Stereochemical Control in Intramolecular Diels–Alder Reactions with Carbene Complexes as Ester Synthons

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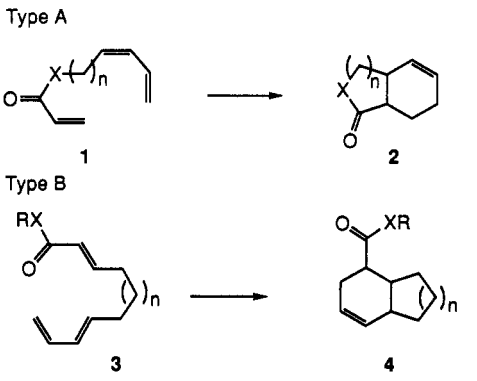
An evaluation of the intramolecular Diels–Alder reactions of Fischer carbene complexes was made for complexes which have an all-carbon tether between the diene and dienophile. Specifically, both the cis- and trans-isomers of the deca-2,7,9-trienyl carbene complexes (**26**-*cis*, **24**-*trans*) and the undeca-2,8,10-trienyl carbene complexes (**27**-*cis*, **25**-*trans*) were prepared and the rates and stereoselectivities of their intramolecular Diels–Alder reactions were in each case compared with those of the known reactions of their corresponding methyl esters. For the deca-2,7,9-trienyl complexes **24** and **26**, the stereoselectivities are comparable to those observed for the Lewis-acid-catalyzed reactions of their corresponding methyl esters and much higher than the thermal reactions of the methyl esters which are completely unselective. The undeca-2,8,10-trienyl complex **25** undergoes intramolecular Diels–Alder reaction with a 93:7 endo/exo selectivity whereas the corresponding methyl ester **7** is known to give a 51:49 selectivity under thermal conditions and to fail with attempts at Lewis acid catalysis. The cis-substituted complex **27** also undergoes a selective reaction where the corresponding reaction of the ester fails. In addition no trace of isomerization of the cis-complex **27** could be observed during its cycloaddition. The triphenylphosphine and isopropoxy complexes **28–30** were prepared, and the stereoselectivity of their intramolecular Diels–Alder reactions is consistent with an s-trans conformation of the vinyl carbene funtionality in the transition state. In all cases the carbene complex cycloadducts can be oxidatively cleaved in high yield to their corresponding esters. The results show that the value of these complexes as synthons for esters is a result of tolerance of the carbene complex functional group to sensitive diene units which do not tolerate traditional Lewis acids utilized in accelerating intramolecular Diels–Alder reactions.

The intramolecular Diels–Alder reaction is an indispensable tool in organic synthesis that is uniformly accepted as standard protocol.[2] The impressive assay of bicylic systems that can be generated by the intramolecular Diels–Alder reaction and the extensive applications of these reactions to natural product synthesis is a function of the large number of configurations for this reaction that have been examined and for which the scope of their tactical applications in synthetic methodology are appreciated. For the purposes of discussion here, these reactions can be divided into two general classes: those in which the alkene and diene units are tethered through the heteroatom of a carbonyl activating group (type A) or those in which the alkene and diene are connected only via carbon atoms (type B). Examples of each class are given in Scheme I in which each class is illustrated by one specific configuration only.

Our interests were drawn to the class of reactions in which there is an all-carbon tether connecting the alkene and diene and specifically to the reactions of the deca-2,7,9-trienyl and the undeca-2,8,11-trienyl esters **5** and **7** indicated in Scheme II. These reactions illustrate one of the limitations that can be encountered in the applications of the intramolecular Diels–Alder reaction: the inability in all cases to achieve high stereoselectivity even under the influence of Lewis acids. The cyclization of the deca-2,7,9-trienyl ester **5** under thermal conditions is not stereoselective giving only a 1.5:1.0 preference for the endo

Scheme I



over the exo cycloadduct but the selectivity for the endo adduct can be made complete if the reaction is accelerated with 0.9 equiv of ethyldichloroaluminum.[3] Such is not the case for the homologated undedeca-2,8,11-trienyl ester **7**. The thermal cyclization of **7** is highly efficient but is completely unselective, and all attempts to affect an increase in selectivity with a number of Lewis acids failed to produce any of the desired cycloadducts but instead lead to only to products of decomposition and/or butadiene polymerization.[4a] Successful Lewis acid mediated asymmetric intramolecular Diels–Alder reactions of chiral oxazolidinone derivatives of **7** have been reported; however, it is unlikely that this chemistry will be applicable to derivatives of the *cis*-ester **58**.[4b] The goal of the work described herein, is to investigate the possibility of

(1) Department of Education GAANN Fellow, 1991–92.

(2) For reviews, see: (a) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. *Natural Products Synthesis Through Pericyclic Reactions*; American Chemical Society: Washington, D.C., 1983; pp 164–191. (b) Cigarek, E., *Org. React.* **1984**, *32*, 1–374. (c) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 187–238. (d) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds., 1991; Vol. 5, pp 513–550.

(3) Roush, W. R.; Gillis, H. R.; Ko, A. I. *J. Am. Chem. Soc.*, **1982**, *104*, 2269.

(4) (a) Roush, W. R.; Hall, S. E. *J. Am. Chem. Soc.* **1981**, *103*, 5200. (b) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.

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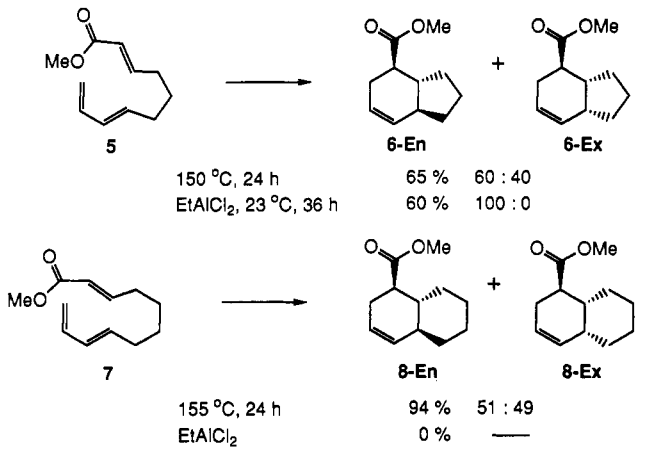
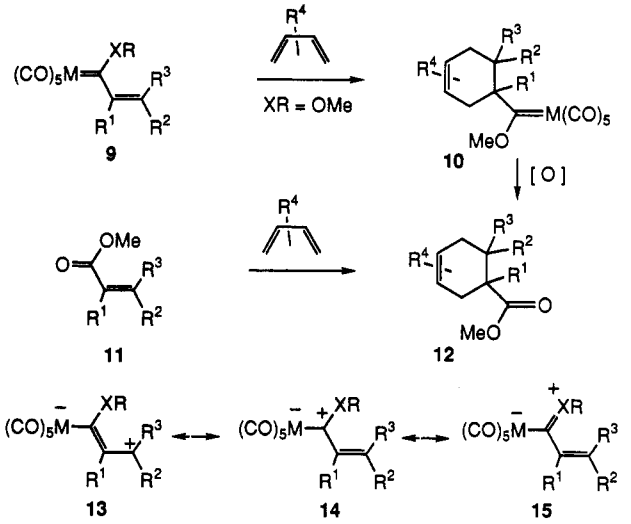
Scheme II



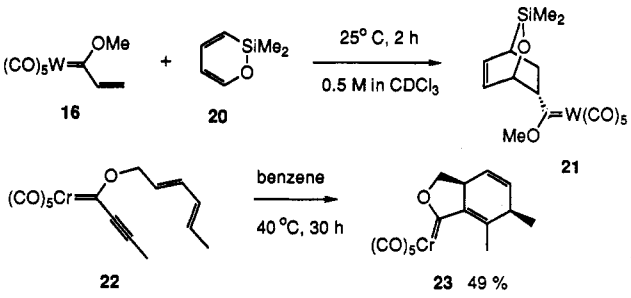
overcoming these types of problems in intramolecular Diels–Alder reactions by employing Fischer carbene complexes as synthons for the ester activating groups in these reactions.[5]

The Diels–Alder reactions of α,β-unsaturated Fischer carbene complexes have been extensively investigated and the metal–carbon doubly-bonded unit is a useful synthon for a number of functional groups, especially carboxylic esters since the cycloadducts can be easily divested of the metal unit in high yields by mild oxidation procedures.[6,7] On the basis of many examples of reactions including a variety of substitution patterns on both the diene and on the carbene complex, it can in general be anticipated that any particular reaction of an α,β-unsaturated carbene complex with a diene will occur with rates and regio- and stereoselectivities that would be associated with those of the Lewis acid-mediated reaction of the corresponding ester (Scheme III). The high reactivity and selectivities of the Diels–Alder reactions of carbene complexes may be associated with the highly polarized metal–carbene-carbon bond which is thought to be a function of the importance of resonance structures of the type **13**–**15** (in addition to **9**). Resonance structure **13** depicts an activation of the double bond due to electronic delocalization into the metal–carbene bond and is analogous to the resonance structures that are invoked to account for the increased reactivity of esters in the Diels–Alder reactions under the influence of Lewis acids. These type of resonance structures also are consistent with the fact that dialkylamino-substituted carbene complexes (XR = R_2N) are less reactive than alkoxy carbene complexes as dienophiles.[7o]

Scheme III



Scheme IV



In effect, carbene complexes are dienophiles with a built in Lewis acid which display the beneficial effect of increased rates and selectivities, but without the deleterious effect of the Lewis acid on sensitive organic functional groups. The latter point is illustrated in the reaction of the vinyl tungsten complex **16** with the silapyran **20** (Scheme IV).[6] This reaction is quantitative at room temperature whereas the corresponding reaction of methyl acrylate with the silapyran **20** fails under thermal conditions as well as with all attempts to accelerate the reaction with a variety of Lewis acids due to the sensitivity of the diene. The high endo selectivity of the Diels–Alder reaction of alkoxy carbene complexes and their tolerance of sensitive functionality foreshadows success in the application of carbene complexes as synthons in the intramolecular Diels–Alder reactions of undeca-2,9,11-trienyl systems of the type **7** in Scheme II.

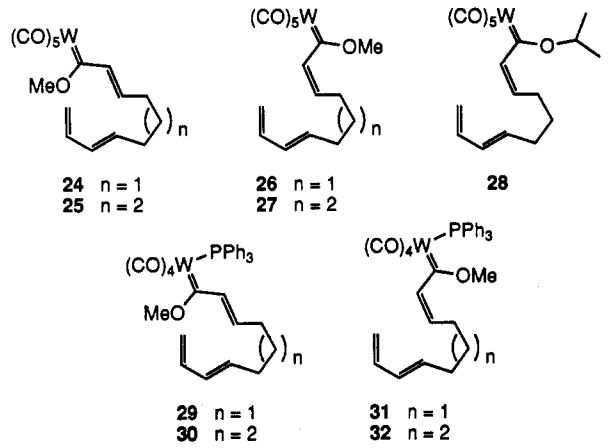
The first example of an intramolecular Diels–Alder reaction of a carbene complex was reported in 1985 for complex **22** where the diene and dienophile are tethered through the oxygen heteroatom of the carbene complex and hence is an example of an intramolecular Diels–Alder reaction of type A indicated in Scheme I.[7c] Since that time there have been a few other reports of intramolecular Diels–Alder reactions of Fischer carbene complexes but

(5) For recent reviews on the chemistry of carbene complexes, see: (a) Dotz, K. H., Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach FL, 1984. (b) Dotz, K. H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587. (c) Dotz, K. H., in H. tom Dieck, A. de Meijere, Eds. *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; Springer: Berlin, 1988. (d) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (e) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press, Inc.: Greenwich, CN, 1989; Vol. 1. (f) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed., Kluwer Academic Publishers: Boston, 1989. (g) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds., Pergamon Press: New York, 1991; Vol. 5.

(6) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. A full account of this work has appeared: (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.

(7) For other examples of Diels–Alder reactions of carbene complexes, see: (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7656. (b) Dötz, K. H.; Kuhn, W., *J. Organomet. Chem.* **1985**, *286*, C23. (c) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (d) Dötz, K. H.; Werner, K.; Mueller, G.; Huber, B.; Alt, H. G. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 812. (e) Paquette, L. A.; Gugelchuk, Y. L.; Hsu, Y. L. *J. Org. Chem.* **1986**, *51*, 3864. (f) Dötz, K. H.; Noack, R.; Müller, G. *J. Chem. Soc. Chem. Commun.* **1988**, 302. (g) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *110*, 2653. (h) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727. (i) Huy, N. H. T.; Mathey, F. *Organometallics* **1988**, *7*, 2233. (j) Dötz, K. H.; Noack, R.; Harms, K.; Mueller, G. *Tetrahecron* **1990**, *46*, 1235. (k) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (l) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413. (m) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (n) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873. (o) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784.

