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Molybdenum-Catalyzed Enantioselective Ring-Closing Metathesis/Kinetic Resolution of Racemic Planar-Chiral 1,1′-Diallylferrocenes

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Abstract: The molybdenum-catalyzed enantioselective ring-closing metathesis/kinetic resolution of a series of racemic planar-chiral 1,1′-diallylferrocene derivatives was reinvestigated utilizing the method of generating catalytically active chiral molybdenum-alkylidene species in situ, which allowed us to examine a variety of chiral molybdenum-alkylidene metathesis precatalysts in the present asymmetric reaction. With the catalyst screening experiments conducted in this study, the more practical reaction conditions, including a choice of a proper chiral molybdenum precatalyst, giving planar-chiral ferrocenes of higher enantiomeric purity and better chemoselectivity could be optimized.

Keywords: ferrocene; planar-chiral; enantioselective; kinetic resolution; olefin metathesis; ring-closing metathesis; molybdenum; alkylidene complex

Citation: Imazu, H.; Masaoka, K.; Uike, S.; Ogasawara, M. Molybdenum-Catalyzed Enantioselective Ring-Closing Metathesis/Kinetic Resolution of Racemic Planar-Chiral 1,1′-Diallylferrocenes. *Catalysts* **2024**, *14*, 123. https://doi.org/10.3390/catal14020123

Academic Editor: Luca Bernardi

Received: 10 January 2024
Revised: 1 February 2024
Accepted: 2 February 2024
Published: 4 February 2024

1. Introduction

The introduction of two (or more) different substituents in a single η^5-cyclopentadienyl ligand in ferrocene breaks the symmetry of the molecule, and so-called planar chirality is induced in it. Planar-chiral ferrocene derivatives have been recognized as being useful chiral scaffolds in organic and organometallic chemistry (Figure 1) [1–8], and various such complexes have been utilized in a wide range of asymmetric reactions as chiral ligands [9–19] or chiral catalysts [19–26]. In spite of their usefulness, enantioselective preparation of planar-chiral ferrocenes is still a challenging problem. Classical methods of obtaining enantiomerically pure (or enantiomerically enriched) planar-chiral ferrocene derivatives are the enantiomeric resolution of preformed racemates [27], including enzymatic resolution [28–30], and diastereoselective metalation utilizing chiral *ortho*-directing groups [31–40]. To the best of our knowledge, the first *catalytic* enantioselective synthesis of planar-chiral ferrocenes was reported in 1997 by Schmaltz and Siegel [41]. In 2006, three research groups (O'Brien [42], Moyano [43], and ourselves [44]) independently reported the catalytic asymmetric reactions giving enantiomerically enriched planar-chiral ferrocene derivatives. Since then, nearly 100 research works related to this topic have been published worldwide [45–48].

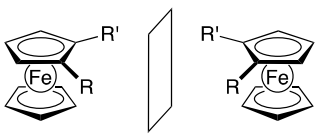


Figure 1. Enantiomeric pair of a planar-chiral ferrocene.

Since 2002, our research group has been interested in utilizing the ring-closing metathesis (RCM) reactions for the modulation of various transition-metal complexes [49–55] using

the Schrock's Mo- [56,57] and the Grubbs' Ru-alkylidene [58–61] complexes. The RCM protocols were extended to the asymmetric counterparts to show the excellent enantioselectivity in the asymmetric synthesis of diverse planar-chiral transition-metal complexes either by the kinetic resolution (KR) of the racemic substrates [44,48,62–64] or by the desymmetrization of the C_s-symmetric substrates [48,65–67].

The chiral catalysts employed in our asymmetric reactions, which produced enantiomerically enriched planar-chiral transition-metal complexes, were chiral Schrock–Hoveyda molybdenum-alkylidene precatalysts [68–71] (Figure 2). At the beginning of the development of these chiral precatalysts, each chiral molybdenum complex needed to be prepared and isolated one by one prior to the catalytic applications, which made the screening of the chiral precatalysts/diolate ligands tedious and time-consuming. In 2006, Schrock and Hoveyda reported molybdenum complex **A**, which served as a universal precursor to generate a variety of chiral molybdenum-alkylidene precatalysts in situ by means of a reaction with an appropriate chiral diol (Scheme 1) [72]. The development of this method enabled rapid and operationally simple screening of the various chiral molybdenum-alkylidene precatalysts in asymmetric olefin metathesis reactions.

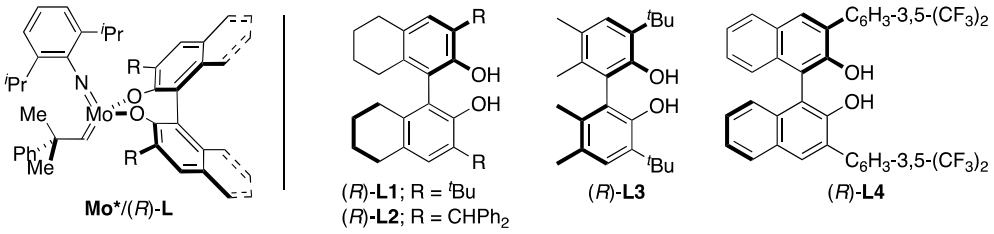
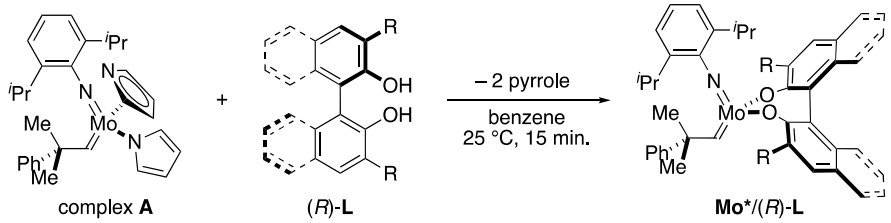
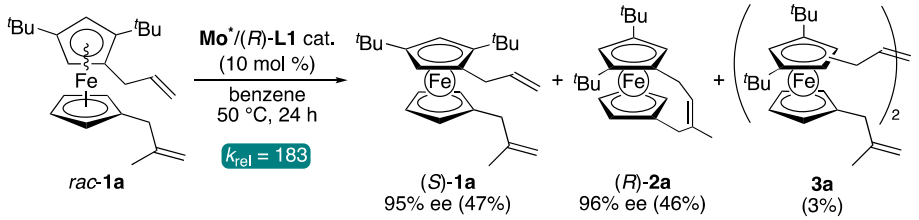


Figure 2. Representative chiral Schrock–Hoveyda molybdenum-alkylidene precatalysts [68–71].



