Asymmetric Synthesis

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Kinetic Resolution of Planar-Chiral (η^6-Arene)Chromium Complexes by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis**

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Planar-chiral (η^6-arene)chromium complexes are useful chiral scaffolds in asymmetric synthesis, and have found widespread application as chiral ligands for asymmetric catalysis, or as chiral building blocks for natural product syntheses.[1] Typical methods for the preparation of enantiomerically enriched planar-chiral (arene)chromium species are based either on the optical resolution of racemates[2] or on stereoselective transformations, which include diastereoselective complexation,[3] diastereo- or enantioselective *ortho*-lithiation by utilizing a chiral directing group or a chiral base,[4] and diastereo- or enantioselective nucleophilic addition/hydride abstraction.[5] Whereas these methods require a stoichiometric amount of chiral reagents or auxiliaries, asymmetric catalysis is an attractive and effective alternative for preparing optically active (η^6-arene)chromium complexes. Since the first report on such a catalytic process by Uemura et al. in 1993,[6] only a handful of examples of the desymmetrization of prochiral (arene)chromium substrates have been reported by Gotov and Schmalz,[7] Kündig and co-workers,[8,9] and Uemura and co-workers[10,11].

Recently, we reported the preparation of phosphine-chelate (η^6-arene)chromium complexes by Ru-catalyzed ring-closing metathesis.[12] We also demonstrated that Mo-catalyzed asymmetric ring-closing metathesis (ARCM) was highly effective for the asymmetric synthesis of the various planar-chiral ferrocenes.[13] Thus, we are interested in controlling the planar chirality of (η^6-arene)chromium complexes by ARCM.[14,15] Indeed, the kinetic resolution of racemic (η^6-1,2-disubstituted benzene)chromium complexes proceeds efficiently in the presence of a chiral Mo-alkylidene species to give the planar-chiral chromium complexes with excellent enantiomeric purity. Furthermore, a highly enantiomerically enriched (η^6-bromoarene)chromium complex that was prepared by using the present method is an excellent precursor to various planar-chiral (arene)chromium derivatives. A (phosphinoarene)chromium species was derived from the (η^6-bromoarene)chromium complex and applied as a chiral ligand in Rh-catalyzed asymmetric reactions, which achieved excellent enantioselectivity of up to 99.5%.

The (η^6-arene)chromium complexes (*rac*-**1**) that were used in this study contain an η^6-(2-substituted alkenylbenzene) ligand, which constructs the planar-chiral environment upon coordination to the chromium atom, and an alkenylphosphine ligand. The chiral catalysts were screened by using racemic [(η^6-2-methylstyrene)$Cr(CO)_2$(methallyldiphenylphosphine)] (**1a**) as a prototypical substrate. The asymmetric reactions were carried out in benzene at 40°C in the presence of an appropriate chiral Mo catalyst (10 mol%), which was generated in situ from the Mo precursor [$(pyrrolyl)_2Mo(=CHCMe_2Ph)(=NC_6H_3$-2,6-$iPr_2$)] and an axially chiral biphenol derivative (Table 1).[16] Under these conditions, the Mo catalyst that was generated with (*R*)-**L1**[17a] gave the ARCM product **2a** in 32% yield with an *ee* value of 79%, and unreacted **1a** was recovered in 66% yield with an *ee* value of 50% (entry 1). The k_{rel} value ([reaction rate of the fast-reacting enantiomer]/[reaction rate of the slow-reacting enantiomer]; selectivity factor) for this reaction is estimated to be 14.[18] The Mo catalyst that was generated with (*R*)-**L2** gives better enantioselectivity and the k_{rel} value improved to 41 (entry 2). Lowering the temperature worsened the selectivity; the k_{rel} value was 12 at 23°C (entry 3). It was found that the reaction with the Mo catalyst coordinated with (*S*)-**L3**[17b] shows excellent enantioselectivity; **2a** was obtained in 96% *ee* and 44% yield, and **1a** was recovered in 88% *ee* and 50% yield. The k_{rel} value for the reaction is 114 (entry 4), and a nearly perfect kinetic resolution of the two enantiomers of *rac*-**1a** was achieved. Considering the structural similarity between **L1**, **L2**, and **L3**, these results are quite surprising and indicate that the slight structural modification to the Mo catalysts affects the enantioselectivity of the asymmetric reaction.[17a]

After the optimization studies, the Mo/(*S*)-**L3** species was applied to the other substrates. The substrate *rac*-**1b**, which has an ethyl substituent in place of the *ortho*-methyl group in **1a**, was also resolved as above. The enantioselectivity and the reaction efficiency (k_{rel} = 75 (entry 5)) of the kinetic resolution of *rac*-**1b** were still high. Substrate **1c** contains an η^6-bromostyrene ligand. As the bromo substituents in **1c**/**2c** can be easily replaced by other functional groups by standard organic transformations (see below),[19] they serve as versatile precursors to various planar-chiral compounds. The reaction of *rac*-**1c** under the optimized conditions afforded complex **2c** in 97% *ee* and 47% yield. Unreacted **1c** was also recovered in 89% *ee* and 50% yield. The k_{rel} value for this reaction is 198

