Palladium-Catalyzed Reactions, 1

Palladium-Catalyzed Enantioselective Hydrophenylation and Hydrohetarylation of Bicyclo[2.2.1]hept-2-ene: Influence of the Chiral Ligand, the Leaving Group, and the Solvent

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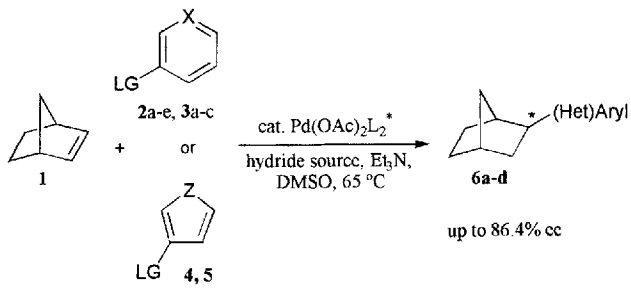
The use of optically active biaryl bisphosphanes **10**−**12**, a diphenylphosphanylphenyloxazoline **8**, and a (β-*N*-sulfonylaminomethyl)bisdiphenylphosphane **7** as ligands in the Pd-catalyzed Heck-type hydroarylation of norbornene (**1**) with phenyl **2** and various hetaryl derivatives **3**−**5** leads exclusively to the formation of exo-2-(het)arylnorbornanes **6** with asymmetric inductions of up to 86.4% ee. In addition to an investigation into the effects of different chiral ligands, a systematic study has been made of the influence of various (het)aryl compounds, leaving groups, and solvents on the chemical and optical yields of this reductive arylation.

Enantioselective C−C bond formation mediated by optically pure transition metal complexes is one of the most important goals in contemporary synthetic chemistry. The palladium-catalyzed arylation and alkenylation of olefins, known as the Heck reaction[1], was first performed enantioselectively in 1989, independently by Shibasaki[2] and Overman[3]. In this way, optically enriched compounds were generated by intramolecular cyclization. In 1991, Hayashi[4] obtained optically active arylated dihydrofurans via an intermolecular asymmetric Heck reaction. In the same year, Brunner[5] reported the formation of optically enriched *exo*-2-arylnorbornanes from norbornene and norbornadiene with iodobenzene and various substituted phenyl iodides via the reductive variant of the Heck arylation[6] using palladium(II) acetate and different chiral bisphosphanes as catalysts. In the case of norbornene, the enantiomeric excess reached a maximum of 37.7%. To the best of our knowledge, there have not been any reports where a better enantioselectivity than this was obtained with chiral directing bisphosphanes in this kind of hydroarylation of bicyclic alkenes. However, using the new P−N ligand (*S*)-Ms-Valphos (**7**), Achiwa[7] achieved a further marked increase in optical induction in the hydrophenylation of norbornene. By varying the organic base, enantiomeric yields ranging from 67.9−73.6% ee were obtained.

Results and Discussion

In view of the fact that no detailed studies of the asymmetrical hydroarylation of bicyclic alkenes have been reported, except with regard to the effect of different organic bases, in our present investigation we have carried out a systematic study of the influence of the chiral ligand, the leaving group, and of the solvent. We used norbornene as the bicyclic alkene substrate because of its availability, and also to allow comparison with the work of Brunner and Achiwa. Furthermore, it is of interest to note that certain 2-phenyl-substituted norbornane derivatives show activity against Parkinsonism[8].

Scheme 1



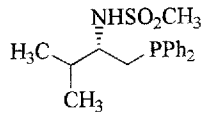
2: X = C; LG = OTf (**a**), ONf (**b**), I (**c**), Br (**d**), I(OAc)$_2$ (**e**); **3**: X = N; LG = OTf (**a**), ONf (**b**), Br (**c**); **4**: 3-bromothiophene; **5**: 3-bromofuran. For deviations from noted conditions see Table 1.