Scheme 1. Reaction generating chiral molybdenum-alkylidene precatalysts in situ from complex **A** and proligand (*R*)-**L** [72].

Whereas our very first contribution to catalytic asymmetric synthesis of planar-chiral transition-metal complexes, which was the enantioselective ring-closing metathesis/kinetic resolution of racemic planar-chiral 1,1′-diallylferrocene derivatives **1** (Scheme 2), was reported prior to the development of complex **A**, only one molybdenum-alkylidene species, **Mo***/(*R*)-**L1**, was examined as a chiral precatalyst in the original publication [44]. In this article, various chiral Mo-alkylidene species were generated in situ, as shown in Scheme 1, and applied in the enantioselective RCM/KR reaction of racemic **1**. After the extensive screening of the chiral Schrock–Hoveyda metathesis precatalysts, the more practical conditions giving planar-chiral ferrocenes of higher enantiomeric purity and better chemoselectivity could be determined. Here, we would like to describe the details of our observations.



Scheme 2. **Mo***/(*R*)-**L1**-catalyzed enantioselective ring-closing metathesis/kinetic resolution of racemic planar-chiral ferrocene *rac*-**1a** [44].

2. Results and Discussion

2.1. Design and Preparation of Racemic Planar-Chiral 1,1′-Diallylferrocene Substrates 1a-c for the Molybdenum-Catalyzed Enantioselective Ring-Closing Metathesis/Kinetic Resolution

Our preliminary studies on the enantioselective RCM/KR of racemic planar-chiral 1,1′-diallylferrocene derivatives **1** [44] postulated that a couple of structural factors in the substrates were crucial to achieve the high enantioselectivity in the molybdenum-catalyzed reactions: (i) steric discrimination of the two allylic groups at the 1- and 1′-positions of the ferrocene core with a methyl substituent in the 2-allylic position of one of the two allylic substituents, and (ii) a bulky substituent R′ in the position adjacent to the unsubstituted (i.e., the more reactive) allyl group (Figure 3).

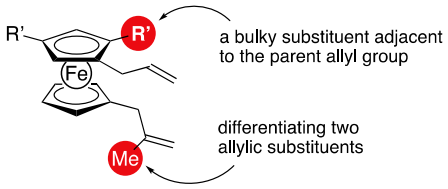
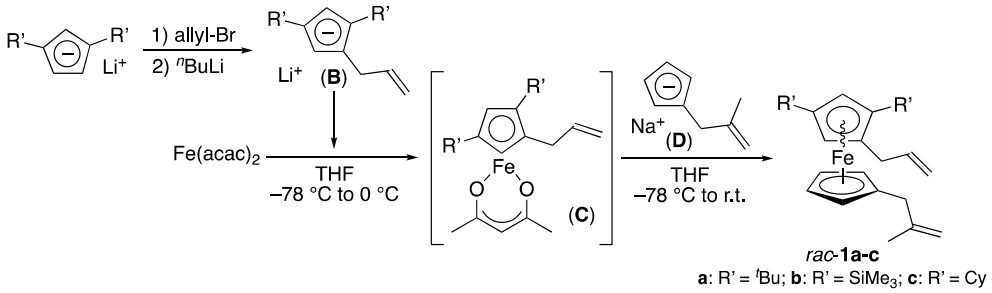


Figure 3. Structural requirements for ferrocene substrates showing high selectivity in molybdenum-catalyzed enantioselective RCM/KR reaction.

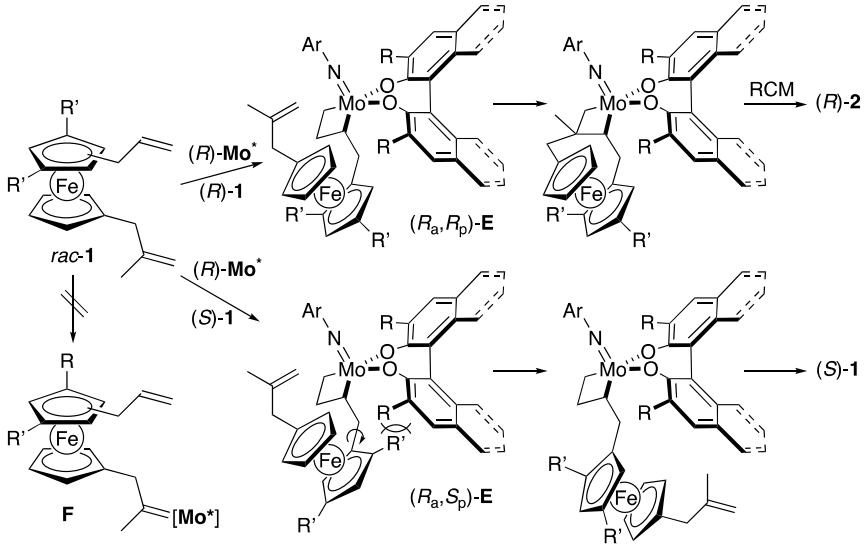
The preparation of the designed unsymmetric ferrocene derivatives *rac*-**1a-c** was achieved by the method developed by Manriquez et al., as shown in Scheme 3 [73]. Allylation of lithium 1,3-R′$_2$-cyclopentadienide with allyl bromide, followed by a deprotonation reaction with butyllithium, provided a THF solution of lithium 1-allyl-2,4-R′$_2$-cyclopentadienide (**B**). The allylation was highly regioselective, and the formation of a regioisomer, lithium 2-allyl-1,3-R′$_2$-cyclopentadienide, was negligible. A reaction of Fe(acac)$_2$ with stoichiometric **B** at –78 °C generated metastable intermediate **C** as a THF solution, and a subsequent reaction with sodium methallylcyclopentadienide (**D**) afforded *rac*-**1a-c** in the yields ranging 20–45%. The reaction conditions were not optimized. The reaction giving *rac*-**1a-c** was not completely hetero-selective, and the formation of homoleptic ferrocene byproducts, (η^5-methallyl-C$_5$H$_4$)$_2$Fe and (η^5-1-allyl-2,4-R′$_2$-C$_5$H$_2$)$_2$Fe, could not be eliminated. The target compounds could be separated from the byproducts by the standard column chromatography on alumina.