Scheme V



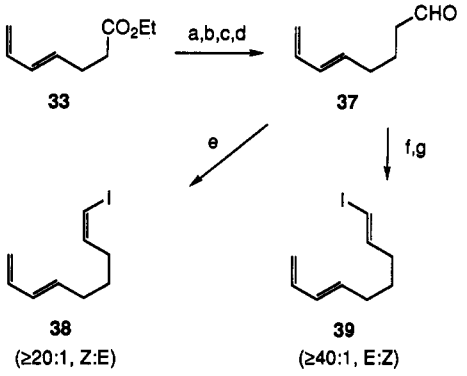
they all are of type A involving tether through the heteroatom of the carbene complex.[7f,j,o] This work was undertaken therefore to provide the first examples of the intramolecular Diels–Alder reactions of Fischer carbene complexes of the type B and to compare the selectivities of these reactions with those that have been reported for their corresponding esters.[9]

The set of carbene complexes that was originally chosen to evaluate the utility of the metal–carbene unit as a synthon in the intramolecular Diels–Alder reaction is shown in Scheme V. Complexes **24–27** were chosen for the purpose of examining the effect of both the ring size and the geometry of the dienophile on the stereoselectivity of the cycloaddition. The isopropoxy and the phosphine-substituted complexes were desired to probe steric effects in the diastereomeric transitions states of the cycloaddition. The metal in each case was deemed best to be tungsten since these complexes display greater thermal stability than either chromium or molybdenum complexes which in part is due to a higher CO dissociation energy.[10] This has direct implications in the likelihood of effecting cycloaddition of cis-substituted dienophiles (**26–28, 31, 32**) without an undersiredisomerization of the dienophiles to their trans-isomers. It has been shown that *cis*-propenyl methoxyl carbene complex of chromium will isomerize slowly to the trans-isomer at room temperature,[11] whereas, the anologous tungsten complex will not begin to isomerize until 70 °C.[6b] As will be discussed, it was in fact possible to prepare and study the reactions of the cis-substituted methoxyl and isopropyloxy complexes, however, the cis-substituted phosphine complexes **31** and **32** could not be isolated but rather isomerized to the trans-complexes during preparation.

Preparation of Carbene Complexes

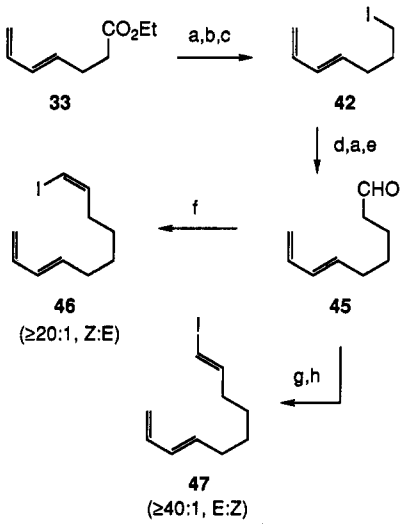
All of the carbene complexes prepared in this work were prepared by the original route of Fischer involving the addition of a organolithium reagent to tungsten hexacarbonyl.[12] The specific strategy involves the use of a vinyllithium reagent that has the trienyl unit intact. For this purpose the vinyl iodides **38, 39, 46,** and **47** were prepared such that the corresponding vinyllithiums could be generated by metal–halogen exchange. While the metal–halogen exchange is expected to stereospecific, this approach relies on the assumption that both the *cis*- and *trans*-vinyl iodides can either be prepared stereoselectively or the stereoisomers can be separated from one another by either analytical or chemical methods. The preparation of these vinyl iodides is summarized in Schemes VI and VII.

Scheme VI[a]



[a] (a) $LiAlH_4$, Et_2O, 0 °C, 70%; (b) CH_3SO_2Cl, Et_3N, CH_2Cl_2, 0 °C; (c) KCN, $EtOH/H_2O$, reflux (80% from ROH); (d) DIBAL, Et_2O, 0 °C, 91%; (e) $Ph_3P(CHI_2)I$, $Na(TMS)_2$, THF, –60 °C, 60% (≥20:1, *Z/E*); (f) $CrCl_2$, CHI_3, THF, 0 °C, 58% (4:1, *E/Z*); (g) NaOH, 1-BuOH, reflux, 80% (≥40:1, *E/Z*).

Scheme VII[a]

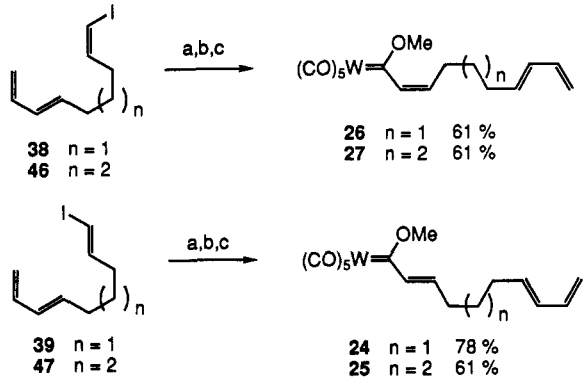


[a] (a) $LiAlH_4$, ET_2O, 0 °C (70%, 85%, respectively); (b) CH_3SO_2Cl, Et_3N, CH_2Cl_2, 0 °C; (c) KI, $EtOH/H_2O$, reflux (75% from ROH); (d) *t*-BuOAc, LDA, HMPA, THF, –78 °C, 85%; (e) ClCOCOCl, DMSO, Et_3N, CH_2Cl_2, –60 °C, 86%; (f) $Ph_3P(CHI_2)I$, $Na(TMS)_2$, THF, –78 °C, 60% (≥20:1, *Z/E*); (g) $CrCl_2$, CHI_3, THF, 0 °C, 60% (4:1, *E/Z*); (h) NaOH, 1-BuOH, reflux, 80% (≥40:1, *E/Z*).

A convenient route to multigram quantities of the nona-1,6,8-trienyl iodides **38** and **39** was accomplished using Roush's approach to aldehyde **37**[3] which serves as a common intermediate on route to both the *cis*- and *trans*-vinyl iodides. The cis-isomer **38** was prepared by using the method of Stork[13] which proved to be quite stereospecific (>20:1, *Z/E*). On the other hand, the synthesis of the trans-isomer **39** proved not to be as stereoselective. Using the procedure of Takai,[14] an inseparable 4:1 mixture of **39**

(8) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 2032.
(9) During the preparation of this manuscript, a related report has been communicated: Müller, G.; Jas, G. *Tetrahedron Lett.* **1992**, *33*, 4417.
(10) (a) Lewis, K. E.; Golden, D. A.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *49*, 3905. (b) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87.
(11) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293.
(12) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 960.
(13) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 2173.

Scheme VIII[a]



[a] (a) *t*-BuLi, THF, −78 °C; (b) $W(CO)_6$, THF, 0 °C; (c) $CH_3OSO_2CF_3$, CH_2Cl_2.

and **38** was obtained in 58% yield. However, enrichment of **39** could be obtained using the technique described by Hayashi[15] to give essentially pure **39** (>40:1, *E*/*Z*). Other known methods for regio- and stereospecific trans-hydrohalogenolysis of terminal alkynes using both Schwartz's reagent[16] and hydroboration[17] proved to be unsuccessful perhaps due to competing reaction at the diene.

The preparation of the one-carbon homologues **46** and **47** was accomplished as outlined in Scheme VII. This synthesis also begins with the ester **33** and the necessary homologation step is accomplished by alkylation of the iodide **42** with *tert*-butyl acetate. The resulting *tert*-butyl ester was reduced with $LiAlH_4$ and then oxidized by the Swern procedure to give aldehyde **45**. This aldehyde was then converted to vinyl iodides **46** and **47** using the same procedures that are described above for **38** and **39** and which also are accompanied with virtually identical stereoselectivity.

With all vinyl iodides now in hand, we prepared carbene complexes **24–27** as shown in Scheme VIII. The appropriate vinyl iodide was trans-metalated at low temperature in THF with *tert*-butyllithium and was then added to a dilute solution of $W(CO)_6$ in THF at 0 °C. After alkylation with methyl triflate followed by standard workup, the carbene complexes were all isolated in good yield as red oils. The cycloaddition of these compounds begins to occur slowly upon standing at room temperature and thus these complexes are best stored in the freezer or used immediately following their preparation. No isomerization of the α,β-unsaturated double bond in the cis-isomers **26** and **27** was detectable and the coupling constant between the H_a and H_b vinyl hydrogens confirmed the stereochemistry in each series (trans J_{HH} = 15.0 Hz, cis J_{HH} = 11.5–11.7 Hz). The isopropyloxy carbene complex **28** was synthesized in 30% yield using the same procedure described above except that isopropyl triflate was used instead of methyl triflate in the final alkylation step. As was the case for the cis-complexes **26** and **27**, no isomerization of the cis-double bond of isopropoxy complex **28** could be detected.

Attempts to prepare the *cis*-vinyl-substituted complexes **31** and **32** with a triphenylphosphine ligand were unsuccessful. The additions of the vinyllithiums generated from the *cis*-iodides **38** and **46** to pentacarbonyl(triphenylphosphine)chromium(0) and subsequent alkylation with methyl triflate proceeded with isomerization of the α,β-unsaturated double bond to give exclusively the *trans*-vinyl carbene complexes **29** and **30** in 49% and 53% yields, respectively. The trans stereochemistry of the products was evident upon inspection of the coupling constants between H_a and H_b (J_{HH} = 15.0 Hz each case). The increased rates for the isomerization of the cis-couble bonds in the phosphine complexes **31** and **32** would not be expected on electronic grounds. Increased rates of isomerization would be expected for complexes with more electron-poor metal centers due to an increase in importance of resonance structures of the type **13** in Scheme III. A related phenomenon has been observed for esters in the presence of strong Lewis acids in work reported by Evans and co-workers in an attempted intermolecular Diels–Alder reaction.[18] Certainly, however, replacement of an σ-electron donating phosphine for a π-electron withdrawing carbon monoxide ligand would be expected to produce a more electron-rich metal center and to a decreased propensity for isomerization due to the fact that resonance structures of the type **13** (Scheme I) would be rendered less important. A reasonable explanation for the isomerization of complexes **31** and **32** may be rationalized in terms of an unfavorable steric interaction between the bulky triphenylphosphine ligand and the α,β-unsaturated carbene ligand (Figure 1). The triphenylphosphine ligand would be expected and was found to be bound to tungsten in a cis disposition with respect to the carbene ligand in the trans complexes **29** and **30** which is revealed by the presence of the three inequivalent CO absorptions in the ^{13}C NMR spectra (see Experimental Section).[19] It is thus reasonable to assume that the cis-*vinyl* phosphine complexes **31** and **32** also had *cis*-phosphine ligands when they were generated. The *cis*-vinyl substituent on the carbene carbon would interact more unfavorably with the phosphine ligand relative to a *trans*-vinyl substituent when adopting the s-cis conformation as shown in Figure 1.

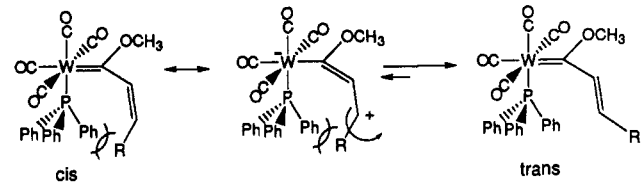


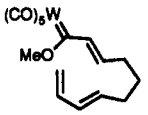
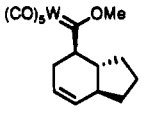
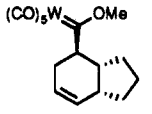
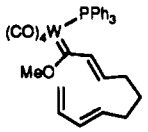
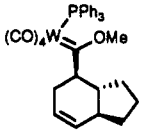
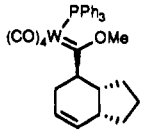
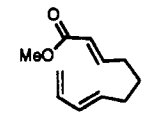
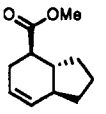
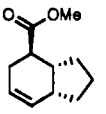
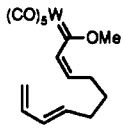
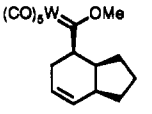
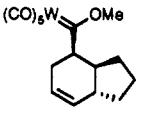
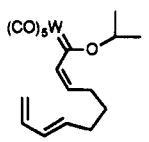
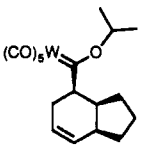
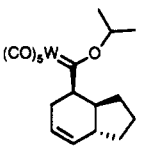
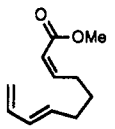
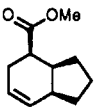
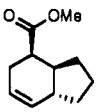
Figure 1.

