3); C1–C2 1.354(4); C2–C3 1.513(4); C3–C4 1.554(4); C1–P1–C5 99.9(1); C1–P1–P2 93.4(1); C4–P2–C3 48.9(1); C4–P2–P1 100.8(1); C3–P2–P1 94.4(1).

The P–C bond lengths (1.877 and 1.879 Å) of the phosphirane ring of **5a** are in the range typical for other phosphiranes (1.78–1.89 Å).[40] The sum of bond angles around P2 ($\Sigma(\angle P2) = 243.1°$) of **5a** reflects strong pyramidalization of the environment at the phosphorus atom comparable with those for other bicyclic phosphiranes.[26,41,42]

Phosphiranes are 3-membered cyclic phosphines with unique stereoelectronic properties, (smaller cone angles and higher inversion barriers compared with their acyclic analogues) and are thought to be poorer σ donors and better π acceptors,[40] but their use as ligands in metal-catalyzed reactions is rare.[43] Chiral phosphiranes are especially rare;[44–47] therefore, the convenient asymmetric cycloaddition reaction reported here is potentially useful for expanding their limited applications in asymmetric catalysis.[48–50]

In conclusion, we have shown that a diastereoselective 1,3-dipolar cycloaddition reaction of 1-alkyl-1,2-diphospholes **1** and **4** with a chiral substituent at phosphorus with diphenyldiazomethane is a new way for the selective synthesis of *P*-chiral bicyclic phosphiranes from cheap and readily available starting materials. The formation of two diastereomers **3a** and **3b** (1 : 1) was observed in the 1,3-dipolar cycloaddition of 1-((1*R*,2*S*,5*R*)-menthyl)oxymethyl-1,2-diphosphole (**1**) with diphenyldiazomethane, while the reaction between 1-(+)-neomenthyl-1,2-diphosphole **4** and diphenyldiazomethane proceeded with high de (71%). Enantiopure 2-(+)-neomenthyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0]hex-3-ene (**5a**) could be obtained by crystallization. This study proves that combination of a chiral auxiliary with the >C=P– group of 1,2-diphospholes facilitates stereoselective 1,3-dipolar cycloaddition reactions, which is important for further developments of asymmetric cycloaddition reactions in the synthesis of chiral *P*-stereogenic phosphines.

Experimental part

NMR spectroscopy

All NMR experiments were performed with a Bruker AVANCE-600 and 500 MHz (600.1 and 500.1 MHz for ^{1}H NMR; 150.9 and 125.7 MHz for ^{13}C NMR; 242.9 and 202.5 MHz for ^{31}P NMR, respectively) spectrometers equipped with a 5 mm diameter gradient inverse broad band probehead and a pulsed gradient unit capable of producing magnetic field pulse gradients in the *z* direction of 53.5 G cm^{-1}. Most of the NMR experiments were carried out at 303 K. For ^{1}H–^{31}P long range correlations, HMBC experiments were optimized for J = 10 Hz. NOE experiments were performed with 1D DPFGNOE techniques.[51] Chemical shifts are reported in the δ (ppm) scale relative to the ^{1}H (7.27 ppm) and ^{13}C (77.0 ppm) signals of $CDCl_3$. ^{31}P chemical shifts were referred to external 85% H_3PO_4 (0.00 ppm).

DNMR experiments were carried out using a Bruker BVT3000 variable-temperature unit (with BTO2000, accuracy ±0.1 K calibrated using a methanol reference). The samples were allowed to equilibrate for 15 min at target temperature.

Elemental analyses were carried out at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences.

Synthesis

All reactions and manipulations were carried out under dry pure N_2 in standard Schlenk devices. All solvents were distilled from sodium/benzophenone or P_2O_5 and stored under nitrogen before use. Starting materials: 1-((1*R*,2*S*,5*R*)-menthyl)oxymethyl-1,2-diphosphole **1**,[27] 3,4,5-triphenyl-1-(+)-neomenthyl-1,2-diphosphole **4**[18] and diphenyldiazomethane[52] were obtained according to literature procedures.

