Practical Catalyst for Cyclic Metathesis. Synthesis of Functional and/or Enantiopure Cycloalkenes

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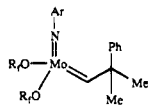
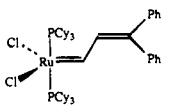
Abstract: The oxo−tungsten complex *trans*-$WOCl_2(OAr)_2$ (Ar = 2,6-dibromophenyl) is prepared by reaction of $WOCl_4$ with 2 equiv of 2,6-dibromophenol. A variety of nonconjugated dienes are cleanly cyclized to the corresponding cycloalkenes using 2 mol % of this catalyst in combination with 4 mol % of tetraethyllead. All three components of the catalyst system are commercially available. The catalytic reactions are typically complete in 1 h at 90 °C and allow the synthesis of chiral cycloalkenes with little or no loss in optical activity. For example, (*R*)- and (*S*)-citronellene have been cyclized to the corresponding (*R*)- or (*S*)-3-methylcyclopentenes in 97% enantiomeric excess. The cyclization is compatible with a variety of functional groups including some ester, amide, and ether derivatives. Tri- (but not tetra-) substituted cycloalkenes could be prepared using this catalyst.

The discovery of efficient catalysts for the cyclic metathesis of nonconjugated dienes stands as one of the premier developments in the field of organic annulations during the past decade. Of particular significance are the molybdenum catalyst **1** (R_f = hexafluoro-*tert*-butyl) reported by Schrock and co-workers[1] and ruthenium catalyst **2** developed by Grubbs and co-workers.[2]

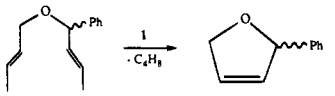


1

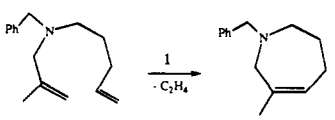


2

These catalysts are highly active and long-lived; unlike earlier olefin metathesis catalysts, they do not require Lewis acidic promoters and are compatible with even sensitive functional groups in the substrate diene. Using catalyst **1**, Fu and Grubbs have demonstrated the cyclization of allylic ethers to cyclic ethers[3] as exemplified by eq 1, as well as the cyclization of unsaturated amines to the corresponding five-, six-, and seven-membered azacycles[4] (e.g., eq 2). Already several exciting applications of cyclic metathesis to synthetic organic chemistry have appeared.[5]



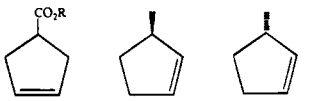
(1)



(2)

From an industrial perspective, cyclic methathesis has a number of potentially attractive features for the large-scale manufacture of cycloalkenes. In particular, this technology utilizes no additional reagents beyond the catalyst, which is often present in 1% or less mol equiv relative to the substrate diene. Cyclizations typically take place under mild conditions, require little or no solvent, and produce only a volatile alkene such as ethylene as side product. However, a significant impediment for many commercial applications of this technology at present is the cost of the catalyst. Indeed, the relative inaccessibility of especially catalyst **1** is a problem for even laboratory-scale applications of this chemistry. Neither **1** nor **2** is at present commercially available; both are the product of multistep synthetic procedures.

Our efforts to develop a practical catalyst for cyclic metathesis grew from local interest in two particular organic building blocks, namely alkyl 3-cyclopentenecarboxylates **3** and enantiopure (*R*)- and (*S*)-3-methylcyclopentenes **4a,b**. Cycloalkenes



3 have already been demonstrated to be broadly useful intermediates for laboratory synthesis,[6,7] yet large-scale manu-

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1995.

(1) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886; Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287−2289. The nonfluorinated analogue of **1** in which R_f is replaced by *tert*-butyl is commercially available from Strem Chemical Co. but does not appear suitable for cyclic metathesis reactions.

(2) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859.

(3) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426−5427.

(4) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324−7325.

(5) Borer, B. C.; Deerenberg, S.; Bieraeugel, H.; Pandit, U. K. *Tetrahedron Lett.* **1994**, *35*, 3191−3194; Martin, S. F.; Liao, Y.; Chen, H.-J.; Paetzel, M.; Ramser, M. N. *Tetrahedron Lett.* **1994**, *35*, 6005−6008; Heiko, J.; Blechert, S. *Tetrahedron Lett.* **1993**, *34*, 3731−3732.

(6) Methyl ester **3a** has been widely utilized in the synthesis of carbocyclic nucleosides including carbovir and aristeromycin: Hodgson, D. M.; Witherington, J.; Moloney, B. A. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3373−3378. Agrofoglio, L.; Condom, R.; Guedj, R.; Challand, S. R.; Selway, J. *Nucleosides Nucleotides* **1994**, *13*, 1147−1160. Jung, M. E.; Rhee, H. *Tetrahedron Lett.* **1993**, *34*, 4449−4452. Norman, M. H.; Almond, M. R.; Reitter, B. E.; Rahim, S. G. *Synth. Commun.* **1992**, *22*, 3197−3204. Hutchison, A.; Grim, M.; Chen, J. *J. Heterocyclic Chem.* **1989**, *26*, 451−452.

(7) Examples of natural products that have been synthesized using **3a** as starting material include (a) (±)-isolobophytollide and (±)-crassin: McMurry, J. E.; Dushin, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6942−6949. (b) (±)-sterpuric acid: Paquette, L. A.; Lin, H. S.; Gunn, B. P.; Coghlan, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 5017−5020. (c) (+)-hirsutic acid: Greene, A. E.; Luche, M. J.; Serra, M. A. *J. Org. Chem.* **1985**, *50*, 3957−3962.

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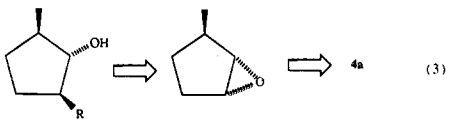
facture of such compounds has been precluded by the requirement for treacherous reagents[8] (lithium hydride, *cis*-1,4-dichloro-2-butene). Corey[9] has pointed out the great potential of **4** as chiral building blocks as exemplified by the retrosynthetic scheme in eq 3. However, attempts[10] to prepare **4** in enantiopure form using conventional technology have thus far been unsuccessful.[11]

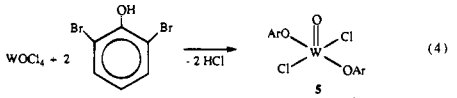


(3)

In this paper we describe a simple tungsten catalyst system which allows the efficient synthesis of many synthetically interesting cycloalkenes including **3b** and **4a,b** by cyclic metathesis of the corresponding dienes. All three components of the catalyst system are commercially available. Although the catalyst lacks the exquisite functional group compatibility which characterizes catalysts **1** and **2**, it is shown to be compatible with a range of functionality including ester, trifluoroacetamide, and ether substituents. The catalyst described in this paper builds on the studies of Bell at Hercules, Inc., who demonstrated that related $O{=}WCl_2(OAr)_2$ derivatives are excellent catalysts for ring-opening metathesis polymerizations.[12a] The important contributions of Basset et al., who demonstrated the high activity of W phenoxide catalysts in metathesis reactions of acyclic functionalized olefins, are also acknowledged.[12b-e]

Results

Catalyst Preparation and Characterization. The catalyst used in these studies was prepared by treatment of tungsten(VI) oxychloride ($WOCl_4$) with 2,6-dibromophenol in refluxing toluene (eq 4). Related halide displacement reactions of $WOCl_4$



(4)

have been known for many years.[13] Simple distillation of the solvent and coproduct HCl affords a brick red solid in essentially quantitative yield which is substantially pure **5**. This crude product can be used as a catalyst for cyclic metathesis reactions in cases where the substrate is not sensitive to traces of protic acid impurities (see below). However, most of the work reported below makes use of recrystallized **5**.

