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Asymmetric hydroformylation of styrene using rhodium and platinum complexes of diphosphites containing chiral chelate backbones and chiral 1,3,2-dioxaphosphorinane moieties

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Abstract

Several chiral diphosphite ligands containing six stereogenic centres were synthesised and tested in order to study chiral cooperativity in the Rh- and Pt-catalysed asymmetric hydroformylation of styrene. The ligands were prepared either by the reaction of 2,4-pentanediol enantiomers with (4*R*,6*R*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane or that of (1*S*,3*S*)-1,3-diphenyl-1,3-propanediol with 4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane enantiomers. Thus the chirality was varied both in the chelate backbone and in the terminal groups of the ligands. In case of Pt-catalysed hydroformylation, the stereogenic elements in the bridge have been found to be determinate for the product configuration with a cooperative effect from the terminal groups when the constellations are matched with 40% e.e. maximum enantioselectivity. Some coordination chemistry and the crystal structure determination of these ligands are also reported. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Asymmetric hydroformylation is an attractive catalytic approach to the synthesis of a large number of chiral products.[1] Diphosphite ligands are gaining increasing importance since their beneficial effect on catalytic activity and/or regioselectivity has been disclosed in Rh-catalysed hydroformylation.[2] The recently developed Rh-based asymmetric hydroformylation catalysts, which utilise chiral bidentate phosphine–phosphite[3] or diphosphite ligands[4] are generally superior to Pt–Sn systems containing chiral diphosphines in terms of regioselectivity.[5]

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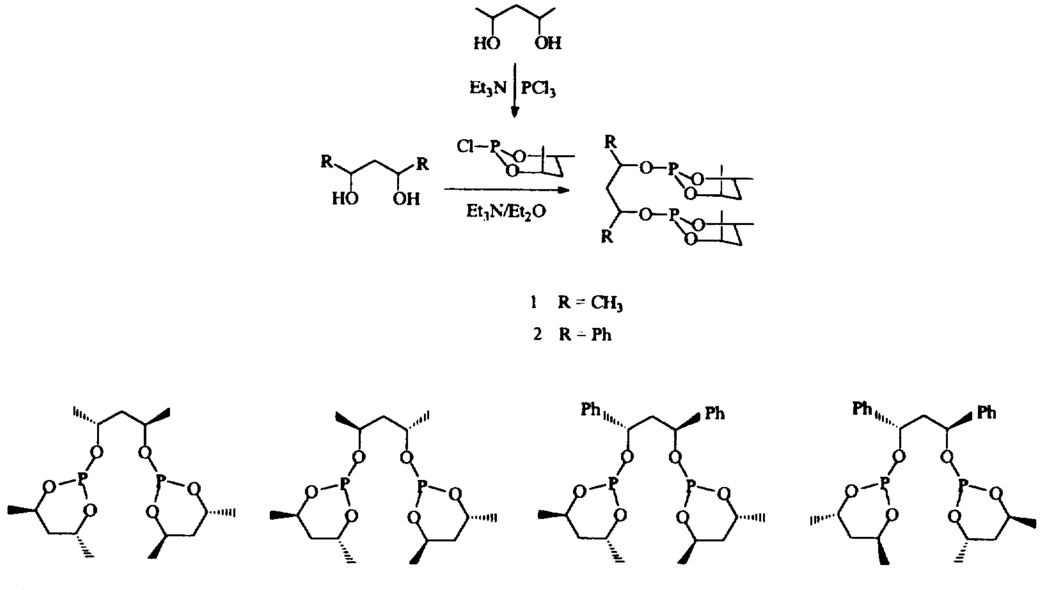
We have already reported on the synthesis and stereochemistry of (2*R*,4*R*)-2,4-bis[(4*R*,6*R*)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]pentane, **1** and (1*S*,3*S*)-1,3-diphenyl-1,3-bis[(4*R*,6*R*)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]propane, **2**.[6] It has been found that the six-membered heterocyclic rings of these compounds prefer to adopt chair conformations in solutions. Furthermore, as the first example for this type of compounds, through-space couplings were found between the P-atoms located six bonds apart. The through-space J_{PP} coupling, which was attributed to the presence of spatially close P atoms and strongly electronegative P-substituents in compounds **1** and **2**, resulted in second order features in the room temperature ^{13}C NMR spectra.[6] As part of our research aimed at the synthesis and use of new chiral diphosphites, we have described the first examples of Pt–diphosphite/$SnCl_2$ catalytic systems for asymmetric hydroformylation in a recent communication.[7] By the use of different 2,4-bis[dinaphtho[*d,f*][1,3,2]dioxaphosphepin-6-yloxy]-pentane diphosphite diastereomers as ligands, which contain stereogenic centres in the backbone and stereogenic axes in the terminal groups, remarkable enantioselective cooperative effects were observed in such reactions.[7] In the light of these findings, we have investigated the catalytic properties and stereochemistry of compounds **1** and **2** in Rh- and Pt-catalysed hydroformylation. In order to be able to study the extent of chiral cooperativity, new homochiral diastereomers of **1** and **2** were prepared. We also report here on the coordination chemistry and X-ray structure determination of these ligands.