Thermal Cyclizations

The results of the thermal cyclizations of carbene complexes **24**, **29**, **26**, and **28** are shown in Table I along with the thermal and Lewis acid-catalyzed reactions of the analogous methyl esters. Thermolysis of the trans-substituted complex **24** at 80 °C in benzene (0.005 M) stereoselectively gave the corresponding trans-fused (endo) Diels–Alder adduct **48**-En in 88% isolated yield as a stable yellow solid. Analysis of complex **48** by 500 MHz ^1H NMR showed only one product (≥40:1). The stereochemical

(14) Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.
(15) Hayashi, T.; Kanishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. J. Org. Chem.* **1986**, *51*, 3772.
(16) Haut, D. W.; Blackburn, T. F.; Schwartz, *J. Chem. Soc. Chem. Commun.* **1974**, *97*, 679.
(17) Brown, H. C.; Bowman, D. H.; Umisumi, S. *J. Am. Chem. Soc.* **1967**, *89*, 4531.
(18) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.
(19) (a) Darensbourg, M. Y.; Couder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919. (b) Dobson, G. R.; Paxson, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5925.

Table I. Cycloadditions of Deca-2,7,9-trienyl Carbene Complexes

substrate endo	conditions[a,b]	products endo	products exo	% yield[c]	ratio[d] endo/exo	Ce^{IV} cleavage[e] to esters, %
 **24**	80 °C, 6 h	 **48-En**	 **48-Ex**	88	≥98:2	95 (6-En)
 **29**	50 °C, 72 h	 **49-En**	 **49-Ex**	50 (60)[f]	≥94:6	83 (6-En)
 **5**	150 °C, 24 h $EtAlCl_2$ 23 °C, 36 h	 **6-En**	 **6-Ex**	65 60	60:40[g] 100:0[g]	
 **26**	40 °C, 24 h	 **50-En**	 **50-Ex**	97	45:55[h]	94 (53-En + 53-Ex) (45:55)
 **28**	40 °C, 36 h	 **51-En**	 **51-Ex**	92	24:76[i]	84 (54-En + 54-Ex) (24:76)
 **52**	180 °C, 5 h $EtAlCl_2$ 23 °C, 40 h	 **53-En**	 **53-Ex**	75 27	35:65[g] 48:52[g]	

[a] Conditions for the esters are those reported for optimal stereoselectivity; ref 3. [b] All carbene complex reactions were run in benzene at 0.005 M. [c] Total isolated yields of products purified by chromatography on silica gel. [d] Determined by capillary GC after oxidative conversion to the esters. [e] Aqueous cerric ammonium nitrate, Et_2O, 25 °C, 1 h. [f] Yield based on unrecovered **29**. [g] Reference 3. [h] Determined by ^1H NMR. [i] Isolated as inseparable mixture.

assignment of **48-En** was confirmed by Ce^{IV} oxidative cleavage of the metal unit in 95% yield to give the known indenyl ester **6-En** which was found to be spectroscopically identical to the compound that was previously reported by Roush.[3] The stereoselectivity of the thermal reaction of the *trans*-carbene complex **24** is superior to the thermal intramolecular Diels–Alder reaction of the analogous of the methyl decatrienoate ester **5** which gives a 60:40 mixture of **6-En** and **6-Ex** in favor of the endo product in 60% combined yield.[3] The carbene complex **24** is also far more reactive towards intramolecular cycloaddition than its organic counterpart. For example, cyclization of **24** is complete within 6 h at 80 °C whereas thermolysis of **5** requires 150 °C for 24 h. On the basis of our previous work,[6] it was not surprising to find that complex **24** cyclizes with approximately the same degree of stereoselectivity as the Lewis acid-catalyzed intramolecular reaction in the analogous organic system, which also give exclusively endo product **6-En**, but requires 1.5 days at room temperature for the reaction to go to completion.

Thermolysis of the cis-substituted complex **26** was carried out at 40 °C to avoid possible isomerization of the dienophile stereochemistry[6b,11] and gave both the endo and exo products **50-En** and **50-Ex** as a 45:55 mixture of products in favor of exo in a total of 97% yield. Control experiments have shown that the cycloadducts **50-En** and **50-Ex** are derived from a kinetically controlled process.[20] The complexes **50-En** and **50-Ex** were separated by flash chromatography on silica gel and oxidized independently to the known esters **53-En** and **53-Ex** for which the stereochemistry was assigned by comparison of their spectral data with that which had been previously reported for these esters.[3] Control experiments have shown that epimerization of either ester **53-En** or **53-Ex** does not occur under the oxidation conditions.[21] It is interesting to note that neither the thermal nor Lewis acid-catalyzed reaction of the corresponding *cis*-methyl decatrienoate ester **52** were stereoselective, giving 65:35 and 56:44 mixtures, respectively, in favor of the trans-fused exo product in each case.

The difference in stereoselectivity between the *trans*- and *cis*-carbene complexes **24** and **26** may be explained by

(20) After separation, the endo and exo carbene complexes were each subjected to the conditions of the cyclization and no interconversion was noted.

(21) After separation, the endo and exo esters were each subjected to the conditions of the oxidative workup with cerric ammonium nitrate, and the esters were each recovered unchanged.

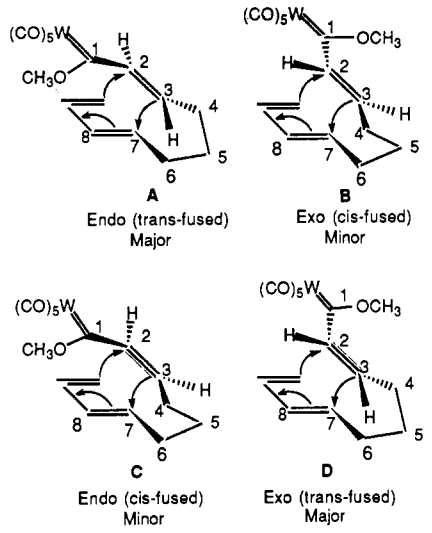


Figure 2.

examination of the transition states giving rise to both endo and exo products. The transition state for these reactions are shown in Figure 2 and, like the transition states that have been proposed for the analogous reactions of the esters **5** and **52**,[3] they include the assumptions that the cycloaddition occurs by way of a concerted mechanism and that carbon–carbon bond formation between the diene and dienophile occurs along a trajectory that is perpendicular to both of the planes containing the π-bonds of the diene and dienophile.[22]

It is observed experimentally that complex **24** cyclizes preferentially through some transition state that gives only the trans-fused endo adduct **48-En**. It is apparent that transition state A is in accordance with the endo rule postulated by Alder and Stein.[23] Although calculations have not been performed on possible secondary orbital overlap stabilization energies of α,β-unsaturated carbene complexes, these energies have been postulated to account for observed endo selectivity in the Lewis acid-catalyzed reactions of organic systems.[24] Theoretical analysis of simple pentacarbonyl carbene complexes of chromium reveal that the LUMO is expected to be largely localized on the carbene carbon.[25] Experimentally this conclusion has been supported by the ESR spectrum of the radical anion of aryl-substituted carbene complexes which show that the unpaired electron is localized on the carbene carbon suggesting that the LUMO of these complexes is also largely localized on the carbene carbon.[26] The presence of possible endo-stabilization due to secondary orbital overlap of the HOMO of the diene with the LUMO of the carbene carbon would certainly energetically favor transition state A relative to B. In addition, the endo transition state would be expected to more energetically accessible due to the presence of an unfavorable nonbonding interaction between the hydrogens at C_4 and the hydrogen at C_8 as they approach one another along the reaction coordinate for the exo-transition state B. This unfavorable interaction has been cited as a contributor to the endo-selectivity of the intramolecular cyclization of the ester **5** and cyclization of related systems.[3]

The lack of stereoselectivity in the cyclization of the *cis*-vinyl carbene complex **26** may be explained by a consideration of the transition states C and D in Figure 2. In transition state C an electronic preference for an endo approach of the dienophile would be present concurrent with the unfavorable nonbonding interaction between C_4-methylene and C_8-H by virtue of the cis stereochemistry in the dienophile. An exo approach in transition state D would not have the unfavorable nonbonding interactions present, but loss of secondary orbital overlap would also be required. With this in mind, we set out to improve the exo-selectivity of **26** by increasing the steric bulk at the heteroatom in hopes of sterically disfavoring endo approach. It is well known in organic systems that increasing steric bulk in the transition state favors exo relative to endo products.[24] We prepared the isopropoxy complex **28** anticipating that the presence of the larger isopropyl group replacing the methyl group in **26** would favor transition state A relative to B, hence increasing the exo-selectivity.

Thermolysis of **28** in benzene gave cycloadducts **51-En** and **51-Ex** in a 24:76 ratio in favor of the exo cycloaddition product **51-Ex** as expected from the considerations discussed above. We anticipated that the even larger triphenylphosphine ligand bound to the metal would favor the exo product to an even greater extent; however, the synthesis of the *cis*-vinyl triphenylphosphine methoxy complex **31** was complicated by isomerism of the double bond on the carbene ligand to give trans-complex **29** as the only isolable product. The Diels–Alder reactions of carbene complexes with phosphine ligands on the metal have not been previously reported; however, it would be expected that the rate of the reaction of the phosphine complex **29** would be slower than the pentacarbonyl complex **24** due to the expected more electron-rich metal center in complex **29** and a consideration of the resonance structures **13–15** in Scheme III. The reaction of **29** is in fact slower than the reaction **24** but not by a great deal. Upon thermolysis of **29** at 50 °C, 72 h were required for 60% conversion to complex **49-En**. The reaction of **24** is complete within 6 h at 80 °C. The analysis of the stereoselectivity was most conveniently carried out after oxidation of the crude reaction mixture to the known ester **6-En** which was shown by capillary GC to be ≥94:6 mixture of endo to exo products. It is interesting that the steric effects of the phosphine ligand in complex **29** plays only a small or negligible role in disfavoring endo relative to exo cyclization and contributes only to a slight loss of reactivity towards cycloaddition.

The fact that the high degree of endo selectivity of the complex **24** is not lost in the phosphine complex **29** can be taken as some indication that these reactions take place via an s-trans conformation of the vinyl carbene complex rather than an s-cis conformation as indicated in transition states E and F in Figure 3. This assumption is supported by the reactions of the *cis*-methoxy complex **26** and the *cis*-isopropoxy complex **28**. Here the increased exo selectivity of the isopropoxy complex **28** could be taken as being consistent with an expected bigger influence of the isopropoxy group on the stereoselectivity for the s-trans

(22) (a) Kikuchi, O. *Tetrahedron* **1971**, *27*, 2791. (b) McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 772. (c) Townsend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190. (d) Boeckmann, R, K., Jr.; Ko, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 7146.

(23) Alder, K.; Stein, G. *Angew. Chem.* **1937**, *50*, 510.

(24) Fleming, I. In *Frontier Orbitals in Organic Reactions*; Wiley: New York, 1976; pp 161–165. Houk, K. N., *Acc. Chem. Res.* **1975**, *8*, 361.

(25) See P. Hoffman in ref 5a.

(26) Krusic, P. J.; Klabunde, U.; Casey, C. P.; Block, T. F. *J. Am. Chem. Soc.* **1987**, *98*, 2015.

(27) Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200.

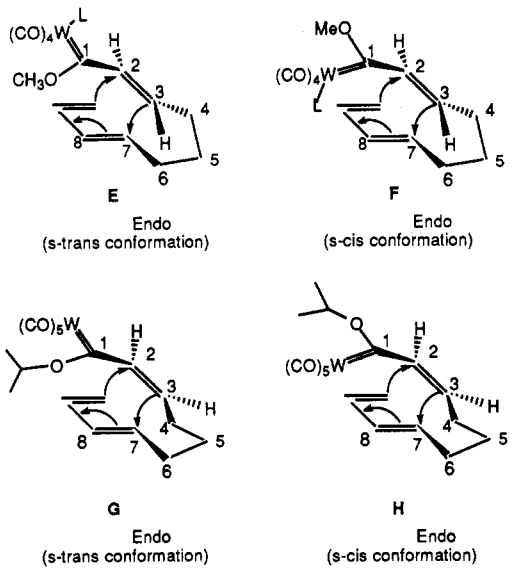


Figure 3.

conformation G than for the s-cis conformation in transition state H. It is unfortunate that the proper control experiment involving the *cis*-vinyl complex **31** with a phosphine ligand could not be carried out. It must be cautioned that present observations are only suggestive that these reactions are occurring via an s-trans conformation of the dienophile; nonetheless, this is an important issue that will be the subject of future investigations.

The intramolecular Diels–Alder reaction of the homologous undeca-2,9,11-trienyl complexes **25**, **30**, and **27** with an extra methylene spacer between the diene and dienophile were examined. The results of our findings are summarized in Table II. The intramolecular Diels–Alder reaction of the *trans*-vinyl carbene complex **25** occurs in high yield and gives a 93:7 selectivity for the endo product **55**-En. This selectivity was determined after oxidative cleavage of the metal and analysis by capillary GC with the aid of authentic samples of **55**-En and **55**-Ex prepared by the thermal intramolecular Diels–Alder reaction of the ester **7** as has been previously described.[4a] The intramolecular Diels–Alder reaction of the trienyl ester **7** has been reported to give an essentially unselective reaction under thermal conditions, and under the influence of Lewis acids the cyclization of **7** has been reported to fail completely leading only to products of decomposition and/or butadiene polymerization. As discussed in the introduction, it was anticipated that the reaction of the carbene complex **25** would be highly stereoselective and succeed where the ester **7** fails due to the tolerance of the carbene complex functional group to sensitive organic functionality. The reaction of the *trans*-vinyl phosphine complex **30** is also stereoselective, but like the complex **29**, its reaction is slower than that of its corresponding pentacarbonyl complex and is also slightly less endo selective.