We routinely crystallize **5** by dissolving the crude complex in a minimum amount of dichloromethane, adding a layer of hexanes, and cooling this two-phase system in a freezer to −15 °C (see the Experimental Section for details). The ensuing crystallization is surprisingly slow, and 7−10 days are required to achieve an optimal recovery (typically 65%) of **5**. The material obtained in this way is an analytically pure green-black crystalline solid.

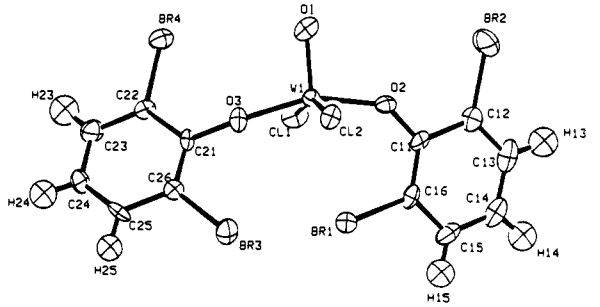


Figure 1. ORTEP representation of complex **5** showing the numbering scheme. Additional bond distances (Å) and angles (deg): W−Cl(1) 2.330(3), W−Cl(2) 2.316(3), O(2)−C(11) 1.362(14), O(3)−C(21) 1.339(12); Cl(1)−W−O(1) 101.4(3), Cl(2)−W−O(1) 100.6(3), O(1)−W−O(2) 99.0(3), O(1)−W−O(3) 102.4(4). For complete structural data see the supporting information.

An X-ray crystallographic study on **5** reveals some interesting structural features. An ORTEP diagram of the complex is shown in Figure 1. The complex most closely conforms to a square pyramidal coordination geometry with the oxo ligand in the apical position. In this regard it resembles the structure of the corresponding complex bearing 2,6-diisopropylphenoxide ligands which was structurally characterized by Bell.[12] Moreover, the W−O(phenoxy) distances in our dibromo derivative at 1.859(8) and 1.854(7) Å are very close to those reported for the diisopropyl analogue, 1.832(6) Å. However, in the case of complex **5**, one of the W−O−C bond angles is more or less linear at 165(1)° while the other is significantly bent at 139.2(8)°. In contrast, the W−O−C angles in the diisopropyl analog[12] are 154.0(6)°. The apparent reason for this distortion is to allow a (presumably weak) bonding interaction between the tungsten atom and bromine atom Br1.

The tungsten−bromine distance for Br1 in **5** is 3.120(1) Å. It is difficult to assess the extent of the bonding interaction in the absence of closely related structures in the literature. It can be noted that the W−O distance for the THF oxygen in $O{=}W(O^tBu)_4(THF)$ is 2.38(3) Å.[14] Since the van der Waals radius for bromine is 0.55 Å greater than that of oxygen (1.95 vs 1.40 Å), this would suggest a W−Br distance of ca. 2.93 Å for a tightly bound bromide donor. However, the presence of this donor ligand seems to have little effect on the tungsten−oxo multiple bond. The tungsten−oxo distance in **5** is 1.646(8) Å, at the short end of the range for tungsten complexes bearing a single oxo ligand.[15]

In order to function as a metathesis catalyst, **5** must be activated with 2 mol equiv of tetraethyllead.[16] The role of this organometallic "promoter" is presumed to be the replacement of the two chloride substituents in **5** with ethyl groups, ultimately leading to a catalytically active ethylidene complex (see below). To date, attempts to replace the tetraethyllead with other main group organometallic compounds have been unsuccessful.

(8) Depres, J.-P.; Greene, A. E. *J. Org. Chem.* **1984**, *49*, 928−931.

(9) Equation 3 is taken from Corey, E. J.; Cheng, X.-M. *The Logic of Chemical Synthesis*; Wiley: New York, 1989; p 75.

(10) Compound **4b** of 4.5% enantiomeric excess has been prepared via asymmetric alkylation: Consiglio, G.; Morandini, F.; Piccolo, O. *Helv. Chim. Acta* **1980**, *63*, 987−989. A kinetic resolution strategy using diisopinocampheylborane afforded **4b** with $[\alpha]^{26}_D$ −34.6. This corresponds to 20% ee. Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1962**, *84*, 4341−4342.

(11) During the preparation of this manuscript, we learned of an unpublished study in which cyclic metathesis employing catalyst **1** has been applied to the synthesis of scalemic **4**: Sita, L. R. Personal communication. We thank Professor Sita for sharing these results with us.

(12) (a) Bell, A. *J. Mol. Catal.* **1992**, *76*, 165−180. (b) Quignard, F.; Leconte, M.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1816−1817. (c) Quignard, F.; Leconte, M.; Basset, J.-M. *J. Mol. Catal.* **1986**, *36*, 13−29. (d) Couturier, J.-L.; Paillet, C.; Leconte, M.; Basset, J.-M.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 628−631. (e) Couturier, J.-L.; Tanaka, K.; Leconte, M.; Basset, J.-M.; Olivier, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 112−115.

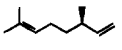
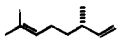
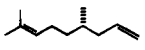
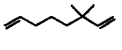
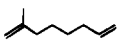
(13) Funk, H.; Mohaupt, G. *Z. Anorg. Allg. Chem.* **1962**, *315*, 204−212.

(14) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *J. Organomet. Chem.* **1985**, *296*, 55−68. For a review of the coordination chemistry of halocarbons, see: Kulawiec, R. J.; Crabtree, R. W. *Coord. Chem. Rev.* **1990**, *99*, 89−115.

(15) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; pp 172−173.

(16) The use of 1 mol equiv of $PbEt_4$ per tungsten also afforded a reactive catalyst. However, rates observed under these conditions were roughly one-half of those obtained with 2 equiv, suggesting that one-half of the tungsten complex had been activated.

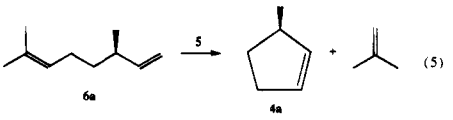
Table 1. Cyclization of Nonfunctional Dienes with Catalyst **5**[a]

Diene	Structure No.	Product	Structure No.	Yield[b] (%)	e.e. (%)[c]
	6a		4a	68	97
	6b		4b	70	97
	7		10	64	99
	8		11	87	--
	9		12	84	--

[a] Conditions: 2 mol % catalyst **5**, 1,2,4-trichlorobenzene, 90 °C, 1 h. [b] Isolated yield; in all cases GC yields were essentially quantitative. [c] Determined by chiral GC, see the Experimental Section.

Cyclization of Nonfunctional Dienes. Results for the cyclization of a series of simple nonconjugated dienes are summarized in Table 1. The volatile nature of these products favors the use of a high-boiling solvent to facilitate recovery of the cycloalkene products by distillation. 1,2,4-Trichlorobenzene proved particularly suitable as a reaction medium.

