ELSEVIER

Journal of Organometallic Chemistry 624 (2001) 162–166

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Chiral 1,2-bis(phosphetano)ethanes

Angela Marinetti [a,*], Sébastien Jus [a], Jean-Pierre Genêt [a], Louis Ricard [b]

[a] *Laboratoire de Synthèse Sélective Organique et Produits Naturels, ENSCP 11, rue Pierre et Marie Curie, F 75231 Paris Cedex 05, France*
[b] *Laboratoire Hétéroéléments et Coordination, Ecole Polytechnique, F 91128 Palaiseau Cedex, France*

Received 9 October 2000; accepted 15 November 2000

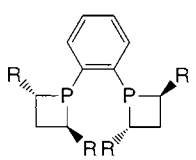
Abstract

Optically pure 1,2-bis(phosphetano)ethanes **3** (BPE-4) have been prepared from 1,2-bis(phosphino)ethane and the cyclic sulfates of symmetrical *anti*-1,3-diols. Diphosphine **3c** (R = cyclohexyl) is an easily accessible, air-stable chiral ligand. Its suitability to the ruthenium-catalysed hydrogenation of functionalised ketones has been examined by using several catalyst precursors. Significant enantiomeric excesses were obtained. A ruthenium complex containing two coordinated diphosphines **3c** was characterised by X-ray diffraction studies. © 2001 Elsevier Science B.V. All rights reserved.

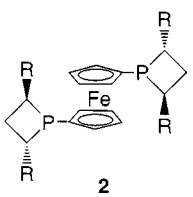
Keywords: Phosphetanes; Asymmetric hydrogenation; Ruthenium

1. Introduction

C_2-Symmetric bidentate ligands bearing phosphetane units are currently outlined as a new class of chiral auxiliaries for asymmetric catalysis. Notably, optically pure 1,2-bis(phosphetano)benzenes, **1** (CnrPHOS) [1] and 1,1′-bis(phosphetano)ferrocenes, **2** [2], are easily accessible ligands which display significant enantioselectivity in ruthenium and rhodium-catalysed hydrogenations, respectively. Albeit the search for their catalytic applications is at an early stage, their high potential cannot be denied in view of the reported preliminary results of catalytic tests [1,2].



1



2

Clearly, the design of phosphetanes **1** and **2** has been drawn by their structural analogy to the well-known, phospholane-based DuPHOS [3] and bis(phospholano)ferrocene ligands [4]. The very restricted information available to date on phosphetanes as catalytic auxiliaries does not allow exhaustive comparison between the two classes of ligands. However, it appears that the presence of the four-membered phosphetane ring in diphosphines **1** and **2** brings about peculiar properties and specific application fields with respect to the analogous phospholane derivatives. Thus, for instance, ligands **2** display better enantioselectivities than the corresponding phospholanes in rhodium-catalysed hydrogenations of itaconic acid derivatives. By contrast, DuPHOS ligands perform better than the corresponding phosphetanes in the rhodium-catalysed hydrogenation of the few model dehydroaminoacid derivatives tested to date. In this reaction, however, an intriguing behaviour of phosphetane-based ligands has been observed [5] when either the 1,2-bis(phosphetano)benzenes **1** or the l,2-bis(phosphetano)ethanes **3** are used as chiral auxiliaries: an unusual, strong increase of the enantioselectivity at higher hydrogen pressure is noticed. Mechanistic implications are currently under study in our group.

The origin of the divergent behaviours of phosphetanes and phospholanes with overall similar structures, should be related to restricted flexibility, specific geometrical features and electronic effects of the constrained four-membered ring. Full rational is not yet available. However, it appears that chiral phosphetanes are interesting targets for both applied purposes and fundamental studies. In this context, we wish to present herein a new family of phosphetane ligands, the ethyli-

* Corresponding author.

