Synthesis of New Chiral Ligands and Their Group VI Metal Alkylidene Complexes

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The new chelating chiral diol ligands (1*S*,2*S*)- and (1*R*,2*R*)-1,2-bis(2-hydroxy-2,2-bis-(trifluoromethyl)ethyl)cyclopentane (TBEC-H_2; **1**) were synthesized. The dilithium alkoxide of TBEC was reacted with Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$dme (**2**; Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) to give the chiral alkylidene complex Mo(CHCMe$_2$Ph)(NAr)(TBEC) (**3**). The ligand also reacts with W(η^2-diphenylcyclopropene)Cl$_2$(O)[P(OMe)$_3$]$_2$ (**4**), W(CHCHCOCH$_2$CH$_2$CH$_2$O)(O)Cl$_2$[P(OMe)$_3$] (**5**), and W(CHCHCPh$_2$)(NAr)Cl$_2$[P(OMe)$_3$]$_2$ (**6**; Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) to the give stable corresponding tungsten oxo vinylalkylidene complexes and tungsten amide vinylalkylidene complexes, respectively. These group VI alkylidene complexes show excellent catalytic activity in both ring-opening metathesis polymerization and in ring-closing metathesis processes.

Introduction

An important class of well-defined catalysts for olefin metathesis reactions are the alkylidene complexes of the group VI metals.[2] Two important reactions included in this category are ring-opening metathesis polymerization (ROMP)[3] and ring-closing metathesis (RCM).[4] Despite enormous amounts of research in this field, there have been very few reports concerning the asymmetric variants of these reactions.[5] To explore the possibility of asymmetric induction in olefin metathesis reactions, we proposed to modify the ubiquitous alkoxide ligands in the molybdenum and tungsten alkylidene complexes. This is the most simple way to introduce chirality to the complexes due to the facile design and synthesis of their parent chiral alcohols. In this paper we report the synthesis of new ligands, their derived chiral molybdenum and tungsten alkylidene complexes, and their respective metathesis activities.

Results and Discussion

(1*S*,2*S*)- and (1*R*,2*R*)-1,2-Bis(2-hydroxy-2,2-bis-(trifluoromethyl)ethyl)cyclopentane (TBEC-H_2) Ligand Synthesis. We designed a new chiral ligand with the following considerations in mind. (1) A bidentate 3° alcohol with at least two perfluoroalkyl groups at the α-carbon was required (Figure 1A). The perfluoroalkyl groups are required to increase the activity of the catalyst.[2a,f] Bidentate coordination can provide a rigid structure that is suited for transfer of asymmetry.[6] In addition, 3° alkoxides are bulky enough to stabilize the catalyst.[2] (2) To differentiate the two faces of the metal−carbon double bond and reduce the number of possible diastereomers upon attachment to the metal center, a C_2-symmetry structure was desired (Figure 1B). (3) A large-membered-ring chelation system (>7) was preferred (Figure 1C), as molecular models revealed that a smaller ring chelate (i.e. 5 or 7) cannot block one of the two faces of the metal−carbon double bond in case of Mo(CHR)(NAr)(OR′)$_2$ within the tetrahedral structure of the complexes (Figure 1D,E).

Geminally perfluoroalkylated diol ligands such as the 1,1,6,6-tetrakis(trifluoromethyl)hexane-1,3,4,6-tetraol de-

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(2) Molybdenum: (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886. (b) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899−6907. (c) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495−4502. (d) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287−2289. (e) Schrock, R. R. *Strem Chem.* **1992**, *14*, 1−6. Tungsten: (f) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423−1435. (g) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Kruger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262−2275. (h) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 793−794. (i) Couturier, J.; Paillet, C.; Leconte, M.; Basset, J. M.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 628−631. (j) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130−8145. (k) Van der Schaaf, P. A.; Abbenhuis, R. A.; Van der Noort, W. P. A.; De Graaf, R.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *Organometallics* **1994**, *13*, 1433−1444.

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(4) (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426−5427. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324−7325. (c) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800−3801. (d) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (e) Fujimura, O.; Fu, G. C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029−4031. (f) Kim, S. H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *115*, 10801−10802. (g) Miller, S. J.; Kim, S. H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108−2109. (h) Miller, S. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 5855−5856. (i) Martin, S. F.; Liao, Y.; Rein, T. *Tetrahedron Lett.* **1994**, *35*, 691−694. (j) Martin, S. F.; Liao, Y.; Chen, H. J.; Patzel, M.; Ramser, M. N. *Tetrahedron Lett.* **1994**, *35*, 6005−6008. (k) Martin, S. F.; Wagman, A. S. *Tetrahedron Lett.* **1995**, *36*, 1169−1170. (l) Houri, A. F.; Xu, Z.; Cogan, D.; Hoveyda, A. *J. Am. Chem. Soc.* **1995**, *117*, 2943−2944.

(5) (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413−4414. (b) O'Dell, R.; McConville, D. H.; Hofmeister, G. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414−3423. (c) Heppert, J. A.; Dietz, S. D.; Eilerts, N. W.; Henning, R. W.; Morton, M. D.; Takusagawa, F. *Organometallics* **1993**, *12*, 2565−2572.

(6) For examples, see: *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993.

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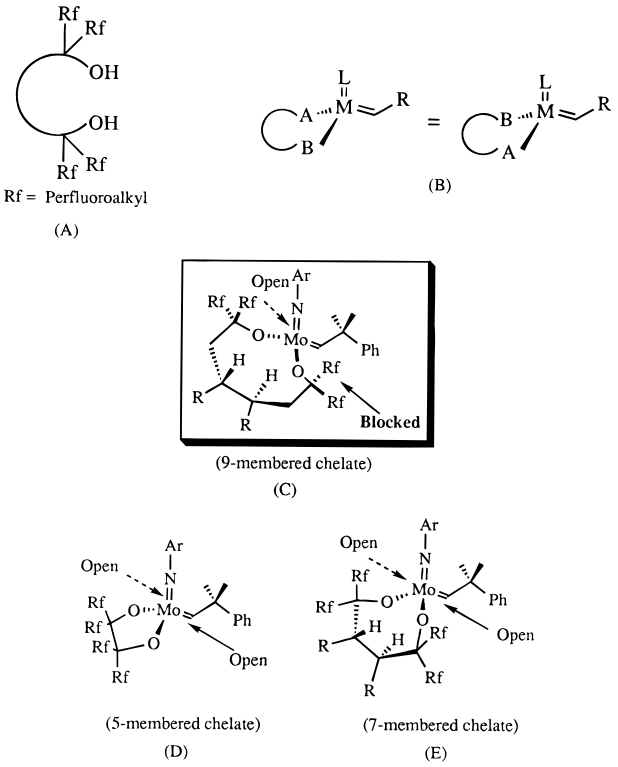
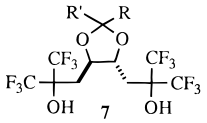


Figure 1. Design features for the chiral ligand.