Scheme 3. Preparation of racemic planar-chiral ferrocene substrates *rac*-**1a-c**.

The ferrocene substrates for this study, *rac*-**1a-c**, possess a trisubstituted cyclopentadienide, η^5-(C_5H_2-1-allyl-2,4-R′$_2$), which is responsible for inducing planar chirality in ferrocene compounds, and the monosubstituted η^5-cyclopentadienyl ligand η^5-(C_5H_4-methallyl). In the presence of an appropriate chiral (*R*)-molybdenum-alkylidene metathesis catalyst, one of the two planar-chiral enantiomers in **1** is preferentially cyclized to give enantiomerically enriched bridged ferrocene (ferrocenophane) (*R*)-**2**, and antipodal (*S*)-**1** is left intact. The major side reaction of this RCM/KR process is the formation of **3**, which is a product of the metathesis dimerization at the unsubstituted allyl group in the trisubstituted cyclopentadienide (Scheme 2).

For the highly enantioselective kinetic resolution of *rac*-**1a-c**, the allyl group in a trisubstituted cyclopentadienyl needs to be more reactive than the methallyl (2-methylallyl) substituent in a monosubstituted cyclopentadienyl. In general, less substituted olefins are more reactive than more substituted ones in olefin metathesis. When a chiral molybdenum-alkylidene species, (*R*)-**Mo***, approaches *rac*-**1**, an initial reaction takes place preferentially at the allyl group in the planar-chiral trisubstituted Cp to give intermediates (R_a,R_p)- and (R_a,S_p)-**E** as a diastereomeric mixture ("R_a" represents the absolute configuration of the axially chiral biaryl moiety in Mo*), and the formation of **F** is unfavorable. While (R_a,R_p)-**E** is transformed into (*R*)-**2** smoothly via the RCM reaction, the epimeric intermediate, (R_a,S_p)-**E**, is forced to take an unfavorable conformation due to the steric repulsion between an R′ group in η^5-C_5H_2R′$_2$(allyl) and an R group in the chiral biaryloxide ligand in (*R*)-**Mo*** to liberate (*S*)-**1** intact (Scheme 4). On the other hand, the unfavorable formation of intermediate **F** is crucial for the high enantioselectivity in the RCM/KR process. Whereas the methallyl group in η^5-C_5H_4-methallyl is remote from the planar-chiral η^5-C_5H_2R′$_2$(allyl) moiety, its reaction with (*R*)-**Mo*** takes place with low diastereoselectivity. Following the RCM step in **F** is an intramolecular process, and, thus, both (R_a,R_p)- and (R_a,S_p)-**F** shall be transformed into the corresponding ferrocenophanes to give **2** with low enantioselection.



Scheme 4. Plausible stereochemical pathways of the molybdenum-catalyzed enantioselective RCM KR of *rac*-**1**.

2.2. Molybdenum-Catalyzed Enantioselective Ring-Closing Metathesis/Kinetic Resolution of Racemic Planar-Chiral 1,1′-Diallylferroce Substrates 1a-c: Catalyst Screening Studies

At the outset, the screening of precatalysts/reaction conditions was examined for the enantioselective RCM/KR reaction of *rac*-**1a**. Precatalyst **Mo***/(*R*)-**L1** (10 mol % to *rac*-**1a**), which was generated in situ as outlined in Scheme 1, showed a nearly identical performance (selectivity and reactivity) to the preformed catalyst [44] in the reaction (Table 1, Entry 1). Although the enantioselectivity of this reaction was quite high, with a k_{rel} value of 109 (k_{rel} = ([reaction rate of the fast-reacting enantiomer]/[reaction rate

