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Tetrahedron: *Asymmetry* 14 (2003) 2127–2131

TETRAHEDRON: *ASYMMETRY*

New chiral amino-phosphoramidite and bisphosphoramidite ligands derived from (*R*,*R*)-1,2-diaminocyclohexane: application in Cu-catalyzed asymmetric conjugate addition of diethylzinc to 2-cyclohexenone

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Received 4 April 2003; accepted 9 June 2003

Abstract—New bidentate amino-phosphoroamidite and diphosphoroamidite ligands derived from inexpensive (*R*,*R*)-1,2-diaminocyclohexane have been synthesized and screened in the Cu-catalyzed asymmetric conjugate addition of Et_2Zn to 2-cyclohexenone. The highest 74% ee value was reached with the *N*,*N*′-dimethyl substituted *P*,*N*-ligand and $Cu(OAc)_2 \cdot H_2O$.

1. Introduction

Catalytic asymmetric conjugate addition of organometallic, Grignard and organolithium reagents to α,β-unsaturated compounds is an attractive synthetic method for carbon–carbon formation.[1] Remarkable advances have been achieved in this area employing a combination of an organozinc reagent, generally Et_2Zn, and a copper complex with a chiral ligand.[2] Several copper complexes of chiral phosphorus ligands[3] have been used in the catalytic conjugate addition of dialkylzinc to enones with good to excellent enantioselectivity. Even though, the use of chiral monodentate phosphoroamidites in the Cu-catalyzed 1,4-addition of R_2Zn gave very high enantioselectivities,[4] some bidentate *P*,*P*-[5] and *P*,*N*-[6] ligands have been described affording excellent results.

Following our interest in developing effective *P*,*P*- and *P*,*N*-chiral ligands for enantioselective homogeneous catalysis,[7] we have designed a series of amino-phosphoramidite and bisphosphoramidite ligands derived from the inexpensive and easily derivatizable chiral source (*R*,*R*)-1,2-diaminocyclohexane. Herein we report the synthesis of these ligands and their application in the asymmetric conjugate addition of diethylzinc to 2-cyclohexenone.

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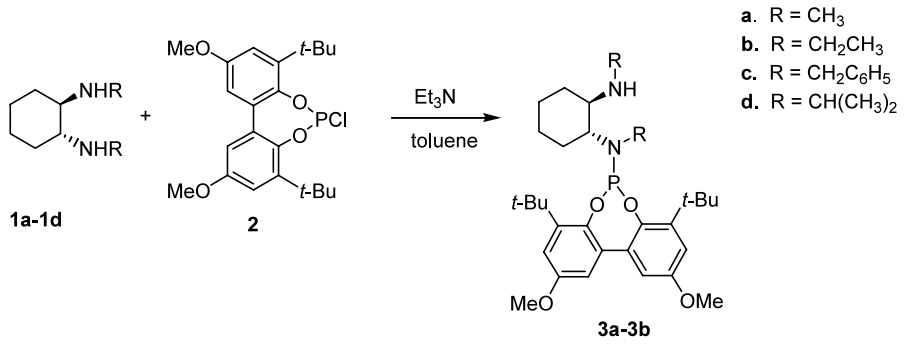
doi:10.1016/S0957-4166(03)00447-6

2. Results and discussion

2.1. Synthesis of the ligands

Reaction of the disubstituted (*R*,*R*)-1,2-diaminocyclohexanes[8] **1a–d** (Scheme 1) with one equivalent of (3,3′-bis-*tert*-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)-phosphorochloridite[9] **2** in toluene in the presence of triethylamine, gave the desired amino-phosphoroamidite ligand **3a** only in the case of the *N*,*N*′-dimethyl substituted amine **1a**, whereas two equivalents of **2** were necessary to obtain the *N*,*N*′-diethyl substituted ligand **3b**. The presence of a larger group, such as benzyl or isopropyl, in the *N*,*N*′-disubstituted diamines **1c–d** did not allow the synthesis of the corresponding *P*,*N*-chiral ligand even upon exposure to a large excess of **2**. Moreover, treatment of *N*,*N*′-dimethyl amine **1a** with **2** excess did not lead to the corresponding diphosphoroamidite. The new chiral ligands **3a–b** were obtained, as white solid, in good yields (75–85%) after purification by chromatography over silica gel. They are stable to air in the solid state. The analytical data were in accordance with the proposed structures, in particular ^{31}P spectroscopy showed one singlet at chemical shift values observed for similar compounds.[10] Because the rapid biphenyl moiety atropoisomerization on the NMR time scale, diastereoisomers expected for the ligands **3a–b** was not detected by low temperature ^{31}P NMR. Finally, steric requirements of the *N*-substituents prevented us from introducing a binaphthol fragment into *N*,*N*′-dialkyl diamines **1a–1d**.



