ELSEVIER

Journal of Molecular Catalysis A: Chemical 185 (2002) 33–39

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Optically active pyrazolylborate: synthesis, characterization and uses in enantioselective cyclopropanation reaction

Udai P. Singh [a,*], Preeti Babbar [a], Bernd Hassler [b,1], H. Nishiyama [b], H. Brunner [c]

[a] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India*
[b] *School of Material Science, Toyohashi University of Technology, Toyohashi 441-8580, Japan*
[c] *Institut für Anorganische Chemie, der Universität Regensburg, D-93040 Regensburg, Germany*

Received 10 September 2001; received in revised form 10 December 2001; accepted 21 January 2002

Abstract

Optically active sodium salt of tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazolyl)borate, [NaB(camphpz)$_4$] (**1**) was synthesized by the reaction of 4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazole and $NaBH_4$ whereas sodium salt of hydrotris((−)-3(5)-methyl-1-phenylethylaminomethylpyrazolyl)borate, [NaHB(P1)$_3$] (**2**) was prepared by the reaction of (−)-3(5)-methyl-1-phenylethylaminomethylpyrazole with $NaBH_4$. Their uses in various metal-catalysed enantioselective cyclopropanation reactions of styrene and several diazoacetates gave the corresponding *trans*- and *cis*-phenylcyclopropane-1-carboxylates with moderate to reasonably good enantioselectivities.

Keywords: Pyrazolylborate; Optical activity; Copper, rhodium and ruthenium catalysts; Cyclopropanation; Enantioselectivity

1. Introduction

The asymmetric catalytic cyclopropanation of olefins with diazoacetates has been intensively studied for three decades, since Nozaki et al. [1] initiated it in 1966. They decomposed ethyl diazoacetate and styrene in the presence of chiral copper complex as a catalyst to give the products *trans*- and *cis*-2-phenylcyclopropane-carboxylate both in optically active form. Fischer [2] also demonstrated that the carbene derived from ethyl diazoacetate is not free but is combined with chiral copper complex to form a carbene–copper complex which is responsible for the asymmetric induction. Recently, several chiral nitrogen-based ligands in combination with copper and rhodium complexes[2] in asymmetric cyclopropanation reaction have been reported. Pyrazole molecules are well-established ligands and tris(pyrazolyl)-hydroborate anions [Tp or HB(pz)$_3^-$] have been demonstrated to be versatile ligands useful for the preparation of complexes of elements from throughout the periodic table that are important from inorganic, organometallic, and/or bioinorganic chemistry perspectives [8]. Several workers have used metal complexes of pyrazolylborate as catalysts in cyclopropanation reaction and reported the products with relatively good yield (80–90%) [9]. Polypyrazolyl ligands have also been employed to induce a signif-

* Corresponding author. Tel.: +91-1332-85329; fax: +91-1332-73560.
E-mail address: udaipfcy@rurkiu.ernet.in (U.P. Singh).

[1] JSPS fellow from Germany in Prof. H. Nishiyama's group, Japan.

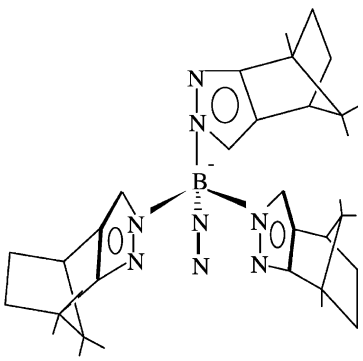
[2] For recent papers on copper catalysts, see [3]. For recent papers on rhodium catalysts, see [7].