Effect of the Chiral Ligand

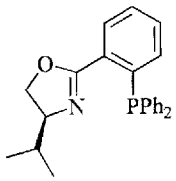
In the course of our studies, we screened both well-known and recently developed phosphanes: the aforementioned amino acid based (*S*)-Ms-Valphos (**7**), a phosphanylaryloxazoline **8**, recently reported by Helmchen[9], Pfaltz[10], and Frost and Williams[11], commercially available (*S*,*S*)-Chiraphos (**9**), and three axially chiral bisphosphanes, the dibenzofuran derivative (*S*)-BIBFUP[12] (**10**), (*R*)-MeO-

BIPHEP[13,14] (**11**), and Noyori's "classical" (*S*)-BINAP[15] (**12**) (Scheme 2 and Table 1).

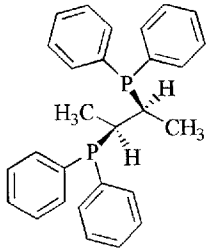
Scheme 2



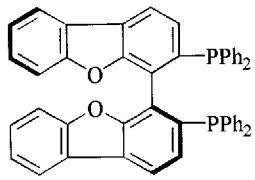
(S)-Ms-Valphos
(**7**)



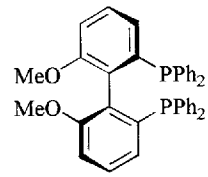
(S)-2-(2-Diphenyl-phosphinophenyl)-4-isopropyl-oxazoline
(**8**)



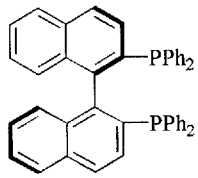
(S,S)-Chiraphos
(**9**)



(S)-BIBFUP
(**10**)



(R)-MeO-BIPHEP
(**11**)



(R)-BINAP
(**12**)

Surprisingly, the palladium-BINAP catalyst that gave an enantiomeric excess of 93% in the hydroalkenylation of norbornene, as reported by Ozawa and Hayashi[16], yielded only very moderate results in the reductive phenylation of the bicyclic alkene, giving enantiomeric excesses of 15% or less. Therefore, for the first time, we also tested the atropisomeric ligands **10** and **11**, which possess a more polar biaryl skeleton of different steric demand. Indeed, use of the axially chiral (*S*)-BIBFUP (**10**) and (*R*)-MeO-BIBHEP (**11**) led to an increase in enantiomeric excess, up to 29% and 35%, respectively. Use of the symmetrical aliphatic bisphosphane (*S,S*)-Chiraphos (**9**) led to an enantioselectivity of about 25% ee. Apparently, the degree of asymmetric induction cannot be improved further, merely by varying the steric and electronic properties of the biphosphane ligands. Therefore, we focussed our attention on unsymmetrical bisdentate ligands with donor groups of different donating ability. The best optical inductions, obtained by varying only the chiral ligand, were achieved with the valine-based P–N ligands: the oxazoline phosphane **8** and (*S*)-Ms-Valphos (**7**) (Scheme 2). The latter facilitated asymmetric hydrophenylation with up to 86.4% ee. Depending on the leaving group and the solvent, chemical yields ranging from 27–82% were obtained. Other ligands with various skeletons and different donor groups, somewhat modified with an appropriate substituent at the nucleophilic center, are currently under investigation. Unless noted otherwise, the following results refer to the ligand (*S*)-Ms-Valphos.

Effects of the Leaving Group and the Solvent

A very promising line of investigation was an examination of the influence of various leaving groups (see Scheme 1 and Table 1). Thus, besides arylhalides, i.e. bromides and iodides, experiments were also conducted with sulfonates. Furthermore, we tested the applicability of two alternative leaving groups that have not hitherto been employed in the field of hydroarylations – diazonium and iodonium functions. Both aryldiazonium salts and aryliodonium compounds have already proved to be useful starting materials in Heck reactions[17,18]. With phenyldiazonium tetrafluoroborate, besides biphenyl only trace amounts of the desired product were obtained, but using phenyliodonium diacetate (**2e**), a maximum product yield of 82% was achieved. Unfortunately, in this case the usually efficient ligand (*S*)-Ms-Valphos gave only poor optical yields (entry 17). It is very striking that on changing the leaving group from iodide to triflate, the enantiomeric yield was improved from 42.6% to 82.4%. The best enantioselectivities, both among the sulfonates and in general, were obtained with arylnonaflates, which were prepared from the corresponding alcohols[19]. Phenylnonaflate (**2b**) provided the highest enantiomeric excess with up to 86.4% ee (entry 11, Table 1). Further investigations need to be carried out in order to account for the improved optical yield obtained using bromobenzene (**2d**) compared to those achieved with iodobenzene (**2c**).

