Rhodium(I)-, iridium(I)-, and ruthenium(II)-catalyzed asymmetric transfer hydrogenation of ketones using diferrocenyl dichalcogenides as chiral ligands

Yoshiaki Nishibayashi [a], Jai Deo Singh [a], Yasuyoshi Arikawa [a], Sakae Uemura [a,*],
Masanobu Hidai [b]

[a] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*
[b] *Department of Chemistry and Biotechnology, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan*

Abstract

[$R,S;R,S$]-Bis[2-[1-(dimethylamino)ethyl]ferrocenyl] dichalcogenides, (R,S)-{[EC$_5$H$_3$CHMe(NMe$_2$)]Fe(C$_5$H$_5$)}$_2$ (E = S, Se, Te), act as chiral ligands for Rh(I)-catalyzed asymmetric transfer hydrogenation of alkyl aryl ketones using a diphenylsilane/methanol system to give the corresponding alcohols in fair to good yields with moderate enantiomeric excess (22–95% *ee*). The transfer of hydrogen from methanol to the resultant alcohol is confirmed by experiment using deuterated methanol (MeOD), and a new catalytic system containing Rh-hydride species is proposed. In the well-known 2-propanol/base system, the stereoselection is not satisfactory for Rh(I)-, Ir(I)- and Ru(II)-catalyzed reactions using these ligands.

Keywords: Rhodium; Iridium; Ruthenium; Hydrogenation; Chalogenide; Chirality

1. Introduction

In a transition metal-catalyzed enantioselective hydrogenation of ketones, that of simple ketones lacking secondary coordinating functional groups is known to be difficult to attain high enantiomeric excess (*ee*) compared with that of functionalized ketones (see for example [1]; very recently Noyori and coworkers [2] reported highly enantioselective hydrogenation of simple ketones by a ruthenium(II) complex). Recently, some complexes of Rh and Ir with chiral nitrogen ligands were shown to work as fair [3] to good [4] catalysts for this purpose via transfer hydrogenation using a 2-propanol/base system, and yet higher temperatures and basic conditions were necessary in these cases. Quite recently, an excellent system for highly enantioselective asymmetric transfer hydrogenation of simple ketones was developed using the new chiral Ru(II) complex and formic acid/triethylamine [5] or 2-propanol/KOH [6]. As another approach, an effective

enantioselective asymmetric hydrosilylation and subsequent hydrolysis were developed for the reduction of unfunctionalized ketones [7]. We reported recently that [$R,S;R,S$]-bis[2-[1-(dimethylamino)ethyl]ferrocenyl] dichalcogenides, (R,S)-{[EC$_5$H$_3$CHMe(NMe$_2$)]Fe-(C$_5$H$_5$)}$_2$ (E = S, Se 2, Te 3), acted efficiently as chiral ligands for the Rh(I)-catalyzed asymmetric hydrosilylation of unfunctionalized alkyl aryl ketones with diphenylsilane in tetrahydrofuran [8,9]. When the reaction was carried out in methanol as solvent, it gave directly a chiral alcohol, not a hydrosilylated compound. Close examination revealed that the reaction proceeded via a transfer hydrogenation pathway under very mild and neutral conditions, not via hydrogenation by evolved hydrogen and also not via hydrosilylation by some silane species. Although *ee* values of the resultant alcohols are yet moderate, our finding seems to present a new catalytic asymmetric transfer hydrogenation system since the combination of diphenylsilane and methanol is so far known only to give hydrogen under the employed conditions [10,11]. Transfer hydrogenation using the well-known 2-propanol/base system was also examined in the presence of an Rh(I), Ir(I) or

---

* Corresponding author.

Ru(II) complex and a dichalcogenide **1**, **2** or **3**. Typical results of these reactions are reported here (paper partly presented at the *68th Annual Meet. of the Chemical Society of Japan, Nagoya, October 1994*, Abstr. p. 27 and at the *6th Int. Kyoto Conf. on New Aspects of Organic Chemistry, Kyoto, November 1994*, Abstr. p. 192).

