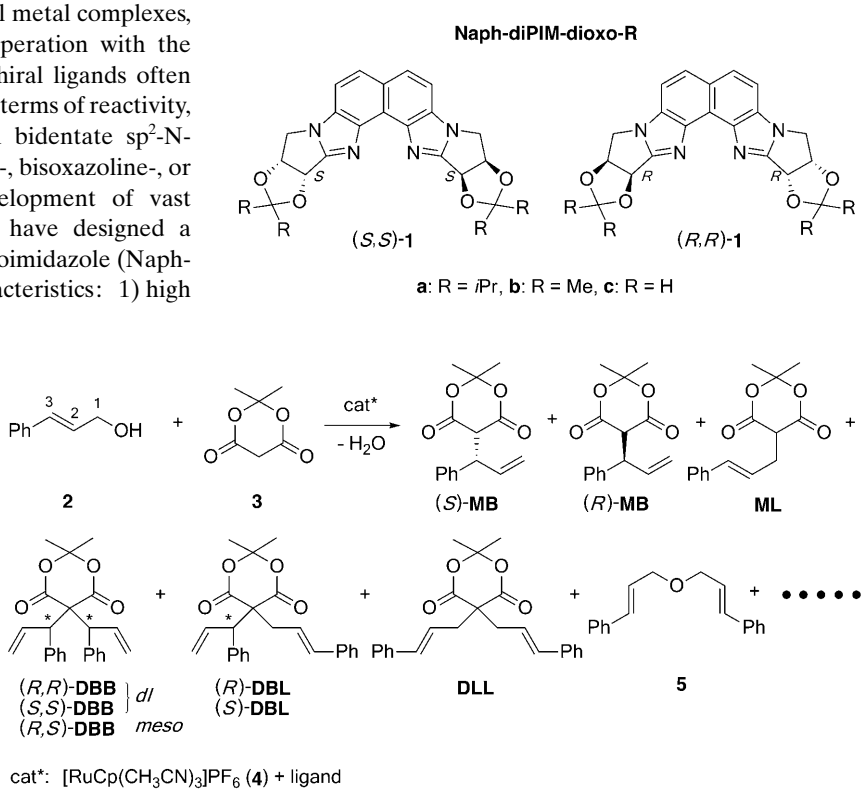
Asymmetric Catalysis

DOI: 10.1002/ange.201100772

A Chiral Bidentate sp^2-N Ligand, Naph-diPIM: Application to CpRu-Catalyzed Asymmetric Dehydrative C-, N-, and O-Allylation**

*Kengo Miyata, Hironori Kutsuna, Sho Kawakami, and Masato Kitamura**

In asymmetric reactions catalyzed by chiral metal complexes, the ligand plays a definitive role in cooperation with the central metal. The introduction of new chiral ligands often revolutionizes the catalytic performance in terms of reactivity, selectivity, and productivity.[1] The chiral bidentate sp^2-N-ligands that possess a privileged bipyridine-, bisoxazoline-, or diimine-skeleton have enabled the development of vast numbers of asymmetric reactions.[2] We have designed a novel ligand, naphtho[1,2-*b*:7,8-*b*′]dipyrroloimidazole (Naph-diPIM), which has the following characteristics: 1) high rigidity and planarity with fixation of two sp^2-hybridized N atoms on the same side, 2) near 90° bite angle, making the coordination plane and Naph-diPIM plane coplanar to stabilize square-planar and octahedral metal complexes, 3) an extended π-conjugated system showing pyridine-level π-acceptability, and 4) high σ-donicity derived from the two amidine units. Introduction of substituents on the pyrrolo moieties, such as C_2 chiral (*S*,*S*)- or (*R*,*R*)-Naph-diPIM-dioxo-R (R = *i*Pr, Me, H) (**1a–c**),[3] should create a well-defined chiral environment (see below).