1381-1169/02/$ – see front matter
PII: S1381-1169(02)00075-4

icant degree of asymmetry in the cyclopropanation reaction. Tolman and co-workers [3] have reported a series of hydrotris(pyrazolyl)borate–copper complexes where the pyrazole ring provides the chirality. Similar results were presented by Brunner et al. [12]. Bis(pyrazolyl)borate–copper compounds have also been employed as the precatalyst [3], as well as related ligands with a phosphorus oxide group instead of the B–H moiety [10]. The great number of existing pyrazoles with a wide range of electronic and steric properties permits the construction of many unsymmetrical bis(pyrazolyl)borates, chiral tripod bis-(pyrazolyl)borates [11] and chiral tris(pyrazolyl)borates with different electronic and steric properties. The possibility of tailoring the pyrazolylborates, in addition to the great stability of their complexes, led us to attempt the synthesis of optically active poly-(pyrazolyl)borates. In this paper, we describe the synthesis and spectroscopic studies of the hydrotris((−)-3 (5)-methyl-1-phenylethy- laminomethylpyrazolyl)borate [NaHB(P1)$_3$] and uses of [NaB(camphpz)$_4$] and [NaHB(P1)$_3$] in copper, rhodium and ruthenium catalysed asymmetric cyclopropanation of styrene and diazoacetates.

2. Results and discussion

(−)-3(5)-Methyl-1-phenylethylaminomethylpyrazole (P1) and [NaB(camphpz)$_4$] (**1**) (Fig. 1) were prepared by the literature method [12,13]. Hydrotris(pyrazolyl)borate salt of (P1), [NaHB(P1)$_3$] (**2**) was obtained as a white solid by heating $NaBH_4$ in the presence of 3 equiv. of (P1) at 220–240 °C until 3 equiv. of hydrogen gas was evolved (Scheme 1).



1

Fig. 1.

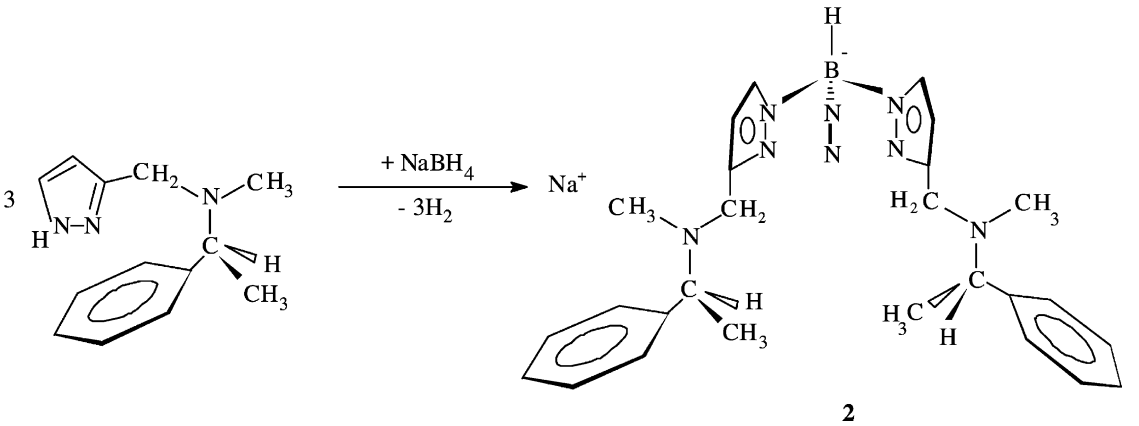
Its infrared spectrum exhibits a BH band at 2410 cm^{-1} and no νN–H band due to free pyrazole. The solubility of this ligand is not very good in organic solvents but it is soluble in dichloromethane, ethanol and methanol. It has optical activity −45.1° and can be stored well as solid. ^{1}H-NMR (250 MHz) spectrum shows pyrazole ring proton signal at 7.36 ppm (s, 3H, pzC(5)–H). These results together with analytical data suggest the chemical formula $C_{39}H_{49}BN_9Na$ for ligand **2**.

The IR spectra of dihydrobis(pyrazolyl)borates show BH_2 bands in the range 2200–2500 cm^{-1} and those of hydrotris(pyrazolyl)borates show a BH band around 2500 cm^{-1} [8]. In contrast, the IR spectrum of **2** shows a BH band at 2410 cm^{-1}, supporting its formulation as a hydrotris derivative, in accordance with the elemental analysis. The negative ion FAB mass spectrum exhibits an *m*/*z* peak at 655 for the anion [HB(P1)$_3$]$^-$. As the ^{1}H-NMR spectrum of **2** shows only one singlet at 7.36 ppm for the C(5) proton, we formulate [NaHB(P1)$_3$] as shown in Scheme 1.