The *cis*-vinyl carbene complex **27** undergoes complete cycloaddition in benzene (0.005 M) at 40 °C in 48 h to give a 86% yield of a 78:22 mixture of **57**-En and **57**-Ex in favor of the endo product **57**-En. Once again, the stereochemical assignment was confirmed by cerium(IV) oxidation to give the known decalins **59**-En and **59**-Ex in the same ratio of 78:22 and 91% total yield and subsequent comparison of the spectral data of these esters and their retention times by capillary GC with those of authentic samples prepared as previously described for the thermal cyclization of ester

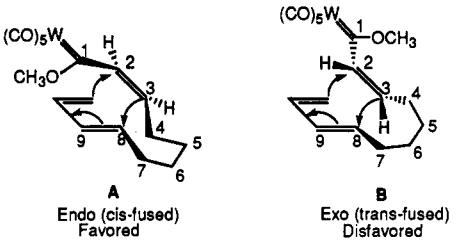


Figure 4.

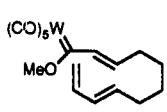
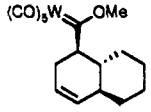
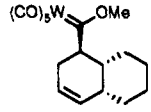
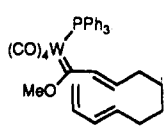
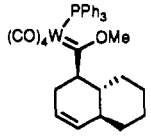
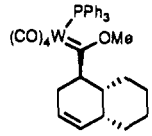
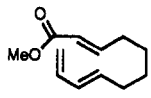
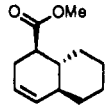
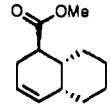
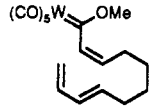
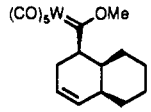
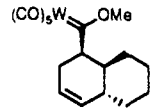
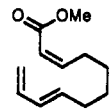
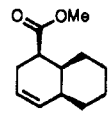
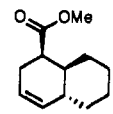
58.[4a] The thermal cyclization of *cis*-trienyl ester **58** requires 45 h at 155 °C to give roughly a 1:1 mixture of the endo and exo cycloadducts.[4a] As was the case for the *trans*-ester **7**, Lewis acid catalysis of the cyclization of the *cis*-ester **58** fails to give any observable products arising from an intramolecular Diels–Alder reaction due to the incompatibility of the substrate with Lewis acids.[4a] To the best of our knowledge, the cycloaddition of complex **27** represents the best stereoselectivity ever observed in this system.

The same type of transition state models used to rationalize the observed endo-selectivity of the complexes reported in Table I can be adapted to the reactions of those complexes in Table II. Secondary orbital interactions seem to control the stereochemical course of the intramolecular reaction of all of the complexes in Table II. For the *cis*-vinyl complex **27** a greater endo selectivity is seen than that for the *cis*-vinyl complex **26** with one less carbon in the tether (Table I). It was also determined by capillary GC with authentic samples of **55**-En and **55**-Ex that less than 0.2% of these compounds are present in the reaction mixture from the thermolysis of **27**, which indicated that virtually no isomerization of the cis-double bond in the dienophile **27** occurs under the reaction conditions. The higher endo selectivity of **27** versus **26** can be explained by a situation where the nonbonding interaction between the C_9-vinyl hydrogen and axial C_4-methylene hydrogen is not as important as in the intramolecular reaction of complex **26** as illustrated for the endo and exo transition state for the reaction of **27** in Figure 4. The boat-like geometry adopted by the tether in transition state A would be predicted to have less severe nonbonding interactions between the methylenes in the tether and the vinyl hydrogen at the C_9 (or C_8)-vinyl hydrogen than in the corresponding transition state C in Figure 2 for the one-carbon shorter tether, and this model has also been utilized to account for related observations in the intramolecular Diels–Alder reactions of esters.[4a]

Summary

The goal of this study was to develop methodology concerning the intramolecular Diels–Alder reactions of alkoxy carbene complexes. The stereochemical aspects of the intramolecular reaction of complexes **24**–**30** were examined. The yields of cycloaddition were excellent and the thermal conditions required to affect cycloaddition were more mild (≤100 °C) than the conditions required to effect cycloaddition of their organic ester analogues. The observed stereoselectivity was far superior to the thermal cycloadditions of the corresponding organic esters and were comparable to those of the Lewis acid-catalyzed reactions of their corresponding esters. High stereoselectivity was observed for the *trans*-undeca-2,9,11-trienyl complex **25** where Lewis acid catalysis fails completely for

Table II. Cycloadditions of Undeca-2,9,11-trienyl Carbene Complexes

substrate endo	conditions[a,b]	products: endo	products: exo	% yield[c]	ratio[d] endo/exo	Ce^{IV} cleavage[e] to esters, %
 **25**	80 °C, 36 h	 **55-En**	 **55-Ex**	87 (97)[f]	93:7	94 (8-En + 8-Ex) (93:7)
 **30**	50 °C, 48 h	 **56-En**	 **56-Ex**	15 (81)[f]	88:12	80 (8-En + 8-Ex) (88:12)
 **7**	150 °C, 45 h $EtAlCl_2$ 23 °C	 **8-En**	 **8-Ex**	94 0	51:49[g] *g*	
 **27**	40 °C, 48 h	 **57-En**	 **57-Ex**	86	78:22[h]	91[i] (**59**-En + **59**-Ex) (78:22)
 **58**	150 °C, 45 h $EtAlCl_2$ 23 °C	 **59-En**	 **59-Ex**	90 00	49:51[g] *g*	

[a] Conditions for the esters are those reported for optimal stereoselectivity; reference 4a. [b] All carbene complexes reactions were run in benzene at 0.005 M. [c] Total isolated yields of products purified by chromatography on silica gel. [d] Determined by capillary GC after oxidative conversion to the esters. [e] Aqueous cerric ammonium nitrate, Et_2O, 25 °C, 1 h. [f] Yield based on unrecovered carbene complex. [g] Reference 4a. [h] Isolated as inseparable mixture. [i] <0.2% trans-isomers 8-En and 8-Ex.

the corresponding ester **7**. The intramolecular Diels–Alder reaction of cis-substituted carbene complexes can also be effected with no detectable isomerization of the cis-double bond of the complex. Facile oxidation of the resulting complexes using cerium(IV) occurred with retention of stereochemistry and all of the corresponding esters were obtained in excellent yields. The origin of stereoselectivity using transition state models were found to be consistent with theoretical considerations and were helpful in achieving greater exo-selectivity in the case of isopropyloxy complex **28**. The potential for the application of this work should be realized in the synthesis of natural products containing carbon frameworks otherwise not obtainable by available intramolecular Diels–Alder methodology.

Experimental Section

Unless otherwise stated, all chemical were obtained from commercial suppliers and used without further purification. Tetrahydrofuran, benzene, and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use. Methylene chloride, diisopropylamine, methyl sulfoxide, and HMPA were distilled from calcium hydride. Elemental analyses were carried out by Galbraith Labs., Inc. Gas chromatography was performed on a Varian STAR 3000 series instrument interfaced with a Spectra-physics Chromjet integrator. A 30 m × 0.32 mm cross-linked fused capillary SE-54 (0.25-μm film) coated column was used with a helium carrier flow of 1.2 mL/min at 20 psi. Flash chromatography was performed with Merck silica gel grade 60, 230–400 mesh.

Ethyl Hepta-4(*E*),6-dienoate (33). This compound was prepared by the procedure of Roush, Gillis, and Ko[3] and purified by distillation under reduced pressure to give **33** as a colorless oil: 31.8 g (70%); bp 115–119 °C (24 mm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, 3 H, J = 7.1 Hz), 2.39–2.41 (m, 4 H), 4.13 (q, 2 H, J = 7.1), 4.98 (d, 1 H, J = 10.2 Hz), 5.10 (d, 1 H, J = 17.2 Hz), 5.66–5.69 (m, 1 H), 6.08 (dd, 1 H, J = 15.2, 10.4 Hz), 6.27 (dt, 1 H, J = 17.0, 10.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.8, 28.4, 34.3, 60.8, 116.1, 132.6, 133.2, 137.5, 173.2; IR (neat) 1735 (vs) cm^{-1}. (This material contained ≤8% of the (*Z*)-butadiene isomer by 500-MHz ^{1}H NMR analysis).

Hepta-4(*E*),6-dienol (34). This compound was prepared from ester **33** by the procedure of Roush, Gillis, and Ko[3] and purified by distillation under reduced pressure to give **34** as a colorless oil: 9.80 g, (90%); bp 115–119 °C (30 mm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66–1.72 (m, 2 H), 2.17–2.21 (m, 2 H), 3.66 (t, 2 H, J = 6.4 Hz), 4.97 (d, 1 H, J = 10.0 Hz), 5.09 (d, 1 H, J = 16.9 Hz), 5.69–5.73 (m, 1 H), 6.07 (dd, 1 H, J = 15.0, 10.4 Hz), 6.29 (dt, 1 H, J = 17.0, 10.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 29.4, 32.6, 62.3, 115.6, 132.0, 135.0, 137.8; IR (neat) 3304 (vs) cm^{-1}.

Hepta-4(*E*),6-dienecarbonitrile (36). This compound was prepared from alcohol **34** via the mesylate **35** by the procedure of Roush, Gillis, and Ko[3] and purified by chromatography on silica gel with EtOAc/hexane (1:1; R_f = 0.70) to give **36** as a colorless oil: 5.48 g, (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55–1.61 (m, 2 H), 2.13–2.16 (m 2 H), 2.35 (t, 2 H, J = 7.0 Hz), 4.98 (t, 1 H, J = 10.2 Hz), 5.10 (d, 1 H, J = 17.0 Hz), 5.62–5.67 (m, 1 H), 6.05 (dd, 1 H, J = 15.1, 11.0 Hz), 6.29 (dt, 1 H, J = 16.9, 10.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 17.0, 25.4, 31.8, 116.6, 120.2, 132.6, 133.4, 137.3; IR (neat) 2252(m) cm^{-1}; mass spectrum, *m/z* (rel inten) 121 M$^+$ (45), 111 (20), 97 (30), 81 (90), 71 (35), 67 (100).

Octa-5(*E*),7-dienal (37). This compound was prepared by a slight modification of the procedure of Roush, Gillis, and Ko.[3] To a stirring solution of 5.48 g (45.0 mmol) of the nitrile **36** in 100 mL of dry hexane under an atmosphere of argon at −70 °C was added 90 mL of 1 M DIBAL (90.0 mmol, in cyclohexane) dropwise over a period of 1 h. This solution was stirred an additional 30 min at this temperature and then at room

temperature for 4 h. The reaction was cooled to 0 °C and quenched by the sequential addition of EtOAc, MeOH, and H_2O. The resulting mixture was diluted with 50 mL of 1 N HCl and stirred at room temperature for 30 min. This mixture was extracted with ether (3 × 30 mL) and the organic extracts were combined, dried over $MgSO_4$, filtered, and concentrated. The crude product was chromatographed on silica gel with CH_2Cl_2 (R_f = 0.50) to give **37** as a colorless oil: 5.08 g, (91%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.74–1.78 (m, 2 H), 2.14–2.17 (m, 2 H), 2.46 (t, 2 H, J = 6.8 Hz), 4.98 (d, 1 H, J = 9.8 Hz), 5.10 (d, 1 H, J = 17.0 Hz), 5.61–5.67 (m, 1 H), 6.05 (dd, 1 H, J = 15.1, 11.0, Hz), 6.29 (dt, 1 H, J = 16.8, 10.1 Hz), 9.74 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.4, 31.7, 43,1, 115.4, 132.0, 134.0, 136.9, 202.3; IR (neat) 3002 (w), 2930 (m), 2878 (w), 1725 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 124 M$^+$ (85), 95 (55), 80 (100), 77 (50), 67 (95), 65 (60). Anal. calcd for $C_8H_{12}O$ m/z 124.0885, measured m/z 124.0931. Alternatively, aldehyde **37** can be prepared by the procedure of Müller and Jas.[9]

Hepta-4(*E*),6-dienyl Iodide (42). To a stirring solution of the mesylate **35** (3.41 g, 17.9 mmol) in 30 mL of 80:20 EtOH–H_2O was added 5.40 g (35.9 mmol) of NaI and the reaction was heated to reflux for 12 h. The reaction mixture was cooled to room temperature, diluted with 100 mL of brine, and extracted with ether (3 × 30 mL). The combined extracts were dried over $MgSO_4$, filtered, and concentrated. The crude reaction mixture was chromatographed on silica gel with hexane (R_f = 0.60) to give **42** as a colorless oil: 3.30 g, (75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91–1.96 (m, 2 H), 2.19–2.23 (m, 2 H), 3.19 (t, 2 H, J = 6.9 Hz), 5.05 (d, 1 H, J = 17.1 Hz), 5.12 (d, 1 H, J = 10.7 Hz), 5.60–5.65 (m, 1 H), 6.09 (dd, 1 H, J = 15.0, 10.6 Hz), 6.29 (dt, 1 H, J = 17.0, 10.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.5, 33.6, 34.0, 116.4, 133.1, 133.3, 137.7; IR (neat) 3007 (m), 2955 (m), 2929 (m) cm^{-1}; mass spectrum, m/z (rel inten) 222 M$^+$ (90), 155 (40), 127 (15), 95 (75), 79 (75), 67 (100). Anal. calcd for $C_7H_{11}I$: C 37.82; H 4.99. Found C 37.69; H 5.05.