2-((1*R*,2*S*,5*R*-Menthyl)oxymethyl)-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0]hex-3-ene (3). A solution of diphenyldiazomethane (0.25 g, 1.27 mmol) in toluene (1.5 mL) was added dropwise to a solution of **1** (0.60 g, 1.21 mmol) in toluene (10 mL). After the addition was complete, the solution was stirred for 18 h at 25 °C. Toluene was evaporated in vacuum and the residue was extracted with 100 mL of petroleum ether. After removal of the solvent, the residue (0.64 g) was purified by flash chromatography (silica gel, petroleum ether/toluene (3 : 1, v/v)) to give 0.30 g (37%) of **3a** as yellowish powder and 0.26 g (32%) of **3b** as yellowish powder.

2-((1*R*,2*S*,5*R*-Menthyl)oxymethyl)-3,4,5,6,6-pentaphenyl-1,2-(P1$_R$P2$_S$C5$_S$)-diphosphabicyclo[3.1.0]hex-3-ene (3a). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 7.65 (d, $^3J_{HH}$ = 7.1 Hz, 2H, C6-*o*-H in Ph), 7.50–7.40 (m, 3H, *m*, *p*-H in Ph), 7.11 (br, 2H, C5-*o*-H in Ph), 7.06–6.80 (m, 14H, Ph), 6.39 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C4-*o*-H in Ph), 6.30 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C3-*o*-H in Ph), 3.95 (ddd, 1H, $^2J_{HH}$ = 14.5 Hz, $^2J_{HP}$ = 11.8 Hz, $^3J_{HP}$ = 2.4 Hz, PCH_2O), 3.62 (ddd, 1H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HP}$ = 11.5 Hz, $^2J_{HP}$ = 3.5 Hz, PCH_2O), 3.01 (td, 1H, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.3 Hz, C1′–H), 2.47 (ttd, 1H, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 2.2 Hz, C7′–H), 2.28 (d, 1H, $^3J_{HH}$ = 12.0 Hz, C6′$_{eq}$ – H), 1.76–1.67 (m, 2H, C4′–H, C3′–H), 1.49–1.42 (m, 1H, C2′–H), 1.40–1.31 (m, 1H, C5′–H), 1.04–0.95 (m, 3H, C3′–H, C4′–H, C6′$_{ax}$ – H), 1.00 (d, 3H, $^3J_{HH}$ = 6.5 Hz, C10′–H), 0.92 (d, 3H, $^3J_{HH}$ = 7.0 Hz, C8′–H), 0.68 (d, 3H, $^3J_{HH}$ = 7.0 Hz, C9′–H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm, *J*, Hz): 151.1 (s, C4), 144.5 (d, $^1J_{CP}$ = 24.2 Hz, C3), 142.7 (br, *ipso*-C6$_{Ph'}$), 139.6 (d, $^2J_{CP}$ = 5.4 Hz, *ipso*-C5$_{Ph}$), 139.1 (s, *ipso*-C4$_{Ph}$), 139.0 (d, $^2J_{CP}$ = 17.7 Hz, *ipso*-C3$_{Ph}$), 138.3 (br, *ipso*-C6$_{Ph}$), 134.8 (s, *o*-C6$_{Ph}$), 134.2 (d, $^3J_{CP}$ = 7.3 Hz, *o*-C5$_{Ph}$), 131.2 (s, *o*-C4$_{Ph}$), 129.5 (d, $^3J_{CP}$ = 14.2 Hz, *o*-C6$_{Ph'}$), 129.0 (d, $^3J_{CP}$ = 6.6 Hz, *o*-C3$_{Ph}$), 127.3 (br, *p*-C$_{Ph}$ + *m*-C$_{Ph}$ + *m*-C$_{Ph}$), 127.0 (s, *p*-C$_{Ph}$), 126.9 (s, *m*-C$_{Ph}$), 126.8 (s, *m*-C$_{Ph}$), 126.5 (s, *m*-C$_{Ph}$), 125.7 (s, *p*-C$_{Ph}$), 125.6 (s, *p*-C$_{Ph}$), 125.3 (s, *p*-C$_{Ph}$), 80.5 (s, C1′), 73.1 (d, $^1J_{CP}$ = 37.8 Hz, C5), 64.8 (dd, $^1J_{CP}$ = 25.4 Hz, $^2J_{CP}$ = 6.2 Hz, P$\underline{C}H_2O$), 54.1 (d, $^1J_{CP}$ = 36.3 Hz, C6), 48.9 (s, C2′), 39.9 (s, C6′), 34.7 (s, C4′), 31.6 (s, C5′), 24.8 (s, C7′), 23.0 (s, C3′), 22.4 (s, C10′), 21.3 (s, C8′), 16.1 (s, C9′). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm, *J*, Hz): 6.2 (d, $^1J_{CP}$ = 264.6 Hz, P2), −121.4 (d, $^1J_{CP}$ = 264.6 Hz, P1). Anal. calcd for $C_{45}H_{46}OP_2$ (M 665): C, 81.30; H, 6.97; O, 2.41; P 9.32. Found: C, 81.14; H, 7.10; O, 2.18; P 9.58.