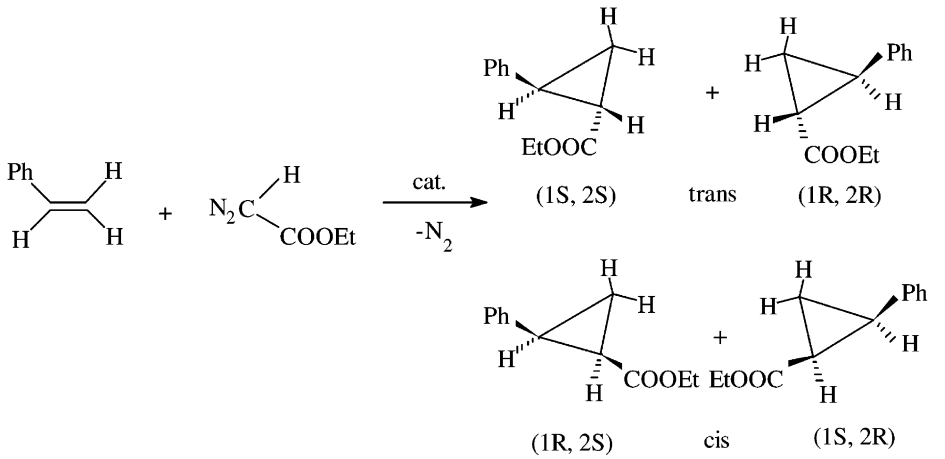
In continuation of our efforts to develop new optically active pyrazolylborate ligands for enantioselective catalysis, we have examined the use of the NaB(camphpz)$_4$/NaHB(P1)$_3$ in cyclopropanation of styrene and ethyl/menthyl diazoacetates brought about by copper(I), copper(II), rhodium(I) and ruthenium(II) in situ catalysts (Scheme 2).

As shown in Table 1, the product of the cyclopropanation is a mixture of *cis*/*trans* isomers [12], with the *cis* isomer as the main component. The chemical yields are in the range 9–69%. The enantiomeric excess is 10–62% for the *cis* isomer and 0.5–42% for the *trans* isomer. The maximum enantiomeric excess is 62% for the *cis* isomer, obtained with a copper(I)triflate/**1** catalyst, and 42% for the *trans* isomer, obtained with a copper(II) acetate/**1** catalyst. However, the cocatalysts Cu(OAc)$_2$, CuI, and Cu(CF$_3$SO$_3$) give very similar results (Table 1, runs 1–3). With the isolated complex Cu(CO)[B(camphpz)$_4$] as the catalyst the enantioselectivity is little lower, and with the in situ catalyst [Rh(cod)Cl]$_2$/**1** it is significantly lower (Table 1, runs 4 and 5).

The reported ee with optically active pyrazolylborate was 85% for *cis* and 81% for *trans* isomer



Scheme 1.



Scheme 2.

[3]. Although the observed ee for the *cis* product in present paper is 62% lower than the literature value, it is a promising indication of useful applications of **1** and other synthesized pyrazolylborate ligands towards asymmetric synthesis. In general, it is reported that diazoacetate with bulky ester groups can improve enantiomeric excess. We, therefore, performed the reaction with ethyl/menthyl diazoacetates

Table 1
Enantioselective cyclopropanation of styrene (8.7 mmol) with ethyl diazoacetate (10.0 mmol) using in situ catalysts Cu^{I}, Cu^{II} and Rh^{I}/**1**; metal salt (0.05 mmol), ligand **1** (0.05 mmol); solvent CH_2Cl_2; reaction temperature 55 °C except for fourth run (25 °C)

