Preparation of New Ferrocenylmonophosphine Ligands Containing Two Planar Chiral Ferrocenyl Moieties and Their Use for Palladium-Catalyzed Asymmetric Hydrosilylation of 1,3-Dienes

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Dedicated to Professor *Dieter Seebach* on the occasion of his sixty-fifth birthday

Bis{(R_p)-2-[(1*S*)-1-methoxyethyl]ferrocenyl}arylphosphines (S,R_p)-**9** (aryl = 4-$MeOC_6H_4$ (**9a**), Ph (**9b**), 4-$CF_3C_6H_4$ (**9c**), 3,5-$(CF_3)_2C_6H_3$ (**9d**)), which contain two planar chiral ferrocenyl moieties, were prepared *via* (R_p)-1-bromo-2-[(1*S*)-1-methoxyethyl]ferrocene ((S,R_p)-**8**). Asymmetric hydrosilylation of linear 1,3-dienes such as deca-1,3-diene (**10a**) with trichlorosilane in the presence of a palladium catalyst coordinated with **9d** gave allylic silanes of up to 93% ee.

1. Introduction. – Palladium-catalyzed asymmetric hydrosilylation of C–C multiple bonds provides one of the most efficient routes to enantiomerically enriched organosilicon compounds[1]). One important point in the palladium-catalyzed hydrosilylation is that no chelating bisphospine ligands can be used because of the low catalytic activity of their palladium complexes. We have reported that high enantioselectivity as well as high catalytic activity in the asymmetric hydrosilylation is achieved by use of chiral monodentate phosphine ligands (MOP) whose chirality is due to the binaphthyl axial chirality [2]. The MOP ligands have an advantage over others in that their fine tuning is readily made by the introduction of a desired group at the 2′ position. In the asymmetric hydrosilylation of simple terminal alkenes [3] and cyclic alkenes [4], high enantioselectivity (> 90% ee) has been observed by use of 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP; **1**). For styrene derivatives, 2-(diphenylphosphino)-1,1′-binaphthyl (H-MOP; **2a**) [5] and its analog **2b** containing the bis[3,5-bis(trifluoromethyl)phenyl]phosphino group [6] are more effective than MeO-MOP at giving the hydrosilylation products of over 95% ee. For the asymmetric hydrosilylation of 1,3-dienes, which is a very useful asymmetric transformation because it produces enantiomerically enriched allylic silanes, we found that MOP ligand **2c** substituted with a 3,5-dimethyl-4-methoxyphenyl group at the 2′ position [7] and its long-chain-alkylated version **2d** [8] are better than others. The ligand **2d** showed 91% ee for the hydrosilylation of cyclopentadiene. However, unfortunately, these MOP ligands are not so effective for linear 1,3-dienes such as deca-1,3-diene. The highest enantioselectivity so far observed for deca-1,3-diene is 77% ee [8]. On the other hand, we have also developed the chiral ferrocenylphosphine ligands, which have ferrocene planar chirality[2])[3]). They possess high modularity, allowing us to prepare both mono-

[1]) For reviews on catalytic asymmetric hydrosilylation, see [1].
[2]) For reviews on chiral ferrocenylphosphines, see [9].
[3]) For recent examples of new types of chiral ferrocenylphosphines, see [10].

phosphines and bisphosphines and to introduce various kinds of functional groups at the side chain according to the demand of the reaction type. Nevertheless, there have been few efforts on the modification of ferrocenylphosphines for the asymmetric hydrosilylation of 1,3-dienes[4])[5]) [12]. Ferrocenylmonophosphines, PPFA **3a**, PPFOMe **3b**, PPFOAc **3c**, and perfluoroalkylated PPFA **3d**, have been used for the catalytic asymmetric hydrosilylation of both cyclic and linear 1,3-dienes, but the enantioselectivity is not satisfactory. The highest was 77% ee, which was observed with **3c** for cyclohexa-1,3-diene [11e]. Here we wish to report the preparation of new ferrocenylmonophosphines containing two chiral ferrocenyl moieties[6]) and their use as highly effective chiral ligands for the palladium-catalyzed asymmetric hydrosilylation of linear 1,3-dienes.