***tert*-Butyl Nona-6(*E*),8-dienoate (43).** To a stirring solution of diisopropylamine (700 mg, 6.93 mmol) in 7 mL of THF was added a solution of *n*-butyllithium (3.65 mL, 1.6 M, 6.93 mmol in pentane) at 0 °C under an argon atmosphere. This solution was transferred via cannula to a solution of *tert*-butyl acetate (810 mg, 6.93 mmol) in 10 mL of THF at −78 °C. After 15 min, 0.20 mL of HMPA was added and the reaction mixture was warmed to −40 °C, upon which a solution of iodide **42** (1.54 g, 6.93 mmol) in 10 mL of THF was added dropwise. This resulting solution was gradually warmed to room temperature over a 30-min period and then quenched with 50 mL of H_2O. This mixture was extracted with CH_2Cl_2 (3 × 20 mL). The extracts were combined, dried over $MgSO_4$, filtered, and concentrated. The resulting oil was chromatographed on silica gel with CH_2Cl_2, (R_f = 0.65) to give the *tert*-butyl ester **43** as a colorless oil: 1.33 g, (85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44–1.49 (m, 2 H), 1.45 (s, 9 H), 1.52–1.64 (m, 2 H), 2.08–2.13 (m, 2 H), 2.22 (t, 2 H, J = 7.3 Hz), 4.94 (d, 1 H, J = 10.2 Hz), 5.08 (d, 1 H, J = 16.8 Hz), 5.66–5.70 (m, 1 H), 6.04 (dd, 1 H, J = 15.2, 10.5 Hz), 6.28 (dt, 1 H, J = 17.0, 10.1 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 25.2, 28.7, 29.2, 32.8, 35.9, 80.4, 115.4, 131.9, 135.2, 137.8, 173.4; IR (neat) 3006 (w), 2978 (m), 2932 (m), 1731 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 210 M$^+$ (45), 154 (100), 137 (85), 94 (95), 79 (75), 67 (80). Anal. calcd for $C_{13}H_{22}O_2$: C 74.23; H 10.55. Found C 74.28; H 10.38.

Nona-6(*E*),8-dienol (44). To a cooled suspension (0 °C) of $LiAlH_4$ (250 mg, 6.33 mmol) in THF (10 mL) under an argon atmosphere was added dropwise a solution of the *tert*-butyl ester *43* (1.33 g, 6.33 mmol) in THF (10 mL). The reaction mixture was warmed to room temperature and stirred for 2 h. The mixture was quenched by the sequential addition of EtOAc, MeOH, and H_2O. The mixture was diluted with 1 N HCl and the two layers were separated. The aqueous layer was washed further with ether (2 × 30 mL) and the combined extracts were dried over $MgSO_4$, filtered, and concentrated to give the crude product which was purified by chromatography on silica gel with EtOAc/hexane (1:1, R_f = 0.55) give alcohol **44** as a colorless oil: 840 mg, (95%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39–1.47 (m, 4 H), 1.56–1.61 (m, 2 H), 2.08–2.13 (m, 2 H), 3.64 (t, 2 H, J = 6.6 Hz), 4.94 (d, 1 H, J = 10.0 Hz), 5.07 (d, 1 H, J = 16.7 Hz), 5.65–5.71 (m, 1 H), 6.03 (dd, 1 H, J = 15.3, 10.4 Hz), 6.28 (dt, 1 H, J = 17.0, 10.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 26.1, 29.7, 33.1, 33.2, 62.8, 115.3, 131.7, 135.7, 137.9; IR (neat) 3315 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 140 M$^+$ (20), 122 (75), 107 (45), 93 (85), 80 (100), 67 (95). Anal. calcd for $C_9H_{16}O$: C 77.08; H 11.50. Found C 77.38; H 11.30.

Nona-6(*E*),8-dienal (45).[4a] A solution of oxalyl chloride (0.69 mL, 7.93 mmol) in CH_2Cl_2 (18 mL) under an argon atmosphere was cooled to −60 °C and 1.13 mL (15.86 mmol) of DMSO was added dropwise. This mixture was stirred for 2 min and alcohol **44** (1.01 g, 7.21 mmol) in CH_2Cl_2 (3 mL) was then added dropwise. After stirring for 15 min at −60 °C, triethylamine (5.02 mL, 36.05 mmol) was added. The reaction mixture was gradually warmed to room temperature over a 30-min period upon which 50 mL of distilled H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL) and the combined organic extracts were washed with brine (2 × 30 mL). The pale yellow solution was dried over $MgSO_4$, filtered, and concentrated. The oily residue was loaded onto a silica gel column and eluted with EtOAc/hexane (1:1, R_f = 0.75) to give aldehyde **45** as a colorless oil: 860 mg, (86%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42–1.48 (m, 2 H), 1.58–1.67 (m, 2 H), 2.10–2.13 (m, 2 H), 2.48 (t, 2 H, J = 6.3 Hz), 4.95 (d, 1 H, J = 10.1 Hz), 5.09 (d, 1 H, J = 16.9 Hz), 5.66–5.72 (m, 1 H), 6.06 (dd, 1 H, J = 15.2, 10.4 Hz), 6.28 (dt, 1 H, J = 17.0, 10.7 Hz), 9.73 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$); δ 22.1, 29.2, 32.8, 44.2, 115.5, 132.0, 135.0, 137.8, 202.7; IR (neat) 2970 (w), 2932 (vs), 2858 (s), 2719 (m), 1725 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 138 M$^+$ (35), 111 (40), 94 (65), 84 (80), 79 (100), 67 (95). Anal. calcd for $C_9H_{14}O$ m/e 138.1045; measured 138.1053.

General Procedure for the Conversion of Aldehydes to *cis*-Vinyl Iodides.[13] To a stirring suspension of (iodomethyl)-triphenylphosphine iodide (1.25 equiv) in THF (0.36 M) at room temperature under an atmosphere of argon was added dropwise 1.25 equiv of sodium bis(trimethylsilyl)amide (1.0 M in THF). After stirring for 1 min, the solution was cooled to −60 °C and HMPA (0.1 equiv) was added dropwise followed by cooling to −78 °C. The proper aldehyde was then added dropwise (1.0 equiv) as a THF solution (1.4 M). The cold bath was removed and the reaction mixture was stirred for an additional 45 min with gradual warming. Hexane was added to dilute the solution by 2-fold and the mixture was washed with brine (2x). The hexane layer was dried over $MgSO_4$, filtered, and concentrated. The resulting residue was chromatographed on silica gel with hexane eluent to give the expected *cis*-vinyl iodides. This procedure produced mixtures of *cis*- and *trans*-vinyl iodides that varied from 8:1 to 12:1 in favor of the cis isomer. In each case the pair of isomers were slightly separable on silica gel chromatography and the yields of **38** and **46** reported below referred to purified materials that were enriched to ≥20:1 cis:trans.

Nona-(*Z,E*)-1,6,8-trienyl Iodide (38). Aldehyde **37** (1.63 g, 13.1 mmol) gave *cis*-vinyl iodide **38** (1.76 g, 60%): pale yellow oil, R_f = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53–1.96 (m, 2 H), 2.11–2.19 (m, 4 H), 4.96 (d, 1 H, J = 10.0 Hz), 5.09 (d, 1 H, J = 16.6 Hz), 5.66–5.72 (m, 1 H), 6.04–6.14 (m, 1 H), 6.15–6.20 (m, 2 H), 6.30 (dt, 1 H, J = 9.9, 6.7 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.2, 32.7, 34.9, 83.5, 115.8, 132.2, 135.2, 137.9, 141.6 cm^{-1}; IR (neat) 2970 (w), 2927 (s), 2855 (m) cm^{-1}; mass spectrum, m/z (rel inten) 248 M$^+$ (10), 180 (15), 167 (20), 127 (30), 119 (100), 105 (30), 91 (90), 79 (85), 67 (70).

Deca-(*Z,E*)-1,7,9-trienyl Iodide (46). Aldehyde **45** (200 mg, 1.44 mmol) gave *cis*-vinyl iodide **46** (220 mg, 58%): pale yellow oil, R_f = 0.65; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43–1.55 (m, 4 H), 2.11–2.17 (m, 4 H), 4.95 (d, 1 H, J = 10.0 Hz), 5.08 (d, 1 H, J = 16.7 Hz), 5.66–5.71 (m, 1 H), 6.06 (dd, 1 H, J = 15.0, 10.4 Hz), 6.15–6.20 (m, 2 H), 6.29 (dt, 1 H, J = 17.0, 10.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.2, 29.4, 33.1, 35.3, 83.4, 115.6, 132.0, 135.6, 138.0, 141.84; IR (neat) 2926 (vs), 2855 (s) cm^{-1}; mass spectrum, m/z (rel inten) 262 M$^+$ (5), 180 (15), 167 (80), 135 (90), 127 (85), 93 (100), 77 (80), 67 (95).

General Procedure for the Conversion of Aldehydes to *trans*-Vinyl Iodides.[14] To a stirring solution of $CrCl_2$ (6.00 equiv) in THF (0.57 M) at 0 °C under an atmosphere of argon was added dropwise a solution of the proper aldehyde (1.00 equiv) and CHI_3 (2.00 equiv) in THF (0.14 M). The resulting solution was stirred at 0 °C for 3 h and then poured into 50 mL of H_2O. The dark green solution was extracted with ether (3x) and the combined extracts were dried over $MgSO_4$, filtered, and con-

centrated. The resulting residue was chromatographed on silica gel with hexane as eluent to give the expected *trans*-vinyl iodide. For both **39** and **47** the material obtained at this point contained ~20% of the cis-isomer which could not be separated by chromatography without significant sacrifice of the trans-isomer. The purity of both **39** and **47** could be enhanced to ≥98% if it was refluxed in sodium hydroxide in butanol according to the procedure of Hayashi[15] and obtained in 80% yield based on the total amount of impure material that was used (nearly quantitative recovery of the trans-isomer).

Nona-(*E,E*)-1,6,8-trienyl Iodide (39). Aldehyde **37** (200 mg, 1.44 mmol) gave *trans*-vinyl iodide **39** (860 mg, 60%): pale yellow oil, R_f = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$ δ 1.49–1.55 (m, 2 H), 2.07–2.11 (m, 4 H), 4.96 (d, 1 H, *J* = 10.1 Hz), 5.02 (d, 1 H, *J* = 16.9 Hz), 5.64 (dt, 1 H, *J* = 15.1, 7.3 Hz), 5.97–6.06 (m, 2 H), 6.28 (dt, 1 H, *J* = 17.0, 10.2 Hz), 6.48 (dt, 1 H, *J* = 16.9, 7.1 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.1, 32.0, 35.8, 75.25, 115.5, 131.9, 134.6, 137.4, 146.5; IR (neat) 2969 (w), 2926 (m), 2855 (m) cm^{-1}; mass spectrum *m/z* (rel inten) 248 (5) M$^+$, 180 (70), 121 (100), 93 (90) 79 (95), 67 (95).

Deca-(*E,E*)-1,7,9-trienyl Iodide (47). Aldehyde **45** (200 mg, 1.44 mmol) was converted to *trans*-vinyl iodide **47** (910 mg, 63%) as described in the general procedure: pale yellow oil, R_f = 0.63); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40–1.50 (m, 4 H), 2.05–2.15 (m, 4 H), 4.95 (d, 1 H, *J* = 16.7 Hz), 5.04 (d, 1 H, *J* = 11.3 Hz), 5.67 (dt, 1 H, *J* = 14.8, 7.1 Hz), 5.96 (d, 1 H, *J* = 14.3 Hz), 6.03 (dd, 1 H, *J* = 15.3, 10.7 Hz), 6.29 (dt, 1 H, *J* = 17.0, 10.3 Hz), 6.46 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.6, 29.2, 33.0, 36.6, 75.6, 115.7, 132.0, 135.4, 137.9, 147.0; IR (neat) 2928 (vs), 2854 (m) cm^{-1}; mass spectrum *m/z* (rel inten) 262 (5) M$^+$, 180 (15), 167 (65); 135 (60), 127 (55), 93 (95), 81 (100), 77 (83).

