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Diastereoselective synthesis of α-silylphosphetanes. An approach to monodentate, P–O chelating and *trans*-chelating chiral ligands

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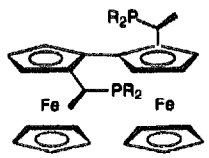
Abstract

Optically pure α-silylphosphetanes have been prepared through stereoselective metallation–silylation reactions of the P-menthylphosphetane oxide **1**. Bridging of two phosphetane units by means of bifunctional chlorosilanes leads to various bidentate ligands and, particularly, to the chiral, *trans*-chelating diphosphine **6b**. Its square planar rhodium complex *trans*-Rh(CO)Cl(**6b**) has been structurally characterized.

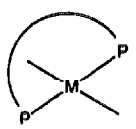
Keywords: Diphosphine; Chirality; Silyl; Rhodium

1. Introduction

Chiral, *cis*-chelating diphosphines are well known as excellent auxiliaries for a variety of catalytic asymmetric reactions. Nevertheless, the design and synthesis of novel chiral phosphines having different structural features, including mixed chelates with P–O [1a], P–N [1b] and P–S [1c] combinations, polydentate [1d] and side-chain functionalized ligands [1d], have played a major role in the recent development of catalytic reactions [1]. Among these, chiral diphosphines which chelate to the central metal in *trans*-fashion have received the attention of Ito and coworkers: a series of 2,2″-bis[1-phosphinoethyl]-1,1″-biferrocenes (TRAPs) [2a] have been prepared and successfully used in rhodium-catalyzed ketone hydrosilylations [2o], olefin hydrogenations [2c] and Michael reactions [2d].



TRAP

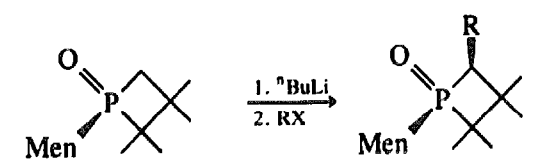


With *trans*-chelating phosphines, a coordination site of the catalytically active species will either be masked or only accessible to very small ligands. Thus, the catalytic properties of their complexes or, at least, their reaction mechanisms and stereoselectivities are expected to be significantly affected. As far as we know, Ito and coworkers' TRAPs are the only chiral *trans*-spanning ligands reported to date [3].

Here we report a new approach to *trans*-chelating diphosphines based on the diastereoselective α-silylation of the optically pure phosphetane oxides **1**.

2. Results and discussion

We have shown previously that both epimers of the phosphetane oxide **1** may be obtained in optically pure form and that substitutions at the intracyclic CH_2 carbon are readily performed through highly selective metallation–alkylation reactions [4]:



(1)

1a, P(R); **1b**, P(S)

Men = l-menthyl

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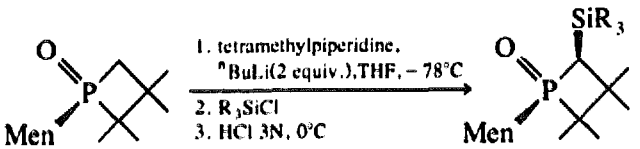
Trans chelating ligands should be accessible via an analogous reaction when a bifunctional alkylating reagent is used to connect two phosphetane units, provided that the bridging chain is sufficiently long to span the central metal atom. For such ligands, it is also desirable that the phosphorus atoms be hindered from taking up mutual *cis*-positions by increasing the sterical requirement of the substituents. In this light, chlorosilyl derivatives of the general formula $ClSiMe_2(CH_2)_n$-$SiMe_2Cl$, with $n \geq 5$ [5], are good starting materials. Thus, we examined the α-silylation reactions of phosphetane oxide **1**, initially towards simple chlorosilanes and then with bis(chlorodimethylsilyl) derivatives.

The phosphetane oxide **1a** (or **1b**) was metallated with ^{n}BuLi at −78 °C and subsequently reacted with various chlorosilanes according to Eq. (2), giving the α-silyl derivatives **2a–f**:



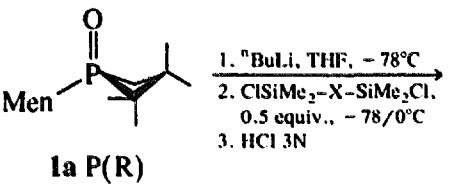
1a, 1b **2a–f** (2)

Entry	Substrate	SiR_3	Product	Yield
1	**1a**	$SiMe_3$	**2a**	76
2	**1b**	$SiMe_3$	**2b**	57
3	**1a**	$SiEt_3$	**2c**	56
4	**1a**	$SiMe_2^iPr$	**2d**	87
5	**1a**	$SiMe_2Ph$	**2e**	83
6	**1a**	$SiMe_2(CH_2)_2Ph$	**2f**	74

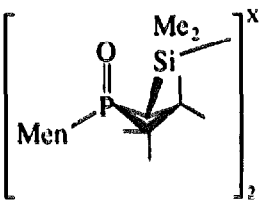
No significant quantities of side products are formed, although some starting material is recovered when the reaction conditions are not optimized. The epimers **1a** P(R) or **1b** P(S) of the phosphetane oxide **1** were used as starting materials in the reaction with trimethylchlorosilane (entries 1, 2); no difference with regard to the reactivity or selectivity was observed.