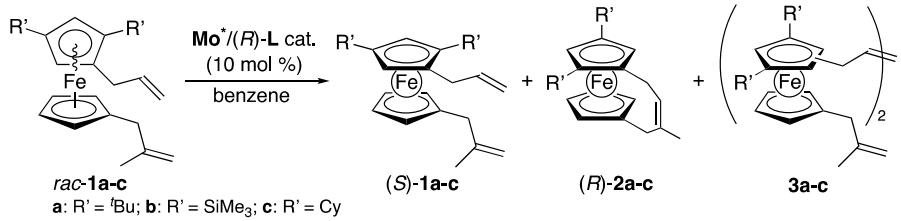
of the slow-reacting enantiomer]; selectivity factor) [74,75], the observed drawbacks of using **Mo***/(*R*)-**L1** were (i) the competition between the RCM reaction giving the desired ferrocenophane **2a** and the bimolecular metathesis giving side-product **3a**, (ii) the necessity of the high-dilution conditions for minimizing the formation of metathesis dimer **3a**, and (iii) the relatively high reaction temperature (50 °C) to retain the reasonable catalytic activity of the molybdenum species under the diluted conditions. It was found that the reaction using **Mo***/(*R*)-**L2** (10 mol % to *rac*-**1a**) promoted the intramolecular RCM reaction giving (*R*)-**2** preferentially, and the formation of **3** via the intermolecular reaction was not observed (Entry 2). The enantioselectivity was reasonably high (k_{rel} = 65) but slightly lower than that in Entry 1. Precatalyst **Mo***/(*R*)-**L2** was catalytically more active than **Mo***/(*R*)-**L1** in the reaction of *rac*-**1a**, and, thus, the reaction could be conducted at a lower temperature. Enantioselectivity was improved to k_{rel} = 95 at 25 °C (Entry 3). Since **Mo***/(*R*)-**L2** did not drive the bimolecular reaction giving **3**, the RCM/KR reaction catalyzed by **Mo***/(*R*)-**L2** could be conducted under the more concentrated conditions, which realized the shorter reaction time whilst retaining a high enantioselectivity. Under these conditions, RCM product (*R*)-**2a** of 96% ee was obtained in a 45% yield, and unreacted (*S*)-**1a** of 75% ee was recovered in 55%, of which k_{rel} was 110 (Entry 4). It is worth mentioning that the "concentrated" reaction could be carried out in an NMR sample tube using C_6D_6 as a solvent, which allowed for the direct monitoring of the reaction progress through ^{1}H-NMR measurements. The catalytic performance of **Mo***/(*R*)-**L3** was similar to that of **Mo***/(*R*)-**L1** (Entry 5). Precatalyst **Mo***/(*R*)-**L4** was the most reactive among the precatalysts examined but far less enantioselective. The reaction of *rac*-**1a** catalyzed by **Mo***/(*R*)-**L4** at 50 °C for 24 h was leading to the complete consumption of the substrate to provide nearly racemic **2a** quantitatively (Entry 6). The reaction at 25 °C realized the kinetic resolution of *rac*-**1a**, but its enantioselectivity was far less satisfactory (k_{rel} = 5.5; Entry 7).

The trends of the molybdenum-catalyzed enantioselective RCM/KR reactions of *rac*-**1b** were similar to those of *rac*-**1a**. Precatalysts **Mo***/(*R*)-**L1** and **Mo***/(*R*)-**L3** showed fairly high enantioselectivity (k_{rel} = 117 and 76, respectively) but with unsatisfactory chemoselection, producing a considerable amount of dimeric **3b** (Entries 8 and 12). On the other hand, **Mo***/(*R*)-**L2** was more reactive in the RCM/KR of *rac*-**1b** and did not catalyze the dimerization reaction (Entries 9-11). The reactivity of **Mo***/(*R*)-**L4** was too high, showing low enantioselectivity (Entries 13 and 14). The best result in the reaction of *rac*-**1b** was obtained using **Mo***/(*R*)-**L2** at the lower temperature (25 °C) under the concentrated conditions in C_6D_6 to give (*R*)-**2b** (97% ee, 47% yield) and recover (*S*)-**1b** (74% ee, 53%). The k_{rel} value of this reaction was estimated to be 146 (Entry 11).

Due to the sterically less-demanding cyclohexyl substituents in **1c** (compared to ^{t}Bu in **1a** and $SiMe_3$ in **1b**), the RCM/KR reaction of *rac*-**1c** was generally less enantioselective (Entries 15–17). The optimized reaction conditions, as in Entries 4 and 11, were applied to the reaction of *rac*-**1c**, and the reasonably good enantioselectivity of k_{rel} = 9.9 was achieved as well (Entry 17). It should be noted that the reactions of *rac*-**1c** under **Mo***/(*R*)-**L2** catalysis did not produce the undesirable metathesis dimer **3c** (Entries 16 and 17), as expected.

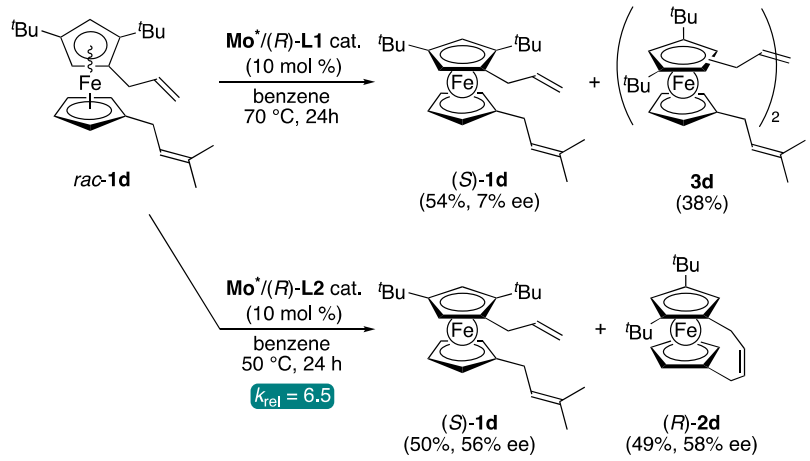
Next, the conditions optimized for the reaction of *rac*-**1a-c** were applied in the enantioselective RCM/KR reaction of substrate *rac*-**1d**, in which the methallyl group in *rac*-**1a** was replaced with a prenyl (3,3-dimethylallyl) substituent. It had been reported previously that the reaction of *rac*-**1d** in the presence of catalytic **Mo***/(*R*)-**L1** provided dimeric **3d** in a 38% yield as a sole metathesis product and that bridged **2d** was not detected. The unreacted substrate was recovered in 54%, of which the enantiopurity was as low as (*S*)-7% ee (Scheme 5, top) [44]. On the other hand, the reaction of *rac*-**1d,** as in Entry 4 in Table 1, afforded ferrocenophane (*R*)-**2d** of 58% ee in a 49% yield together with recovered (*S*)-**1d** of 56% ee in a 50% yield. The k_{rel} value for this reaction was determined to be 6.5 (Scheme 5, bottom).