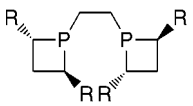
PII: S0022-328X(00)00910-4

Table 1
Hydrogenation reactions promoted by ruthenium–**3c** complexes [a]

Entry	Ru-catalyst	Substrate	Conditions	e.e. (config)
1	$Cl_2Ru(PPh_3)_3$	$MeCOCH_2CO_2Me$	50 bars, 80°C	15(*S*) [b]
2	(COD)Ru(2-Me-allyl)$_2$ + 2HBr		80 bars, 80°C	87(*R*)
3	$[(C_6H_6)RuCl_2]_2$		10 bars, 80°C	91(*R*)
4	$[(C_6H_6)RuCl_2]_2$ + HCl		10bars, 80°C	73(*R*)
5	$[(C_6H_6)RuCl_2]_2 + NH_4PF_6$		10 bars, 80°C	92(*R*)
6	(COD)Ru(2-Me-allyl)$_2$ + 2HBr	$EtCOCH_2CO_2Et$	80 bars, 80°C	91(*R*) [b]
7	$[(C_6H_6)RuCl_2]_2$		10 bars, 80°C	90(*R*)
8	(COD)Ru(2-Me-allyl)$_2$ + 2HBr	$PhCOCH_2CO_2Et$	80 bars, 80°C	80(*S*) [b]
9	$[(C_6H_6)RuCl_2]_2$		10 bars, 80°C	90(*S*)
10	(COD)Ru(2-Me-allyl)$_2$ + 2HBr	$iPrCOCH_2CO_2Et$	80 bars, 80°C	95(*S*) [b]
11	$[(C_6H_6)RuCl_2]_2 + NH_4PF_6$		10 bars, 80°C	92(*S*)
12	(COD)Ru(2-Me-allyl)$_2$ + 2HBr	$MeCOCH_2COMe$	80 bars, 80°C	98(*R,R*) [c]

[a] Conditions: 1 mmol substrate, solvent MeOH or EtOH (1.5 ml), catalysts formed in situ from ruthenium complexes (1% molar amount) and ligand **3c** (Cy-BPE-4) (1:1 ratio to Ru). Reaction times of 20 h (non-optimised) led to complete conversions.
[b] Enantiomeric excesses were determined by GC on a Lipodex A column.
[c] Diastereomeric excess = 95%; the enantiomeric excess was determined by ^{1}H-NMR or GC analysis of the Mosher diester prepared from the crude diol and (*S*)-MPTA-Cl.

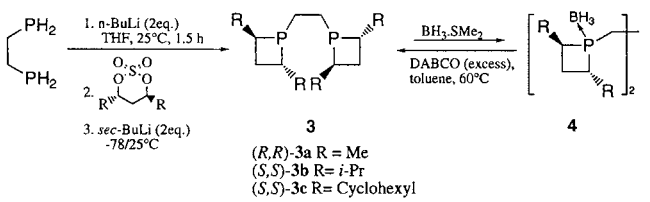
dene bridged [6] l,2-bis(phosphetano)ethanes **3** (BPE-4). The experimental procedure for their synthesis as well as several data on their coordinating properties and catalytic behaviour in ruthenium promoted hydrogenations are reported hereafter.



3

2. Results and discussion

The preparation of the 1,2-bis(phosphetano)ethanes **3** follows the well-established method based on the nucleophilic cyclisation of a lithiated primary phosphine with the cyclic sulfate of an optically pure 1,3-diol. Starting materials are the commercially available 1,2-diphosphinoethane (Strem Chemicals, Inc.) and chiral *anti*-1,3-diols, easily obtained by enantioselective ruthenium-catalysed hydrogenation of the corresponding symmetrical diketones.[1]



(1)

The procedure in Eq. (1) gives access to 1,2-bis(phosphetano)ethanes, symmetrically substituted on the α-carbons, as their air stable borane complexes **4**, in reasonably good yields (40–65%). The best yields are obtained for the cyclohexyl-substituted phosphine. After purification of **4**, the borane protecting group is removed by heating at 60°C for several hours with an excess DABCO. Longer reaction times and harder conditions are needed for the decomplexation of **3** compared to the analogous reactions on the bis(phosphetano)benzenes **1**, owing probably to their higher basicity. The l,2-bis(2,4-dimethylphosphetano)ethane **3a** (Me-BPE-4) is an extremely air sensitive compound. It has been characterised only by ^{1}H- and ^{31}P-NMR spectroscopy in the crude reaction mixture of the deboronation reaction. The sterically hindered phosphines **3b** (*i*-Pr-BPE-4) and **3c** are less sensitive compounds that can be purified by column chromatography. Phosphetane **3c** (Cy-BPE-4) can be handled in air in the solid state, and oxidises very slowly in solution. It is then a well-suited representative substrate for initial studies on the coordination chemistry and catalytic behaviour of the new diphosphines **3**.