Considering the choice of solvent, dimethyl sulfoxide and, in a few cases tested, tetrahydrofuran, proved to be the best reaction media, with rapid conversion of the starting materials (usually 2–14 hours) and the highest ee values. Using dimethyl sulfoxide, propylene carbonate, tetrahydrofuran or dimethylformamide, we obtained comparable chemical and enantiomeric yields with phenyl triflate (**2a**) as the aromatic substrate (entries 1–4, Table 1), but with iodobenzene (**2c**) in DMF, the enantioselectivity was drastically decreased (entry 16). The use of 1,2-dichloroethane and phenyl triflate also resulted in a marked drop in the chemical and optical yields. A point worthy of note is that the replacement of triethylamine in our system by other organic bases, e.g. piperidine or Proton sponge, did not significantly affect the chemical yields or the degree of asymmetric induction.

Variation of the Aryl Compound

To explore the scope of this hydroarylation reaction (Scheme 1), we have for the first time extended its application to a number of heteroaromatic compounds. Thus, experiments were performed with the 3-pyridyl derivatives **3a–c**, and the bromides of the activated heteroaromatics thiophene **4** and furan **5**. The new hetarylnorbornanes **6c, d** were obtained from the commercially available 3-bromoaryl compounds **4**, **5** in acceptable chemical (39 and 40%) and

Table 1. Hydroarylation of norbornene

Entry	Product	Aryl compound	Chiral ligand	Conditions	Time [h]	Conv. [%]	Yield[c] [%]	% ee[d]
1	**6a**		7	[a]	2	100	37	80.9–82.4
2	**6a**		7	[a](DMF)	10	100	31	79.3
3	**6a**		7	[a](PC)	12	100	27	78.7
4	**6a**		7	[a](THF)	16	100	44	79.5
5	**6a**	phenyl triflate (**2a**)	7	[b]	24	20	13	77.7
6	**6a**		8	[a]	14	100	12	71.2
7	**6a**		9	[a]	14	100	58	23.7–24.8
8	**6a**		10	[a]	36	80	18	26.2–28.7
9	**6a**		11	[a]	12	100	17	34.5
10	**6a**		12	[a]	12	100	9	7.6–11.4
11	**6a**	phenyl nonaflate (**2b**)	7	[a]	4	100	47	80.2–86.4
12	**6a**	phenyl nonaflate (**2b**)	7	[a](THF)	12	100	41	78.6
13	**6a**	iodobenzene (**2c**)	7	[a]	12	100	55	42.6
14	**6a**	iodobenzene (**2c**)	8	[a]	10	100	16	46.9–49.5
15	**6a**	iodobenzene (**2c**)	12	[a]	18	100	23	14.8
16	**6a**	iodobenzene (**2c**)	12	[a](DMF)	12	100	51	6.4–8.2
17	**6a**	$PhI(OAc)_2$ (**2e**)	7	[a](HCOOK)	12	100	82	7.7
18	**6b**	3-pyridyl nonaflate (**3b**)	7	[a]	16	100	11	55.5
19	**6b**	3-pyridyl triflate (**3a**)	7	[a]	18	100	17	54.3–56.4
20	**6a**	bromobenzene (**2d**)	7	[a]	12	100	37	48.4–50.6
21	**6b**	3-bromopyridine (**3c**)	7	[a]	12	100	23	26.4
22	**6c**	3-bromothiophene (**4**)	7	[a]	11	100	40	61.6
23	**6d**	3-bromofuran (**5**)	7	[a]	12	100	39	46.4

