Experimental Section

A typical experimental procedure: aldehyde (0.25 mmol) and silyl enolate (0.375 mmol) were added successively at 30 °C to a stirred white suspension of diphenylborinic acid (0.025 mmol), benzoic acid (0.0025 mmol), and SDS (0.025 mmol) in water (1.5 mL). After 24 h, saturated aq. $NaHCO_3$ (5 mL) and brine (5 mL) were added, and the mixture was extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. The aldol product was purified by preparative thin layer chromatography (TLC; SiO_2, ethyl acetate/hexane = 1/3).

Received: March 27, 2001 [Z16861]

[1] For boron-mediated aldol reactions, see: a) B.-M. Kim, S. F. Williams, S. Masamune in *Comprehensive Organic Synthesis*, *Vol. 2* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, pp. 239–268; b) W. Fenzl, R. Köster, *Liebigs Ann. Chem.* **1975**, 1322–1338; c) T. Inoue, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 174–178; d) D. A. Evans, J. V. Nelson, E. Vogel, T. R. Taber, *J. Am. Chem. Soc.* **1981**, *103*, 3099–3111; e) S. Masamune, S. Mori, D. Van Horn, D. W. Brooks, *Tetrahedron Lett.* **1979**, *19*, 1665–1668.

[2] For LASC-mediated carbon–carbon bond forming reactions in water, see: a) S. Kobayashi, T. Wakabayashi, *Tetrahedron Lett.* **1998**, *39*, 5389–5392; b) S. Otto, J. B. F. N. Engberts, J. C. T. Kwak, *J. Am. Chem. Soc.* **1998**, *120*, 9517–9525; c) K. Manabe, S. Kobayashi, *Synlett* **1999**, 547–548; d) K. Manabe, S. Kobayashi, *Tetrahedron Lett.* **1999**, *40*, 3773–3776; e) S. Kobayashi, Y. Mori, S. Nagayama, K. Manabe, *Green Chem.* **1999**, 175–177; f) K. Manabe, Y. Mori, S. Nagayama, K. Odashima, S. Kobayashi, *Inorg. Chim. Acta* **1999**, *296*, 158–163; g) K. Manabe, Y. Mori, S. Kobayashi, *Tetrahedron* **1999**, *55*, 11203–11208; h) Y. Mori, K. Kakumoto, K. Manabe, S. Kobayashi, *Tetrahedron Lett.* **2000**, *41*, 3107–3111; i) K. Manabe, Y. Mori, T. Wakabayashi, S. Nagayama, S. Kobayashi, *J. Am. Chem. Soc.* **2000**, *122*, 7202–7207.

[3] Ph_2BOH can be easily prepared from its ethanolamine ester, see: G. E. Coates, J. G. Livingstone, *J. Chem. Soc.* **1961**, 4909–4911.

[4] Ph_2BOH was used for the generation of a boron enolate from ethoxyacetylene, see: M. Murakami, T. Mukaiyama, *Chem. Lett.* **1982**, 241–244.

[5] Anionic surfactants are effective, see the Supporting Information.

[6] When a Lewis acid (for example, $Sc(O_3SOC_{12}H_{25})_3$) was used in water, the diastereoselectivity was *syn*/*anti* = 49/51 (substrates: aldehyde **4** and silyl enolate **2**), see: refs. [2a, i].

[7] Diarylborinic acids with electron-withdrawing substituents at their aryl groups are known to function as Lewis acids for Mukaiyama aldol reactions in dichloromethane, see: K. Ishihara, H. Kurihara, H. Yamamoto, *Synlett* **1997**, 597–599.

[8] The examples of catalytic use of metals for generating metal enolates from silyl enolates in stereoselective aldol reactions have been reported, see: a) G. A. Slough, R. G. Bergman, C. H. Heathcock, *J. Am. Chem. Soc.* **1989**, *111*, 938–949; b) M. Sodeoka, K. Ohrai, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 2648–2649; c) J. Krüger, E. M. Carreira, *J. Am. Chem. Soc.* **1998**, *120*, 837–838; d) O. Fujimura, *J. Am. Chem. Soc.* **1998**, *120*, 10032–10039.

[9] Y. Li, M. N. Paddon-Row, K. N. Houk, *J. Org. Chem.* **1990**, *55*, 481–493.