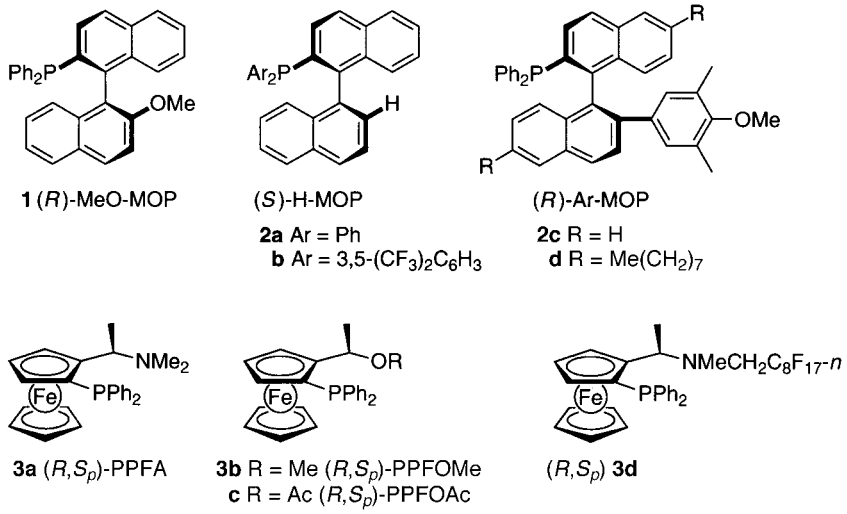

Fig. 1. *MOP and Ferrocenylphosphine ligands for palladium-catalyzed asymmetric hydrosilylation of olefins*

2. Results and Discussion. – In 1980, we reported [14] the preparation of chiral bis(ferrocenyl)monophosphine (S,R_p)-**4**[7]), which contains two planar chiral ferrocene moieties, by way of ferrocenylstannane derivative (S,R_p)-**5** starting from (*S*)-*N*,*N*-dimethyl-1-ferrocenylethylamine ((*S*)-**6**) [15] (*Scheme 1*). Attempts to obtain (S,R_p)-**4** in a one-pot reaction by the lithiation of (*S*)-**6** with BuLi and then addition of dichlorophenylphosphine failed, probably due to the low conversion of (*S*)-**6** to the lithiated ferrocene, which causes the reaction of remaining BuLi with chlorophosphines giving butylphosphines. By use of the route involving the ferrocenylstannane (S,R_p)-**5**, we succeeded in the preparation of (S,R_p)-**4**, but the yields for the two steps in *Scheme 1* are still not high enough.

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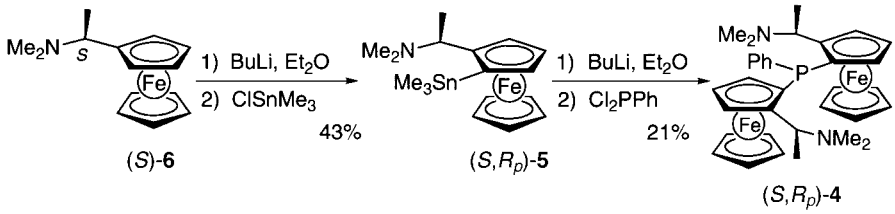
4) For palladium-catalyzed hydrosilylation of 1,3-dienes with chiral ferrocenylphosphine ligands, see [11].

5) For palladium-catalyzed hydrosilylation of trinorbornene and styrene with chiral ferrocenylphosphine ligands, see [12].

6) A C_3-symmetric tri(ferrocenyl)monophosphine has been reported [13].

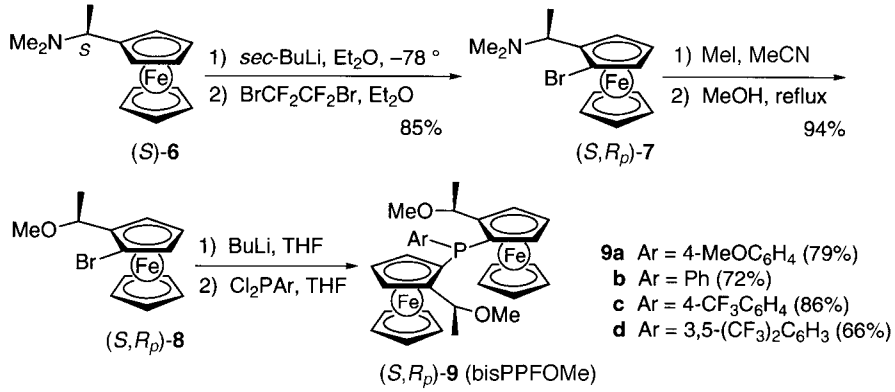
7) Subscript *p* means planar.