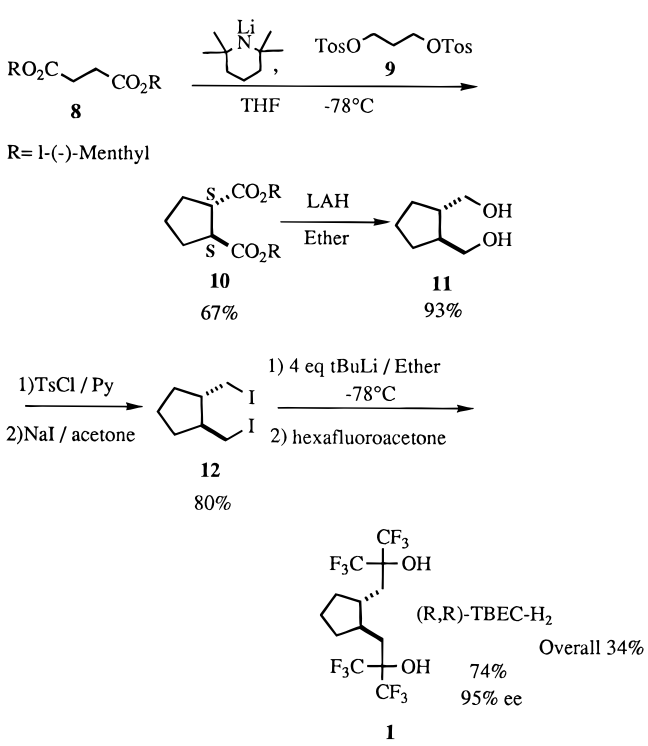
rivatives **7** seemed to meet our design criteria. However, after several attempts to prepare these diols, we found that replacement of the oxygen atom in the acetal moiety with a $-CH_2-$ group was necessary to avoid β-elimination.[7] Thus, **1** became our target ligand.



7

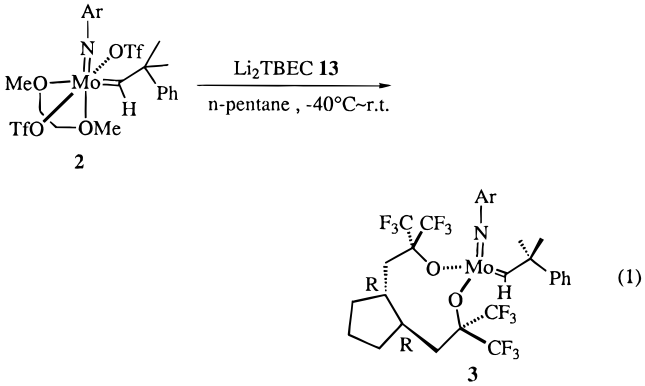
The starting (1*S*,2*S*)-bis((−)-menthyl) 1,2-cyclopentanedicarboxylate (**10**) was prepared with excellent diastereoselectivity by the reaction of the 1,3-propanediol bis(tosylate) species **9** and the dilithium enolate of bis((−)-menthyl) succinate (**8**).[8,9] Diester **10** was reduced with lithium aluminum hydride to give the diol **11** in good yield.[10] The two-step transformation of diol **11** into diiodide **12** was carried out by conventional means. The lithiation of diiodide **12** by *tert*-butyllithium at −78 °C and successive reaction with hexafluoroacetone afforded the desired chiral diol (1*R*,2*R*)-1,2-bis-(2-hydroxy-2,2-bis(trifluoromethyl)ethyl)cyclopentane

Scheme 1



(TBEC-H_2; **1**) in good yield (34% overall) and high enantiomeric excess (95% ee) (Scheme 1).[11,12]

Synthesis of a Chiral Molybdenum Alkylidene Complex. The molybdenum alkylidene bis(triflate) precursor Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$dme (**2**; Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) was prepared via known methods.[13] The reaction of 1 equiv of **2** with 1 equiv of the dilithium alkoxide derivative of TBEC, **13**, in *n*-pentane at −40 °C afforded the chiral molybdenum alkylidene (*R*,*R*)-Mo(CHCMe$_2$Ph)(NAr)(TBEC) (**3**), which can be isolated as a brown yellow solid in 85% yield (eq 1).

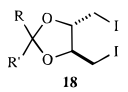


2

3 (1)

Complex **3** can be stored under N_2 at low temperature (−10 °C) for several months without any decomposition. Even in benzene solution at ambient temperature, **3** is stable for more than 1 week. Whereas the two methyl groups of the neophylidene analogue of achiral Mo(CHCMe$_2$Ph)(NAr)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$)

(7) For the synthesis of **7**, we tried the Grignard reaction of diiodide **18** (derived from threitol 2,3-acetal) with hexafluoroacetone. However, the Grignard reagent of **18** could not be prepared because of spontaneous decomposition by β-elimination. We also tried lithiation of **18** with *n*-butyllithium at −78 °C, but this resulted in decomposition of **18** in the same fashion.



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(8) Misumi, A.; Iwanaga, K.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 3343−3345.

(9) By using the bis((+)-menthyl) succinate dilithium enolate, bis-((+)-menthyl) (1*R*,2*R*)-1,2-cyclopentanedicarboxylate was prepared in the same way.

(10) Hollis, T. K.; Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 2812−2816.

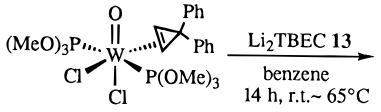
(11) The enantiomeric excess was determined by chiral GC. See the Experimental Section for details.

(12) (1*S*,2*S*)-TBEC-H_2 was also prepared in the same manner by starting from (1*R*,2*R*)-bis((+)-menthyl) 1,2-cyclopentanedicarboxylate.

(13) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185−198.

are equivalent (^{13}C NMR δ 30.6 in C_6D_6), they are no longer equivalent in **3**. The chemical shifts of these methyl groups are δ 31.0 and 31.2, respectively. This implies differentiation of the two faces of the metal−carbon double bond by the chiral ligand. The monomeric structure of this complex was confirmed by a molecular weight determination by the vapor pressure equilibrium method. The molecular weight calculated for **3** is 831 and is found to be 811 (see Experimental Section).

