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Metathesis Route to Bridged Metallocenes

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Connecting two cyclopentadienyl ligands in a bis(η^5-cyclopentadienyl)metal complex is one of the most important methods to modify steric characteristics of the metallocene. The interannular bridge restricts a free rotation of the Cp ligands about the Cp-metal axes with respect to each other. It changes a dihedral angle between the two Cp ligands. The metallocenophanes have attracted attention because of their interesting structures, chemical reactivity, and potential use as building blocks for new materials.[1] On the other hand, *ansa*-metallocenes of group III or group IV metals have been demonstrated as useful catalysts/reagents in polymerization/organic synthesis.[2]

Here we wish to report a novel method of preparing a variety of bridged metallocenes, which include compounds of Fe(II), Ru(II), Zr(IV), and Hf(IV), by the ring-closing metathesis reaction (Scheme 1).[3] The method was extended to diastereoselective kinetic resolution of *meso*- and *dl*-isomeric mixtures and showed excellent selectivity.[4]

It was found that transformation of 1,1′-diallylferrocene (**1a**), which was readily prepared from allylcyclopentadienyllithium and anhydrous $FeCl_2$, into the corresponding ferrocenophane **2a** is efficiently catalyzed by 3 mol % of the Grubbs' complex $RuCl_2(=CHPh)(PCy_3)_2$ (**3**).[5] Thus, a mixture of **1a** (203 mg, 763 μmol) and **3** (21 mg, 26 μmol) was dissolved in CH_2Cl_2 (5 mL), and the solution was heated to reflux. The reaction was complete within 3 h, and 180 mg of **2a** (>99% yield) was isolated as a yellow-orange crystalline solid by column chromatography on Al_2O_3 (Table 1, entry 1). 1,1′-Di(2-butenyl)ferrocene (**1b**), which is a mixture of three possible geometrical isomers, is also an excellent precursor to **2a** and afforded **2a** as a single product in quantitative yield with a longer reaction time (entry 2). The reaction of diallyloctamethylferrocene (**1c**) was carried out under analogous conditions (3 mol % of **3**, [**1c**] = 0.11 mol/L). The substrate **1c** was completely consumed within 48 h, and the homogeneous solution turned into a heterogeneous mixture with a considerable amount of an insoluble solid. Expected ferrocenophane **2c** was not detected in the reaction mixture by a GC-MS analysis (entry 3). Apparently, an intermolecular metathesis reaction giving the polymeric material was dominant for **1c** because of the sterically more congested Cp ligands. The intermolecular reaction was effectively eliminated under the high-dilution conditions ([**1c**] = 5.3×10^{-3} mol/L), and **2c** was obtained in 94% isolated yield as a reddish-orange crystalline solid (entry 4).[6] An X-ray structure determination of **2c** revealed that the two cyclopentadienyl moieties are eclipsed and the dihedral angle between the two Cp rings is 4.5°.[7]

The reaction allowed access to the isostructural ruthenocenophane **2d** in 92% yield under the high-dilution conditions (entry 5). The yield of **2d** was somewhat decreased under the more concentrated conditions (entry 6). The relatively low yield of **2d** is attributed to the larger central metal in **2d**, which imposes a larger tilt angle (8.3°)[7] between the two Cp planes.

Scheme 1

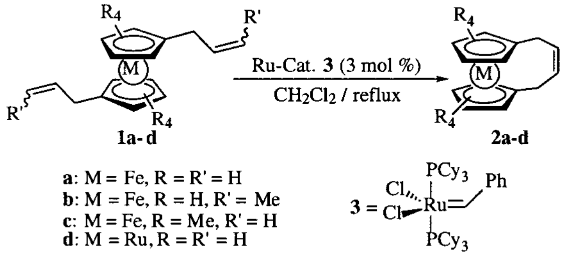
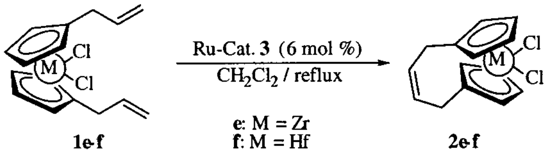


Table 1. Ruthenium-Catalyzed Synthesis of Bridged Metallocenes[a]

entry	substrate	[**1**] (mol/L)[b]	[**3**] (mol %)	time (h)[c]	yield of **2** (%)[d]
1	**1a**	1.5×10^{-1}	3	3	>99 (**2a**)
2	**1b**	1.1×10^{-1}	3	12	>99 (**2a**)
3	**1c**	1.1×10^{-1}	3	48	0
4	**1c**	5.2×10^{-3}	3	12	94 (**2c**)
5	**1d**	9.1×10^{-3}	3	12	92 (**2d**)
6	**1d**	6.8×10^{-2}	3	12	55 (**2d**)
7	**1e**	2.7×10^{-3}	6	36	88 (**2e**)
8	**1f**	2.7×10^{-3}	6	36	83 (**2f**)

[a] The reaction was carried out in CH_2Cl_2 in the presence of the ruthenium catalyst **3**. [b] Initial concentration of the substrate. [c] No remaining substrate was detected. [d] Yield of isolated product.