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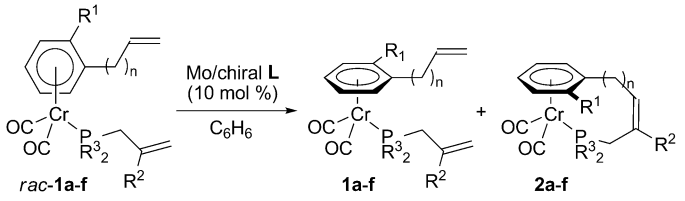
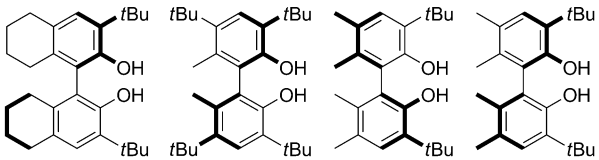
Table 1: Mo-catalyzed ARCM kinetic resolution of planar-chiral (η^6-arene)chromium complexes.[a]



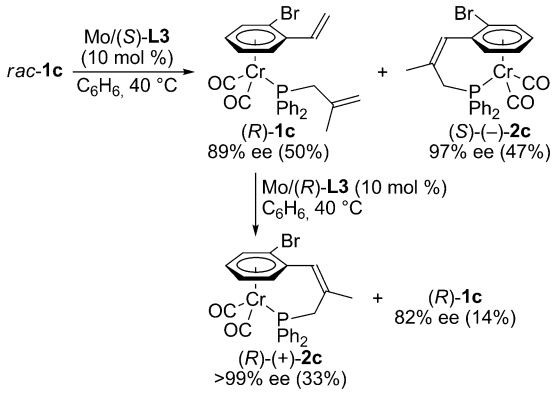
a: R^1 = Me, R^2 = Me, R^3 = Ph, n = 0
b: R^1 = Et, R^2 = Me, R^3 = Ph, n = 0
c: R^1 = Br, R^2 = Me, R^3 = Ph, n = 0
d: R^1 = Me, R^2 = Me, R^3 = *i*Pr, n = 0
e: R^1 = Me, R^2 = H, R^3 = Ph, n = 0
f: R^1 = Me, R^2 = Me, R^3 = Ph, n = 1



Entry	1	L	Temp. [°C][b]	Time [h]	*ee* (yield) of recovered **1** [%][c,d,e]	*ee* (yield) of **2** [%][d,e]	Config./optical rotation sign of **2**	k_{rel}[f]
1	**1a**	(*R*)-**L1**	40	12	50 (66)	79 (32)	(*R*)-(−)	14
2	**1a**	(*R*)-**L2**	40	12	72 (48)	90 (42)	(*R*)-(−)	41
3	**1a**	(*R*)-**L2**	23	12	48 (61)	76 (30)	(*R*)-(−)	12
4	**1a**	(*S*)-**L3**	40	18	88 (50)	96 (44)	(*S*)-(+)	114
5[g]	**1b**	(*S*)-**L3**	40	12	63 (55)	95 (42)	(*S*)-(−)	75
6	**1c**	(*S*)-**L3**	40	12	89 (50)	97 (47)	(*S*)-(−)	198
7	**1d**	(*R*)-**L3**	40	8	98 (42)	90 (49)	(−)	87
8[h]	**1e**	(*R*)-**L3**	23	1	3 (69)	14 (14)	(+)	1.4
9	**1f**	(*R*)-**L3**	40	12	12 (55)	45 (34)	(−)	3.0

[a] The reaction was carried out in benzene in the presence of an appropriate metathesis catalyst that was generated in situ (10 mol%) unless otherwise noted. [b] Oil bath temperature. [c] The *ee* value of recovered **1** was determined after conversion into **2** by treatment with the 2nd-generation Grubbs' catalyst. [d] The *ee* value was determined by HPLC on a chiral stationary phase (see the Supporting Information for details). [e] Yield of isolated product is given after purification by chromatography on a silica gel column. [f] Calculated based on a first-order equation (Ref. [18]). [g] With 20 mol% catalyst loading. [h] With 5 mol% catalyst loading.

