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Chiral Nonracemic α-Alkylidene and α-Silylidene Cyclopentenones from Chiral Allenes Using an Intramolecular Allenic Pauson−Khand-Type Cycloaddition

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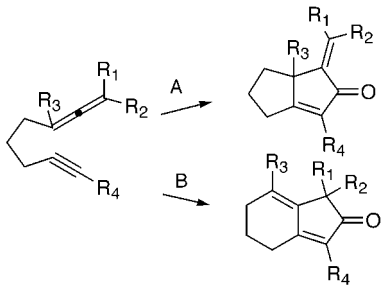
We have successfully effected a transfer of chirality from a chiral nonracemic allene to an α-alkylidene and an α-silylidene cyclopentenone. The molybdenum-mediated examples possessing a silyl group on the terminus of the allene show good facial selectivities, but isomerization of the (*E*)-silylidene cyclopentenone to the (*Z*)-silylidene cyclopentenone occurs upon purification of these products. Alternatively, an alkyl group on the terminus of the allene undergoes cycloaddition with moderate selectivities but gives products that undergo an isomerization of the (*Z*)-alkylidene cyclopentenone to the (*E*)-alkylidene cyclopentenone when exposed to acidic conditions. Thus, erosion of the enantiomeric excesses is observed for one of the two products as a result of this isomerization. The allenic Pauson−Khand-type cycloaddition has also been effected by first isolation the (η^6-arene)-molybdenum tricarbonyl complex, demonstrating for the first time that this is most likely the active complex in the molybdenum-mediated reactions. Attempts to increase the facial selectivity by increasing the size of the arene moiety resulted in a marginal increase in the selectivity at the expense of the yield. Based upon these results, we have concluded that altering the approach for the preparation of nonracemic α-alkylidene cyclopentenones is necessary in order to obtain synthetically useful levels of stereocontrol.

Introduction

In the past three decades, allenes have most certainly reached the status of important and useful functional groups in organic synthesis.[1] One interesting facet of an allene is the cumulated double bond, which was originally thought to be very unstable, and in fact, upon undergoing any addition reaction does experience a relief in strain of about 10 kcal/mol.[2] This inherent instability imparted by the cumulated double bond has been exploited by many research groups taking advantage of the facility in which cycloaddition reactions take place relative to that of an isolated double bond.[3] Previously, in our group we have shown that an intramolecular formal [2 + 2 + 1] cycloaddition reaction can occur between an alkyne and an allene to afford α-alkylidene and/or 4-alkylidene cyclopentenones depending upon which double bond of the allene reacts (Scheme 1). Early results from our group show that the double bond of the allene that undergoes reaction depends on the substitution pattern of the allene. While there is some variability in predicting the regioselectivity in this manner, when effecting this reaction

SCHEME 1



using molybdenum hexacarbonyl, trends have been observed. For instance, if R_1 and R_2 are hydrogen and R_3 is an alkyl group, the reaction takes place regioselectively with the less substituted, external olefin of the allene to give the corresponding 4-alkylidene cyclopentenone shown in reaction pathway B. However, if R_1 is an alkyl or silyl group and R_2 and R_3 are hydrogen, then the reaction occurs regioselectively with the internal double bond of the allene to give the α-alkylidene cyclopentenone designated by reaction pathway A.[4] The value of accessing substructures in this manner has recently been demonstrated by the application of the allenic Pauson−Khand reaction to the synthesis of the anticancer compound hydroxymethylacylfulvene.[5]

(1) Prior to the 1970s, allenes were regarded as curiosities, and it is not stated more completely and succinctly than: Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 3rd ed.; McGraw-Hill Book Co.: New York, 1970; pp 104−105.

(2) Padwa, A.; Filipkowski, M. A.; Meske, M.; Murphree, S. S.; Watterson, S. H.; Ni, Z. *J. Org. Chem.* **1994**, *59*, 591.

(3) Schuster, H. F.; Coppola, G. M. In *Allenes in Organic Synthesis*; Wiley-Interscience: New York, 1983; pp 286−330.

(4) Brummond, K. M.; Wan, H.; Kent, J. L. *J. Org. Chem.* **1998**, *63*, 6535.

(5) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087.

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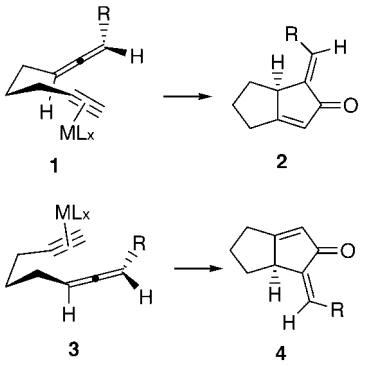
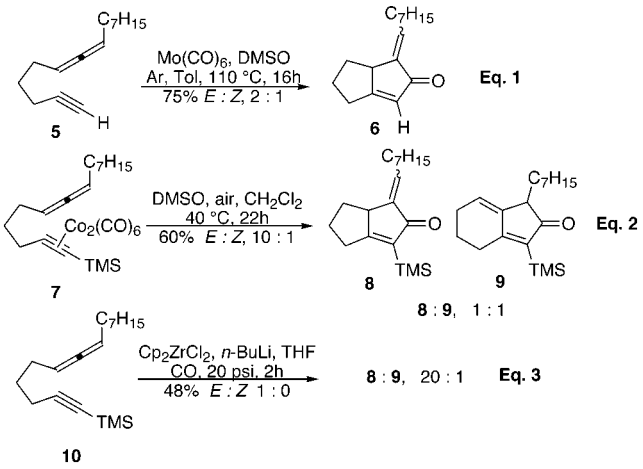
SCHEME 2



Another interesting facet of an allene is that a 1,3-disubstitution pattern renders the allene chiral. An idea that seemed particularly intriguing, although not new with regard to other allenic cycloadditions, is to take advantage of this chirality for the preparation of nonracemic building blocks, in our case α-alkylidene cyclopentenones. We reasoned that the axial chirality of a 1,3-disubstituted allene could be transferred to the stereocenter at the ring fusion of the α-alkylidene cyclopentenone via a selective addition of the metal−alkyne complex to one face of the allene. The two potential reaction conformers are shown in Scheme 2. In reaction conformer **1**, the addition of the metal−alkyne complex to the less hindered face of the allene provides the (*E*)-α-alkylidene cyclopentenone **2** with the designated stereochemistry at the newly formed stereogenic carbon. Alternatively, in reaction conformer **3**, the addition of the metal−alkyne complex to the more hindered face of the allene would afford the (*Z*)-α-alkylidene cyclopentenone **4** with the opposite stereochemistry at the newly formed stereogenic carbon. It is predicted that reaction conformer **1** will be preferred over conformer **3** on the basis of steric control. Thus, an allenic Pauson−Khand-type cycloaddition involving a chiral nonracemic allene should afford enantiomerically enriched α-alkylidene cyclopentenones. In order for this method to be useful in the application to the preparation of chiral α-alkylidene cyclopentenones, high levels of facial selectivity must be achieved. Accordingly, our initial task was to learn to how control the *E*/*Z* selectivity obtained in the Pauson−Khand-type reaction, and we set out to do this by altering the metal that was used to mediate the process. These results are described below.

