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BINOL derived monodentate acylphosphite ligands for homogeneously catalyzed enantioselective hydrogenation

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Abstract—Enantiopure acylphosphites have been prepared based upon chiral nonsubstituted and 3,3′-disubstituted binaphthols in order to elucidate steric and electronic effects on the Rh(I)-catalyzed asymmetric hydrogenation of functionalized olefins. With these new types of ligands, up to 80% ee was obtained. Rate as well as enantioselectivity of the hydrogenation were strongly dependent on the precatalyst preparation and substitution pattern of the ligand.

1. Introduction

Asymmetric homogeneous catalysis with transitions metal complexes has made considerable progress over the last 30 years. Several approaches, which have focused on the development of new and more efficient chiral ligands, have resulted in remarkable achievements, for example, in the enantioselective hydrogenation of prochiral olefins, imines, and ketones.[1] To date, hydrogenation is probably the most important enantioselective homogeneously catalyzed process in industry.[2] Until recently, most efforts have concentrated on the employment of chiral bidentate P-ligands. However, in recent years, monodentate ligands have also been reported to be highly efficient and stereoselective.[3] Interestingly, the majority of monodentate ligands reported up to now bear a 1,1′-substituted binaphthyl backbone.[4] In particular, complexes that have been based on ligands easily derived from enantiopure nonsubstituted BINOL such as phosphites,[5] phosphonites,[6] and phosphoramidites[7] have been shown to be highly effective in the hydrogenation of different types of substrates. Apparently the BINOL backbone is pivotal for the stereo-discriminating abilities of the catalysts. In contrast, the effect of a third substituent at the phosphorus atom is less clear.

Recently, we introduced bis-acylphosphites as a new type of bidentate ligands in homogeneous catalysis.[8] These organophosphorus compounds contain a P–O–C(O) fragment and have been known for many years. In spite of this fact their potential as ligands for homogeneous catalysis remains surprisingly unexplored. The first use of acylphosphites in Rh-catalyzed *n*-regioselective hydroformylation of olefins gave promising results and prompted us to broaden the range of the ligands and their catalytic applications. Herein we report a straightforward synthesis of chiral BINOL-derived acylphosphite ligands. The main aim of our investigations is to assess the effect of acyl groups on the enantioselective hydrogenation of functionalized olefins. Moreover, we are interested in clarifying the role of substituents in 3,3′-positions of the binaphthyl moiety.

2. Results and discussion

The new ligands **3a**–**f** were obtained from nonsubstituted or 3,3′-disubstituted (*R*)-BINOL in two steps (Scheme 1). Thus, treatment of chlorophosphites **2**, easily derived from BINOLs by condensation with PCl_3, with sodium carboxylates afforded analytically pure acylphosphites **3** in more than 80% yield. It is

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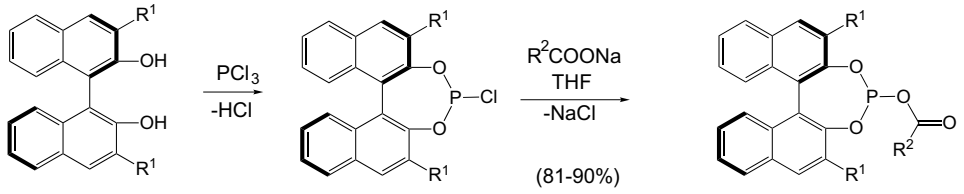

1a (R^1 = H)
1b (R^1 = Br)
1c (R^1 = Me)
1d (R^1 = Ph)
1e (R^1 = $SiMe_3$)

2a-e

3a (R^1 = H, R^2 = Me)
3b (R^1 = H, R^2 = Ph)
3c (R^1 = Br, R^2 = Ph)
3d (R^1 = Me, R^2 = Ph)
3e (R^1 = Ph, R^2 = Ph)
3f (R^1 = $SiMe_3$, R^2 = Ph)

Scheme 1.

noteworthy that preliminary attempts to react **2a** with the corresponding triethylammonium carboxylates gave crude **3a** and **b** contaminated by varying amounts of byproducts, which could not be removed by standard purification procedures. In general, acylphosphites of type **3** were white crystalline compounds, which were reasonably soluble in common non-protic solvents and stable under dry conditions.