The main features of these high yielding reactions are their tolerance of some sterical hindrance at silicon (entry 4) and their high diastereoselectivity; a single isomer of each silylated phosphetane oxide **2** was obtained according to ^{31}P NMR analysis of the crude reaction mixture. The SiR_3 group is expected to lie in the equatorial position, *anti* to the menthyl substituent, by analogy to previous results in alkylation reactions [4]. Nevertheless, because the ^2J(H–P) coupling constants of the PC*H*Si hydrogen were significantly larger (ca. 12 Hz) than in analogous α-substituted phosphetane oxides of known *anti* stereochemistry ($J = 5$ to 7 Hz [4]), the carbon configuration could not be unambiguously defined on the basis of the NMR data. A subsequent X-ray crystal structure of a rhodium complex containing a silylated phosphetane (see below) confirmed the assumed stereochemistry. Detailed NMR data for **2d** are given in Table 1. Selected ^{1}H and ^{13}C NMR data for compounds **2a,b,c,e,f** are reported in Tables 2 and 3.

As far as the synthesis of bridged diphosphetanes is concerned, the crucial point is the stereospecificity of reaction (2), regardless of the precise stereochemistry of the final products. Consequently, analogous silylation reactions allow the facile synthesis of optically pure diphosphetane dioxides: the phosphetane oxide **1a** was reacted successively with 1 equivalent of ^{n}BuLi and 0.5 equivalents of a difunctional chlorosilane, e.g. 1,3-dichlorotetramethyldisiloxane, 1,2-bis(chlorodimethylsilyl)ethane or 1,6-bis(chlorodimethylsilyl)hexane, according to Eq. (3), to afford compounds **3a–c** respectively.



1a P(R)



3a–c P(R)C(R) (3)

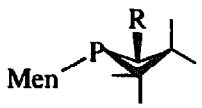
Entry	X	Product	Yield (%)
1	O	**3a**	80
2	CH_2CH_2	**3b**	64
3	$(CH_2)_6$	**3c**	74

A single isomer of each phosphetane oxide was obtained, within the detection limits of our ^{31}P NMR experiments. The stereochemistry was assigned on the basis of the X-ray structure of the rhodium complex given hereafter. Selected NMR data for oxides **3a–c** are presented in Tables 2 and 3.

Eq. (3) represents a convenient method for bridging two phosphetane units via silylated chains of various length. Up to date, three, five and eight atom chains have been incorporated, however, the synthetic approach is likely to have more general applications.

Reduction of the phosphetane oxides **2** and **3** with $HSiCl_3$–Et_3N at room temperature proceeds stereo-

specifically, presumably with retention of the phosphorus configuration [4]. After the usual workup (see Experimental section), the new chiral ligands **4–6** (see below) were obtained.



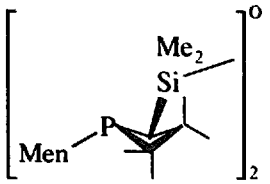
4a, R = $SiMe_3$

4c, R = $SiEt_3$

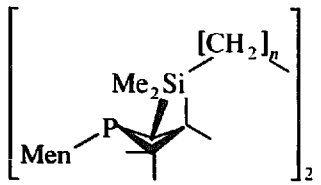
4d, R = $SiMe_2{}^iPr$

4e, R = $SiMe_2Ph$

4f, R = $SiMe_2(CH_2CH_2Ph)$



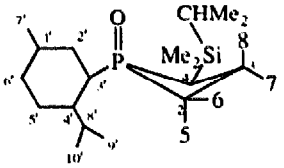
5

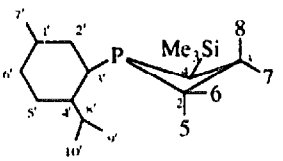


6a, $n = 1$
6b, $n = 3$

Compounds **4–6** have peculiar properties: phosphetanes **4** are electron rich, highly hindered monodentate ligands. Phosphetane **5** is a potentially tridentate species, because the oxygen atom of phosphorus–oxygen ligands is often involved in hemilabile bonds to transition metals [6]. In the case of phosphetanes **5** and

Table 1
^1H and ^{13}C spectral data for compounds **2d** and **4a** [a]





		2d				**4a**			
		$^{13}C(C_6D_6)$		$^1H(C_6D_6)$		$^{13}C(C_6D_6)$		$^1H(C_6D_6)$	
		δ(ppm)	J(C–P)	δ(ppm) [J_{H-H}]	J(H–P)	δ(ppm)	J(C–P)	δ(ppm) [J_{H-H}]	J(H–P)
C	2	50.3	55.0			43.2 *	2.8		
C	3	40.3	15.4			40.6 *	—		
CH	4	40.3	36.5	1.73	12.3	27.8	16.8	1.38	3.6
Me	5	21.6	—	0.91	18.2	22.4	5.7	1.19	4.6
Me	6	18.1	3.2	1.13	16.4	23.8	22.0	1.06	15.4
Me	7	27.6	16.8	0.85	—	27.1	5.9	0.84	—
Me	8	25.6	4.8	1.32	—	25.5	7.7	1.33	—
CH	1′	33.5	12.1			34.0	5.6	°	
CH_2	2′	35.6	—			39.0	5.6	°	
CH	3′	40.1	41.7			35.7	34.4	°	
CH	4′	41.5	3.1			48.8	24.4	°	
CH_2	5′	24.6	10.3			25.3	9.9	°	
CH_2	6′	34.3	—			35.1	—	°	
Me	7′	22.6	—	0.94 [6.1]		22.7	—	0.92 [6.4]	
CH	8′	30.4	3.2			29.8	14.9	1.9 m	
Me	9′	17.4	—	0.77 [6.9]		16.7	—	0.77 [6.8]	
Me	10′	22.2	—	1.08 [6.7]		22.6	—	0.98 [6.8]	
$SiMe_2$		−2.8	—	0.23					
		−2.4	—	0.38					
SiCH*Me*$_2$		17.8	—	0.9–1°					
		18.1	—						
Si*CH*Me$_2$		14.2	4.6						
$SiMe_3$						1.8	2.7	0.19	