Table 1. Molybdenum-catalyzed enantioselective ring-closing metathesis/kinetic resolution of racemic planar-chiral ferrocenes *rac*-**1a-c** [a].



Entry	Substrate [b]	Ligand	Conditions	Yields (%) of 1/2/3 [c]	% ee of (S)-1/(R)-2 [d,e]	k_{rel} [f]
1	**1a** (0.005)	(*R*)-**L1**	50 °C, 24 h	46/52/2	99/91	109
2	**1a** (0.005)	(*R*)-**L2**	50 °C, 24 h	45/55/0	97/88	65
3	**1a** (0.005)	(*R*)-**L2**	25 °C, 24 h	53/47/0	67/96	95
4 [g]	**1a** (0.05)	(*R*)-**L2**	25 °C, 1 h	55/45/0	75/96	110
5	**1a** (0.005)	(*R*)-**L3**	50 °C, 24 h	35/45/20	94/91	75
6	**1a** (0.005)	(*R*)-**L4**	50 °C, 24 h	0/100/0	--- [h]/--- [h]	--- [h]
7	**1a** (0.005)	(*R*)-**L4**	25 °C, 24 h	12/88/0	99/18	5.5
8	**1b** (0.005)	(*R*)-**L1**	50 °C, 24 h	51/38/11	89/95	117
9	**1b** (0.005)	(*R*)-**L2**	50 °C, 24 h	45/55/0	92/88	51
10	**1b** (0.005)	(*R*)-**L2**	25 °C, 24 h	45/55/0	97/91	89
11 [g]	**1b** (0.05)	(*R*)-**L2**	25 °C, 2 h	53/47/0	74/97	146
12	**1b** (0.005)	(*R*)-**L3**	50 °C, 24 h	44/52/4	91/92	76
13	**1b** (0.005)	(*R*)-**L4**	50 °C, 24 h	0/100/0	--- [h]/--- [h]	--- [h]
14	**1b** (0.005)	(*R*)-**L4**	25 °C, 24 h	20/80/0	90/26	4.4
15	**1c** (0.005)	(*R*)-**L1**	50 °C, 24 h	28/52/20	98/54	15
16	**1c** (0.005)	(*R*)-**L2**	50 °C, 24 h	1/99/0	--- [h]/5	--- [h]
17 [g]	**1c** (0.05)	(*R*)-**L2**	25 °C, 1 h	45/55/0	84/59	9.9

[a] The reaction was carried out with *rac*-**1** (0.10 mmol) in benzene using a molybdenum catalyst generated in situ (10 mol %), unless otherwise noted. [b] Initial concentration of substrate **1** in parentheses. [c] Determined via the ^{1}H-NMR analysis of the crude reaction mixture. [d] Determined by chiral HPLC analysis (see Materials and Methods Section for detail). [e] Enantiomeric excess of recovered **1a-c** was determined after converting them into the corresponding **2a-c** via the RCM reaction using the Grubbs-II catalyst. [f] Calculated based on a first-order equation [74,75]. [g] The reaction was carried out in C_6D_6. [h] Not determined.



Scheme 5. Molybdenum-catalyzed enantioselective ring-closing metathesis/kinetic resolution of racemic planar-chiral ferrocene *rac*-**1d**.

3. Materials and Methods

3.1. General Information

All air- and/or moisture-sensitive reactions were conducted with standard Schlenk techniques under pre-dried nitrogen or with glovebox techniques under pre-purified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100 MHz) chemical shifts were reported in

ppm downfield of internal tetramethylsilane. Tetrahydrofuran was distilled from sodium benzophenone-ketyl under dry nitrogen prior to use. Benzene and C_6D_6 were dried over a Na/K alloy and distilled and deoxygenated under high-vacuum conditions prior to use. Chloroform-*d* was distilled and deoxygenated from P_2O_5 under high-vacuum conditions and stored in a glovebox. $C_5H_4{}^tBu_2$ [76], $C_5H_4(SiMe_3)_2$ [77], $C_5H_4Cy_2$ [78], $(pyrrolyl)_2Mo(=CHCMe_2Ph)(=N\text{-}C_6H_3\text{-}2,6\text{-}{}^iPr_2)$ [72], (*R*)-**L1** [69], (*S*)-**L3** [68], (*R*)-**L4** [71], and the Grubbs-II catalyst [79,80] were prepared as reported. All the other chemicals were purchased from commercial suppliers and used without further purification, unless otherwise noted.

*3.2. Preparation of Racemic Diallylferrocene Substrates rac-***1a-d** *[44]*

A typical procedure is hereby given for the synthesis of *rac*-**1a**. To a THF (8 mL) solution of $Fe(acac)_2$ (2.54 g, 10.0 mmol) was added a solution of lithium 1-allyl-2,4-$^tBu_2$-cyclopentadienide, which was prepared from $C_5H_3(allyl)^tBu_2$ (2.18 g, 10.0 mmol) and ^{n}BuLi (1.60 M hexane solution, 6.3 mL, 10.1 mmol) in THF (25 mL), at –78 °C, and the mixture was stirred at 0 °C for 1h. After cooling the mixture to −78 °C, to this was added a solution of sodium methallylcyclopentadienide, which was prepared from C_5H_5-methallyl (1.06 g, 10.0 mmol) and NaH (240 mg, 10.0 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 3 h. The mixture was diluted with hexane and filtered through a pad of Celite. After removal of the solvent under reduced pressure, the remaining dark-red oil was purified by column chromatography on alumina using hexane as an eluent, and following vacuum transfer gave *rac*-**1a** as a dark-red oil. The reaction conditions were not optimized. The characterization data of the diallylferrocene substrates *rac*-**1a-d** are given below.