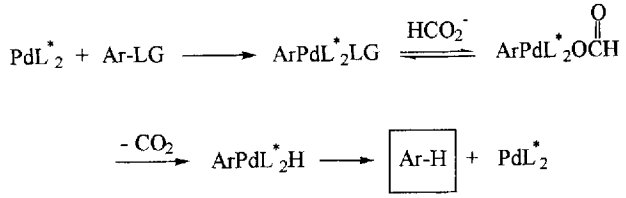
[a] Solvent: dimethyl sulfoxide (DMSO), hydride source: formic acid; possible variations are noted: dimethylformamide (DMF), propylene carbonate (PC), tetrahydrofuran (THF). – [b] Solvent: DMSO, hydride source: polymethylenehydrogensilane (PMHS). – [c] Chemical yields refer to isolated products. – [d] Optical yields determined by chiral GC (see Experimental Section).

optical yields (46–62% ee). In the case of 3-bromopyridine (**3c**), the enantioselectivity was moderate (26.4% ee), but by changing the leaving group to sulfonate **3a**, **b**, the enantiomeric excess of the resulting 2-(3′-pyridyl)norbornane (**6b**) was as high as 56.4% (entry 19).

An Undesirable Side-Reaction

As noted above, the highest chemical yield (82%) was obtained with phenyliodonium diacetate (**2e**). However, the product yields were more typically in the range 30–60%, even though the starting material was completely consumed. It is known that a competing reaction pathway can proceed under comparable conditions, i.e. that reductive dehalogenation (hydrodehalogenation) of the arylhalides[20], or reduction of the sulfonates[21], respectively, with loss of the leaving group (Scheme 3). The only difference between the reaction conditions of the desired hydroarylation and the undesirable side-reaction is the requirement for the presence of an alkene in the first case. Attempts to improve the chemical yield of the arylnorbornane by increasing the molar ratio aryl compound/alkene have hitherto been unsuccessful. The reduced aryl compounds were identified by GC retention times and by ^{1}H-NMR spectroscopy. This reduction seems to be favoured if the ligand has decreased donor properties, as in the case of the double-bonded nitrogen atom in the oxazoline **8** (see entry 6: 71.2% ee, but only 12% chem. yield), or if the aryl compound is electron-deficient, as in the case of the pyridine derivative **6b** (entries 18, 19).

Scheme 3



To overcome this reduction problem, we tried to find a more selective hydride source than formic acid or potassium formate. First attempts with polymethylenehydrogensilane (PMHS) gave nearly identical ee values, but did not produce higher chemical yields due to incomplete conversion[22] (20% conv., 13% chem. yield; Table 1, entry 5). Therefore, it is our intention to test other silanes as well as PMHS under modified reaction conditions, e.g. with an additional phase-transfer catalyst. Another approach to suppress the unwanted reduction pathway might be a further search for alternative solvents.

In conclusion, by testing the directing ability of structurally different chiral ligands, varying the reagents and reaction conditions, and focussing on alternative leaving groups, we have obtained several (het)arylnorbornanes from the hydroarylation of norbornene, with enantiomeric excesses up

to 86.4% ee, in acceptable to good chemical yields. Best enantioselectivities have been achieved in dimethyl sulfoxide with (het)arylnonaflates and the aminophosphane (*S*)-Ms-Valphos as the chiral directing ligand. In general, P−N ligands have proved to lead to a higher degree of asymmetric induction than bisphosphanes.