Discussion of Results

Facial Selectivity as a Function of the Metal. The regiochemical outcome (pathway A vs pathway B, Scheme 1) of the allenic Pauson−Khand-type cycloaddition of 1,3-disubstituted allenes varies as a function of the metal employed in the reaction.[4] For example, treatment of 6,7-pentadecadien-1-yne (**5**) to molybdenum hexacarbonyl and DMSO afforded a 75% yield of only the α-octylidene cyclopentenone (**6**) (eq 1). Alternatively, effecting the cycloaddition of the cobalt−alkyne complex **7**, resulted in compound **8** and the 4-alkylidene cyclopentenone **9** in a 1:1 ratio (eq 2). Finally, treatment of 1-(trimethylsilyl)-6,7-pentadecadien-1-yne (**10**) to the Negishi cyclization protocol gave the corresponding cycloadducts **8** and **9** in moderate yield and in a 20:1 ratio, respectively (eq 3). By comparison of the regiochemical results and the yields of the reactions in eqs 1−3, one can conclude that

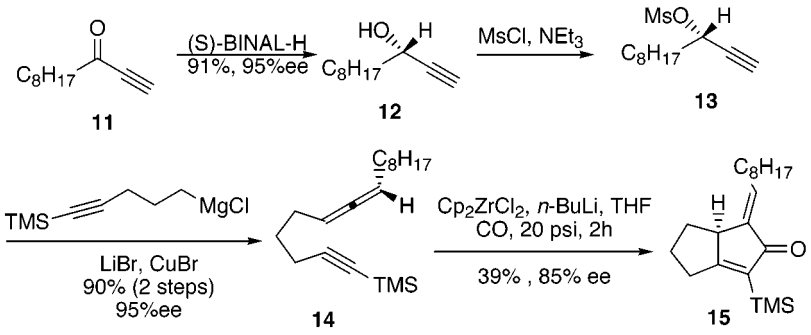


molybdenum hexacarbonyl is the metal of choice for effecting this reaction. However, comparison of the stereochemical results of these same reactions forces one to rethink the metal of choice, since the molybdenum-mediated reaction gives only a 2:1 *E*/*Z* selectivity (eq 1). (Facial selectivity is inferred by examining the *E*/*Z* ratio of the cyclization product with the supposition that an isomerization is not taking place after the cyclization.) Whereas the cobalt-mediated reaction gave a 10:1 *E*/*Z* ratio (eq 2). The reaction shown in eq 2 was also performed in benzene instead of CH_2Cl_2 at 80 °C; these conditions resulted in formation of only (*E*)-alkylidene cyclopentenone and none of the Z-isomer; however, a 2:1 ratio of **8**/**9** was observed. This experiment strongly suggests that the regio- and stereoselectivity changes are not simply a result of the temperature changes between reactions in eqs 1 and 2. Finally, the zirconium-mediated reaction gave only the *E*-isomer (eq 3). Thus, on the basis of the excellent selectivity obtained in the Negishi version of the alkynyl allene cycloaddition process, we set out to test the feasibility of the transfer of chirality from an allene to an α-alkylidene cyclopentenone using the zirconium-mediated conditions despite the moderate yields that were obtained.

Transfer of Stereochemistry in the Allenic P−K Cycloaddition. It has previously been demonstrated that the axial chirality of an allene can be transferred to a newly formed stereogenic center.[6] Most relevant to this work is that described by Sato where he has shown that a titanium(II)-mediated allenyne formal [2 + 2 + 1] cycloaddition affords cyclopentenones with complete transfer of chirality.[6e] Even so, the product possessing the α-alkylidene functionality is not isolated, but instead undergoes a subsequent electrophilic addition via a

(6) (a) Gibbs, R.; Bartels, K.; Lee, R. W. K.; Ojamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 3717. (b) Ikeda, I.; Honda, K.; Osawa, E.; Shiro, M.; Aso, M.; Kanematsu, K. *J. Org. Chem.* **1996**, *61*, 2031. (c) Shepard, M. S.; Carreira, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 2597. (d) Jin, J.; Weinreb, S. M.; *J. Am. Chem. Soc.* **1997**, *119*, 5773. (e) Urabe, H.; Takeda, T.; Hideura, D.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 11295. (f) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348. (g) Hu, H.; Smith, D.; Cramer, R. E.; Tius, M. *J. Am. Chem. Soc.* **1999**, *121*, 9895. (h) Buisine, O.; Aubert, C.; Malacria, M. *Synthesis* **2000**, *7*, 985.