Scheme 1. *Preparation of Chiral Bis(ferrocenyl)monophosphine* **4** *as Reported in* [14]



We decided to take the synthetic route shown in *Scheme 2*, which involves bromoferrocene (S,R_p)-**7** as a key intermediate, because bromoferrocenes are known to be converted to lithioferrocenes with high efficiency [16]. Considering that phosphine ligands substituted with a dialkylamino group are not suitable for the catalytic hydrosilylation with trichlorosilane due to their insolubility in the reaction media, the dimethylamino group in (S,R_p)-**4** was replaced by an alkoxy group in our target ferrocenylphosphines (S,R_p)-**9**. Thus, first, (S)-**6** was brominated in 85% yield by lithiation with *sec*-BuLi followed by bromination with 1,2-dibromo-1,1,2,2-tetrafluoroethane according to modified procedures based on the reported method [16] to give the bromoferrocene (S,R_p)-**7**, which is diastereoisomerically pure. The dimethylamino group of (S,R_p)-**7** was replaced by a MeO group by methanolysis of its ammonium salt in refluxing MeOH, which proceeded with retention of configuration at the stereogenic ferrocenylmethyl position to give 94% yield of (S,R_p)-**8**. Lithiation of (S,R_p)-**8** with 1 equiv. on BuLi at $-78°$ for 1 h followed by addition of 0.5 equiv. of aryldichlorophosphine gave high yields of the bis(ferrocenyl)monophosphines (bisPPFOMe) (S,R_p)-**9**. During our previous studies on the palladium-catalyzed asymmetric hydrosilylation by means of MOP ligands [6], we observed that substituents at the phenyl rings at the P-atom have strong electronic effects on the catalytic activity and enantioselectivity. To examine the electronic effects in the bis(ferrocenyl)monophosphines, we introduced both electron-donating and -withdrawing groups at the phenyl ring. The monophosphine **9a** is substituted with a 4-methoxyphenyl group, while **9c** and **9d** contain trifluoromethyl groups.

Scheme 2. *Preparation of Chiral Bis(ferrocenyl)monophosphines* (S,R_p)-**9**



The bis(ferrocenyl)monophosphine ligands (S,R_p)-**9** were examined for their enantioselectivity in the palladium-catalyzed asymmetric hydrosilylation of deca-1,3-diene (**10a**) with trichlorosilane (*Scheme 3*). The reaction was carried out without solvents at 20° in the presence of 1 mol-% of the palladium catalyst generated *in situ* by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with one of the bis(ferrocenyl)monophosphines (S,R_p)-**9**. The hydrosilylation proceeded in a 1,4-fashion to give (*Z*)-**4**-(trichlorosilyl)-dec-2-ene (**11a**) as a major product with over 80% selectivity, together with a minor amount of regioisomers (*E*)-2-(trichlorosilyl)-dec-3-ene (**12a**) and (*Z*)-1-(trichlorosilyl)-dec-2-ene (**13a**), the ratio being slightly dependent on the ligand employed (*Entries 1–4* in the *Table 1*). The enantiomer excess of **11a** was measured by HPLC analysis (*Chiralcel*

Scheme 3. *Palladium-Catalyzed Asymmetric Hydrosilylation of Linear 1,3-Dienes* **10**

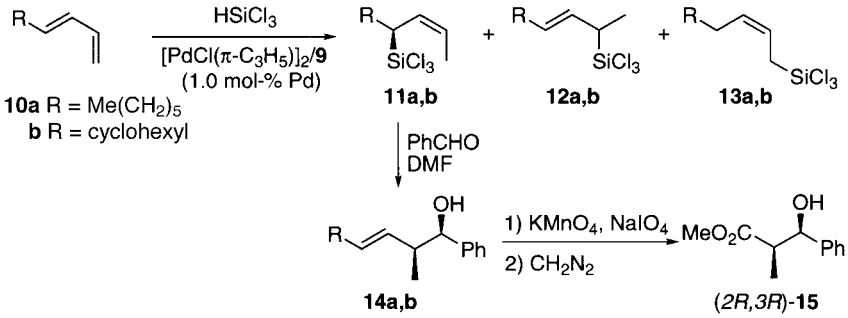


Table. *Palladium-Catalyzed Asymmetric Hydrosilylation of Dienes* **10** *with Trichlorosilane*[a])

