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A new asymmetric synthesis of optically active allenes via metal catalyzed hydrosilylation☆

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Abstract

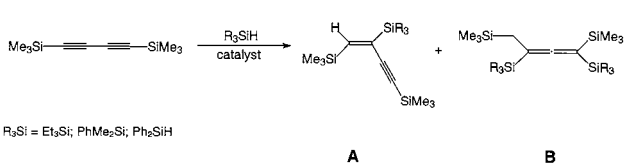
The Rh and Ni catalyzed hydrosilylation of butadiynes to chiral allenes in the presence of chiral phosphine ligands is described. For the first time an enantiomeric excess up to 27% was achieved using $[Rh(COD)Cl]_2$/(−)-PPM and up to 11% using $NiCl_2$[(−)-DIOP]. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Asymmetric hydrosilylation; Butadiynes; Chiral allenes; Rhodium complexes; Nickel complexes; Chiral phosphines

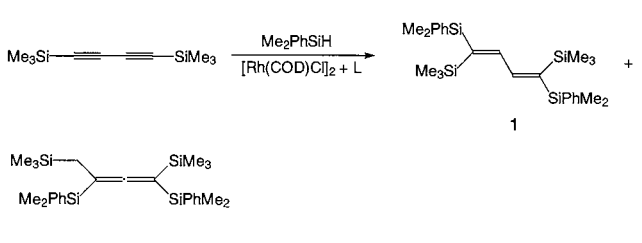
1. Introduction

Allenes are of great importance in organic chemistry as very useful intermediates, their synthesis and application are described in detail in the literature [1]. In particular, allenylsilanes serve as valuable three-carbon components in a general [3 + 2] annulation method, which provides efficient access to a variety of highly substituted furan derivatives, these again represent important intermediates for the syntheses of pharmaceuticals and flavors and fragrant compounds [2]. Many syntheses of chiral allenes of high enantiomeric purity start from chiral precursors [3], but relatively few syntheses are known in which the chirality is induced by a chiral catalyst. To the best of our knowledge the Palladium catalyzed cross-coupling reaction of 4,4-dimethyl-1,2-pentadiene and iodobenzene in the presence of chiral phosphine ligands is the only example of a transition metal catalyzed enantioselective allene synthesis [4]. Here we report on a further example of a transition metal catalyzed synthesis of chiral allenes via asymmetric hydrosilylation. In general, allenes can be synthesized in high yields by hydrosilylation of enynes [5] and butadiynes. In 1985, Kusumoto and Hiyama reported the first example of a hydrosilylation of 1,4-bis(trimethylsilyl)-1,3-butadiyne catalyzed by H_2PtCl_6, $RhCl(PPh_3)_3$ or $Pt(PPh_3)_4$, which gives an enyne (**A**) and/or an allene (**B**) (Scheme 1) [6].

Recently, we reported on the hydrosilylation of disubstituted butadiynes to allene derivatives in the presence of achiral $L_2Ni(0)$-butadiyne catalysts [7]. Now we started investigations of asymmetric hydrosilylation of substituted 1,3-butadiynes in the presence of transition metal complexes (e.g. Rh, Ir, Ni, Pd, Pt) and chiral ligands.



Scheme 1.



Scheme 2.

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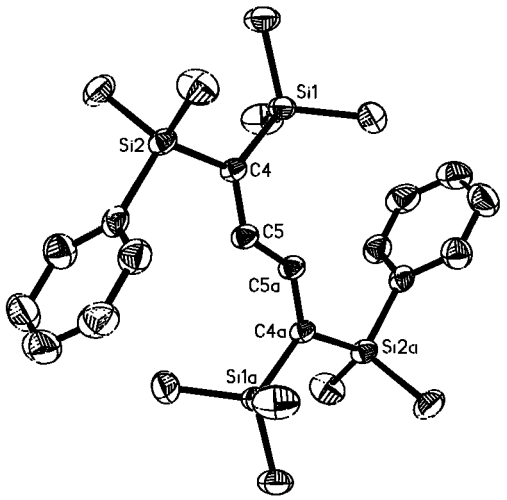
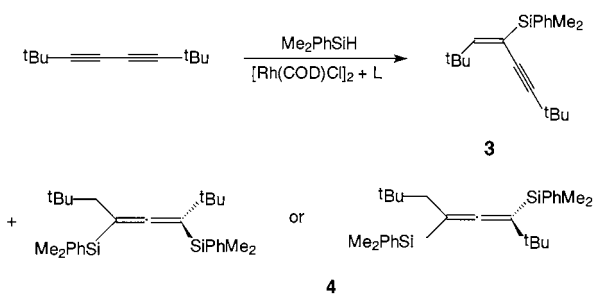