2. Results and discussion

2.1. Rhodium(I)-catalyzed asymmetric transfer hydrogenation of ketones using diphenylsilane and methanol as a new hydrogen source

The chiral dichalcogenides **1–3** and the chiral diselenides without an amino group, such as **4** and **5** (Scheme 1), were prepared by the reported method [8,9,12–14]. The reduction of acetophenone in the presence of these chiral ligands was first examined under a variety of conditions. A methanol (1 ml) solution of [Rh(cod)Cl]₂ (0.025 mmol; 2.5 mol%; cod = cycloocta-1,5-diene) and the chiral diselenide **2** (0.05 mmol; 5 mol%) was stirred at room temperature for 1 h under argon and then a diphenylsilane (1.5 mmol) was added. Shortly afterwards, a vigorous gas evolution was observed in the dark red solution. The solution was cooled to 0 °C, acetophenone (1.0 mmol) in methanol (1 ml) added and the resulting mixture stirred at 0 °C for an appropriate time. The chiral 1-phenylethanol was obtained in good chemical yield and moderate *ee* together with diphenyldimethoxysilane Ph₂Si(OMe)₂. The *ee* values were determined by HPLC using Daicel Chiralcel OB, OD and OJ columns. Typical results and reaction conditions are summarized in Table 1 (Scheme 1). Higher enantioselectivity was observed at lower temperature (48% *ee* at 0 °C and 32% *ee* at 25 °C), but the reaction did not proceed at −20 °C. In other alcohols,
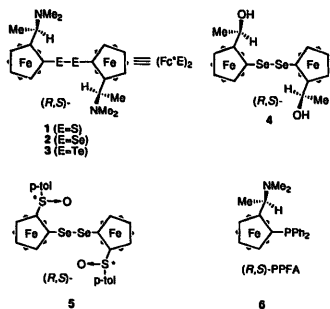
Table 1
Asymmetric transfer hydrogenation of acetophenone catalyzed by Rh(I)-(**1–6**) [a]

Run	Ligand	Reaction condition		1-Phenylethanol (R)	
		Solvent	Temperature (°C)/time (h)	GLC yield (%)	ee (%)
1	2	MeOH	0/70	46	48
2	2	MeOH	25/70	50	32
3 [b]	2	MeOH	25/70	3	--
4	2	EtOH	0/70	0	—
5	2	ⁱPrOH	0/70	0	—
6	1	MeOH	0/40	56	10
7	3	MeOH	0/40	72	27
8	4	MeOH	0/40	< 10	—
9	5	MeOH	25/120	0	—
8	6	MeOH	0/40	< 10	—
9	Ph₃P	MeOH	0/40	< 10	—
10 [c]	2	MeOH	0/70	0	—
11 [d]	2	MeOH	0/70	0	—

[a] All reactions were carried out in the presence of [Rh(cod)Cl]₂ (2.5 mol%) and **2** (5 mol%) with acetophenone (1.0 mmol) and diphenylsilane (1.5 mmol) in alcohol (2 ml).
[b] [Rh(cod)₂]BF₄ (5.0 mol%) was used instead of [Rh(cod)Cl]₂.
[c] [Ir(cod)Cl]₂ (2.5 mol%) was used instead of [Rh(cod)Cl]₂ (2.5 mol%).
[d] [Ru(cod)Cl₂]ₙ (5.0 mol%) was used instead of [Rh(cod)Cl]₂ (2.5 mol%).

such as ethanol and 2-propanol, the reaction did not proceed at all. The compounds **1** and **3** could also be used as ligands, but they were less effective for stereoselection than **2**; 10% *ee* and 27% *ee* respectively. When the diselenides **4** and **5** were used, phosphine ligands such as (*R,S*)-[2-[(1-dimethylamino)ethyl]ferrocenyl] diphenylphosphine (**6**; (*R,S*)-PPFA) [15] and PPh₃ were used in place of **1–3** as ligands, the transfer hydrogenation did not occur at all. The result shows another utility of our chiral diferrocenyl dichalcogenides. However, the reaction did not proceed at all when the Rh(I) complex was replaced by corresponding Ir(I) and Ru(II) complexes such as [Ir(cod)Cl]₂ and [Ru(cod)Cl₂]ₙ (see Table 1).

