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Kinetic Resolution of Planar-Chiral 1,2-Disubstituted Ferrocenes by Molybdenum-Catalyzed Asymmetric Intraannular Ring-Closing Metathesis

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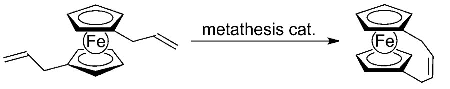
Metal-catalyzed structural modification of transition-metal complexes within their coordination spheres has been an interesting subject in inorganic/organometallic synthesis.[1] This strategy is potentially extendable to stereoselective processes, and the development of the enantioselective counterparts would be particularly attractive. Among metal-containing chiral scaffolds, planar-chiral ferrocenes[2] are by far the most widely utilized in asymmetric synthesis and have found widespread application as chiral ligands[3] or catalysts.[4] In spite of their usefulness, enantioselective preparations of such ferrocene derivatives are rather limited; the majority of optically active planar-chiral ferrocenes were obtained either by diastereoselective metalation by utilizing chiral *ortho*-directing groups[5] or by classical resolution of preformed racemates. Enantioselective lithiation of prochiral ferrocenes by a stoichiometric chiral base has also shown fair success.[6] On the other hand, examples of catalytic asymmetric syntheses of planar-chiral ferrocenes are extremely rare,[7,8] and further breakthroughs have been clearly awaited.

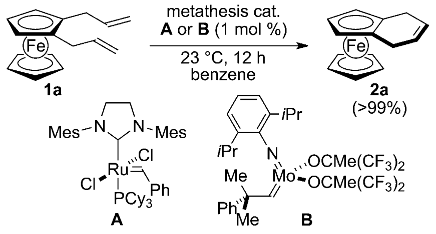
Recently, we and others independently reported the preparation of various bridged metallocenes by interannular ring-closing metathesis (RCM) of 1,1′-diallylmetallocenes [Eq. (1)].[9] The reaction was extended to the enantioselective variants in our group,[8] and various planar-chiral bridged metallocenes were prepared with excellent enantioselectivity. Here, we would like to report an alternative protocol for the catalytic asymmetric synthesis of planar-chiral metallocenes: the “intraannular” RCM of 1,2-diallylmetallocenes [Eq. (2)]. Kinetic resolution of racemic **1b**–**1i**, which are planar chiral with the two different allylic substituents, is facilitated by the molybdenum-catalyzed asymmetric ring-closing metathesis (ARCM) giving the optically active metallocenes in up to 99% *ee* (*ee* = enantiomeric excess). It should be noted that the present protocol allows direct access to scalemic planar-chiral indenyl motifs.

Interannular RCM of 1,1'-diallylferrocene (Ref. [9])



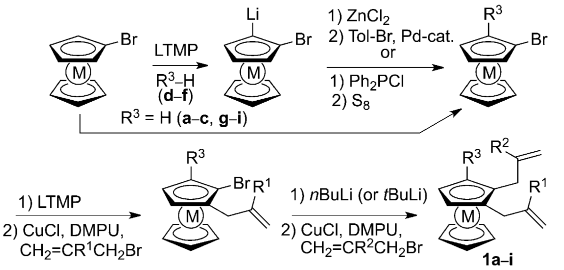
(1)

Intraannular RCM of 1,2-diallylferrocene



(2)

A series of 1,2-diallylmetallocene substrates (**1a**–**1i**) were prepared by the method outlined in Scheme 1. The two modes of lithiation on bromoferrocenes, that is, *ortho* lithiation by lithium tetramethylpiperidide (LTMP)[10] and lithium–bromine exchange by butyllithium, were utilized for the regioselective and stepwise introduction of the proper substituents in **1**.



a: M = Fe, $R^1 = R^2 = R^3 = H$
b: M = Fe, $R^1 = R^3 = H$, $R^2 = Me$
c: M = Ru, $R^1 = R^3 = H$, $R^2 = Me$
d: M = Fe, $R^1 = H$, $R^2 = Me$, $R^3 = p$-Tol
e: M = Fe, $R^1 = Me$, $R^2 = H$, $R^3 = p$-Tol
f: M = Fe, $R^1 = H$, $R^2 = Me$, $R^3 = P(S)Ph_2$
g: M = Fe, $R^1 = R^3 = H$, $R^2 = Et$
h: M = Fe, $R^1 = R^3 = H$, $R^2 = CH_2Ph$
i : M = Fe, $R^1 = R^3 = H$, $R^2 = SiMe_3$

Scheme 1. Preparation of 1,2-diallylmetallocene substrates **1a**–**1i**. Tol = *para*-methylphenyl, DMPU = *N*,*N*′-dimethylpropyleneurea.