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Experimental Section

All reactions were carried out under dry nitrogen by using standard Schlenk techniques. All solvents were carefully dried by standard procedures (tetrahydrofuran with Na/K alloy, diethyl ether with sodium, dimethylformamide with calcium hydride). Triethylamine was dried with calcium hydride, and potassium formate was dried in vacuo before use. Trifluoromethanesulfonates (triflates) were prepared by standard procedures from the corresponding alcohols and triflic anhydride; nonafluorobutanesulfonates were synthesized by reaction of the sodium salts of the aromatic alcohols with nonafluorobutanesulfonyl fluoride in diethyl ether or ether/tetrahydrofuran in case of 3-hydroxypyridine, in analogy to a literature procedure[19]. Phenyliodonium diacetate was prepared from iodobenzene and peracetic acid in acetic acid[23]. Other reagents and catalysts are commercially available or were obtained as free samples, and were used as received. − NMR: Bruker AMX 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) with $CDCl_3$ as solvent and TMS as internal standard. − Enantioselectivities were determined by chiral GC, using a 25-m capillary column coated with either heptakis-(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin or oktakis-(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin.

Hydroarylation Reactions − General Procedure: 5.6 mg (25 μmol) of palladium(II) acetate and 55 μmol of the chiral ligand were dissolved in 1.5 ml of dry dimethyl sulfoxide and the solution was stirred at 65°C for 15 min. Then, 127 mg (1.35 mmol) norbornene, 1.00 mmol of the aryl compound, 488 μl (3.50 mmol) of triethylamine, and 3.00 mmol of the hydride source were added rapidly in one portion. After stirring until conversion was complete (see Table 1 for reaction times), all products **6a−d** could be isolated directly from the reaction mixtures by flash column chromatography (SiO_2, 40−63 μm; Machercy-Nagel, Düren, Germany). Selected data for **6a** and characterization of the new products **6b−d**.

2-Phenylnorbornane (**6a**): Colorless oil; R_f = 0.69 (SiO_2, petroleum ether). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15−1.39 (m, 3H), 1.51−1.81 (m, 5H), 2.32−2.39 (m, 2H), 2.74 (dd, *J* = 8.7, 5.7 Hz, 1H, 2-H_{endo}), 7.11−7.31 (m, 5H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9 (−), 30.6 (−), 36.1 (−), 36.8 (+), 39.1 (−), 42.9 (+), 47.3 (+), 125.3 (+), 127.0 (+), 128.2 (+) and 147.6 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 172 (41) [M^+], 144 (13) [$M^+ - C_2H_4$], 129 (14) [$M^+ - C_3H_7$], 115 (20) [$M^+ - C_4H_9$], 104 (100) [$PhCH{=}CH_2^+$], 95 (13) [$M^+ - C_6H_5$].

2-(3′-Pyridiyl)norbornane (**6b**): Colorless oil; R_f = 0.35 (SiO_2; petroleum ether/AcOEt, 7:1). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20−1.42 (m, 3H), 1.47−1.67 (m, 4H), 1.76−1.84 (m, 1H), 2.36 and 2.38 (s, 2H, 1,4-H), 2.74 (dd, *J* = 8.7, 5.7 Hz, 1H, 2-H_{endo}), 7.18 (dd, *J* = 8.1, 4.7 Hz, 1H, 4′-$H_{pyridyl}$), 7.50 (d, *J* = 7.6 Hz, 1H, 5′-$H_{pyridyl}$), 8.39 (dd, *J* = 4.7, 1.7 Hz, 1H, 6′-$H_{pyridyl}$), 8.48 (d, *J* = 1.7 Hz, 1H, 2′-$H_{pyridyl}$). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7 (−), 30.5 (−), 36.0 (−), 36.8 (+), 38.8 (−), 42.7 (+), 44.9 (+), 123.1 (+, $C_{pyridyl}$-5′), 134.1 (+, $C_{pyridyl}$-4′), 142.5 ($C_{quat.}$, $C_{pyridyl}$-3′), 146.8 (+, $C_{pyridyl}$-6′), 149.3 (+, $C_{pyridyl}$-2′). − MS (70 eV); *m/z* (%): 173 (5) [M^+], 144 (35), 130 (12) [$M^+ - C_3H_7$], 117 (15), 106 (100) [$PyC_2H_4^+$]. − HRMS: $C_{12}H_{15}N$: calcd. 173.1204; found 173.1204.