[a] ^{13}C NMR assignments for the menthyl moieties have been made by analogy to the reported spectra of menthyldiphenylphosphine and phosphine oxide [7a]. For the phosphetane moiety, data from Refs. [7b,c] have been used. * C(2) and C(3) may be reversed. ° Unresolved. ^1H–^{13}C correlations have been established by 2D spectroscopy.

Table 2
^{31}P and selected ^{1}H NMR data for phosphetane oxides **2** and **3**

Compound	^{31}P	^{1}H					
		Me(5) [a]	Me(6)	Me(7)	Me(8)	PCHSi	SiR_3
2a	68.0	0.90 [18.0]	1.12 [16.4]	0.81	1.38	1.46 [11.8]	0.28 (s, SiMe)
2b	61.8	1.03 [17.2]	1.23 [15.8]	0.95	1.27	1.96 [11.8]	0.29 (s, SiMe)
2c	68.7	°	1.14 [16.4]	0.85	1.33	1.76 [12.5]	1.08° (t, J_{HH} = 6.7, $SiCH_2CH_3$)
2e *	72.7	1.10 [18.6]	1.06 [16.8]	0.87	1.31	2.02 [11.9]	0.51 (s, 6H, $SiMe_2$), 7.2–7.6 (m, SiPh)
2f *	71.7	1.14 [18.5]	1.11 [16.8]	1.04	1.36	1.85 [12.0]	0.22, 0.27 (s, SiMe), 2.6 (m, CH_2Ph), 7.1–7.3 (m, Ph)
3a	65.9	0.94 [17]	1.19 [16.5]	1.00	1.55	1.77 [12.3]	0.49, 0.63 (s, SiMe)
3b *	71.3	1.11 [18.4]	1.07 [16.7]	1.00	1.32	1.81 [11.8]	0.16, 0.18 (s, SiMe)
3c	67.8	0.92 [18.0]	1.15 [16.4]	0.87	1.41	1.61 [12.0]	0.35, 0.37 (s, SiMe)

Solvent C_6D_6 or $CDCl_3$ *. [a] Assignments for methyls 5, 6, 7, 8 have been made on the basis of literature data [7b,c and references cited theirein]. Me(5) and Me(6) may be reversed. ° Unresolved or tentative assignment.

6, *cis*-coordination of the two phosphorus atoms on the same metal should be prevented by sterical hindrance, however, the synthesis of bimetallic complexes or, for **6b**, of *trans*-chelated monometallic compounds, is envisaged.

Phosphetanes **4–6** have been fully characterized by NMR spectroscopy. As an example the principal ^{1}H and ^{13}C NMR data for **4a** are given in Table 1. Assignments have been made on the basis of literature data [7] and confirmed by ^{1}H–^{13}C correlation and DEPT experiments.

In order to check its *trans*-chelating properties, phosphetane **6b** was reacted with $(Rh(CO)_2Cl)_2$ in dilute benzene solution (7×10^{-3} mmol ml^{-1}):

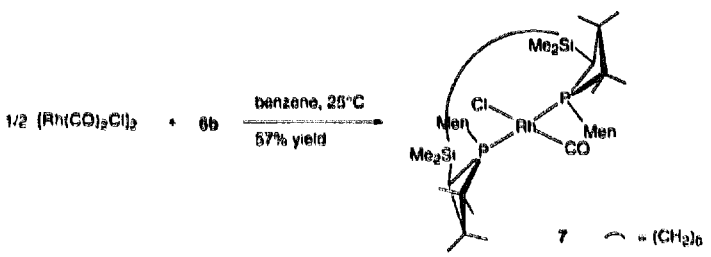


Table 3
Selected ^{13}C NMR data for phosphetane oxides **2** and **3**

Compound	C-2	C-3	CH-4	CH-3'	Me-5'	Me-6'	Me-7	Me-8	SiR_3
2a	50.4 [56.0]	40.7 [15.2]	42.2 [37.6]	40.0 [41.6]	21.6	17.8 [4.5]	27.0 [18.4]	25.7 [2.8]	1.8 [2.7] $SiMe_3$
2b	51.3 [56.3]	40.4 [13.8]	44.7 [‡] [36.0]	46.8 [‡] [39.4]	°	19.7 [4.5]	28.5 [14.3]	25.2 [7.3]	1.4, 1.5 $SiMe_3$
2c	50.3 [55.0]	40.2 [15.1]	39.7 [37.9]	40.2 [42.3]	21.6	18.1 [4.7]	27.7 [16.8]	25.8 [4.7]	5.2 [2.5] $SiCH_2$, 8.1 $SiCH_2Me$
2e *	50.8 [55.2]	40.8 [15.0]	42.0 [37.5]	39.9 [41.7]	21.7	17.6 [4.0]	27.1 [17.5]	25.4 [2.9]	−0.4 [4.0] SiMe, −0.3 SiMe
2f *	50.5 [55.1]	40.4 [14.0]	41.4 [38.1]	39.8 [41.8]	21.8	17.9 [4.0]	27.7 [17.0]	25.6 [4.6]	−0.5 $SiMe_2$, 19.1 $SiCH_2$
3a	50.4 [55.8]	40.3 [15.1]	44.4 [36.9]	40.4 [42.5]	21.6	18.6 [4.2]	27.6 [17.6]	25.6 [3.2]	
3b *	50.3 [55.1]	40.0 [14.1]	41.3 [38.2]	39.6 [41.4]	21.8	17.8 [4.4]	27.5 [17.3]	25.6 [4.2]	−1.3, −1.2 $SiMe_2$, 9.4 [2.7] $SiCH_2$
3c	50.4 [55.4]	40.6 [14]	41.7 [37.6]	40.1 [41.5]	21.7	18.0 [4]	27.4 [18.1]	25.8 [2.9]	−0.1 $SiMe_2$, 17.9 $SiCH_2$