Next, we applied this Rh(I)-catalyzed reaction system using **2** to a variety of alkyl aryl ketones (Table 2). The product yield was much dependent on the nature of the alkyl and aryl groups. It decreased in order of bulkiness of the alkyl group as expected; Me (46%) > Et (28%) > ⁱBu (11%): the introduction of an electron-withdrawing group such as NO₂ (92%) and Cl (51%) to an aryl group or the use of a thienyl group (100%) increased the yield, while the introduction of an electron-releasing group such as *p*-Me or *p*-MeO inhibited the reaction completely. The enantioselectivity was generally mod-

Scheme 1.

Scheme 2.

Table 2
Asymmetric transfer hydrogenation of alkyl aryl ketones catalyzed by Rh(I)-(2) [a]

Run	Ketone		Time (h)	Product (R)	
	Ar	R		GLC yield (%)	ee (%)
1	Ph	Me	70	46	48
2	Ph	Et	40	28	31
3	Ph	CH_2Cl	70	68	25 [b]
4 [c]	Ph	CO_2Me	25	95	41
5	Ph	^tBu	170	11	95
6	indanone	—	170	15 [d]	31
7	p-$NO_2C_6H_4$	Me	50	92 [d]	25 [e]
8	p-ClC_6H_4	Me	70	51	22 [b]
9	p-$CH_3C_6H_4$	Me	70	0	—
10	p-$CH_3OC_6H_4$	Me	70	0	—
11	2-naphthyl	Me	70	24	37 [b]
12	2-thienyl	Me	70	100	43

[a] All reactions were carried out in the presence of [Rh(cod)Cl]$_2$ (2.5 mol%) and 2 (5 mol%) with alkyl aryl ketone (1.0 mmol) and diphenylsilane (1.5 mmol) in MeOH (2 ml) at 0 °C.
[b] The absolute configuration of the product is S.
[c] At 25 °C.
[d] Isolated yield.
[e] The absolute configuration of the product is not determined.

erate (22–48% ee), 95% ee in the case of 2,2-dimethyl-propiophenone being the highest. This tendency was the same as that in the case of asymmetric hydrosilylation using chiral diferrocenyl dichalcogenides as ligands [8,9].

The reduction seems to proceed as follows. The first step is the ligand exchange of cyclooctadiene on the Rh(I) complex with dichalcogenide. In the second step, a resultant Rh(I)–dichalcogenide complex catalyzes the reaction of diphenylsilane with methanol to generate hydrogen and methoxydiphenylsilane. It is known that Rh(I) compounds catalyze such reactions (Scheme 3(i)) [10,11]. Then, the Rh(I) complex transfers hydrogen of methoxydiphenylsilane and/or methanol to the carbonyl compound enantioselectively (Scheme 3(ii)). We confirmed separately that the reduction did not proceed at all with 1 atm hydrogen in place of diphenylsilane, even in the presence of 2. The presence of methoxy-diphenylsilane and the absence of hydrosilylated product such as ArCH(R)OSiHPh$_2$ were also confirmed. It is worth noting that the reduction did not proceed when ethanol or 2-propanol was used as solvent, probably because the rhodium(I) complex cannot catalyze the reaction between diphenylsilane and ethanol or 2-pro-
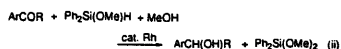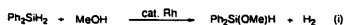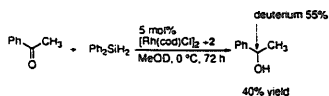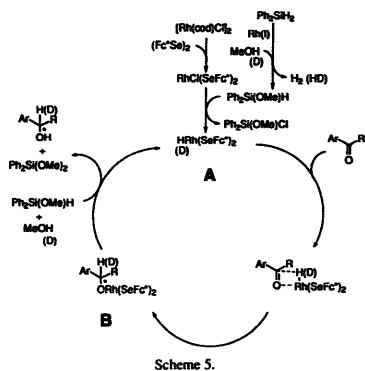
Scheme 4.