Fig. 1. Molecular structure of compound **1** shown by an ORTEP plot at the 30% probability level. Selected bond distances (Å) and angles (°): C(4)–C(5) 1.346(3), C(5)–C(5a) 1.460(4), Si(1)–C(4) 1.886(2), Si(2)–C(4) 1.880(2); C(4)–C(5)–C(5a) 127.6(2), C(5)–C(4)–Si(1) 121.7(2), Si(2)–C(4)–Si(1) 121.04(11), C(5)–C(4)–Si(2) 117.3(2).



Scheme 3.

2. Results and discussion

2.1. Catalysis with Rh complexes

In order to find an appropriate model reaction, we investigated the reaction of different butadiynes (Ph–C≡C–C≡C–Ph, Me_3Si–C≡C–C≡C–$SiMe_3$, ^{t}Bu–C≡C–C≡C–^{t}Bu) using different silanes (Ph_2SiH_2, Me_2PhSiH, Et_3SiH) in the presence of $[Rh(COD)Cl]_2$ and DIOP. Me_2PhSiH was found to be most suitable. Formation of disilanes was observed when Ph_2SiH_2 was used. Due to the formation of hydrogen, hydrogenation products could be detected as well as the desired hydrosilylation components, and it was not worth working up the reaction mixture. On the other hand, Et_3SiH was not reactive enough. The investigated butadiynes showed different behavior. No formation of allenes could be observed when Ph–C≡C–C≡C–Ph was reacted in the presence of Me_2PhSiH. Two disilylation products have been found when Me_3Si–C≡C–C≡C–$SiMe_3$ was used (Scheme 2). (*E*,*E*)-1,4-bis(dimethylphenylsilyl)-1,4-bis(trimethylsilyl)-1,3-butadiene (**1**) crystallized from the reaction mixture. The structure was proved by X-ray analysis (Fig. 1). Compound **1** was formed via *cis*-addition of the silane. It was the first time that we observed addition of both silyl groups at the outer C-atoms. IR spectroscopy revealed the presence of a second product in the reaction mixture, which was proved to be an allene (**2**) because of the characteristic absorption at 1883 cm^{-1} (ν(C=C=C)). However, isolation from the isomeric mixture was not possible.

Table 1
Results of catalytic hydrosilylation of ^{t}Bu–C≡C–C≡C–^{t}Bu with Me_2PhSiH in the presence of $[Rh(COD)Cl]_2$/L at 70°C in toluene (substrate:silane = 1:4, substrate:Rh = 50:1, 24 h)

Entry	Ligand	Yield (%)		*ee* (%) (conf.) [a]
		2	**3**	
1	(*S*)-(+)-NMDPP	>90	<1	n.d.
2	(2*S*,3*S*)-(+)-Norphos	>90	<1	n.d.
3	(*R*)-(+)-QUINAP	92	7	n.d.
4	(3*R*,4*R*)-Pyrphos	67	4	n.d.
5	(4*R*,5*R*)-(−)-DIOP	53	25	Racemate
6	(*R*)-(+)-BINAP	41	30	Racemate
7	(2*S*,4*S*)-(−)-BPPM	56	21	Racemate
8	(3*R*,4*R*)-(−)-POP-BZ	56	35	5
9	(2*S*,4*S*)-(−)-PPM	66	27	22

[a] The absolute configuration was not determined; optical rotation sign of crude product: (−) (THF).

Thus, as a model reaction the hydrosilylation of 2,2,7,7-tetramethyl-3,5-octadiyne with dimethylphenylsilane was studied (Scheme 3). Depending on the reaction conditions the hydrosilylation gives two reaction products, the monohydrosilylation product **3** and the dihydrosilylation product (allene) **4**.