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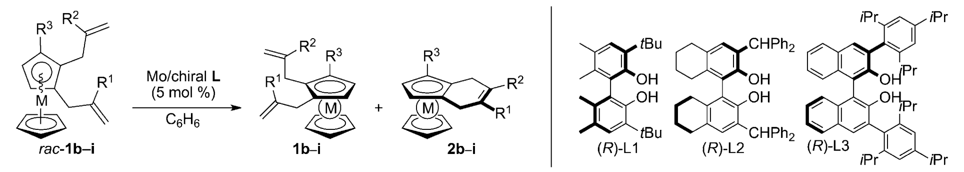
At the outset, the feasibility of the intraannular RCM process was examined. The reaction of 1,2-diallylferrocene (**1a**) proceeded smoothly in the presence of the Grubbs II catalyst[11] **A** (1 mol %) or the Schrock Mo catalyst[12] **B** (1 mol %) to give (η^5-4,7-dihydroindenyl)FeCp (**2a**, Cp = cyclopentadienyl) in >99 % yield [Eq. (2)].

Substrates **1b**–**1i** are planar chiral because the two adjacent allylic substituents are non-identical, and their racemates were subjected to the kinetic resolution studies by using a chiral Mo–alkylidene catalyst (Table 1).[13] Screening of the chiral catalysts was examined on racemic 1-allyl-2-methallylferrocene (**1b**) as a prototypical substrate. The reactions were carried out in benzene at 23 °C in the presence of an appropriate chiral Mo catalyst (5 mol %), that was generated in situ from the Mo precursor (pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=N-C$_6$H$_3$-2,6-iPr$_2$) and an axially chiral biphenol derivative.[14] Under these conditions, the Mo catalyst generated with (*R*)-L1[15a] gave the RCM product **2b** with 53 % *ee* in 66 % yield, and the unreacted **1b** with 98 % *ee* was recovered in 24 % yield (Table 1, 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.[16] The Mo/(*R*)-L2 species[15b] was highly active; the reaction of *rac*-**1b** by using this catalyst showed complete conversion to *rac*-**2b** within 4 h. Thus, the kinetic resolution study by using Mo/(*R*)-L2 was conducted at 0 °C in toluene for 1 h, but the enantioselectivity was minimal (k_{rel} = 2.0; Table 1, entry 2). The Mo catalyst coordinated with (*R*)-L3[15c] showed excellent enantioselectivity giving **1b** with 96 % *ee* in 37 % yield and **2b** with 72 % *ee* in 60 % yield, respectively. The k_{rel} value for the reaction is as high as 22 (Table 1, entry 3).

After the optimization studies, Mo/(*R*)-L1 or Mo/(*R*)-L3 was applied to the other substrates. Substrate *rac*-**1c**, which has a ruthenocene core in place of the ferrocene in **1b**, was also resolved as described above, however the enantioselectivity was somewhat lower (k_{rel} = 11; Table 1, entry 4). The position of R^3 in **1** is crucial for a high enantioselectivity of the ARCM reaction. Substrate **1d**, which possesses a *p*-tolyl group adjacent to the methallyl substituent, was resolved efficiently by using Mo/(*R*)-L1, and **1d** with 91 % *ee* was recovered in 30 % yield (Table 1, entry 5). On the other hand, the reaction of **1e**, which has a *p*-tolyl substituent next to the allyl group, under the identical conditions gave recovered **1e** with 4 % *ee* and cyclized **2e** with less than 1 % *ee* (Table 1, entry 6). Based on our previous studies,[9] it is postulated that the initial metathesis between the Mo*–alkylidene precatalyst and a substrate takes place at the unsubstituted allyl group. In the diastereomeric intermediates [(*R*)-Mo*]/(*R*/*S*)-**1d** that are derived from *rac*-**1d** and (*R*)-Mo*–alkylidene, the steric factors between the two substituents adjacent to the [(*R*)-Mo*]-binding tether are fairly different (C–H vs. C–methallyl). As a result, [(*R*)-Mo*]/(*R*)-**1d** forms preferentially over the other diastereomeric intermediate (Scheme 2, left). On the other hand, the two substituents proximal to the allyl group are sterically comparable in *rac*-**1e**. And thus, the (*R*)-Mo* species failed to distinguish the two enantiomers in **1e** leading to the low enantioselectivity in its kinetic resolution (Scheme 2, right). Ferrocenylphosphine sulfide (**1f**), in which the relative arrangement of the three substituents is similar to that in **1d**, was also a suitable substrate for the kinetic resolution, and unreacted **1f** was recovered with 99 % *ee* and 32 % yield with a k_{rel} value of 25 (Table 1, entry 7).