The Naph-diPIM-dioxo-R ligands **1a–c** were synthesized from 2,7-dibromo-1,8-dinitronaphthalene and appropriate acetonides of enantiomerically pure 3,4-dihydroxypyrrolidine-2-one by a Buchwald coupling/NO_2-reduction/dehydrative cyclization protocol.[4] We decided to access the utility of the new chiral ligands in intermolecular dehydrative C-allylation between (*E*)-3-phenylprop-2-en-1-ol ((*E*)-**2**) and Meldrum's acid (**3**). This particular reaction was chosen because it remains intractable. There have, however, been some recent breakthroughs in the development of new asymmetric metal complex catalysts for other important intramolecular dehydrative reactions, namely, chiral bisphosphine/Au-catalyzed Friedel–Crafts C-allylation of indoles,[5] chiral picolinic acid/CpRu-catalyzed cyclization (Cp = cyclopentadienyl) of ω-hydroxy allyl alcohols,[6] and chiral bisphosphine/Hg-catalyzed cyclization of anilino sulfonamide allyl alcohols.[7] In contrast, there are numerous metal complexes that catalyze C-, N-, and O-allylations using activated allyl alcohols such as allyl esters or halides.[8,9] From among these complexes, we focused on the high potential ability of $CpRu^{II}$ complexes for direct activation of allylic alcohols through π-allyl $CpRu^{IV}$ species based on both our own experiments[6,10] and those of others.[11,12] The standard conditions were set as $[[RuCp(CH_3CN)_3]PF_6$ (**4**)$]$[13] = [(*S*,*S*)-**1a**] = 0.5 mM, [(*E*)-**2**] = 500 mM, [**3**] = 2500 mM, CH_2Cl_2, reflux, 4 h, in which mono/di (M/D), branch/linear (B/L), *R* and *S* (*R*/*S* or enantiomeric ratio (e.r.)), and C- and O-allylation (C/O) selectivities are involved to give (*S*)-**MB**, (*R*)-**MB**, **ML**, (*R*,*R*)-**DBB**, (*S*,*S*)-**DBB**, (*R*,*S*)-**DBB**, (*R*)-**DBL**, (*S*)-**DBL**, **DLL**, and others.

[*] K. Miyata, H. Kutsuna, S. Kawakami, Prof. Dr. M. Kitamura
Research Center for Materials Science and
Department of Chemistry, Nagoya University
Chikusa, Nagoya 464-8602 (Japan)
Fax: (+81) 52-789-2958
E-mail: kitamura@os.rcms.nagoya-u.ac.jp

[**] This work was aided by a Grant-in-Aid for Scientific Research (No. 25E07B212) from the Ministry of Education, Science, Sports and Culture (Japan). Naph-diPIM = naphtho[1,2-*b*:7,8-*b*′]dipyrroloimidazole; Cp = cyclopentadienyl.

Supporting information (synthesis of ligands and substrates, general procedure for asymmetric allylation, X-ray crystallographic analysis of CpRu complexes, and NMR spectral data of ligands, substrates, and products) for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100772.