Scheme 1.

In view of these results, it appears that the *N*-substituents in (*R*,*R*)-1,2-diaminocyclohexane, **1**, determine the course of these *P*,*N*-ligand syntheses reaction. Spilling et al.[11] reported similar results on the synthesis of a new series of amino-phosphine ligands derived from (*R*,*R*)-1,2-cyclohexanediamine.

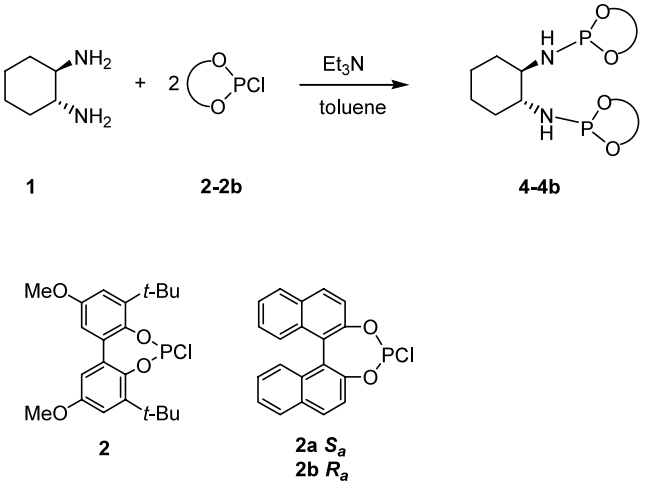
The chiral bisphosphoroamidite ligands **4**–**4b** were prepared in 80–90% isolated yields from the (*R*,*R*)-1,2-diaminocyclohexane, **1**, and either **2** or the corresponding enantiomer of the (2,2′-binaphthol)phosphorochloridite[9] **2a**–**b** in a 1:2 molar ratio, in toluene in the presence of triethylamine (Scheme 2). Ligand **4** was purified by chromatography over silica gel and it is stable to air. In contrast to **4**, ligands **4a**–**b** have to be stored under nitrogen. One singlet was observed for **4**–**4b**, in the ^{31}P NMR spectrum at chemical shift values agree with those expected for phosphoroamidites compounds.[12]

2.2. Asymmetric conjugate addition of Et_2Zn to 2-cyclohexenone

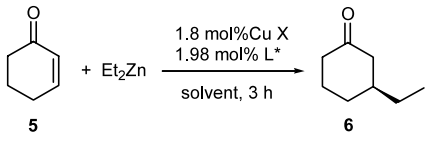
The new chiral *P*,*N*-**3a**–**3b** and *P*,*P*-**4**–**4b** ligands were tested in the Cu-catalyzed addition of diethylzinc to 2-cyclohexenone **6** (Scheme 3). The catalytic system was formed in situ by adding the corresponding ligand to a suspension of $Cu(OTf)_2$ or $Cu(OAc)_2{\cdot}H_2O$. The results are summarized in Table 1. Complete chemoselectivity was found since no 1,2 product was detected by GC analysis. Using the amino-phosphoroamidite ligands **3a**, the highest enantioselectivity was achieved (74% ee, entry 3) with $Cu(OAc)_2{\cdot}H_2O$ in toluene at −20°C. As reported by Alexakis,[4e] the degree of enantioselectivity increased using $Cu(OAc)_2{\cdot}H_2O$ (entry 3) compared to $Cu(OTf)_2$ (entry 1) while the catalytic activity is higher with $Cu(OTf)_2$. However, in contrast to Alexakis's findings, in this case the catalyst performance in ether is very low (entry 6). Adding a one-fold excess of ligand led to a decrease of the catalytic activity as well as the enantioselectivity (entry 7 versus 3).

Surprisingly, the catalytic system $Cu(OAc)_2{\cdot}H_2O$/**3b** in toluene at −20°C gave a lower reaction rate and was not selective (63% conv, 8% ee, entry 8). Probably, the active catalyst was not stable under these reaction conditions. Indeed, metallic copper was observed in the reaction vessel after 3 h. Employing the system $Cu(OTf)_2$/**3b** the conversion reached 80% and (*S*)-3-ethylcyclohexenone **6** was obtained in 57% ee (entry 9). Comparing the results obtained with ligands **3a** and **3b** (entry 1 and 9), it is worth noting that a slight increase in the steric hindrance at nitrogen in *N*,*N*′-dialkyl diamines **1a**–**b** lead to a depletion of the conversion and stereoselectivity. It is plain that amino-phosphoroamidites derived from (*R*,*R*)-1,2-diaminocyclohexane show a low tolerance to an increase of the sterically demanding substituent at the nitrogen in the asymmetric copper-catalyzed 1,4-addition to cyclohexenone.