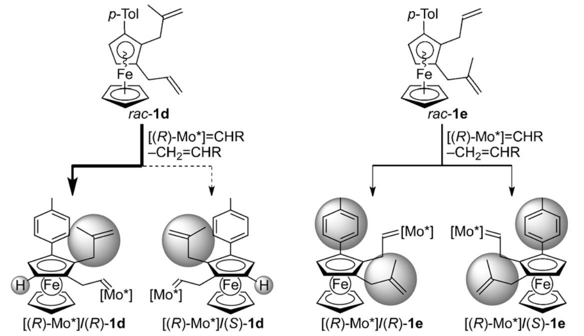
The enantioselectivity of the kinetic resolution was sensitive to the substituent at the allylic 2-position (R^2 group in **1**). Introduction of a bulkier substituent in place of the methyl group in **1b** improved the enantioselectivity. The ARCM of *rac*-**1g**, which has a 2-ethylallyl tether, proceeded with excellent selectivity (k_{rel} = 30) to give the recovered substrate with 99 % *ee* in 37 % yield (Table 1, entry 8). With a benzyl group as the R^2 substituent in *rac*-**1h**, the k_{rel} value was further improved to 33 (Table 1, entry 9). Substrate **1i**, possessing a 2-(trimethylsilyl)allyl tether, was less reactive probably due to the excessively bulky SiMe$_3$ substituent. Both Mo/(*R*)-L1 and Mo/(*R*)-L3 failed to afford the cyclized product for the reaction with **1i**. It was found that the

Table 1. Molybdenum-catalyzed intraannular ARCM kinetic resolution of planar-chiral 1,2-diallylmetallocenes.[a]



	1	Chiral L	T [°C], t [h]	*ee* (yield) of recovered **1** [%][b,c,d]	*ee* (yield) of cyclized **2** [%][b,c]	Config./optical rotation of **2**	k_{rel}[e]
1	*rac*-**1b**	(*R*)-L1	23, 24	98 (24)	53 (66)	(+)	14
2[f]	*rac*-**1b**	(*R*)-L2	0, 1	5 (80)	31 (15)	(+)	2.0
3	*rac*-**1b**	(*R*)-L3	23, 12	96 (37)	72 (60)	(+)	22
4	*rac*-**1c**	(*R*)-L3	23, 12	96 (31)	52 (60)	(+)	11
5	*rac*-**1d**	(*R*)-L1	23, 0.5	91 (30)	31 (66)	(−)	5.3
6	*rac*-**1e**	(*R*)-L1	23, 0.5	4 (26)	<1 (74)	(−)	<1.1
7	*rac*-**1f**	(*R*)-L3	23, 12	99 (32)	67 (67)	(*R*)-(+)	25
8	*rac*-**1g**	(*R*)-L3	23, 12	99 (37)	74 (59)	(+)	30
9	*rac*-**1h**	(*R*)-L3	23, 12	96 (41)	79 (53)	(+)	33
10	*rac*-**1i**	(*R*)-L2	23, 3	97 (35)	87 (57)	(−)	60

[a] The reaction was carried out in benzene in the presence of a metathesis catalyst (5 mol %) generated in situ unless otherwise noted. [b] The enantiomeric excess was determined by chiral HPLC (see the Supporting Information for details). [c] The yield of the product isolated by silica gel chromatography is given in parentheses. [d] The enantiomeric excess of recovered **1** was determined after conversion into **2** by a reaction with the Grubbs II catalyst. [e] Calculated based on a first-order equation (Ref. [16]). [f] In toluene.



Scheme 2. Comparison between **1d** and **1e** in the reaction with the chiral Mo–alkylidene precatalyst [(*R*)-Mo*]=CHR.

molybdenum species coordinated with (*R*)-L2, which is a more active but less enantioselective catalyst for the reaction of *rac*-**1b** (see Table 1, entries 1–3), was the catalyst of choice for the kinetic resolution of *rac*-**1i**. With this catalyst, the ARCM of *rac*-**1i** proceeded smoothly to give the cyclized product (**2i**) with 87 % *ee* in 57 % yield, and unreacted **1i** was recovered with 97 % *ee* and 35 % yield. The selectivity factor for the reaction is remarkably high being $k_{\mathrm{rel}} = 60$ (Table 1, entry 10).

