Preparation of a New MOP Ligand Containing a Long-Chain Alkyl Group and Its Use for Palladium-Catalyzed Asymmetric Hydrosilylation of Cyclic 1,3-Dienes

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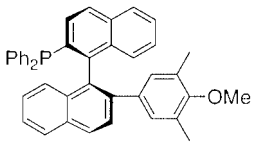
A new MOP ligand containing *n*-octyl group at 6 and 6' positions of (*R*)-2-(diphenylphosphino)-2'-aryl-1,1'-binaphthyl skeleton was prepared and used for palladium-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes with trichlorosilane. By introduction of the *n*-octyl group, the palladium-phosphine catalyst became soluble in the reaction system, realizing high catalytic activity at a low reaction temperature.

Palladium-catalyzed asymmetric hydrosilylation of 1,3-dienes is one of the important synthetic methods for optically active allylsilanes,[1] which are readily transformed to a wide variety of enantiomerically enriched compounds by the reaction with electrophiles in an S_E' fashion.[2] We have recently reported that the palladium-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes such as cyclohexadiene and cyclopentadiene is efficiently catalyzed by palladium complexes coordinated with (*R*)-2-diphenylphosphino-2'-aryl-1,1'-binaphthyls.[3] Thus, for example, the most effective Ar-MOP ligand for this hydrosilylation is (*R*)-2-(diphenylphosphino)-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (**1**), which gave 90% ee of the corresponding allylsilanes. However, the catalytic reactivity is not high enough due to the low solubility of a palladium complex coordinated with the MOP ligand in the reaction media. Although the concept of introducing a long-chain alkyl group to enhance solubility has often appeared in polymer chemistry,[4] there have been few reports in the field of homogeneous asymmetric catalysis.[5] Here we wish to report that appropriate modification of the Ar-MOP ligand by introducing a long-chain alkyl group at 6 and 6' positions leads to the higher catalytic reactivity and enantioselectivity for cyclic 1,3-dienes.



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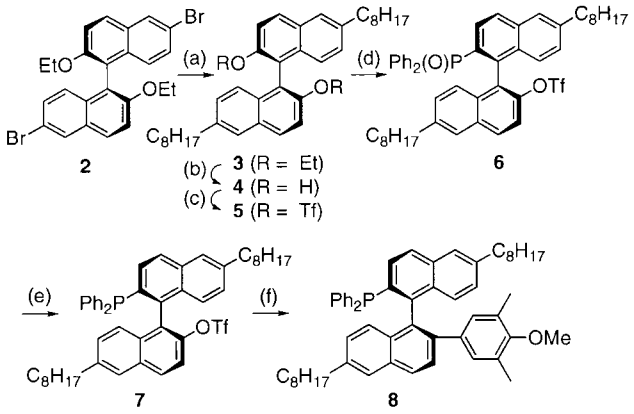
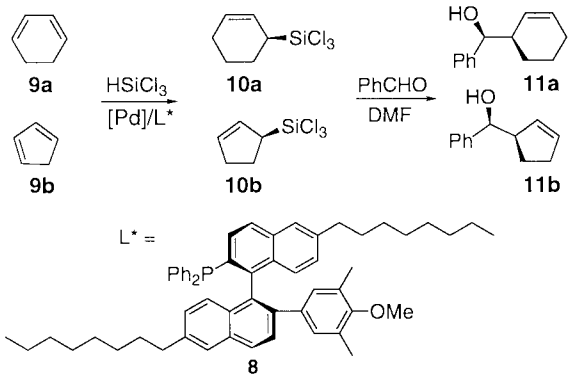
The Ar-MOP ligand which contains *n*-octyl group at 6 and 6' positions of binaphthyl was prepared starting from (*R*)-6,6'-dibromo-2,2'-diethoxy-1,1-binaphthyl (**2**)[6] (Scheme 1). The *n*-octyl group was introduced into binaphthyl skeleton by the palladium-catalyzed cross-coupling reaction of **2** with the *n*-octyl Grignard reagent in the presence of $PdCl_2$(dppf) catalyst[7] in high yield. The *n*-octyl substituted binaphthol **4** was prepared by deprotection of ethyl ether **3** with BBr_3. The binaphthol **4** was converted into (*R*)-2-diphenylphosphino-2'-(3,5-dimethyl-4-methoxyphenyl)-6,6'-dioctyl-1,1'-binaphthyl (**8**) according to the reported procedures.[8] Thus, the selective monophosphinylation of the ditriflate **5**, readily obtained by treatment of **4** with Tf_2O, with diphenylphosphine oxide in the presence of a palladium catalyst at 130 °C gave a high yield of the monophosphinylation product **6**. The reduction of phosphine oxide in **6** with trichlorosilane followed by replacement of the remaining triflate in **7** by 3,5-dimethyl-4-methoxyphenyl group by the nickel-catalyzed Grignard cross-coupling gave the Ar-MOP ligand **8**.[9]