General Procedure for the Preparation of Trienyl Pentacarbonyltungsten Carbene Complexes 24–27. To a cooled solution (−78 °C) of the proper vinyl iodide (1.00 equiv) in THF (0.20 M) under an atmosphere of argon was added dropwise a solution of *tert*-butyllithium (2.00 equiv, 1.7 M in pentane). After 1 h at −78 °C, the solution was transferred via cannula to a 0.05 M solution of tungsten hexacarbonyl (1.10 equiv) in THF at 0 °C. After the addition was complete, the mixture was stirred at 0 °C for an additional 30 min and then room temperature for 2 h. This orange solution was then concentrated on a rotary evaporator and dried under high vaccum (0.01 mm) for 30 min. The residue was then dissolved in ~100 mL of ether and filtered through a plug of Celite. This solution was concentrated and redissolved in CH_2Cl_2 (1.0 M). This solution was cooled (0 °C) and methyl triflate (1.20 equiv) was added. The mixture was gradually warmed to room temperature and stirred for 1 h upon which the solution turned deep red. The reaction was quenched by the rapid addition of saturated $NaHCO_3$ (excess) and the two-phase reaction mixture was transferred to a separatory funnel. After diluting with diethyl ether and discarding the water layer, the ether layer was washed with saturated aqueous $NaHCO_3$ (1x) and brine (2x). The ether layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude reaction mixture was chromatographed on silica gel with hexane as eluent to give the expected carbene complex. Note: Although these complexes are relatively stable to both air and water, they are best stored in the freezer or used immediately since the intramolecular cycloaddition does begin to occur slowly upon standing at room temperature.

[(*E,E*)-Deca-2,7,9-trienyl(methoxy)methylene]pentacarbonyltungsten(0) (24). Vinyl iodide **39** (341 mg, 1.37 mmol) gave complex **24** (521 mg, 78%): deep-red oil, R_f = 0.35, ^{1}H NMR (500 MHz, $CDCl_3$ δ 1.55–1.65 (m, 2 H), 2.13–2.25 (m, 4 H), 4.57 (s, 3 H), 4.98 (d, 1 H, *J* = 10.2 Hz), 5.09 (d, 1 H, *J* = 17.0 Hz), 5.65 (dt, 1 H, *J* = 15.2, 7.7 Hz), 6.05 (dd, 1 H, *J* = 15.1, 6.8 Hz), 6.30 (dt, 1 H, *J* = 16.7, 10.1 Hz), 6.53 (dt, 1 H, *J* = 15.1, 7.6 Hz), 7.17 (d, 1 H, *J* = 15.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$ δ 27.5, 31.9, 32.1, 69.0, 115.2, 131.8, 133.89, 137.0, 141.7, 148.0, 197.5, 203.5, 309.9; IF (neat) 2934 (m), 2066 (vs), 1948 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 488 M$^+$ (^{184}W) (60), 432 (45), 346 (100), 329 (90); 301 (91).

[(*Z,E*)-Deca-2,7,9-trienyl(methoxy)methylene]pentacarbonyltungsten(0) (26). Vinyl iodide **38** (385 mg, 1.01 mmol) gave complex **26** (301 mg, 61%): deep red oil, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52–1.58 (m, 2 H), 2.09–2.14 (m, 2 H), 2.20–2.25 (m, 2 H), 4.60 (s, 3 H), 4.99 (d, 1 H, *J* = 10.1 Hz), 5.09 (d, 1 H, *J* = 16.8 Hz), 5.41 (dt, 1 H, *J* = 11.5, 7.6 Hz), 5.65 (dt, 1 H, *J* = 15.2, 7.5 Hz), 6.05 (dd, 1 H, *J* = 15.1, 10.4, Hz), 6.31 (dt, 1 H, *J* = 16.7, 10.1 Hz), 7.18 (d, 1 H, *J* = 11.7 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.6, 30.1, 32.0, 69.2, 115.3, 131.7, 134.15, 135.0, 137.0, 146.3, 197.3, 203.7, 316.1; IR (neat) 2067 (vs), 1922 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 488 M$^+$ (^{184}W) (55), 432 (30), 404 (50), 387 (55), 374 (55), 346 (100), 331 (95), 301 (95), 268 (40), 238 (25), 91 (55), 79 (55), 67 (53).

[(*E,E*)-Undeca-2,8,10-trienyl(methoxy)methylene]pentacarbonyltungsten(0) (25). Vinyl iodide **47** (272 mg, 1.04 mmol) gave complex **24** (318 mg, 61%): deep red oil, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50–1.55 (m, 4 H), 2.05–2.20 (m, 4 H), 4.59 (s, 3 H), 4.97 (d, 1 H, *J* = 10.1 Hz), 5.09 (d, 1, H, *J* = 16.9 Hz), 5.70 (dt, 1 H, *J* = 15.0, 7.5 Hz), 6.06 (dd, 1 H, *J* = 15.3, 10.7 Hz), 6.31 (dt, 1 H, *J* = 17.2, 10.4 Hz), 6.55 (dt, 1 H, *J* = 15.3, 6.9 Hz), 7.18 (d, 1 H, *J* = 15.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 27.5, 28.6, 32.2, 32.5, 68.9, 114.8, 131.4, 134.9, 137.1, 142.0, 147.9, 197.5, 203.5, 310.1; IR (neat) 2066 (s), 1917 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 502 M$^+$ (^{184}W) (45), 474 (10), 446 (65), 360 (100), 343 (90), 313 (90), 331 (95), 285 (15).

[(*Z,E*)-Undeca-2,8,10-trienyl(methoxy)methylene]pentacarbonyltungsten(0) (27). Vinyl iodide **46** (241 mg, 1.04 mmol) gave complex **27** (318 mg, 61%): deep red oil, R_f = 0.37; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44–1.67 (m, 4 H), 2.10–2.13 (m, 2 H), 2.20–2.23 (m, 2 H), 4.61 (s, 3 H), 4.96 (d, 1 H, *J* = 10.2 Hz), 5.08 (d, 1 H, *J* = 17.2 Hz), 5.42 (dt, 1 H, *J* = 11.5, 7.6 Hz), 5.68 (dt, 1 H, *J* = 14.6, 7.6 Hz), 6.04 (dd, 1 H, *J* = 15.1, 10.9 Hz), 6.30 (dt, 1 H, *J* = 16.9, 10.3 H), 7.17 (d, 1 H, *J* = 11.5 Hz); ^{13}C NMR (500 MHz, $CDCl_3$) V 28.7, 32.2, 32.2, 69.2, 114.9, 130.9, 131.2, 134.7, 135.37, 137.1, 146.2, 197.5, 203.8, 316.2; IR (neat) 2930 (w), 2067 (vs), 1919 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 502 M$^+$ (^{184}W) (45), 446 (20), 418 (60), 401 (100), 360 (55), 345 (90), 315 (90), 280 (80), 157 (15), 67 (23).

Preparation of [(*Z,E*)-Deca-2,7,9-trienyl(isopropyloxy)methylene]pentacarbonyltungsten(0) (28). To a cooled solution (−78 °C) of vinyl iodide **38** (360 mg, 1.45 mmol) in 15 mL of THF under an atmosphere of argon was added dropwise 1.70 mL of a *tert*-butyllithium solution in pentane (1.7 M, 2.90 mmol). After 30 min at −78 °C, the solution was transfered via canula to 560 mg of tungsten hexacarbonyl (1.60 mmol) in 150 mL of THF at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 h. The orange solution was then concentrated on a rotavap and the residue was dissolved in 100 mL of ether and filtered through a pad of Celite. The filtrate was concentrated on a rotory evaporator and dried under high vacuum (0.01 mm) for 30 min. The resulting brown solid was dissolved in 50 mL of CH_2Cl_2 and isopropyl triflate (420 mg, 2.18 mmol) dissolved in CH_2Cl_2 (10 mL) was added dropwise at 0 °C. The resulting solution was stirred for an additional 1 h at room temperature and then quenched by the rapid addition of 50 mL of saturated aqueous $NaHCO_3$. The mixture was transferred to a separatory funnel and the aqueous layer was discarded. The remaining ether layer was washed with brine (1x), dried over $MgSO_4$, filtered, and concentrated on a rotorary evaporator. The crude product was chromatographed on silica gel with hexane as eluent (R_f = 0.30) give 224 mg (30%) of complex **28** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (d, 6 H, *J* = 6.1 Hz), 1.60–1.70 (m, 2 H), 2.08–2.27 (m 4 H), 4.97 (d, 1 H, *J* = 10.0 Hz), 5.10 (d, 1 H, *J* = 16.9 Hz), 5.35 (dt, 1 H, *J* = 11.6, 7.5 Hz), 5.55–5.72 (m, 2 H), 6.08 (dt, 1 H, *J* = 15.0, 11.5 Hz), 6.27 (dt, 1 H, *J* = 15.2, 10.3 Hz), 7.08 (d, 1 H, *J* = 10.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 22.2, 22.6, 29.8, 32.1, 89.1, 115.2, 130.0, 131.7, 134.0, 137.0, 146.3, 197.1, 203.8, 309.5; IR (neat) 2934 (w), 2066 (vs), 1919 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 516 M$^+$ (^{184}W) (55), 488 (15), 473 (20), 460 (20), 387 (100), 359 (95), 331 (90), 301 (70), 121 (25).

Preparation of the Trienyl Tetracarbonyltriphenylphosphinetungsten Carbene Complexes. An identical procedure to that described above for the pentacarbonyl complexes was used except that tungsten pentacarbonyl triphenylphosphine[27] was used instead of tungsten hexacarbonyl. These complexes were purified by flash chromatography on silica gel eluting with a 3:1 mixture of hexane/CH_2Cl_2. These deep reddish-purple oils, although obtained in lower yields than the pentacarbonyl derivatives, are slightly more stable than the pentacarbonyl complexes, and like the pentacarbonyl complexes when obtained

in pure form should be stored in the freezer or used immediately after preparation.

[(*E,E*)-Deca-2,7,9-trienyl(methoxy)methylene]tetracarbonyltriphenylphosphinetungsten(0) (29). Vinyl iodide **38** (300 mg, 1.21 mmol) gave complex **29** (420 mg, 49%: deep reddish-purple oil, R_f = 0.30; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30–1.36 (m, 2 H), 1.70–1.75 (m, 2H), 1.97–2.01 (m, 2 H), 4.34 (s, 3 H), 4.97 (d, 1 H, J = 10.2 Hz), 5.08 (d, 1 H, J = 16.9 Hz), 5.59–5.62 (m, 1 H), 6.00 (dt, 1 H, J = 15.2, 7.2 Hz), 6.29 (dt, 1 H, J = 17.0, 7.1 Hz), 6.83 (d, 1 H, J = 15.0 Hz), 7.25–7.42 (m, 15 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 27.2, 31.6, 31.8, 67.4, 114.9, 128.2 (d, $^2J_{CP}$ = 8.8 Hz), 129.9, 131.5, 132.9, 133.2 (d, $^2J_{CP}$ = 11.5 Hz), 134.2, 135.5 (d, $^2J_{CP}$ = 36 Hz), 137.0, 148.4, 203.3 (d, $^2J_{CP}$ = 6.6 Hz), 206.2 (d, $^2J_{CP}$ = 23.2 Hz), 210.9, (d, $^2J_{CP}$ = 6.6 Hz), 310.2 (d, $^2J_{CP}$ = 5.3 Hz); IR (neat) 2012 (vs), 1885 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 586 [$Ph_3P^{184}W(CO)_5$] (10), 460 [M^+ – 262 (Ph_3P)] (5), 446 (15), 262 (100), 183 (50), 135 (25).

[(*E,E*)-Undeca-2,8,10-trienyl(methoxy)methylene]tetracarbonyltriphenylphosphinetungsten(0) (30). Vinyl iodide **46** (380 mg, 1.45 mmol) gave complex **30** (566 mg, 53%): deep reddish-purple oil, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$ δ 1.25–1.35 (m, 4 H), 1.70–1.80 (m, 2 H), 2.05–2.10 (m, 2 H), 4.35 (s, 3 H), 4.96 (d, 1 H, J = 10.2 Hz), 5.08 (d, 1 H, J = 17.2 Hz), 5.64 (dt, 1 H, J = 15.2, 7.7), 6.02–6.05 (m, 1 H), 6.29 (dt, 1 H, J = 17.0, 6.7 Hz), 6.85 (d, 1 H, J = 15.0 Hz), 7.25–7.42 (m, 15 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 27.3, 28.6, 32.0, 32.2, 67.4, 114.8, 128.2, (d, $^2J_{CP}$ = 9.9 Hz), 129.9, 131.1, 133.2 (d, $^2J_{CP}$ = 11.5 Hz), 133.2, 134.8, 135.5 (d, $^2J_{CP}$ = 38.0 Hz), 137.1, 148.2, 203.2 (d, $^2J_{CP}$ = 6.6 Hz), 206.9 (d, $^2J_{CP}$ = 23.1 Hz), 211.9 (d, $^2J_{CP}$ = 6.6 Hz), 310.3 (d, $^2J_{CP}$ = 6.6 Hz); IR (neat) 2012 s, 1887 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 586 [$Ph_3P^{184}W(CO)_5$] (10), 462 [M^+ – 262 (Ph_3P)] (10), 446 (35), 366 (20), 340 (10), 262 (100), 183 (50), 135 (25).