Run	Metal compound	Yield (%)	*cis*/*trans*	ee for *cis* isomer (%)	ee for *trans* isomer (%)
1	$Cu(OAc)_2$/**1**	69	76/24	58 (1*R*,2*S*)	42 (1*R*,2*R*)
2	CuI/**1**	48	68/32	54 (1*R*,2*S*)	36 (1*R*,2*R*)
3	$Cu(CF_3SO_3)$/**1**	53	76/24	62 (1*R*,2*S*)	40 (1*R*,2*R*)
4	Cu(CO)[B(camphpz)$_4$]	40	60/40	46 (1*R*,2*S*)	28 (1*R*,2*R*)
5	$[Rh(cod)Cl]_2$/**1**	9	44/56	10 (1*R*,2*S*)	0.5 (1*R*,2*R*)

Table 2
Enantioselective cyclopropanation of styrene (5.0 mmol) with ethyl/menthyl diazoacetate (1.0 mmol) using in situ catalyst copper(I)triflate–benzene/**1**; copper(I)triflate–benzene complex (0.025 mmol); ligand **1** (0.060 mmol); solvent 1,2-$ClCH_2CH_2Cl$; reaction temperature 45 °C

Run	Diazo compound	Yield (%)	*cis*/*trans*	ee for *cis* isomer (%)	ee for *trans* isomer (%)
1	Ethyl	88	50/50	39 (1*R*,2*S*)	39 (1*R*,2*R*)
2	L-Menthyl	64	01/99	19 (1*R*,2*S*)	23 (1*R*,2*R*)
3	D-Menthyl	53	04/96	24 (1*R*,2*S*)	0

Table 3
Enantioselective cyclopropanation of styrene (5.0 mmol) with ethyl/menthyl diazoacetate (1.0 mmol) using in situ catalyst copper(I)triflate–benzene/**2**; copper(I)triflate–benzene complex (0.025 mmol); ligand **2** (0.060 mmol); reaction temperature 45 °C except for first run (25–27 °C)

Run	Diazo compound	Yield (%)	*cis*/*trans*	ee for *cis* isomer (%)	ee for *trans* isomer (%)
1	Ethyl[a]	23	58/42	32 (1*R*,2*S*)	4 (1*S*,2*S*)
2	Ethyl[b]	59	42/58	22 (1*R*,2*S*)	16 (1*R*,2*R*)
3	L-Menthyl	91	3/97	0	12 (1*R*,2*R*)
4	D-Menthyl	66	0.5/99.5	n.d.[c]	5 (1*R*,2*R*)

[a] Ethyl diazoacetate as a solution in CH_2Cl_2.
[b] Ethyl diazoacetate as a solution in 1,2-$ClCH_2CH_2Cl$.
[c] No detection in NMR of any *cis*-compound, in GC *cis* can be seen as very small peaks, probably a racemic mixture, but even after several attempts no detection by integrator was possible.

using copper(I)triflate–benzene/**1** or **2** catalyst. In comparison to the results reported in Table 1, the *cis*-selectivity is lower with only 50:50 (Table 2, run 1) and are obtained higher diastereoselectivity and highest ee (39% for both *cis* and *trans*) of all runs with copper(I)triflate–benzene/**1** catalyst. With menthyl diazoacetates, the *cis*/*trans* ratio changes extremely to *trans* (99% *trans* for L-menthyl and 96% *trans* for D-menthyl) but ee decreases (19% ee for *cis* and 23% ee for *trans* in the case of L-menthyl, 24% ee for *cis* and 0% ee for *trans* in case of D-menthyl) (Table 2, runs 2 and 3), which is in accordance with the previously observed results reported by other workers that diazoacetate with bulky ester groups afford a high *trans* selectivity with any catalytic systems [14].