[10] The examples of the generation of boron enolates from silyl enolates using stoichiometric amounts of boron sources in organic solvents have been reported, see: a) I. Kuwajima, M. Kato, A. Mori, *Tetrahedron Lett.* **1980**, *21*, 4291–4294; b) M. Wada, *Chem. Lett.* **1981**, 153–156.

[11] Various Brønsted acids are effective, see the Supporting Information.

[12] The reaction also showed first-order dependence with respect to the catalyst combination (**1**-SDS-$PhCO_2H$ (1:1:0.1)), see the Supporting Information.

CH/π Attraction: The Origin of Enantioselectivity in Transfer Hydrogenation of Aromatic Carbonyl Compounds Catalyzed by Chiral η^6-Arene-Ruthenium(II) Complexes**

Masashi Yamakawa, Issaku Yamada, and Ryoji Noyori*

In asymmetric catalysis using chiral transition metal complexes, metal ligands generally affect the stability of stereodetermining transition states (TSs) by exerting electronic influences on metallic centers and also by through-space interactions with the assembled substrates. In our enantioselective asymmetric transfer hydrogenation of aryl alkyl ketones[1–3] or [1-^{2}H]benzaldehydes[4] by using 2-propanol or formic acid, we intuitively selected $Ru^{II}(\eta^6$-arene) catalysts that possess a chiral 2-amino alcohol or related auxiliary. A theoretical study has now revealed that the enantioselectivity originates not only from the chiral geometry of the five-membered chelate ring but also from the CH/π attractive interaction[5] between the η^6-arene ligand and the carbonyl aryl substituent, instead of conventional nonbonded repulsion. This TS stabilization is reminiscent of the origin of *endo* selectivity in the Diels–Alder reaction that is based on an attractive secondary interaction between nonreacting sites.[6]

A combined system of [RuCl{(*R*,*R*)-$YCH(C_6H_5)CH(C_6H_5)NH_2$}($\eta^6$-arene)] (Y = O or NTs) and an alkaline base in 2-propanol catalyzes transfer hydrogenation of aromatic ketones or aldehydes to give the corresponding *R* alcohols with fair to excellent enantiomeric purity.[1–4] The real reducing complex is [RuH{(*R*,*R*)-$YCH(C_6H_5)CH(C_6H_5)NH_2$}($\eta^6$-arene)].[2c, 7, 8] The general stereochemical outcome[1–4] prompted us to study the TS structures by hybrid density functional theory-based (DFT) calculations.[9, 10]

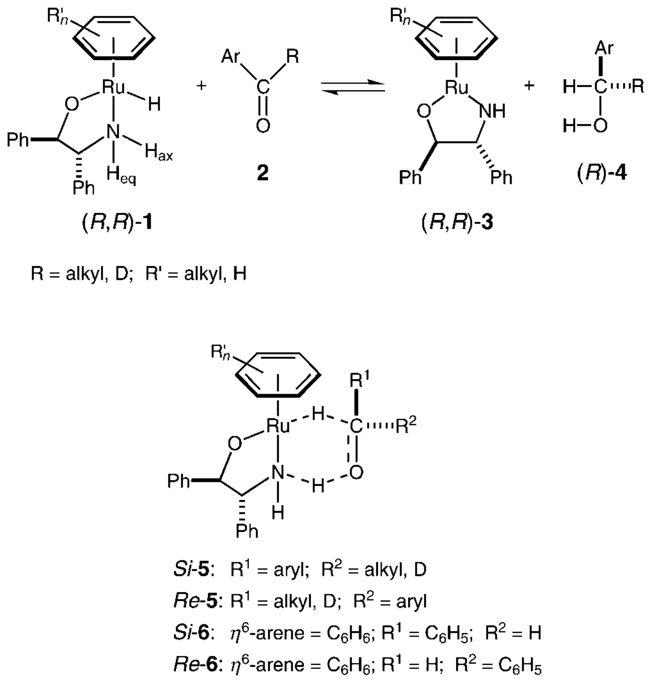
Transfer hydrogenation of carbonyl substrates with **1** occurs by a novel metal–ligand bifunctional catalysis[1, 2c, 7, 8] (Scheme 1). The hydridic Ru–H and protic N–H_{ax} in the 18e complex **1** are transferred simultaneously to the C=O bond in **2** to form the 16e complex **3** and alcohol **4**. The process is reversible. The chiral complex (*R*,*R*)-**1** reacts with **2** preferentially via "proximal" TS *Si*-**5** instead of "distal" *Re*-**5**, giving *R*-enriched **4**. The calculation for the reaction of (*R*,*R*)-**1** (η^6-arene = C_6H_6) and benzaldehyde at the RMP2/BS-II//B3LYP/LANL2DZ level[10] indicated that 1) the hydrogen