With (*S*,*S*)-Naph-diPIM-dioxo-*i*Pr (**1a**), 28% of (*E*)-**2** was converted to give the (*S*)- and (*R*)-**MB** in a 99:1 e.r. with very high **MB**/**ML** ratio (>200:1).[4] Addition of *p*-TsOH (0.5 mM) into this standard system (**4**/(*S*,*S*)-**1a** (0.5 mM)) completed the reaction to give **MB**, **ML**, *dl*-**DBB**, dicinnamyl ether (**5**), 2-(1-phenylallyl)malonic acid (**6**), and dicinnamyl malonate (**7**) in the ratio 93.6:0.4:2.2:1.2:2.5:0.2 (**MB**/**ML** 228:1; **MB**/*dl*-**DBB** 43:1) and greater than 99:1 (*S*)-/(*R*)-**MB**. Neither *meso*-**DBB**, **DBL**, nor **DLL** could be detected in the reaction mixture. With concentrations [**4**/(*S*,*S*)-**1a**] = 5 mM and [*p*-TsOH] = 0.5 mM, a similar result was obtained. The best results were achieved by increasing the concentrations of both **4**/(*S*,*S*)-**1a** and *p*-TsOH to 5 mM. The reaction was completed within 1 h to give a mixture of **MB**/**ML**/*dl*-**DBB** only in a ratio of 98.9:0.35:0.7 and a high e.r. (>99:1 (*S*)-/(*R*)-**MB** and >99:1 (*R*,*R*)-/(*S*,*S*)-**DBB**).[14] Using this approach there was no detectable formation of **5**, **6**, or **7**. Decreasing the concentration of **3** to 500 mM gave **MB** in 84% yield together with **DBB** in 15% yield without change in the e.r. values. The enantiomeric ligand (*R*,*R*)-**1a** afforded nearly enantiomerically pure (*R*)-**MB**. The acceleration effect was lowered in the order of *p*-TsOH, *p*-TsOH/Py, CF_3SO_3H, and *p*-TsOH/$(C_2H_5)_3N$, and *p*-TsOH/2Py retarded the reaction. Less acidic $(C_6H_5)_2PO_2H$ or C_6H_5COOH showed no effect. $B(C_6F_5)_3$ as well as $Zn(OTf)_2$ could be used, although the formation of **5**–**7** became significant. $In(OTf)_3$ and $Sm(OTf)_3$ led to the formation of insoluble compounds of undetermined structure, probably as a result of polymerization. CH_2Cl_2, $CHCl_3$, and toluene were the solvents of choice. In THF or DMF, the major reaction route was alcoholysis of **3** by **2** to afford **7**. The reaction was sluggish in *t*-C_4H_9OH or CH_3CN, albeit with no detrimental effect on the e.r. of **MB**. Replacement of the *i*Pr group of (*S*,*S*)-**1a** with a Me group (**1b**) decreased the e.r. from >99:1 to 98:2 and **MB**/**ML** ratio from 228:1 to 60:1. The values were further decreased with (*S*,*S*)-**1c** (R = H). Using conditions that gave the best result with **1a**, chiral bisoxazoline ligands **La**[15] and **Lb**[15] as well as BINAP[15] or replacement of Cp with Cp* afforded mainly **7** with no **MB**.

The scope and limitations of the present method are shown in Table 1. Electron-donative substituents as well as the electron-withdrawing NO_2 group at the *para* position of the phenyl group of (*E*)-**2** exerted little negative effect on reactivity and selectivity (Table 1, entries 1–5), while saturation of the phenyl group or introduction of a methyl substituent at C(3) led to no detectable C-allylation (Table 1, entries 8 and 11). Alkenyl or alkynyl group at C(3) instead of a phenyl group was tolerable to give the corresponding branched product with e.r. of 96:4–99:1 (Table 1, entries 6, 7). (*Z*)-3-Phenylprop-2-en-1-ol ((*Z*)-**2**) gave (*S*)- and (*R*)-**MB** in 97:3 e.r. (Table 1, entry 9). The predominant formation of (*S*)-**MB** both from *E* and *Z* stereoisomers implies that π–σ–π interconversion should be faster than the intermolecular nucleophilic attack on a π-allyl intermediate (see below). This view can be supported by the high level of asymmetric induction in dynamic kinetic resolution (DKR) of racemic 1-phenylprop-2-en-1-ol (Table 1, entry 10). 5-Methyl Meldrum's acid, tetronic acid, and 3-methyl tetronic acid can

Table 1: Inter- and intramolecular enantioselective dehydrative allylation using the (*S*,*S*)-Naph-diPIM-dioxo-*i*Pr/$[RuCp(CH_3CN)_3]PF_6$/*p*-TsOH combined catalyst.[a]