All attempts to synthesize bis-acylphosphites via the reaction of sodium oxalate or the dipotassium salt of phthalic acid with 2 equiv. chlorophosphite **2** failed to give the desired product, under these conditions pyrophosphites were obtained.[9]

Rhodium precatalysts $[Rh(COD)L_2]BF_4$ were prepared by the reaction of $[Rh(COD)_2]BF_4$ with two equivalents of the ligand in CH_2Cl_2. Using **3a** and **b** only doublets characterizing the desired complexes were found in the ^{31}P NMR spectra of the reaction solutions (**3a**: δ 132.1, $^1J = 258.0$ Hz; **3b**: δ 133.1, $^1J = 258.0$ Hz). $[Rh(COD)(\mathbf{3b})_2]BF_4$ could be isolated as a pure material, while the solid complex based on ligand **3a** contained significant amounts of byproducts. Complexation of **3c** and **d** with $[Rh(COD)_2]BF_4$ proceeded analogously to ligand **3a** (^{31}P NMR, **3c**: δ 120.5, $^1J = 267.7$ Hz; **3d**: δ 126.0, $^1J = 259.4$ Hz). When the solid products were isolated and subsequently subjected to ^{31}P NMR spectroscopy, complex mixtures were observed. In contrast to **3a**–**d**, ligands **3e** and **f** bearing bulky 3,3′-substituents, reacted with $[Rh(COD)_2]BF_4$ unselectively and gave mixtures of rhodium complexes already in CH_2Cl_2 reaction solution.

The new ligands were tested in the Rh-catalyzed hydrogenation of common benchmark substrates, namely methyl α-acetylaminocinnamate (AMe) and dimethyl itaconate ($ItMe_2$). Precatalysts were generated in situ or isolated prior to use. The results are summarized in Table 1.

As can be seen from Table 1, the rate of the reaction and the enantioselectivity were strongly dependent on the solvent, the substitution pattern of the ligand and the preparation method of the precatalyst employed. Enantioselectivities in the broad range of 1–80% ee were observed. In general, enantioselectivities were inferior in comparison to those reported with monodentate phosphites or phosphoamidites as ligands.[5,7] Apparently, the strong electron-withdrawing acyl group has a disadvantageous influence on the outcome of the reaction. Moreover, any additional substituent in 3,3′-positions of the BINOL-framework decreased the activity of the catalyst in comparison to the parent complex. No beneficial effect on the enantioselectivity was achieved due to this increase of the bulk so close to the rhodium center.

An interesting issue in the use of monodentate BINOL-derived P-ligands in Rh-catalyzed hydrogenation is the results observed due to the variation of the ligand/rhodium ratio. Reetz et al. noted the same catalytic performance in the hydrogenation of $ItMe_2$ with a monophosphite-Rh-complex using 1, 2, or 4 equivalents of the ligand with respect to rhodium.[5a] In contrast, Feringa et al. showed that the L/Rh ratio in the case of phosphoramidites strongly influenced the rate of the olefin hydrogenation.[7d] Thus, the hydrogen consumption ceased when the L/Rh ratio was increased to 3/1. In contrast, an increase in rate was observed when the ratio was lowered to 1.5/1. Remarkably, for both monophosphites and phosphoramidites, the ee remained the same when less than 2 equivalents of the ligand were used.