Synthesis of Chiral Tungsten Oxo and Amide Alkylidene Complexes. We recently reported the synthesis of $W(CHCHCPh_2)(O)(OCMe(CF_3)_2)_2[P(OMe)_3]$.[14] Although the complex was observed in solution, it was not isolated as a solid due to the lability of the W−P(OMe$_3$) bond. We projected that the bulkier alkoxide TBEC would stabilize the final vinyl alkylidene complex without loss of activity because of the analogous electronic nature of both alkoxide ligands. Reaction of W(η^2-diphenylcyclopropene)Cl_2(O)[P(OMe$_3$)$_2$ (**4**)[14] with 1 equiv of the dilithium alkoxide derivative of TBEC, **13**, in toluene for 12 h at room temperature and then 2 h at 65 °C afforded the chiral tungsten oxo vinylalkylidene complex $W(CHCHCPh_2)(O)$(TBEC)-[P(OMe$_3$)] (**14**). As expected, this complex is stable and was isolated as a yellow crystalline solid in 80−90% yield (eq 2).[15]



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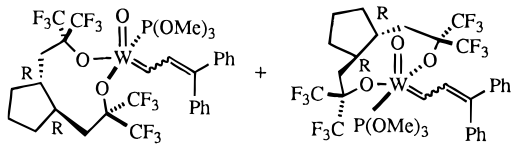
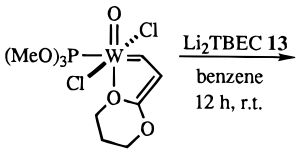


(2)

14a **14b**

In the same manner as for **14**, the reaction of $W(CHCHCOCH_2CH_2CH_2O)(O)Cl_2[P(OMe_3)]$ (**5**)[14] with 1 equiv of **13** in toluene afforded the new chiral tungsten oxo vinylalkylidene complex $W(CHCHCOCH_2CH_2CH_2O)$-(O)(TBEC)[P(OMe$_3$)] (**15**), which was isolated as a yellow crystalline solid in 85−90% yield (eq 3).



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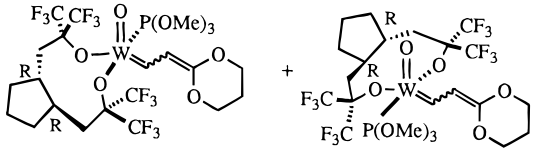


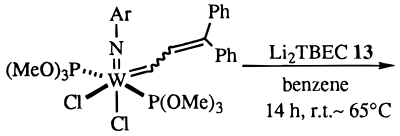
(3)

15a **15b**

Complexes **14** and **15** are sensitive to air but can be stored under argon at −10 °C for several months without any decomposition. Both complexes are highly soluble in a variety of solvents.

The coordination of TBEC to the metal center in **14** and **15** can produce two diastereomers, depending on the coordination geometry of the TBEC ligand. Each one of these isomers can present syn and anti rotamers, giving a total of four possible isomers for complexes **14** and **15**. The ^{1}H NMR spectra of both complexes show the presence of these four isomers (Figure 2).[16] The two isomers, due to the different coordination of TBEC, appeared in a 4:1 ratio in **14** and **15**, and both contained the syn rotamer as the major isomer. Syn and anti assignments were made on the basis of the coupling constant values.[17]

In addition, $W(CHCHCPh_2)(NAr)$(TBEC)[P(OMe$_3$)] (**16**) can be prepared by the reaction of $W(CHCHCPh_2)$-$(NAr)Cl_2[P(OMe_3)]_2$ (**6**)[18a] with 1 equiv of **13**. The syn rotamer is also the major isomer (eq 4). In this case,



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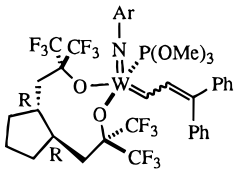
Ar= 2,6-*i*Pr-C_6H_3



(4)

16

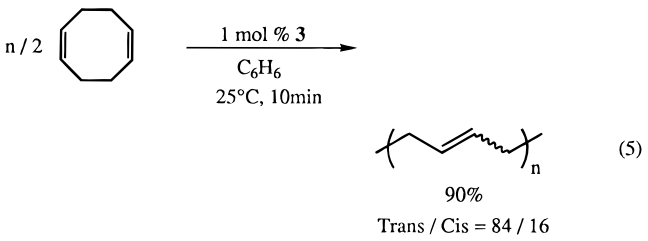
only one coordination mode of the TBEC ligand is observed by ^{1}H NMR, probably due to steric reasons that may make the other conformation quite unfavorable.

The spectroscopic data for **14**−**16** (see Experimental Section) are similar to those observed for analogous oxo and imido complexes.[18] The chemical shifts and coupling constants corresponding to H_α and H_β of the vinylalkylidene ligand are also similar. Accordingly, we proposed for these complexes a structure analogous to that solved by X-ray diffraction methods in a previous report; that is, a distorted trigonal bipyramid, where the oxo (or imido) and vinylalkylidene ligands are cis to each other and are placed in the equatorial plane, the TBEC ligand occupies the other equatorial position and one of the axial positions, and the remaining axial position is occupied by the phosphite ligand.

Metathesis Activity of Molybdenum and Tungsten TBEC Complexes. The complex **3** is a very active catalyst for the olefin metathesis reactions. For example, cyclooctadiene was polymerized in good yield (eq 5).

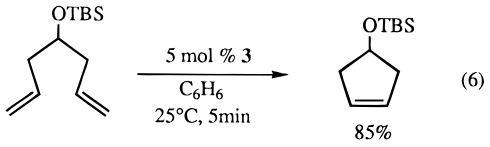
(14) de la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 577.
(15) Heating the reaction mixture from the beginning causes the decomposition of **4**.[14]

(16) ^{1}H NMR of **14** shows, besides the signals corresponding to the four isomers, resonances corresponding to small amounts (about 2%) of free phosphite carbene species.
(17) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; Di Mare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832−1843.
(18) (a) Johson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130−8145. (b) Claverie, J. P.; de la Mata, F. J.; Grubbs, R. H. Unpublished results.



(5)

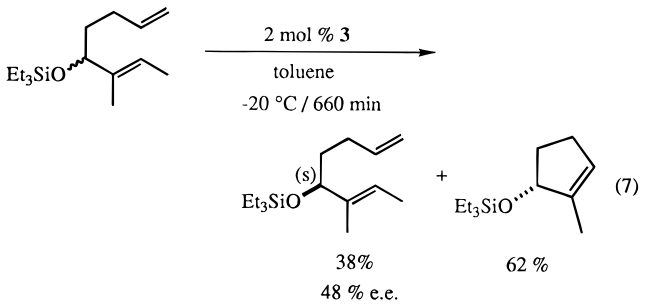
Complex **3** also catalyzes a ring-closing metathesis reaction at ambient temperature (eq 6).



(6)

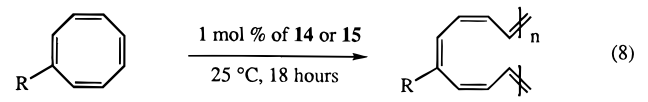
The reactivity of **3** is essentially identical with that of the typical metathesis catalyst Mo(CHCMe$_2$Ph)(NAr)(OCMe(CF$_3$)$_2$)$_2$ (**17**; Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$).[1a,4a−c,e] **17** polymerizes 1,5-cyclooctadiene under the same conditions shown in eq 5 (25 °C, 10 min, yield 89%, trans/cis = 85/15) and cyclizes 4-(*tert*-butyldimethylsiloxy)-1,6-heptadiene in 90% yield under the same conditions shown in eq 6.