2. Results and discussion

New diastereomers of **1** and **2** were prepared by the reaction of homochiral (2*S*,4*S*)-2,4-pentanediol and (1*S*,3*S*)-1,3-diphenylpropane-1,3-diol with (4*R*,6*R*)- and (4*S*,6*S*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane, respectively, analogous to the earlier reported method (Scheme 1).[6] (4*R*,6*R*)- and (2*S*,4*S*)-4,6-Dimethyl-2-chloro-1,3,2-dioxaphosphorinane can be obtained from the homochiral enantiomers of 2,4-pentanediol and PCl_3 in the presence of triethylamine.[8]



(2R,4R)-bis(4R,6R)-1 (2S,4S)-bis(4R,6R)-1 (1S,3S)-bis(4R,6R)-2 (1S,3S)-bis(4S,6S)-2

Scheme 1. Synthesis of chiral diphosphite with C_2 symmetry

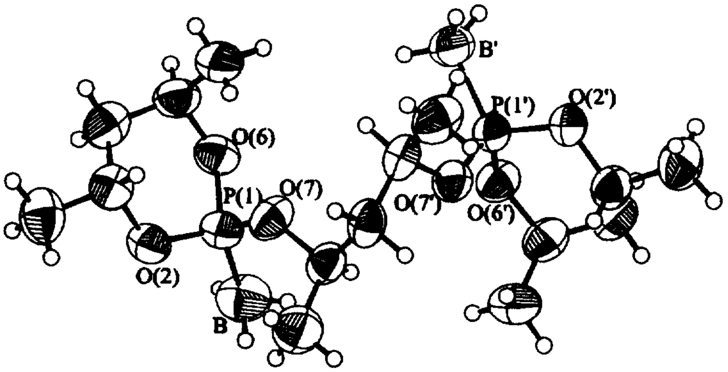


Fig. 1. ORTEP drawing of the (2*R*,4*R*)-bis(4*R*,6*R*)-**1** borane adduct

The (2*R*,4*R*)- and (2*S*,4*S*)-(2,4)-bis[(4*R*,6*R*)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]pentane diastereomers **1** differ only in the configuration of the carbon atoms in the bridge. In the case of **2**, the two diastereomers differ in the configuration of the carbon atoms in the terminal units, while the configuration of the carbon atoms in the bridge are the same. ^{31}P NMR spectra of the ligands exhibit singlet patterns which indicate that pure diastereomers have been obtained.