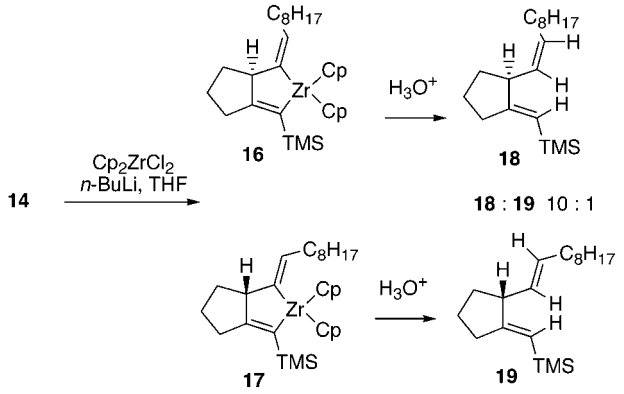
SCHEME 3



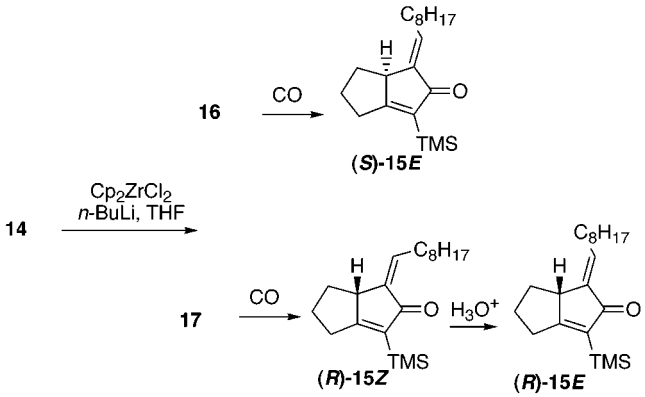
titanium homoenolate equivalent. We are interested in the preparation of nonracemic α-alkylidene cyclopentenones since access to this particular building block using existing chemistries is not so straightforward and it will ultimately be used in the synthesis of biologically interesting natural products such as cyclopentenone prostaglandins. To test the feasibility of the transfer of chirality of an allenic Pauson−Khand-type cycloaddition for the preparation of this substructure, chiral allene **14** was prepared (Scheme 3). Preparation of the nonracemic, chiral allene was accomplished as follows: asymmetric reduction of the undec-1-yn-3-one (**11**) using the Noyori protocol [(*S*)-BINAL-H][7] afforded the chiral propargylic alcohol **12** in 91% yield and 95% ee on the basis of the preparation of the Mosher ester and analysis of the ^{1}H NMR spectrum. Conversion of the propargylic alcohol **12** to the propargylic mesylate **13** was effected using standard conditions. Next, addition of the organocopper species,[8] prepared from 5-(trimethylsilyl)-4-pentynylmagnesium chloride, lithium bromide, and copper bromide, to the propargyl mesylate afforded the chiral allene **14** in 90% yield in 95% ee. The enantiomeric purity of the allene was determined by chiral shift reagent analysis of the ^{1}H NMR spectrum with the aid of a silver(I) compound and an optically active lanthanide complex. Following a procedure reported by Manshreck,[9] treatment of the allene to silver (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) [AgFOD] and ytterbium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate) [Yb(hfc)$_3$] in a ratio of 2.0:1.5:1.0 resulted in separation of the allenyl protons of the resulting diastereomeric complexes. The enantiomeric excesses were then determined by the integration of the diastereomeric allenic protons. Treatment of the chiral alkynyl allene **14** to the Negishi cyclization protocol[10] resulted in the formation of the bicyclo[3.3.0]octenone **15** in only 39% yield and an 85% ee as determined by ^{1}H NMR analysis using the chiral shift reagent europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate (Eu(hfc)$_3$). This decrease in enantiomeric excess of **15** was unexpected since formation of only the (*E*)-α-alkylidene cyclopentenone was observed.

In an effort to determine where the enantiomeric purity had been compromised, α-alkylidene cyclopentenone **15-*Z***, prepared independently, was treated to the standard workup conditions in 3 M HCl. Within 15 min, the *Z*-isomer had totally isomerized to α-alkylidene cyclopentenone **15-*E***. This indicates that the loss of enantiomeric purity might be due to an isomerization of the diastereomeric (*Z*)-α-alkylidene cyclopentenone to the (*E*)-α-alkylidene cyclopentenone. To further support this possibility, hydrolysis of the intermediate zirconacycles **16** and **17** as shown in Scheme 4 revealed that the facial selectivity obtained from the zirconium cyclization protocol was in fact 10:1, not 1:0 as originally thought. This ratio was based upon the isolation of cis and trans olefins of the dienes **18** and **19** in a 10:1 ratio.

SCHEME 4



SCHEME 5



Thus, the loss in enantiomeric excesses during the cycloaddition can be explained as follows (Scheme 5). In the first step of the cyclization process, zirconacyles **16** and **17** are formed in 10:1 ratio. Subsequent CO insertion also afforded a 10:1 ratio of (*E*)- and (*Z*)-α-alkylidene cyclopentenones **(*S*)-15*E*** and **(*R*)-15*Z***, respectively. Hy-

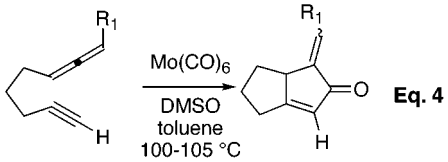
(7) Noyori, R.; Tomino, Y.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717.

(8) Elsevier: C. J.; Vermeer, P. *J. Org. Chem.* **1989**, *54*, 3726.

(9) Mannshreck, A.; Munninger, W.; Burgemeister, T.; Gore, J.; Cazes, B. *Tetrahedron* **1986**, *42*, 399.

(10) Negishi, E.i.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568.

TABLE 1. $Mo(CO)_6$-Mediated Cycloadditions



entry	R_1	time (h)	yield (%)	*E*/*Z*
1	C_7H_{15}	10	75	2:1
2	Ph	10	70	5:1
3	TMS	16	44	4:1
4	TBDMS	10	49	6:1
5	DPS	22	59	8:1

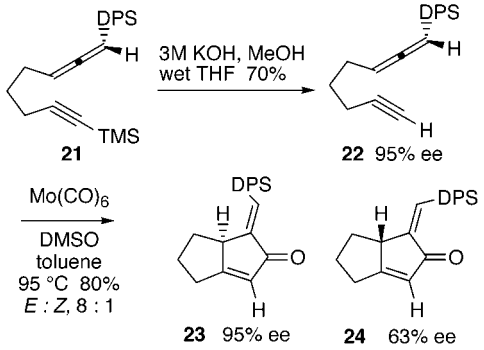
drolytic workup conditions resulted in the isomerization of **(*R*)-15*Z*** to the isomer **(*S*)-15*Z*,** resulting in the 10:1 ratio that is evidenced by the observed decrease in ee.

Attempts to increase the facial selectivity by using larger ligands on the metal (Cp*or indene) were investigated but neither of these zirconium complexes gave rise to cycloadducts. Furthermore, the yields were always low when zirconium was used to effect these cycloadditions. So we decided at this point to focus on improving our facial selectivity under the molybdenum cyclization conditions (eq 1) by increasing the size of the ligand on the terminus of the allene.

Facial Selectivity in the Molybdenum-Mediated Cycloaddition Based on Substitution on the Terminus of the Allene. Preliminary results utilizing the molybdenum conditions with 1,3-disubstituted allenes revealed a 2:1 *E*/*Z* ratio when R_1 was a heptyl moiety (eq 4 and entry 1, Table 1). We felt that facial selectivity might be enhanced by increasing the steric bulk of R_1. For example, replacement of the heptyl moiety with a phenyl group afforded a slightly higher *E*/*Z* ratio of 5:1 (eq 4, entry 2, Table 1). Based on these results though, we decided that a much larger stereocontrolling group would be needed. In addition, we reasoned that this transfer of chirality would be more synthetically appealing if a potentially removable stereocontrolling group could be incorporated into the cycloaddition process. Efforts were then directed toward the development of a traceless stereocontrolling moiety. Initially, substitution of the trimethylsilyl (TMS) moiety on the terminus of the allene was examined. Subjection of this substrate to the molybdenum P−K cyclization conditions gave a modest 4:1 *E*/*Z* ratio in a 44% yield (eq 4, entry 3, Table 1). Next, a *tert*-butyldimethylsilyl (TBDMS) moiety was placed on the terminus of the allene. Cyclization afforded the α-alkylidene cyclopentenone in a 6:1 *E*/*Z* ratio in a 49% yield (eq 4, entry 4, Table 1). Finally, subjection of an allenyne possessing a dimethylphenylsilyl (DPS) moiety on the terminus of the allene to cyclization conditions gave an 8:1 *E*/*Z* ratio in a 59% yield (eq 4, entry 5, Table 1). While the *E*/*Z* selectivities were not at the level that we had anticipated, the facial selectivity was sufficient to be synthetically useful and to examine the feasibility of the transfer of chirality.