---

[*] Prof. Dr. R. Noyori, Dr. I. Yamada
Department of Chemistry and Research Center for
Materials Science
Nagoya University, Chikusa, Nagoya 464-8602 (Japan)
Fax: (+81) 52-783-4177
E-mail: noyori@chem3.chem.nagoya-u.ac.jp
Prof. M. Yamakawa
Kinjo Gakuin University
Omori, Moriyama, Nagoya 463-8521 (Japan)
Fax: (+81) 52-798-0370

[**] This work was financially supported by a Grant-in-Aid for Scientific Research (No. 07CE2004) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 1. Asymmetric hydrogen transfer via a metal–ligand bifunctional mechanism.

transfer, which gives (*R*,*R*)-**3** and benzyl alcohol, occurs via a hydrogen-bonded intermediate[7] with an endothermicity of 14.5 kJ mol^{-1}, while dehydrogenation of 2-propanol with (*R*,*R*)-**3** is exothermic by 9.1 kJ mol^{-1}; 2) the spatially congested TS, *Si*-**6**, is more stable than the uncrowded TS, *Re*-**6**, by 8.6 kJ mol^{-1} ($E_a = 47.8$ versus 56.4 kJ mol^{-1}); 3) the 5/6-fused bicyclic core structures of *Si*-**6** and *Re*-**6** are geometrically very similar; 4) in both TSs, no aggravating steric effects arise from the two phenyl rings in the N,O-chelate ligand, the shortest H···H distance in the less stable *Re*-**6** being 2.620 Å (much longer than the sum of the van der Waals radii, 2.4 Å); and 5) the more stable *Si*-**6** contains a short interatomic distance (2.993 Å) between a η^6-benzene C*H* and a phenyl C(sp^2) atom (Figure 1).

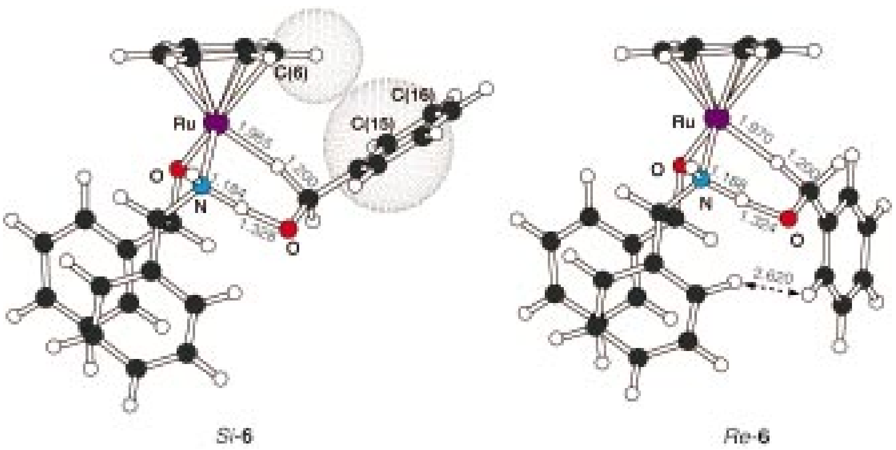
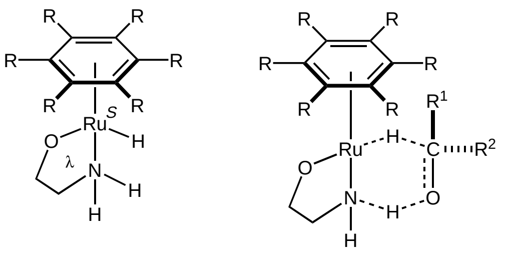


Figure 1. Diastereomeric transition structures, *Si*-**6** (favored) and *Re*-**6** (less favored). The geometries were optimized at the B3LYP/LANL2DZ level. *Si*-**6**: C(6)H···C(15) 2.993 Å, C(6)H···C(16) 3.372 Å; Ru-H-C 152.0°, N-H-O 167.4°, RuH-C-O 109.8°, H-Ru-N-HO 12.0°. *Re*-**6**: Ru-H-C 148.7°, N-H-O 167.6°, RuH-C-O 110.0°, H-Ru-N-HO 15.0°. The bond lengths are given in Å. The dotted surfaces indicate the van der Waals radii of the atoms.