Scheme 2



The present method is effective in the preparation of group IV *ansa*-metallocenes. 1,1′-Diallylzirconocene dichloride (**1e**) was treated with the Grubbs' catalyst **3** (6 mol %) in refluxing CH_2Cl_2 under the high-dilution conditions (Scheme 2). The RCM reaction proceeded smoothly, and the *ansa*-zirconocene **2e** was isolated in 88% yield by vacuum sublimation (entry 7). Analogous *ansa*-hafnocene **2f** was prepared in a similar manner and isolated in 83% yield (entry 8). These reactions are very few examples of constructing the bridging bis(cyclopentadienyl) framework on the air- and moisture-sensitive group IV metallocene species.[8] The reaction also demonstrates excellent tolerance of the Ru complex **3** to the electrophilic Zr and Hf metal centers.

The present RCM reaction was extended to diastereoselective kinetic resolution of *meso*- and *dl*-isomeric mixtures and showed excellent selectivity. Diallylmetallocenes with central or planar chirality could be used as substrates for the diastereoselective reaction.[4] The ferrocene substrate **1g**, which possesses two stereogenic centers, exists as a 50/50 mixture of *meso*- and *dl*-isomers.[9]

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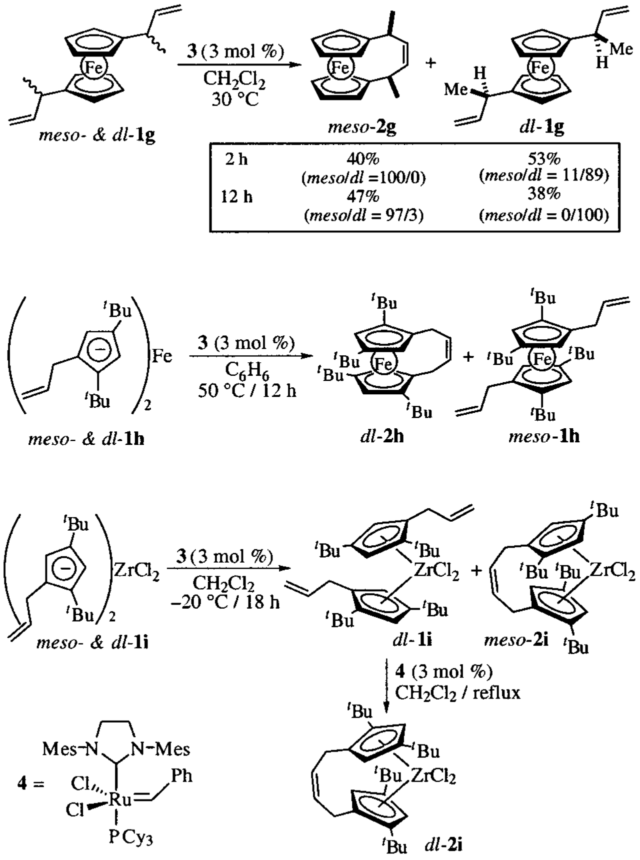
Scheme 3. Diastereoselective RCM Kinetic Resolution of Diallylmetallocenes



	meso-2g	dl-1g
2 h	40% (meso/dl = 100/0)	53% (meso/dl = 11/89)
12 h	47% (meso/dl = 97/3)	38% (meso/dl = 0/100)

As shown in Scheme 3, in the presence of 3 mol % of **3**, the *meso*-**1g** was selectively cyclized to give *meso*-**2g**, while *dl*-**1g** remained virtually untouched. From the mixture reacted for 2 h, the bridged **2g** (*meso*-**2g** only)[7] and the nonbridged **1g** (*meso*-**1g**/*dl*-**1g** = 11/89) were easily separated by preparative GPC[10] in 40 and 53% yields, respectively. The pure *dl*-**1g** was recovered in 38% yield (76% of theory) after being reacted for 12 h, and 47% of the bridged **2g** was obtained with *meso*-**2g**/*dl*-**2g** = 97/3. The recovered less-reactive *dl*-**1g** was transformed into the corresponding bridged *dl*-**2g** in 83% yield using more powerful second-generation Grubbs' catalyst **4**.[11]