General Procedure for Thermal Cycloadditions of Trienyl Carbene Complexes. To a flame-dried single-necked round-bottom flask equipped with a threaded vacuum Teflon stopcock and a Teflon-coated stir bar was added the appropriate carbene complex. The carbene complex was dissolved in freshly distilled benzene to make a 0.005 M solution and the mixture was then deoxygenated by the freeze–thaw method (–196 ⇒ 25 °C, three cycles). On the final cycle the flask was backfilled with 1 atm of argon, and after the flask was sealed at 25 °C with the threaded stopcock, the flask was heated at the appropriate temperature. The extent of reaction was monitored by TLC. All aliquots taken from the reaction mixtures were removed under a steady stream of argon flow. After the reactions were complete, the crude mixtures were concentrated on a rotavap, dried under high vacuum (0.01 mm) for 10 min, and then chromatographed on silica gel with the appropriate solvent. Once obtained in pure form, all carbene complex cycloaddition products were extremely stable (<5% decomposition when stored under argon at –30 °C after ~2 years).

[2,3,3aα,4,5,7aα-Hexahydroindenyl-4β-(methoxy)methylene]pentacarbonyltungsten(0) (48-En). Complex **24** (149 mg, 0.305 mmol) was heated in 60 mL of benzene at 80 °C for 5 h. Flash chromatography using hexane/CH_2Cl_2 (4:1) gave 131 mg (88%, R_f = 0.38) of **48-En** as a yellow solid: mp 87–89 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10–1.19 (m, 1 H), 1.23–1.35 (m, 1 H), 1.46–2.00 (m, 7 H), 2.45 (d of multiplets, 1 H, J = 17.4 Hz), 4.23 (td, 1 H, J = 10.6, 5.7 Hz), 4.62 (s, 3 H), 5.56–5.60 (m, 1 H), 5.83 (broad d, 1 H, J = 10.1 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 23.3, 27.1, 28.0, 31.0, 44.4, 47.0, 70.5, 73.9, 125.4, 130.1, 197.4, 203.3, 342–8; IR (neat) 2955 (m), 2871 (w), 2069 (vs), 1920 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 488 M^+ (^{184}W) (65), 432 (45), 376 (38), 374 (40), 348 (95), 346 (100), 329 (95), 301 (75), 91 (45). Anal. calcd for $C_{16}H_{16}O_6{}^{184}W$: C 39.35; H. 3.30. Found C 39.09; H 3.42.

[2,3,3aα,4,5,7aβ-Hexahydroindenyl-4β-(methoxy)methylene]pentacarbonyltungsten(0) (50-Ex) and [2,3,3aα,4,5,7aα-Hexahydroindenyl-4β-(methoxy)methylene]pentacarbonyltungsten(0) (50-En). Complex **26** (199 mg, 0.407 mmol) was heated in 80 mL of benzene at 40 °C for 24 h. The two products could be separated by flash chromatography on silica gel with hexane as eluent to give 106 mg of **50-Ex** (53%, R_f = 0.27) and 88 mg of **50-En** (45%, R_f = 0.22) as yellow solids.[20]

Spectral data for 50-En: mp 67–69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83–0.92 (m, 1 H), 1.42–1.49 (m, 2 H), 1.50–1.58 (m, 1 H), 1.60–1.68 (m, 1 H), 1.80–1.84 (m, 1 H), 1.95 (d of multiplets, 1 H, J = 16.9 Hz), 2.18–2.23 (m, 1 H), 2.43–2.51 (m, 1 H), 2.78 (br s, 1 H), 4.41 (ddd, 1 H, J = 11.7, 5.7, 3.8 Hz), 4.60 (s, 3 H), 5.41 (broad d, 1 H, J = 9.7 Hz), 5.58 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 22.2, 23.4, 24.2, 29.7, 31.0, 40.0, 41.1, 70.3, 70.5, 124.0, 131.7, 197.4, 203.0, 341.1; IR (neat) 2955 (m) 2872 (w), 2068 (vs), 1937 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 488 M^+ (^{184}W) (45), 460 (15), 432 (25), 404 (75), 387 (100), 346 (40), 331 (55), 301 (60). Anal. calcd for $C_{16}H_{16}O_6{}^{184}W$ m/z 488.0456, measured m/z 488.0463.

Spectral data for 50-Ex: mp 93–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84–0.93 (m, 1 H), 1.05–1.17 (m, 1 H), 1.50–1.58 (m, 1 H), 1.63–1.70 (m, 2 H), 1.80–1.85 (m, 1 H), 1.87–1.95 (m, 1 H), 1.97–2.00 (m, 2 H), 2.27 (d of m, 1 H, J = 16.2), 4.59 (s, 3 H), 4.81 (dd, 1 H, J = 8.3, 5.2 Hz), 5.51 (d of multiplets, 1 H, J = 10.1 Hz), 5.85 (d, 1 H, J = 9.8 Hz); ^{13}C NMR (500 MHz, $CDCl_3$) δ 22.2, 26.9, 28.2, 29.7, 40.0, 46.7, 66.4, 70.4, 124.5, 130.5, 197.6, 203.5, 345.1; IR (neat) 2954 (m), 2972 (m), 2068 (vs), 1937 (vs); cm^{-1}; mass spectrum, m/z (rel inten) 488 M^+ (^{184}W) (40), 432 (25), 404 (75), 374 (60), 348 (85), 346 (100), 331 (60), 329 (70), 301 (65). Anal. calcd for $C_{16}H_{16}O_6{}^{184}W$ m/z 488.0456, measured m/z 488.0459.

[2,3,3aα,4,5,7aβ-Hexahydroindenyl-4β-(isopropyloxy)methylene]pentacarbonyltungsten(0) (51-Ex) and [2,3,3aα,4,5,7α-Hexahydroindenyl-4β-(isopropyloxy)methylene]pentacarbonyltungsten(0) (51-En). Complex **28** (125 mg, 241 mmol) was heated in 48 mL of benzene at 40 °C for 36 h. The crude product was purified by flash chromatography on silica gel with hexane to give 114 mg (92%, R_f = 0.38) of **51-Ex** and **51-En** as an inseparable mixture in a ratio of 76:24. Spectral data were collected on the mixture: yellow solid, mp 76–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$) **51-En** δ 4.36 (dt, 1 H, J = 9.5, 2.9 Hz, H α to carbene carbon); **51-Ex** δ 4.70 (dd, 1 H, J = 8.3, 5.2 Hz, H α to carbene carbon); ^{13}C NMR (300 MHz, $CDCl_3$) **51-En** δ 332.9 (carbene); **51-Ex** δ 335.8 (carbene); IR (neat) 2941 (w), 2872 (w), 2067 (s), 1916 (vs) cm^{-1}; mass spectrum, m/z (% rel inten) 516 M^+ (^{184}W) 329 (21), 299 (10), 262 (100), 183 (75), 108 (35). Anal. calcd for $C_{18}H_{20}O_6{}^{184}W$ (mixture): C 41.86; H 3.91. Found C 41.85; H 4.01.

[2,3,3aβ,4,5,7aα-Hexahydroindenyl-4β-(methoxy)methylene]tetracarbonyltriphenylphosphinetungsten(0) (49-En). Complex **29** (240 mg, 330 mmol) was heated in 66 mL of benzene at 50 °C for 72 h. The dark reddish-brown material was chromatographed on silica gel with hexane/CH_2Cl_2 (3:1) to give 120 mg of **49-En** (50% yield, 60% based on unrecovered starting material, R_f = 0.35) as an orange solid and 41 mg of the starting carbene complex **29**. Spectral data for **49-En**: mp 134–136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84–0.95 (m, 1 H), 1.05–1.17 (m, 2 H), 1.63–1.83 (m, 6 H), 2.08 (d of multiplets, 1 H, J = 17.5 Hz), 4.01 (td, 1 H, J = 10.5, 5.5 Hz), 4.36 (s, 3 H), 5.40 (m, 1 H), 5.70 (d, 1 H, J = 9.8 Hz), 7.36–7.47 (m, 15 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 22.3, 27.2, 28.3, 32.0, 44.4, 47.3, 68.7, 72.8, 125.9, 128.3 (d, J_{CP} = 10.0 Hz), 129.9, 130.0, 133.2 (d, J_{CP} = 11.7 Hz), 135.8 9d, J_{CP} = 38.5 Hz), 203.1 (d, J_{CP} = 6.7 Hz), 203.6 (d, J_{Cp} = 6.7 Hz), 206.0 (d, J_{CP} = 21.7 Hz), 210.9 (d, J_{CP} = 6.7 Hz), 340.4 (d, J_{CP} = 6.7 Hz); IR (neat) 2947 (m), 2014 (s), 1885 (s) cm^{-1}; mass spectrum, m/z (rel inten) 460 (M^+ – 262; ^{184}W) (5), 329 (10), 299 (10), 262 (100), 183 (75), 108 (35). Anal. calcd for $C_{34}H_{33}O_5P^{184}W$: C 54.82; H 4.33. Found C 54.43; H 4.46.

[1,2,3,4,4aβ,5,6,8aα-Octahydronaphthyl-5β-(methoxy)methylene]pentacarbonyltungsten(0) (55-En). Complex **25** (89 mg, 177 mmol) was heated in 35 mL of benzene at 80 °C for 36 h. Flash chromatography on silica gel with hexane gave 77 mg of **55-En** (97% based on unrecovered starting material, R_f = 0.31) as yellow solid and 10 mg of the starting carbene complex **25**. Spectral data for **55-En**: mp 91–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85–0.95 (m, 2 H), 1.05–1.07 (m, 1 H), 1.30–1.40 (m, 1 H), 1.50–1.56 (m, 2 H), 1.70–1.79 (m, 3 H), 1.80–1.85 (m, 2 H), 2.30 (d of multiplets, 1 H, J = 15.0 Hz), 4.19 (td, 1 H, J = 10.4, 4.7 Hz), 4.65 (s, 3 H), 5.41 (br d, 1 H, J = 9.7 Hz), 5.57–5.60 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 27.1, 27.4, 30.7, 30.8, 33.5, 42.4, 45.2, 70.9, 74.0, 124.4, 132.6, 197.8, 203.9, 347.0; IR (neat) 2926 (s), 2853 (m), 2069 (vs), 1979 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 502 M^+ (55, ^{184}W), 446 (65), 362 (100), 345 (75), 315 (60), 285 (15), 157 (13), 91 (15); m/z calcd for $C_{17}H_{18}O_6{}^{184}W$ 502.0613, measured 502.0607.

[1,2,3,4,4aα,5,6,8aα-Octahydronaphthyl-5β-(methoxy)methylene]pentacarbonyltungsten(0) (57-En) and [1,2,3,4,-

4aα,5,6,8aβ-Octahydronaphthyl-5β-(methoxy)methylene]-pentacarbonyltungsten(0) (57-Ex). Complex **27** (100 mg, 199 mmol) was heated in 40 mL of benzene at 40 °C for 48 h. The crude product was purified by flash chromatography on silica gel with hexane to give 86 mg (86%, R_f – 0.28) of **57**-En and **57**-Ex as an inseparable mixture (78:22) mixture of yellow solids. Spectral data were collected on the mixture: mp 60–62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64 (s, OCH_3, major), 4.59 (s, OCH_3, minor); ^{13}C NMR (125 MHz, $CDCl_3$) δ 340.1 (carbene), 346.5 (carbene), 203.6 (*trans*-CO) 202.9 (*trans*-CO), 197.4 (*cis*-CO), 197.5 (*cis*-CO); IR (neat) 2928 (m), 2855 (w), 2068 (s), 1916 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 502 M$^+$ – (55, ^{184}W), 474 (15), 446 (30), 418 (55), 401 (100), 362 (35), 360 (37), 343 (45), 315 (60), 280 (25), 67 (20); *m/z* calcd for $C_{17}H_{18}O_6{}^{184}W$ 502.0613, measured 502.0600.