2-(3′-Thienyl)norbornane (**6c**): Colorless oil; R_f = 0.65 (SiO_2, petroleum ether). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13−1.37 (m, 3H), 1.42−1.76 (m, 5H), 2.32 ('s', 2H, 1,4-H), 2.75 (dd, *J* = 8.5, 5.5 Hz, 1H, 2-H_{endo}), 6.88 (m, 1H, 2′-$H_{thienyl}$), 6.94 (d, *J* = 5.1 Hz, 1H, 4′-$H_{thienyl}$), 7.20−7.24 (m, 1H, 5′-$H_{thienyl}$). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9 (−), 30.0 (−), 35.9 (−), 36.7 (+), 38.8 (−), 43.1 (+), 43.1 (+), 118.2 (+, C_{aryl}-2′), 125.1 (+, C_{aryl}-5′), 127.9 (+, C_{aryl}-4′), 148.8 ($C_{quat.}$, C_{aryl}-3′). − MS (70 eV); *m/z* (%): 178 (46) [M^+], 135 (12) [$M^+ - C_3H_7$], 110 (51) [$ArCH{=}CH_2^+$], 98 (100) [$ArCH_3^+$]. − HRMS: $C_{11}H_{14}S$: calcd. 178.0816; found 178.0816.

2-(3′-Furyl)norbornane (**6d**): Colorless oil; R_f = 0.51 (SiO_2, petroleum ether). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12−1.18 (m, 1H), 1.19−1.35 (m, 2H), 1.39−1.45 (m, 1H), 1.46−1.63 (m, 3H), 1.64−1.72 (m, 1H), 2.22 and 2.30 ('s', 2H, 1,4-H), 2.55 (dd, *J* = 8.5, 4.9 Hz, 1H, 2-H_{endo}), 6.26 (s, 1H, 4′-H_{furyl}), 7.16 (s, 1H, 2′-H_{furyl}), 7.28−7.35 (m, 1H, 5′-H_{furyl}). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9 (−), 29.8 (−), 35.8 (−), 36.5 (+), 38.3 (−), 38.4 (+), 43.0 (+), 110.5 (+, C_{aryl}-4′), 131.4 ($C_{quat.}$, C_{aryl}-3′), 137.9 (+, C_{aryl}-2′), 142.7 (+, C_{aryl}-5′). − MS (70 eV); *m/z* (%): 162 (46) [M^+], 119 (7) [$M^+ - C_3H_7$], 105 (9) [$M^+ - C_4H_9$], 94 (71) [$ArCH{=}CH_2^+$], 82 (100) [$ArCH_3^+$]. − HRMS: $C_{11}H_{14}O$: calcd. 162.1045; found 162.1045.