Entry	Diene	Ligand	Temp. [°]	Time [h]	Yield[b])	[%] of **11** + **12** + **13**	Ratio[c]) **11**/**12**/**13** % ee[d]) of **11** (config.)[e])
1	**10a**	**9a**	20	96	43	82 : 3 : 15	68 (*S*)
2	**a**	**b**	20	29	78	90 : 9 : 1	76 (*S*)
3	**a**	**c**	20	8	89	90 : 8 : 2	78 (*S*)
4	**a**	**d**	20	25	91	87 : 10 : 3	87 (*S*)
5	**a**	**d**	−5	168	81	89 : 9 : 2	93 (*S*)
6	**b**	**d**	20	26	94	92 : 6 : 2	88 (*S*)
7	**b**	**d**	−5	168	81	93 : 5 : 2	90 (*S*)

[a]) The hydrosilylation was carried out without solvent. The catalyst was generated *in situ* by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and a chiral ligand (S,R_p)-**9**. The initial ratio diene/$HSiCl_3$/Pd/(S,R_p)-**9** was 1.0 : 1.2 : 0.01 : 0.02. [b]) Isolated yield of a mixture of allyltrichlorosilanes **11**, **12**, and **13** by bulb-to-bulb distillation. [c]) Determined by ^{1}H-NMR analysis of the allyltrichlorosilanes. [d]) Determined by HPLC analysis of homoallyl alcohols **14** with a chiral-stationary-phase column (*Chiralcel OD-H*). [e]) Determined by the optical rotation of homoallyl alcohols **14** (see *Exper. Part*). For *Entry 5* (**14a**), $[\alpha]_D^{20} = +16.5$ ($c = 1.0$, $CHCl_3$). For *Entry 7* (**14b**), $[\alpha]_D^{20} = +15.7$ ($c = 1.0$, $CHCl_3$).

OD-H) of the homoallyl alcohol **14a** [7] obtained by the reaction with benzaldehyde in DMF, which proceeds *via* a six-membered cyclic transition state [17], and the absolute configuration was determined by correlation with the known hydroxy ester **15** [18]. The highest enantioselectivity (87% ee) was observed with ligand **9d** where Ar at the P-atom is 3,5-$(CF_3)_2C_6H_3$ (*Entry 4*) an the enantioselectivity decreased in the order **9d** (Ar = 3,5-$(CF_3)_2C_6H_3$) > **9c** (Ar = 4-$CF_3C_6H_4$) > **9b** (Ar=Ph) > **9a** (Ar = 4-$MeOC_6H_4$).

The reaction at $-5°$ with **9d** gave the allylsilane (*S*)-**11a** of 93% ee (*Entry 5*). The ligand **9d** was also effective for the asymmetric hydrosilylation of 1-cyclohexyl-buta-1,3-diene (**10b**). The reactions at 20 and $-5°$ gave allylsilane (*S*)-**11b** of 88 and 90% ee, respectively (*Entries 6* and *7*). The regioselectivity forming **11b** is also high.

3. Conclusions. – The enantioselectivity of 93% observed here with the bis(ferrocenyl)monophosphine **9d** is the highest for asymmetric hydrosilylation of 1,3-dienes, especially for linear 1,3-dienes. Recently, it was also found that one of the bis(ferrocenyl)monophosphines **9b** is effective for the palladium-catalyzed asymmetric hydrosilylation of 1-en-3-ynes giving axially chiral allenylsilanes [19]. Further work is ongoing to design more enantioselective structures based on the ferrocene planar chirality and to apply them to catalytic asymmetric reactions.

Experimental Part

1. *General*. All manipulations were carried out under N_2. N_2 Gas was dried by passage through P_2O_5. HPLC: *Jasco PU-980* liquid chromatograph system with a chiral-stationary-phase column, *Chiralcel OD-H*. Column chromatography = CC. $[\alpha]_D$: *Jasco DIP-370* polarimeter. NMR Spectra: *Jeol JNM-LA-500* spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P); chemical shifts δ are reported in ppm referenced to internal $SiMe_4$ (δ(H)), $CDCl_3$ (δ(C) 77.00) or (D_6)benzene- (δ(C) 128.39), and external 85% H_3PO_4 soln. (δ(P)).