2-((1*R*,2*S*,5*R*-Menthyl)oxymethyl)-3,4,5,6,6-pentaphenyl-1,2-(P1$_S$P2$_R$C5$_R$)-diphosphabicyclo[3.1.0]hex-3-ene (3b). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 7.65 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C6-*o*-H in Ph), 7.50–7.40 (m, 3H, *m*, *p*-H in Ph), 7.09 (br, 2H, C5-*o*-H in Ph), 7.05–6.81 (m, 14H, Ph), 6.41 (d, $^3J_{HH}$ = 7.8 Hz, 2H, C4-*o*-H in Ph), 6.31 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C3-*o*-H in Ph), 4.07 (ddd, 1H, $^3J_{HP}$ = 14.0 Hz, $^2J_{HH}$ = 12.6 Hz, $^2J_{HP}$ = 1.6 Hz, P–CH_2–O), 3.62 (ddd, 1H, $^2J_{HH}$ = 12.6 Hz, $^2J_{HP}$ = 12.7 Hz, $^3J_{HP}$ = 5.3 Hz, P–CH_2–O), 3.05 (td, 1H, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.0 Hz, C1′–H), 2.58 (ttd, 1H, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 2.2 Hz, C7′–H), 1.89 (d, 1H, $^3J_{HH}$ = 12.7 Hz, C6′$_{eq}$ – H), 1.70–1.62 (m, 2H, C4′–H, C3′–H), 1.37–1.30 (m, 1H, C2′–H), 1.27–1.19 (m, 1H, C5′–H), 1.02 (d, 3H, $^3J_{HH}$ = 7.2 Hz, C8′–H), 0.88–0.84 (m, 6H, C9′–H, C10′–H), 1.00–0.70 (m, 3H, C3′–H, C4′–H, C6′$_{ax}$ – H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm, *J*, Hz): 150.8 (s, C4), 145.35 (d, $^1J_{CP}$ = 24.1, C3), 142.6 (d, $^2J_{CP}$ = 8.8 Hz, *ipso*-C6$_{Ph'}$), 139.5 (d, $^2J_{CP}$ = 4.4 Hz, *ipso*-C5$_{Ph}$), 139.1 (s, *ipso*-C4$_{Ph}$), 139.0 (d, $^2J_{CP}$ = 16.3 Hz, *ipso*-C3$_{Ph}$), 138.1 (br, *ipso*-C6$_{Ph}$), 134.9 (s, *o*-C6$_{Ph}$), 134.1 (d, $^3J_{CP}$ = 6.8 Hz, *o*-C5$_{Ph}$), 131.2 (s, *o*-C4$_{Ph}$), 129.5 (d, $^3J_{CP}$ = 14.3 Hz, *o*-C6$_{Ph'}$), 129.0 (d, $^3J_{CP}$ = 6.9 Hz, *o*-C3$_{Ph}$), 127.3 (s, *p*-C$_{Ph}$ + *m*-C$_{Ph}$ + *m*-C$_{Ph}$), 127.0 (s, *p*-C$_{Ph}$), 126.9 (s, *m*-C$_{Ph}$), 126.8 (s, *m*-C$_{Ph}$), 126.6 (s, *m*-C$_{Ph}$), 125.8 (s, *p*-C$_{Ph}$), 125.7 (s, *p*-C$_{Ph}$), 125.3 (s, *p*-C$_{Ph}$), 80.2 (s, C1′), 73.5 (d, $^1J_{CP}$ = 37.8 Hz, C5), 66.1 (dd, $^1J_{CP}$ = 23.1 Hz, $^2J_{CP}$ = 9.3 Hz, P$\underline{C}H_2O$), 54.8 (d, $^1J_{CP}$ = 35.9 Hz, C6), 48.6 (s, C2′), 40.0 (s, C6′), 34.6 (s, C4′), 31.5 (s, C5′), 25.4 (s, C7′), 23.1 (s, C3′), 22.3 (s, C10′), 21.3 (s, C8′), 16.2 (s, C9′). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm, *J*, Hz): 5.3 (d, $^1J_{CP}$ = 265.3 Hz, P2), −118.3 (d, $^1J_{CP}$ = 264.6 Hz, P1). Anal. calcd for $C_{45}H_{46}OP_2$ (M 665): C, 81.30; H, 6.97; O, 2.41; P, 9.32. Found: C, 81.34; H, 7.05; O, 2.17; P, 9.44.