We studied the influence of the L/Rh ratio on the example of acylphosphites **3a** and **b** (Table 2). Increasing the **3b**/Rh ratio to 4/1 decelerated the hydrogenation of both AMe and $ItMe_2$ (entries 8 and 16). Apparently, acylphosphites have more in common with phosphoramidites than with phosphites. One more analogy with phosphoramidites is that lowering the L/Rh ratio resulted in an enhanced reaction rate. However, in contrast to the use of phosphoramidites, the ee was lowered in comparison to the results obtained with the ligand/Rh ratio equal to 2/1.

3. Conclusion

In conclusion, several chiral acylphosphites were obtained for the first time by a simple two-step synthe-

Table 1. Rh(I)-catalyzed hydrogenation of prochiral olefins

Run	Substrate	Ligand	Solvent	Time (min)	Conversion (%)	Ee (%)
1	AMe	**3a**[a]	CH_2Cl_2	180	100	50 (*S*)
2	AMe	**3a**	CH_2Cl_2	60	100	18 (*S*)
3	AMe	**3b**[a]	CH_2Cl_2	180	100	52 (*S*)
4	AMe	**3b**	CH_2Cl_2	130	100	44 (*S*)
5	AMe	**3b**	THF	60	100	4 (*S*)
6	AMe	**3b**	CH_3OH	8	100	37 (*S*)
7	AMe	**3b**	Toluene	50	100	75 (*S*)
8	AMe	**3b**	EtOAc	90	100	24 (*S*)
9	$ItMe_2$	**3a**[a]	CH_2Cl_2	130	100	67 (*R*)
10	$ItMe_2$	**3a**	CH_2Cl_2	55	100	55 (*R*)
11	$ItMe_2$	**3b**[a]	CH_2Cl_2	100	100	80 (*R*)
12	$ItMe_2$	**3b**	CH_2Cl_2	45	100	74 (*R*)
13	$ItMe_2$	**3b**	THF	50	100	22 (*S*)
14	$ItMe_2$	**3b**	CH_3OH	40	100	43 (*R*)
15	$ItMe_2$	**3b**	Toluene	720	100	78 (*R*)
16	$ItMe_2$	**3b**	EtOAc	240	100	51 (*R*)
17	AMe	**3c**	CH_2Cl_2	1200	96	38 (*R*)
18	AMe	**3e**	CH_2Cl_2	180	100	41 (*R*)
19	AMe	**3e**	THF	90	100	2 (*S*)
20	AMe	**3e**	CH_3OH	400	100	41 (*R*)
21	AMe	**3e**	Toluene	1200	100	21 (*R*)
22	AMe	**3f**[a]	CH_2Cl_2	480	100	15 (*R*)
23	AMe	**3f**	CH_2Cl_2	180	100	1 (*R*)
24	$ItMe_2$	**3c**[a]	CH_2Cl_2	1200	49	34 (*S*)
25	$ItMe_2$	**3c**	CH_2Cl_2	1200	27	40 (*S*)
26	$ItMe_2$	**3d**[a]	CH_2Cl_2	480	21	2 (*R*)
27	$ItMe_2$	**3e**[a]	CH_2Cl_2	320	62	65 (*S*)
28	$ItMe_2$	**3e**	CH_2Cl_2	120	100	68 (*S*)
29	$ItMe_2$	**3e**	THF	600	100	45 (*R*)
30	$ItMe_2$	**3e**	CH_3OH	240	100	30 (*S*)
31	$ItMe_2$	**3e**	Toluene	900	60	12 (*R*)
32	$ItMe_2$	**3f**[a]	CH_2Cl_2	300	100	3 (*S*)
33	$ItMe_2$	**3f**	CH_2Cl_2	30	100	30 (*S*)

[a] Rh(I)-precatalyst was prepared and used in situ.