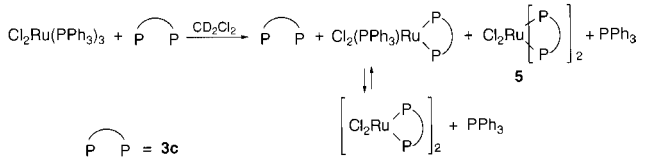
Phosphetane **3c** has been evaluated in the ruthenium-catalysed hydrogenations of model β-ketoesters and 1,3-diketones, as shown in Table 1. Several catalyst precursors have been tested in the hydrogenation of methyl acetoacetate (entries 1–5): the catalyst formed in situ from (COD)Ru(2-Me-allyl)$_2$ and ligand **3c** by addition of two equivalents of HBr (entry 2) [7] gave complete conversion and high enantiomeric excesses when the reaction was performed in hard conditions (80 bars, 80°C, 20 h). Under milder conditions both conversions and e.e. decreased significantly, and somewhat inconsistent results were obtained.

With the catalyst formed by mixing $Cl_2Ru(PPh_3)_3$ and ligand **3c**, according to the procedure already suc-

[1] See Ref. [1b] and references therein.

cessfully applied to the reduction of β-dicarbonyls [8], the hydroxybutanoate was obtained in very low e.e., with the *S*-configurated product as the major enantiomer (entry 1). The highest catalytic activities, associated with high enantioselectivity, were attained by using $[(benzene)RuCl_2]_2$ as the catalyst precursor [9]. Neither acid additives (the beneficial effect of acid additives in analogous hydrogenations has been reported in Ref. [10]) (aq. HCl, entry 4), nor addition of NH_4PF_6 (counter-ion exchange, entry 5) did not improve substantially the catalytic properties. The few hydrogenations of other β-ketoesters and 1,3-diketones (entries 6–12), which have been tested to date, show analogous trends and high enantioselectivities.

The catalyst precursors formed from the three ruthenium complexes above and ligand **3c**, have been examined by ^{31}P-NMR spectroscopy. A 1:1 mixture of $RuCl_2(PPh_3)_3$ and phosphetane **3c** in CD_2Cl_2 after 2 h at room temperature, shows the presence of a large amount (50%) of free **3c** and three ruthenium complexes.