2-((+)-Neomenthyl)-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0]hex-3-ene (5). A solution of diphenyldiazomethane (0.13 g, 0.67 mmol) in toluene (1.0 mL) was added dropwise to a solution of **4** (0.29 g, 0.62 mmol) in toluene (10 mL). After the addition was complete, the solution was stirred for 24 h at 25 °C. Toluene was evaporated in vacuum and the residue was extracted with 200 mL of a mixture of *n*-hexane/toluene (1 : 2, v/v), this solution was passed through a silica-gel pad (2 cm). Removal of solvents gave 0.34 g (87%) of a mixture of isomers **5a** and **5b**. The major diastereomer **5a** was crystallized from the isomer mixture from methanol as a yellowish crystals.

2-((+)-Neomenthyl)-3,4,5,6,6-pentaphenyl-1,2-(P1$_R$P2$_R$C5$_S$)-diphosphabicyclo[3.1.0]hex-3-ene (5a). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 7.62 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C6-*o*-H in Ph), 7.53–6.79 (m, 19H, *m*, *p*-Ph, C5-*o*-H in Ph), 6.37 (d, $^3J_{HH}$ = 7.8 Hz, 2H, C4-*o*-H in Ph), 6.23 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C3-*o*-H in Ph), 3.11–3.00 (m, 1H, C5′–H), 2.24 (d, 1H, $^3J_{HH}$ = 13.8 Hz, C6′$_{eq}$ – H), 2.11–2.00 (m, 2H, C4′–H, C1′–H), 1.98–1.87 (m, 2H, C3′–H, C7′–H), 1.43 (q, 1H, $^3J_{HH}$ = 10.4 Hz, C3′–H), 1.24–1.13 (m, 1H, C6′$_{ax}$ – H), 1.17 (d, 3H, $^3J_{HH}$ = 6.3 Hz, C10′–H), 1.14–1.04 (m, 1H, C2′–H), 1.07–0.96 (m, 1H, C4′–H), 0.95 (d, 3H, $^3J_{HH}$ = 6.3 Hz, C9′–H), 0.57 (d, 3H, $^3J_{HH}$ = 6.5 Hz, C8′–H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm, *J*, Hz): 149.5 (d, $^2J_{CP}$ = 5.8 Hz, C4), 148.1 (d, $^1J_{CP}$ = 26.2 Hz, C3), 143.3 (d, $^2J_{CP}$ = 10.8 Hz, *ipso*-C6$_{Ph'}$), 140.2 (d, $^2J_{CP}$ = 6.5 Hz, *ipso*-C5$_{Ph}$), 139.5 (d, $^2J_{CP}$ = 15.5 Hz, *ipso*-C3$_{Ph}$), 139.2 (d, $^2J_{CP}$ = 3.6 Hz, *ipso*-C4$_{Ph}$), 136.7 (br, *ipso*-C6$_{Ph}$), 135.3 (d, $^3J_{CP}$ = 2.9 Hz, *o*-C6$_{Ph}$), 133.9 (d, $^3J_{CP}$ = 6.5 Hz, *o*-C5$_{Ph}$), 131.4 (d, $^3J_{CP}$ = 11.5 Hz, *o*-C4$_{Ph}$), 129.5 (d, $^3J_{CP}$ = 14.3 Hz, *o*-C6$_{Ph'}$), 129.0 (d, $^3J_{CP}$ = 6.9 Hz, *o*-C3$_{Ph}$), 128.4 (s, *m*-C3$_{Ph}$), 127.7–126.3 (*p*-C6$_{Ph}$ + *p*-C5$_{Ph}$ + *m*-C6$_{Ph}$ + *m*-C6$_{Ph'}$ + *m*-C4$_{Ph}$), 125.6 (s, *p*-C4$_{Ph}$), 125.5 (s, *p*-C3$_{Ph}$), 125.1 (s, *p*-C6$_{Ph'}$), 75.2 (d, $^1J_{CP}$ = 40.7 Hz, C5), 55.3 (dd, $^1J_{CP}$ = 38.6 Hz, $^2J_{CP}$ = 2.3 Hz, C6), 48.8 (d, $^2J_{CP}$ = 11.8 Hz, C2′), 38.5 (d, $^2J_{CP}$ = 4.3 Hz, C6′), 36.0 (s, C4′), 35.8 (d, $^1J_{CP}$ = 34.8 Hz, C1′), 30.5 (d, $^3J_{CP}$ = 17.6 Hz, C5′), 30.3 (d, $^3J_{CP}$ = 17.6 Hz, C7′), 28.3 (s, C3′), 22.8 (s, C10′), 21.3 (s, C9′), 20.7 (d, $^4J_{CP}$ = 3.3 Hz, C8′). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm, *J*, Hz): 16.0 (d, $^1J_{CP}$ = 298.1 Hz, P2), −103.3 (d,