3.3. Characterization Data of Racemic 1,1′-Diallylferrocene Substrates **1a-d** *[44]*

rac-1-Allyl-1′-(2-methylallyl)-2,4-di(*tert*-butyl)ferrocene (**1a**). Yield: 45%. ^{1}H NMR ($CDCl_3$): δ 5.88–5.97 (m, 1H), 5.03 (d, *J* = 4.8 Hz, 1H), 4.99 (s, 1H), 4.62 (s, 1H), 4.59 (s, 1H), 4.13 (br, 1H), 4.08 (br, 1H), 3.93 (br, 2H), 3.76 (br, 1H), 3.72 (br, 1H), 3.22 (dd, *J* = 15.8 and 6.7 Hz, 1H), 3.07–3.12 (m, 1H), 3.01 (br, 2H), 1.65 (s, 3H), 1.27 (s, 9H), 1.18 (s, 9H). $^3C\{^1H\}$ NMR ($CDCl_3$): δ 146.5, 138.2, 115.0, 110.8, 98.8, 96.8, 86.0, 81.7, 71.2, 70.1, 68.8, 68.1, 67.7, 64.1, 38.5, 34.3, 32.4, 31.9, 31.5, 30.5, 22.2. Anal. Calcd for $C_{25}H_{36}Fe$: C, 76.52; H, 9.25. Found: C, 76.30; H, 9.03. HRMS Calcd for $C_{25}H_{36}Fe$: 392.2165. Found: 392.2165.

rac-1-Allyl-1′-(2-methylallyl)-2,4-bis(trimethylsilyl)ferrocene (**1b**). Yield: 20%. ^{1}H NMR ($CDCl_3$): δ 5.87–5.97 (m, 1H), 5.01 (d, *J* = 3.9 Hz, 1H), 4.98 (s, 1H), 4.62 (s, 1H), 4.58 (s, 1H), 4.07 (s, 1H), 4.02 (s, 1H), 3.96 (s, 1H), 3.90 (s, 1H), 3.88 (s, 1H), 3.79 (s, 1H), 3.13 (d, *J* = 6.2 Hz, 2H), 3.00 (br, 2H), 1.64 (s, 3H), 0.26 (s, 9H), 0.22 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.2, 138.2, 115.0, 110.3, 94.4, 86.5, 79.4, 78.2, 74.0, 73.3, 70.8, 69.7, 68.4, 68.1, 38.4, 34.2, 22.2, 0.6, 0.1. Anal. Calcd for $C_{23}H_{36}FeSi_2$: C, 65.07; H, 8.55. Found: C, 65.13; H, 8.43. HRMS Calcd for $C_{23}H_{36}FeSi_2$: 424.1703. Found: 424.1702.

rac-1-Allyl-1′-(2-methylallyl)-2,4-dicyclohexylferrocene (**1c**). Yield: 30%. ^{1}H NMR ($CDCl_3$): δ 5.91–6.01 (m, 1H), 4.99–5.06 (m, 2H), 4.63 (br, 1H), 4.58 (br, 1H), 3.77–3.97 (m, 6H), 2.94–3.09 (m, 4H), 2.13–2.25 (m, 3H), 1.84-1.93 (m, 3H), 1.66 (s, 3H), 1.61–1.78 (m, 6H), 1.15–1.40 (m, 9H), 0.91 (qd, *J* = 12.3 and 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.5, 138.0, 115.0, 110.1, 92.9, 92.5, 86.2, 82.9, 71.0, 70.5, 69.1, 69.0, 66.9, 64.0, 38.1, 37.4, 36.4, 36.3, 34.4, 34.3, 32.29, 32.26, 27.0, 26.9, 26.8 (2C), 26.6, 26.5, 22.3. Anal. Calcd for $C_{29}H_{40}Fe$: C, 78.36; H, 9.07. Found: C, 78.47; H, 9.20. HRMS Calcd for $C_{29}H_{40}Fe$: 444.2477. Found: 444.2484.

rac-1-Allyl-1′-(3-methyl-2-butenyl)-2,4-di(*tert*-butyl)ferrocene (**1d**). Yield: 33%. ^{1}H NMR ($CDCl_3$): δ 5.96–5.86 (m, 1H), 5.24–5.21 (m, 1H), 5.01 (d, *J* = 4.8 Hz, 1H), 4.98 (br, 1H), 4.15 (br, 1H), 4.09 (br, 1H), 3.95 (br, 1H), 3.92 (br, 1H), 3.83 (br, 1H), 3.79 (br, 1H), 3.19 (dd, *J* = 16.4 and 7.2 Hz, 1H), 3.07–2.99 (m, 3H), 1.68 (s, 3H), 1.65 (s, 3H), 1.25 (s, 9H), 1.16 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.4, 131.1, 124.3, 114.9, 98.7, 96.7, 88.4, 81.7, 70.2, 69.1, 68.4, 67.9, 67.6, 63.8, 34.3, 32.4, 31.9, 31.5, 30.5, 27.8, 25.7, 17.8. Anal. Calcd for $C_{26}H_{38}Fe$: C, 76.84; H, 9.42. Found: C, 76.70; H, 9.59. HRMS Calcd for $C_{26}H_{38}Fe$: 406.2321. Found: 406.2328.