Table 2. Rh(I)-catalyzed hydrogenation of prochiral olefins with various Rh/L ratios (in CH_2Cl_2)

Entry	Substrate	Ligand	L*/Rh	Time (min)	Ee (%)
1	AMe	**3a**[a]	2/1	180	50 (*S*)
2	AMe	**3a**[a]	1.5/1	100	27 (*S*)
3	AMe	**3a**[a]	1/1	45	12 (*S*)
4	AMe	**3b**[a]	2/1	180	52 (*S*)
5	AMe	**3b**	2/1	130	44 (*S*)
6	AMe	**3b**[a]	1/1	140	7 (*S*)
7	AMe	**3b**	1/1	35	7 (*S*)
8	AMe	**3b**	4/1	1200[b]	51 (*S*)
9	$ItMe_2$	**3a**[a]	2/1	130	67 (*R*)
10	$ItMe_2$	**3a**[a]	1.5/1	10	56 (*R*)
11	$ItMe_2$	**3a**[a]	1/1	60	50 (*R*)
12	$ItMe_2$	**3b**[a]	2/1	100	80 (*R*)
13	$ItMe_2$	**3b**	2/1	45	74 (*R*)
14	$ItMe_2$	**3b**[a]	1/1	30	56 (*R*)
15	$ItMe_2$	**3b**	1/1	10	61 (*R*)
16	$ItMe_2$	**3b**	4/1	1200[c]	—

[a] Rh(I)-precatalyst was prepared and used in situ.
[b] 61% conversion.
[c] 2.5% conversion.

sis. The new ligands were used in Rh-catalyzed hydrogenation where up to 80% ee were achieved in the benchmark test with $ItMe_2$ (ligand **3b**). Increasing the L/Rh ratio was found to result in diminishing the hydrogenation rate, while lowering of the L/Rh ratio accelerated the reaction. Other possible catalytic applications of chiral acylphosphite ligands are under investigation in our group.

4. Experimental part

4.1. General methods

All reactions were carried out under argon in dry solvents. (*R*)-3,3′-disubstituted binaphthols[10] and chlorophosphites **2a**–**e**[9,11] were obtained using literature procedures. NMR spectra were recorded on a Bruker AMX-400 instrument at 400.13 (^{1}H), 100.63 (^{13}C), or 161.98 MHz (^{31}P). Chemical shifts (ppm) are quoted relative to TMS (^{13}C and ^{1}H NMR) and 85% H_3PO_4 (^{31}P NMR). Mass spectra were recorded on an AMD 402 spectrometer. Elemental analyses were performed at a Leco CHNS-932. Melting points are uncorrected. Optical rotations were measured on a Gyromat-HP polarimeter. Hydrogenation experiments have been carried out under normal pressure and isobaric conditions with an automatically registrating gas measuring device (1.0 atm overall pressure over the solution). The

conversion of the prochiral substrates and the ees were determined by GC (AMe: Lipodex E, 25 m × 0.25 mm, 145 °C, 1 mL/min; $ItMe_2$: Lipodex E, 25 m × 0.25 mm, 80 °C, 1 mL/min).

4.2. (*R*)-Acetyl-(1,1′-binaphthyl-2,2′-diyl)phosphite 3a

A solution of chlorophosphite **2a** (1.225 g, 3.5 mmol) in THF (15 mL) was added to a warm (45 °C) suspension of sodium acetate (0.41 g, 5.0 mmol) in THF (15 mL) and the resulting mixture then stirred at the same temperature for 4 h. The solvent was removed under reduced pressure, the residue dissolved in toluene (40 mL), filtered through celite and the obtained filtrate concentrated in vacuum to give a white amorphous solid (1.15 g, 88% yield). Mp 72 °C. $[\alpha]_D^{23} = -463.6$ (*c* 1.07, CH_2Cl_2). IR (KBr): *v* (C=O) 1736 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 142.0. ^{13}C NMR ($CDCl_3$): 21.0 (*C*H_3), 120.1 (CH), 120.5 (CH), 121.8 (C), 123.3 (C), 124.2, 124.4, 125.4, 125.5, 125.9, 127.3, 127.4, 129.0, 129.7 (all CH), 130.3, 130.7, 131.5, 131.7 (all C), 145.5 (d, $J_{C,P} = 1.9$ Hz, *C*O), 146.4 (d, $J_{C,P} = 3.8$ Hz, *C*O), 168.8 (d, $J_{C,P} = 4.8$ Hz, *C*OO). ^1H NMR ($CDCl_3$): δ 2.05 (d, $J_{H,P} = 1.0$ Hz, 3H, CH_3), 7.20 (m, 2H), 7.30 (m, 3H), 7.38 (m, 2H), 7.48 (d, $J = 8.6$ Hz, 1H), 7.89 (m, 4H). MS (EI, 70 eV): 374 (81) $[M]^+$, 332 (100), 268 (13). Found: C 70.60, H 4.53. Calcd for $C_{22}H_{15}O_4P$: C 70.59, H 4.04.