Solvent C_6d_6 or $CDCl_3$ *, ‡ May be reversed. ° Non-assigned. ' May be reversed.

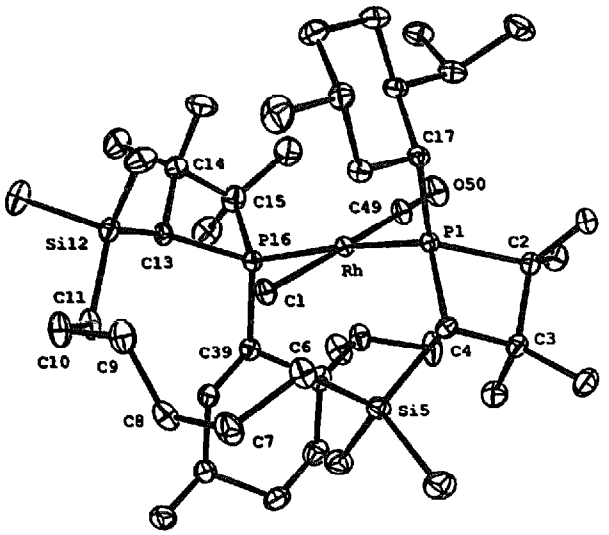


Fig. 1. ORTEP drawing of the rhodium complex 7.

After chromatography on alumina with pentane as eluent, complex **7** was obtained in 57% yield as an air stable, pale yellow solid. Recrystallization from pentane afforded crystals suitable for an X-ray diffraction study, the results of which are given in Fig. 1 (ORTEP plot) and Table 4 (main bond distances and angles).

The X-ray structure of Fig. 1 confirms the assumed stereochemistry of the phosphetane moiety: both the menthyl and the silyl substituents occupy equatorial positions (a relative *anti*-configuration) and the phosphorus atoms show *S*-configuration. In complex **7** the tetracoordinate rhodium atom is planar. The eight-atom chain bridging the phosphetane units lies roughly in the coordination plane and surrounds the chlorine ligand. The whole molecule has C_2 symmetry, where the C_2 axis passes through the linear Cl–Rh–CO framework. The other known complexes of *trans*-chelating chiral ligands (TRAP complexes [8]) adopt a quite different arrangement in the solid state, the phosphorus-bridging chain being almost perpendicular to the coordination plane of the metal.

In summary, this work shows the wide potential of metallation–silylation reactions of phosphetane oxides for the synthesis of new mono- and polydentate chiral ligands. A *trans*-chelating, optically pure phosphine has been prepared and its rhodium complex **7** fully characterized.

The next target will be the use of such complexes or their analogues in appropriate catalytic reactions. Previous work having shown that phosphetanes are more effective ligands for palladium- than for rhodium-catalyzed reactions, the catalytic activity of palladium complexes of **6b** will be targeted initially. In this respect, some exploratory work is needed because *trans*-chelating diphosphines have not yet been used in enantioselective palladium chemistry. Moreover, the eventual use of **6b** in chiral organometallic species displaying Lewis acid-like catalytic activity [9] should be feasible, given the known catalysis of Michael reactions by TRAP–rhodium complexes [2d].

3. Experimental section

All reactions were carried out under argon in dry solvents. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P NMR. Most of the NMR data for the new compounds are given in Tables 1–3; additional selected data are reported in this section. All the chlorosilanes are commercially available.

3.1. General procedure for the synthesis of the phosphetane oxides 2a–f

0.51 g (1.8 mmol) of **1a** (or **1b**) and 0.31 ml (1.8 mmol) of 2,2,6,6-tetramethylpiperidine were dissolved in 25 ml of THF. The reaction mixture was cooled to −78 °C. To this solution were added dropwise 2.4 ml of n-butyllithium (1.6 M in hexane) and, after 15 min, 1 to 3 equivalents of the appropriate chlorosilane. The solution was allowed to warm to room temperature over 2 h. It was then hydrolysed at 0 °C with 3 N HCl (2 ml). THF was removed in vacuo, and after extraction of the residue with ether and drying over $MgSO_4$, the final product was purified by column chromatography on neutral aluminium oxide with hexane–ether (80:20) as eluent.