*3.4. General Procedure for Molybdenum-Catalyzed Enantioselective RCM/Kinetic Resolution of rac-***1**

The detailed reaction conditions are summarized in Table 1. A mixture of Mo(=NC_6H_3-2,6-$^i Pr_2$)(=$CHCMe_2Ph$)(NC_4H_4)$_2$ (5.4 mg, 10 μmol) and an appropriate chiral ligand **L** (11 μmol) were placed in a test tube (with a Teflon-sealed screw cap) and dissolved in dry benzene (3.0 mL) in a glovebox under pre-purified argon. The mixture was stirred for 15 min at room temperature, and then to this was added a solution of substrate *rac*-**1** (0.10 mmol) in benzene (17.0 mL). The sealed test tube was taken out of the glovebox and was immersed in an oil bath maintained at 50 °C or 25 °C. After stirring the mixture for 24 h, the reaction was quenched by the addition of acetone (ca. 100 μL). The reaction mixture was passed through a short pad of silica gel (eluent: hexane/Et_2O = 9/1). The volatiles were removed under reduced pressure, and the conversion of the reaction was determined by the ^{1}H-NMR measurement of the crude residue. The residue was purified by preparative HPLC [LC-908 recycle HPLC system (Japan Analytical Industry Co., Ltd., Tokyo, Japan) with a GPC column (JAIGEL-H, chloroform, 3.5 mL/min)] to provide RCM product **2** and recovered substrate **1**, respectively. Recovered unreacted **1** was treated with Grubbs-II catalyst (5 mol %) in benzene to give the corresponding **2** quantitatively, which was used for a chiral HPLC analysis. The absolute configurations of ferrocenophanes **2** as well as recovered unreacted substrates **1** were determined through the comparison of their signs of the specific rotations with those of the known compounds [44]. The characterization data of the RCM products and the conditions for the chiral HPLC analysis are listed below.

3.5. Characterization Data of Ferrocenophanes **2a-d** *[44]*

1,1′-(3-Methyl-2-buten-1,4-diyl)-2,4-di(*tert*-butyl)ferrocene (**2a**). ^{1}H NMR ($CDCl_3$): δ 5.67 (t, *J* = 7.4 Hz, 1H), 4.14 (s, 1H), 4.02 (s, 1H), 3.99 (s, 1H), 3.89 (s, 1H), 3.82 (s, 1H), 3.73 (s, 1H), 3.28 (dd, *J* = 14.7 and 7.4 Hz, 1H), 3.12 (d, *J* = 14.7 Hz, 1H), 2.59-2.67 (m, 2H), 1.93 (s, 3H), 1.28 (s, 9H), 1.14 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.1, 124.1, 99.9, 98.3, 85.3, 83.1, 70.6, 70.3, 66.8, 66.1, 66.0, 63.6, 32.6, 32.1, 31.4, 30.4, 29.4, 26.7, 24.8. Anal. Calcd for $C_{23}H_{32}Fe$: C, 75.82; H, 8.85. Found: C, 76.08; H, 8.91. HRMS Calcd for $C_{23}H_{32}Fe$: 364.1852. Found: 364.1856. $[\alpha]^{30}_D$ = +22 (*c* 0.50, $CHCl_3$ for the sample of (*R*)-96% ee). Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 2000/1; flow rate: 1.0 mL/min; t_1 = 17.7 min (*R*-isomer), t_2 = 20.6 min (*S*-isomer).

1,1′-(3-Methyl-2-buten-1,4-diyl)-2,4-bis(trimethylsilyl)ferrocene (**2b**). ^{1}H NMR ($CDCl_3$): δ 5.76 (t, *J* = 7.8 Hz, 1H), 4.10 (s, 1H), 4.02 (s, 1H), 3.97 (s, 1H), 3.92 (s, 1H), 3.87 (s, 1H), 3.84 (s, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 3.02 (dd, *J* = 14.8 and 7.3 Hz, 1H), 2.75 (dd, *J* = 14.8 and 8.2 Hz, 1H), 2.69 (d, *J* = 14.4 Hz, 1H), 1.94 (s, 3H), 0.27 (s, 9H), 0.17 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.1, 124.1, 96.3, 86.1, 78.5, 76.2, 74.8, 74.7, 70.1, 69.7, 66.5, 66.4, 29.4, 26.7, 25.0, 0.9, −0.1. Anal. Calcd for $C_{21}H_{32}FeSi_2$: C, 63.61; H, 8.13. Found: C, 63.46; H, 8.04. HRMS Calcd for $C_{21}H_{32}FeSi_2$: 396.1390. Found: 396.1395. $[\alpha]^{31}_D$ = +50 (*c* 2.0, $CHCl_3$ for the sample of (*R*)-97% ee). Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent: hexane/^{i}PrOH = 2000/1; flow rate: 1.0 mL/min; t_1 = 15.5 min (*R*-isomer), t_2 = 16.5 min (*S*-isomer).

1,1′-(3-Methyl-2-buten-1,4-diyl)-2,4-dicyclohexylferrocene (**2c**). ^{1}H NMR ($CDCl_3$): δ 5.74 (t, *J* = 8.0 Hz, 1H), 4.09–4.07 (m, 1H), 3.94–3.93 (m, 1H), 3.86–3.85 (m, 1H), 3.85–3.84 (m, 1H), 3.76–3.74 (m, 1H), 3.53-3.52 (m, 1H), 3.04 (d, *J* = 14.4 Hz, 1H), 2.94 (dd, *J* = 15.2 and 7.8 Hz, 1H), 2.81 (d, *J* = 14.4 Hz, 1H), 2.70 (dd, *J* = 14.8 and 7.8 Hz, 1H), 2.42–2.35 (m, 1H), 2.11-2.02 (m, 2H), 1.98-1.83 (m, 3H), 1.94 (s, 3H), 1.75-1.66 (m, 6H), 1.43–1.08 (m, 9H), 0.96–0.86 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.1, 123.6, 93.8, 93.0, 86.3, 84.9, 71.9, 70.3, 67.6, 66.6, 66.5, 63.2, 37.33, 37.25, 36.3, 34.5, 34.4, 31.7, 31.5, 29.6, 27.1, 26.8, 26.74, 26.65, 23.6, 22.8, 14.3. Anal. Calcd for $C_{27}H_{36}Fe$: C, 77.88; H, 8.71. Found: C, 77.70; H, 8.92. HRMS Calcd for $C_{27}H_{36}Fe$: 416.2165. Found: 416.2166. $[\alpha]^{30}_D$ = +23 (*c* 1.3, $CHCl_3$ for the sample of (*S*)-84% ee derived from recovered (*S*)-**1c**). Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent: hexane; flow rate: 0.5 mL/min; t_1 = 78.3 min (*R*-isomer), t_2 = 86.4 min (*S*-isomer).