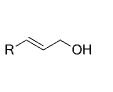
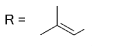
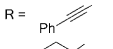
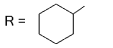
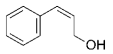
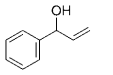
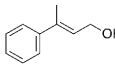
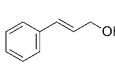
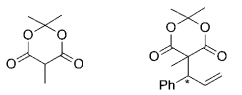
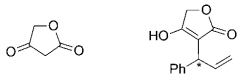
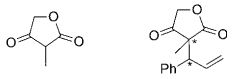
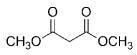
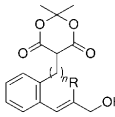
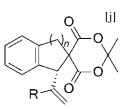
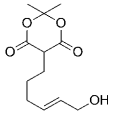
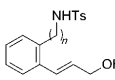
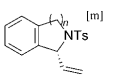
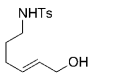
No.	Reactant(s)	Product	Yield [%][b] (e.r.)
1	 X = H	 [c]	96 (>99:1)
2	X = OCH_3		95 (98:2)
3	X = CH_3		96 (99:1)
4	X = Cl		94 (99:1)
5	X = NO_2		–[d] (99:1)
6			73 (96:4)
7			89 (99:1)
8		–	–[e]
9			93 (97:3)[f]
10			96 (96:4)[f]
11		–	no reaction
12			87 (99:1)
13			89 (>99:1)[g]
14			88 (95:5, 95:5)[h]
15		–	–[i]
16	 **8a**: *n* = 1, R = H	 [j]	98 (>99:1)[k]
17	**8b**: *n* = 1, R = CH_3		98 (>99:1)
18	**8c**: *n* = 2, R = H		97 (>99:1)[k]
19	 **9**		57 (88:12)[l]
20		 [m]	99 (>99:1)[k]
21	**10a**: *n* = 1		99 (99:1)[k]
22	**10b**: *n* = 2		95 (99:1)[n]
23			83 (95:5)[o]
24	 **11**		97 (82:18)

Table 1: (Continued)

No.	Reactant(s)	Product	Yield [%][b] (e.r.)
25	**12a**: $n=1$, R = H	[p]	89 (99:1)[k]
26	**12b**: $n=2$, R = H		98 (>99:1)[k]
27			
28	**12c**: $n=2$, R = CH_3		93 (94:6)[n]
29	**13**	[q]	94 (99:1) (60:40)

[a] Conditions: 1.0 mmol scale; [allyl alcohol] = 500 mM; [**4**] = [(*S*,*S*)-**1a**] = [*p*-TsOH] = 5 mM; CH_2Cl_2; reflux; 1 h. In the intermolecular case, the concentrations of nucleophiles were set to 2500 mM. The absolute configurations (AC) were not determined unless otherwise specified. For the details of the results in Table 1, see the Supporting Information. [b] Yield of isolated product. [c] The AC was determined with R = H. [d] Quantitative by ^{1}H NMR spectroscopic analysis but difficult in separation from **3**. Isolated as ethyl 3-(4-nitrophenyl)pent-4-enoate in 72% yield. [e] Major product: allylidenecyclohexane. [f] Five times more dilute than the standard. [g] HPLC analysis after acetylation. [h] Diastereomeric ratio: ca. 1:1. e.r. values of 96:4 and 94:6 are also possible. [i] Major product: dicinnamyl ether (**5**). [j] The AC was determined with $n=1$, R = H. [k] S/C = 1000 ([(*S*,*S*)-**1a**] = [*p*-TsOH] = 0.5 mM). [l] A 61:39 mixture of (*Z*)- and (*E*)-5-(hexa-3,5-dienyl)-2,2-dimethyl-1,3-dioxane-4,6-dione was isolated in 13% yield. [m] The AC was determined with $n=1$. [n] S/C = 5000 ([sub] = 1 M; [**4**/(*S*,*S*)-**1a**] = 0.2 mM; [*p*-TsOH] = 0.4 mM; 6 h). [o] S/C = 10000 ([sub] = 1 M; [**4**/(*S*,*S*)-**1a**] = 0.1 mM; [*p*-TsOH] = 0.4 mM; 12 h). [p] The AC was determined with $n=2$, R = H. [q] Not isolated. Quantitative by GC analysis.