(entry 6). The kinetic resolution of substrate **1d**, which contains a diisopropylmethallylphosphine, catalyzed by Mo/(*R*)-**L3** is also highly efficient and shows a k_{rel} value of 87. Both the recovered substrate (**1d**) and the ARCM product (**2d**) were obtained in greater than 90% *ee* (entry 7). The enantioselectivity of the ARCM kinetic resolution was strongly dependent on the structures of the alkenyl groups in both the η^6-arene ligand and the phosphine ligand (entries 8 and 9).[13a] Introduction of a Ph_2P(allyl) ligand in place of the Ph_2P(methallyl) ligand in *rac*-**1e** diminishes the enantioselectivity of the asymmetric reaction. With the two monosubstituted olefin moieties in the substrate, the ARCM of **1e** was extremely rapid and was complete within 1 h at 40 °C. For this reason, the kinetic resolution of *rac*-**1e** was conducted at 23 °C for 1 h with a lower loading of the catalyst. The reaction with Mo/(*R*)-**L3** gave the ARCM product **2e** in 14% *ee* and the *ee* value for recovered **1e** was 3%. The selectivity factor for the reaction is only 1.4 (entry 8). Likewise, the selectivity of the kinetic resolution reaction was decreased when the vinyl group in the η^6-arene ligand was replaced by an allyl group, as in **1f** (entry 9).

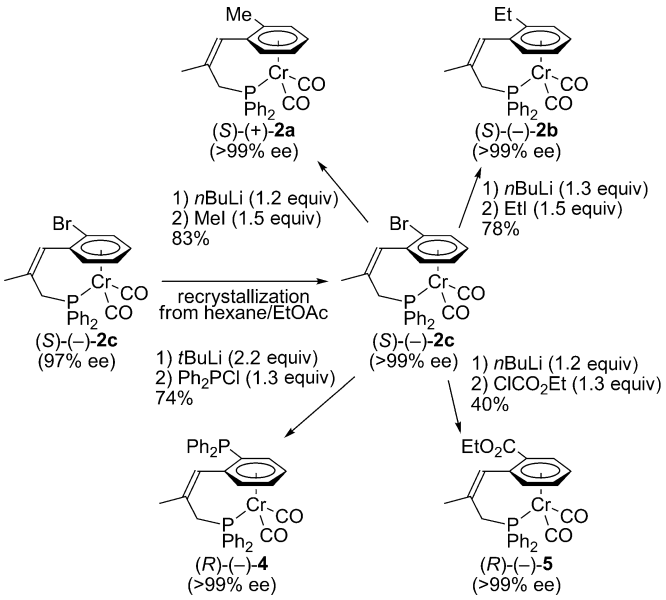


Scheme 1. Two successive ARCM kinetic resolutions of **1c** give (*R*)-(+)-**2c** in over 99% *ee*.

The absolute configuration of (−)-**2c** ($[\alpha]_D^{25} = -61.4$ ($c = 0.40$ in EtOAc for 97% *ee*)), which is the enantiomer that is preferentially cyclized by Mo/(*S*)-**L3**, was determined as the *S* configuration by single-crystal X-ray crystallography (see the Supporting Information for details).[20] The absolute configurations of (+)-**2a** and (−)-**2b** were also determined as the *S* configurations by stereoretentive derivatization from (*S*)-(−)-**2c** (see Scheme 2). The configurations of the other ARCM products were assigned by analogy.

By the combination of the two successive ARCM operations, (*R*)-(+)-**2c** could be obtained in almost enantiomerically pure form. After the first kinetic resolution of *rac*-**1c** catalyzed by Mo/(*S*)-**L3** (Table 1, entry 6), the recovered substrate, (*R*)-**1c** with an *ee* value of 89%, was subjected to a second ARCM kinetic resolution with Mo/(*R*)-**L3** to give (*R*)-(+)-**2c** in greater than 99% *ee* (Scheme 1).

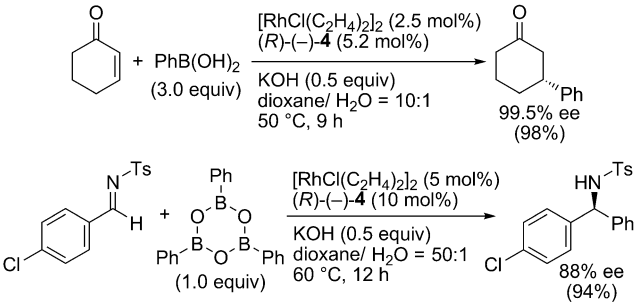
Enantiomerically pure (*S*)-**2c** was also obtained by the recrystallization of (*S*)-**2c** (97% *ee*), which was produced by Mo-catalyzed ARCM, from hexane/EtOAc. The bromo substituent in **2c** is lithiated under standard conditions, and subsequent reactions with an appropriate electrophile give the corresponding planar-chiral (arene)chromium complexes in good yields with complete retention of optical purity in (*S*)-**2c** (Scheme 2). The absolute configurations of the planar-



Scheme 2. Stereoretentive conversion of (*S*)-(−)-**2c** into various planar-chiral (η^6-arene)chromium complexes.