Using the catalytic system formed by $Cu(OTf)_2$ and bidentate phosphoroamidites **4**–**4b**, a marked decrease



Scheme 2.



Scheme 3.

Table 1. Asymmetric conjugate addition of Et_2Zn to 2-cyclohexenone

Entry[a]	L	Copper salt	Solvent	T (°C)	Conv. (%)[b]	ee (%)[b]
1	**3a**	$Cu(OTf)_2$	Toluene	−20	95	70 (*R*)
2[c]	**3a**	$Cu(OTf)_2$	Toluene	0	>99	66 (*R*)
3	**3a**	$Cu(OAc)_2{\cdot}H_2O$	Toluene	−20	92	74 (*R*)
4	**3a**	$Cu(OAc)_2{\cdot}H_2O$	Toluene	0	99	64 (*R*)
5	**3a**	$Cu(OAc)_2{\cdot}H_2O$	CH_2Cl_2	−20	94	61 (*R*)
6	**3a**	$Cu(OAc)_2{\cdot}H_2O$	Et_2O	−20	45	51 (*R*)
7[d]	**3a**	$Cu(OAc)_2{\cdot}H_2O$	Toluene	−20	80	70 (*R*)
8	**3b**	$Cu(OAc)_2{\cdot}H_2O$	Toluene	−20	63	8 (*R*)
9	**3b**	$Cu(OTf)_2$	Toluene	−20	89	57 (*R*)
10	**4**	$Cu(OTf)_2$	Toluene	−20	96	6 (*R*)
11	**4a**	$Cu(OTf)_2$	Toluene	−20	97	40 (*S*)
12	**4b**	$Cu(OTf)_2$	Toluene	−20	97	0

[a] Conditions, see Scheme 3 and Section 4.
[b] % Conversions and enantiomeric excesses determined by GC (Lipodex E column, 90°C).[4e]
[c] Determined after 1 h.
[d] Ligand:copper salt = 2.2:1

in the enantioselectivity was observed (0–40% entries 10–12) in comparison to *P*,*N*-ligands, while no significant difference was observed in the reaction rates. Poor results were obtained when $Cu(OAc)_2{\cdot}H_2O$ was used as the copper salt. Substitution of the biphenol fragment with the (*S*)-binaphthol groups afforded a relevant improvement in the ee value (6%, entry 10 versus 40%, entry 11) together an inversion in the absolute configuration of the 3-ethylcyclohexanone **6** (*R* versus *S*). In contrast to (S_aS_aRR) **4a**, when the diastereomer (R_aR_aRR) **4b**, was employed the enantioselectivity dropped to 0 (entry 12). Evidently the relative configurations of binaphthol and cyclohexanediamine moieties play an important role in determining the reaction stereoselectivity. On the other hand, matching and mismatching combinations of chirality elements were found for related bidentate phosphoroamidite ligands.[12]

3. Conclusions

New bidentate amino-phosphoroamidite and bisphosphoroamidite ligands derived from inexpensive and easily derivatizable chiral source (*R*,*R*)-1,2-diaminocyclohexane were synthesized and screened in the Cu-catalyzed asymmetric conjugate addition of Et_2Zn to 2-cyclohexenone. The highest 74% ee value was reached with *N*,*N*′-dimethyl substituted *P*,*N*-ligand **3a** and $Cu(OAc)_2{\cdot}H_2O$. The asymmetric induction is strikingly dependent on the steric hindrance of the nitrogen substituent. The bidentate phosphoroamidites **4**–**4b** afforded lower ee values. An enantiomeric excess of 40% was obtained with ligand **4a** in which the chiral elements (S_a)-binaphthol and (*R*,*R*)-1,2-diaminocyclohexane proved to be the matched combination, while the alternative R_aR_aRR combination in **4b** gave no stereoselectivity.

Further screening of these new chiral ligands with respect to other enones and studies on the structure of the actual catalyst complex are currently in progress.

4. Experimental

All syntheses were performed under purified nitrogen using standard Schlenk techniques. Solvents were dried by standard procedures. NMR experiments were carried out using Bruker AMX R300 spectrometer. ^1H and ^{13}C NMR spectra were referenced to internal tetramethylsilane and $^{31}P\{^1H\}$ spectra to external 85% H_3PO_4 ($\delta = 0$ ppm).Unless otherwise indicated, all materials were commercially available and were used without further purification. (*R*,*R*)-1,2-diaminocyclohexane was dried over NaOH pellets for several days prior to use. For column chromatography, silica gel 60 (220–440 mesh) purchased from Fluka was used. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano. Gas chromatographic analyses were run on a Fisons GC 8000 instrument.