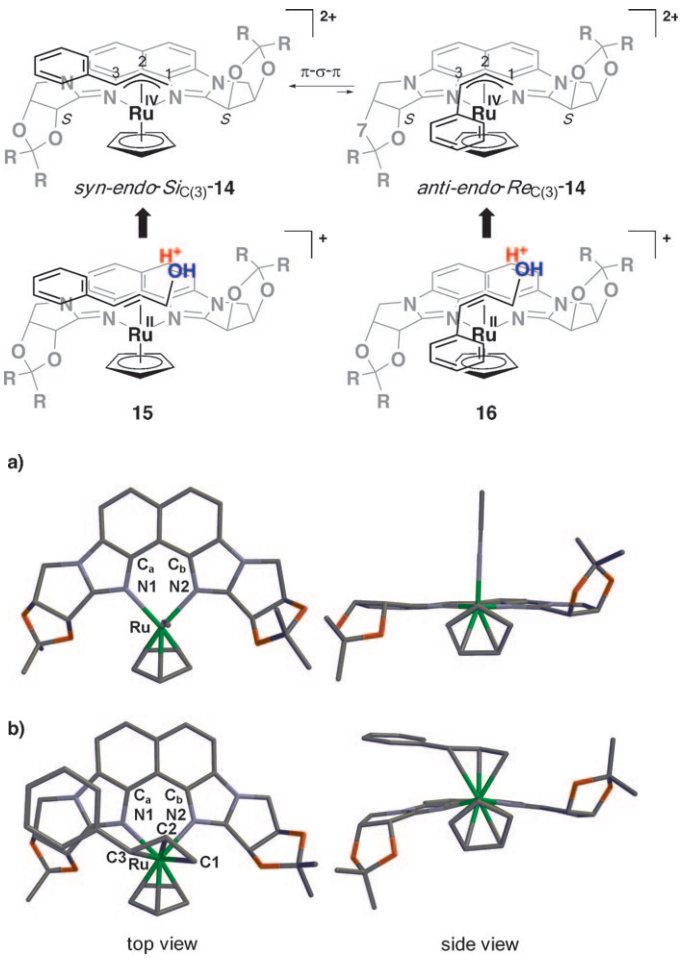


Figure 1. Molecular structures of a) [RuCp(CH_3CN)((*S*,*S*)-**1b**)]PF_6 ($P2_1$, $a=10.037(3)$, $b=27.534(7)$, $c=24.106(6)$ Å, $\beta=98.742(5)°$, $V=6585(3)$ Å^3, $Z=8$, $R=0.1177$, $R_W=0.1280$. Ru–N1 2.169 Å, Ru–N2 2.107 Å, N1-Ru-N2 86.3°, C_a-N1-Ru-N2 0.2°, C_b-N2-Ru-N1 3.6°) and b) [RuCp($C_6H_5CHCHCH_2$)((*S*,*S*)-**1b**)]$(PF_6)_2$ ($P1$, $a=10.189(5)$, $b=19.427(9)$, $c=10.554(5)$ Å, $\beta=96.668(8)°$, $V=2074.9(17)$ Å^3, $Z=2$, $R=0.0627$, $R_W=0.0755$. Ru–N1 2.156 Å, Ru–N2 2.137 Å, Ru–C1 2.228 Å, Ru–C2 2.193 Å, Ru–C3 2.455 Å, N1-Ru-N2 86.4°, C_a-N1-Ru-N2 −22.84°, C_b-N2-Ru-N1 16.74°). PF_6 is omitted for clarity.

be also used as C-nucleophiles, but no reaction occurred with dimethyl malonate (Table 1, entries 12–15).

Intramolecular C-allylation using **8a–c** quantitatively afforded the 2,3-dihydro-1*H*-indene and 1,2,3,4-tetrahydronaphthalene derivatives with >99:1 e.r. in all cases (Table 1, entries 16–18). Enantioselectivity deteriorated when the aliphatic substrate **9** was used, in which the benzene ring is removed from **8a** (Table 1, entry 19). Not only C-nucleophiles but also N- and O-nucleophiles can be used in the intramolecular cyclization of **10** and **12** to give 1,2,3,4-tetrahydroisoquinoline, isoindoline, isochroman, and phthalan derivatives quantitatively with high enantioselectivity (Table 1, entries 20–23, 25–28). In most intramolecular cyclizations, the reaction proceeds with an a substrate/catalyst (S/C) ratio of 1000–10000. The C(3) aliphatic compounds **11** and **13**, having no cinnamyl alcohol unit, were poor substrates (Table 1, entries 24 and 29).