Our interest then turned to the other optically active hydrotris(pyrazolyl)borate ligand and we performed the cyclopropanation reaction with ethyl diazoacetate and styrene in dichloromethane in the presence of copper(I)triflate–benzene/**2** catalyst. The enantiomeric excess of the *cis* isomer was 32% ee with 58% yield (Table 3, run 1). The same reaction was performed at 45 °C in 1,2-dichloroethane solvent and the products obtained were 42% *cis* and 58% *trans* isomers with lower enantiomeric excess of *cis* isomer than previous case (Table 3, run 2). The reaction of the menthyl diazoacetate proceeded smoothly at 45 °C and gave *trans* isomer as the sole product in 97% with L-menthyl diazoacetate and 99.5% with D-menthyl diazoacetate but the enantiomeric excesses decrease (Table 3, runs 3 and 4). Run 1 (ethyl diazoacetate compound at room temperature) exhibits a high selectivity in both criteria, diastereoselectivity and enantioselectivity, but yield is only 23%. With dichloroethane at 45 °C (Table 3, run 2) the yield is much better, but diastereoselectivity for the *cis*-compound decreases. Of certain interest is here the fact that compared to run 1 the ee of the *cis*-compound decreases while the ee of the *trans*-compound not only switches from (1*S*,2*S*) to (1*R*,2*R*) in run 2 but also increases. Cyclopropanation was also tried with ruthenium/**1** system but the results were not encouraging (Table 4). Several other copper complexes with bis(oxazoline) ligand have been used in asymmetric cyclopropanation reaction of olefins by various workers with better yield and enantiomeric excess than present results.[3] Nishiyama and co-workers [5] have reported the maximum enantiomeric excess of 99% for *cis* isomer, whereas Evans et al. [6] have

[3] For recent papers on copper bis(oxazoline) catalyst, see [4].

Table 4
Enantioselective cyclopropanation of styrene (5.0 mmol) with ethyl diazoacetate (EDA) (1.0 mmol) using in situ catalysts $RuCl_2$(*p*-cymene)/**1**; $RuCl_2$(*p*-cymene)/**2** (0.025 mmol, 5 mol% Ru to EDA), ligand **1** (0.06 mmol); EDA solution (3.0 ml); solvent CH_2Cl_2

Run	Temperature (°C)	Yield (%)	*cis*/*trans*	ee for racemic (%)
1	<40	0	0	0
2	50	18	73/27	0
3	70	20	70/30	0

reported the maximum enantiomeric excess of 99% for *trans* isomer.

The exact mechanism of cyclopropanation in the present case is not known. Based on the mechanism reported for asymmetric cyclopropanation in literatures, it may be proposed that the metal pyrazolylborate complex reacts with diazoacetate compound and form the metal stabilized carbene with the extrusion of nitrogen. The metal stabilized carbene then reacts with styrene and generates the catalytically active species in the reaction. As shown in various tables, several metal salts have been tested for in situ catalysis but copper appears one of the most efficient catalyst in the present study. Among various copper salts used, copper(I)triflate is very effective as reported in literature. This is due to a simple reason that the triflate like perchlorate is an extremely weak coordinating anion and metal salt of copper(I) is extremely ionized even in non-aqueous solution. Thus, the electrophillic metal ion is capable of multiple coordination which makes the cyclopropanation process extremely facile.

In conclusion, we have demonstrated the use of optically active tetrakis and hydrotris pyrazolylborate in asymmetric cyclopropanation reaction. The highest ee obtained was 62% for *cis* isomer and 42% for *trans* isomer. With the use of menthyl diazoacetate drastic changes were observed from *cis* to *trans* and enantiomeric excesses decrease. Although the stereoselectivity induced by optically active pyrazolylborate and copper catalyst in the present work is not very high and results are not encouraging as with copper bis(oxazoline) catalyst but offering future opportunity for synthesizing more effective pyrazole based chiral ligand for asymmetric catalysis.

3. Experimental

All solvents and reagents are commercially available and were used without further purification. Elemental analysis were performed microanalytically at a Perkin-Elmer model 240 C elemental analyser. IR spectra were registered on a Perkin-Elmer model 1600 FT-IR spectrometer and optical rotation were measured on a Perkin-Elmer Polarimeter 241. ^{1}H-NMR spectra were recorded on a Brucker WM 250 (250 MHz) NMR spectrometer and mass spectra were recorded on Finnigan Mat 311A instruments. Sodium salt of tetrakis(4,5,6,7-tetrahydro-7,8,8-trimethyl-2*H*-4,7-methanoindazolyl)borate was synthesized by literature method [12]. (−)-3(5)-Methyl-1-phenylethylaminomethylpyrazole (P1) was also synthesized by the method described earlier [13].