The cyclization of (*R*)-citronellene (**6a**) to (*R*)-3-methylcyclopentene is illustrated in eq 5. A solution of **6a** in 1,2,4-



(5)

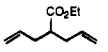
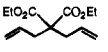
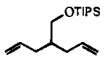
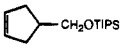
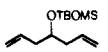
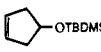
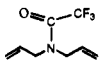
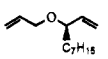
trichlorobenzene containing 2 mol % of catalyst **5** and 4 mol % of tetraethyllead was heated in a 90 °C oil bath for 1 h. At the end of this period, crude **4a** could be distilled from the reaction mixture. Interestingly, the product recovered in this way still retained a significant amount of dissolved isobutylene coproduct. Consequently, the crude product from eq 5 was heated at reflux under air briefly and redistilled to afford analytically pure **4a**, $[\alpha]^{25}_D$ +167.4 (*c* 5.23, chloroform), lit.[17] $[\alpha]^{25}_D$ +174.5 (neat) in 70% isolated yield. In similar fashion, the epimeric (*S*)-citronellene (**6b**) could be cyclized to (*S*)-3-methylcyclopentene (**4b**).

Chiral GLC analysis of the **4a,b** prepared by via cyclic metathesis (after conversion to a mixture of cis and trans epoxides) indicates that the products are formed in 97% enantiomeric excess. Although the enantiomeric excess of the citronellene starting material is not known with certainty, the results for the analogous cyclization of **18** (see below) suggest that the cyclization proceeds without significant epimerization at the allylic position.

Other nonfunctional substrates were examined in Table 1 to probe the scope of the cyclization reaction. For example, cyclization of readily available **7** afforded (*S*)-(−)-4-methylcyclohexene in 99% ee and illustrates the extension of eq 5 to an enantiopure six-membered cycloalkene. Remarkably, sterically encumbered **8** bearing a quaternary center adjacent to the C=C double bond readily cyclized to **11**. We also examined a single case where the product cycloalkene contains a trisubstituted double bond. Thus, cyclization of **9** proceeded cleanly to give 1-methylcyclohexene (**12**).

(17) Schurig, V.; Gil-Av, E. *Israel J. Chem.* **1976/77**, *15*, 96−98.

Table 2. Cyclization of Functional Dienes with Catalyst **5**[a]

Diene	Structure No.	Product	Structure No.	Yield (%)[b]
	13		3b	74
	14		19	86
	15		20	91
	16		21	81
	17		22	83
	18		23	58[c,d]

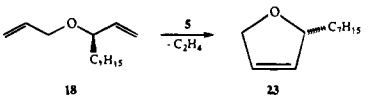
[a] Conditions: 2 mol % catalyst **5**, toluene, 90 °C, 1 h. [b] Isolated yield after distillation or flash chromatography. [c] Run with 5% catalyst **5** and hindered base; see text. [d] Product obtained in 96% ee by chiral GC.

Attempts to further extend these results to the cyclization of substrates such as 1,9-decadiene, 1,13-tetradecadiene, and diallyldimethylsilane instead led to polymeric materials with only trace amounts of the corresponding cycloalkenes being formed. This is consistent with basic thermodynamic considerations; similar observations have been made using conventional organometallic catalysts.[18]

Cyclization of Functional Dienes. The cyclization of a series of 1,6-dienes bearing a variety of functional groups is summarized in Table 2. The higher boiling points of these products as compared to those in Table 1 dictated that these cyclizations should be run in a lower boiling solvent which was removed by distillation at the completion of the reaction. Toluene proved suitable for this purpose.

The substrates in Table 2 include examples of the ester, ether, and amide functional groups. For all dienes except **18**, use of 2% catalyst **5** was sufficient to achieve essentially complete conversion to the corresponding cycloalkene. Gas chromatographic analysis suggests that the selectivity of these cyclizations is also high. For the cyclization of diethyl diallylmalonate (**14**), GLC analysis after 15 min indicated the presence of the cyclopentene **19** (99.8%) and **14** (0.2%) as the only volatile products (0.5 M **14** in toluene, 90 °C).

Substrate **18** presented a special challenge due to the lability of the diallyl ether structure in the presence of traces of acidic impurities. To effect eq 6 in synthetically useful conversions,



(6)

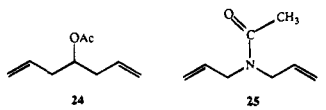
the amount of catalyst **5** was increased to 5 mol %. In addition, the sterically hindered[19] base 2,6-di-*tert*-butyl-4-methyl pyridine (9 mol %) was added to the system to scavenge any traces of protic acid. Under these conditions, conversions of 70% were routinely achieved. Significantly, little racemization of the sensitive chiral substrate was observed. A sample of **18**

(18) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983.

(19) Use of this base was suggested by our colleague T.-V. RajanBabu, one of many critical suggestions he has contributed to our program over the years. We express our heartfelt thanks to Babu and extend our best wishes for his continued success in his new position at The Ohio State University.

prepared from *R*-(−)-1-decen-3-ol of 97.7% ee provided **23** of 96.0% ee (both analyses by chiral capillary GLC). Similarly, another sample of **18** of 88.8% ee gave **23** of 87.7% ee. Most of the unreacted **18** can be recovered during chromatographic workup so that yields based on recovered starting material as high as 87% were demonstrated for eq 6.

Consistent with the Lewis acidic nature of the tungsten(VI) metal center, attempts to extend the cyclization to substrates which are potentially strong chelators were unsuccessful. In contrast to the ready cyclization of **16** and **17**, substrates **24** and **25** under identical conditions gave no more than a trace of cyclized product.



24 **25**

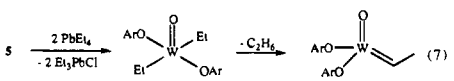
Cyclization Using "Crude" Catalyst Preparation. Attempts to generate catalyst **5** in situ from tungsten oxychloride and 2,6-dibromophenol were not successful. Not surprisingly, the hydrogen chloride coproduct of catalyst synthesis inhibits the metathesis reaction, presumably by protonolysis of the organotungsten species formed upon addition of tetraethyllead. However, as an alternative to *in situ* catalyst generation, it did prove feasible to use a crude catalyst preparation. This procedure circumvents the fairly time-consuming recrystallization of catalyst **5**.

To apply this procedure, a quantity of $WOCl_4$ and 2,6-dibromophenol sufficient to provide a nominal 2% catalyst loading is heated at reflux in toluene after which the solvent and byproduct HCl are removed at reduced pressure. The substrate diene along with 4 mol % of tetraethyllead are introduced as a toluene solution. The cyclization is then conducted as usual (1 h, 90 °C). In this way **13** was successfully cyclized to **3b** in 76% yield.[20] Crude **5** also catalyzed the cyclization of diethyl diallylmalonate (**14**) to **19** in 91% yield.