(2*R*,4*R*)-Bis(4*R*,6*R*)-**1** reacts with BH_3·THF[9] to yield the borane adduct as a crystalline solid.[6] This material was recrystallised from diethylether at −20°C yielding crystals suitable for analysis by X-ray diffraction. The molecular structure of (2*R*,4*R*)-bis(4*R*,6*R*)-**1** borane adduct is shown in Fig. 1. The coordination sphere around the phosphorus atom is distorted tetrahedral. In agreement with the solution NMR spectra[6] the X-ray structure determination of this compound shows chair conformations for the dioxaphosphorinane rings.

Selected bond lengths and angles for (2*R*,4*R*)-bis(4*R*,6*R*)-**1** borane adduct[10] are as follows: P(1)–O(6) 1.571(2), P(1)–O(7) 1.576(2), P(1)–O(2) 1.578(2), P(1)–B 1.861(3), P(1′)–O(2′) 1.566(2), P(1′)–O(6′), 1.567(2), P(1′)–O(7′) 1.578(2), P(1′)–B′ 1.869(3), O(2′)–P(1′)–O(6′) 105.6(1), O(2′)–P(1′)–O(7′) 105.1(1), O(6′)–P(1′)–O(7′) 103.0(1), O(2′)–P(1′)–B′ 111.6(1), O(6′)–P(1′)–B′ 112.3(1), O(7′)–P(1′)–B′ 118.3(1), O(2′)–P(1′)–O(6′) 105.6(1), O(2′)–P(1′)–O(7′) 105.1(1), O(6′)–P(1′)–O(7′) 103.0(1), O(2′)–P(1′)–B′ 111.6(1), O(6′)–P(1′)–B′ 112.3(1), O(7′)–P(1′)–B′ 118.3(1).

The X-ray crystal structure of (1*S*,3*S*)-bis(4*R*,6*R*)-**2**[11] has also been determined (Fig. 2). In the solid state, an intramolecular P–P distance of 4.27 Å is found which is greater than the sum of their van der Waals radii. However, the collisional and vibrational energy of (1*S*,3*S*)-bis(4*R*,6*R*)-**2** in solution may lead to the population of states with shortened distances in relevance to the observed through-space coupling in solution.[6] The dioxaphosphorinane rings also clearly show chair conformations.

Selected bond lengths and angles for (1*S*,3*S*)-bis(4*R*,6*R*)-**2** are as follows: P(1)–O(2) 1.584(3), P(1)–O(6) 1.598(3), P(1)–O(7) 1.627(3), P(1′)–O(2′) 1.595(4), P(1′)–O(6′) 1.602(3), P(1′)–O(7′) 1.633(3), O(2)–P(1)–O(6) 103.0(2), O(2)–P(1)–O(7) 98.3(2), O(6)–P(1)–O(7) 103.1(2), O(2′)–P(1′)–O(6′) 102.9(2), O(2′)–P(1′)–O(7′) 97.2(2), O(6′)–P(1′)–O(7′) 102.4(2).

Each diastereomer of **1** and **2** reacts at room temperature with $PtCl_2(PhCN)_2$ by replacing PhCN at the metal. The formed platinum complexes were identified by their characteristic ^{31}P NMR spectra. These show singlet patterns supplemented with $J_{^{195}\mathrm{Pt-P}}$ satellites at 63.6 ppm ($J_{\mathrm{Pt-P}}$=5817.7 Hz) for $PtCl_2$((2*R*,4*R*)-bis(4*R*,6*R*)-**1**) and at 62.3 ppm ($J_{\mathrm{Pt-P}}$=5790.6 Hz) for $PtCl_2$((2*S*,4*S*)-bis(4*R*,6*R*)-**1**), respectively. The phosphorous resonance of the ligand in the latter complex appears ~70.0 ppm upfield to that of the non-coordinated free ligand at 132.3 ppm. Similar coordination shift trends are also