By using **3** as a catalyst, asymmetric ring-closing metathesis was accomplished for the first time (eq 7).[19]



(7)

Although complexes **14** and **15** are less active than W(CHCMe$_3$)(NAr)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-(*i*Pr)$_2$C$_6$H$_3$)[2f] due to their Lewis base (P(OMe)$_3$) coordination,[20] they also show significant metathesis activity. In addition to the cyclic strained olefins such as norbornene, cyclooctene, and 1,5-cyclooctadiene, these catalysts even can polymerize less strained olefins such as substituted cyclooctatetraenes, leading to substituted polyacetylenes (eq 8).[21] Due to the lability of the W−P(OMe)$_3$ bond, there is no need to use a phosphite sponge to activate the catalyst.[18]



(8)

R = CH(CH$_3$)CH$_2$CH$_3$

Conclusion

The new chiral ligands (1*S*,2*S*)- and (1*R*,2*R*)-1,2-bis-(2-hydroxy-2,2-bis(trifluoromethyl)cyclopentane (TBEC) were synthesized. The ligands have C_2 symmetry and contain bulky 3° alcohols bearing two electron-withdrawing trifluoromethyl groups at the α-carbons. The dilithium alkoxide derivative of TBEC reacts with various Mo and W alkylidene precursors to give stable chiral alkoxy alkylidene complexes. Particularly, in the case of tungsten, this ligand produces complexes which exhibit excellent stability, whereas the complexes synthesized using hexafluoro-*tert*-butoxide are not stable enough to be isolated. These complexes are quite active in olefin metathesis reactions. The application of these complexes to asymmetric ring-closing metathesis reactions (i.e. kinetic resolution) will be reported in detail, and the stereoregulation of ring-opening polymerization is also currently under investigation.

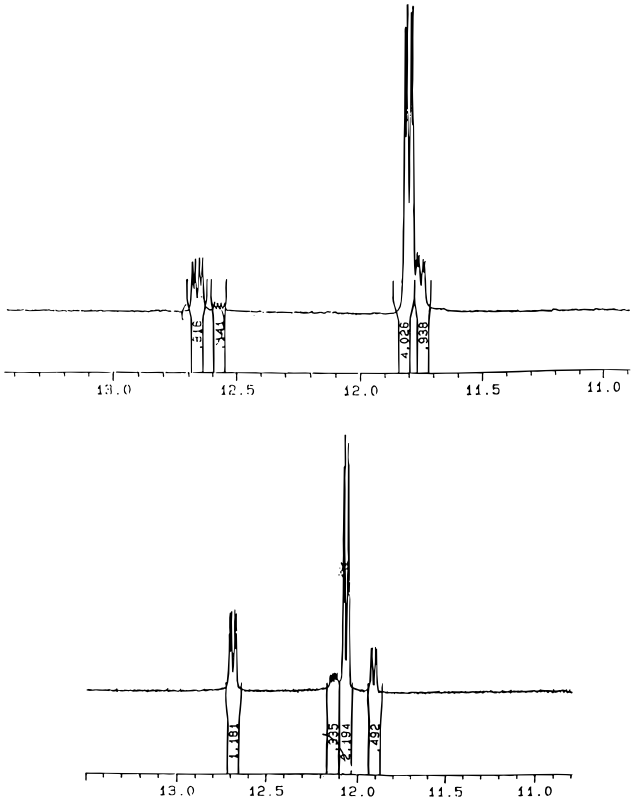


Figure 2. Alkylidene regions (H$_\alpha$) of the ^{1}H NMR spectra of (a) **14** and (b) **15**.

Experimental Section

General Methods. ^{1}H spectra were recorded on a General Electric QE-300 spectrometer or a Bruker 500 AM spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale) with the solvent resonance employed as an internal standard (C$_6$D$_6$ at δ 7.15, CDCl$_3$ at δ 7.26), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), integration, and assignment.

^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer at ambient temperature. ^{13}C chemical shifts are reported in parts per million downfield from tetramethylsilane (δ scale) and the solvent resonance employed as an internal standard (C$_6$D$_6$ at δ 128.0). All ^{13}C spectra were determined with complete proton decoupling.

^{31}P NMR (202.69 MHz) and ^{19}F NMR (470.56 MHz) spectra were recorded on a Bruker 500 AM spectrometer at ambient temperature. ^{31}P chemical shifts are reported in δ scale with

(19) Fujimura, O.; Grubbs, R. H. *J. Am. Chem. Soc.*, in press.

(20) In the case of *sec*-butylcyclooctatetraene polymerization, THF was added to slow down the reaction when W(CHCMe$_3$)(NAr)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) was used; polymerization was still completed within minutes at 25 °C. See also ref 24.

(21) Even the most reactive molybdenum alkylidene complex such as Mo(CHCMe$_2$Ph)(NAr)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) cannot polymerize *sec*-butylcyclooctatetraene.

trimethyl phosphite at 140 ppm as standard. ^{19}F chemical shifts are reported in parts per million downfield from $CFCl_3$ (δ scale).

Infrared spectra were obtained on a Perkin-Elmer 1600 Series FTIR. High resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California, Riverside, CA). Analytical thin-layer chromatography was accomplished using EM Reagents 0.25 mm silica gel 60 plates. Flash chromatography was performed on EM Reagents silica gel (230−400 mesh). Elemental analysis was performed at the California Institute of Technology Elemental Analysis Facility. Optical rotations were obtained on a JASCO DIP-181 digital polarimeter.

GLC analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph.

The molecular weight of **3** was determined by the vapor pressure equilibrium method described by Bercaw.[22] Freshly recrystallized $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ (Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$).[1a,4a−c,e] was used as standard.

Argon was purified by passage through a column of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves.

All manipulations were performed under an argon atmosphere using standard Schlenk techniques with a double-manifold vacuum line or in a N_2-filled drybox using oven-dried glassware with magnetic stirring.