2. *Chiral Ferrocenyl Compounds: (1S)-*N,N*-Dimethyl-1-[(*R_p*)-2-bromoferrocenyl]ethylamine* ((*S*,*R_p*)-**7**). To a soln. of 2.3 g (8.9 mmol) of (1*S*)-*N*,*N*-dimethyl-1-ferrocenylethylamine ((*S*)-**6**) [15] in Et_2O 30 ml) was added dropwise 11.1 ml (10.7 mmol; 0.96M in cyclohexane/hexane) of *sec*-BuLi at r.t. After stirring at r.t. for 2 h, the mixture was cooled to $-78°$, and then 2.1 ml (17.8 mmol) of 1,2-dibromo-1,1,2,2-tetrafluoroethane was added slowly. After 1 h, excess *sec*-BuLi was quenched with aq. $NaHCO_3$ soln. The mixture was extracted with Et_2O, the extract washed with H_2O, dried ($MgSO_4$), and evaporated, and the crude product purified by CC (silica gel, hexane/Et_2O/Et_3N 5:3:0.8): 2.82 g (95%) of (*S*,*R_p*)-**7** (diastereomer ratio 98:2). Yellow solid. The diastereoisomerically pure compound was obtained by recrystallization from MeCN (2.52 g, 85%). $[\alpha]_D^{20} = -8.6$ ($c = 1.0$, $CHCl_3$). ^1H-NMR ($CDCl_3$): 1.52 (*d*, $J = 6.6$, 3 H); 2.13 (*s*, 6 H); 3.75 (*q*, $J = 6.8$, 1 H); 4.09 (*s*, 1 H); 4.13 (*s*, 1 H); 4.15 (*s*, 5 H); 4.45 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 16.73; 41.10; 56.04; 65.13; 65.63; 69.77; 71.16; 79.75; 87.33. Anal. calc. for $C_{14}H_{18}BrFeN$: C 50.04, H 5.40, N 4.17; found: C 49.91, H 5.18, N 4.25.

(R_p*)-1-Bromo-2-(1S)-1-methoxyethyl]ferrocene* ((*S*,*R_p*)-**8**). To a soln. of 2.4 g (7.3 mmol) of (*S*,*R_p*)-**7** in 15 ml of MeCN was added 2 ml of MeI. The mixture was stirred at r.t. for 2 h, and then all volatiles were evaporated. The remaining yellow residue was dissolved in 15 ml of MeON. After refluxing for 30 min, the mixture was cooled to r.t., and MeOH was evaporated. The mixture was extracted with Et_2O, the extract washed with aq. NH_4Cl soln. dried ($MgSO_4$), and evaporated, and the crude product purified by CC (silica gel, hexane/AcOEt 10:1): 2.2 g (94%) of (*S*,*R_p*)-**8**. Orange oil. $[\alpha]_D^{20} = +13.4$ ($c = 1.0$, $CHCl_3$). ^1H-NMR ($CDCl_3$): 1.63 (*d*, $J = 6.3$, 3 H); 3.24 (*s*, 3 H); 4.16 (*s*, 6 H); 4.22 (*s*, 1 H); 4.44 (*q*, $J = 6.4$, 1 H); 4.48 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 19.82; 55.86; 64.66; 66.39; 70.23; 71.19; 72.68; 79.83; 87.33. Anal. calc. for $C_{13}H_{15}BrFeO$: C 48.34, H 4.68; found: C 48.32, H 4.71.