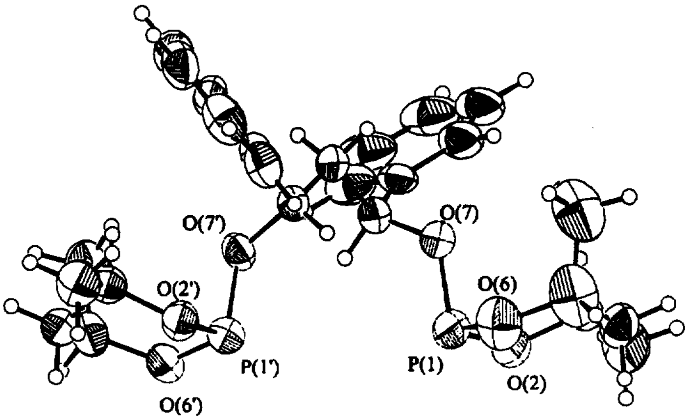


Fig. 2. ORTEP drawing of (1*S*,3*S*)-bis(4*R*,6*R*)-**2**

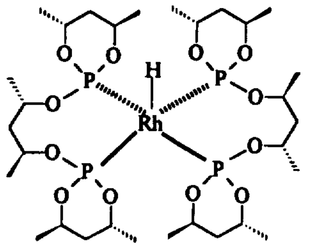


Fig. 3.

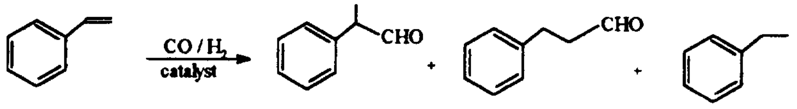
observed for the rest of the $PtCl_2$-complexes. When anhydrous $SnCl_2$ was added to the solution of $PtCl_2$((2*R*,4*R*)-bis(4*R*,6*R*)-**1**), a new complex was formed. The ^{31}P NMR spectrum of this complex showed the presence of two different P-atoms each being coupled by a platinum and a phosphorous atom (δ 73.7 ppm (J_{Pt-P}=5710 Hz), 85.8 ppm (J_{Pt-P}=5126 Hz), J_{P-P}=23 Hz). Accordingly, the complex was assigned to the structure of $Pt(SnCl_3)Cl$((2*R*,4*R*)-bis(4*R*,6*R*)-**1**). When 2 equiv. of $SnCl_2$ (per Pt) were added, the phosphorus atoms became equivalent again giving rise to a new complex, $Pt(SnCl_3)_2$((2*R*,4*R*)-bis(4*R*,6*R*)-**1**) which showed the ^{31}P resonance at 86.9 ppm with J_{Pt-P}=4000 Hz.

The treatment of an excess amount of (2*R*,4*R*)-bis(4*R*,6*R*)-**1** with $Rh(CO)_2(acac)$ (P/Rh=4.04) in $CDCl_3$ under CO/H_2 atmosphere resulted in the formation of only one complex. This complex gave a doublet ^{31}P resonance at 163.4 ppm, (J_{Rh-P}=217.2 Hz, coordination shift 31.1 ppm). In the ^1H NMR spectrum a doublet of quintet resonance is found at the hydride region at δ −11.22 ppm (J_{Rh-H} 10.6 Hz, J_{P-H} 38.8 Hz).

The IR spectrum showed a significant ν(Rh–H) hydride band at 2246 cm^{-1} without any detectable carbonyl bands. It was concluded from these results that in the presence of excess phosphite under 1 atm of CO and H_2 atmosphere, the concentration of the Rh–carbonyl species is very low due to the easy displacement of CO by the ligand to give a tetragonal pyramidal $HRh(PP)_2$ complex (Fig. 3).