Materials. Commercial reagents were used as received, with the following exceptions. Benzene and diethyl ether were purified by passage through a column of La Roche A-2 alumina and Engelhard Q-5 reactant (supported copper oxide), degassed by freeze−pump−thaw (FPT) three times, and stored under argon in a flask with a Teflon valve. *n*-Pentane was stirred over concentrated H_2SO_4, dried over CaH_2 and $MgSO_4$, vacuum-transferred from sodium−benzophenone ketyl, degassed by FPT, and stored under argon in a flask with a Teflon valve. $P(OMe)_3$ was vacuum-transferred from sodium and then subjected to several freeze−pump−thaw cycles. 3,3-Diphenylcyclopropene was synthesized according to the method described in the literature.[23] Cyclooctadiene was dried over CaH_2 and distilled. *sec*-Butylcyclooctatetraene was prepared according to the literature.[24]

(1*S*,2*S*)-Bis(*l*-menthyl) 1,2-Cyclopentanedicarboxylate ((1*S*,2*S*)-10).[8] To a solution of 2,2,6,6-tetramethylpiperidine (35.6 g, 211 mmol) in dry THF (300 mL) was added dropwise a solution of *n*-butyllithium in hexane (1.6 M, 132 mL, 211 mmol) at −20 °C under argon, and the mixture was stirred for 20 min. The resulting mixture was cooled to −78 °C, and (−)-bis(*l*-menthyl)succinate (40 g, 101 mmol) in dry THF (100 mL) was added and stirred at −78 °C for 1 h. To this bis enolate solution was added dropwise 1,3-propanediol ditosylate (32.5 g, 85 mmol) in dry THF (100 mL). After being stirred for 3 h at the same temperature, 2-methylpropanal (3.6 mL) was added to quench excess reagent. The reaction mixture was opened to ice-cooled 1 M aqueous hydrochloric acid solution (500 mL) and extracted with ether (150 mL × 3). The ether extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo. The concentrate was passed through a short silica gel plug to remove polar byproducts (hexane/EtOAc = 40/1). The filtrate was concentrated, and flash chromatography (EM Reagents silica gel 60, 230−400 mesh, hexane/EtOAc = 40/1) yielded 24.7 g (67%) of **11** as a white solid.

(1*S*,2*S*)-Bis(*l*-menthyl) 1,2-cyclopentanedicarboxylate ((1*S*,2*S*)-10): ^1H NMR (300 MHz, C_6D_6) δ 4.90 (td, J = 10.7, 4.3, 2H, −OC**H**(CH)CH_2), 3.41−3.32 (m, 2H, C**H**CO_2R), 2.17−2.00 (m, 4H, CH_3C**H**CH_3, OCHC**H**CH_2), 2.00−1.78 (m, 4H, CH_2C**H$_2$**$CHCO_2$R), 1.52−1.34 (m, 6H, OCHC**H$_2$**CH, CH_3C**H**-$(CH_2)CH_2$), 1.26−1.10 (m, 2H, OCHCHC**H**H), 0.95−0.60 (m, 8H, CH_2C**H$_2$**CH_2, OCHCHCH**H**, OCHCH_2CHC**H$_2$**CH_2), 0.90 (d, J = 7.0, 6H, C**H$_3$**$CHCH_3$), 0.85 (d, J = 7.0, 6H, CH_3CHC**H$_3$**), 0.77 (d, J = 6.4, 6H, C**H$_3$**$CH(CH_2)CH_2$); $[\alpha]_D^{25}$ = −33.0° (c = 1.0, $CHCl_3$; lit.[8] −32.8°); mass spectrum (EI) m/z (relative intensity) 419 (M^+ − CH_3, 5), 297 (5), 207 (10), 159 (100).

(1*R*,2*R*)-Bis(*d*-menthyl) 1,2-cyclopentanedicarboxylate ((1*R*,2*R*)-10).[8] (1*R*,2*R*)-**10** was synthesized in the same procedure as above, except (+)-bis(*d*-menthyl) succinate was used instead of (−)-bis(*l*-menthyl) succinate. Yield 63%.

(1*R*,2*R*)-10: ^1H NMR (300 MHz, C_6D_6) δ 4.90 (td, J = 10.7, 4.3, 2H, −OC**H**(CH)CH_2), 3.41−3.32 (m, 2H, C**H**CO_2R), 2.17−2.00 (m, 4H, CH_3C**H**CH_3, OCHC**H**CH_2), 2.00−1.78 (m, 4H, CH_2C**H$_2$**$CHCO_2$R), 1.52−1.34 (m, 6H, OCHC**H$_2$**CH, CH_3C**H**-$(CH_2)CH_2$), 1.26−1.10 (m, 2H, OCHCHC**H**H), 0.95−0.60 (m, 8H, CH_2C**H$_2$**CH_2, OCHCHCH**H**, OCHCH_2CHC**H$_2$**CH_2), 0.90 (d, J = 7.0, 6H, C**H$_3$**$CHCH_3$), 0.85 (d, J = 7.0, 6H, CH_3CHC**H$_3$**), 0.77 (d, J = 6.4, 6H, C**H$_3$**$CH(CH_2)CH_2$); $[\alpha]_D^{25}$ = +31.0° (c = 1.0, $CHCl_3$; lit.[8] +33.8°).

(1*S*,2*S*)-1,2-Bis(hydroxymethyl)cyclopentane ((1*S*,2*S*)-11).[10] To lithium aluminum hydride (4.8 g, 120 mmol) suspended in dry ether (300 mL) was added dropwise (1*S*,2*S*)-**10** (24.7 g, 57 mmol) in dry ether (75 mL) for 1 h under argon. After being stirred for 10 h at ambient temperature, the reaction mixture was cooled to 0 °C and water (4.8 mL) was added carefully, followed by the addition of 15% aqueous NaOH (4.8 mL) and water (14.4 mL). The reaction mixture was then heated to reflux for 5 min and cooled to room temperature. The white precipitates were filtered off, and the filtrate was concentrated in vacuo. Flash chromatography (EM Reagents silica gel 60, 230−400 mesh, hexane/EtOAc = 3/1) yielded 6.9 g (93%) of **11** as colorless oil.

(1*S*,2*S*)-1,2-bis(hydroxymethyl)cyclopentane ((1*S*,2*S*)-**11**): ^1H NMR (300 MHz, C_6D_6) δ 5.12 (s, 2H, O**H**), 3.71 (d, J = 10.0, 2H, CHC**H**HOH), 3.30 (dd, J = 10.0, 10.0, 2H, CHCH**H**OH), 1.83−1.69 (m, 2H, C**H**CH_2OH), 1.62−1.49 (m, 2H, CH_2C**H**HCH), 1.45−1.39 (m, 2H, CH_2CH**H**CH), 1.12−0.97 (m, 2H, CH_2C**H$_2$**CH_2).

(1*R*,2*R*)-1,2-Bis(hydroxymethyl)cyclopentane ((1*R*,2*R*).[10] (1*R*,2*R*)-**11** was synthesized by the same procedure as above, except (1*R*,2*R*)-**10** was used instead of (1*S*,2*S*)-**10**. Yield: 93%.

(1*S*,2*S*)-1,2-Bis((tosyloxy)methyl)cyclopentane ((1*S*,2*S*)-17). To (1*S*,2*S*)-**11** (6.9 g, 53 mmol) in pyridine (150 mL) was added tosyl chloride (27.3 g, 143 mmol) portionwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 18 h. The reaction mixture was opened to water (300 mL) and extracted by AcOEt (100 mL × 3). The extracts were combined, washed with saturated aqueous $CuSO_4$, dried over $MgSO_4$, and concentrated in vacuo. The solid thus obtained (21 g, 90%) was virtually pure according to ^1H and ^{13}C NMR spectra.