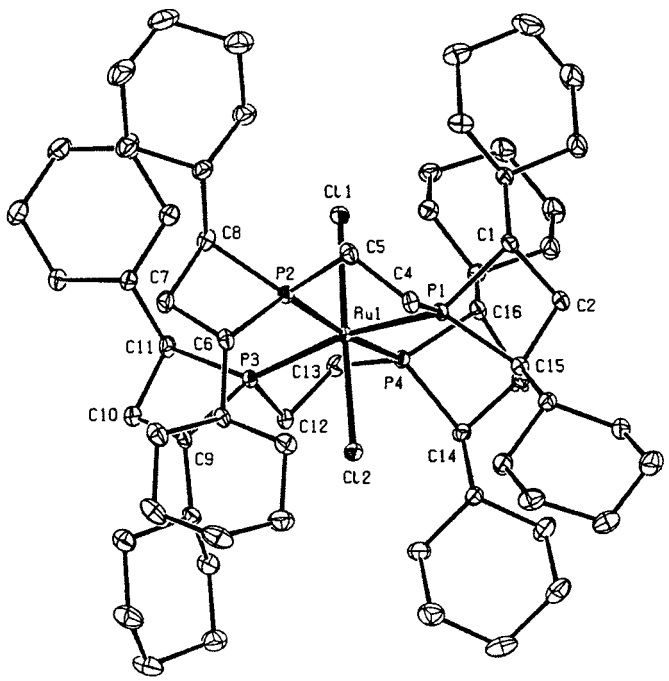


Fig. 1. ORTEP drawing of the ruthenium complex **5**, $Cl_2Ru(\mathbf{3c})_2$. Selected bond distances: Ru–P(1) 2.3443(7), Ru–P(2) 2.3522(8), Ru–Cl(1) 2.4325(6), P(1)–C(1) 1.889(3), C(1)–C(2) 1.540(4), C(2)–C(3) 1.559(4), P(1)–C(3) 1.867(3), P(1)–C(4) 1.852(3), C(4)–C(5) 1.529(4). Selected bond angles: C(1)–P(1)–C(3) 77.8(1), C(1)–P(1)–C(4) 102.7(1), C(3)–P(1)–C(4) 110.8(1), C(4)–P(1)–Ru 107.1(1), P(1)–Ru–P(2) 83.11(3), P(1)–Ru–P(4) 97.31(3).

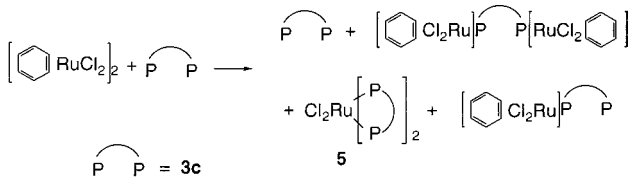
One of them displays an ABC spectrum at δ 128.2 (dd, $J = 11$ and 27 Hz), 115.2 (dd, $J = 11$ and 32 Hz), 42.9 (dd, $J = 27$ and 32 Hz), which suggests coordination of **3c** and triphenylphosphine to the same ruthenium centre. However, the ^{31}P-NMR spectrum is not fully consistent with the formation of the expected $Cl_2Ru(PPh_3)(\mathbf{3c})$ complex, which should give a large $^2J_{P-P}$ coupling between PPh_3 and the phosphorus atom of the bidentate ligand which occupies the *trans* coordination site [8], unless the complex adopts an *fac* coordination mode with three *cis* phosphorus atoms. The second complex shows an AB spectrum at $\delta = 50.7$ and 50.0 ppm ($J_{AB} = 39$ Hz) which could be assigned to the dimeric $[(\mathbf{3c})RuCl_2]_2$ complex. A third complex, **5**, is formed ($\delta^{31}P = 86$ ppm) which becomes the main product on heating or when an excess **3c** is added. Complex **5** (*trans*-$Cl_2Ru((S,S)$-$\mathbf{3c})_2$) is a poorly soluble compound which has been isolated by crystallisation and characterised by X-ray diffraction studies. ORTEP drawing of **5** is shown in Fig. 1.

The phosphetane ring is bent, with a flapping angle of 15.2°. The four phosphorus atoms occupy equatorial positions in the distorted octahedral ruthenium complex. The $P(CH_2)_2P$ framework adopts a twist δ conformation which closely resembles that of the ethano bridge in the cationic (COD)Rh((*R,R*)-Me-BPE)$^+SbF_6^-$ complex [3]. The δ conformation minimises sterical interactions by moving the *syn*-cyclohexyl group to an axial position, back away from the ruthenium centre. The observed twist conformation contrasts with the geometry of the analogous chiral ruthenium–chiraphos and ruthenium–bnpe complexes [11] in which the chelate rings adopt envelope conformation in the solid state (conformational mobility is expected to be facile in solution). The envelope conformation induces loss of the C_2 symmetric arrangement of the phenyl rings of the chiraphos and bnpe ligands, giving a nearly centrosymmetric molecule, while the twist conformation of complex **5** retains the C_2 symmetry of the molecule. The isolated complex **5** is catalytically inactive in the hydrogenation of methyl acetoacetate at 10 bars, 80°C.