Bis{(R_p*)-2-(1S)-1-methoxyethyl]ferrocenyl}arylphosphine* ((*S*,*R_p*)-**9**). A typical procedure is given for the preparation of *bis{(*R*)-2-[(1S)-1-methoxyethyl]ferrocenyl}phenylphosphine* (**9b**): To a soln. of 1.7 g (5.3 mmol) of (*S*,*R_p*)-**8** in 20 ml of THF was added dropwise 3.4 ml (5.3 mmol, 1.55M in hexane) of BuLi at $-78°$. After stirring at $-78°$ for 1 h, 0.36 ml (2.65 mmol) of dichlorophenylphosphine was added slowly. The mixture was refluxed for 2 h, and then hydrolyzed with aq. NH_4Cl soln. at r.t. The mixture was extracted with Et_2O, the extract washed with H_2O, dried ($MgSO_4$), and evaporated, and the crude product purified by CC (silica gel, hexane/AcOEt 10:1): 1.13 g (72%) of **9b**. Orange solid. $[\alpha]_D^{20} = +447.4$ ($c = 1.1$, benzene). ^1H-NMR (C_6D_6): 1.54 (*d*, $J = 6.5$, 3 H); 1.70 (*d*, $J = 6.4$, 3 H); 2.78 (*s*, 3 H); 3.44 (*s*, 3 H); 3.61 (*s*, 5 H); 4.07 (*s*, 5 H); 4.13 (*t*, $J = 2.4$, 1 H); 4.16 (*t*, $J = 2.4$, 1 H); 4.29 (*m*, 1 H); 4.35 (*m*, 1 H); 4.39 (*m*, 1 H); 4.40 (*m*, 1 H); 4.68 (*qd*, $J = 6.5, 2.8$, 1 H); 4.95 (*qd*, $J = 6.4, 2.9$, 1 H); 7.03–7.11 (*m*, 3 H); 7.76–7.79 (*m*, 2 H). ^{13}C-NMR (C_6D_6): 20.04; 20.29; 54.90; 56.33; 68.71 (*d*, $J = 6.2$); 68.91; 69.45 (*d*, $J = 4.1$); 69.81; 70.31; 70.54; 71.40 (*d*, $J = 4.2$); 72.94 (*d*, $J = 5.1$); 73.68 (*d*, $J = 8.3$); 74.12 (*d*, $J = 10.4$); 77.84 (*d*, $J = 16.5$); 80.59 (*d*, $J = 9.3$); 95.12 (*d*, $J = 23.8$); 97.36 (*d*, $J = 32.1$); 128.06 (*d*, $J = 9.3$); 128.95, 135.09 (*d*, $J = 23.8$); 142.39 (*d*, $J = 8.2$). $^{31}P\{^1H\}$-NMR (C_6D_6): -44.27 (*s*). Anal. calc. for $C_{32}H_{35}Fe_2O_2P$: C 64.67, H 5.94; found: C 64.68, H 6.04.

Bis{(R_p*)-2-[(1S)-1-methoxyethyl]ferrocenyl}(4-methoxyphenyl)phosphine* (**9a**): Yield 79%. Orange solid. $[\alpha]_D^{20} = +419.1$ ($c = 1.0$, benzene). ^{1}H-NMR (C_6D_6): 1.59 (d, $J = 6.4$, 3 H); 1.71 (d, $J = 6.3$, 3 H); 2.86 (s, 3 H); 3.24 (s, 3 H); 3.46 (s, 3 H); 3.67 (s, 5 H); 4.08 (s, 5 H); 4.15 (t, $J = 2.3$, 1 H); 4.18 (t, $J = 2.5$, 1 H); 4.31 (m, 1 H); 4.37 (m, 1 H); 4.41 (m, 2 H); 4.72 (qd, $J = 6.5$, 2.8, 1 H); 4.99 (qd, $J = 6.4$, 3.1, 1 H); 6.74 (d, $J = 8.6$, 2 H); 7.72 (dd, $J = 8.5$, 7.9, 2 H). ^{13}C-NMR (C_6D_6): 19.92; 20.58; 55.00; 55.09; 56.36; 68.62 (d, $J = 5.2$); 68.87; 69.32 (d, $J = 4.1$); 69.75; 70.28; 70.54; 71.26 (d, $J = 4.1$); 72.90 (d, $J = 5.2$); 73.69 (d, $J = 9.3$); 74.13 (d, $J = 11.4$); 78.84 (d, $J = 15.5$); 81.18 (d, $J = 8.3$); 95.05 (d, $J = 24.8$); 97.28 (d, $J = 30.0$); 113.71 (d, $J = 9.3$); 133.53 (d, $J = 5.2$); 136.52 (d, $J = 24.8$); 160.84. ^{31}P{^{1}H}-NMR (C_6D_6): -45.98 (s). Anal. calc. for $C_{33}H_{37}Fe_2O_3P$: C 63.46, H 5.88; found: C 63.49, H 5.97.