Discussion

The results summarized in Tables 1 and 2 indicate that cyclic metathesis with catalyst **5** can provide a truly practical synthetic route to many cycloalkenes and heterocycles. It is noteworthy that, with the exception of dienes **15** and **18**, all of the dienes used in this study were prepared in a single chemical step from commercially available starting materials.[21]

The role of tetraethyllead in generating the active catalyst is presumably to replace the chloride ligands on tungsten with ethyl groups. Consistent with the generally accepted "Chauvin mechanism",[22] the resultant organotungsten intermediate would then undergo α elimination to afford the corresponding tungsten ethylidene derivative following eq 7. It is tempting to attribute

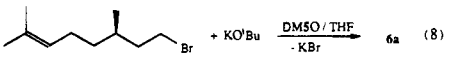


(7)

the unusually robust character of catalyst **5** to the stabilization provided by the bromide donor atom at the stage of the alkylidene intermediate. Related tungsten alkylidenes bearing β hydrogen atoms have been shown[23] to be unstable toward β hydrogen elimination processes. The short W−Br distance observed in the structure of **5** is consistent with this argument. However, in the absence of a crystal structure for the alkylidene derivative itself, this line of reasoning remains speculative.

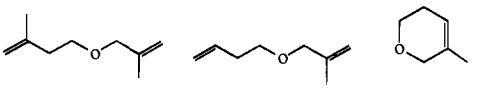
The 2,6-dibromophenol used in these studies could be replaced with other 2,6-dihalophenols with only a modest loss of reactivity and catalyst life. Isolated $WOCl_2(OAr)_2$ derivatives prepared from 2,6-dibromo-4-methylphenol, 2,4,6-tribromophenol, and even 2,6-dichlorophenol were active catalysts for the cyclization of **14**. A slight decrease in activity could usually be compensated by somewhat longer reaction times. For example, using 2 mol % of **5** as catalyst, the conversion of **14** to **19** was 99.8% after 15 min (90 °C, 0.5 M **14** in toluene). Using the analogous catalyst prepared from 2,6-dichlorophenol,[24] the conversion was 93.3% after 15 min and 97.7% after 45 min. However, we were less successful in replacing 2,6-dibromophenol in the "crude catalyst" protocol described above. An attempt to replace the 2,6-dibromophenol in this procedure with an equimolar amount of cheaper 2,6-dichlorophenol caused the conversion of **14** to **19** to drop to 85%.

Given the special interest in enantiopure 3-methylcyclopentene, it is worth noting that the enantiopure β-citronellene starting materials referred to in Table 1 were prepared by base-induced elimination of commercial (*R*)- or (*S*)-citronellyl bromide from Aldrich Chemical Co.[25] (eq 8).



(8)

The ready cyclization of **9** to **12** is noteworthy in that a trisubstituted double bond is formed. An attempt was made to extend this result to the case of a tetrasubstituted cyclic olefin. Methallyl ether (**26**) failed to cyclize.[26] In contrast, under identical conditions, the less substituted allyl ether **27** was shown (GC/MS, NMR) to cyclize, affording the trisubstituted cycloalkene **28**. We tentatively conclude that at least one non-β-substituted double bond is required for cyclization to proceed under these conditions.



26 **27** **28**

The principal limitation of catalyst **5**, as compared with the conventional organometallic catalysts **1** and **2**, is its sensitivity to Lewis basic donor functionality. In this regard we are encouraged by the results summarized in Table 2 in which dienes bearing the ether, ester, and trifluoroacetamide functional groups were successfully cyclized. The failure of potentially chelating dienes **24** and **25** to undergo cyclization in the presence of catalyst **5** is noteworthy. Moreover, we note that conversions for eq 6 were usually[27] limited to ca. 70% even under our optimized conditions. Yet we were able to demonstrate that

(20) The crude **19** produced in this way could be directly decarboxylated to **3b** by treatment with 2 equiv of NaCN in DMSO under the same conditions (160 °C, 6 h) used to prepare **13** (see the Experimental Section). Moreover, **19** itself can serve as a useful synthetic intermediate. See, for example: Cipollina, J. A.; Ruediger, E. H.; New, J. S.; Wire, M. E.; Shepherd, T. A.; Smith, D. W.; Yevich, J. P. *J. Med. Chem.* **1991**, *34*, 3316−3328.

(21) In fact, diethyl diallylmalonate is commercially available from a variety of vendors including Aldrich and Lancaster Synthesis.

(22) Herrison, J.-P.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161−176.

(23) See, for example: 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.

(24) Synthesis and characterization of this complex has been reported by Bell. See ref 12.

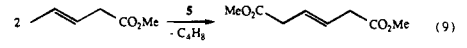
(25) Commercial (*R*)- and (*S*)-β-citronellene from Fluka also readily cyclized but gave product of significantly lower optical purity (72% ee for **4a** and 87% ee for **4b**). The analogous cyclization of "(*R*)-(+)-5,7-dimethyl-1,6-octadiene" from Fluka gave the (*S*)-(−) isomer **4b** in 41% ee, indicating that the absolute stereochemistry of the commercial starting material has been misassigned.

(26) Conditions: 0.5 M toluene solution, 5% catalyst **1**, 90 °C, 2 h. Conversion was quantitative.

(27) In a single run, an anomalously high conversion of 83% was obtained, suggesting that there remains opportunity to further optimize this procedure.

substrate **18** was cleanly cyclized with the Schrock catalyst **1** (3% catalyst, room temperature, 1 h, 88% isolated yield); as with catalyst **5**, there was no significant loss of optical activity.

Although extensions of this chemistry to intermolecular metathesis reactions fall outside the scope of this paper, we note that catalyst **5** was discovered during the course of scouting studies on such a process. The conversion of methyl 3-pentenoate to the corresponding hexenedioate (eq 9) is of interest as an alternative route to the nylon intermediate adipic acid.



(9)

Using 2% of catalyst **5**, eq 9 was accomplished (no solvent, 130 °C, 2 h) in 70% conversion with 90% selectivity to the desired dehydroadipate. Similar activity was observed using catalyst **1**, while catalyst **2** was ineffective for this transformation.

Cyclic metathesis using **5** is remarkably "user friendly" even for organic chemists having little experience with homogeneous catalysis. Many additional synthetically useful transformations based on this chemistry can be anticipated. We encourage our colleagues in the field of organic synthesis to explore these exciting applications.

Experimental Section

Tetrahydrofuran was distilled from sodium benzophenone radical anion under nitrogen. All other solvents were stored over activated 4A sieves for at least 48 h prior to use.

Methyltriphenylphosphonium bromide and 4A molecular sieves were dried at 200 °C in high vacuum prior to use. Except where indicated, other reagents were purchased from Aldrich Chemical Co. and used as received. All synthetic reactions were carried out under dry nitrogen except as indicated.

Flash chromatography was carried out on 230−400 mesh silica (EM Reagents) following the general procedure of Still.[28] Except where indicated, 300 MHz ^{1}H NMR and 75.5 MHz {^{1}H}^{13}C NMR spectra were obtained in $CDCl_3$. Chemical shifts (δ) are in parts per million (ppm) downfield from internal reference tetramethylsilane, and coupling constants (J) are in hertz.

Analysis of Enantiomeric Excess for 4a,b, 10, and 23. Samples of the products were epoxidized with a slight excess of 3-chloroperoxybenzoic acid in dichloromethane. In each case this produced a mixture of the diastereomeric cis and trans epoxides. The enantiomeric excess was then determined by capillary GLC analysis using a Cyclodex-B stationary phase (J & W Scientific). Column temperatures for these analyses were 70 °C for **4a,b**, 80 °C for **10**, and 140 °C for **23**. Comparison of the ee's for the diastereomeric epoxides provided an independent internal check; in all cases values were identical to within ±0.3%.