The pure diastereomers of compound **1** and **2** have been tested both in the Pt- and Rh-catalysed asymmetric hydroformylation of styrene (Table 1). The catalyst solutions for the hydroformylation experiments were prepared in situ by simply mixing $PtCl_2(PhCN)_2$ in toluene or $Rh(CO)_2(acac)$ in benzene with the ligands (**1**–**2**). With the platinum precursor, anhydrous $SnCl_2$ was used as cocatalyst, which is essential for catalytic activity. In the case of rhodium systems, an excess amount of diphosphite ligand was always added to the catalyst precursor to exclude the formation of $HRh(CO)_4$, which is an

Table 1
Hydroformylation of styrene with chiral Pt and Rh diphosphite catalysts[a]



3 **4** **5**

Entry	Ligand	t/h	T/°C	Conv. (%)[b]	5 (%)[b]	(b/n)[b]	ee of 3 (%)[c]	Config.[d]
1	(2R,4R)-bis(4R,6R)-**1**[e]	24	60	72	16	71/29	40	(S)
2	(2R,4R)-bis(4R,6R)-**1**[e]	18	100	56	25	71/29	12	(S)
3	(2S,4S)-bis(4R,6R)-**1**[e]	22	60	100	15	71/29	26	(R)
4	(1S,3S)-bis(4R,6R)-**2**[e]	116	25	62	34	76/24	35	(S)
5	(1S,3S)-bis(4R,6R)-**2**[e]	19	60	49	42	76/24	18	(S)
6	(1S,3S)-bis(4S,6S)-**2**[e]	26	60	80	40	70/30	12	(S)
7	(2R,4R)-bis(4R,6R)-**1**[f]	73	24	10	0	87/13	17	(R)
8	(2R,4R)-bis(4R,6R)-**1**[f]	5	60	69	0	83/17	15	(R)
9	(2S,4S)-bis(4R,6R)-**1**[f]	24	60	65	0	83/17	1	(R)
10	(1S,3S)-bis(4S,6S)-**2**[f]	19	60	14	0	83/17	5	(R)
11	(1S,3S)-bis(4R,6R)-**2**[f]	42	60	8	0	85/15	2	(S)

[a] Reactions were carried out in 20 ml stainless-steel autoclave under an atmosphere of H_2 and CO (1:1) at 100 atm initial total pressure. [b] Conversions and composition of the reaction mixture (b:l:h branched:linear:hydrogenated) were determined by GC (SPB-1) using decane as an internal standard. [c] Determined by GC analysis (β-DEX, 30 m, id 0.25 mm) of the corresponding acid. [d] Determined by the sign of optical rotation of the corresponding aldehyde. [e] Catalyst: $Pt(PhCN)_2Cl_2$-$SnCl_2$-L, solvent: toluene, substr/catalyst molar ratio is 2000. [f] Catalyst: $Rh(CO)_2(acac)$, solvent: benzene, substr/catalyst molar ratio is 2000.

active achiral hydroformylation catalyst.[12] The catalytic reactions were carried out under the conditions shown in Table 1.

The hydroformylation results show that in the platinum-catalysed asymmetric hydroformylation the enantioselection is dictated by the stereogenic centres located in the bridging backbone. In the case of (2*R*,4*R*)-bis(4*R*,6*R*)-**1** and (1*S*,3*S*)-bis(4*R*,6*R*)-**2** (matched constellations), there is a co-operative effect of the chiral elements of the bridge and the ones of the dioxaphosphorinane ring. Diastereomers afforded the opposite prevailing enantiomers in the product when the configuration of the stereogenic centres on the backbone linking the two P atoms are changed [40% (*S*) vs. 26% (*R*) in the case of **1** and 18% (*S*) vs.

12% (*R*) in case of **2**]. Diastereomers differing in the configuration of the terminal groups afforded the same prevailing enantiomer in the product in both cases (see entry 5 vs. 6).

The fact that **2** gave higher hydrogenation activity than **1** points, probably, to the larger π-acceptor strength of **2**. No significant differences in regioselectivities were noted between diastereomers. Both diastereomers of **1** and **2** afforded higher enantioselectivity in combination with platinum than with rhodium, but the rhodium system gave higher chemo- and regioselectivity. With the rhodium system, ethylbenzene, the hydrogenated product of styrene was not detected.