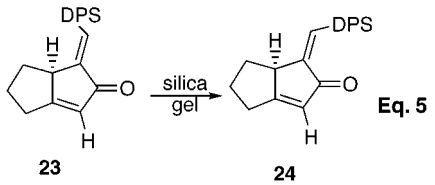
Transfer of Chirality from an Allenyl Silane to an α-Silylidene Cyclopentenone. Chiral alkynyl allene **21** was prepared using a known procedure[6e] and removal of the trimethylsilyl moiety from the terminus of the alkyne was effected using basic conditions to afford

SCHEME 6



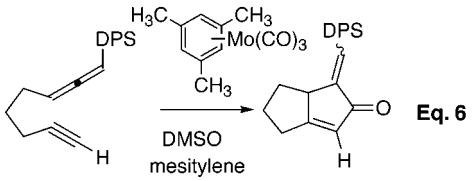
P−K precursor **22** in 70% yield (Scheme 6). The enantiomeric purity of allenyne **21** was determined to be 95% ee by ^{1}H NMR analysis using AgFOD and the chiral shift reagent $Yb(hfc)_3$. Subjection of alkynyl allene **22** to the molybdenum-mediated cycloaddition conditions gave an 8:1 *E*/*Z* mixture of α-silylidene cyclopentenones **23** and **24** in a combined isolated yield of 80%. Approximately 20% of the starting alkynyl allene **22** was recovered. Compounds **23** and **24** were easily separated by silica gel column chromatography and the enantiomeric purity of each isomer was determined.

Compound **23,** resulting from cycloaddition from the least hindered face (cf. Scheme 2) was obtained in 95% enantiomeric excess as determined by ^{1}H NMR analysis using the chiral shift reagent $Eu(hfc)_3$. Thus, the (*E*)-α-silylidene cyclopentenone **23** was obtained with a complete transfer of chirality from the allene to the product. However, for the (*Z*)-α-silylidene cyclopentenone **24**, the enantiomeric purity was only 63% ee. It was postulated that this loss in enantiomeric purity may be a result of an isomerization of the (*E*)-α-silylidene cyclopentenone to the *Z*-isomer during the purification process since our crude *E*/*Z* ratios are higher than our chromatographically pure ratios as determined by ^{1}H NMR and GC. To test this hypothesis, the pure *E*-isomer (>150:1 by GC integration) was subjected to column chromatography. A dramatic decrease in the *E*/*Z* ratio of 13:1 was observed (eq 5). The *Z*-isomer *ent*-**24** obtained in this isomerization possesses the opposite stereochemistry at the stereogenic center as that of **24** (Scheme 6). Thus, it appears that this facile silica gel isomerization process is responsible for the low ee's obtained for the *Z*-isomer **24**. Attempts to purify the crude products by filtering through Florisil or neutral alumina resulted in decomposition of the product, which is attributed to the presence of metal impurities. It is interesting to note that under acidic conditions the (*E*)-silylidene isomerizes to the *Z*-isomer. In contrast the (*Z*)-alkylidene cyclopentenone isomerizes to the *E*-isomer. This isomerization most likely results from an $A^{1,3}$ interaction between the silicon and methylene group α to the ring fusion.



Increasing Facial Selectivity by Changing the Ligands of the Molybdenum Promoter. The molyb-

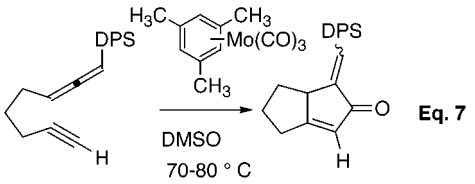
TABLE 2. $Mo(CO)_3$-Mesitylene-Mediated Cycloadditions



Eq. 6

entry	*T* (°C)	time (h)	yield (%)	*E*/*Z*
1	60	7.5	40	10:1
2	80	7.5	58	7:1
3	110	6	39	7:1

TABLE 3. $Mo(CO)_3$-Mesitylene-Mediated Cycloadditions



Eq. 7

entry	solvent	time (h)	yield (%)	*E*/*Z*
1	benzene	6.5	68	6:1
2	toluene	19	35	6:1
3	mesitylene	7.5	58	7:1

denum-mediated cycloaddition requires heating of the reaction solution to >100 °C to effect dissolution of the molybdenum hexacarbonyl. During the course of cycloaddition, the reaction solution becomes bright canary yellow in color. It is assumed at this stage of the reaction that an (η^6-arene) molybdenum tricarbonyl species is formed by the reaction of molybdenum hexacarbonyl with the aromatic solvent. Based upon this assumption, we felt that it might be possible to effect the cycloaddition reaction at a lower temperature and consequently higher facial selectivity by first preparing the (η^6-arene) molybdenum tricarbonyl complex and using this preformed metal complex to effect the cycloaddition. Moreover, it was postulated that a larger arene moiety on the molybdenum may also lead to higher facial selectivities assuming the arene is present on the molybdenum during the course of the cycloaddition process. Thus, the (η^6-mesitylene) molybdenum tricarbonyl complex was prepared[11] and its promotion of the allenic P−K cycloaddition was examined. The (η^6-mesitylene) molybdenum tricarbonyl complex was found to effect the cycloaddition at lower temperature. In a temperature study using the (η^6-mesitylene) molybdenum tricarbonyl complex (eq 6, Table 2), lower temperatures gives rise to a modest increase in the *E*/*Z* ratio (compare entries 1 and 2, Table 2) but at the expense of yield. The mass balance in these reactions consisted largely of starting material. It is also interesting to note that dimethyl sulfoxide is still needed in these reactions even after the (η^6-mesitylene) molybdenum tricarbonyl complex had been formed.

Different aromatic solvents were examined with little change in the *E*/*Z* ratio of the cycloadducts (eq 7, Table 3). However, significantly higher yields were observed when benzene was used as the solvent. On the basis of this brief ligand study, it is conceivable that the (η^6-arene) molybdenum tricarbonyl complex is the active species in the molybdenum hexacarbonyl mediated cycloadditions. In addition, the reactions can be effected at lower temperatures when using the prepared (η^6-arene) molybdenum tricarbonyl complex. However, while the *E*/*Z* ratios are modestly higher, reaction yields are decreased. Finally, the size of the arene moiety on the molybdenum has almost no effect on the *E*/*Z* product ratio, but the smaller arene moiety gives substantially higher yields and faster reaction times at lower temperatures.

(11) Nesmeyanov, A. N.; Krivykh, V. V.; Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1975**, *102*, 185.