panol at lower temperatures such as 0–25 °C as described so far [10]. When acetophenone was treated in deuterated methanol (MeOD), nearly equal amounts of deuterated and non-deuterated (at carbon) 1-phenyl-ethanols were obtained (Scheme 4), the result indicating that the introduced hydrogen in this reduction comes from both methanol and diphenylsilane. We also confirmed separately that deuterium exchange between diphenylsilane and deuterated methanol to give species such as Ph$_2$Si(OMe)D did not occur under the present reaction conditions. These facts clearly exclude the intervention of a hydrosilylation pathway. Considering these results we propose a new catalytic cycle for transfer hydrogenation, using diphenylsilane and methanol as hydrogen source, in which an Rh-hydride species (A) [3] might be involved as shown in Scheme 5, though we do not have any direct evidence for the presence of such species. A detailed mechanism for the formation of A from the species having an O–Rh bond (B), Ph$_2$Si(OMe)H and methanol is not yet known. To the best of our knowledge, this is the first example of transfer hydrogenation of ketones using diphenylsilane and methanol as hydrogen source (hydrogenation of alkenes and alkynes using diphenylsilane and methanol in the presence of palladium catalyst was reported, in which an evolved hydrogen acted as a reactant [16]). In addition, this Rh(I)-catalyzed system could be applied to the asymmetric reduction of ketones.
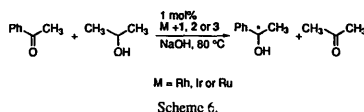
Scheme 3.

Scheme 5.

2.2. Rhodium(I)-, iridium(I)-, and ruthenium(II)-catalyzed asymmetric transfer hydrogenation of alkyl aryl ketones using 2-propanol and base

In the studies of asymmetric transfer hydrogenation, the 2-propanol/base [3,4] and formic acid/triethylamine [5,17] systems have so far been used as a source of hydrogen. We also examined the transition metal-catalyzed asymmetric transfer hydrogenation of simple ketones by using a 2-propanol/base system in the presence of a catalytic amount of chiral ligands 1–3.

A typical procedure using acetophenone as substrate was as follows. A 2-propanol (1 ml) solution of [Rh(cod)Cl]₂ (0.005 mmol; 0.5 mol%) and .he diselenide 2 (0.01 mmol; 1 mol%) was stirred at 80 °C for 15 min under argon. Acetophenone (1.0 mmol) in 2-propanol (1 ml) was then added and the mixture stirred at 80 °C for another 15 min. The solid NaOH (8 mg, 0.20 mmol) was then added portionwise and the mixture further stirred at 80 °C for 1 h. The chiral 1-phenylethanol was obtained in good chemical yield and moderate *ee*. The *ee* values were determined by HPLC using Daicel Chiralcel columns as described above. The reaction was also carried out in the presence of [Ir(cod)Cl]₂ or [Ru(cod)Cl₂]ₙ as catalyst. Typical results and reaction conditions are summarized in Table 3 (Scheme 6). Although the enatioselectivity was not satisfactory in all cases, a suitable combination of transition metal and dichalcogenide was important for stereoselection. With the rhodium complex ([Rh(cod)Cl]₂), the diselenide 2

Table 3
Asymmetric transfer hydrogenation of acetophenone catalyzed by Rh(I)-, Ir(I)- or Ru(II)-(1–3) [a]