To fully elucidate the origin of the preference for the more crowded TS, we performed the more reliable calculation by using [RuH(OCH$_2$CH$_2$NH$_2$)(η^6-C$_6$H$_6$)] (**7**) and the higher quality basis sets (RMP2/BS-III//B3LYP/BS-I). This model, like the real system (*R*,*R*)-**1** (η^6-arene = C$_6$H$_6$), possesses a λ conformation for the chiral N,O-chelate ring and an *S* configuration at the Ru stereogenic center. This result is consistent with the above energy profile. The reaction of **7** and benzaldehyde to give the 16e Ru amide complex and benzyl alcohol takes place with an endothermicity of 20.8 kJ mol^{-1}, whereas regeneration of **7** by 2-propanol is exothermic by 18.3 kJ mol^{-1}. In the aldehyde reduction, the proximal TS, *Si*-**9**, is favored over the distal isomer, *Re*-**9**, by 12.3 kJ mol^{-1} ($E_a = 40.1$ versus 52.4 kJ mol^{-1}) (see Supporting Information for details). Most significantly, *Si*-**9** is more stabilized by the CH/π attraction between the η^6-benzene and the phenyl substituent (Figure 2a). The C(6)H···C(15) distance in *Si*-**9**, 2.860 Å, is close to the sum of the van der Waals radii, 2.9 Å. In fact, C(6)H with a significant positive natural population analysis (NPA) charge interacts with highly negative C(15) and C(16) by means of largely electrostatic and slight covalent attractions, with Mulliken bond populations of +0.0080 and +0.0040, respectively. The C(sp^2)H/π attraction between the two aromatic rings becomes conspicuous with the through-bond linkage of the Ru···H···C moiety, and this feature is distinct from the conventional T-shaped interaction.[5] The C*H* donating property of benzene is greatly enhanced upon metal complexation;[11] in going from free benzene to *Si*-**9**, the positive charge of C(sp^2)H increases from +0.235 au to +0.267–0.278 au, or even to +0.286 au at C(6)H. In contrast, the hydride approach to the carbonyl carbon atom in benzaldehyde reverses the relative charge distribution at the *ortho*/*para* versus *meta* positions, resulting in an increase in the C*H*-accepting ability at the *ortho* and *para* carbon atoms. In particular, the negative charges at the interacting C(15) (−0.245 au) is much larger than in free



7: R = H
8: R = CH$_3$

Si-**9**: R = H; R^1 = C$_6$H$_5$; R^2 = H
Re-**9**: R = H; R^1 = H; R^2 = C$_6$H$_5$
Si-**10**: R = CH$_3$; R^1 = C$_6$H$_5$; R^2 = H
Re-**10**: R = CH$_3$; R^1 = H; R^2 = C$_6$H$_5$