Based on the molecular structures of CpRu^{II}/(*S*,*S*)-**1b** and CpRu^{IV}($C_6H_5CHCHCH_2$)/(*S*,*S*)-**1b** complexes shown in Figure 1,[4,16] we assume that the reaction of (*E*)-**2** with **3** proceeds via *syn-endo-Si*$_{C(3)}$-**14**, which has a C(2)H/C(3)Ph *syn* stereochemistry in the more stable *endo*-π-allyl ligand[12,17] with *Si* face selection at C(3). Steric repulsion between the 2,2-dialkyl-1,3-dioxolane moiety of Naph-diPIM ligand and C(3)Ph group would destabilize *syn-endo-Re*$_{C(3)}$-**14**. The stereoisomeric *anti-endo-Re*$_{C(3)}$-**14**, which is generated from (*Z*)-**2** or (±)-1-phenylprop-2-en-1-ol (Table 1, entries 9 and 10), is then isomerized to *syn-endo-Si*$_{C(3)}$-**14** via an σ-allyl intermediate so as to avoid a C(3)Ph/Cp steric repulsion. Outside attack of nucleophile **3** onto C(3), which is more electrophilic than C(1) (Ru-C(3): 2.455 Å vs. Ru-C(1): 2.228 Å),[12a,17a] affords (*S*)-**MB**. Indeed, reaction of [RuCp($C_6H_5CHCHCH_2$)((*S*,*S*)-**1b**)]$(PF_6)_2$ with **3** in a 1:5 ratio in CD_3CN[18] at 60 °C afforded a 96:4 mixture of (*S*)- and (*R*)-**MB** in 49% yield. Moreover, the mechanism outlined above explains the increased enantioselectivity and **MB**/**ML** ratio with a bulkier R group as well as the enantioface selection observed in the reactions with **8a**, **10a**, and **12b**. The π-allyl intermediates *syn-endo-Si*$_{C(3)}$-**14** and *anti-endo-Re*$_{C(3)}$-**14** are thought to be generated from the structurally similar catalyst/(*E*)-**2** complex **15** and catalyst/(*Z*)-**2** complex **16**, respectively. Here, the electrophilicity of C(3) is enhanced by protonation of *p*-TsOH on the hydroxy oxygen atom. Moreover, nucleophilicity of the Ru^{II} central metal is enhanced by the coordination of electron-donative Cp ligand and the amidine-based bidentate Naph-diPIM ligand. The synergistic

effect of the "redox-mediated donor–acceptor bifunctional catalyst"[1c,19] facilitates π-allyl formation even without activation of the allyl alcohol as an ester or halide. The lack of catalytic activity of the electronically richer Cp*Ru complex would be ascribed to the steric crowding around the central metal, inhibiting the coordination of substrate.

In summary, we have developed a new chiral bidentate sp^2-N-ligand and demonstrated the high utility of this CpRu complex in enantioselective dehydrative C-, N-, and O-allylation. The reaction proceeds with high reactivity and selectivity without stoichiometric activation of allylic alcohols as esters or halides and without the use of extra additives. Water is the only co-product, thereby making the reaction clean and simplifying product isolation. Various allylic alcohols having an sp^2- or sp-hybridized carbon at C(3) can be used both in inter- and intramolecular systems. Of particular importance is the highly enantioselective construction of five- and six-membered cycloalkanes and N- and O-heterocycles, all of which are versatile key intermediates for a wide range of biologically active natural products.[8] We are currently exploring the applications of this novel catalytic system for asymmetric synthesis and elucidation of detailed reaction mechanisms as well as expansion of the utility of Naph-diPIM-related ligands to other asymmetric catalysis reactions.