^{31}P-NMR analysis of the catalyst formed in situ from $(COD)Ru(2\text{-Me-allyl})_2$ and **3c** by addition of HBr (Table 1, entry 2), shows formation of a major component with $\delta^{31}P$ at 82 ppm. This sparingly soluble complex can be isolated by precipitation from acetone–ether mixtures. Analytical data for this compound suggest formation of the $Br_2Ru(\mathbf{3c})_2$ complex, the bromo-analogue of **5**. This complex is also catalytically inactive in the reduction of β-ketoesters. Thus, it seems that the observed catalytic activity comes from minor components of the mixture which cannot be detected by ^{31}P-NMR.[2] This could explain the low and somewhat erratic catalytic activity.

[2] Alternatively, the catalytically active species could be formed under the hydrogenation conditions, upon heating the mixture at 80°C.

Finally, the catalyst precursor used in entry 3 of Table 1 was checked by ^{31}P-NMR. The reaction between **3c** and the dimeric [(benzene)$RuCl_2$)]$_2$ complex at room temperature is slow.



After 3 h some free ligands are still present, together with equal amounts of the Cl_2Ru(**3c**)$_2$ complex **5** and two other species whose structures are tentatively assigned as the non-chelated complexes (benzene)$RuCl_2$(**3c**) (δ^{31}P at 68.7 and 23.7 ppm, $J_{P-P} = 27$ Hz) and [(benzene)$RuCl_2$]$_2$(**3c**) ($\delta^{31}P = 66.2$ ppm). Addition of NH_4PF_6, which should favour cationic chelated species through Cl^-/PF_6^- exchange, did not change the product ratios in the reaction mixture significantly.

In summary, the NMR data above point out that any of the catalyst precursors examined to date afford a single, catalytically active ruthenium complex. Diphosphine **3c** displays a slow complexation rate as well as propensity to form the dihalide complexes X_2Ru(**3c**)$_2$ (X = halide). From previous studies [11] it appears that dihalide-bis-phosphine ruthenium complexes analogous to **5** are especially favoured in the case of diphosphines giving five-membered chelate rings, while they cannot be prepared with, for instance, Josiphos or Binap ligands which form six- and seven-membered chelate rings, respectively. The main drawback of the easy formation of **5** is a consequent decrease of the catalytic activity. Thus, albeit the enantiomeric excesses obtained, for instance, with the [(benzene)$RuCl_2$]$_2$ precursor are rather satisfying, we guess that the catalytic performances of the 1,2-bis(phosphetano)ethanes **3** could be improved by the choice of a more suitable catalyst precursor. Further studies are in progress.

3. Experimental section

All reactions were performed under argon in dry solvents. NMR spectra were recorded either on a Bruker AM 200 (at 200.13 MHz for ^{1}H and 50.32 MHz for ^{31}P) or on a Bruker 400 (at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C and 161.97 MHz for ^{31}P) spectrometers.

(*S*,*S*)-2,4-Pentanediol, (*R*,*R*)-2,6-dimethyl-3,5-heptanediol and (*R*,*R*)-1,3-dicyclohexyl-1,3-propanediol have been prepared via ruthenium/(*S*)-MeO-Biphep-catalysed hydrogenations of 2,4-pentanedione, 2,6-dimethyl-3,5-heptanedione and 1,3-dicyclohexyl-1,3-propanedione, respectively, according to the published procedure [1b]. The cyclic sulfates have been prepared according to Ref. [1b].

3.1. Synthesis of the 1,2-bis(phosphetano)ethane bis-borane complexes **4**

The synthesis of **4c** is given hereafter as a representative example.