More than 30 chiral phosphine ligands have been tested in situ in the presence of $[Rh(COD)Cl]_2$; for instance, monophosphines (e.g. (*S*)-(+)-NMDPP), chelate ligands (P/P and P/N ligands, e.g. (2*S*,3*S*)-(+)-Norphos, (2*S*,3*S*)-(−)-Chiraphos, (2*S*,3*S*,4*S*,5*S*)-Rophos-benzene [8], (3*R*,4*R*)-Pyrphos [9], (*R*)-(+)-QUINAP, (*S*)-(−)-Amphos [9], (2*S*,3*S*)-(−)-BDPP, (4*R*,5*R*)-(−)-DIOP, (*R*)-(+)-BINAP, (2*S*,4*S*)-(−)-BPPM, (2*S*,4*S*)-(−)-PPM, (3*R*,4*R*)-(−)-POP-BZ [9], Ph-β-Glup [9], (R_C,S_{Fe})-(−)-BPPFA, (*S*)-(+)-Prolophos [9]. Selected results are given in Table 1 (ligand structures see Fig. 2). Monophosphines and five- and six-membered chelates favor the formation of **3**.

Allene **4** is obtained by using ligands forming seven-membered chelates. For the first time an enantiomeric excess of 5% and 22% was obtained in the presence of ligands POP-BZ and PPM. In contrast to PPM, no enantioselection was obtained with BPPM, a ligand with an electron-withdrawing substituent at the pyrrolidine nitrogen atom.

Both ligands differ in the substituent at the nitrogen atom. Achiwa [10] showed that an additional coordination of the nitrogen to the rhodium atom exists in the non-substituted PPM. This hemilabile effect seems to influence positively the induction of chirality. The role of this N-substituent must still be clarified.

Furthermore, the effect of different reaction conditions such as temperature, reaction time, solvents, and additives on the enantiomeric excess was investigated (Table 2). An increase in temperature up to 90°C or a decrease in reaction time down to 8 h did not show a substantial difference in the yield or in the enantiomeric excess. The conversion is too low when the temperature is decreased down to 50°C. Also THF and chloroform as solvents cause a drastic lowering in conversion. Without any solvent, but an excess of silane, the conversion increases, followed by a decrease in the *ee* values.

We observed a slight increase of the *ee* values with Et_3N as solvent. However, due to the lower solubility of the starting compounds, the yields turned to be much lower.

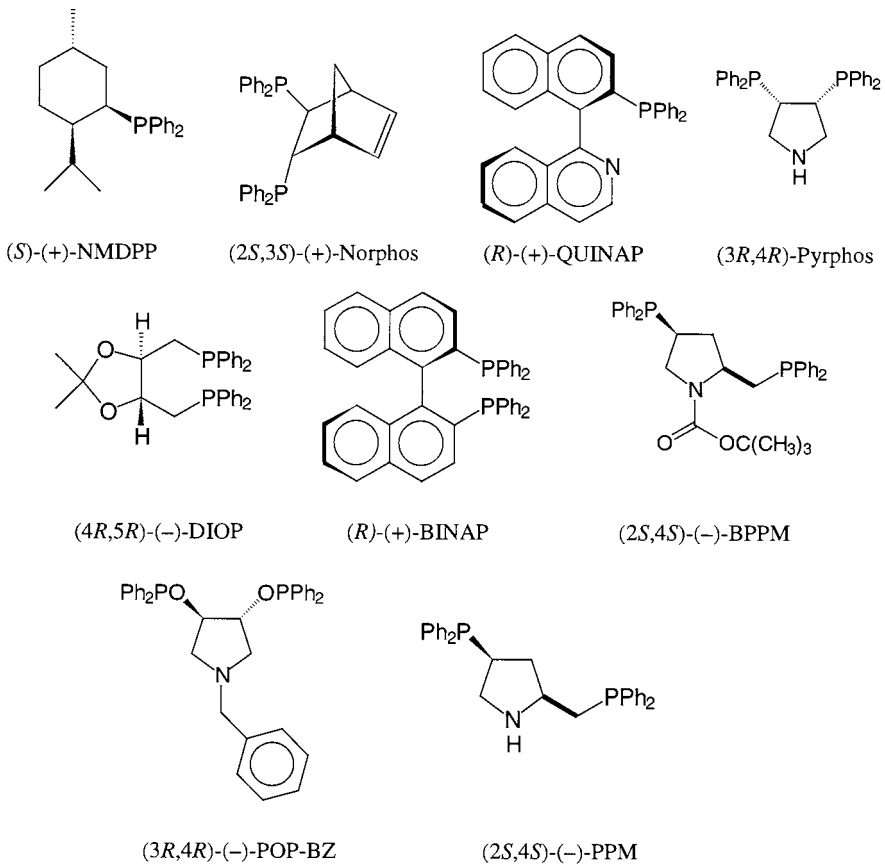


Fig. 2. Selected phosphine ligands (see Table 1).