Run	Metal	Ligand	Time (h)	1-Phenylethanol (R)	
				GLC yield (%)	ee (%)
1	Rh [b]	2	1	65	27
2	Rh [b]	2 [c]	1.5	41	33
3	Rh [b]	2	2 [d]	30	14
4	Rh [b]	2	10 [e]	100	7
5	Rh [b]	1	1	0	—
6	Rh [b]	3	1	43	13
7	Ir [f]	2	1	47	32
8	Ir [f]	1	1	0	—
9	Ir [f]	3	1	40	35
10	Ru [g]	2 [c]	2	32	18
11	Ru [g]	2	1 [e]	44	27
12	Ru [f]	1	1 [e]	51	15
13	Ru [g]	3	1 [e]	48	29

[a] All reactions were carried out in the presence of metal catalyst (0.5 mol%) and 1–3 (1 mol%) with NaOH (20 mol%) and acetophenone (1.0 mmol) in ¹PrOH (2 ml) at 80 °C (reflux).
[b] [Rh(cod)Cl]₂.
[c] 2 (0.5 mol%) was used.
[d] ¹PrOH (1 ml) was used.
[e] ¹PrOH (4 ml) was used.
[f] [Ir(cod)Cl]₂.
[g] [Ru(cod)Cl₂]ₙ.

M = Rh, Ir or Ru

Scheme 6.

was better than other dichalcogenides, while with the iridium complex ([Ir(cod)Cl]₂) and ruthenium complex ([Ru(cod)Cl₂]ₙ) [18], the ditelluride 3 was slightly better than others. Application to other alkyl aryl ketones such as propiophenone, indanone and *t*-butyl phenyl ketone resulted in a lower product yield (6–38%) and lower stereoselectivity (0–22% *ee*). On hydrosilylation [8,9] using these dichalcogenides as chiral ligands, the absolute configuration of the resultant alcohols was completely opposite in Rh and Ir cases. However, in this transfer hydrogenation the configuration of the produced alcohol was the same in all cases.

3. Experimental section

¹H NMR spectra were recorded on a Jeol GSX-270 (270 MHz) spectrometer as solutions in CDCl₃. GLC analyses were performed on a Hitachi 163 instrument (1 m × 3 mm stainless steel column packed with 20% EGSS on Shimalite) and a Shimadzu GC-14A instrument (25 m HiCap-CBP-10-S25 capillary column) with flame-ionization detectors and N₂ as carrier gas. Column chromatographies on Al₂O₃ and SiO₂ were performed with ICN Alumina N, Akt. I and with Wakogel C-300 (hexane and hexane/ethyl acetate as eluents) respectively. All the solvents were distilled from CaH₂ or LiAlH₄ and stored over 4 Å molecular sieves under nitrogen. The chiral diferrocenyl dichalcogendies (1–3) were prepared by the reported method from the chiral N,N-dimethyl-1-ferrocenylethylamines [13,14]. The other chiral diferrocenyl diselenides (4 and 5) were prepared by following the literature method [9]. The chiral PPFA [2-(1-dimethylaminoethyl)ferrocenyl]-diphenylphosphine (6) was prepared by the Hayashi procedure [15,19]. All the starting ketones, resultant alcohols and deuterium compounds are known compounds and commercially available.