4.3. (*R*)-Benzoyl-(1,1′-binaphthyl-2,2′-diyl)phosphite 3b

Application of the same method as detailed above for the synthesis of **3a**, using sodium benzoate (0.72 g, 5.0 mmol). White solid, 1.32 g (87% yield). Mp 125 °C. $[\alpha]_D^{21} = -371.0$ (*c* 0.5, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 142.8. ^{13}C NMR ($CDCl_3$): δ 121.8 (CH), 122.1 (CH), 123.5 (d, $J_{C,P} = 1.9$ Hz, C), 124.8 (d, $J_{C,P} = 5.7$ Hz, C), 125.7, 125.9, 127.5, 128.81, 128.89, 128.95, 129.0 (all CH), 129.3 (d, $J_{C,P} = 2.9$ Hz, C), 130.6, 130.9, 131.3 (all CH), 131.9, 132.3, 133.1, 133.3 (all C), 134.6 (CH), 147.20 (d, $J_{C,P} = 1.9$ Hz, *C*O), 148.2 (d, $J_{C,P} = 4.8$ Hz, *C*O), 165.6 (d, $J_{C,P} = 6.7$ Hz, *C*OO). ^1H NMR ($CDCl_3$): δ 7.15–7.25 (m, 2H), 7.28–7.41 (m, 7H), 7.45–7.55 (m, 2H), 7.82–7.95 (m, 6H). IR (KBr): *v* (C=O) 1716 cm^{-1}. MS (EI, 70 eV): 436 (100) $[M]^+$, 331 (12), 268 (15), 239 (12), 105 (100). EI-HRMS (70 eV): 436.0842 (calcd for $C_{27}H_{17}O_4P$: 436.0865). Found: C 74.24, H 4.45. Calcd for $C_{27}H_{17}O_4P$: C 74.31, H 3.93.

4.4. (*R*)-Benzoyl-(3,3′-dibromo-1,1′-binaphthyl-2,2′-diyl)phosphite 3c

Application of the same method as detailed above for the synthesis of **3a**, starting from chlorophosphite **2b** (1.78 g, 3.5 mmol) and sodium benzoate (0.72 g, 5.0 mmol). Beige solid, 1.77 g (85% yield). Mp 113 °C. $[\alpha]_D^{23} = -375.3$ (*c* 0.64, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 142.6. ^1H NMR ($CDCl_3$): δ 8.33 (s, 1H), 8.29 (s, 1H), 8.03 (m, 2H), 7.87 (m, 2H), 7.59 (m, 1H), 7.40–7.52 (m, 5H), 7.26–7.33 (m, 3H). IR (KBr): *v* (C=O) 1720 cm^{-1}. $C_{27}H_{15}Br_2O_4P$ (594.2); MS (EI, 70 eV): 594 (11) $[M]^+$, 489 (4), 105 (100).