(1*S*,2*S*)-1,2-Bis((tosyloxy)methyl)cyclopentane ((1*S*,2*S*)-**17**): IR (thin film) 2956.3, 2872.8, 1597.9, 1452.6, 1359.9, 1173.8, 1097.1, 962, 816, 666 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.79 (d, J = 8.3, 4H, aromatic), 6.78 (d, J = 8.3, 4H, aromatic), 3.78−3.67 (m, 4H, CHC**H$_2$**O), 1.85 (s, 6H, C**H$_3$**C), 1.61−1.50 (m, 2H, C**H**CH_2O), 1.34−1.22 (m, 2H, CH_2C**H**HCH), 1.13−1.04 (m, 2H, CH_2CH**H**CH), 1.00−0.89 (m, 2H, CH_2C**H$_2$**CH_2); ^{13}C NMR (75 MHz, C_6D_6) δ 144.5, 134.0, 130.0, 128.1, 72.7, 41.4, 29.2, 24.3, 21.2; mass spectrum (EI) m/z (relative intensity) 438 (M^+, 5), 267 (3), 173 (6), 155 (24), 111 (15), 95 (100), 81 (22); HRMS m/z calcd for $C_{21}H_{26}O_6S_2$ (M^+), 438.1171, found 438.1149.

(1*R*,2*R*)-1,2-Bis((tosyloxy)methyl)cyclopentane ((1*R*,2*R*)-17). (1*R*,2*R*)-**18** was synthesized by the same procedure as above, except (1*R*,2*R*)-**11** was used instead of (1*S*,2*S*)-**11**. Yield: 80%.

(1*S*,2*S*)-1,2-Bis(iodomethyl)cyclopentane ((1*S*,2*S*)-12). To (1*S*,2*S*)-**17** (19.9 g, 46 mmol) in acetone (200 mL) was added NaI (40.9 g, 273 mmol), and the mixture was heated to reflux.

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(24) Gorman, C. B.; Ginsburg, E. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 1397−1409.

The reaction mixture was stirred at the same temperature for 18 h and then cooled to room temperature. The reaction mixture was opened to water (500 mL) and extracted by *n*-hexane (150 mL × 3). *n*-Hexane extracts were washed with saturated aqueous $Na_2S_2O_3$ solution, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography (EM reagents silica gel 60, 230−400 mesh, hexane) yielded 14.2 g (89%) of **12** as a light orange oil.

(1*S*,2*S*)-1,2-bis(iodomethyl)cyclopentane ((1*S*,2*S*)-**12**): IR (neat) 2949.6, 2863.6, 1446.9, 1422.8, 1259.3, 1184.7 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 2.74 (dd, J = 10.0, 3.5, 2H, CHC**H**HI), 2.55 (dd, J = 10.0, 6.9, 2H, CHCH**H**I), 1.62−1.49 (m, 2H, C**H**CH_2I), 1.31−1.17 (m, 4H, C**H**$_2$$CH_2$C**H**$_2$), 1.17−1.04 (m, 2H, CH_2C**H**$_2$$CH_2$); ^{13}C NMR (75 MHz, C_6D_6) δ 47.7, 34.3, 23.2, 12.2; mass spectrum (EI) *m*/*z* (relative intensity): 350 (M^+, 11), 223 (24), 169 (10), 155 (7), 128 (3), 95 (100), 80 (7), 67 (53), 55 (54); HRMS *m*/*z* calcd for $C_7H_{12}I_2$ (M^+) 349.9029, found 349.9041.

(1*R*,2*R*)-1,2-Bis(iodomethyl)cyclopentane ((1*R*,2*R*)-12). (1*R*,2*R*)-**12** was synthesized by the same procedure as above, except (1*R*,2*R*)-**18** was used instead of (1*S*,2*S*)-**18**. Yield: 78%.

(1*R*,2*R*)-1,2-Bis(2-hydroxy-2,2-bis(trifluoromethyl)ethyl)cyclopentane ((*R*,*R*)-TBEC-H$_2$, (1*R*,2*R*)-1). To the diiodide (1*S*,2*S*)-**12** (8.0 g, 23 mmol) in dry ether (150 mL) was added dropwise a solution of *tert*-butyllithium in pentane (1.7 M, 54 mL, 92 mmol) at −78 °C under argon, and the mixture was stirred for 5 min. To the stirred reaction mixture, excess hexafluoroacetone was introduced via a long hypodermic needle which penetrated the liquid surface. The reaction mixture turned pale yellow and was then warmed to room temperature. The reaction mixture was opened to 1 M aqueous hydrochloric acid solution (300 mL) and extracted by ether (150 mL × 3). Ether extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (EM Reagents silica gel 60, 230−400 mesh, hexane) yielded 7.3 g (74%) of **1** as a colorless oil. The enantiomeric excess (ee) was determined as 95% by GLC with a CHIRASIL-VAL (25 m × 0.25 mm) chiral column by Alltech Associates, Inc. (at column temperature 90 °C, the retention time for (1*R*,2*R*)-**1** was 94 min).

(1*R*,2*R*)-1,2-bis(2-hydroxy-2,2-bis(trifluoromethyl)ethyl)cyclopentane ((*R*,*R*)-TBEC-H$_2$, (1*R*,2*R*)-**1**): IR (neat) 3418.1 (br), 2963.6, 2878.1, 1622.4, 1454.8, 1209.4, 1147.6, 1030.5, 995.1, 962.4, 724.5 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 2.59 (s, 2H, O**H**), 1.95 (d, J = 13.6, 2H, CHC**H**HC$(CF_3)_2$OH), 1.72−1.60 (m, 2H, C**H**CH_2C$(CF_3)_2$OH), 1.54 (dd, J = 13.6, 7.4, 2H, CHCH**H**C$(CF_3)_2$OH), 1.53−1.44 (m, 2H, CH_2C**H**HCH), 1.24 (m, 2H, CH_2CH**H**CH), 0.91−0.79 (m, 2H, CH_2C**H**$_2$$CH_2$); ^{13}C NMR (75 MHz, C_6D_6) δ 123.6 (q, J_{CF} = 288.1), 76.8 (sept, J_{CCF} = 23.0), 40.8, 34.9, 33.3, 24.2; $[\alpha]_D^{25}$ = +26.3° (c = 0.9, $CHCl_3$); mass spectrum (EI) *m*/*z* (relative intensity) 430 (M^+, 2), 392 (10), 373 (3), 248 (7), 235 (7), 222 (10), 207 (13), 135 (5), 73 (20), 55 (100); HRMS *m*/*z* calcd for $C_{13}H_{14}O_2F_{12}$ (M^+) 430.0802, found 430.0781.