4.1. *N*-[(3,3′-Bis-*tert*-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)phosphate]-(*R*,*R*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane 3a

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane[8] (300 mg, 2.1 mmol) and Et_3N (640 mg, 6.33 mmol) in toluene (5 mL) were added slowly to a solution of (3,3′-bis-*tert*-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)phosphorochloridite[9] **2** (889 mg, 2.1 mmol) in the same solvent (10 mL) at 0°C. After the addition was complete, the resulting solution was stirred overnight at room temperature and then $Et_3N{\cdot}HCl$ precipitate was removed by filtration. The solvent was evaporated in vacuum to afford a white foam which was purified by column chromatography (SiO_2, hexane:EtOAc = 3:2). Yield (85%, 1.78 mmol, 943 mg). $[\alpha]_D^{21} = -168$ (*c* 3.1, hexane). Anal. calcd for $C_{30}H_{45}N_2O_4P$: C. 68.16; H. 8.58; N. 5.30. Found: C, 68.31; H, 8.60; N, 5.19. ^1H NMR (C_6D_6): δ 0.99–1.56 (m, 7H); 1.66 (s, 9H), 1.72 (s, 9H), 1.90 (m, 2H), 2.15 (m, 1H), 2.30 (s, 1H), 2.41 (d, $J_{PH} = 3.0$ Hz, 3H), 2.51 (s, 3H), 3.47 (s, 3H), 3.51 (s, 3H), 6.85 (d, $J = 3.0$ Hz, 1H), 6.91 (d, $J = 3.0$ Hz, 1H), 7.30 (d, $J = 3.0$ Hz, 1H), 7.32 (d, $J = 3.0$ Hz, 1H). ^{31}P NMR (C_6D_6): δ 148.6 (s). ^{13}C NMR (C_6D_6): δ 24.3,

26.6, 27.0, 30.4, 30.6, 31.0, 33.4, 35.2, 54.7, 58.7, 58.7, 112.6, 113.0, 114.4, 114.5, 135.1, 136.1, 141.4, 142.4, 144.0, 144.9, 152.2, 155.6.

4.2. *N*-[(3,3′-Bis-*tert*-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)phosphate]-(*R*,*R*)-N]-(*R*,*R*)-*N*,*N*′-diethyl-1,2-diaminocyclohexane 3b

(*R*,*R*)-*N*,*N*′-Diethyl-1,2-diaminocyclohexane[8] (255 mg, 1.5 mmol) and Et_3N (607 mg, 6 mmol) in toluene (5 mL) were added dropwise to a solution of (3,3′-bis-*tert*-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)phosphorochloridite **2** (1268 mg, 3 mmol) in the same solvent (10 mL) at 0°C. The reaction mixture was allowed to warm to room temperature over 3 h and then filtered under N_2. Evaporation of the solvent afforded a yellowish foam which was purified over SiO_2 (hexane:EtOAc = 3:2) to give a white foam (75%, 1.12 mmol, 626 mg). $[\alpha]_D^{21} = -65.4$ (*c* 1.3, hexane). Anal. calcd for $C_{32}H_{49}N_2O_4P$: C, 69.04; H, 8.87; N, 5.03. Found: C, 69.19; H, 8.90; N, 4.98. ^{1}H NMR (C_6D_6): δ 0.99 (m, 2H), 1.20 (m, 5H), 1.31 (m, 5H), 1.64 (m, 2H), 1.69 (s, 9H), 1.74 (s, 9H), 2.00 (m, 2H), 2.63 (m, 2H), 2.96 (s, 3H), 3.23 (m, 1H), 3.47 (s, 3H), 3.48 (s, 3H), 6.86 (d, $J = 3.0$ Hz, 1H), 7.33 (d, $J = 3.0$ Hz, 2H). ^{31}P NMR (C_6D_6): δ 151.4 (s). ^{13}C NMR (C_6D_6): δ 15.7, 17.2, 24.2, 26.0, 30.4, 30.8, 30.6, 31.0, 31.2, 32.1, 32.7, 35.3, 38.7, 40.7, 54.6, 54.7, 59.5, 59.6, 112.9, 114.4, 133.1, 134.1, 141.3, 142.2, 144.1, 145.0, 155.0, 155.6.