Conclusions

We have successfully effected a transfer of chirality from a chiral nonracemic allene to an α-alkylidene and an α-silylidene cyclopentenone. The molybdenum-mediated examples possessing a silyl group on the terminus of the allene show good facial selectivities but isomerization of the (*E*)-silylidene cyclopentenone to the (*Z*)-silylidene cyclopentenone occurs upon purification of these products. Alternatively, an alkyl group on the terminus of the allene undergoes cycloaddition with moderate selectivities but gives products that undergo an isomerization of the (*Z*)-alkylidene cyclopentenone to the (*E*)-alkylidene cyclopentenone when exposed to acidic conditions. Thus, erosion of the enantiomeric excesses is observed for one of the two products as a result of this isomerization. The allenic Pauson−Khand-type cycloaddition has also been effected by first isolating the (η^6-arene) molybdenum tricarbonyl complex, demonstrating for the first time that this is most likely the active complex in the molybdenum-mediated reactions. Attempts to increase the facial selectivity by increasing the size of the arene moiety resulted in a marginal increase in the selectivity at the expense of the yield. Based upon the results, we have concluded that altering the approach for the preparation of nonracemic α-alkylidene cyclopentenones is necessary in order to obtain synthetically useful levels of stereocontrol. These efforts will be described in the future.

Experimental Section

General Methods. Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. Solvents were dried according to established procedures by distillation from an appropriate drying agent under an inert atmosphere. Reactions involving air- or moisture-sensitive reagents or intermediates were performed under argon or nitrogen in glassware that had been flame-dried. Flash chromatography was performed using Merck silica gel 60 (230−400 mesh). All samples were purified by column chromatography and characterized by ^{1}H NMR (270 MHz) and ^{13}C NMR (67.9 M Hz).

(*S*)-3-(Methylsulfonyloxy)-1-undecyne (13). To a solution of (*S*)-1-trimethylsilyl-1-undecyn-3-ol (236 mg, 1.4 mmol) in CH_2Cl_2 at 0 °C were added triethylamine (284 μL, 2.1 mmol) and methanesulfonyl chloride (130 μL, 1.7 mmol). The resulting solution was stirred for 15 min at 0 °C and poured into 1 M HCl, the mixture was extracted with ether, and the combined organic layers were washed with saturated $NaHCO_3$ and dried over $MgSO_4$. Removal of the solvent in vacuo and purification by flash chromatography on silica gel (eluting with 25% EtOAc/hexanes) furnished the title compound **13** (328 mg) in 95% yield: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.16 (dt, J = 6.6, 2.2 Hz, 1H), 3.12 (s, 3H), 2.70 (d, J = 2.2 Hz. 1H), 1.99−1.80

(m, 2H), 1.56−1.42 (m, 2H), 1.38−1.21 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H); MS (GC/MS) *m/z* 175, 148, 133, 121, 95, 93, 79.

(*R*)-1-Trimethylsilyl-6,7-hexadecadien-1-yne (14). To a flask containing anhydrous magnesium chloride (1.25 g, 13.1 mmol) and THF (13 mL) was added potassium metal (978 mg, 25.0 mmol). The mixture was heated to reflux for 2 h and then cooled to rt. During this time, a finely divided black powder is deposited on the walls of the flask. A solution of 1-chloro-5-(trimethylsilyl)-4-pentyne (1.75 g, 10.0 mmol) in THF (10 mL) was added slowly to the mixture, and the reaction was stirred at rt for an additional 25 min. The reaction is a gray-black heterogeneous mixture. The reaction was checked by TLC for the disappearance of the alkyl halide, and then the concentration of the resulting Grignard was found by titration (the Grignard reagent was titrated with menthol in THF and 1,10-phenanthroline according to the literature procedure).[12] Copper(I) bromide (191 mg, 1.33 mmol) and lithium bromide (116 mg, 1.33 mmol) were placed into a flask, dried under vacuum (1 mmHg) with stirring at 130 °C for 3 h, and then cooled to rt under Ar. THF (2 mL) was added to these solids, and the resulting suspension was cooled to −65 °C. The Grignard reagent (5.55 mL, 1.33 mmol, 0.24 M) was added dropwise to the LiBr−CuBr mixture via syringe. The mixture was stirred at −60 °C for 30 min, and then a solution of (*S*)-3-(methylsulfonyloxy)-1-undecyne (**13**) (328 mg, 1.33 mmol) in THF (2 mL) was added dropwise to the organocopper reagent via cannula over 4 min. The reaction was allowed to stir at −60 °C for an additional 15 min and then allowed to slowly warm to rt. The reaction was stirred at rt for 1.5 h, diluted with pentane, and poured into a separatory funnel containing a solution of NaCN (0.5 g) in saturated NH_4Cl (50 mL). After vigorous shaking, the aqueous layer was extracted with pentane. The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed in vacuo (cooled bath to 10 °C) to provide (*R*)-1-trimethylsilyl-6,7-hexadecadien-1-yne **(14)** as a colorless liquid (367 mg, 1.26 mmol, 95%): R_f = 0.27 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.15−5.00 (m, 2H), 2.26 (t, J = 7.1 Hz, 2H), 2.12−1.91 (m, 4H), 1.62 (quint, J = 7.3 Hz, 2H), 1.43−1.20 (m, 12H), 0.88 (t, J = 6.5 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 204.1, 107.1, 91.3, 89.8, 84.4, 31.9, 29.5, 29.3, 29.2, 29.1, 28.9, 28.1, 28.0, 22.7, 19.2, 14.1, 0.12; IR (neat) 2923, 2854, 2175, 1962, 1458, 1249, 1048, 842 cm^{-1}; MS (GC/MS) *m/z* 290, 275, 261, 247, 233, 217; HRMS for $C_{19}H_{34}Si$ calcd 275.2195, obsd 275.2205. The enantiomeric excess was determined as follows: Ag(fod) (2.0 equiv) and Yb(hfc)$_3$ (1.5 equiv) were added to the NMR tube and suspended in $CDCl_3$. 1-Trimethylsilyl-6,7-hexadecadien-1-yne (1.05 equiv) in $CDCl_3$ was the added via syringe. The ^{1}H NMR was then taken, and the enatiomeric excess was determined by the integration of the diastereomeric allenyl proton resonance (integration of the racemic allenyl proton resonance showed a 1:1 ratio). The enantiomeric excess of (*R*)-1-trimethylsilyl-6,7-hexadecadien1-yne (**14**) was determined to be greater than 95% on the basis of this protocol.