chiral chromium complexes are retained during the lithiation/substitution sequence.[19] The levorotatory enantiomer (*S*)-(−)-**2c** affords (+)-**2a** and (−)-**2b**, after the lithiation/alkylation sequence, respectively. With these analyses, both (+)-**2a** and (−)-**2b**, which are the enantiomers that are preferentially cyclized in the Mo/(*S*)-**L3**-catalyzed ARCM, were identified as the *S* enantiomers. In the same way, the η^6-(diphenylphosphino)arene species (*R*)-(−)-**4** and the η^6-benzoate derivative (*R*)-(−)-**5** were obtained from (*S*)-**2c** in optically pure forms (Scheme 2). The structure of complex **4** was confirmed by X-ray crystal-structure analysis (see the Supporting Information for details).[20]

The synthetic utility of (*R*)-(−)-**4** as a chiral ligand[21] was examined in two Rh(I)-catalyzed asymmetric reactions. It was found that (*R*)-(−)-**4** is an extremely effective chiral ligand in the asymmetric 1,4-addition of phenylboronic acid to cyclohexenone,[22] and (*R*)-3-phenylcyclohexanone was obtained with a 99.5% *ee* in 98% yield (Scheme 3, top). The usefulness of (*R*)-(−)-**4** was also demonstrated in the Rh-catalyzed addition of arylboroxine to an *N*-tosyl aldimine.[23] The reaction of the *N*-tosyl imine of *p*-chlorobenzaldehyde with phenylboroxine in the presence of Rh/(*R*)-**4** gave the asymmetric addition product in 94% yield with 88% *ee* (Scheme 3, bottom). Applications of (*R*)-**4** in other reactions that are catalyzed by transition metals are now under investigation and will be reported in due course.[24,25]



Scheme 3. Asymmetric reactions catalyzed by Rh/(*R*)-(−)-**4**. Ts = toluene-4-sulfonyl.

In summary, we have developed an effective method for the kinetic resolution of racemic planar-chiral (η^6-arene)-chromium complexes by Mo-catalyzed asymmetric ring-closing metathesis. After the appropriate derivatization, the obtained optically active (diphenylphosphinoarene)chromium complex can be utilized as an excellent chiral ligand in Rh-catalyzed asymmetric reactions.

Experimental Section

General procedure for the Mo-catalyzed ARCM kinetic resolution of **1**: [(pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-*i*Pr$_2$)] (5.4 mg, 10 μmol) and 3,3′-*t*Bu$_2$-5,5′,6,6′-tetramethyl-2,2′-biphenol (**L3**, 3.5 mg, 10 μmol) were dissolved in dry benzene (1 mL) in a test tube with a Teflon-sealed screw cap in a glovebox under prepurified argon. After stirring the mixture for 15 min at room temperature, benzene (3 mL) and the (η^6-arene)chromium complex **1** (100 μmol) were added. The test tube was sealed tightly and taken out of the glovebox. The test tube was immersed in an oil bath that was maintained at 40 °C, and the mixture was stirred for 12 h. After quenching the reaction by the addition of acetone (ca. 100 μL), the reaction mixture was evaporated to dryness under reduced pressure. The crude product was purified by chromatography on a silica gel (hexane/benzene = 1:2) under nitrogen to give the ARCM product **2** and the recovered substrate **1**. Recovered **1** was converted into the corresponding **2** by treatment with the second-generation Grubbs' catalyst (2 mol%) in dichloromethane for analysis by HPLC on a chiral stationary phase. The characterization data of the ARCM products and the conditions for the HPLC analysis are described in the Supporting Information.

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[20] CCDC 854841 ((*S*)-(−)-**2c**) and 854842 (*rac*-**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[24] The two potential electron donors, the diphenylphosphino group and the olefin moiety, are located in proximity to each other in (*R*)-**4**. Thus, the compound may function as a bidentate phosphine-olefin hybrid ligand. Preliminary NMR studies imply that a Rh–olefin interaction exists in the mixture of $[RhCl(C_2H_4)_2]_2$ and (*R*)-**4**. The coordination chemistry of **4** is now under investigation. For selected examples of phosphine-olefin hybrid ligands, see: a) P. Maire, S. Deblon, F. Breher, J. Geier, C. Böhler, H. Rüegger, H. Schönberg, H. Grützmacher, *Chem. Eur. J.* **2004**, *10*, 4198; b) R. Shintani, W. L. Duan, T. Nagano, A. Okada, T. Hayashi, *Angew. Chem.* **2005**, *117*, 4687; *Angew. Chem. Int. Ed.* **2005**, *44*, 4611; c) C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira, *Angew. Chem.* **2007**, *119*, 3200; *Angew. Chem. Int. Ed.* **2007**, *46*, 3139; d) W.-L. Duan, H. Iwamura, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 2130. See also: ref. [23i] and references therein.

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