3.1. General procedure for asymmetric transfer hydrogenation of ketones with rhodium(I) complex and chiral ligand using diphenylsilane and methanol as hydrogen source

In a 20 ml round-bottomed flask were placed a metal complex (0.025 mmol) and a chiral ligand (0.05 mmol) under argon. Anhydrous MeOH (1.0 ml) was added, and the mixture was then magnetically stirred at room temperature for 1 h. After the reaction flask was dipped in a

thermoregulated bath at 0°C, diphenylsilane (1.5 mmol) was added. After gas evolution ceased, the ketone (1.0 mmol) in MeOH (1.0 ml) was slowly added by syringe. The reaction mixture was kept at 0°C for an appropriate time. For the work-up, the reaction mixture was extracted with brine (50 ml) and diethyl ether (3 × 50 ml). For GLC analyses, 1,2-diphenylethane was added as internal standard. For isolation, the extract was dried over anhydrous $MgSO_4$, concentrated under reduced pressure by an aspirator, and then distilled in vacuum by Kugelrohr to give the corresponding alcohol together with the unreacted starting ketone. Dimethoxydiphenylsilane was left in the residue. The ee value and the configuration of the alcohols of the distillate were determined by HPLC on Daicel Chiralcel OJ, OD, OB and OF columns (2-propanol/hexane as eluent).

3.2. General procedure for asymmetric transfer hydrogenation of ketones with rhodium(I), iridium(I), and ruthenium(II) complex and chiral ligand using 2-propanol and NaOH

In a 20 ml round-bottomed flask were placed a metal complex (0.005 mmol) and a chiral ligand (0.01 mmol) under argon. Anhydrous 2-propanol (1.0 ml) was added, and the mixture was then magnetically stirred at reflux temperature for 15 min. After the addition of acetophenone (1.0 mmol) in anhydrous 2-propanol (1.0 ml), the reaction mixture was stirred at reflux temperature for 15 min. Then the solid NaOH (8 mg, 0.20 mmol) was added portionwise and the mixture stirred at 80°C for 1 h. For the work-up, 1 N HCl aq. (5 ml) and then brine (50 ml) were added to the reaction mixture and the mixture was extracted with diethyl ether (3 × 50 ml). The analysis and determination of the products were carried out as described above.

3.3. The reaction of diphenylsilane with methanol and deuterated methanol

Diphenylsilane (1.5 mmol) was added to the chilled mixture (at 0°C) of $[Rh(cod)Cl]_2$ (0.025 mmol), the chiral diselenide 2 (0.05 mmol), deuterated methanol (1 mmol) and anhydrous diethyl ether (1 ml) under nitrogen and the mixture was stirred for 5–10 min [10]. A similar reaction was also carried out using methanol. ^{1}H NMR analysis of the Kugelrohr distillation product (ca. 0.15 g; 200°C/5–10 mmHg) revealed the presence of $Ph_2Si(OMe)H$ [^{1}H NMR: δ 3.61 (–OMe), 5.39 (Si–H)] and showed that the ratio of peak area of two signals [3:1] was almost the same in both cases, suggesting no deuterium incorporation in the case of MeOD.

3.4. Analysis of the deuterium distribution

The deuterium distribution in 1-phenylethanol was evaluated by comparison of the integral intensity of the methine proton with the intensity of the phenyl and methyl protons.

References

[1] H. Takaya, T. Ohta and R. Noyori, in I. Ojima (ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 1.

[2] T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya and R. Noyori, J. Am. Chem. Soc., 117 (1995) 2675.

[3] G. Zassinovich and G. Mestroni, Chem. Rev., 92 (1992) 1051; G. Zassinovich, R. Bettella, G. Mestroni, N. Bresciani-Pahor, S. Geremia and L. Randaccio, J. Organomet. Chem., 370 (1989) 187; C. Bolm, Angew. Chem., Int. Ed. Engl., 30 (1991) 542 and references cited therein; S. Gladiali, L. Pinna, G. Deloga, S.D. Martin, G. Zassinovich and G. Mestroni, Tetrahedron: Asymm., 1 (1990) 635; P. Gamez, F. Fache, P. Mangeney and M. Lemaire, Tetrahedron Lett., 34 (1993) 6897; P. Gamez, B. Dunjic, F. Fache and M. Lemaire, J. Chem. Soc., Chem. Commun., (1994) 1417; P. Gamez, F. Fache and M. Lemaire, Bull. Soc. Chim. Fr., 131 (1994) 600; P. Gamez, F. Fache and M. Lemaire, Tetrahedron: Asymm., 6 (1995) 705.