Table 2
Hydrosilylation of ^{t}Bu–C≡C–C≡C–^{t}Bu with Me_2PhSiH in the presence of $[Rh(COD)Cl_2]$/PPM under different reaction conditions

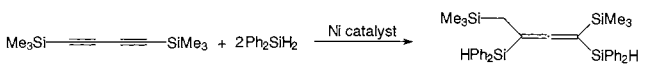
Entry	Solvent	Temperature (°C)	*t* (h)	Yield (%)		*ee* (%) [a]
				2	**3**	
1	Toluene	70	24	66	27	22
2	Toluene	70	8	58	21	23
3	Toluene	90	6	73	23	21
4	THF	70	24	83	6	n.d.
5	$CHCl_3$	70	24	47	2	n.d.
6	Et_3N	70	24	80	15	25
7	Without	70	24	51	39	15

[a] Optical rotation sign of crude product: (−) (THF).

Table 3
Effect of Et_3N as additive at the hydrosilylation of ^{t}Bu–C≡C–C≡C–^{t}Bu with Me_2PhSiH in the presence of $[Rh(COD)Cl_2]$/PPM (toluene; 70°C; 24 h; substrate:silane = 1:4, substrate:Rh = 50:1)

Entry	$n(NEt_3)$ (mmol)	Yield (%)		*ee* (%) [a]
		2	**3**	
1	0.02	60	35	22
2	0.05	53	31	25
3	0.07	50	34	20
4	0.10	54	30	27

[a] Optical rotation sign of crude product: (−) (THF).



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Scheme 4.

It is known that achiral additives can influence drastically the enantioselectivity and yields [11]. We investigated this effect in the case of Et_3N. A remarkable influence could not be observed (Table 3). The *ee* values reached 27% when 0.1 mmol Et_3N was added to the reaction mixture (Table 3, entry 4). Small amounts of additives did not change the solubility considerably, and that is why yields were not affected compared with the reaction when using Et_3N as solvent. Now the influence of other achiral amine additives is investigated.

Hiyama [6b] discussed the fact that hydrosilylation of butadiynes proceeds stepwise. The first addition of hydridosilane leads to the *cis*-product with a regioselectivity that hydrogen adds at C(1) and silicon at C(2) to give products of type **3** (enynes). The second addition of hydridosilane leads to products of 1,3-butadiynes via another 1,2-addition of C≡C bond of enyne but with different regioselectivity or, alternatively, to allene via 1,4-addition. We assume that the hydrosilylation does not proceed in a two-step mechanism. It is likely to be a concerted reaction because the allene did not form when the enyne **3** was used instead of the ^{t}Bu–C≡C–C≡C–^{t}Bu under the same conditions described above. We also observed only *cis*-addition of the silanes in the reaction. Whether the silyl groups are added at the inner or outer C-atoms depends on the substrate, the silane, and the catalyst.

2.2. Catalysis with Ir, Pd and Pt complexes

Besides Rh catalysts, $(COD)PtCl_2$, $(COD)PdCl_2$ and $[Ir(COD)Cl]_2$ with PPM were also investigated as precatalysts with ^{t}Bu–C≡C–C≡C–^{t}Bu in the presence of the silanes Me_2PhSiH and Ph_2SiH_2. The Pd complex decomposed with precipitation of metal during the reaction after the silanes have been added. On the other hand, when the Ir complex was used no reaction occurred in the presence of Me_2PhSiH, whereas the Pt complex only formed the enyne **3**. With Ph_2SiH_2 as reagent, in both cases, formation of the allene was not observed.