A solution of l,2-bis(phosphino)ethane (0.30 g, 3.2 mmol) in THF (40 ml) was cooled to −78°C and *n*-BuLi (2.4 M solution in hexane, 2.8 ml, 6.7 mmol.) was added. After warming to room temperature, the yellow solution was stirred for 1.5 h and added then to a solution of (*R*,*R*)-l,3-dicyclohexyl-l,3-propanediol cyclic sulfate (2.0 g, 6.6 mmol) in THF (200 ml) at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for about 1 h. After cooling to −78°C, *s*-BuLi (1.3 M solution, 5.2 ml, 6.7 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 3 h. Then, $BH_3{\cdot}SMe_2$ complex (1 ml, 10 mmol) was added. After hydrolysis, the crude mixture was concentrated under vacuum. Ether was added, the organic phase was washed with water and dried over $MgSO_4$. The colourless solution was evaporated and the residue chromatographed on alumina with cyclohexane–ether 98:2 as eluent. The 1,2-bis((*S*,*S*)-2,4-dicyclohexylphosphetano)ethane bis(borane) complex was obtained as a colourless solid (1.1 g, 65% yield) and recrystallised from an ether–pentane mixture. ^{31}P-NMR (C_6D_6) δ 57.7; ^{13}C-NMR (C_6D) δ 17.4 (pseudo-t, PCH_2), 25.8, 25.9, 26.2, 26.3, 26.4, 26.6 (CH_2), 28.6 (pseudo-t, CH_2), 30.5 (pseudo-t, CH_2), 31.0 (pseudo-t, CH_2), 32.6 (CH_2), 33.3 (CH_2), 38.2 (CH), 38.6 (d, $^1J_{C-P} = 36.1$ Hz, CH), 39.0 (t, $J_{C-P} = 2.6$ Hz, CH), 39.5 (d, $^1J_{C-P} = 38.0$ Hz, CH) ppm. Mass spectrum (EI): *m*/*e* 529 ($M^+ - H$, 40%), 516 ($M^+ - BH_3$, 40%), 310 (85%), 82 (100%). $[\alpha]_D = +39$ ($c = 0.5$, CH_2Cl_2). Anal. Calc. for $C_{32}H_{62}B_2P_2$: C, 72.46; H, 11.78. Found, C, 72.55; H, 11.86.

Following the same procedure, the 1,2-bis-((*S*,*S*)-2,4-diisopropylphosphetano)ethane borane complex **4b** was obtained as a colourless solid (0.25 g, 31% yield) and recrystallised from an ether–pentane mixture. ^{31}P-NMR (C_6D_6) δ 56.6; ^{1}H-NMR (C_6D_6) δ 0.54 (d, $^3J_{H-H} = 6.4$ Hz, 2Me), 0.72 (d, $^3J_{H-H} = 6.5$ Hz, 2Me), 0.88 (d, $^3J_{H-H} = 6.4$ Hz, 2Me), 1.07 (d, $^3J_{H-H} = 6.5$ Hz, 2Me), 1.2–2.5 (m, 16H); ^{13}C-NMR (C_6D_6) δ 17.0 (pseudo-t, PCH_2), 20.0 (pseudo-t, Me), 20.4 (pseudo-t, Me), 22.1 (2Me), 29.1 (CH), 29.5 (CH), 30.0 (pseudo-t, CH_2), 39.7 (d, $^1J_{C-P} = 36.2$ Hz, CH), 40.8 (d, $^1J_{C-P} = 38.1$ Hz, CH) ppm. Mass spectrum (EI): *m*/*e* 342 ($M^+ - 2BH_3$, 5%), 314 (70%), 245 (80%), 190 (100%). $[\alpha]_D = +62$ ($c = 0.5$, CH_2Cl_2). Anal. Calc. for $C_{20}H_{46}B_2P_2$: C, 64.9; H, 12.53. Found, C, 64.79; H, 12.42.