1,1′-(2-Buten-1,4-diyl)-2,4-di(*tert*-butyl)ferrocene (**2d**). ^{1}H NMR ($CDCl_3$): δ 5.93–6.02 (m, 1H), 4.13 (s, 1H), 3.98–3.99 (m, 2H), 3.93 (s, 1H), 3.80 (s, 1H), 3.79 (s, 1H), 3.48 (dd, *J* = 15.1 and 6.0 Hz, 1H), 3.02 (dd, *J* = 15.1 and 6.0 Hz, 1H), 2.88 (dd, *J* = 14.6 and 7.3 Hz, 1H), 2.74 (dd, *J* = 14.6 and 7.3 Hz, 1H), 1.31 (s, 9H), 1.15 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 131.6, 130.2, 99.6, 97.6, 86.2, 82.0, 70.6, 70.1, 66.9, 66.3, 65.7, 63.3, 32.6, 32.0, 31.4, 30.4, 24.3, 24.1. Anal. Calcd for $C_{22}H_{30}Fe$: C, 75.43; H, 8.63. Found: C, 75.29; H, 8.77. HRMS Calcd for $C_{22}H_{30}Fe$: 350.1695. Found: 350.1697. $[\alpha]^{31}_{D}$ = −8.2 (*c* 0.56, $CHCl_3$ for the sample of (*R*)-58% ee). Chiral HPLC Analysis Conditions: Chiralcel OD-H × 2; eluent: hexane/^{i}PrOH = 3000/1; flow rate: 0.1 mL/min; t_1 = 94.2 min (*R*-isomer), t_2 = 101.4 min (*S*-isomer).

3.6. Calculation of Selectivity Factors "k_{rel}" in Table 1 and in Scheme 5

Selectivity factors (k_{rel}, k_{rel}′) of the first-order KR reaction are calculated by equations 1 or 2 [74,75], where *c* ($0 \leq c \leq 1$) stands for the conversion of the reaction, and ee_{sub} and ee_{pro} ($0 \leq ee \leq 1$) are the enantiomeric excesses of recovered (*S*)-**1** and RCM product (*R*)-**2**, respectively.

$$k_{rel} = \frac{\ln[(1-c)(1-ee_{sub})]}{\ln[(1-c)(1+ee_{sub})]} \quad (1)$$

$$k'_{rel} = \frac{\ln[1-c(1+ee_{pro})]}{\ln[1-c(1-ee_{pro})]} \quad (2)$$

Among the three variables in Equations (1) and (2) (*c*, ee_{sub}, and ee_{pro}), conversion "*c*", which was determined by the ^{1}H-NMR measurement of the unpurified reaction mixture, contained up to 5% experimental errors. On the other hand, the ee_{sub} and ee_{pro} values were much more accurate. The %ee values of recovered substrate (*S*)-**1** and RCM product (*R*)-**2** in Table 1 and in Scheme 5 were determined by chiral HPLC analysis, which is usually reproducible within 1% of errors, if the two enantiomers are clearly separated in the chromatograms. The k_{rel} value (determined from eq. 1) and the k_{rel}′ value (determined from eq. 2) in a single reaction should be identical, in theory. Accordingly, logical conversion of the reaction could be determined from ee_{sub} (%ee of recovered (*S*)-**1**) and ee_{pro} (%ee of (*R*)-**2**) using Equations (1) and (2). The logical conversion values thus obtained showed reasonable agreement with the experimental observations. The k_{rel} values in Table 1 and in Scheme 5 were calculated using logical conversion, ee_{sub}, and ee_{pro}.

4. Conclusions

The molybdenum-catalyzed enantioselective ring-closing metathesis/kinetic resolution of planar-chiral 1,1′-diallylferrocene derivatives **1a-d** was reinvestigated utilizing the method of generating various catalytically active molybdenum species in situ. Among the molybdenum catalysts screened, **Mo***/(*R*)-**L2** showed the best overall performance with good enantioselectivity and excellent chemoselectivity. Since **Mo***/(*R*)-**L2** did not drive the undesirable bimolecular reaction giving **3**, the RCM/KR reaction could be conducted under the concentrated conditions using this catalyst, which realized a shorter reaction time whilst retaining excellent enantioselectivity.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal14020123/s1: Figures S1–S8: ^{1}H-NMR spectra of substrates **1a-d** and RCM products **2a-d**; Figures S9–S12: chiral HPLC chromatograms of **2a-d**.

Author Contributions: Conceptualization, M.O.; investigation, H.I., K.M., and S.U.; writing—original draft preparation, M.O.; writing—review and editing, M.O.; supervision, M.O.; funding acquisition, M.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Grant-in-Aids for Scientific Research (21H01940) from MEXT, Japan.

Data Availability Statement: All the available data have been made available through the Supplementary Material.

Conflicts of Interest: The authors declare no conflicts of interest.

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