3.1.1. (P(R),C(R)) 1-menthyl-3,3,4,4-tetramethyl-2-(trimethylsilyl)phosphetane oxide, 2a

0.49 g (76%) of **2a** was recovered as a colorless solid from **1a** and 1 equivalent of Me_3SiCl; m.p. 154 °C. Anal. Found: C, 67.52; H, 11.58. $C_{20}H_{41}POSi$ Calc.: C, 67.36; H, 11.59%. Mass spectrum (C.I.) m/e 357 (M + 1). $[\alpha]_D = -47°$ ($c = 1$, $CHCl_3$).

Table 4
Selected bond angles and distances for complex 7

Distances (Å)		Angles (deg)	
Rh–P1	2.3523(7)	P1–Rh–P16	169.79(2)
Rh–P16	2.3302(8)	C1–Rh–C49	178.8(1)
Rh–C49	1.825(3)	C1–Rh–P1	84.57(3)
Rh–C1	2.3114(7)	C1–Rh–P16	85.33(3)
P1–C2	1.889(3)	P1–Rh–C49	94.5(1)
P1–C4	1.882(3)	P16–Rh–C49	95.6(1)
C2–C3	1.583(4)	C2–P1–C4	77.6(1)
C49–O	1.153(4)	P1–C4–Si5	130.8(2)

3.1.2. (P(S),C(S)) 1-menthyl-3,3,4,4-tetramethyl-2-(trimethylsilyl)phosphetane oxide, 2b

0.36 g (56%) of **2b** was recovered as a colorless solid from **1b** and 1 equivalent of Me_3SiCl; m.p. 122 °C. $[\alpha]_D = -33°$ ($c = 1$, $CHCl_3$).

3.1.3. (P(R),C(R)) 1-menthyl-3,3,4,4-tetramethyl-2-(triethylsilyl)phosphetane oxide, 2c

0.40 g (56%) of **2c** was obtained as a colorless oil from **1a** (1.8 mmol) and Et_3SiCl (5.4 mmol). Mass spectrum (E.I.) m/e 398 (M, 9%), 369 (M–C_2H_5, 29%), 69 (100%). $[\alpha]_D = -45°$ ($c = 1$, $CHCl_3$).

3.1.4. (P(R),C(R)) 1-menthyl-3,3,4,4-tetramethyl-2-(dimethylisopropylsilyl)phosphetane, 2d

0.60 g (87%) of **2d** was obtained as a colorless solid from **1a** (1.8 mmol) and $^iPrMe_2SiCl$ (1.8 mmol); m.p. 94 °C. Anal. Found: C, 68.63; H, 12.02. $C_{22}H_{45}POSi$ Calc.: C, 68.70; H, 11.79%. Mass spectrum m/e 384 (M, 8%), 369 (M–CH_3, 10%), 341 (M–C_3H_7, 100%). $[\alpha]_D = -40°$ ($c = 1$, $CHCl_3$).

3.1.5. (P(R),C(R)) 1-menthyl-3,3,4,4-tetramethyl-2-(dimethylphenylsilyl)phosphetane oxide, 2e

0.63 g (83%) of **2e** was obtained as a colorless solid from **1a** and 1.1 equivalents of $PhMe_2SiCl$; m.p. 156 °C. Anal. Found: C, 72.37; H, 10.52. $C_{25}H_{43}POSi$ Calc.: C, 71.72; H, 10.35%. Mass spectrum m/e 418 (M, 21%), 135 ($PhSiMe_2$, 100%). $[\alpha]_D = -45°$ ($c = 1$, $CHCl_3$).

3.1.6. (P(R),C(R))-1-menthyl-3,3,4,4-tetramethyl-2-(dimethyl(2-phenylethyl)silyl)phosphetane oxide, 2f

0.60 g (74%) of **2f** was recovered as a colorless oil from **1a** and 1.1 equivalents of $Me_2(PhCH_2CH_2)SiCl$. Mass spectrum m/e 446 (M, 32%), 341 (M–CH_2CH_2Ph, 100%).

3.2. General procedure for the synthesis of phosphetane oxides 3a–c

^{n}BuLi (1.20 ml, 1.6 M solution in hexane, 1.9 mmol) was added slowly to a THF solution (25 ml) of **1a** (0.51 g, 1.8 mmol) at −78 °C. After a few minutes, 0.9 mmol of chlorosilane was added. After 1 h at −78 °C, the solution was warmed to 0 °C over a period of 2 h and subsequently hydrolysed with 0.5 ml HCl 3 N. After extraction with ether, the organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by chromatography on a short alumina column with hexane–ether mixtures as eluent.

3a was obtained as a colorless solid from **1a** and 1,3-dichlorotetramethyldisiloxane in 80% yield (0.50 g); m.p. 212 °C. Anal. Found: C, 64.86; H, 10.99. $C_{38}H_{76}O_3P_2Si_2$ Calc.: C, 65.28; H, 10.96%. Mass spectrum m/e 700 (M + 2, 6%), 415 (M–$C_{17}H_{32}PO$, 100%). $[\alpha]_D = -50°$ ($c = 1$, $CHCl_3$).

3b was obtained as a colorless solid from **1a** and 1,2-bis(chlorodimethylsilyl)ethane in 64% yield. Small amounts of side products were observed in the reaction mixture by ^{31}P NMR analysis. Anal. Found: C, 67.59; H, 11.37. $C_{40}H_{80}O_2Si_2P_2$ Calc.: C, 67.55; H, 11.34%. Mass spectrum m/e 710 (M, 3%), 427 (M–$C_{17}H_{32}PO$, 30%), 341 ($C_{19}H_{38}OPSi$, 66%), 284 ($C_{17}H_{33}PO$, 70%), 55 (100%).