Following the experimental procedure above, the 1,2-bis((*S*,*S*)-2,4-dimethylphosphetano)ethane borane complex **4a** was obtained as a colourless solid (0.26 g, 32% yield) after purification by column chromatography (cyclohexane–ether 90:10 as eluent). Complex **4a** was recrystallised from an ether–pentane mixture. ^{31}P-NMR ($CDCl_3$) δ 57.7 ($J_{P-B} = 47$ Hz); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.24 (dd, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-P} = 15.4$ Hz, 2Me), 1.29 (dd, $^3J_{H-H} = 7.1$ Hz, $^3J_{H-P} = 18.4$ Hz, 2Me), 2.0–2.1 (m, 4H), 2.3 (m, 4H), 2.4–2.5 (m, 2H), 2.6–2.7 (m, 2H); ^{13}C-NMR (100.61 MHz, $CDCl_3$) δ 14.3 (Me), 15.5 (Me), 16.0 (pseudo-t, CH_2), 26.3 (d, $^1J_{C-P} = 38.9$ Hz, CH), 27.0 (d, $^1J_{C-P} = 38.5$ Hz, CH), 35.8 (pseudo-t, CH_2) ppm. Mass spectrum (EI): *m*/*e* 230 ($M^+ - 2BH_3$, 5%), 202 (80%), 160 (100%). $[\alpha]_D = -23$ ($c = 1$, CH_2Cl_2). Anal. Calc. for $C_{12}H_{30}B_2P_2$: C, 55.88; H, 11.72. Found, C, 55.64; H, 11.87.

3.2. Removal of the bis(phosphetano)ethanes *3* from their borane complexes

General procedure. The 1,2-bis(phosphetano)ethane bis(borane) complexes **4b** or **4c** (0.40 mmol) were reacted with 1,4-diazabicyclo[2.2.2]octane (160 mg, 1.4 mmol) in benzene (3 ml) at 60°C for 6 h. The reaction mixture was diluted with benzene (5 ml) and directly chromatographed under argon on a short alumina column with cyclohexane–ether 99:1 as eluent.

1,2-Bis((*S*,*S*)-2,4-diisopropylphosphetano)ethane, **3b**, was obtained in quantitative yield as a colourless oil. ^{31}P-NMR (C_6D_6) δ 22; ^{1}H-NMR (400.13 MHz, C_6D_6) δ 0.71 (d, $^3J_{H-H} = 6.4$ Hz, 2Me), 0.86 (d, $^3J_{H-H} = 6.5$ Hz, 2Me), 0.96 (d, $^3J_{H-H} = 6.5$ Hz, 2Me), 1.15 (d, $^3J_{H-H} = 6.6$ Hz, 2Me), 1.6–2.2 (m, 12H), 2.4–2.5 (m, 2H) 2.6–2.7 (m, 2H); ^{13}C-NMR (100.6 MHz, C_6D_6) δ 18.8 (Me), 19.2 (d $^1J_{C-P} = 10.5$ Hz, PCH_2), 19.9 (Me), 20.2 (Me), 20.4 (t, $J_{C-P} = 5.8$ Hz, Me), 29.4 (CH), 30.4 (t, $J_{C-P} = 8.0$ Hz, CH), 33.2 (CH_2), 34.6 (CH), 36.2 (CH) ppm.

1,2-Bis((*S*,*S*)-2,4-dicyclohexylphosphetano)ethane, **3c**, was obtained in 87% yield as a colourless solid. ^{31}P-NMR (C_6D_6) δ 23.3; ^{13}C-NMR (62.9 MHz, C_6D_6, selected data) δ 20.9 (d, $^1J_{C-P} = 11.0$ Hz, PCH_2), 34.3 (t, $J_{C-P} = 3.3$ Hz, CH), 36.5 (t, $J_{C-P} = 3.7$ Hz, CH), 40.1 (CH), 40.9 (t, $J_{C-P} = 7.5$ Hz, CH) ppm.. Mass spectrum (EI): *m*/*e* 502 (M^+, 5%), 474(10%), 237 ($PC_{15}H_{26}$, 20%), 311(20%), 81 (100%). $[\alpha]_D = +266$ ($c = 0.5$, CH_2Cl_2). Anal. Calc. for $C_{32}H_{56}P_2$: C, 76.45; H, 11.23. Found: C, 76.35; H, 11.37.

1,2-Bis((*R*,*R*)-2,4-dimethylphosphetano)ethane, **3a,** has been displaced from its borane complex by heating with DABCO (two equivalents) for 6 h in C_6D_6. It has been characterised by NMR in the crude mixture: ^{31}P-NMR (C_6D_6) δ 26.3; ^{1}H-NMR (400.13 MHz, C_6D_6) δ 0.96 (t, $^3J = 7.3$ Hz, 2Me), 1.29 (dd, $^3J = 16.5$ and 7.4 Hz, 2Me) ppm.