2.3. Catalysis with Ni complexes

For the investigation of hydrosilylation with chiral Ni(II) complexes, such as $NiCl_2$[(−)-DIOP] and $NiCl_2$[(−)-PPM], Me_3Si–C≡C–C≡C–$SiMe_3$ was chosen as substrate and Ph_2SiH_2 as silane component (Scheme 4).

Neither formation of disilane or hydrogen nor reaction to the enyne was observed in the presence of Ph_2SiH_2.

In contrast to the Rh catalyzed reaction, *ee* values were found in both cases (Table 4). We were able to show that besides Rh complexes, it is also possible to induce chirality using chiral Ni complexes.

3. Experimental

All operations were carried out in an inert atmosphere (argon). Toluene and THF were freshly distilled from sodium tetraethylaluminate under argon prior to use. Chloroform was distilled from CaH_2. The starting materials, metal complexes, butadiynes, silanes and ligands (NMDPP, Norphos, Chiraphos, QUINAP, BDPP, DIOP, BINAP, BPPM, PPM, BPPFA), were commercially available (STREM, Fluka, Aldrich). $NiCl_2$[(−)-DIOP] was synthesized according to the literature method [12]. The following spectrometer were

Table 4
Results of catalytic hydrosilylation of Me_3Si–C≡C–C≡C–$SiMe_3$ with Ph_2SiH_2 in toluene (substrate:silane = 1:4, substrate:Ni = 50:1, 24 h)

Entry	Catalyst	Temperature (°C)	Yield (%)	*ee* (%) (sign of rot.)
1	$NiCl_2$[(−)-DIOP]	70	9	9 (+)
2	$NiCl_2$[(−)-DIOP] [a]	70	8	8 (+)
3	$NiCl_2$[(−)-DIOP]	90	11	11 (+)
4	$NiCl_2$[(−)-PPM]	70	49	7 (+)

[a] Without solvent.

used: NMR, Bruker ARX 400; IR, Nicolet Magna 550; MS, AMD 402; C,H-analysis, Leco CHNS 932-Analyzer. Melting points were measured on a Büchi 535 apparatus. HPLC was performed with a Liquid Chromatograph 1090 series II equipped with DAD (Hewlett–Packard) and Chiralyser (IBZ Messtechnik GmbH, Hanover). Separations were carried out on CHIRALCEL OD-H analytical column 4.6 × 250 mm I.D (Daicel).

3.1. General procedures of hydrosilylation

Under inert conditions, a mixture of 1 mmol of butadiyne, 0.02 mmol of the ligand and 0.01 mmol of $[Rh(COD)Cl]_2$ (or 0.02 mmol of L_2NiCl_2) were dissolved in 1 ml of solvent and stirred for 10 min at room temperature.

A certain amount of amine was added in the case when additives were used (see Table 3). Then 4 mmol of silane were added and the mixture was stirred for 24 h at 70°C. The yields were determined by gas chromatography and dodecane was used as internal standard.

Afterwards, toluene and silane were removed in vacuo. The residue was purified by column chromatography (eluent: *n*-hexane; Silica Gel 60 (Merck)).

3.2. Characterization of reaction products

3.2.1. (E,E)-1,4-Bis(dimethylphenylsilyl)-1,4-bis(trimethylsilyl)-1,3-butadiene (1)

Colorless crystals (*n*-hexane); yield 10%; m.p. 93–94°C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.00 (s, 18H, SiMe_3); 0.39 (s, 12H, SiMe_2); 7.33 (m, 4H, *m*-Ph); 7.33 (m, 2H, *p*-Ph); 7.42 (s, 2H, CH); 7.46 (m, 4H, *o*-Ph). ^{13}C-NMR ($CDCl_3$): δ (ppm) −1.0 (2SiMe_2); 1.6 (2 SiMe_3); 127.8 (4*m*-Ph); 128.8 (2*p*-Ph); 134.0 (4*o*-Ph); 139.6 (2*i*-Ph); 147.8 (2CSi$_2$); 154.9 (2CH). ^{29}Si-NMR ($CDCl_3$): δ(ppm) −8.9 ($^2J_{Si-H} \approx 6.5$ Hz, 2SiMe$_3$); −4.1 ($^2J_{Si-H} \approx 6.5$ Hz, 2SiMe$_2$). MS (70 eV): *m*/*z* (rel. int. (%)) 466 (4) [M^+], 316 (31), 243 (34), 135 (100) [$(SiPhMe_2)^+$], 73 (66) [$(SiMe_3)^+$]. IR (KBr, cm^{-1}): 1428 and 1114 (ν(Ph–Si)), 1251 (δ_s(CH_3–Si)). Anal. Calc. (%) for $C_{26}H_{42}Si_4$ (466.96): C, 66.88; H, 9.07. Found: C, 66.72; H, 9.18%.