Bis{(R_p*)-2-[(1S)-1-methoxyethyl]ferrocenyl}[4-(trifluoromethyl)phenyl]phosphine* (**9c**): Yield 86%. Orange solid. $[\alpha]_D^{20} = +414.6$ ($c = 1.0$, benzene). ^{1}H-NMR (C_6D_6): 1.44 (d, $J = 6.3$, 3 H); 1.66 (d, $J = 6.3$, 3 H); 2.73 (s, 3 H); 3.41 (s, 3 H); 3.54 (s, 5 H); 4.04 (s, 5 H); 4.12 (t, $J = 2.5$, 1 H); 4.13 (t, $J = 2.6$, 1 H); 4.16 (m, 1 H); 4.24 (m, 1 H); 4.28 (m, 1 H); 4.38 (m, 1 H); 4.61 (qd, $J = 6.5$, 2.8, 1 H); 4.87 (qd, $J = 6.3$, 2.8, 1 H); 7.33 (d, $J = 8.4$, 2 H); 7.69 (t, $J = 7.6$, 2 H). ^{13}C-NMR (C_6D_6): 19.02; 19.75; 54.57; 56.26; 68.98 (d, $J = 5.2$); 69.04; 69.56 (d, $J = 4.1$); 70.07; 70.31; 70.59; 71.47 (d, $J = 5.2$); 72.78 (d, $J = 5.2$); 73.68 (d, $J = 8.3$); 74.00 (d, $J = 10.3$); 76.14 (d, $J = 15.5$); 80.10 (d, $J = 9.3$); 94.68 (d, $J = 24.8$); 97.22 (d, $J = 31.0$); 124.65 (dq, $J = 7.2$, 4.1); 125.34 (q, $J = 274.1$); 130.63 (q, $J = 34.1$); 135.16 (d, $J = 22.8$); 147.27 (d, $J = 11.4$). ^{31}P{^{1}H}-NMR (C_6D_6): -43.52 (s). Anal. calc. for $C_{33}H_{34}F_3Fe_2O_2P$: C 59.72, H 5.20; found: C 59.85, H 5.17.

Bis{(R_p*)-2-[(1S)-1-methoxyethyl]ferrocenyl}[3,5-bis(trifluoromethyl)phenyl]phosphine* (**9d**): Yield 66%. Orange solid. $[\alpha]_D^{20} = +471.6$ ($c = 1.0$, benzene). ^{1}H-NMR (C_6D_6): 1.38 (d, $J = 6.4$, 3 H); 1.59 (d, $J = 6.4$, 3 H); 2.90 (s, 3 H); 3.44 (s, 3 H); 3.62 (s, 5 H); 4.02 (s, 5 H); 4.07 (t, $J = 2.5$, 1 H); 4.15 (t, $J = 2.6$, 1 H); 4.17 (m, 1 H); 4.22 (m, 1 H); 4.27 (m, 1 H); 4.36 (m, 1 H); 4.68 (qd, $J = 6.5$, 2.7, 1 H); 4.82 (qd, $J = 6.4$, 2.8, 1 H); 7.73 (s, 1 H); 8.43 (d, $J = 6.6$, 2 H). ^{13}C-NMR (C_6D_6): 17.76; 18.89; 54.23; 56.26; 69.10 (d, $J = 6.2$); 69.55; 69.58 (d, $J = 4.1$); 70.25; 70.56; 70.62; 71.20 (d, $J = 5.2$); 72.51 (d, $J = 5.2$); 73.71 (d, $J = 8.3$); 73.88 (d, $J = 10.3$); 75.40 (d, $J = 14.5$); 79.87 (d, $J = 9.3$); 94.32 (d, $J = 24.8$); 97.09 (d, $J = 33.1$); 122.03 (br. s); 124.53 (q, $J = 273.1$); 131.02 (qd, $J = 33.1$, 8.3); 134.50 (br. d, $J = 23.8$); 147.18 (d, $J = 15.5$). ^{31}P{^{1}H}-NMR (C_6D_6): -41.94 (s). Anal. calc. for $C_{34}H_{33}F_6Fe_2O_2P$: C 55.77, H 4.49; found: C 55.92, H 4.55.

3. *Palladium-Catalyzed Asymmetric Hydrosilylation of 1,3-Dienes.* The reaction conditions and results are summarized in the *Table.* A typical procedure is given for *Entry 6:* To a mixture of 1.9 mg (0.0052 mmol) of $[PdCl(\pi\text{-}C_3H_5)]_2$, 14.6 mg (0.02 mmol) of chiral ligand **9d**, and 137 mg (1.00 mmol) of 4-cyclohexylbuta-1,3-diene (**10b**) was added 0.12 ml (1.2 mmol) of trichlorosilane at 20°. The mixture was stirred in a sealed tube at 20° for 26 h, and then bulb-to-bulb distilled *in vacuo* to give 255 mg (94%) of a mixture of *(2*Z*)-1-cyclohexyl-1-(trichlorosilyl)but-2-ene* (**11b**), *(1*E*)-1-cyclohexyl-3-(trichlorosilyl)but-1-ene* (**12b**), and *(2*Z*)-1-cyclohexyl-4-(trichlorosilyl)but-2-ene* (**13b**) in a ratio 92 : 6 : 2.