(1*S*,2*S*)-1,2-Bis(2-hydroxy-2,2-bis(trifluoromethyl)ethyl)cyclopentane ((*S*,*S*)-TBEC-H$_2$), (1*S*,2*S*)-1). (1*S*,2*S*)-**1** was synthesized in the same procedure as above, except (1*R*,2*R*)-**12** was used instead of (1*S*,2*S*)-**12**. Yield: 63%. The ee was determined as 90% by GLC with a CHIRASIL-VAL (25 m × 0.25 mm) chiral column by Alltech Associates, Inc. (at column temperature 90 °C, the retention time for (1*S*,2*S*)-**1** was 90 min).

(1*S*,2*S*)-1,2-bis(2-hydroxy-2,2-bis(trifluoromethyl)ethyl)cyclopentane ((*S*,*S*)-TBEC-H$_2$, (1*S*,2*S*)-**1**): $[\alpha]_D^{25}$ = −21.6° (c = 1.8, $CHCl_3$).

Preparation of the Dilithium Alkoxide Derivative of (*R*,*R*)-TBEC-H$_2$. A solution of *n*-butyllithium in hexane (1.6 M, 13.2 mL, 21 mmol) was added dropwise to a stirred *n*-hexane (75 mL) solution of (1*R*,2*R*)-**1** (4.52 g, 10.5 mmol) at 0 °C under argon. The reaction mixture was stirred for 3 h, and the solvent was removed to yield 4.31 g (93%) of a white solid. The dilithium alkoxide was pure as shown by its ^1H NMR spectra. No residual *n*-BuLi nor free −OH was observed.

(*R*,*R*)-TBEC-Li$_2$ (**13**): ^1H NMR (300 MHz, THF-d_8) δ 2.15−1.92 (m, 2H, CHC**H**HC$(CF_3)_2$OLi), 1.90−1.62 (m, 6H, CHCH**H**C$(CF_3)_2$OLi, C**H**CH_2C$(CF_3)_2$OLi, CH_2CH**H**CH), 1.52 (m, 2H, CH_2C**H**HCH), 1.38−1.20 (m, 2H, CH_2C**H**$_2$$CH_2$).

(*R*,*R*)-Mo(CHCMe$_2$Ph)(NAr)TBEC (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$; 3). Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$dme (**2**; Ar = 2,6-(*i*-Pr)$_2$$C_6H_3$)[13] (871 mg, 1.1 mmol) was suspended in dry *n*-pentane (50 mL). To this heterogeneous mixture was added (*R*,*R*)-TBEC-Li$_2$ (486 mg, 1.1 mmol) in dry *n*-pentane (20 mL) at −40 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The lithium triflate precipitated was filtered off through Celite, and the filtrate was evaporated to dryness in vacuo to give an orange-yellow solid (780 mg, 85%). The solid thus obtained was virtually pure according to ^1H and ^{13}C NMR spectra and elemental analysis.

(*R*,*R*)-Mo(CHCMe$_2$Ph)(NAr)TBEC (Ar = 2,6-(*i*-Pr)$_2$$C_6H_3$); **3**): ^1H NMR (300 MHz, C_6D_6) δ 12.51 (s, 1H, C**H**CMe$_2$Ph), 7.27 (d, J = 8.2, 2H, aromatic), 7.13 (dd, J = 8.1, 8.1, 2H, aromatic), 7.00−6.95 (m, 4H, aromatic), 4.10 (septet, J = 6.8, 2H, C**H**CMe$_2$), 2.23−1.88 (m, 6H, CHC**H**$_2$C$(CF_3)_2$O, C**H**CH_2C$(CF_3)_2$O), 1.69 (s, 3H, CHC**Me**MePh), 1.67 (s, 3H, CHCMe**Me**Ph), 1.66−1.10 (m, 4H, C**H**$_2$$CH_2$C**H**$_2$), 1.25 (d, J = 6.8, 6H, C**H**$_3$CHCH$_3$), 1.24 (d, J = 6.8, 6H, CH_3CHC**H**$_3$), 1.00−0.80 (m, 2H, CH_2C**H**$_2$$CH_2$); ^{13}C NMR (75 MHz, C_6D_6) δ 291.2 (**C**HCMe$_2$Ph), 154.7, 148.6, 147.6, 129.4, 128.5, 126.6, 126.2, 123.4 (aromatic), 85.0 (sept, J_{CCF} = 27.6, CH_2**C**$(CF_3)_2$O), 83.1 (sept, J_{CCF} = 27.6, CH_2**C**$(CF_3)_2$O), 56.4 (CH**C**Me$_2$Ph), 43.5, 41.0 (CH**C**H_2C$(CF_3)_2$), 39.2, 39.0 (CH_2C**H**C**H**CH_2), 33.6, 33.2 (**C**$H_2$$CH_2$C**H**$_2$), 31.2 (CHC**Me**MePh), 31.0 (CHCMe**Me**Ph), 29.3 (**C**HMe$_2$), 28.7 (CH**Me**Me), 23.8 (CHMe**Me**), 23.4 (CH_2C**H**$_2$$CH_2$) (trifluoromethyl groups, δ 124, were not assigned); ^{19}F NMR (470 MHz, C_6D_6) δ −77.64, −77.80, −79.87, −82.50 (four nonequivalent trifluoromethyl groups); molecular weight[22] calcd for $C_{35}H_{41}O_2NF_{12}Mo$ 831.64, found 811. Anal. Calcd for $C_{35}H_{41}O_2NF_{12}Mo$: C, 50.55; H, 4.97; N, 1.68. Found: C, 51.19; H, 5.00; N, 1.80.

(*R*,*R*)-W(CHCHCPh$_2$)(O)(TBEC)[P(OMe)$_3$] (14). To a yellow solution of W(η^2-diphenylcyclopropene)Cl$_2$(O)[P(OMe)$_3$]$_2$ (0.75 g, 1.05 mmol) in benzene (20 mL) was added (*R*,*R*)-TBEC-Li$_2$ (0.47 g, 1.05 mmol) in benzene (10 mL) via cannula. The solution was stirred for 12 h at room temperature and then 2 h at 65 °C. The resulting yellow-brown solution was filtered to remove the LiCl. The filtrate was concentrated and transferred over pentane at −78 °C, yielding a yellow powder that was separated by filtration, dried under vacuum, and characterized as **14** (0.8 g, 80%). Two isomers were observed in a 4:1 ratio, and the diagnostic NMR signals are as follows. ^1H NMR (500 MHz, C_6D_6): major isomer (anti rotamer), δ 12.65 (dd, J_{HH} = 14.7, J_{HP} = 6.3, H$_\alpha$), 8.95 (dd, J_{HH} = 14.7, J_{HP} = 2.1, H$_\beta$); major isomer (syn rotamer), δ 11.8 (dd, J_{HH} = 11.3, J_{HP} = 4.6, H$_\alpha$), 9.14 (dd, J_{HH} = 11.3, J_{HP} = 1.5, H$_\beta$); minor isomer (anti rotamer), δ 12.57 (dd, J_{HH} = 14.5, J_{HP} = 6.8, H$_\alpha$), 8.88 (dd, J_{HH} = 14.5, H$_\beta$); minor isomer (syn rotamer), δ 11.76 (dd, J_{HH} = 11.4, J_{HP} = 4.1, H$_\alpha$), 9.10 (dd, partially overlapped, H$_\beta$). ^{13}C NMR (75 MHz, C_6D_6): major isomer, δ 268.3 (d, J_{CP} = 21.0, C$_\alpha$). ^{31}P NMR (203 MHz, C_6D_6): major isomer, δ 146.8 (P(OMe)$_3$). ^{19}F NMR (470 MHz, C_6D_6): major isomer, δ −71.6, −73.58, −73.77, −77.75 (four nonequivalent trifluoromethyl groups). Anal. Calcd for $C_{31}H_{33}F_{12}O_6PW$: C, 39.42; H, 3.52. Found: C, 39.51; H, 3.65.