(5*S*)-(*E*)-4-Nonylidene-2-(trimethylsilyl)bicyclo[3.3.0]-oct-1-en-3-one (15). To a solution of Cp_2ZrCl_2 (55 mg, 0.19 mmol) in THF (2 mL) at −78 °C under argon was added *n*-butyllithium (0.25 mL of a 1.6 M solution in hexane, 0.40 mmol). Upon completion of addition, stirring was continued at −78 °C for 1 h, and then 1-(trimethylsilyl)-6,7-hexadecadien-1-yne (**14**) (52.4 mg, 0.18 mmol) in THF (0.5 mL) was added. The reaction mixture was warmed to rt over 2 h and then stirred for an additional 4 h, whereupon it was transferred to a sealed tube and cooled to 0 °C. The argon atmosphere in the sealed tube was replaced with CO by partial evacuation under vacuum and then flushed with CO. This process was repeated three times, and then the solution was placed under CO pressure (20 psi) and stirred at 0 °C for 2 h. Air was bubbled into the reaction mixture via a balloon at rt for 20 min with stirring, and the color of the solution turned from orange-red to yellow. HCl (3 M) and pentane were then added. The aqueous layer was extracted with pentane, and the combined extracts were washed with $NaHCO_3$ and brine and then dried over $MgSO_4$. Removal of the solvent in vacuo and purification by flash chromatography on silica gel (eluting with 2% EtOAc/hexane) afforded (5*S*)-(*E*)-4-nonylidene-2-(trimethylsilyl)bicyclo-[3.3.0]oct-1-en-3-one (**15**) (22.4 mg, 39%). The enantiomeric excess was determined as follows. (5*S*)-(*E*)-4-Nonylidene-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-en-3-one (**15**) was diluted in $CDCl_3$ and added to an NMR tube. Eu(hfc)$_3$ diluted in $CDCl_3$ was added via syringe portionwise (0.05−0.1 equiv each portion). An ^{1}H NMR spectrum was taken after each addition until clear resolution was achieved. Analysis of the vinyl proton resonances in the ^{1}H NMR spectrum showed an enantiomeric excess of 85% (12.4:1 ratio): ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.44 (dt, J = 7.7, 2.0 Hz, 1H), 3.30 (dd, J = 12.0, 7.3 Hz, 1H), 2.73−2.46 (m, 2H), 2.33−2.16 (m, 3H), 2.13−2.05 (m, 2H), 1.52−1.39 (m, 2H), 1.26−1.09 (m, 11H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 201.8, 192.7, 139.6, 136.7, 133.1, 50.6, 31.8, 29.8, 29.4, 29.2, 29.1, 28.9, 26.9, 26.1, 22.6, 14.1, −1.1; IR (neat) 2925, 2855, 1694, 1658 cm^{-1}; MS (GC/MS) *m/z* 318 (M^+) 303, 245, 220, 189, 178, 131, 115, 73.

(*S*)-8-(Trimethylsilyl)-6,7-octadien-1-yne (Entry 3, Table 1). General Procedure for the Desilylation of Alkynyl Allenes. (*S*)-8-(Trimethylsilyl)-6,7-octadien-1-yne was prepared by treatment of a solution of (*S*)-1,8-bis(trimethylsilyl)-6,7-octadien-1-yne[13] (661 mg, 2.64 mmol) in wet THF (20 mL) at 0 °C with 3 M KOH/MeOH (1.3 mL, 3.97 mmol) dropwise. The reaction was allowed to warm to rt and stir for 12 h. The reaction was diluted with pentane, and the layers were separated. The aqueous layer was extracted with pentane. The combined organic phase was washed with H_2O and brine and dried over Na_2SO_4 to afford, after silica gel chromatography (pentane), (*S*)-8-(trimethylsilyl)-6,7-octadien-1-yne **(13)** (372 mg, 2.09 mmol, 79%) as a colorless liquid: R_f = 0.60 (pentane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.92 (dt, J = 6.9, 3.6 Hz, 1H), 4.76 (q, J = 6.8 Hz, 1H), 2.24 (dt, J = 7.2, 2.6 Hz, 2H), 2.08 (dq, J = 7.4, 3.7 Hz, 2H), 1.95 (t, J = 2.7 Hz, 1H), 1.62 (quint, J = 7.2 Hz, 2H), 0.09 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 210.0, 83.9, 82.7, 82.3, 68.4, 28.3, 26.7, 17.8, −1.01; IR (neat) 3312, 2956, 2854, 1939 cm^{-1}; HRMS calcd for $C_{11}H_{18}Si$ *m/z* (MH^+) calcd 179.1256, obsd 179.1253.

(*S*)-(*Z*)-4-[(Trimethylsilyl)methylidene]bicyclo[3.3.0]-oct-1-en-3-one (Entry 3, Table 1). General Procedure for the Molybdenum Hexacarbonyl Mediated Cycloaddition. Molybdenum hexacarbonyl (79.3 mg, 0.130 mmol) was weighed into a 10 mL two-neck flask equipped with a reflux condenser in a glovebox under a N_2 atmosphere. DMSO (119 μL, 1.67 mmol) and toluene (2.0 mL) were deoxygenated and then added via cannula to (*S*)-8-(trimethylsilyl)-6,7-octadien-1-yne (29.6 mg, 0.166 mmol). This solution was added to the $Mo(CO)_6$ by cannula. The reaction mixture was heated at 100 °C until there appeared to be no further product formation by TLC. The reaction was cooled to rt, filtered, and then washed with Et_2O through a plug of Celite topped with a thin layer of silica gel. The Et_2O was removed in vacuo, and the crude reaction mixture was purified by flash chromatography on silica gel using a solvent gradient (pentane; 10% ether/pentane) to give (*S*)-(*Z*)-4-[(Trimethylsilyl)methylidene]bicyclo-[3.3.0]oct-1-en-3-one (entry 3, Table 1) (3.0 mg, 0.015 mmol, 9%) as a yellow oil: R_f = 0.44 (10% EtOAc/hexanes); ^{1}H NMR (270 MHz, $CDCl_3$) 6.05−6.02 (m, 2H), 3.33−3.29 (m, 1H), 2.67−2.48 (m, 2H), 2.22−2.04 (m, 4H), 1.27−1.14 (m, 1H), 0.19 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198, 154, 136.5, 126.5, 52.0, 29.1, 26.5, 26.0, −0.8; IR (neat) 2952, 1694, 1613, 1282, 1243, 1158, 1096, 864 cm^{-1}; HRMS calcd for $C_{12}H_{18}OSi$ *m/z* (MH^+) calcd 207.1205, obsd 207.1209.

(*R*)-(*E*)-4-[(Trimethylsilyl)methylidene]bicyclo[3.3.0]-oct-1-en-3-one (Entry 3, Table 1) (12 mg, 0.058 mmol, 35%) as a yellow oil: R_f = 0.27 (10% EtOAc/hexanes); ^{1}H NMR (270 MHz, $CDCl_3$) 6.72 (d, J = 1.5 Hz, 1H), 6.12 (s, 1H), 3.40 (t, J = 9.9 Hz, 1H), 2.67−2.52 (m, 2H), 2.32−2.23 (m, 1H), 2.18−2.03 (m, 2H), 1.24 (quint, J = 10.6 Hz, 1H), 0.20 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 197.0, 185.9, 152.3, 132.0, 125.6,

49.9, 30.0, 26.0, 25.5, −0.68; IR (neat) 2956, 2871, 1695, 1613 cm^{-1}; HRMS calcd for $C_{12}H_{18}OSi$ *m/z* (MH^+) calcd 207.1205, obsd 207.0804.