4.3. General procedure for bisphosphoroamidite ligands

To a stirred solution of the appropriate phosphorochloridite[9] (4.4 mmol) in toluene (10 mL) was added dropwise (*R*,*R*)-cyclohexane-1,2-diamine (2.2 mmol) and Et_3N (8.8 mmol) in the same solvent (5 mL) at 0°C. The reaction mixture was stirred overnight at room temperature and the precipitate of $Et_3N{\cdot}HCl$ formed was removed by filtration. The toluene was evaporated from filtrate to give the crude product.

4.4. *N*,*N*′-[Bis-(3,3′-bis-*tert*-butyl-5,5′-bis-methoxy-1,1′-biphenyl-2,2′-diyl)phosphite]-(*R*,*R*)-1,2-diaminocyclohexane 4

The crude product was obtained as a yellowish foam which was purified by column chromatography (SiO_2, hexane:EtOAc = 3:2) to give **4** in 80% yield (1.76 mmol, 1,56 g). Anal. calcd for $C_{50}H_{68}N_2O_8P_2$: C. 67.70; H. 7.73; N, 3.16. Found: C, 67.79; H, 7.77; N, 3.06. ^{1}H NMR (C_6D_6): δ 1.0 (s br, 2H); 1.35 (s br, 4H), 1.63 (s, 18H), 1.67 (s, 18H), 1.99 (m, 2H), 3.42 (s br, 1H), 3.47 (s, 3H), 3.50 (s, 3H), 6.87 (d, $J = 3.0$ Hz, 2H), 6.91 (d, $J = 3.0$ Hz, 2H), 7.31 (m, 4H). ^{31}P NMR (C_6D_6): δ 150.5 (s). ^{13}C NMR (C_6D_6): δ 23.2, 25.6, 30.87, 31.03, 35,1, 54.6, 54.7, 56.4, 112.9, 114.3, 134.2, 142.2, 144.4, 155.6.

4.5. *N*,*N*′-Bis[-(*S*)-1,1′-binaphthyl-2,2′-diyl)phosphite]-(*R*,*R*)-1,2-diaminocyclohexane 4a

The crude product was obtained as a white solid which was washed with cold hexane (3 mL) and dried to give **4a** in 90% yield (1.98 mmol, 1.47 g). Anal. calcd for $C_{46}H_{36}N_2O_4P$: C, 74.39; H, 4.89; N, 3.77. Found: C, 74.50; H, 5.08; N, 3.65. ^{1}H NMR (C_6D_6): δ 1.03 (m, 2H); 1.3 (m, 4H), 1.87 (m, 2H), 2.67 (m, 2H), 3.10 (m br, 2H), 6.91–7.70 (m, 24H). ^{31}P NMR (C_6D_6): δ 151.9 (s). ^{13}C NMR (C_6D_6): δ 24.6, 35.7, 56.3, 56.5, 121.0, 124.2, 126.0, 127.0, 128.3, 129.5, 130.3, 131.0, 133.0, 149.8.

4.6. *N*,*N*′-Bis[-(*R*)-1,1′-binaphthyl-2,2′-diyl)phosphite]-(*R*,*R*)-1,2-diaminocyclohexane 4b

The crude product was obtained as a white solid which was washed with hexane (3 mL) and dried to give **4b** in 85% yield (1.87 mmol, 1.39 g). Anal. calcd for $C_{46}H_{36}N_2O_4P$: C, 74.39; H, 4.89; N, 3.77. Found: C, 74.48; H, 5.05; N, 3.63. ^{1}H NMR (C_6D_6): δ 0.98 (m, 2H); 1.38 (m, 4H), 2.1 (m, 2H), 2.96 (m, 2H), 3.22 (m, 2H), 6.70–7.90 (m, 24H). ^{31}P NMR (C_6D_6): δ 154.2 (s). ^{13}C NMR (C_6D_6): δ 24.9, 35.9, 56.5, 56.8, 121.5, 124.6, 126.3, 127.0, 128.3, 130.0, 131.7, 134.0, 149.0.

4.7. General procedure for asymmetric 1,4-conjugate addition

0.017 mmol of copper salt and 0.019 mmol of ligand in toluene (9 mL), were stirred, at room temperature, for 1 h. After cooling to (−20°C), 2-cyclohexen-1-one (3 mmol) and 3 mL of Et_2Zn (1.1 M solution in toluene) were added slowly. The resulting mixture was stirred at −20°C and monitored by GC. The reaction was quenched with HCl 1 M. The conversions and ee values were determined by GC with a Lipodex E column.[4e]

Acknowledgements

We thank MURST for financial support.

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