(a) *n*-$C_8H_{17}MgBr$, $PdCl_2$(dppf), ether, 50 °C, 20 h, 91%.
(b) BBr_3, CH_2Cl_2, 12 h, 95%. (c) Tf_2O, py, CH_2Cl_2, 2 h, 95%.
(d) Ph_2POH, $Pd(OAc)_2$, dppb, *i*-Pr_2NEt, DMSO, 130 °C, 18 h, 78%.
(e) $HSiCl_3$, Et_3N, xylene, 100 °C, 12 h, 93%.
(f) 3,5-Me_2-4-$MeOC_6H_2MgBr$, $NiCl_2(PPh_3)_2$, THF, 80 °C, 24 h, 80%.

Scheme 1.

The Ar-MOP containing two *n*-octyl groups at 6 and 6' positions of binaphthyl skeleton **8** thus obtained was examined for its catalytic reactivity and enantioselectivity in the palladium-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes **9** with trichlorosilane (Scheme 2). The hydrosilylation was carried out without solvent in the presence of 0.25 mol% of the palladium catalyst generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with 2 equiv (to palladium) of chiral ligand **8**. The resulting allyl(trichloro)silane was allowed to react with benzaldehyde in DMF according to Kobayashi's procedure[10] to give the homoallylic alcohol, which was subjected to GLC or HPLC analysis with a chiral stationary phase column for the determination of the enantioselectivity. The results are summarized in Table 1, which also contains the data obtained with (*R*)-2-diphenylphosphino-2'-(3,5-dimethyl-4-methoxyphenyl)-1,1'-binaphthyl (**1**) for comparison. In the reaction of 1,3-cyclohexadiene (**9a**), the highest enantioselectivity so far recorded was 79% ee, which was observed with Ar-MOP ligand **1** at 0 °C (entry 1).[3] At a lower temperature, the hydrosilylation of **9a** did not proceed at all even if the reaction time was prolonged, which is due to the insolubility of the palladium catalyst coordinated with ligand **1** in the reaction media consisting of 1,3-cyclohexadiene (**9a**) and trichlorosilane (entry 3). Actually, a considerable amount of off-white precipitates were observed in the reaction flask.[11] On



Scheme 2.

Table 1. Pd-cat. asymmetric hydrosilylation of 1,3-dienes with $HSiCl_3$[a]

Entry	Diene	Ligand	Temp /°C	Time /h	Yield[b] /%	%ee[c]	Config.[d]
1	**9a**	**1**	0	72	75	79	*S*
2	**9a**	**8**	0	72	80	80	*S*
3	**9a**	**1**	−10	168	0	—	—
4	**9a**	**8**	−10	168	70	83	*S*
5	**9b**	**1**	−20	72	89	90	*S*
6	**9b**	**8**	−20	72	86	90	*S*
7	**9b**	**1**	−30	168	0	—	—
8	**9b**	**8**	−30	168	75	91	*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 **1** or **8**. The initial ratio of diene/$HSiCl_3$/Pd/L* was 1.0/1.2/0.0025/0.0050. [b]Isolated yield by bulb-to-bulb distillation. [c]Determined by GLC analysis of alcohol **11a** with a chiral stationary column (CP-Chiralsil-Dex CB) for **10a**. Determined by HPLC analysis of alcohol **11b** with a chiral stationary column (Daicel Chiralpak OB-H) for **10b**. [d]Determined by optical rotation of alcohols **11**.