$^1J_{CP}$ = 298.1 Hz, P1). Anal. calcd for $C_{44}H_{44}P_2$ (M 635): C, 83.25; H, 6.99; P, 9.76. Found: C, 83.41; H, 6.85; P 9.69.

2-((+)-Neomenthyl)-3,4,5,6,6-pentaphenyl-1,2-(P1$_S$P2$_S$C5$_R$)-diphosphabicyclo[3.1.0]hex-3-ene (5b). The bicyclic phosphiranes fragment signals in ^{1}H and ^{13}C NMR spectra cannot be resolved due to intensive overlap with the main isomer (**5a**) signals therefore only the data for the neomenthyl fragment is given. ^{1}H NMR ($CDCl_3$, δ, ppm, J, Hz): 6.28 (d, $^3J_{HH}$ = 7.5 Hz, 2H, C4-*o*-H in Ph), 6.21 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C3-*o*-H in Ph), 2.85–2.80 (m, 1H, C1′–H), 2.21–2.14 (m, 1H, C7′–H), 2.07–2.02 (m, 1H, C6′$_{eq}$ − H), 1.61–1.55 (m, 1H, C3′–H), 1.52–1.46 (m, 1H, C4′–H), 1.27–1.2 (m, 1H, C2′–H), 1.21 (d, 3H, $^3J_{HH}$ = 6.3 Hz, C8′–H), 1.19–1.14 (m, 3H, C3′–H, C5′–H, C6′$_{ax}$ − H), 0.99 (d, 3H, $^3J_{HH}$ = 6.7 Hz, C9′–H), 0.75–0.7 (m, 1H, C4′–H), 0.37 (d, 3H, $^3J_{HH}$ = 5.8 Hz, C10′–H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm, J, Hz): 75.1 (d, $^1J_{CP}$ = 39.5 Hz, C5), 54.7 (dd, $^1J_{CP}$ = 37.0 Hz, $^2J_{CP}$ = 1.3 Hz, C6), 50.7 (d, $^2J_{CP}$ = 11.5 Hz, C2′), 42.6 (dd, $^1J_{CP}$ = 30.6 Hz, $^2J_{CP}$ = 10.2 Hz, C1′), 40.7 (dd, $^2J_{CP}$ = 5.7 Hz, $^3J_{CP}$ = 5.7 Hz, C6′), 35.8 (s, C4′), 30.3 (d, $^3J_{CP}$ = 17.6 Hz, C7′), 28.3 (C5′), 26.0 (d, $^3J_{CP}$ = 6.4 Hz, C3′), 23.0 (d, $^4J_{CP}$ = 6.1 Hz, C8′), 22.0 (s, C10′), 21.2 (s, C9′). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm, J, Hz): 8.1 (d, $^1J_{CP}$ = 279.9 Hz, P2), −114.2 (d, $^1J_{CP}$ = 279.9 Hz, P1).

Conflicts of interest

There are no conflicts to declare.

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