3c was obtained from **1a** and 1,6-bis(chlorodimethylsilyl)hexane in 74% yield after chromatography with ether as eluent. Colorless solid; m.p. 160 °C. Anal. Found: C, 68.37; H, 11.50. $C_{44}H_{88}O_2P_2Si_2$ Calc.: C, 68.88; H, 11.56%. Mass spectrum m/e 767 (M + 1, 8%), 483 (M–$C_{17}H_{32}PO$, 100%). $[\alpha]_D = -47°$ ($c = 1$, $CHCl_3$).

3.3. Reduction procedure

The phosphetane oxide **2** or **3** (1 mmol) was dissolved in dry benzene (5 ml) and triethylamine (2 equiv. for each phosphine oxide function to be reduced) was added. The mixture was cooled to 5 °C and trichlorosilane (2 equiv. for each phosphine oxide function) was added. The reaction mixture was stirred at room temperature and monitored by ^{31}P NMR. Reaction times varied between 2 and 5 h. The solution was then cooled to 5 °C and hydrolized with 20% aqueous sodium hydroxide solution. The organic layer was directly chromatographed on a short alumina column with hexane–ether (95:5) as eluent, under argon. All reductions were quantitative and stereospecific according to ^{31}P NMR analysis of the crude reaction mixtures. Yields ranging from 70 to 95% were obtained after chromatography. Phosphetanes **4**, **5** and **6**, which are slightly air sensitive, must be handled under inert atmosphere.

4a Quantitative yield obtained after 3 h at room temperature. Colorless solid; m.p. 79 °C. Mass spectrum m/e 340 (M, 12%), 267 (M–$SiMe_3$, 18%), 212 (MenP=CMe_2, 30%), 73 ($SiMe_3$, 100%). ^{31}P NMR (C_6D_6) δ 28.2 ppm. $[\alpha]_D = -180°$ ($c = 1$, C_6H_6).

4b was formed quantitatively after 3 h at room temperature according to ^{31}P NMR analysis of the reaction mixture. Colorless solid. ^{31}P NMR (C_6D_6) δ 22.6 ppm. ^1H NMR (C_6D_6) δ 0.20 (s, $SiMe_3$), 0.88 (s, Me-7), 1.13 (d, $^3J_{H-P} = 15.6$ Hz, Me-6), 1.29 (d, $^3J_{H-P} = 4.2$ Hz, Me-5), 1.34 (s, Me-8), 1.78 (d, $^2J_{H-P} = 3.3$ Hz, PCHSi) ppm. ^{13}C NMR (C_6D_6) δ 0.96 (d, $^3J_{C-P} = 4.0$ Hz, $SiMe_3$), 21.6 (d, $^2J_{C-P} = 5.2$ Hz, Me-5), 25.1 (d, $^3J_{C-P} = 9.4$ Hz, Me-8), 25.6 (d, $^2J_{C-P} = 23.0$, Me-6), 27.1 (d, $^3J_{C-P} = 5.9$ Hz, Me-7), 29.1 (d, $^1J_{C-P} = 19.6$ Hz, PCHSi), 41.6 (*C*), 44.5 (d, $J_{C-P} = 2.7$ Hz, *C*) ppm. Mass spectrum m/e 340 (M, 5%), 325 (M–Me, 5%), 267 (M–$SiMe_3$, 10%), 212 (MenP=CMe_2, 15%), 73 ($SiMe_3$, 100%).

4c was obtained after 3 h at room temperature. Colorless oil. ^{31}P NMR (C_6D_6) δ 28.9 ppm. ^1H NMR

(C_6D_6) δ 0.97 (s, Me-7), 1.19 (d, $^3J_{H-P}$ = 15.3 Hz, Me-6), 1.29 (d, $^3J_{H-P}$ = 4.5 Hz, Me-5), 1.47 (s, Me-8), 1.71 (d, $^2J_{H-P}$ = 3.2 Hz, PCHSi) ppm. ^{13}C NMR (C_6D_6) δ 5.2 (d, $^3J_{C-P}$ = 2.8 Hz, $SiCH_2$), 7.9 (s, $SiCH_2CH_3$), 22.1 (d, $^2J_{C-P}$ = 4.5 Hz, Me-5), 23.9 (d, $^2J_{C-P}$ = 22.8 Hz, Me-6), 24.4 (d, $^1J_{C-P}$ = 18.3 Hz, PCHSi), 25.7 (d, $^3J_{C-P}$ = 8.9 Hz, Me-8), 27.3 (d, $^3J_{C-P}$ = 6.0 Hz, Me-7), 40.5 (*C*), 43.6 (*C*) ppm. $[\alpha]_D = -123°$ (c = 1, C_6H_6).