Nearly perfect diastereoselectivity was achieved in the kinetic resolution of *meso*- and *dl*-bis(η^5-1-allyl-2,4-di-*tert*-butylcyclopentadienyl)iron(II) (**1h**). Because of planar chirality induced by the η^5-coordination of the unsymmetrically substituted cyclopentadienyls, **1h** exists as a mixture of two diastereomers (*meso*-**1h**/*dl*-**1h** = 66/34).[9] It was found that the Grubbs' catalyst **3** perfectly distinguishes the two isomers under the conditions illustrated in Scheme 3 and cyclized *dl*-**1h** selectively to give *dl*-**2h** quantitatively (NMR analysis).[7] After the reaction, neither *dl*-**1h** nor *meso*-**2h** was detected in the solution. From the reaction mixture, *meso*-**1h** and *dl*-**2h** were easily separated by GPC[10] and isolated in pure form in 61% (90% of theory) and 27% (80% of theory) yields, respectively.

Similarly, bis(η^5-1-allyl-2,4-di-*tert*-butylcyclopenta-dienyl)zirconium(IV) dichloride (*meso*-**1i**/*dl*-**1i** = 74/26) was applied to the RCM reaction and showed excellent diastereoselectivity. The diastereomeric mixture of the bent metallocene was treated with 3 mol % of **3** for 18 h at −20 °C. Under these conditions, *meso*-**1i** was preferentially cyclized, and the *ansa*-zirconocene dichloride **2i** was formed with *meso*-**2i**/*dl*-**2i** = 96/4 selectivity.[12] The pure *meso*-**2i** was isolated in 67% yield (91% of theory) by the preparative GPC[10] followed by recrystallization from CH_2Cl_2/MeOH. The unreacted **1i**, which consisted of the *dl*-isomer only, was recovered in 21% yield (81% of theory), from which the *dl*-*ansa*-**2i** was prepared in 83% isolated yield by the RCM reaction using the Ru-dihydroimidazolylidene catalyst **4**.[11] The method described here provides a novel strategy for preparing C_2-symmetric planar chiral *ansa*-metallocene species,[8a,13] which are important catalyst precursors for stereoregular polymerization.[2]

In summary, we have developed a general and efficient method of converting a variety of 1,1′-diallylmetallocene derivatives into the corresponding bridged metallocenes by the ruthenium-catalyzed ring-closing metathesis.

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Supporting Information Available: Detailed experimental procedures, compound characterization data, and crystallographic data for **2c**, **2d**, *meso*-**2g**, and *dl*-**2h** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Examples of diastereomeric mixtures whose components underwent RCM at different rates, see: (a) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108. (b) Miller, S. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 5855. (c) Schmidt, B.; Sattelkau, T. *Tetrahedron* **1997**, *53*, 12991. (d) Lloyd-Jones, G. C.; Murray, M.; Stentiford, R. A.; Worthington, P. A. *Eur. J. Org. Chem.* **2000**, 975.

(5) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(6) The isolated ferrocenophane **2c** was treated with **3** (3 mol %) in refluxing CH_2Cl_2 (initial concentration of **2c** was 1.1×10^{-1} mol/L). In 30 h, ca. 40% of **2c** was converted into an insoluble polymeric material.

(7) The complexes **2c**, **2d**, *meso*-**2g**, and *dl*-**2h** were characterized by X-ray crystal structure studies. See Supporting Information for details.

(8) (a) Erker, G.; Wilker, S.; Krüger, C.; Goddard, R. *J. Am. Chem. Soc.* **1992**, *114*, 10983. (b) Knüppel, S.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1923. (c) Bai, S.-D.; Wei, X.-H.; Guo, J.-P.; Liu, D.-S.; Zhou, Z.-Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 1926.

(9) Because of their close similarity, two isomers were not separable by column chromatography, HPLC, GPC, or GC with a capillary column. The ratio between the two isomers was determined by ^{1}H NMR (for **1h** and **1i**) or ^{13}C NMR (for **1g**, accumulated with a 120 s delay time). In the ^{1}H NMR (500 MHz) spectrum of the isomeric mixture of **1g**, all of the signals were observed as overlapped resonances from both of the isomers, and thus the *dl*/*meso* molar ratio could not be determined by ^{1}H NMR.

(10) GPC separation of *dl*-**1g**/*meso*-**2g**, *meso*-**1h**/*dl*-**2h**, and *dl*-**1i**/*meso*-**2i** was performed on a LC-908 recycle HPLC system (Japan Analytical Industry Co. Ltd.) with a GPC column (JAIGEL-H, chloroform, 3.5 mL/min).

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(12) The configurations of the stereoisomers in **2i** were determined by ^{1}H NMR after coverting them into the corresponding $ZrMe_2$ derivatives by a MeLi treatment. A single $ZrMe_2$ signal (δ −0.22) was detected for *dl*-**2i**, while *meso*-**2i** gave two $ZrMe_2$ resonances (δ −0.23 and −0.20) in $CDCl_3$.

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