3. Conclusion

The bisphosphite diastereomers of **1–2** in Pt- and Rh-complexes are both active catalysts for the asymmetric hydroformylation of styrene, albeit with moderate enantioselectivity. These model ligands are unique in the sense that they contain stereogenic centres both in the bridge and the terminal groups. Thus the notion of chiral cooperativity could be conveniently studied. The highest enantioselectivity (40%) has been obtained with the platinum(II)–$SnCl_2$ catalytic system associated with (2*R*,4*R*)-bis(4*R*,6*R*)-**1**, which is attributed to a positive chiral cooperation effect. Since the latter ligand contains no aryl groups, the extent of enantiodiscrimination is rather remarkable.

4. Experimental

4.1. General information

All reactions were carried out in oven-dried glassware using standard Schlenk techniques under an atmosphere of argon. Benzene and toluene were distilled from sodium/benzophenone. Triethylamine and dichloromethane were distilled from CaH_2 and stored under an atmosphere of argon. Infrared (IR) spectra were recorded on a Specord IR-75A spectrometer. ^{31}P (121.421 MHz), ^{13}C (75 MHz) and ^{1}H (300 MHz) NMR spectra were obtained on a Varian Unity instrument. Optical rotations were measured on a Schmidt Haensch 21245 polarimeter. Gas chromatographic analyses were run on a Hewlett Packard 5830A gas chromatograph (SPB-1 30 m column, film thickness 0.1 μm, carrier gas 2 ml/min). Gas and mass spectroscopy analyses were carried out on a Hewlett Packard 5980 II gas chromatograph (ULTRA-2 25 m column, film thickness 0.3 μm, carrier gas helium) and a 5971 A mass spectrometer (70 eV), respectively.

4.2. Catalysis

In a typical experiment, the autoclave was filled with the solvent, olefin and catalyst precursor. It was then purged with syngas ($CO:H_2=1:1$) and pressurised to the appropriate initial pressure with gas mixture. At the end of the reaction the autoclave was cooled and depressurised. The reaction mixture was directly vacuum distilled to remove the catalyst. The reaction mixture and the distilled products were analysed by gas chromatography. The enantiomeric excess was determined by measuring the optical rotation of the aldehyde[13] and by GC analysis of the corresponding acid (β-DEX, 30 m, id 0.25 mm).

4.3. Materials and methods

Enantiomerically pure 2,4-pentanediols or 1,3-diphenylpropane-1,3-diols were synthesised by asymmetric hydrogenation of 2,4-pentanedione or dibenzoylmethane, respectively, over a Raney nickel catalyst modified with the corresponding enantiomer of tartaric acid and NaBr (TA–NaBr–MRNi).[14,15] (4*R*,6*R*)- and (2*S*,4*S*)-4,6-Dimethyl-2-chloro-1,3,2-dioxaphosphorinane[8] were prepared as follows. A 500 ml three-necked, round-bottomed flask equipped with a dropping funnel was filled with homochiral 2,4-pentanediol (61.5 mmol, 6.4 g) in 200 ml of ether and 17.7 ml (123 mmol) of triethylamine. PCl_3 (5.36 ml, 75 mmol) was dissolved in 50 ml of ether and added dropwise to the solution of 2,3-pentanediol at −20°C. The amine-salt was then filtered off and the solvent was removed under reduced pressure. The obtained crude product was purified by vacuum distillation (111°C/20 mmHg) to yield 9.1 g of colourless liquid (85%). The bis[(4,6)-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]alkane derivatives were prepared by a method described previously.[6]

4.4. Analytical data

4.4.1. *(2R,4R)-2,4-Bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]-pentane, (2R,4R)-bis(4R,6R)-1*[6]

$[\alpha]_D^{20}$ +71.3 (c 1.15, CH_2Cl_2).

4.4.2. *(2R,4R)-2,4-Bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]pentane borane adduct*

Anal. calcd for $C_{15}H_{36}B_2O_6P_2$: C, 45.47; H, 9.09. Found: C, 45.76; H, 9.10.