*3.1. Synthesis of hydrotris((−)-3(5)-methyl-1-phenylethylaminomethylpyrazolyl)borate [NaHB(P1)$_3$] (**2**)*

The 7.132 g (33.0 mmol) of P1 and 0.418 g $NaBH_4$ (11.0 mmol) were gradually heated at 210–230 °C with monitoring of H_2 evolution. Heating was continued at that temperature till 3 equiv. of hydrogen gas was evolved. The mixture was then allowed to cool to room temperature. The solid mass was washed two times with 80 ml hot petroleum ether and dried in vacuum. Yield: 16%, $[\alpha]_d^{25} = -45.1^\circ$ (c 1.00, ethanol). Mass spectrum (PI-FAB:glycerin/MeOH, *m*/*e*); 655, anion of [NaHB(P1)$_3$]. IR (KBr, cm^{-1}), 3056, 3024(w) (ν(=C–H)); 2960, 2945 (ν(–C–H)); 2410 (νB–H); 1615, 1510, 1460 (νC=N, C=C). ^{1}H-NMR (250 MHz, $CDCl_3$/TMS), δ (ppm): 7.36 (s, 3H, pzC(5)–H), 7.30–6.90 (m, 5H, C_6H_5), 6.20–5.95 (m, 3H, pzC(4)–CH), 3.80–3.18 (m, 9H, CH–CH_3 + pzC(3)–CH_2), 2.16–1.70 (m, 9H, *N*-CH_3), 1.40–0.97 (m, 9H, CH–CH_3). $C_{39}H_{49}BN_9Na$ (677.68): calculated: C 69.12%, H 7.29%, N 18.60%; found: C 67.98%, H 7.42%, N 18.42%.

3.2. Cyclopropanation procedure

The solution of copper(I)triflate–benzene complex (0.025 mmol), styrene (5.0 mmol) and [NaB(camphpz)$_4$]/[NaHB(P1)$_3$] (0.060 mmol) in the used solvent (3.0 ml) was stirred for 1–2 h at 45 °C under

an argon atmosphere. Then the diazo compound (1.0 mmol) in dichloromethane/1,2-dichloroethane (3.0 ml) was added at the specified reaction temperature through a microsyringe controlled by a feeder (ca. 0.4 ml/h) for 7 h. After stirring for an additional 10 h at the reaction temperature (25 or 45 °C), the mixture was concentrated under reduced pressure. The residual oil was subjected to silica gel column chromatography, at first with hexane to remove the excess of styrene, then with hexane–ethyl acetate (10:1) as the eluent to give, after evaporation, an oily mixture of the *cis*- and *trans*-2-phenylcyclopropane-carboxylate esters. The yield is determined by weight of the above described cyclopropane oil residue. The *cis*/*trans* ratio is obtained by NMR ($CDCl_3$/TMS, 270 MHz): *cis*, 3.87 ppm (CH_2O, q), *trans*, 4.17 ppm (CH_2, q).

3.3. Optical yield

The ethyl and menthyl cyclopropane esters were converted to the corresponding methyl ester by the following procedure: 30–40 mg of the cyclopropane ester mixture was refluxed for 2 h (ethyl ester) or 6 h (menthyl ester) in a mixture of 2 ml ethanol and 1 ml 1 N NaOH. After evaporation of the ethanol, the solution is acidified with 10% HCl to a pH of about 1. The obtained cyclopropane acid is extracted with 3×5 ml of CH_2Cl_2, then dried over $MgSO_4$ and Na_2SO_4. The solvent is evaporated and the acid is treated with a solution of CH_2N_2 in ether to give the corresponding methyl cyclopropane ester. The optical yield is determined by gas chromatography using a chiral B-DX 30m (Astec chiraldex 30m) column on a Shimazu Capillary Gas Chromatograph 14A at column temperature 110 °C, injection temperature 130 °C and detection temperature 130 °C. The retention times were: *cis* (1*R*,2*S*), 54.5 min; *cis* (1*S*,2*R*), 56.1 min; *trans* (1*S*,2*S*), 65.9 min; *trans* (1*R*,2*R*), 67.1 min (configurations are all relative to the ethyl ester).