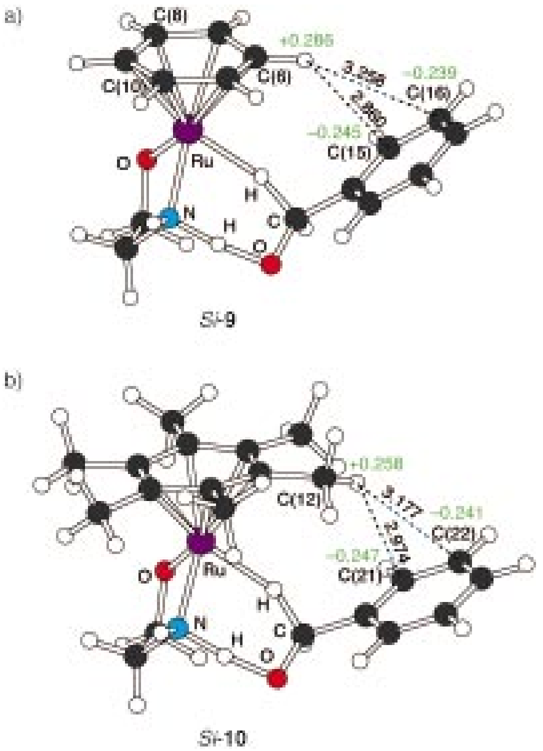


Figure 2. CH/π attractive interaction between the η^6-arene ligand and phenyl group in a) *Si*-**9** and b) *Si*-**10**. The geometries were optimized at the B3LYP/BS-I level. *Si*-**9**: Ru-H 1.990 Å, RuH-C 1.204 Å, O-H 1.269 Å, N-HO 1.217 Å, N-Ru 2.090 Å; Ru-H-C 152.5°, N-H-O 168.0°, RuH-C-O 110.4°, H-Ru-N-HO 13.9°. *Si*-**10**: Ru-H 2.010 Å, RuH-C 1.200 Å, O-H 1.289 Å, N-HO 1.204 Å, N-Ru 2.095 Å; Ru-H-C 153.4°, N-H-O 168.0°, RuH-C-O 110.8°, H-Ru-N-HO 11.0°. The interatomic distances are shown by dashed lines (Å) and the NPA charges (au) are given in green.

benzaldehyde (−0.195), whereas C(16) is inherently electron-rich (−0.239 in *Si*-**9** versus −0.236 in benzaldehyde). The RMP2/BS-I optimizations have led to the same conclusion, suggesting a greater CH/π interaction with a very short C(6)H⋯C(15) distance, 2.609 Å (see Supporting Information).

This mechanism uniformly explains the role of aryl substituents in asymmetric reactions of aromatic aldehydes and ketones[1–4] catalyzed by **1** and its analogues. The reaction of aliphatic aldehydes in 2-propanol is much less enantioselective.[4] Electron-donating substituents in [1-^{2}H]benzaldehyde tend to increase the enantioselectivity owing to the greater secondary interaction caused by the higher CH-accepting ability of the π-electron-rich aromatic ring, whereas electron-withdrawing groups lower the enantioselectivity.[4] The *ee* value of the *R* product in the reaction of substituted [1-^{2}H]benzaldehydes with (*R*,*R*)-**1** (arene = C_6H_6) decreases from 61 % for the *p*-CH_3O derivative to 45 % for the parent benzaldehyde and to 20 % for the *p*-CF_3 compound.[4, 12] The reaction of 4-cyano-4′-methoxybenzophenone, a skeletally symmetrical but electronically unsymmetrical diaryl ketone, in the presence of (*R*,*R*)-**1** (arene = C_6H_6; 0.025 M 2-propanol solution, ketone/RuCl precursor/*t*BuOK 50:1:2, 20 °C, 12 h) gives *p*-cyano-*p*′-methoxybenzhydrol in an *R*/*S* ratio of 67:33 (100 % conversion) as a result of the greater η^6-benzene/*p*-methoxyphenyl CH/π interaction.

The rate and stereoselectivity are influenced by the electronic and steric properties of alkyl groups in the η^6-arene ligand. Because both *Si*-**9** and *Re*-**9** possess smaller negative NPA charges at C(6), C(8), and C(10) (−0.218, −0.196, and −0.227 au, respectively, for *Si*-**9** (Figure 2 a)) in comparison to other carbon atoms (−0.258 to −0.278 au), electron-donating alkyl groups at such positions stabilize the TSs. Despite the presence of six methyl groups, the Ru complex **8** is predicted to reduce benzaldehyde with a lower activation energy (28.5 versus 40.1 kJ mol^{-1}) than and with a similar endothermicity (17.6 versus 20.8 kJ mol^{-1}) to **7**. The TS for dehydrogenation of 2-propanol is also more stabilized with the hexamethylbenzene complex (28.6 versus 33.6 kJ mol^{-1}). Furthermore, the aldehyde reduction with **8** proceeds preferentially via TS *Si*-**10** (Figure 2 b), giving the same sense of asymmetric induction as with **7**. The C(sp^3)H/π attractions[13] stabilize the sterically congested *Si*-TS more than the uncrowded isomer by 7.0 kJ mol^{-1} ($E_a = 28.5$ versus 35.5 kJ mol^{-1}), although the presence of methyl groups distorts the core six-membered geometry considerably from that of nonmethylated *Si*-**9**.[13] In *Si*-**10**, the atomic distances between C(12)H and C(21) and C(22) in the aldehyde phenyl are 2.974 and 3.177 Å, respectively. The attraction reflects the distinct positive NPA charge at C(12)H (+0.258 au; free hexamethylbenzene +0.237 to +0.239 au) and the large negative charges at C(21) (−0.247 au) and C(22) (−0.241 au). In agreement with such calculations, the catalytic reduction of [1-^{2}H]benzaldehyde with (*R*,*R*)-**1** (arene = $C_6(CH_3)_6$) in 2-propanol takes place 3.4 times faster than the reaction with (*R*,*R*)-**1** (arene = C_6H_6) and gives (*R*)-[1-^{2}H]-benzyl alcohol with somewhat lower *ee* (32 % versus 45 %).[12]