Single-crystal X-ray crystallography revealed that the absolute configuration of the levorotatory **2f** ($[\alpha]_D^{25} = -26.0$ ($c = 1.6$ in $CHCl_3$) for the sample with 99 % *ee*), which was derived from recovered **1f** (Table 1, entry 7), was *S* as shown in Figure 1 (see the Supporting Information for details).[17] The configurations of the other ARCM products were deduced by analogy.

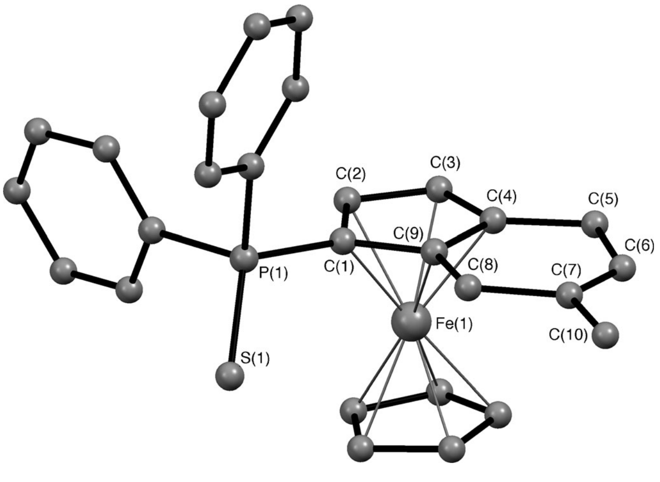
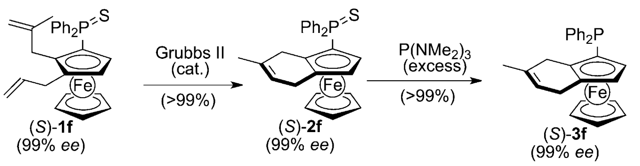


Figure 1. Ball-and-stick drawing of the levorotatory planar-chiral phosphine sulfide (*S*)-(−)-**2f**. All hydrogen atoms are omitted for clarity.

Phosphine sulfide (*S*)-**2f** (99 % *ee*), which was obtained from recovered (*S*)-**1f** by the RCM reaction by using the Grubbs II catalyst, could be reduced to the corresponding phosphine quantitatively by treating with an excess of $P(NMe_2)_3$.[18] The enantiopurity of (*S*)-**1f** was retained during the transformation (Scheme 3). Phosphine (*S*)-**3f** is a novel chiral ligand with a unique structure.[19] Its applications are now under investigation in our group and will be reported in due course.



Scheme 3. Stereoretentive conversion of (*S*)-**1f** into the planar-chiral ferrocenylphosphine (*S*)-**3f**.

In summary, we have developed an efficient method for the kinetic resolution of racemic planar-chiral 1,2-disubstituted ferrocene derivatives through a molybdenum-catalyzed asymmetric intraannular ring-closing metathesis reaction.

Experimental Section

General procedure for the molybdenum-catalyzed ARCM kinetic resolution of 1: In a glovebox under prepurified argon, $Mo(=NC_6H_3\text{-}2,6\text{-}iPr_2)(=CHCMe_2Ph)(NC_4H_4)_2$ (4.9 mg, 9.1 µmol) and L3 (6.3 mg, 9.1 µmol) were dissolved in dry benzene (5 mL) in a test tube with a Teflon-sealed screw cap. After stirring the mixture for 15 min at room temperature, benzene (13 mL) and the metallocene substrate **1** (180 µmol) were added. The test tube was sealed tightly and taken out of the glovebox. The test tube was immersed in an oil bath maintained at 23 °C and the mixture was stirred for 12 h. After quenching the reaction by addition of acetone (≈100 µL), the reaction mixture was passed through a pad of silica gel by using hexane/Et_2O (9:1) as the eluent. The solvent was removed under reduced pressure and the residue was purified by preparative HPLC [LC-908 recycle HPLC system (Japan Analytical Industry Co. Ltd.) with a GPC column (JAIGEL-H, chloroform, 3.5 mL min^{-1})] to give the ARCM product **2** and the recovered substrate **1**. Recovered **1** was converted to the corresponding compound **2** by treatment with the Grubbs II catalyst (5 mol %) in benzene for a chiral HPLC analysis. The characterization data of the ARCM products and the conditions for the chiral HPLC analysis are described in the Supporting Information.

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Keywords: asymmetric synthesis · chirality · kinetic resolution · metallocene · planar chirality · ring-closing metathesis

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[17] CCDC-902537 ((*S*)-(−)-**2f**.) contains 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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