Acknowledgements

Authors (UPS and PB) are very grateful to Department of Science and Technology, Government of India, New Delhi, for financial support in the form of young scientist project (No. HR/OY/C-20/96).

References

[1] H. Nozaki, S. Moriuti, H. Takaya, R. Noyori, Tetrahedron Lett. (1966) 5239;
M.P. Doyle, Chem. Rev. 86 (1986) 919;
M. Brookhart, W.B. Studebaker, Chem. Rev. 89 (1987) 411;
M.P. Doyle, Recl. Trav. Chim. Pays-Bas 110 (1991) 305;
M.P. Doyle, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 63;
R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994, p. 199.
[2] E.O. Fischer, Pure Appl. Chem. 24 (1970) 407.
[3] M.E. Wright, S.A. Svejda, M.I. Jin, M.A. Peterson, Organometallics 9 (1990) 136;
R.E. Lowenthal, A. Abiko, S. Masamune, Tetrahedron Lett. 31 (1990) 6005;
D. Müller, G. Umbricht, B. Weber, A. Pfaltz, Helv. Chim. Acta 74 (1991) 232;
U. Leutenegger, G. Umbricht, C. Fahrni, P. Von Matt, A. Pfaltz, Tetrahedron 48 (1992) 2143;
H. Brunner, K. Wutz, New J. Chem. 16 (1992) 57;
K. Ito, T. Katsuki, Tetrahedron Lett. 34 (1993) 2661;
D.L. Christenson, C.J. Tokar, W.B. Tolman, Organometallics 14 (1995) 2148;
V.K. Singh, A.D. Gupta, G. Sekar, Synthesis (1997) 137;
M.C. Keyes, B.M. Chamberlain, S.A. Caltagirona, J.A. Halfen, W.B. Tolman, Organometallics 17 (1998) 1984;
G. Sekar, A.D. Gupta, V.K. Singh, J. Org. Chem. 63 (1998) 2961.
[4] A.D. Gupta, D. Bhuniya, V.K. Singh, Tetrahedron 50 (1994) 13725;
S.-B. Park, H. Nishiyama, Y. Itoh, K. Itoh, J. Chem. Soc., Chem. Commun. (1994) 1315;
H. Brunner, C. Henrichs, Tetrahedron-Asymmetr. 6 (1995) 653;
S.-B. Park, K. Murata, H. Matsumoto, H. Nishiyama, Tetrahedron-Asymmetr. 6 (1995) 2487;
H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki, K. Itoh, Bull. Chem. Soc. Jpn. 68 (1995) 1247;
Y. Uozumi, H. Kyota, E. Kishi, K. Kitayama, T. Hayashi, Tetrahedron-Asymmetr. 7 (1996) 1603;
A.M. Harm, J.G. Knight, G. Stemp, Tetrahedron Lett. 37 (1996) 6189;
X.Y. Wu, X.H. Li, Q.L. Zhou, Tetrahedron-Asymmetr. 9 (1998) 4143;
H. Brunner, B. Hassler, Z. Naturforsch 53b (1998) 476;
H. Brunner, B. Hassler, Z. Naturforsch 53b (1998) 126;
J.M. Fraile, J.I. Garcia, J.A. Mayoral, T. Tarnai, J. Mol. Catal. A 144 (1999) 85;
J.M. Fraile, J.I. Garcia, J.A. Mayoral, T. Tarnai, M.A. Harmer, J. Catal. 186 (1999) 214;
M.I. Burguete, J.M. Fraile, J.I. Garcia, E. Garcia-Verdugo, S.V. Luis, J.A. Mayoral, Org. Lett. 2 (2000) 3905.
[5] S.-B. Park, N. Sakata, H. Nishiyama, Chem. Eur. J. 2 (1996) 303.
[6] D.A. Evans, K.A. Woerpel, M.M. Hinman, M.M. Faul, J. Am. Chem. Soc. 113 (1991) 726.