Data of **11b**: ^{1}H-NMR ($CDCl_3$): 1.06–1.33 (m, 6 H); 1.64 (dd, $J = 7.0$, 1.9, 3 H); 1.60–1.90 (m, 5 H); 2.57 (dd, $J = 11.5$, 4.8, 1 H); 5.35 (ddq, $J = 11.6$, 11.0, 1.9, 1 H); 5.81 (dq, $J = 10.9$, 6.9, 1 H).

Data of **11a**: ^{1}H-NMR: see [8].

4. *Reaction of Allyltrichlorosilanes* **11** *with Benzaldehyde in DMF.* To a soln. of a mixture of allyltrichlorosilanes (0.40 mmol) containing **11** as a major isomer in 1.0 ml of DMF was added benzaldehyde (21 µl, 0.20 mmol), and the mixture was stirred at 0° for 2 h. Sat. aq. $NaHCO_3$ soln. was added to quench the reaction, and the aq. layer was extracted with Et_2O. The extract was dried ($MgSO_4$) and evaporated. The crude product was purified by prep. TLC (silica gel, hexane/AcOEt 4 : 1) to a high yield of homoallyl alcohol **14**.

*(1*R*,2*S*)-(3*E*)-4-Cyclohexyl-2-methyl-1-phenylbut-3-en-1-ol* (**14b**): $[\alpha]_D^{20} = +15.7$ ($c = 1.0$, $CHCl_3$) for 90% ee. ^{1}H-NMR ($CDCl_3$): 0.99 (d, $J = 6.9$, 3 H); 1.02 (m, 2 H); 1.10–1.29 (m, 3 H); 1.60–1.73 (m, 5 H); 1.90 (m, 1 H); 2.05 (br. s, 1 H); 2.47–2.57 (m, 1 H); 4.58 (d, $J = 4.3$, 1 H); 5.27 (dd, $J = 16.2$, 6.9, 1 H); 5.40 (dd, $J = 16.0$, 6.6, 1 H); 7.25–7.30 (m, 3 H); 7.33–7.36 (m, 2 H). ^{13}C-NMR ($CDCl_3$): 14.90; 25.97; 26.10; 33.02; 40.67; 43.72; 77.44; 126.55; 127.11; 127.86; 128.78; 138.12; 142.60. Anal. calc. for $C_{17}H_{24}O$: C 83.55, H 9.90; found: C 83.30, H 9.98.

5. *Oxidation of* **14b** *with* $KMnO_4$ *and* $NaIO_4$. To a soln. of **14b** (133 mg, 0.593 mmol) in 15.0 ml of *tert*-butyl alcohol was added a solution of K_2CO_3 (246 mg, 1.78 mmol) in 10.0 ml of H_2O. A soln. of $NaIO_4$ (1.01 g, 4.72 mmol) and $KMnO_4$ (121 mg, 0.766 mmol) in 10.0 ml of H_2O was added, and the resulting soln. was adjusted to pH 8.5 with 2N NaOH. After stirring for 24 h, *tert*-butyl alcohol was evaporated. The residue was acidified with conc. HCl soln. and 10% aq. $NaHSO_3$ soln. was added to destroy the MnO_2. The soln. was made basic with 2N NaOH. The mixture was extracted with Et_2O and washed with H_2O. The extract was dried ($MgSO_4$) and evaporated. A soln. of the crude acid in Et_2O was treated with diazomethane at 0° for 1 h. AcOH was added to quench excess diazomethane, and the mixture was extracted with Et_2O. The extract was washed with sat. aq.

$NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. Prep. TLC (silica gel, hexane/AcOEt 4:1) gave 32 mg (28%) of *methyl (2*R*,3*R*)-3-hydroxy-2-methyl-3-phenylpropanoate* (**15**) [18]. $[\alpha]_D^{20} = 17.0$ ($c = 1.5$, $CHCl_3$) for 90% ee.

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