the other hand, the palladium catalyst of the new ligand **8** became soluble in the reaction media, forming a clear solution even at –10 °C. As a result, the hydrosilylation of **9a** was catalyzed by the palladium/**8** at –10 °C to give (*S*)-3-trichlorosilylcyclohexene (**10a**) of 83% ee, which is the highest value for the reaction of **9a** (entry 4). The enantioselecctivity of the Ar-MOP ligands was not influenced greatly by introduction of the *n*-octyl group, which is shown by the same stereochemical outcome obtained in the hydrosilylation at 0 °C (entries 1 and 2). The highest enantioselectivity was also observed in the hydrosilylation of cyclopentadiene (**9b**) by use of the *n*-octylated MOP ligand **8**. Thus, the reaction of **9b** proceeded at –30 °C in the presence of the palladium/**8** as a catalyst, to give (*S*)-3-trichlorosilylcyclopentene (**10b**) of 91% ee (entry 8). Here again, the reaction with ligand **1** did not take place at the same temperature (entry 7).

In summary, the introduction of two *n*-octyl groups into the Ar-MOP ligand made the palladium catalyst soluble in the hydrosilylation media. The high solubility of the chiral palladium catalyst realized the hydrosilylation at a lower reaction temperature, resulting in the higher enantioselectivity in the asymmetric hydrosilyaltion of 1,3-dienes.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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9 Characterization of compounds: (**3**) colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.1 Hz, 6H), 1.04 (t, *J* = 7.0 Hz, 6H), 1.20–1.43 (m, 20H), 1.62–1.68 (m, 4H), 2.69 (t, *J* = 7.8 Hz, 4H), 3.98–4.03 (m, 4H), 7.04 (s, 4H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.60 (s, 2H), 7.84 (d, *J* = 8.9 Hz, 2H). $[\alpha]^{20}_D$ +0.4 (*c* 1.3, $CHCl_3$). (**4**) colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.1 Hz, 6H), 1.21–1.38 (m, 20H), 1.63–1.69 (m, 4H), 2.71 (t, *J* = 7.8 Hz, 4H), 4.97 (s, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.65 (s, 2H), 7.88 (d, *J* = 9.0 Hz, 2H). $[\alpha]^{20}_D$ –66 °(*c* 1.4, $CHCl_3$). (**5**) colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 6H), 1.21–1.39 (m, 20H), 1.54–1.72 (m, 4H), 2.76 (t, *J* = 7.6 Hz, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 9.1 Hz, 2H), 7.75 (s, 2H), 8.04 (d, *J* = 9.1 Hz, 2H). $[\alpha]^{20}_D$ –108 °(*c* 1.3, $CHCl_3$). (**6**) colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.85–0.89 (m, 6H), 1.19–1.43 (m, 20H), 1.62–1.73 (m, 4H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.20–7.27 (m, 5H), 7.33–7.38 (m, 2H), 7.40–7.48 (m, 4H), 7.57 (s, 1H), 7.62 (dd, *J* = 11.5, 8.6 Hz, 1H), 7.69 (s, 1H), 7.79 (d, *J* = 9.1 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 28.9 (s). $[\alpha]^{20}_D$ +30 °(*c* 1.3, $CHCl_3$). (**7**) colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.84–0.88 (m, 6H), 1.23–1.32 (m, 20H), 1.62–1.73 (m, 4H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.71 (t, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.98–7.01 (m, 2H), 7.05–7.17 (m, 5H), 7.22–7.29 (m, 5H), 7.39 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.47 (d, *J* = 9.3 Hz, 1H), 7.64 (s, 1H), 7.67 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 9.3 Hz, 1H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –12.07 (s). $[\alpha]^{20}_D$ –11 °(*c* 1.3, $CHCl_3$). (**8**) colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.85–0.90 (m, 6H), 1.20–1.33 (m, 20H), 1.64–1.69 (m, 4H), 1.83 (s, 6H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 3.60 (s, 3H), 6.61 (s, 2H), 6.66 (t, *J* = 7.1 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 2H), 7.01–7.23 (m, 8H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.66 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –14.20 (s). FAB MS *m/z* (M^+ + H) Calcd for $C_{57}H_{66}OP$: 797.48 Found: 797.51. $[\alpha]^{20}_D$ +130 ° (*c* 0.3, $CHCl_3$).

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11 Use of polar solvents such as dichloromethane makes the reaction mixture homogeneous, but the hydrosilylation is slow in the polar solvents.