(*R*,*R*)-W(CHCHCOCH$_2$CH$_2$CH$_2$O)(O)(TBEC)[P(OMe)$_3$] (15). To a red solution of W(CHCHCOCH$_2$CH$_2$CH$_2$O)(O)Cl$_2$[P(OMe)$_3$] (0.65 g, 1.3 mmol) in benzene (20 mL) was added (*R*,*R*)-TBEC-Li$_2$ (0.57 g, 1.3 mmol) in benzene (10 mL) via cannula. A procedure similar to that above afforded **15** as a yellow powder (0.94 g, 85%). Two isomers are observed, each of which has syn and anti rotamers, and the diagnostic NMR signals are as follows: ^1H NMR (500 MHz, C_6D_6): major isomer (anti rotamer), δ 12.69 (dd, J_{HH} = 14.0, J_{HP} = 4.9, H$_\alpha$), 6.69 (dd, J_{HH} = 14.0, J_{HP} = 1.2, H$_\beta$); major isomer (syn rotamer), δ 12.06 (dd, J_{HH} = 11.5, J_{HP} = 3.8, H$_\alpha$), 6.91 (dd,

$J_{HH} = 11.5$, $J_{HP} = 1.2$, H_β); minor isomer (anti rotamer), δ 12.13 (dd, $J_{HH} = 14.1$, $J_{HP} = 5.1$ H_α) (signal corresponding to H_β is overlapped); minor isomer (syn rotamer), δ 11.91 (dd, $J_{HH} = 11.4$, $J_{HP} = 3.8$, H_α), 6.40 (dd, $J_{HH} = 11.4$, H_β). ^{13}C NMR (75 MHz, C_6D_6): major isomer, δ 258.1 (d, $J_{CP} = 20.5$, C_α), 152.7 (d, $J_{CP} = 5.4$, C_γ), 96.6 (d, $J_{CP} = 6.2$, C_β), 64.9 (O**C**$H_2CH_2CH_2O-$), 64.5 ($-OCH_2CH_2$**C**H_2O-). ^{31}P NMR (203 MHz, C_6D_6): major isomer, δ 146.8. ^{19}F NMR (470 MHz, C_6D_6): major isomer, δ −72.4, −73.7, −73.8, −77.9 (four nonequivalent trifluoromethyl groups). Anal. Calcd for ($C_{22}H_{29}F_{12}O_8PW$): C, 30.58; H, 3.38. Found: C, 30.86; H, 3.41.

***(R,R)*-W(CHCHCPh$_2$)(NAr)(TBEC)[P(OMe)$_3$] (16).** To a yellow-brown solution of W(CHCHCPh$_2$)Cl$_2$(NAr)[P(OMe)$_3$]$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) (0.83 g, 0.95 mmol) in benzene (20 mL) was added (*R,R*)-TBEC-Li$_2$ (0.42 g, 0.95 mmol) in benzene (10 mL) via cannula. The solution was stirred for 12 h at room temperature. The resulting yellow-brown suspension was filtered to remove the LiCl, and the dark yellow solution was concentrated under vacuum and transferred over pentane at −78 °C, yielding a dark yellow powder that was separated by filtration, dried under vacuum, and characterized as **16** (0.79 g, 75%). Only one set of syn and anti rotamers was observed by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6): anti rotamer, δ 12.51 (dd, $J_{HH} = 14.7$, $J_{HP} = 5.4$, H_α), 9.10 (dd, $J_{HH} = 14.7$, $J_{HP} = 2.0$ Hz, H_β); syn rotamer, δ 11.98 (dd, $J_{HH} = 11.4$, $J_{HP} = 5.1$ H_α), 9.0 (dd, $J_{HH} = 11.4$, $J_{HP} = 2.4$, H_β). ^{31}P NMR (203 MHz, C_6D_6): anti rotamer, δ 147.2; syn rotamer, δ 147.5. Anal. Calcd for $C_{43}H_{50}F_{12}NO_5PW$: C, 46.80; H, 4.56. Found: C, 47.03; H, 4.68.

Polymerization of Cyclooctadiene Catalyzed by 3. Cyclooctadiene (100 mg, 0.92 mmol) was dissolved in dry benzene (0.6 mL). (*R,R*)-**3** (7.6 mg, 0.0092 mmol) in dry benzene (200 μL) was added to the vigorously stirred monomer solution at room temperature. The reaction mixture was stirred for 10 min. The reaction was quenched by addition of methanol. The polymer was dissolved in a minimal amount of dichloromethane, passed through a short silica gel column, and dried in vacuo (90 mg, 90%). The cis/trans ratio was determined by ^{13}C NMR analysis of the polymer (cis/trans = 14/86).

Ring-Closing Metathesis of 4-(*tert*-Butyldimethylsiloxy)-1,6-heptadiene. (*R,R*)-**3** (8.3 mg, 0.01 mmol) was dissolved in dry benzene (0.5 mL). 4-(*tert*-Butyldimethylsiloxy)-1,6-heptadiene (45.3 mg, 0.20 mmol) in dry benzene (0.5 mL) was added to the catalyst solution. The reaction mixture was stirred at ambient temperature for 5 min. The reaction was quenched by the addition of MeOH (0.2 mL), and the solution was concentrated in vacuo. Flash chromatography (EM Reagents silica gel 60, 230−400 mesh, hexane) yielded 34 mg (85%) of 4-(*tert*-butyldimethylsiloxy)-1-cyclopentene as a colorless oil (identical with the authentic sample).[3c]

Polymerization of *sec*-Butylcyclooctatetraene. To *sec*-butylcyclooctatetraene (80 mg, 0.50 mmol) was added (*R,R*)-**14** or (*R,R*)-**15** (0.005 mmol) in dry toluene (200 μL) to the vigorously stirred monomer at room temperature. The reaction mixture was stirred for 18 h. The reaction was quenched by addition of benzaldehyde (10 μL). The polymer was dissolved in a minimal amount of dichloromethane, passed through a short silica gel column, and dried in vacuo and analyzed by ^{1}H NMR according to the literature.[24]

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