4d was obtained in 89% yield after 3 h. Colorless oil. ^{31}P NMR (C_6D_6) δ 28.8 ppm. ^{1}H NMR (C_6D_6) δ 0.14 (s, SiMe), 0.22 (s, SiMe), 0.88 (s, Me-7), 1.19 (d, $^3J_{H-P}$ = 4.7 Hz, Me-5), 1.34 (s, Me-8), 1.57 (d, $^2J_{H-P}$ = 3.3 Hz, PCHSi) ppm. ^{13}C NMR (C_6D_6) δ −3.2 (d, $^3J_{C-P}$ = 5.7 Hz, SiMe), −3.1 (d, $^3J_{C-P}$ = 3.3 Hz, SiMe), 14.0 (d, $^3J_{C-P}$ = 2.9 Hz, $SiCHMe_2$), 22.2 (d, $^2J_{C-P}$ = 5.0 Hz, Me-5), 23.9 (d, $^2J_{C-P}$ = 22.6 Hz, Me-6), 25.7 (d, $^3J_{C-P}$ = 7.7 Hz, Me-8), 25.8 (d, $^1J_{C-P}$ = 18.3, PCHSi), 27.3 (d, $^3J_{C-P}$ = 5.0 Hz, Me-7), 40.5 (s, *C*), 43.6 (s, *C*).

4e Colorless solid; m.p. 79 °C. ^{31}P NMR ($CDCl_3$) δ 29.9 ppm. ^{1}H NMR ($CDCl_3$) δ 0.40 (SiMe), 0.41 (SiMe), 0.76 (s, Me-7), 0.98 (d, $^3J_{H-P}$ = 16.5 Hz, Me-6), 1.21 (d, $^3J_{H-P}$ = 5.0 Hz, Me-5), 1.26 (s, Me-8), 1.71 (d, $^2J_{H-P}$ = 4.3 Hz, PCHSi), 7.2–7.6 (m, Ph) ppm. ^{13}C NMR ($CDCl_3$) δ −1.0 (d, $^3J_{C-P}$ = 3.9 Hz, SiMe), −0.5 (d, $^3J_{C-P}$ = 4.6 Hz, SiMe), 22.0 (d, $^2J_{C-P}$ = 5.1 Hz, Me-5), 23.6 (d, $^2J_{C-P}$ = 21.6 Hz, Me-6), 25.2 (d, $^3J_{C-P}$ = 8.4 Hz, Me-8), 27.0 (d, $^3J_{C-P}$ = 5.6 Hz, Me-7), 27.7 (d, $^1J_{C-P}$ = 15.7 Hz, PCHSi), 40.8 (s, *C*), 43.6 (s, *C*) ppm. Mass spectrum m/e 402 (M, 3%), 135 ($SiMe_2Ph$, 100%). $[\alpha]_D = -142°$ (c = 1, C_6H_6).

4f Colorless oil. ^{31}P NMR ($CDCl_3$) δ 29.0 ppm. ^{1}H NMR ($CDCl_3$) δ 0.13 (s, SiMe), 0.16 (s, SiMe), 0.92 (s, Me-7), 1.03 (d, $^3J_{H-P}$ = 15.8 Hz, Me-6), 1.24 (d, $^3J_{H-P}$ = 5.1 Hz, Me-5), 1.32 (s, Me-8), 2.65 (m, 2H), 7.0–7.3 (m, Ph) ppm. ^{13}C NMR ($CDCl_3$) δ −1.0 (d, $^3J_{C-P}$ = 3.9 Hz, SiMe), −0.9 (d, $^3J_{C-P}$ = 3.8 Hz, SiMe), 18.9 (d, $^3J_{C-P}$ = 4.0 Hz, $SiCH_2$), 22.1 (d, $^2J_{C-P}$ = 4.9 Hz, Me-5), 23.6 (d, $^2J_{C-P}$ = 21.3 Hz, Me-6), 25.4 (d, $^3J_{C-P}$ = 8.4 Hz, Me-8), 27.2 (d, $^3J_{C-P}$ = 6.2 Hz, Me-7), 30.1 (s, CH_2Ph), 27.0 (d, $^1J_{C-P}$ = 16.5, PCHSi), 41.3 (s, *C*), 44.1 (s, *C*) ppm.

5 was obtained quantitatively after 5 h at room temperature. Low melting solid. Mass spectrum m/e 666 (M, 5%), 527 (M–$C_{10}H_{19}$, 53%), 399 (M–$C_{17}H_{32}P$, 100%). ^{31}P NMR (C_6D_6) δ 28.3 ppm. ^{1}H NMR (C_6D_6) δ 0.39 (s, SiMe), 0.47 (s, SiMe), 1.03 (s, Me-7), 1.12 (d, $^3J_{H-P}$ = 15.6 Hz, Me-6), 1.24 (d, $^3J_{H-P}$ = 4.6 Hz, Me-5), 1.54 (s, Me-8) ppm. ^{13}C NMR (C_6D_6) δ 3.7 (d, $^3J_{C-P}$ = 2.7 Hz, SiMe), 4.1 (s, SiMe), 22.4 (d, $^2J_{C-P}$ = 4.9 Hz, Me-5), 24.0 (d, $^2J_{C-P}$ = 22.2 Hz, Me-6), 25.6 (d, $^3J_{C-P}$ = 9.1 Hz, Me-8), 27.5 (d, $^3J_{C-P}$ = 5.0 Hz, Me-7), 29.4 (d, $^1J_{C-P}$ = 16.6 Hz, PCHSi), 40.3 (s, *C*), 43.3 (s, *C*) ppm.