Three-Step Preparation of 8-(*tert*-Butyldimethylsilyl)-6,7-octadien-1-yne (Entry 4, Table 1). 1-(*tert*-Butyldimethylsilyl)-8-(trimethylsilyl)-octa-1,7-diyn-3-ol. To a flask charged with *tert*-butyldimethylsilylacetylene (1.0 g, 7.1 mmol) and THF (8 mL) at 0 °C was added *n*-BuLi (1.6 M, 4.5 mL, 7.2 mmol) dropwise. The reaction was allowed to stir at 0 °C for 30 min. The reaction flask was cooled to −78 °C, and a solution of 6-(trimethylsilyl)-5-hexynal[14] (1.12 g, 6.65 mmol) in THF (2.5 mL) was added dropwise. The reaction was slowly warmed to rt and stirred for an additional 5 h. The reaction was diluted in Et_2O and poured onto ice−water. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was removed in vacuo and purification by flash chromatography on silica gel (10% ethyl acetate/hexanes) gives **(28)** as a colorless liquid (1.47 g, 4.76 mmol, 72%): R_f = 0.38 (10% EtOAc/hexanes); ^1H NMR (270 MHz, $CDCl_3$) δ 4.43−4.39 (m, 1H), 2.29 (t, J = 6.8 Hz, 2H), 1.86−1.67 (m, 4H), 0.93 (s, 9H), 0.14 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 107.2, 106.8, 87.8, 84.9, 62.3, 36.7, 26.0, 24.2, 19.4, 16.4, 0.10, −4.70, −4.71; IR (neat) 3318, 2955, 2857, 2174 cm^{-1}; HRMS calcd for $C_{17}H_{32}OSi_2$ *m/z* (MH^+) calcd 309.2070, obsd 309.2077.

8-(*tert*-Butyldimethylsilyl)-1-(trimethylsilyl)-6,7-octadien-1-yne (Entry 4, Table 1). To a flame-dried 25 mL round-bottom flask were added triphenylphosphine (381 mg, 1.45 mmol) and THF (3 mL). The flask was cooled to −15 °C (NaCl/ice), and a solution of diethyl azodicarboxylate (254 mg, 1.45 mmol) in THF (3 mL) was added dropwise via syringe. The reaction was alowed to stir for 10 min at −15 °C, and then a solution of 1-(*tert*-butyldimethylsilyl)-8-(trimethylsilyl)octa-1,7-diyn-3-ol (341 mg, 1.11 mmol) in THF (3 mL) was added via cannula over 5 min. The reaction was allowed to stir at −15 °C for 10 min. A solution of *o*-nitrobenzenesulfonyl hydrazine[12] (318 mg, 1.46 mmol) in THF (3 mL) was added via cannula over 5 min. The resulting solution was stirred at −15 °C for an additional 2 h (until TLC indicated the consumption of the alcohol), after which time the reaction was allowed to warm slowly to rt and continue stirring for 18 h. The crude reaction is filtered through a plug of Florisil (pentane) and concentrated in vacuo to furnish 8-(*tert*-butyldimethylsilyl)-1-(trimethylsilyl)-6,7-octadien-1-yne (320 mg, 1.09 mmol) as a pale yellow liquid that can be taken on directly for removal of the trimethylsilyl group. The product can be further purified by flash chromatography on silica gel (pentane): R_f = 0.56 (pentane); ^1H NMR (270 MHz, $CDCl_3$) δ 4.89 (dt, J = 6.8, 3.6 Hz, 1H), 4.74 (q, J = 6.8 Hz, 1H), 2.26 (t, J = 7.1 Hz, 2H), 2.07 (dq, J = 7.5, 3.7 Hz, 2H), 1.61 (quint, J = 7.3 Hz, 2H), 0.89 (s, 9H), 0.14 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 210.8, 107.2, 84.6, 82.2, 79.9, 28.7, 27.0, 26.3, 19.3, 16.9, 0.17, −5.70, −5.80; IR (neat) 2953, 2929, 2856, 2175, 1938, 1650, 1462, 1249, 839 cm^{-1}; HRMS calcd for $C_{17}H_{33}Si_2$ *m/z* (MH^+) calcd 293.2121, obsd 293.2121. 8-(*tert*-Butyldimethylsilyl)-1-(trimethylsilyl)-6,7-octadien-1-yne (320 mg, 1.09 mmol) was subjected to the general procedure for the desilylation of alkynyl allenes to afford, after silica gel chromatography (pentane), 8-(*tert*-butyldimethylsilyl)-6,7-octadien-1-yne (145 mg, 0.659 mmol, 60%, two steps) as a colorless liquid: R_f = 0.65 (pentane); ^1H NMR (270 MHz, $CDCl_3$) δ 4.90 (dt, J = 6.7, 3.5 Hz, 1H), 4.74 (q, J = 6.8 Hz, 1H), 2.23 (dt, J = 7.2, 2.6 Hz, 2H), 2.08 (dq, J = 7.3, 3.6 Hz, 2H), 1.94 (t, J = 2.7 Hz, 1H), 1.63 (quint, J = 7.3 Hz, 2H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 210.8, 84.2, 82.1, 79.9, 68.3, 28.5, 26.9, 26.2, 17.9, 16.9, −5.73, −5.82; IR (neat) 3313, 2951, 2929, 2857, 1939 cm^{-1}; GC/MS *m/z* 220.

4-[(*tert*-Butyldimethylsilyl)methylidene]bicyclo[3.3.0]-oct-1-en-3-one (Entry 4, Table 1). Following the general procedure for the molybdenum hexacarbonyl mediated [2 + 2 + 1] cycloaddition, 8-(*tert*-butyldimethylsilyl)-6,7-octadien-1-yne (64.1 mg, 0.291 mmol) yielded, after purification on flash chromatography on silica gel, the product (*Z*)-4-[(*tert*-butyldimethylsilyl)methylidene]bicyclo[3.3.0]oct-1-en-3-one (5.2 mg, 0.209 mmol, 7%) as a colorless oil [R_f = 0.50 (10% EtOAc/hexanes; ^1H NMR (270 MHz, $CDCl_3$) δ 6.07−6.04 (m, 2H), 3.39−3.32 (m, 1H), 2.70−2.50 (m, 2H), 2.27−2.02 (m, 4H), 1.27−1.17 (m, 1H), 0.92 (s, 9H), 0.23 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.1, 184.7, 155.4, 133.5, 126.8, 52.5, 29.1, 26.4, 25.9, 17.0, −5.61, −6.00; IR (neat) 2952, 2926, 2855, 1696 cm^{-1}; HRMS calcd for $C_{15}H_{24}OSi$ *m/z* (MH^+) calcd 249.1675, obsd 249.1502] and (*E*)-4-[(*tert*-butyldimethylsilyl)-methylidene]bicyclo[3.3.0]oct-1-en-3-one (29.9 mg, 0.120 mmol, 41%) as a colorless oil: R_f = 0.60 (20% EtOAc/hexanes; ^1H NMR (270 MHz, $CDCl_3$) δ 6.78 (d, J = 1.9 Hz, 1H), 6.12 (s, 1H), 3.39 (t, J = 9.8 Hz, 1H), 2.66−2.58 (m, 2H), 2.33−2.23 (m, 1H), 2.17−2.05 (m, 2H), 1.32−1.17 (m, 1H), 0.94 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 196.6, 185.9, 153.1, 129.8, 125.4, 49.9, 30.3, 26.4, 26.0, 25.5, 16.7, −4.92, −5.32; IR (neat) 2945, 2845, 1699, 1612 cm^{-1}; HRMS calcd for $C_{15}H_{24}OSi$ *m/z* (MH^+) calcd 249.1675, obsd 249.1682.]