***trans*-Dichlorobis(2,6-dibromophenoxy)oxotungsten(VI) (5).** A mixture of tungsten(VI) oxotetrachloride (1.71 g, 5.00 mmol) and 2,6-dibromophenol (2.52 g, 10.0 mmol) in toluene (25 mL) was heated at reflux for 1 h. After the mixture was cooled, the solvent was removed on a rotary evaporator with minimal exposure to atmospheric moisture. The residue was stirred with dichloromethane (100 mL) under nitrogen for 10 min. The solution was filtered under nitrogen, and a layer of hexanes (100 mL) was carefully added. The resulting two-phase system was placed in a −20 °C freezer for 10 days. Filtration and removal of the last traces of solvent in high vacuum afforded **5** (2.50 g, 65%) as a green-black crystalline solid. ^{1}H NMR: δ 6.89 (t, J = 9, 2H), 7.62 (d, J = 9, 4H). Anal. Calcd for $C_{12}H_6Br_4Cl_2O_3W$: C, 18.66; H, 0.78. Found: C, 18.29; H, 0.75.

Structural Details for 5. Suitable crystals were obtained by cooling a dichloromethane/hexane solution as described above. The crystallographic investigation was carried out on an Enraf-Nonius CAD4 diffractometer (graphite monochrometer, Mo Kα radiation, λ = 0.710 69 Å) equipped with a low-temperature apparatus. The crystal system, space group, and approximate unit cell dimensions were determined during preliminary investigations. Crystal quality was found to be adequate on the basis of ω scans which showed the peak width at half-height to be ca. 0.16° ω. The unit cell parameters were refined from the Bragg angles of 25 computer-centered reflections. Intensity data were collected using the ω scan technique. The intensities of two standard reflections were taken 54 times (4% fluctuation, 56.6% variation on azimuthal scan, corrected for azimuthal absorption). The structure was solved by automated Patterson analysis (PHASE). The atomic scattering factors were taken from the tabulations of Cromer and Waber;[29a] anomalous corrections for W, Br, and Cl were taken from Cromer.[29b] In the full-matrix least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights, w, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$.

Crystal data for $WBr_4Cl_2O_3C_{12}H_6$: black irregular block, ~0.35 × 0.21 × 0.36 mm, orthorhombic, $P2_12_12_1$ (No. 19), a = 7.903(3) Å, b = 14.568(1) Å, c = 15.211(2) Å, T = −60 °C, V = 1751.3 Å^3, Z = 4, FW = 772.57, D_c = 2.930 g/cm^3, μ(Mo) = 160.97 cm^{-1}. A total of 8323 data were collected (scan width 1.20−1.90° ω, variable scan speed = 1.80−5.00 deg/min, 2.7° < 2θ < 55.0°). The asymmetric unit consists of one molecule in a general position. Refined anisotropic: W, Br, Cl, O, C (one carbon atom, C26, was kept isotropic due to abnormal anisotropy, possible a consequence of the absorption method). Hydrogen atoms were fixed with idealized C−H = 0.95 Å. The refinement of 195 parameters using 1798 reflections with $I > 3\sigma(I)$ converged at R = 0.038 and R_w = 0.027. The enantiomorph was chosen on the basis of the best R-value agreement. The largest peak in the residual density was 1.14 e/A^3, near W1.

(*S*)-(+)-Citronellene (6b). Potassium *tert*-butoxide (19.2 g, 171 mmol) was added over the course of several minutes to a solution of (*S*)-(+)-citronellyl bromide (25.0 g, 114 mmol) in tetrahydrofuran (150 mL). After 48 h, the mixture was added to water (500 mL) and was extracted into pentane (2 × 100 mL). After the mixture was dried ($MgSO_4$), the pentane was distilled off. The residue, which contains ca. 5% of the *tert*-butyl ether, was distilled at 140−144 °C to afford **6b** (9.63 g, 61%) as a colorless liquid, $[\alpha]^{25}_D$ +10.7 (*c* 9.53, chloroform), lit. $[\alpha]^{D}_{25}$ +8.62 (neat),[30] +9.24 (neat).[31] ^{1}H NMR: δ 0.99 (d, J = 7, 3H), 1.32 (m, 2H), 1.59 (s, 3H), 1.68 (s, 3H), 1.96 (br q, J = 8, 2H), 2.12 (m, 1H), 4.88−5.00 (m, 2H), 5.10 (m, 1H), 5.70 (m, 1H). ^{13}C NMR: δ 17.68, 20.18, 25.73, 25.79, 36.80, 37.41, 112.44, 124.66, 131.18, 144.69. Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.62; H, 13.42.

(*R*)-(−)-Citronellene (6a). The compound prepared as above from (*R*)-(−)-citronellyl bromide had spectroscopic properties identical to those of the *S* isomer, $[\alpha]^{25}_D$ −9.7 (*c* 8.40, chloroform), lit.[31] $[\alpha]^{25}_D$ −9.70 (neat).

(*S*)-(−)-4,8-Dimethyl-1,7-nonadiene (7). A suspension of triphenylmethyl-phosphonium bromide (22.9 g, 64.1 mmol) in tetrahydrofuran (400 mL) in a side-arm flask was cooled to −20 °C, and 1.60 M butyllithium in hexane (38.0 mL, 60.8 mmol) was added via syringe. The bath was removed, and the mixture was stirred for 0.5 h and then cooled to −78 °C. (*S*)-(−)-Citronellal (11.0 mL, 60.7 mmol) was added via syringe. The mixture was stirred for 1 h at −78 °C and was then allowed to warm to room temperature in the bath. Acetone (10 mL) was added to quench excess reagent. After 0.5 h, the mixture was added to hexane (800 mL) and filtered. After removal of solvent at reduced pressure, the residue was distilled (70−72 °C at 15 Torr) to afford **7** (6.92 g, 75%) as a colorless liquid, $[\alpha]^{25}_D$ −3.0 (*c* 10.38, chloroform). ^{1}H NMR: δ 0.87 (d, J = 7, 3H), 1.06−1.21 (m, 1H), 1.26−1.42 (m, 1H), 1.42−1.57 (m, 1H), 1.61 (s, 3H), 1.69 (s, 3H), 1.81−2.13 (m, 4H), 4.94−5.15 (m, 3H), 5.70−5.88 (m, 1H). ^{13}C NMR: δ 9.94, 17.61, 19.39, 25.67, 32.50, 36.72, 41.40, 115.40, 124.89, 130.99, 137.58. Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.50; H, 13.13.

3,3-Dimethyl-1,7-octadiene (8). The Grignard reagent was prepared from 5-bromo-1-pentene (25.0 g, 168 mmol) and magnesium turnings (4.40 g, 181 mmol) in ether (200 mL). The filtered solution was added dropwise to a mixture of 4-bromo-2-methyl-2-butene (20.0 g, 168 mmol) and copper(I) cyanide (0.70 g, 7.8 mmol) in ether (60 mL) at 0 °C. After the solution was quenched with aqueous ammonium chloride (100 mL), the ether layer was washed with water (50 mL)

(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(29) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; (a) Table 2.2B, (b) Table 2.3.1.

(30) Eschenmoser, A.; Schinz, H. *Helv. Chim. Acta* **1950**, *33*, 171−177.