[4] D. Müller, G. Umbricht, B. Weber and A. Pfaltz, Helv. Chim. Acta, 74 (1991) 232.

[5] A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya and R. Noyori, J. Am. Chem. Soc., 118 (1996) 2521.

[6] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya and R. Noyori, J. Am. Chem. Soc., 117 (1995) 7562; J. Takehara, S. Hashiguchi, A. Fujii, S. Inoue, T. Ikariya and R. Noyori, J. Chem. Soc., Chem. Commun., (1996) 233; J.-X. Gao, T. Ikariya and R. Noyori, Organometallics, 15 (1996) 1087.

[7] H. Brunner, H. Nishiyama and K. Itoh, in I. Ojima (ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 303; Y. Nishibayashi, K. Segawa, K. Ohe and S. Uemura, Organometallics, 14 (1995) 5486; Y. Nishibayashi, K. Segawa, H. Takada, K. Ohe and S. Uemura, J. Chem. Soc., Chem. Commun., (1996) 847.

[8] Y. Nishibayashi, J.D. Singh, K. Segawa, S. Fukuzawa and S. Uemura, J. Chem. Soc., Chem. Commun., (1994) 1375.

[9] Y. Nishibayashi, J.D. Singh, K. Segawa, S. Fukuzawa, K. Ohe and S. Uemura, Organometallics, 15 (1996) 370.

[10] I. Ojima, T. Kogure, M. Nihonyanagi, H. Kono and S. Inaba, Chem. Lett., (1973) 501.

[11] R.J.P. Corriu and J.J.E. Moreau, J. Chem. Soc., Chem. Commun., (1973) 38; L.H. Sommer and J.E. Lyons, J. Am. Chem. Soc., 91 (1969) 7061.

[12] Y. Nishibayashi, J.D. Singh, S. Fukuzawa and S. Uemura, Tetrahedron Lett., 35 (1994) 3115.

[13] Y. Nishibayashi, J.D. Singh, S. Fukuzawa and S. Uemura, J. Org. Chem., 60 (1995) 4114.

[14] Y. Nishibayashi, J.D. Singh, S. Fukuzawa and S. Uemura, J. Chem. Soc., Perkin Trans. 1, (1995) 2871.

[15] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, Bull. Chem. Soc. Jpn., 53 (1980) 1138.

[16] H. Sakurai, J. Abe and K. Sakamoto, *Main Group Metal Chem.*, *13* (1990) 203.

[17] J.M. Brown, H. Brunner, W. Leitner and M. Rose, *Tetrahedron: Asymm.*, *2* (1991) 331 and references cited therein.

[18] J.E. Bäckvall, R.L. Chowdhury and U. Karlsson, *J. Chem. Soc., Chem. Commun.*, (1991) 473; R.L. Chowdhury and J.E. Bäckvall, *J. Chem. Soc., Chem. Commun.*, (1991) 1063; G.Z. Wang and J.E. Bäckvall, *J. Chem. Soc., Chem. Commun.*, (1992) 337; G.Z. Wang and J.E. Bäckvall, *J. Chem. Soc.,*

Chem. Commun., (1992) 980; P. Krasik and H. Alper, *Tetrahedron, 50* (1994) 4347; J.P. Genet, V. Ratovelomanana-Vidal and C. Pinel, *Synlett*, (1993) 478; M. Bianchi, U. Matteoli, G. Menchi, P. Frediani, S. Pratesi and F. Piacenti, *J. Organomet. Chem., 198* (1980) 73.

[19] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann and I. Ugi, *J. Am. Chem. Soc., 92* (1970) 5396; D. Marquarding, H. Burghard, I. Ugi, R. Urban and H. Klueacek, *J. Chem. Res.(S)*, (1977) 82.