(*S*)-8-(Phenyldimethylsilyl)-6,7-octadien-1-yne (22). To a solution containing (*S*)-8-(phenyldimethylsilyl)-1-(trimethylsilyl)-6,7-octadien-1-yne **(21)** (270 mg, 0.864 mmol) in wet THF (10 mL) at 0 °C was added 3 M KOH/MeOH (0.86 mL) dropwise. The reaction was allowed to warm to rt and stir for 15 h. The reaction was diluted in pentane, and the layers were separated. The aqueous layer was extracted with pentane. The combined organic phase was washed with H_2O and brine and dried over Na_2SO_4. Removal of the solvent in vacuo (water bath cooled to <15 °C) and purification of the residue by flash chromatography on silica gel, eluting with pentane (R_f = 0.28) afforded (*S*)-8-(phenyldimethylsilyl)-6,7-octadien-1-yne **(22)** (146 mg, 0.607 mmol, 70%) as a colorless liquid: ^1H NMR (270 MHz, $CDCl_3$) δ 7.56−7.53 (m, 2H), 7.37−7.35 (m, 3H), 5.09 (dt, J = 6.8, 3.6 Hz, 1H), 4.83 (q, J = 6.8 Hz, 1H), 2.22 (dt, J = 7.2, 2.6 Hz, 2H), 2.11 (dq, J = 7.2, 3.7 Hz, 2H), 1.96 (t, J = 2.6 Hz, 1H), 1.62 (quint, J = 7.2 Hz, 2H), 0.38 (s, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 211.1, 138.5, 133.7, 129.1, 127.7, 84.3, 82.9, 81.4, 68.4, 28.3, 26.7, 17.8, −2.25, −2.32; IR (neat) 3298, 3071, 2943, 2359, 2109, 1934 cm^{-1}; HRMS calcd for $C_{16}H_{20}Si$ *m/z* (MH^+) calcd 241.1413, obsd 241.1085.

(*R*)-(*E*)-4-[(Phenyldimethylsilyl)methylidene]bicyclo-[3.3.0]oct-1-en-3-one (23) (95% ee) and (*S*)-(*Z*)-4-[(Phenyldimethylsilyl)methylidene]bicyclo[3.3.0]oct-1-en-3-one (23) (63% ee). Following the general procedure for the molybdenum hexacarbonyl mediated cycloadditon. Molybdenum hexacarbonyl (89.9 mg, 0.341 mmol) was weighed into a 10 mL two-neck flask equipped with a reflux condenser in a glovebox under a N_2 atmosphere. DMSO (0.12 mL, 1.69 mmol) and toluene (2.0 mL) were deoxygenated and then added via cannula to (*S*)-8-(phenyldimethylsilyl)-6,7-octadien-1-yne **(22)** (39.9 mg, 0.166 mmol). This solution was added to the $Mo(CO)_6$ by cannula. The reaction mixture was heated at 100 °C until there appeared to be no further product formation by TLC. The reaction was cooled to rt and filtered, washing with Et_2O (15 mL), through a plug of Celite with a thin layer of silica gel on top. The Et_2O was removed in vacuo, and the crude reaction mixture was purified by flash chromatography on silica gel (hexanes, 10%, 20% ethyl acetate/hexanes) to give (*R*)-(*E*)-4-[(phenyldimethylsilyl)methylidene]bicyclo[3.3.0]oct-1-en-3-one **(23)** (31.8 mg, 0.118 mmol, 71%, 95% ee) as a yellow oil and (*S*)−(*Z*)-4-[(phenyldimethylsilyl)methylidene]bicyclo-[3.3.0]oct-1-en-3-one **(23)** (4.0 mg, 0.015 mmol, 9%, 63% ee) as a yellow oil. **(*S*)-(*Z*)-4-[(Phenyldimethylsilyl)methylidene]-bicyclo[3.3.0]oct-1-en-3-one (23):** R_f = 0.41 (10% EtOAc/hexane); ^1H NMR (270 MHz, $CDCl_3$) δ 7.61−7.57 (m, 2H), 7.40−7.34 (m, 3H), 6.15 (s, 1H), 6.05 (s, 1H), 3.36 (m, 1H), 2.72−2.47 (m, 2H), 2.22−2.03 (m, 3H), 1.20 (m, 1H), 0.51 (s,

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3H), 0.48 (s, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 197.9, 185.3, 154.9, 140.2, 134.1, 133.7, 128.6, 127.6, 126.6, 52.1, 28.9, 26.4, 25.9, −1.98, −2.26; IR (neat) 3063, 2945, 2863, 1694, 1608 cm^{-1}; HRMS calcd for $C_{17}H_{20}OSi$ *m*/*z* (MH^+) calcd 269.1362, obsd 269.1323.

(*R*)-(*E*)-4-[(Phenyldimethylsilyl)methylidene]bicyclo-[3.3.0]oct-1-en-3-one (23): R_f = 0.24 (10% EtOAc/hexanes); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56−7.52 (m, 2H), 7.39−7.34 (m, 3H), 6.85 (d, J = 1.8 Hz, 1H), 6.10 (s, 1H), 3.14 (m, 1H), 2.58−2.50 (m, 2H), 1.98−1.81 (m, 3H), 1.13−0.97 (m, 1H), 0.47 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 196.8, 186.2, 153.5, 137.5, 133.9, 129.8, 129.3, 127.9, 125.4, 50.0, 29.8, 26.0, 25.4, −1.53, −1.99; IR (neat) 3063, 2957, 2871, 1691, 1613 cm^{-1}; HRMS calcd for $C_{17}H_{20}OSi$ *m*/*z* (M^+) calcd 268.1283, obsd 268.1283.

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Supporting Information Available: Characterization data and full experimental procedures are provided for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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