Organometallic chemistry often utilizes arene ligands. The two- to six-electron donors affect the electronic properties of the metallic center and also exert steric influences on neighboring ligands.[14] Here we show previously unrecognized effects of arene ligands. Thus in some cases[1–3] (though not always), ring alkylation can facilitate reactions and also generate a larger asymmetric bias through enhanced electron donation and/or attractive secondary interaction, only if other perturbations remain similar. This possibility is in contrast to the long-held view that ring alkylation decelerates reactions but increases stereoselectivity through the enhanced nonbonded repulsion. In fact, the η^6-*p*-cymene, -mesitylene, or -hexamethylbenzene ligands are superior to η^6-benzene in asymmetric reactions of certain aromatic ketones.[1–3] This study not only explains a range of experimental findings with Ru^{II}-catalyzed asymmetric transfer hydrogenation but also encourages a reconsideration of the origin of selectivity and reactivity observed in many other reactions promoted by transition metal–arene/cyclopentadienyl complexes.[15, 16]

Calculation Method

The Gaussian 98 program[9] was used for all calculations. All geometries of **1**, **3** (η^6-arene = C_6H_6), and TSs **6** were fully optimized by the Becke's three-parameter hybrid density functional method[10] using the LANL2DZ basis set (B3LYP/LANL2DZ). The structures of TSs **9** and **10** as well as the equilibrium structures **7** and **8** were optimized by the B3LYP level using the decontracted LANL2DZ basis set for Ru and the 6-31G(d) basis sets for other atoms (B3LYP/BS-I). The vibrational frequencies and zero-point energy (ZPE) were also calculated. The ground states and TSs were determined by the number of imaginary frequencies. The energies of **1**, **3** (η^6-arene = C_6H_6), and TSs **6** were obtained by the single-point calculations of the second-order Møller-Plesset method using the decontracted LANL2DZ basis set with an f-polarization function ($\alpha = 1.235$)[17] for Ru, 6-311 + G(d) for the phenyl groups, and 6-311 ++ G(d,p) for other atoms (RMP2/BS-II). Energies of the other compounds were obtained by single-point calculations of the RMP2 method using the same basis set as BS-II for Ru and 6-311 ++ G(d,p) for remaining atoms (RMP2/BS-III). Relative energies were corrected with unscaled ZPE. NPA[18] was carried out at the B3LYP/BS-I level. The Mulliken bond population was calculated by the restricted Hartree–Fock (RHF/BS-I) procedure using the geometries obtained by B3LYP/BS-I.

Received: August 9, 2000
Revised: May 29, 2001 [Z15610]

---

[1] a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102; b) M. J. Palmer, M. Wills, *Tetrahedron: Asymmetry* **1999**, *10*, 2045–2061.

[2] a) S. Hashiguchi, A. Fujii, T. Takehara, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563; b) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522; c) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 297–300; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288; d) S. Hashiguchi, A. Fujii, K.-J. Haack, K. Matsumura, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 300–303; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 288–290; e) K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1997**, *119*, 8738–8739.

[3] J. Takehara, S. Hashiguchi, A. Fujii, S. Inoue, T. Ikariya, R. Noyori, *Chem. Commun.* **1996**, 233–234.

[4] I. Yamada, R. Noyori, *Org. Lett.* **2000**, *2*, 3425–3427.

[5] a) M. Nishio, M. Hirota, Y. Umezawa in *The CH/π Interaction: Evidence, Nature, and Consequences* (Ed.: A. P. Marchand), Wiley-VCH, Weinheim, **1998**, chap. 2, pp. 11–45; b) Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa, M. Nishio, *Tetrahedron* **1999**, *55*, 10047–10056; c) J. H. Williams, *Acc. Chem. Res.* **1993**, *26*, 593–598; d) P. Hobza, H. L. Selzle, E. W. Schlag, *J. Am. Chem. Soc.* **1994**, *116*, 3500–3506; e) S. V. Lindeman, D. Kosynkin, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 13268–13269, and references therein.