Experimental Section

A 150 mL Young-type Schlenk tube was charged with [RuCp-$(CH_3CN)_3$]PF_6 (14.9 mg, 34.4 μmol), (*S*,*S*)-**1a** (18.8 mg, 34.4 μmol), and acetone (2.0 mL). The mixture was stirred at room temperature for 30 min, and then the resulting pale yellow solution was concentrated in vacuo. To this solution was added CH_2Cl_2 (35.0 mL), *p*-TsOH·H_2O (6.5 mg, 34.4 μmol), and **8a** (10.0 g, 34.4 mmol). After stirring at reflux temperature for 3 h followed by cooling to room temperature, the mixture was concentrated, and the residue was passed through a pad of silica gel (15 g, 3.5 cm $\phi \times 3.7$ cm). The filtrate was concentrated to give the 5-*endo*-*trig*-cyclized product (9.18 g, 98% yield) with a 99.7:0.3 *S*/*R* e.r. The white solid was recrystallized from EtOAc (20 mL) and hexane (60 mL) to give enantiomerically pure 2,2-dimethyl-1′-vinyl-1′,3′-dihydrospiro[{1,3}dioxane-5,2′-indene]-4,6-dione (8.00 g, 85% yield) as prismatic crystals: m.p. 84 °C, $[\alpha]_D^{20} = -108.5$ deg cm^3 g^{-1} dm^{-1} ($c = 0.01$ g cm^{-3}, $CHCl_3$).

Received: January 30, 2011
Revised: February 21, 2011
Published online: April 15, 2011

Keywords: allylation · asymmetric catalysis · chirality · cyclopentadienyl ligands · heterocycles

[1] a) R. Noyori, *Science* **1990**, *248*, 1194–1199; b) R. Noyori, M. Kitamura, T. Ohkuma, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5356–5362; c) M. Kitamura, H. Nakatsuka, *Chem. Commun.* **2011**, *47*, 842–846; see also: K. Mikami, M. Lautens in *New Frontiers in Asymmetric Catalysis*, Wiley-VCH, New York, **2007**, pp. 1–418.

[2] Reviews for N-based ligands: a) M. Lemaire, P. Mangeney in *Chiral Diaza-Ligands for Asymmetric Synthesis in Topics in Organometallic Chemistry*, Vol. 15, Springer, Berlin, **2005**, pp. 1–301; b) G. Desimoni, G. Faita, K. A. Jørgensen, *Chem. Rev.* **2006**, *106*, 3561–3651; c) N. C. Fletcher, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1831–1842; d) G. Chelucci, R. P. Thummel, *Chem. Rev.* **2002**, *102*, 3129–3170; e) A. Togni, L. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517–547; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497–526.

[3] For example, (*S*,*S*)-Naph-diPIM-dioxo-*i*Pr represents (3a*R*,11a-*R*,14a*S*,16b*S*)-2,2,13,13-tetraisopropyl-3a,11a,14a,16b-tetrahydrobis(1,3-dioxolano[4′,5′:3,4]pyrrolo)[1,2-*a*:1′,2′-*a*]naphtho[1,2-*d*:8,7-*d*′]diimidazole.

[4] For details, see the Supporting Information.

[5] M. Bandini, A. Eichholzer, *Angew. Chem.* **2009**, *121*, 9697–9701; *Angew. Chem. Int. Ed.* **2009**, *48*, 9533–9537.

[6] S. Tanaka, T. Seki, M. Kitamura, *Angew. Chem.* **2009**, *121*, 9110–9113; *Angew. Chem. Int. Ed.* **2009**, *48*, 8948–8951.

[7] H. Yamamoto, E. Ho, K. Namba, H. Imagawa, M. Nishizawa, *Chem. Eur. J.* **2010**, *16*, 11271–11274.

[8] Reviews for asymmetric Tsuji–Trost-type reactions: a) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2943; b) J. T. Mohr, B. M. Stoltz, *Chem. Asian J.* **2007**, *2*, 1476–1491; c) G. Helmchen, A. Dahnz, P. Dübon, M. Schelwies, R. Weihofen, *Chem. Commun.* **2007**, 675–691; d) Z. Lu, S. Ma, *Angew. Chem.* **2008**, *120*, 264–303; *Angew. Chem. Int. Ed.* **2008**, *47*, 258–297; See also, J. F. Teichert, B. L. Feringa, *Angew. Chem.* **2010**, *122*, 2538–2582; *Angew. Chem. Int. Ed.* **2010**, *49*, 2486–2528.

[9] For in situ activation of allylic alcohols, see: 9-BBN-C_6H_{13}: a) B. M. Trost, J. Quancard, *J. Am. Chem. Soc.* **2006**, *128*, 6314–6315; $Nb(OC_2H_5)_3$ or $B(C_6H_5)_3$/MS 4 A: b) Y. Yamashita, A. Gopalarathnam, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 7508–7509; SO_3NH_3/DMF: c) C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira, *Angew. Chem.* **2007**, *119*, 3200–3204; *Angew. Chem. Int. Ed.* **2007**, *46*, 3139–3143.