4.4.3. *(2S,4S)-2,4-Bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]pentane, (2S,4S)-bis(4R,6R)-1*

$[\alpha]_D^{20}$ +97.9 (c 0.735, CH_2Cl_2), bp 138–142/1 mm. ^{31}P NMR ($CDCl_3$) δ 131.9 ppm. ^{1}H NMR ($CDCl_3$): δ 1.23 (d, $^3J_{HH}$=6.4 Hz, 3H, eq.), 1.29 (d, $^3J_{HH}$=6.2 Hz, 3H), 1.44 (d, $^3J_{HH}$=6.8 Hz, 3H, ax.), 1.7 (m, 2H), 1.96 (m, 2H), 4.3 (m, 1H, ax.), 4.3 (m, 1H), 4.5 (m, 1H, eq.). ^{13}C NMR ($CDCl_3$) δ 23.0, 23.1 (d, $^3J_{POCC}$=2.1 Hz), 22.6 (d, $^3J_{POCC}$=1.7 Hz), 39.8 (d, $^3J_{POCC}$=7.4 Hz), 47.7 (t, $^3J_{POCC}$=5.2 Hz), 60.5, 66.8 (d, $^2J_{POC}$=19 Hz), 68.1. MS m/z 368 (0.29%, M^+); 367 (0.39%, M^+-1); 299 (13.8%, $M^+-C_5H_{10}$); 267 (10.2%, $M^+-C_5H_{10}O_2{}^+$); 133 (76.2%, $C_5H_{10}O_2P^+$); 69 (100%, C_5H_{10}).

4.4.4. *(1S,3S)-1,3-Diphenyl-1,3-bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]propane, (1S,3S)-bis(4R,6R)-2*[6]

$[\alpha]_D^{20}$ +121.0 (c 1.255, C_6H_6).

4.4.5. *(1S,3S)-1,3-Diphenyl-1,3-bis[(4S,6S)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]propane (1S,3S)-bis(4S,6S)-2*

$[\alpha]_D^{20}$ −75 (c 12, CH_2Cl_2). ^{31}P NMR ($CDCl_3$) δ 132.3. ^{1}H NMR ($CDCl_3$): δ 1.2 (d, $^3J_{HH}$=6 Hz, 3H, eq.), 1.25 (d, $^3J_{HH}$=6.8 Hz, 3H, ax.), 1.6 (m, 2H), 2.2 (t, $^3J_{HH}$=6.8 Hz, 2H), 4.6 (m, 1H, ax.), 4.55 (m, 1H), 5.1 (m, 1H), 7.2 (m, 10H-aromatic). ^{13}C NMR ($CDCl_3$) δ 22.8, 22.7, 39.3 (d, $^3J_{POCC}$=4.1 Hz), 48.3 (t, $^3J_{POCC}$=4.1 Hz) 62.1 (d, $^2J_{POC}$=1.95 Hz), 72.8 (d, $^2J_{POC}$=22.5 Hz), 68.2 (d, $^2J_{POC}$=6.5 Hz), 126–128 (m, Ph). Anal. calcd for $C_{25}H_{34}O_6P_2$: C, 60.69; H, 6.91. Found: C, 60.49; H, 6.97.

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11. Crystal data for (1*S*,3*S*)-bis(4*R*,6*R*)-**2**: $C_{25}H_{34}O_6P_2$, M=492.46, orthorhombic, space group $P2_12_12_1$, a=11.393(1), b=12.375(1), c=20.590(1) Å, U=2647.9(4) Å^3, Z=4, D_c=1.235 g cm^{-3}, μ=1.791 mm^{-1}, $F(000)$=1048. Reflections measured=2600 (1373 with $I \geq 2\sigma(I)$, 302 refined parameters). Final R values: $R1$=0.0402 and R_w2=0.0866 (observed), $R1$=0.0644 and R_w2=0.0908 (all data); absolute structure parameter=−0.007(35). Full structural details have been deposited at the Cambridge Crystallographic Centre.
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