3.3. Synthesis of the ruthenium complex *5*

Two equivalents of the bis(phosphetano)ethane **3c** (50 mg, 0.1 mmol) were added to a solution of the $Cl_2Ru(PPh_3)_2$ complex (43 mg, 0.05 mmol) in CH_2Cl_2 (1.5 ml) at room temperature. Complex **5** was formed quantitatively after 1 h at room temperature. It was isolated as a yellow solid after addition of pentane to the crude reaction mixture. Complex **5** was characterised by ^{1}H- and ^{31}P-NMR spectroscopy. Its structure was established by X-ray diffraction studies.

References

[1] (a) A. Marinetti, V. Kruger, F.-X. Buzin, Tetrahedron Lett. 38 (1997) 2947. (b) A. Marinetti, J.-P. Genêt, S. Jus, D. Blanc, V. Ratovelomanana-Vidal, Chem. Eur. J. 5 (1999) 1160. (c) A. Marinetti, S. Jus, J.-P. Genêt, L. Ricard, Tetrahedron 56 (2000) 95.

[2] (a) A. Marinetti, F. Labrue, J.-P. Genêt, Synlett (1999) 1975. (b) U. Berens, M.J. Burk, A. Gerlach, W. Hems, Angew. Chem. Int. Ed. Engl. 39 (2000) 1981.

[3] M.J. Burk, J.E. Feaster, W.A. Nugent, R.L. Harlow, J. Am. Chem. Soc. 115 (1993) 10125.

[4] M.J. Burk, M.F. Gross, Tetrahedron Lett. 35 (1994) 9363.

[5] A. Marinetti, S. Jus, J.-P. Genêt, Tetrahedron Lett. 40 (1999) 8365.

[6] Representative examples of chiral diphosphines with ethano bridges connecting two phosphorus atoms are the phospholane-based BPE ligands (see Ref. [4]), the P-chiral DIPAMP (W.S. Knowles, M.J. Sabacky, B.D. Vineyard, D.J. Weinkauff, J. Am. Chem. Soc. 97 (1975) 2567) and bisP* ligands (T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, J. Am. Chem. Soc. 120 (1998) 1635; A.R. Muci, K.R. Campos, D.A. Evans, J. Am. Chem. Soc. 117 (1995) 9075).

[7] (a) J.-P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, L. Bischoff, M.C. Cano De Andrade, S. Darses, C. Galopin, J.A. Laffitte, Tetrahedron: Asymmetry 5 (1994) 675. (b) For a recent review see V. Ratovelomanana-Vidal, J.-P. Genêt, J. Organomet. Chem. 567 (1998) 163.

[8] (a) A. Mezzetti, G. Consiglio, J. Chem. Soc. Chem. Commun. (1991) 1675. (b) A. Mezzetti, A. Tschumper, G. Consiglio, J. Chem. Soc. Dalton Trans. (1995) 49. (c) R.M. Stoop, A. Mezzetti, F. Spindler, Organometallics 17 (1998) 668.

[9] For recent applications of the $[(benzene)RuCl_2]_2$ catalyst precursor see (a) A.E. Sollewijn Gelpke, H. Kooijman, A.L. Spek, H. Hiemstra, Chem. Eur. J. 5 (1999) 2472. (b) M. Kitamura, M. Yoshimura, N. Kanda, R. Noyori, Tetrahedron 55 (1999) 8769. (c) Q.-H. Fan, C.-Y. Ren, C.-H. Yeung, W.-H. Hu, A.S.C. Chan, J. Am. Chem. Soc. 121 (1999) 7407. (d) T. Benincori, E. Cesarotti, O. Piccolo, F. Sannicolò, J. Org. Chem. 65 (2000) 2043.

[10] M. Kitamura, N. Yoshimura, R. Kanda, Noyori, Tetrahedron 55 (1999) 8769.

[11] R.M. Stoop, C. Bauer, P. Setz, M. Wörle, T.Y.H. Wong, A. Mezzetti, Organometallics 18 (1999) 5691.