[10] a) H. Saburi, S. Tanaka, M. Kitamura, *Angew. Chem.* **2005**, *117*, 1758–1760; *Angew. Chem. Int. Ed.* **2005**, *44*, 1730–1732; b) S. Tanaka, P. K. Pradhan, Y. Maegawa, M. Kitamura, *Chem. Commun.* **2010**, *46*, 3996–3998.

[11] a) T. Kondo, Y. Morisaki, S. Uenoyama, K. Wada, T. Mitsudo, *J. Am. Chem. Soc.* **1999**, *121*, 8657–8658; b) S. Gruber, P. S. Pregosin, *Adv. Synth. Catal.* **2009**, *351*, 3235–3242; c) I. F. Nieves, D. Schott, S. Gruber, P. S. Pregosin, *Helv. Chim. Acta* **2007**, *90*, 271–275; d) J. A. van Rijn, M. A. Siegler, A. L. Spek, E. Bouwman, E. Drent, *Organometallics* **2009**, *28*, 7006–7014.

[12] Review for the utility of Cp*Ru catalysts (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) in allylation using allyl esters and halides: a) C. Bruneau, J.-L. Renaud, B. Demerseman, *Chem. Eur. J.* **2006**, *12*, 5178–5187; The related-asymmetric versions: b) Y. Matsushima, K. Onitsuka, T. Kondo, T. Mitsudo, S. Takahashi, *J. Am. Chem. Soc.* **2001**, *123*, 10405–10406; c) M. D. Mbaye, J.-L. Renaud, B. Demerseman, C. Bruneau, *Chem. Commun.* **2004**, 1870–1871; d) K. Onitsuka, H. Okuda, H. Sasai, *Angew. Chem.* **2008**, *120*, 1476–1479; *Angew. Chem. Int. Ed.* **2008**, *47*, 1454–1457; e) M. Austeri, D. Linder, J. Lacour, *Chem. Eur. J.* **2008**, *14*, 5737–5741.

[13] Review for the utility in organic synthesis: B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem.* **2005**, *117*, 6788–6825; *Angew. Chem. Int. Ed.* **2005**, *44*, 6630–6666.

[14] The *R*/*S* indication is reversed between **MB** and **DBB** because of the priority rule.

[15] **La**: (*S*,*S*)-(−)-2,2′-isopropylidenebis(4-*tert*-butyl-2-oxazoline); **Lb**: (+)-2,2′-methylenebis[(3a*R*,8a*S*)-3a,8a-dihydro-8*H*-indeno-[1,2-*d*]oxazole]; BINAP: (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl).

[16] The dicationic $CpRu^{IV}$-π-allyl complex was prepared from the $CpRu^{II}$ complex, cinnamyl chloride, and $AgPF_6$ by reference to: M. D. Mbaye, B. Demerseman, J.-L. Renaud, L. Toupet, C. Bruneau, *Angew. Chem.* **2003**, *115*, 5220–5222; *Angew. Chem. Int. Ed.* **2003**, *42*, 5066–5068.

[17] a) S. Bi, A. Ariafard, G. Jia, Z. Lin, *Organometallics* **2005**, *24*, 680–686; b) R. Hermatschweiler, I. Fernández, P. S. Pregosin, E. J. Watson, A. Albinati, S. Rizzato, L. F. Veiros, M. J. Calhorda, *Organometallics* **2005**, *24*, 1809–1812.

[18] CD_2Cl_2 could not be used for the ^1H NMR experiment because of the low solubility of the CpRu complex. CD_3CN also affords high enantioselectivity, albeit with low reactivity.[4]

[19] For the original reaction of the donor–acceptor bifunctional catalyst concept: a) M. Kitamura, S. Suga, K. Kawai, R. Noyori, *J. Am. Chem. Soc.* **1986**, *108*, 6071–6072; b) R. Noyori, M. Kitamura, *Angew. Chem.* **1991**, *103*, 34–55; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49–69.