4.5. (*R*)-Benzoyl-(3,3′-dimethyl-1,1′-binaphthyl-2,2′-diyl)phosphite 3d

Application of the same method as detailed above for the synthesis of **3a**, starting from chlorophosphite **2c** (1.32 g, 3.5 mmol) and sodium benzoate (0.72 g, 5.0 mmol). White solid, 1.32 g (81 % yield). Mp 128 °C. $[\alpha]_D^{25} = -351.4$ (*c* 0.46, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 138.8. ^1H NMR ($CDCl_3$): δ 7.86–7.93 (m, 2H), 7.75–7.84 (m, 4H), 7.52 (m, 1H), 7.37 (m, 4H), 7.10–7.26 (m, 4H), 2.60 (s, 3H), 2.49 (s, 3H). IR (KBr): *v* (C=O) 1720 cm^{-1}. $C_{29}H_{21}O_4P$ (464.1) MS (EI, 70 eV): 464 (40) $[M]^+$, 360 (31), 105 (100).

4.6. (*R*)-Benzoyl-(3,3′-diphenyl-1,1′-binaphthyl-2,2′-diyl)phosphite 3e

Application of the same method as detailed above for the synthesis of **3a**, starting from chlorophosphite **2d** (1.76 g, 3.5 mmol) and sodium benzoate (0.72 g, 5.0 mmol). Beige solid, 1.85 g (90 % yield). Mp 103 °C. $[\alpha]_D^{25} = -324.7$ (*c* 0.38, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 138.8. IR (KBr): *v* (C=O) 1718 cm^{-1}. $C_{39}H_{25}O_4P$ (588.1); MS (EI, 70 eV): 588 (36) $[M]^+$, 483 (28), 105 (100).

4.7. (*R*)-Benzoyl-[3,3′-bis(trimethylsilyl)-1,1′-binaphthyl-2,2′-diyl]phosphite 3f

Application of the same method as detailed above for the synthesis of **3a**, starting from chlorophosphite **2e** (1.73 g, 3.5 mmol) and sodium benzoate (0.72 g, 5.0 mmol). White solid, 1.685 g (83% yield). Mp 111 °C. ^{31}P NMR ($CDCl_3$): δ 143.1. $C_{33}H_{33}O_4PSi_2$ (580.2); MS (EI, 70 eV): 508 (51) $[M-SiMe_3]^+$, 105 (100).

4.8. Preparation of Rh complexes with ligands 3a–f (general procedure)

A solution of the relevant ligand (0.3 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of $[Rh(COD)_2]BF_4$ (0.061 g, 0.15 mmol) in CH_2Cl_2 (20 mL) at 20 °C. The reaction mixture was stirred for 30 min and aliquots taken for use in catalysis. In order to isolate solid complexes, the solution was concentrated in vacuum and 10 mL of hexane then added to the residue. The obtained solid rhodium products were washed with hexane (2 × 10 mL) and dried in vacuum.

4.8.1. $[Rh(COD)(3b)_2]BF_4$. Yellow solid, 0.137 g (73% yield). Mp >300 °C. ^{31}P NMR ($CDCl_3$): δ 135.2 (d, $^1J_{P,Rh} = 258.0$ Hz). ^1H NMR ($CDCl_3$): δ 1.61 (m, 2H), 2.18 (m, 2H), 2.60 (m, br, 4H), 4.35 (m, 2H), 6.36 (m, 2H), 7.28–7.44 (m, 14H), 7.48 (m, 2H), 7.55–7.67 (m, 4H), 7.91 (m, 8H), 8.10 (m, 4H), 8.29 (d, $J = 8.9$ Hz,

2H). MS (FAB): 976 (49) $[RhL_2]^+$, 647 (20), 511 (55), 136 (100).

4.9. Catalytic hydrogenations (General procedure)

The prochiral olefin (1 mmol) was dissolved in CH_2Cl_2 (13 mL) under a hydrogen atmosphere. The rhodium precatalyst [0.01 mmol, either pre-isolated or formed in situ in CH_2Cl_2 (2 mL)] was subsequently added and the reaction mixture vigorously stirred under hydrogen (1 atm) at 25 °C until the calculated amount of H_2 had been consumed. Both conversion and enantioselectivity of hydrogenation were determined by GC.

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