(31) Rienaecker, R.; Ohloff, G. *Angew. Chem.* **1961**, *73*, 240.

and dried ($MgSO_4$). After distillation of the solvent, gas chromatographic analysis indicated that the residue was a 77:23 mixture of the desired product and isomeric 2-methyl-2,8-nonadiene. Therefore the crude product was dissolved in dichloromethane (50 mL) and a solution of *m*-chloroperoxybenzoic acid (8.00 g, 57% purity, 26 mmol) in dichloromethane (125 mL) was added dropwise at 0 °C to selectively oxidize the trisubstituted olefin. The resultant mixture was extracted with 5% aqueous sodium bisulfite, saturated aqueous $NaHCO_3$, and water (50 mL each), and the solvent was removed at reduced pressure. The product was distilled in a Vigreux apparatus, and the fraction boiling 42−46 °C at 15 Torr was collected (6.45 g, 36% overall yield). Gas chromatographic analysis indicated the isomeric purity to be 98.5%. ^{1}H NMR: δ 0.97 (s, 6H), 1.23−1.38 (m, 4H), 2.02 (br q, J = 7, 2H), 4.85−5.04 (m, 4H), 5.71−5.87 (m, 2H). ^{13}C NMR: δ 23.95, 26.72, 34.47, 36.47, 42.22, 110.12, 114.20, 139.01, 148.48. Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.94; H, 13.21.

2-Methyl-1,7-octadiene (9). The Grignard reagent was prepared from 5-bromo-1-pentene (11.04 g, 74.1 mmol) and magnesium turnings (1.94 g, 79.8 mmol) in ether (100 mL). The filtered solution was added dropwise to a mixture of 3-bromo-2-methylpropene (8.00 g, 59.3 mmol) and copper(I) cyanide (0.30 g, 3.3 mmol) in ether (25 mL) at 0 °C. After the solution was quenched with aqueous ammonium chloride (50 mL), the ether layer was washed with water (25 mL) and dried ($MgSO_4$). After distillation of the solvent, the residue was distilled (142−143 °C) under nitrogen to give a colorless liquid (5.89 g, nominal 80% yield) which, however, contained 5% of the homocoupling product 1,9-decadiene by GC analysis. ^{1}H NMR: δ 1.41 (m, 4H), 1.70 (s, 3H), 1.97−2.10 (m, 4H), 4.68 (m, 2H), 4.90−5.06 (m, 2H), 5.74−5.90 (m, 1H). ^{13}C NMR: δ 22.36, 27.09, 28.58, 33.68, 37.66, 109.68, 114.24, 138.94, 145.97. Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.86; H, 13.01.

(*S*)-(−)-3-Methylcyclopentene (4b). A flask was charged with (*S*)-(+)-citronellene (9.38 g, 67.8 mmol) and catalyst **5** (1.12 g, 1.45 mmol) in 1,2,4-trichlorobenzene (50 mL). Tetraethyllead (0.94 g, 2.91 mmol) was added, and the mixture was heated in a 90 °C oil bath for 2 h. After cooling, the mixture was filtered through a short pad of 220−400 mesh silica and the crude **4b** was distilled out under nitrogen. After the mixture was heated at reflux under air for 0.5 h to remove some dissolved isobutylene, **4b** (3.92 g, 70%) was obtained as a colorless liquid, bp 60−64 °C, $[\alpha]^{25}_D$ −166.6 (*c* 5.14, chloroform). ^{1}H NMR: δ 1.02 (d, J = 7, 3H), 1.25−1.39 (m, 1H), 2.00−2.14 (m, 1H), 2.20−2.43 (m, 2H), 2.73 (m, 1H), 5.60−5.72 (m, 2H). ^{13}C NMR: δ 21.02, 31.99, 32.17, 39.96, 129.58, 136.97. Anal. Calcd for C_6H_{10}: C, 87.73; H, 12.27. Found: C, 87.43; H,12.15. Gas chromatographic analysis as described above indicated the product was formed in 97% enantiomeric excess.

(*R*)-(+)-3-Methylcyclopentene (4a). The compound prepared as above from (*R*)-(−)-citronellene had spectroscopic properties identical to those of the *S* isomer, $[\alpha]^{25}_D$ +167.4 (*c* 5.23, chloroform), lit.[17] $[\alpha]^{25}_D$ +174.5 (neat).

(*S*)-(−)-4-Methylcyclohexene (10). A flask was charged with (*S*)-(−)-4,8-dimethyl-1,7-nonadiene (11.68 g, 76.7 mmol), catalyst **5** (1.26 g, 1.63 mmol), and 1,2,4-trichlorobenzene (60 mL). Tetraethyllead (1.05 g, 3.25 mmol) was added, and the mixture was heated in a 90 °C oil bath for 2 h. After cooling, the solution was stirred briefly with silica (10 g) and filtered to produce a colorless solution. Initial distillation at 97−120 °C afforded crude **10** (5.76 g) still containing dissolved isobutylene. After the solution was heated, at gentle reflux in air for 0.5 h, the product was redistilled to produce a colorless liquid (4.71 g, 64%), bp 92−94 °C, $[\alpha]^{25}_D$ −128.7 (*c* 4.59, chloroform), lit. for the (*R*)-(+) isomer $[\alpha]^{25}_D$ 107.05 (neat),[32a] 110.0 (neat).[32b] ^{1}H NMR: δ 0.95 (d, J = 7, 3H), 1.11 (m, 1H), 1.65 (m, 3H), 2.04 (m, 3H), 5.65 (m, 1H). ^{13}C NMR: δ 21.98, 25.31, 28.55, 30.92, 33.79, 126.63, 126.74. Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.54; H, 12.67. Gas chromatographic analysis as described above indicated that the product was formed in 99% enantiomeric excess.

3,3-Dimethylcyclohexene (11). Tetraethyllead (0.57 g, 1.8 mmol) was added to a solution of 3,3-dimethyl-1,7-octadiene (6.12 g, 44.3 mmol) and catalyst **5** (0.68 g, 0.88 mmol) in 1,2,4-trichlorobenzene (10 mL). After heating in a 90 °C oil bath for 1 h, the reflux condenser was replaced with a distillation head and the colorless product (4.23 g, 87%) was distilled under nitrogen at 109−112 °C. ^{1}H NMR: δ 0.97 (s, 6H), 1.41−1.48 (m, 2H), 1.62 (m, 2H), 1.90 (m, 2H), 5.40 (br d, J = 10, 1H), 5.54 (dt, J = 10, 4, 1H). ^{13}C NMR: δ 19.82, 25.41, 30.15, 31.73, 37.58, 124.74, 138.02. Anal. Calcd for C_8H_{14}: C, 87.19; 12.81. Found: C, 87.15; H, 12.79.

1-Methylcyclohexene (12). Tetraethyllead (0.60 g, 1.9 mmol) was added to a solution of 2-methyl-1,7-octadiene (5.74 g, 95% pure, 43.9 mmol) and catalyst **5** (0.71 g, 0.92 mmol) in 1,2,4-trichlorobenzene (15 mL). The mixture was heated in a 90 °C oil bath for 1 h. The reflux condenser was replaced with a distillation head, and the fraction (4.12 g) boiling at 106−110 °C was collected. This material was redistilled (108−112 °C) to give **12** (3.55 g, 84%) as a colorless liquid. ^{1}H NMR: δ 1.46−1.66 (m, 4H), 1.63 (s, 3H), 1.90 (m, 2H), 1.95 (m, 2H), 5.38 (m, 1H). ^{13}C NMR: δ 22.64, 23.26, 24.19, 25.53, 30.28, 121.31, 134.25. Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.06; H, 12.62.