[7] M.P. Doyle, B.D. Brandes, A.P. Kazala, R.J. Poeters, M.B. Jarstfer, L.M. Watkins, C.T. Eagle, Tetrahedron Lett. 31 (1990) 6613;
M.P. Doyle, R.J. Pieters, S.F. Martin, R.E. Austin, C.J. Oalmann, P. Muller, J. Am. Chem. Soc. 113 (1991) 1423;
M.N. Protopopova, M.P. Doyle, J. Am. Chem. Soc. 114 (1992) 2755;
S.F. Martin, R.E. Austin, C.J. Oalmann, W.R. Baker, S.L. Condon, E. deLara, S.H. Rosenberg, K.P. Spina, H.H. Stein, J. Cohen, H.D. Kleinert, J. Med. Chem. 35 (1992) 1710;
J.L. Maxwell, S. O'Malley, K.C. Brown, T. Kodadek, Organometallics 11 (1992) 645;
S. O'Malley, T. Kodadek, Organometallics 11 (1992) 2299;
M.P. Doyle, M.N. Protopopova, B.D. Brandes, H.M.L. Davies, N.J.S. Huby, J.K. Whitesell, Synletters (1993) 151;
M.P. Doyle, W.R. Winchester, J.A.A. Hoorn, V. Lynch, S.H. Somonsen, R. Ghosh, J. Am. Chem. Soc. 115 (1993) 9968;
S.F. Martin, C.J. Oalmann, S. Liras, Tetrahedron 49 (1993) 3521;
S.F. Martin, M.R. Spaller, S. Liras, B. Hartmann, J. Am. Chem. Soc. 116 (1994) 4493.

[8] S. Trofimenko, J. Am. Chem. Soc. 86 (1967) 6288;
S. Trofimenko, Inorg. Synth. 12 (1970) 99;
S. Trofimenko, Acc. Chem. Res. 4 (1971) 17;
S. Trofimenko, Chem. Rev. 72 (1972) 497;
S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115;
S. Trofimenko, Chem. Rev. 93 (1993) 943;
A.L. Rheingold, R.L. Ostrander, B.S. Haggerty, S. Trofimenko, Inorg. Chem. 33 (1994) 3666;
N. Kitajima, W.B. Tolman, Prog. Inorg. Chem. 43 (1995) 420;
D.L. Reger, Coord. Chem. Rev. 147 (1996) 571.

[9] M.M. Diaz-Requejo, M.C. Nicasio, P.J. Perez, Organometallics 17 (1998) 3051;
M.M. Diaz-Requejo, T.R. Belderrain, M.C. Nicasio, P.J. Perez, Organometallics 19 (2000) 285;
M.M. Diaz-Requejo, P.J. Perez, J. Organomet. Chem. 617 (2001) 110;
P. Babbar, H. Brunner, U.P. Singh, Indian J. Chem. A 40 (2001) 225.

[10] C.J. Tokar, P.B. Kettler, W.B. Tolman, Organometallics 11 (1992) 2737;
D.D. LeCloux, W.B. Tolman, J. Am. Chem. Soc. 115 (1993) 1153.

[11] J.S. Thompson, J.L. Zitzmann, T.J. Marks, J.A. Ibers, Inorg. Chim. Acta 46 (1980) L101.

[12] H. Brunner, U.P. Singh, T. Boeck, S. Altmann, T. Scheck, B. Wrackmeyer, J. Organomet. Chem. 443 (1993) C16.

[13] H. Brunner, T. Scheck, Chem. Ber. 125 (1992) 701.

[14] M.P. Doyle, V. Bagheri, T.J. Wandless, N.K. Harn, D.A. Brinker, C.T. Eagle, K.-L. Loh, J. Am. Chem. Soc. 112 (1990) 1906.