3.2.2. (E)-4-Dimethylphenylsilyl-2,2,7,7-tetramethyl-3-octen-5-yne (3) [7]

^{1}H-NMR ($CDCl_3$): δ (ppm) 0.38 (s, 6H, SiMe_2Ph); 1.18 and 1.19 (s, 18H, CMe_3); 5.92 (s, 1H, CH); 7.33 (m, 3H, *m*-/*p*-Ph); 7.56 (m, 2H, *o*-Ph). ^{13}C-NMR ($CDCl_3$): δ (ppm) −3.1 (SiMe_2); 28.5 (C≡C–CMe$_3$); 29.6 (Me_3C–C=); 30.8 (Me_3C–C≡); 35.7 (Me_3C–C=); 78.6 (C≡C–CMe$_3$); 109.6 (C≡C–CMe$_3$); 120.2 (=C–SiMe$_2$Ph); 127.5 (*m*-Ph); 128.9 (*p*-Ph); 134.1 (*o*-Ph); 138.2 (*i*-Ph); 159.2 (CH). ^{29}Si-NMR ($CDCl_3$): δ (ppm) −7.3 (SiPhMe$_2$). MS (70 eV): *m*/*z* (rel. int. (%)) 298 (23) [M^+], 283 (20) [M^+ − Me], 241 (9) [M^+ − ^{t}Bu], 163 (4) [M^+ − SiMe$_2$Ph], 135 (100) [$(SiPhMe_2)^+$], 57 (6) [^{t}Bu$^+$]. IR (neat, cm^{-1}): 1428 and 1113 (ν(Ph–Si)), 1249 (δ_s(Me–Si)). Anal. Calc. for $C_{20}H_{30}Si$ (298.54): C, 80.46; H, 10.13. Found: C, 80.35; H, 10.59%.

3.2.3. 3,5-Bis(dimethylphenylsilyl)-2,2,7,7-tetramethyl-3,4-octadiene (4) [7]

^{1}H-NMR ($CDCl_3$): δ (ppm) 0.34, 0.36, 0.39, 0.43 (4s, 12H, SiMe_2Ph); 0.89, 1.01 (2s, 18H, CMe_3); 1.70 (d, 1H, $J_{Ha,Hb} \approx 14.5$ Hz, H_b, CH_2); 1.83 (d, 1H, $J_{Ha,Hb} \approx 14.5$ Hz, H_a, CH_2); 7.30–7.35, 7.45-7.55 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): δ (ppm) −2.8, −2.3, 0.0, 0.1 (SiPhMe_2); 29.7, 31.5 (CMe_3); 32.3, 35.0 (CMe$_3$); 42.5 (CH$_2$); 85.7, 96.9 (C=C=C); 128.5, 128.7 (*p*-Ph); 127.3, 127.4, 134.0, 134.1, (2*m*-Ph, 2*o*-Ph); 138.4, 140.0 (*i*-Ph); 206.9 (C=C=C). ^{29}Si-NMR ($CDCl_3$): δ (ppm) −9.6, −7.2 (SiPhMe$_2$). MS (70 eV): *m*/*z* (rel. int. (%)) 434 (19) [M^+], 419 (9) [M^+ − Me], 377 (5) [M^+ − ^{t}Bu], 135 (100) [$(SiPhMe_2)^+$], 57 (12) [^{t}Bu$^+$]. IR (neat, cm^{-1}): 1880 (ν(C=C=C)), 1428 and 1111 (ν(Ph–Si)), 1246 (δ_s(Me–Si)). Anal. Calc. for $C_{28}H_{42}Si_2$ (434.81): C, 77.35; H, 9.74. Found: C, 77.52; H, 9.97%.