4-Carbethoxy-1,6-heptadiene (13). A mixture of diethyl diallylmalonate (50.0 g, 208 mmol), sodium cyanide (20.7 g, 422 mmol), and dimethyl sulfoxide (166 mL, not dried) was heated in a 160 °C oil bath for 6 h. After being cooled, the mixture was added to 300 mL of water and the product was extracted into hexane (3 × 100 mL). After distillation of the solvent at reduced pressure, the residue was distilled (90−92 °C, 15 Torr) to give **13** (28.6 g, 82%) as a colorless liquid. ^{1}H NMR: δ 1.25 (t, J = 7, 3H), 2.20−2.37 (m, 4H), 4.14 (q, J = 2H), 4.98−5.12 (m, 4H), 5.75 (m, 2H). ^{13}C NMR: δ 14.49, 35.95, 45.05, 60.38, 116.98, 135.38, 174.88. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.69; H, 9.80.

4-((Triisopropylsiloxy)methyl)-1,6-heptadiene (15). A 1.0 M solution of lithium aluminum hydride (15.0 mL, 15 mmol) was added via syringe to a solution of 4-carbethoxy-1,6-heptadiene (5.00 g, 29.7 mmol) in tetrahydrofuran (100 mL) at −78 °C. After 0.5 h, the dry ice bath was replaced with a 0 °C bath and stirring was continued for 1 h, whereupon 1 N aqueous sodium hydroxide (100 mL) was added dropwise at 0 °C. The organic layer was separated, and the aqueous layer was further extracted with ether (2 × 50 mL). The combined organics were washed with saturated aqueous KH_2PO_4 and water (20 mL each). The solvent was removed at reduced pressure, and the residue was azeotropically dried with methanol and dichloromethane. The residue was taken up in dichloromethane and dried over 4A molecular sieves for 72 h. The solution was then added dropwise to a solution of triisopropylsilyl trifluoromethanesulfonate (6.92 g, 22.6 mmol) in pyridine (15 mL) and dichloromethane (15 mL). After 18 h, the mixture was added to water (75 mL) and extracted into ether (2 × 75 mL). After removal of volatiles at reduced pressure, the residue was subjected to flash chromatography (95% hexane, 5% ether). Removal of solvent from the product-containing cuts afforded **15** (5.80 g, 69% overall yield) as a colorless liquid. ^{1}H NMR: δ 1.06 (m, 21H), 1.65 (m, 1H), 2.12 (m, 4H), 3.58 (d, J = 7, 2H), 4.99 (br s, 2H), 5.04 (br d, J = 9, 2H), 5.80 (m, 2H). ^{13}C NMR: δ 12.10, 18.10, 35.08, 40.83, 65.04, 115.94, 137.11. Anal. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.42; H, 12.26.

4-((*tert*-Butyldimethylsilyl)oxy)-1,6-heptadiene (16). A solution of *tert*-butyldimethylsilyl trifluoromethanesulfonate (5.29 g, 20.0 mmol) in dichloromethane (15 mL) was added dropwise to a solution of 1,6-heptadien-4-ol (2.24 g, 20.0 mmol) in pyridine (15 mL) and dichloromethane (15 mL). The mixture was allowed to stand overnight whereupon volatiles were removed at reduced pressure. The residue was dissolved in ether (100 mL) and was extracted with 1 N HCl, saturated aqueous $NaHCO_3$, and water (25 mL each). After the mixture was dried ($MgSO_4$), the solvent was removed at reduced pressure and the residue was purified by flash chromatography (90% hexane, 10% benzene) to give **16** (3.37 g, 74%) as a colorless liquid. ^{1}H NMR: δ 0.05 (s, 6H), 0.89 (s, 9H), 2.20 (m, 4H), 3.73 (quintet, J = 6, 1H), 5.01 (m, 2H), 5.05 (m, 2H), 5.73−5.88 (m, 2H). ^{13}C NMR: δ −4.44, 18.18, 25.90, 41.54, 71.76, 116.81, 135.22. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.87; H, 11.40.

***N,N*-Diallyltrifluoroacetamide (17).** A solution of trifluoroacetic anhydride (6.30 g, 30.0 mmol) in dichloromethane (25 mL) was added dropwise to a solution of *N,N*-diallylamine (2.91 g, 30.0 mmol) and pyridine (2.38 g, 30.0 mmol) in dichloromethane (25 mL). The mixture was diluted with ether (100 mL) and was extracted with 1 N HCl (50

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mL) then with water (2 × 50 mL). After the mixture was dried ($MgSO_4$ then 4A sieves), removal of solvent at reduced pressure afforded **17** (4.65 g, 80%) as a pale yellow liquid. ^1H NMR: δ 4.00 (m, 4H), 5.16 (m, 4H), 5.68−5.84 (m, 2H). ^{13}C NMR: δ 48.32, 49.23, 116.64 (q, $J^{13}C^{19}F$ = 287.7), 118.89, 119.28, 131.00, 131.85, 156.84 (q, $J^{13}C^{19}F$ = 36.0). Anal. Calcd for $C_8H_{10}NOF_3$: C, 49.74; H, 5.22; N, 7.25. Found: C, 49.51; H, 5.03; N, 6.88.

(*R*)-(+)-3-(Allyloxy)-1-decene (18). A solution of (*R*)-(−)-1-decen-3-ol (2.46 g, 15.7 mmol, prepared as described previously[33]) in THF (24 mL) was added dropwise to a suspension of potassium hydride (0.72 g, 18 mmol) in tetrahydrofuran (12 mL). The filtered solution was added all at once to a solution of allyl bromide (3.82 g, 31.6 mmol) in DMSO (36 mL). After standing overnight, the mixture was added to water (500 mL) and the product was extracted into hexane (3 × 100 mL). The combined hexane extracts were washed with water (50 mL), and the solvent was removed at reduced pressure. The residue was subjected to flash chromatography to afford **18** (2.26 g, 73%) as a colorless liquid. ^1H NMR: δ 0.88 (t, J = 7, 3H), 1.15−1.54 (m, 10H), 1.60 (m, 2H), 3.67 (q, J = 7, 1H), 3.78−3.86 (m, 1H), 4.00−4.08 (m, 1H), 5.11−5.30 (m, 4H), 5.60−5.76 (m, 1H), 5.83−5.98 (m, 1H). ^{13}C NMR: δ 14.04, 22.66, 25.37, 29.26, 29.60, 31.68, 35.54, 69.17, 80.74, 116.28, 116.43, 135.36, 139.35. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.43; H, 12.24. If desired, some unreacted allylic alcohol (0.44 g in this example) could be recovered from the later chromatographic cuts.