[6] R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797–869; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781–853.

[7] M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478.

[8] D. A. Alonso, P. Brandt, S. J. M. Nordin, P. G. Andersson, *J. Am. Chem. Soc.* **1999**, *121*, 9580–9588.

[9] Gaussian 98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**..

[10] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[11] M. F. Semmelhack, *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36–51.

[12] The reaction of these substrates catalyzed by $[\mathrm{RuH}\{(R,R)\text{-}\mathrm{NTsCH}(C_6H_5)\mathrm{CH}(C_6H_5)\mathrm{NH_2}\}(\eta^6\text{-}C_6H_6)]$ affords the *R* alcohols with 99, 97, and 96 % *ee*, respectively.[4] The enhanced enantioselectivity is a result of an additional *N*-Ts/η^6-arene nonbonded interaction that destabilizes the *Re*-TS to some extent. Unlike in the reaction catalyzed by **1**, replacement of the C_6H_6 ligand by $C_6(CH_3)_6$ lowers the reaction rate.

[13] a) Y. Kodama, K. Nishihata, M. Nishio, N. Nakagawa, *Tetrahedron Lett.* **1977**, *24*, 2105–2108; b) P. J. Breen, J. A. Warren, E. R. Bernstein, J. I. Seeman, *J. Am. Chem. Soc.* **1987**, *109*, 3453–3455; c) Y. Nakai, K. Inoue, G. Yamamoto, M. Oki, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2923–2931; d) J. E. Anderson, V. Bru-Capdeville, P. A. Kirsch, J. S. Lomas, *J. Chem. Soc. Chem. Commun.* **1994**, 1077–1078.

[14] a) W. E. Silverhorn, *Adv. Organomet. Chem.*, **1975**, *13*, 47–137; b) E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, T. A. Albright, *Chem. Rev.* **1982**, *82*, 499–525.

[15] a) K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, 1199–1200; b) K. Murata, T. Ikariya, R. Noyori, *J. Org. Chem.* **1999**, *64*, 2186–2187; c) J. Mao, D. C. Baker, *Org. Lett.* **1999**, *1*, 841–843.

[16] Related phenomena: a) H. Brunner, *Angew. Chem.* **1983**, *95*, 921–931; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 897–907; b) R. W. Quan, Z. Li, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, *118*, 8156–8157; c) J. A. Gladysz, B. J. Boone, *Angew. Chem.* **1997**, *109*, 566–602; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 550–583; d) E. P. Kündig, C. M. Saudan, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 1298–1301; *Angew. Chem. Int. Ed.* **1999**, *38*, 1220–1223.

[17] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111–114.

[18] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO, version 3.1, Gaussian, Inc., Pittsburgh, PA, **1998**.

Architecture of Polymeric Superstructures: Self-Color Tone Films Constructed by Mesoscopically Ordered Cubic Lattices

Koji Ishizu,* Susumu Shiratori,* and
Takafumi Hosokawa*

It is well known that submicron-sized colloidal spheres form a body-centered cubic (BCC) or face-centered cubic (FCC) lattice in aqueous solution.[1] Ascher et al.[2] have developed an approach to permanently lock the ordering of a crystalline colloidal array in a hydrogel matrix. We have also constructed polymeric superstructures by the free-radical polymerization of *N*-vinylpyrrolidone (VP) monomer after polypyrrole microspheres had become arranged into a BCC lattice in a solution of the VP monomer.[3] More recently, we demonstrated that core–shell polymer microspheres[4] and highly branched star polymers[5] led to a hierarchical structural transformation of the cubic lattices. That is, these radially branched polymers formed a lattice with a BCC structure near the overlap threshold (*C**, concentration where the coils begin to become densely packed). This structure changed to a FCC lattice in the bulk region of the films. After these branched polymers had formed a cubic lattice in polymerizable vinyl monomer, the polymeric superstructures were locked permanently into an ordered lattice in a solid matrix by means of free-radical polymerization.[6] This technique is one of the best methods for creating nanoscopic polymeric superstructures composed of two or three phase-separated

---

[*] Prof. Dr. K. Ishizu, S. Shiratori, T. Hosokawa
Department of Organic Materials and Macromolecules
Tokyo Institute of Technology
2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552 (Japan)
Fax: (+81) 3-5734-2888
E-mail: kishizu@polymer.titech.ac.jp

1433-7851/01/4015-2821 $ 17.50+.50/0