[1] [1a] R. F. Heck, J. P. Nolley, Jr., *J. Org. Chem.* **1972**, *37*, 2320−2322. − [1b] R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146−151. − [1c] R. F. Heck, *Org. React.* **1982**, *27*, 345−390. − [1d] A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473−2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379−2411.
[2] Y. Sato, M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1989**, *54*, 4738−4739.
[3] N. E. Carpenter, D. J. Kucera, L. E. Overman, *J. Org. Chem.* **1989**, *54*, 5846−5848.
[4] [4a] F. Ozawa, A. Kubo, T. Hayashi, *J. Am. Chem. Soc.* **1991**, *113*, 1417−1419. − [4b] F. Ozawa, A. Kubo, T. Hayashi, *Tetrahedron Lett.* **1992**, *33*, 1485−1488. − [4c] F. Ozawa, A. Kubo, T. Hayashi, *Pure & Appl. Chem.* **1992**, *64*, 421−427. − [4d] F. Ozawa, Y. Matsumoto, T. Hayashi, *Organometallics* **1993**, *12*, 4188−4196.
[5] H. Brunner, K. Kramler, *Synthesis* **1991**, 1121−1124.
[6] [6a] A. Arcadi, F. Marinelli, S. Cacchi, E. Bernocchi, G. Ortar, *J. Organomet. Chem.* **1989**, *368*, 249−256. − [6b] R. C. Larock, P. L. Johnson, *J. Chem. Soc., Chem. Commun.* **1989**, 1368−1370.
[7] S. Sakuraba, T. Okada, T. Morimoto, K. Achiwa, *Chem. Pharm. Bull.* **1995**, *43*, 927−933.
[8] H.-P. Bächtold, A. Fürst, Th. Struller, H. Kreiskott, *Ullmanns Encyclopädie der technischen Chemie (W. Foerst) 4th ed.* **1980**, vol. 21, p. 628.
[9] [9a] J. Sprinz, G. Helmchen, *Tetrahedron Lett.* **1993**, *34*, 1769−1772. − [9b] M. Peer, J. C. de Long, M. Kiefer, T. Langer, H. Rieck, H. Schell, P. Sennhenn, J. Sprinz, H. Steinhagen, B. Wiese, G. Helmchen, *Tetrahedron* **1996**, *52*, 7547−7583 and refs. cited therein.
[10] O. Loiseleur, P. Meier, A. Pfaltz, *Angew. Chem.* **1996**, *108*, 218−220; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 200−202.
[11] G. J. Dawson, C. G. Frost, J. M. J. Williams, *Tetrahedron Lett.* **1993**, *34*, 3149−3150.
[12] Chr. Laue, G. Schroeder, D. Arlt, R. Grosser (Bayer AG), EP 643.065, **1995** [*Chem. Abstr.* **1995**, *123*, 112406b].
[13] [13a] R. Schmid, J. Foricher, M. Cereghetti, P. Schönholzer, *Helv. Chim. Acta* **1991**, *74*, 370−389. − [13b] R. Schmid, E. A. Broger,

M. Cereghetti, Y. Crameri, J. Foricher, M. Lalonde, R. K. Müller, M. Scalone, G. Schoettel, U. Zutter, *Pure & Appl. Chem.* **1996**, *68*, 131–138.
[14] We acknowledge Dr. R. Schmid of Hoffman-La Roche, Switzerland, for a free sample of this axially chiral phosphane.
[15] A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934.
[16] F. Ozawa, Y. Kobatake, A. Kubo, T. Hayashi, *J. Chem. Soc., Chem. Commun.* **1994**, 1323–1324.
[17] [17a] K. Kikukawa, K. Nagira, N. Terao, K. Wada, T. Matsuda, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2609–2610. – [17b] M. Beller, K. Kühlein, *Synlett* **1995**, 441–442 and refs. cited therein.
[18] For example see: [18a] M. Ochiai, K. Sumi, Y. Takaoda, M. Kunishima, Y. Nagao, M. Shiro, E. Fujita, *Tetrahedron* **1988**, *44*, 4095–4112. – [18b] R. M. Moriarty, W. R. Epa, A. K. Awasthi, *J. Am. Chem. Soc.* **1991**, *113*, 6315–6317. – [18c] Y. Kurihara, M. Sodeoka, M. Shibasaki, *Chem. Pharm. Bull.* **1994**, *42*, 2357–2359. – For a review see: [18d] P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123–1178.
[19] L. R. Subramanian, H. Bentz, M. Hanack, *Synthesis* **1973**, 293–294.
[20] N. A. Cortese, R. F. Heck, *J. Org. Chem.* **1977**, *42*, 3491–3494.
[21] [21a] Q.-Y. Chen, Y.-B. He, Z.-Y. Yang, *Tetrahedron Lett.* **1986**, *27*, 1452–1453. – [21b] S. Cacchi, P. G. Ciattini, E. Morera, G. Ortar, *Tetrahedron Lett.* **1986**, *27*, 5541–5544.
[22] The reaction mixture was inhomogenous after 24 hours and showed rubber-like PMHS.
[23] J. G. Sharefkin, H. Saltzman, J. Diekmann, B. C. McKusick, *Org. Synth.* **1963**, *43*, 62–65.

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