3-Cyclopentene-1,1-dicarboxylic Acid, Diethyl Ester (19). Tetraethyllead (0.46 g, 1.4 mmol) was added to a solution of diethyl diallylmalonate (15.86 g, 66.0 mmol) and catalyst **5** (1.08 g, 1.40 mmol) in toluene (85 mL). The mixture was heated in a 90 °C oil bath for 1 h. After cooling the product solution was filtered through a short pad of silica and washed with 1 N aqueous sodium hydroxide and water (25 mL each). Removal of solvent at reduced pressure followed by vacuum distillation (68−75 °C, 0.3 Torr) afforded **19** (12.10 g, 86%) as a colorless liquid. ^1H NMR: δ 1.16 (t, J = 7, 6H), 3.02 (s, 4H), 4.19 (q, J = 7, 4H), 5.62 (s, 2H). ^{13}C NMR: δ 14.06, 40.88, 58.86, 61.50, 127.79, 172.12. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.32; H, 7.75.

3-Cyclopentenecarboxylic Acid, Ethyl Ester (3b). Tetraethyllead (1.07 g, 3.31 mmol) was added to a solution of 4-carbethoxy-1,6-heptadiene (26.38 g, 156.8 mmol), catalyst **5** (1.28 g, 1.66 mmol), and toluene (200 mL). The mixture was heated in a 90 °C oil bath for 1 h. Workup as in the preceding example and distillation (60−64 °C, 15 Torr) provided **3b** (16.28 g, 74%) as a colorless liquid. ^1H NMR: δ 1.16 (t, J = 7, 3H), 2.65 (d, J = 7, 4H), 3.11 (quintet, J = 7, 1H), 4.15 (q, J = 7, 2H), 5.66 (s, 2H). ^{13}C NMR: δ 14.37, 36.43, 41.70, 60.52, 129.03, 176.20. Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.40; H, 8.86.

3-((Triisopropylsiloxy)methyl)cyclopentene (20). Tetraethyllead (0.69 g, 2.1 mmol) was added to a solution of 4-((triisopropylsiloxy)-methyl)-1,6-heptadiene (15.03 g, 53.2 mmol) and catalyst **5** (0.82, 1.1 mmol) in toluene (100 mL). The mixture was heated in a 90 °C oil bath for 1 h. Workup as in the preceding examples and distillation (71−79 °C, 0.25 Torr) afforded **20** (12.35 g, 91%) as a colorless liquid. ^1H NMR: (δ) 1.07 (m, 21H), 2.14 (m, 2H), 2.36−2.56 (m, 3H), 3.57 (d, J = 7, 2H), 5.65 (s, 2H). ^{13}C NMR: δ 12.34, 18.30, 35.70, 39.94, 67.52, 129.82. Anal. for $C_{15}H_{30}OSi$. Calcd: C, 70.79; H, 11.88. Found: C, 70.66; H, 11.97.

3-((*tert*-Butyldimethylsilyl)oxy)cyclopentene (21). Tetraethyllead (0.26 g, 0.80 mmol) was added to a solution of 4-((*tert*-butyldimethylsilyl)oxy)-1,6-heptadiene (3.97 g, 17.5 mmol) and catalyst **5** (0.31 g, 0.40 mmol) in toluene (25 mL). The mixture was heated in a 90 °C bath for 1 h. After cooling, the mixture was stirred with silica (3.0 g) and filtered and the resultant colorless solution was washed with 1 N NaOH and water (25 mL each). Removal of solvent at reduced pressure produced a residue which was distilled (32 °C, 0.5 Torr) to afford **21** (2.82 g, 81%) as a colorless liquid. ^1H NMR: δ 0.06 (s, 6H), 0.90 (s, 9H), 2.27 (dd, J = 14, 4, 2H), 2.57 (dd, J = 14, 7, 2H), 4.53 (m, 1H), 5.65 (s, 2H). ^{13}C NMR: δ −4.45, 18.51, 26.20, 42.41, 72.69, 128.55. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.32; H, 11.10.

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***N*-(Trifluoroacetyl)-3-pyrroline (22).** A solution of *N,N*-diallyltrifluoroacetamide (3.88 g, 20.1 mmol) in benzene (20 mL) was dried over 4A molecular sieves for 72 h. To the filtered solution were added catalyst **5** (0.31 g, 0.40 mmol) and tetraethyllead (0.26 g, 0.80 mmol). The mixture was heated for 2 h at reflux. The cooled solution was applied directly to a flash chromatography column and was eluted with 70:30 hexane/ethyl acetate. Removal of solvent from cuts 16−24 on a rotary evaporator afforded **22** (2.75 g, 83%). ^1H NMR: δ 4.36 (m, 2H), 4.48 (m, 2H), 5.88 (m, 2H). ^{13}C NMR: δ 53.13, 53.18, 54.79, 116.39 (q, $J^{13}C^{19}F$ = 287.2), 124.74, 124.99, 155.51 (q, $J^{13}C^{19}F$ = 37.1). HRMS. Calcd for $C_6H_6NOF_3$: *m/z* 165.0401. Found: 165.0397. The product darkens upon standing several days at room temperature under air. However, when stored in a −10 °C freezer under nitrogen, it solidifies to a mass of white needles and no decomposition could be detected after several months.

(*R*)-(−)-2-Heptyl-2,5-dihydrofuran (23). A solution of **18** (2.27 g, 11.6 mmol) and tetraethyllead (0.38 g, 1.2 mmol) in toluene (25 mL) was added to a flask containing catalyst **5** (0.45 g, 0.58 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.20 g, 1.0 mmol). After being heated at 90 °C for 1 h, the cooled mixture was stirred with 220−400 mesh silica (2.0 g), filtered and then washed with 1 N sodium hydroxide then water (10 mL each). This solution was applied to a flash chromatography column and was eluted with 90:10 hexane/ether. Unreacted starting material (0.53 g) could be recovered from the early cuts. Distillation of solvent from the product containing cuts afforded **23** (1.14 g, 58%) as a colorless liquid, $[\alpha]^{25}_D$ −100.0 (*c* 4.97, chloroform). ^1H NMR: δ 0.88 (t, J = 7, 3H), 1.20−1.45 (m, 10H), 1.53 (m, 2H), 4.62 (m, 2H), 4.82 (m, 1H), 5.79 (m, 1H), 5.87 (m, 1H). ^{13}C NMR: δ 14.02, 22.64, 25.30, 29.27, 29.71, 31.82, 36.08, 74.86, 86.10, 126.22, 129.91. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.46; H, 11.81. Gas chromatographic analysis as described above indicated that the product was formed in 96% enantiomeric excess.

Cyclization Using Crude 5 (General Procedure). A 200-mL round-bottomed flask was charged with tungsten oxychloride (0.43 g, 1.3), 2,6-dibromophenol (0.63 g, 2.5 mmol), and toluene (10 mL). The mixture was heated at reflux for 1 h, and the solvent was then removed on a rotary evaporator. The solid residue was broken up with a spatula and was dried in high vacuum for 15 min. To the flask were added diethyl diallylmalonate (15.0 g, 62.4 mmol), tetraethyllead (0.81 g, 2.5 mmol), and toluene (75 mL). The mixture was heated in a 90 °C oil bath for 1 h. After cooling, the mixture was filtered through a ca. 3 mm bed of 230−400 mesh silica, rinsing the silica with additional toluene (50 mL). The combined toluene solution was washed with 1% aqueous NaOH (15 mL) and water (15 mL). After removal of the solvent at reduced pressure, the product was distilled (62−66 °C, 15 Torr) to afford **19** (12.00 g, 91%) with properties identical to those described above.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles for **5** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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