3.2.4. 1,3-Bis(diphenylsilyl)-1,4-bis(trimethylsilyl)-1,2-butadiene (5) [7]

^{1}H-NMR: δ (ppm) −0.07 (s, 9H, 1-SiMe_3); −0.04 (s, 9H, 4-SiMe_3); 1.07 (d, 1H, $J_{Ha,Hb} \approx 15.0$ Hz, H_b, CH_2); 1.31 (d, 1H, $J_{Ha,Hb} \approx 15.0$ Hz, H_a, CH_2); 5.09 (s, 1H, 3-SiH); 5.11 (s, 1H, 1-SiH); 7.27–7.52 (m, 20H, Ph). ^{13}C-NMR: δ (ppm) −0.8 (4-SiMe_3); −0.1 (1-

Table 5
Crystallographic data for compound **1**

	1
Formula	$C_{26}H_{42}Si_4$
Formula weight (g mol^{-1})	466.96
Crystal	Prism
Color	Colorless
Crystal size (mm)	0.5 × 0.3 × 0.2
Space group	$P\bar{1}$
Z	2
a (Å)	6.6070(10)
b (Å)	11.134(2)
c (Å)	11.960(2)
α (°)	117.42(3)
β (°)	104.14(3)
γ (°)	91.49(3)
V (Å^3)	747.4(2)
D_{calc} (g cm^{-3})	1.037
Absorption coefficient (mm^{-1})	0.209
Reflection measured	2225
Unique reflections	2225
Observed reflection ($I \geq 2\sigma I$)	1818
No. of parameters	140
R_1	0.0372
wR_2 (all data)	0.1366

Si*Me*$_3$); 16.0 (4-*C*); 69.1 (3-*C*); 73.9 (1-*C*); 127.7 (2*m*-Ph); 127.79, 127.82 (*m*-Ph); 129.5 (4*p*-Ph); 133.4, 133.5 (3-*i*-Ph); 134.2, 134.5 (1-*i*-Ph); 135.6 (3*o*-Ph); 135.8 (*o*-Ph); 210.7 (2-C). ^{29}Si-NMR: δ (ppm) −20.5 ($^1J_{Si-H} \approx 189.9$ Hz, 1-*Si*Ph); −13.9 ($^1J_{Si-H} \approx 192.0$ Hz, 3-SiPh); −1.6 ($^2J_{Si-H} \approx 23.7$ Hz, 1-*Si*Me$_3$); 2.5 ($^2J_{Si-H} \approx 22.6$ Hz, 4-*Si*Me$_3$).

3.2.5. Preparation of NiCl$_2$[(−)-PPM]

NiCl$_2$[(−)-PPM] was prepared according to the procedure for the synthesis of NiCl$_2$[(−)-DIOP] [12b].

Green solid; MS (FAB): *m*/*z* (rel. int. (%)) 546 [90, $M^+ - Cl$], 511 [34, $M^+ - 2Cl$].

*3.2.6. X-ray structure determination of **1***

X-ray diffraction data were collected on a STOE-IPDS diffractometer using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods [13a] and refined by full-matrix least-squares techniques against F^2 [13b]. Crystallographic data for **1** are given in Table 5.

3.2.7. Methods of determination of enantiomeric excess

In general, enantiomeric excesses are determined by gas chromatography and HPLC, respectively. The determination of enantiomers of allene **5** was carried out by HPLC (see Table 4). In order to achieve the enantiomeric resolution normal phase systems with different chiral stationary phases were used. A Chiralcel OD-H column showed the best results. Baseline resolution was obtained with an 100% *n*-hexane eluent. Various chiral columns were tested to separate both enantiomers of allene **4**. In the case of GC no separation could be observed whereas a partial separation could be achieved by means of HPLC, which was unfortunately too inaccurate for an *ee* determination. Therefore, investigations with shift reagents were carried out to determine the enantiomeric purity by NMR spectroscopy. It is known that certain chiral lanthanoid shift reagents (CLSR) together with silver(I) complexes induce a signal separation in several alkenes [14]. In the ^{1}H-NMR spectra of **4** with Yb(hfc)$_3$/Ag(fod) the signals of both the CH_2 and the *tert*-butyl group were separated. Details will be given in [15]. The enantiomeric excess was determined using the *tert*-butyl signals. The results are given in Tables 1–3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 136870 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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