A Chiral Bidentate sp²-N Ligand, Naph-diPIM: Application to CpRu-Catalyzed Asymmetric Dehydrative C-, N-, and O-Allylation**

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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 sp²-Nligands 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 (NaphdiPIM), which has the following characteristics: 1) high

rigidity and planarity with fixation of two sp²-hybridized N atoms on the same side, 2) near 90° bite angle, making the coordination plane and Naph-diPIM plane coplanar to stabilize squareplanar 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-diPIMdioxo-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 2,7dibromo-1,8-dinitronaphthalene and

appropriate acetonides of enantiomerically pure 3,4-dihydroxypyrrolidine-2-one by a Buchwald coupling/NO₂-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-1ol ((*E*)-2) and Meldrum's acid (3). This particular reaction was chosen because it remains intractable. There have,

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- [***] 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.

Naph-diPIM-dioxo-R



a: R = *i*Pr, **b**: R = Me, **c**: R = H



cat*: $[RuCp(CH_3CN)_3]PF_6$ (4) + ligand

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(CH₃CN)₃]PF₆ $(\mathbf{4})]^{[13]} = [(S,S) - \mathbf{1}\mathbf{a}] = 0.5 \text{ mM},$ [(E)-2] = 500 mM,[3] = 2500 mm, CH₂Cl₂, 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.

Communications

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-(1phenylallyl)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, CF₃SO₃H, and p-TsOH/ (C₂H₅)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. CH₂Cl₂, CHCl₃, 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-C₄H₉OH or CH₃CN, 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)-1 c (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 NO2 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>i</i> Pr/[RuCp(CH ₃ CN) ₃]PF ₆ / <i>p</i> -TsOH
combined catalyst. ^[a]

No.		Reactant(s)		Product	Yield [%] ^[b] (e.r.)
	R OH				
1 2 3 4 5	R = X	X=H OCH ₃ CH ₃ Cl NO ₂			96 (>99:1) 95 (98:2) 96 (99:1) 94 (99:1) _ ^[d] (99:1)
6	R =				73 (96:4)
7	R = Ph				89 (99:1)
8	R = ()			-	_[e]
9	ОН				93 (97:3) ^[f]
10	U U				96 (96:4) ^[f]
11	ОН			-	no reac- tion
12	ОН			O O Ph	87 (99:1)
13			0 0	HO O Ph *	89 (>99:1) ^[g]
14			0	O Ph*	88 (95:5, 95:5) ^[h]
15			CH ₃ O OCH ₃	-	_[1]
16 17 18	о о о , , , , , , , , , , , , , , , , ,	8a: n=1 8b: n=1 8c: n=2,	, R = H , R = CH ₃ , R = H		98 (>99:1) ^[k] 98 (>99:1) 97 (>99:1) ^[k]
19	O O O	9			57 (88:12) ^[I]
20 21 22 23	№НТѕ ↓), ОН	10a: n= 10b: n=	1 2	NTs	99 (>99:1) ^[k] 99 (99:1) ^[k] 95 (99:1) ^[n] 83
24	NHTs OH	11		NTs	(95:5) 97 (82:18)

Table 1: (Continued)



[a] Conditions: 1.0 mmol scale; [allyl alcohol]=500 mm; [4]=[(S,S)-1a]=[p-TsOH]=5 mm; CH₂Cl₂; 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 ¹H 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)-1 a]=[p-TsOH]=0.5 mм). [l] A 61:39 mixture of (Z)- and (E)-5-(hexa-3,5-dienyl)-2,2-dimethyl-1,3-dioxane-4,6dione was isolated in 13 % yield. [m] The AC was determined with n = 1. [n] S/C=5000 ([sub]=1м; [4/(S,S)-1а]=0.2 mм; [p-TsOH]=0.4 mм; 6 h). [o] S/C=10000 ([sub]=1м; [4/(S,S)-1а]=0.1 mм; [p-TsOH]= 0.4 mm; 12 h). [p] The AC was determined with n=2, R=H. [q] Not isolated. Quantitative by GC analysis.

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*)-1**b** and CpRu^{IV}(C₆H₅CHCHCH₂)/(*S*,*S*)-1**b** 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 (\pm)-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



Figure 1. Molecular structures of a) [RuCp(CH₃CN)((S,S)-**1b**)]PF₆ (P2₁, a = 10.037(3), b = 27.534(7), c = 24.106(6) Å, $\beta = 98.742(5)^{\circ}$, V = 6585(3) Å³, 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(C₆H₅CHCHCH₂)((S,S)-**1b**)](PF₆)₂ (P1, a = 10.189(5), b = 19.427(9), c = 10.554(5) Å, $\beta = 96.668(8)^{\circ}$, V = 2074.9(17) Å³, 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°). PF₆ is omitted for clarity.

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 CD₃CN^[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

Communications

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 sp²-N-ligand and demonstrated the high utility of this CpRu complex in enantioselective dehydrative C-, N-, and Oallylation. 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 sp²- 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 Oheterocycles, 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-(CH₃CN)₃]PF₆ (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 CH₂Cl₂ (35.0 mL), p-TsOH·H₂O (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 2,2-dimethyl-1'-vinyl-1',3'-dihydrospiro[{1,3}dioxane-5,2'pure indene]-4,6-dione (8.00 g, 85% yield) as prismatic crystals: m.p. 84°C, $[\alpha]_{D}^{20} = -108.5 \text{ deg cm}^{3}\text{g}^{-1}\text{dm}^{-1}$ ($c = 0.01 \text{ g cm}^{-3}$, CHCl₃).

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 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).
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