[1,2,3,4,4aβ,5,6,8aα-Octahydronaphthyl-5β-(methoxy)-methylene]tetracarbonyltriphenylphosphinetungsten(0) (56-En). Complex **30** (233 mg, 320 mmol) was heated in 60 mL of benzene for 48 h. The crude product was purified by flash chromatography on silica gel with a mixture of hexane/CH_2Cl_2 (3:1) as eluent to give 35 mg (15%; 81% based on unrecovered starting material, R_f = 0.40) of **56**-En as an orange oil and 187 mg of the starting complex **30**. Spectral data for **56**-En: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95–1.85 (m, 12 H), 3.98 (td, 1 H, *J* = 10.6, 5.4 Hz), 4.37 (s, 3 H), 5.27 (br d, 1 H, *J* = 9.9 Hz), 5.33–5.36 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 26.6, 27.0, 29.9, 30.8, 33.2, 41.9, 44.9, 68.8, 72.5, 124.3, 128.3 (d, J_{CP} = 9.8 Hz), 128.7, 130.0, 133.2 (d, J_{CP} = 9.8 Hz), 136.1 (d, J_{CP} ~30 Hz), 202.8 (d, J_{CP} = 4.9 Hz), 203.7 (d, J_{CP} = 7.3 Hz), 206.5 (d, J_{CP} = 22 Hz), 211.2 (d, J_{CP} = 4.9 Hz), 342.8 (d, J_{CP} = 7.3 Hz); IR (neat) 2926 (m), 2851 (w), 2014 (vs), 1888 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 474 (M$^+$ – 262 (PPh_3)) (5, ^{184}W), 446 (5), 418 (3), 390 (5), 362 (14), 360 (15), 343 (15), 313 (15), 262 (100), 183 (85), 108 (73).

General Procedure for Oxidation of the Carbene Complex Cycloadducts Using Cerium(IV) and the Determination of the Stereoselectivity of the Intramolecular Diels–Alder Reactions of the Trienyl Carbene Complexes. The oxidations were carried out on the cycloadduct carbene complexes that were first grossly purified on silica gel where several fractions were generously included before and after the yellow carbene complex band to ensure that no separation of diastereomeric carbene complexes was affected and such that the ratio of diastereomeric esters corresponds to the ratio of diastereomeric carbene cycloadducts. The appropriate carbene complex cycloadduct was dissolved in diethyl ether (0.15 M) and treated in the presence of air and at room temperature with 6.0 equiv of cerric ammonium nitrate as a 0.50 M stock solution in water containing 2% nitric acid. The two-layer reaction mixture was stirred until the ether layer became colorless (~1 h). The mixture was then diluted with ether (~10 mL) and poured into a separatory funnel. The aqueous layer was separated and washed with ether (1 × 10 mL). The combined ether layers were washed with saturated aqueous $NaHCO_3$ (1 × 10 mL) and brine (1 × 10 mL). The ether layer was then dried over $MgSO_4$, filtered, and concentrated on a rotavap. All crude reaction mixtures were analyzed by capillary GC to determine the stereoselectivity prior to purification of the ester products by flash chromatography.

Methyl 2,3,3aβ,4,5,7aα-Hexahydroindene-4β-carboxylate (6-En). Complex **48**-En (49 mg, 0.10 mmol) was oxidized as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo ratio of **6**-En/**6**-Ex of ≥ 98:2 (30 m DB-5, 135 °C for 1 min and then 5 °C/min to 250 *C*., t_R (major) = 4.42 min; t_R (minor) = 4.55 min). The limits of detection for the exo isomer were set by integration to the largest unknown peak in the GC trace. The mixture was purified by flash chromatography on silica gel with hexane/ether (3:1) to give **6**-En (17.1 mg, 95%) as a colorless oil (R_f – 0.49). The following spectral data for **6**-En matches that which has been previously reported for this compound:[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20–1.25 (m, 2 H), 1.52–1.62 (m, 1 H), 1.70–1.95 (m, 5 H), 2.35–2.40 (m, 2 H), 2.54 (dt, 1 H, *J* = 10.2, 7.2 Hz), 3.68 (s, 3 H), 5.58 (ddd, 1 H, *J* = 9.4, 6.0, 3.0 Hz), 5.82 (br d, 1 H, *J* = 9.6 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.8, 28.1, 29.0, 30.0, 44.2, 45.3, 45.9, 65.8, 125.5, 129.7, 176.1; IR (neat) 2954 (s), 2855 (m), 1740 (vs); mass spectrum, *m/z* (rel inten) 180 M$^+$ (25), 148 (50), 121 (100), 91 (60), 79 (85), 67 (33). Analysis of capillary GC also indicted that the endo/exo ratio was still ≥98:2).

Complex **49**-En (70 mg, 0.097 mmol) was oxidized as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo of **6**-En/**6**-Ex of ≥94:6 where the ^{1}H NMR of the major product matched that of **6**-En.[3] The mixture was purified by flash chromatography on silica gel with hexane/ether (3:1) to give pure **6**-En (14.5 mg, 83%).

Methyl 2,3,3aα,4,5,7aβ-Hexahydroindene-4β-carboxylate (53-Ex) and Methyl 2,3,3aα,4,5,7aα-Hexahydroindene-4β-carboxylate (53-En). A 45:55 mixture (by ^{1}H NMR) of complexes **50**-En and **50**-Ex (47 mg, 0.096 mmol) was oxidized as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo ratio of **53**-En to **53**-Ex of 45:55 (30 m DB-5, 135 °C for 1 min and then 5 °C/min to 250 °C., t_R (major) = 4.50 min; t_R (minor) = 4.80 min). The esters were separated by flash chromatography on silica gel with hexane/ether (3:1) to give samples of both **53**-Ex (9.1 mg, 52%) and **53**-En (7.4 mg, 42%) as a colorless oils whose stereochemistry was assigned on the basis of the spectral data that has been previously reported for these compounds.[3,21] The spectral data for **53**-Ex[3] (R_f = 0.49): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08–1.21 (m, 1 H), 1.40–1.48 (m, 1 H), 1.60–1.62 (m, 1 H), 1.63–1.72 (m, 3 H), 1.85–1.93 (m, 1 H), 2.01–2.06 (m, 1 H), 2.30 (d of multiplets, 1 H, *J* = 16.9 Hz), 2.45 (d of multiplets, 1 H, *J* = 17.8 Hz), 3.00 (dd, 1 H, *J* = 7.1, 4.2 Hz), 3.66 (s, 3 H), 5.57 (d of multiples, 1 H, *J* = 9.7 Hz), 5.84 (br d, 1 H, *J* = 10.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.8, 27.1, 29.0, 29.0, 39.0, 40.4, 44.8, 51.0, 124.9, 130.0, 174.7; IR (neat) 2952 (s), 2954 (s), 2870 (m), 1736 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 180 (15) M$^+$, 148 (40), 120 (100), 91 (55), 79 (90), 67 (40). The spectral data for **53**-En[3] (R_f = 0.53); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40–1.48 (m, 2 H), 1.50–1.60 (m, 3 H), 1.75–1.83 (m, 1 H), 2.14 (br d, 1 H, *J* = 18.0 Hz), 2.26–2.30 (m, 1 H), 2.50–2.58 (m, 1 H), 2.60–2.76 (m, 1 H), 2.81 (dt, 1 H, *J* = 11.8, 4.3 Hz), 3.68 (s, 3 H), 5.40 (br d, 1 H, *J* = 10.4 Hz), 5.59 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 22.5, 28.8, 29.7, 30.7, 44.9, 46.0, 46.6, 52.1, 126.2, 130.4, 176.8; IR (neat) 2951 (s), 2870 (s), 1738 (vs) cm^{-1}; mass spectrum, *m/z* (rel inten) 180 M$^+$ (25), 148 (25), 121 (100), 91 (60), 79 (75), 67 (30).

Isopropyl 2,3,3aα,4,5,7aβ-Hexahydroindene-4β-carboxylate (54-Ex) and Isopropyl 2,3,3aα,4,5,7aα-Hexahydroindene-4β-carboxylate (54-En). An 29:76 (by ^{1}H NMR) mixture of complexes **51**-En and **51**-Ex (125 mg, 241 mmol) was oxidized as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo ratio of esters **54**-En to **54**-Ex of 24:76 (30 m DB-5, 135 °C for 1 min and then 5 °C/min to 250 °C., t_R (major) = 5.57 min; t_R (minor) = 6.07 min). The mixture was purified by flash chromatography silica gel with hexane/ether (3:1) to give **54**-En and **54**-En as an inseparable mixture of colorless oils (84%, 42.2 mg). The assignment of stereochemistry was made on the following spectral data collected on the mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.75 (dt 1 H, *J* = 11.5, 4.5 Hz, minor), 2.92 (dd, 1 H, *J* = 7.1, 4.0 Hz, major); ^{13}C NMR (300 MHz, $CDCl_3$) major isomer δ 175.1 (CO_2-*i*Pr), 129.9, 125.1, 67.3 ($OCHMe_2$); minor isomer δ 174.7 (CO_2-*i*Pr), 131.5, 124.2, 67.2 ($OCHMe_2$); IR (neat) 2936 (m), 2871 (m), 1729 (vs) cm^{-1}; mass spectrum (mixture), *m/z* (rel inten) 208 M$^+$ (20), 166 (60), 148 (50), 121 (100), 91 (60), 79 (88), 67 (50); *m/z* calcd for $C_{13}H_{20}O_2$ 208.1463, measured 208.1469.

Methyl 1,2,3,4,4aβ,5,6,8aα-Octahydronaphthalene-5β-carboxylate (8-En). Complex **55**-En (32 mg, 0.063 mmol) was oxidized as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo ratio 8-En to 8-Ex of 93:7 (30 m DB-5, 135 °C for 1 min and then 5 °C/min to 250 *C*., t_R (major) = 5.69 min; t_R (minor) = 5.95 min). The assignment of the stereochemistry and the retention times on GC were made by comparison of the ^{1}H NMR spectra and GC retention times of authentic samples of 8-En and 8-Ex that were prepared as described in the literature.[4a] The ester **8** was purified from the crude reaction mixture by flash chromatography on silica gel with hexane/ether (3:1) to give 8-En (13.1 mg, 94%) as a colorless oil (R_f = 0.48). Spectral data for 8-En:[4a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05–1.15 (m, 2 H), 1.32–1.42 (m, 2 H), 1.55–1.65 (m, 2 H), 1.75–1.82 (m, 4 H), 2.20–2.30 (m, 1 H), 2.35–2.42 (m, 2 H), 3.67 (s, 3 H), 5.41 (br d, 1 H, *J* = 10.2 Hz), 5.55–5.58 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 26.3, 26.6, 29.5, 30.3, 32.9,

41.4, 42.4, 46.2, 51.3, 124.1, 132.0, 176.5; IR (neat) 2924 (s), 2852 (m), 1736 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 194 (10) M^+, 162 (5), 135 (100), 119 (8), 105 (8), 91 (27), 79 (20), 67 (23).

The phosphine-substituted complex **56**-En (30 mg, 0.041 mmol) was also oxidized to 8-En as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo ratio of 8-En to 8-Ex of 88:12. The ester 8 was purified by flash chromatography on silica gel with hexane/ether (3:1) to give purified mixture of 8-En and 8-Ex in 80% yield (6.3 mg).

Methyl 1,2,3,4,4aα,5,6,8aβ-Octahydronaphthalene-5β-carboxylate (59-Ex) and Methyl 1,2,3,4,4aα,5,6,8aα-Octahydronaphthalene-5β-carboxylate (59-En). A 78:22 mixture (^1H NMR) of complexes **57**-En and **57-Ex** (40 mg, 0.080 mmol) was oxidized as described in the general procedure. Analysis of the crude reaction mixture by capillary GC indicated an endo/exo ratio of **59**-En to **59**-Ex of 78:22 (30 m DB-5, 135 °C for 1 min and then 5 °C/min to 250 °C, t_R (major) = 6.13 min; t_R (minor) = 5.51 min). The assignment of the stereochemistry and the retention times on GC were made by comparison of the ^1H NMR spectra and GC retention times of authentic samples of **59**-En and **59**-Ex that were prepared as described in the literature.[4a] Also with the aid of authentic samples of the esters 8-En and 8-Ex prepared as described in the literature,[4a] it could be determined by capillary GC that the crude reaction mixture contained less than 0.2% of these esters demonstrating that cis-complex **27** does not undergo any detectable isomerization to the trans-complex **25** during the cycloaddition. The esters **59** were purified by flash chromatography on silica gel with hexane to give **59**-En and **59**-Ex as an inseparable mixture (78:22) of colorless oils in 91% yield (13.3 mg, R_f = 0.28). The following spectral data were collected on the mixture of **59**-En and **59**-Ex.[4a] ^1H NMR (500 MHz, $CDCl_3$) **59**-En (major) δ 3.69 (s, OCH_3), 5.39 (br d, 1 H, J = 9.8 Hz, H_7), 5.64–5.67 (m, H_8); **59**-Ex (minor) δ 3.66 (s, OCH_3), 5.40–5.45 (m, 1 H), 5.46–5.59 (m, 1 H, H_8); ^{13}C NMR (500 MHz, $CDCl_3$) **59**-En (major) δ 176.5 (CO_2CH_3), 130.8, 125.4, 51.5 (OCH_3); **59**-Ex (minor) δ 175.2 (CO_2CH_3), 132.0, 124.1, 51.3 (OCH_3); IR (neat) 2925 (vs), 2853 (m), 1736 (vs) cm^{-1}; mass spectrum, m/z (rel inten) 194 M^+ (15), 162 (15), 135 (100), 119 (18), 105 (20), 91 (83), 79 (65), 67 (85).

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