6a Colorless oil. Mass spectrum m/e 678 (M, 4%), 539 (M–$C_{10}H_{19}$, 64%), 455 (100%). ^{31}P NMR (C_6D_6) δ 27.3 ppm. ^{1}H NMR (C_6D_6) δ 0.28 (s, SiMe), 0.30 (s, SiMe), 0.92 (s, Me-7), 1.08 (d, $^3J_{H-P}$ = 15.4 Hz, Me-6), 1.22 (d, $^3J_{H-P}$ = 4.6 Hz, Me-5), 1.42 (s, Me-8), 1.52 (d, $^2J_{H-P}$ = 3.3 Hz, PCHSi) ppm. ^{13}C NMR (C_6D_6) δ −1.3, −1.2 (SiMe), 9.7 (s, $SiCH_2$), 22.4 (d, $^2J_{C-P}$ = 5.2 Hz, Me-5), 23.9 (d, $^2J_{C-P}$ = 22.5 Hz, Me-6), 25.8 (d, $^3J_{C-P}$ = 8.7 Hz, Me-8), 27.4 (d, $^3J_{C-P}$ = 5.9 Hz, Me-7), 27.0 (d, $^1J_{C-P}$ = 17.8 Hz, P*CH*Si), 40.7 (s, *C*), 43.6 (s, *C*) ppm.

6b was obtained in 81% yield after chromatography. Colorless oil. Mass spectrum m/e 734 (M, 3%), 692 (M–CMe_2, 6%), 595 (M–$C_{10}H_{19}$, 8%), 511 (M–$C_{10}H_{19}$–C_6H_{12}, 100%). ^{31}P NMR (C_6D_6) δ 26.8 ppm. ^{1}H NMR (C_6D_6) δ 0.24 (s, SiMe), 0.26 (s, SiMe), 0.90 (s, Me-7), 1.10 (d, $^3J_{H-P}$ = 15.4 Hz, Me-6), 1.22 (d, $^3J_{H-P}$ = 4.6 Hz, Me-5), 1.39 (s, Me-8) ppm. ^{13}C NMR (C_6D_6) δ −0.7 (d, $^3J_{C-P}$ = 3.0 Hz, SiMe), −0.6 (d, $^3J_{C-P}$ = 4.1 Hz, SiMe), 17.6 (d, $SiCH_2$), 22.4 (d, $^2J_{C-P}$ = 4.9 Hz, Me-5), 23.9 (d, $^2J_{C-P}$ = 22.0 Hz, Me-6), 24.6 (CH_2), 25.7 (d, $^3J_{C-P}$ = 8.1 Hz, Me-8), 27.3 (d, $^3J_{C-P}$ = 5.9 Hz, Me-7), 27.0 (d, $^1J_{C-P}$ = 18.2 Hz, PCHSi), 40.6 (s, *C*), 43.6 (s, *C*) ppm.

3.4. Synthesis of complex 7

$[RhCl(CO)_2]_2$ (49 mg, 0.13 mmol) was dissolved in 40 ml of benzene. A solution containing 0.18 g (0.25 mmol) of the phosphetane **6b** in 30 ml of benzene was added at room temperature and the mixture was then stirred for about 3 h. After evaporation of the solvent, the residue was dissolved in pentane. The crude product was passed through an alumina column. Elution with pentane gave complex **7** as a pale yellow solid (R_F ~ 0.8). Yield 0.13 g (57%). Complex **7** was recrystallized from pentane.

^{31}P NMR (pentane) δ 94.2 ($^1J_{P-Rh}$ = 116 Hz). Anal. Found: C, 59.98; H, 10.13. $C_{45}H_{88}ClOP_2RhSi_2$ Calc.: C, 59.94; H, 9.84%. ^{1}H NMR (C_6D_6) δ 0.28 (s, SiMe), 0.51 (s, SiMe), 0.84 (s, Me-7), unresolved Me signals, 1.69 (s, Me-8) ppm. ^{13}C NMR (C_6D_6) δ 3.4 (s, SiMe), 4.0 (s, SiMe), 17.7 (s, $SiCH_2$), 18.0 (s, $CHMe_2$), 21.8 (s, CH_2), 22.7, 22.9, 24.4, 25.2 (t, J_{C-P} = 5.4 Hz, CH_2), 26.8, 27.2 (t, J_{C-P} = 7.9 Hz, Me), 28.9 (CH_2), 30.2, 34.1 (t, J_{C-P} = 4.8 Hz, CH), 34.4 (CH_2), 36.2, 37.4 (t, J_{C-P} = 8.9 Hz, CH), 42.0, 45.3 (*C*), 47.2 (t, J_{C-P} = 14.6 Hz, *C*), 47.2, 189.0 (dt, $^1J_{C-Rh}$ = 73.2 Hz, $^2J_{C-P}$ = 13.7 Hz, CO). IR (CH_2Cl_2) ν(CO) 1951 cm^{-1}. $[\alpha]_D = +44°$ (c = 0.2, $CHCl_3$).

3.5. X-ray data for complex 7

Crystals of **7**, $C_{45}H_{88}ClOP_2RhSi_2 \cdot C_6H_{14}$, were grown from a hexane solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The crystal

structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group $P2_1$, $a = 11.946(1)$ Å, $b = 14.835(2)$ Å, $c = 15.681(2)$ Å, $\beta = 100.43(1)°$; $V = 2733.16(9)$ Å^3; $Z = 2$; $d_{calc} = 1.200$ g cm^{-3}; $\mu = 4.9$ cm^{-1}; $F(000) = 1072$. A total of 7621 unique reflections were recorded in the range $2° \leq 2\theta \leq 56.1°$, of which 1056 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 6565 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.032$, $R_w = 0.045$, GOF 1.01.

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