m), 5.55 (1 H, ddd, J_1 = 48 Hz, J_2 = 8 Hz, J_3 = 2 Hz), 3.4–3.8 (2 H, m), 1.2 (9 H, s); ^{19}F NMR −149.3 ppm (m); ^{13}C NMR (ppm) 128–125 (C_{arom}), 93.6 (d, $^1J_{CF}$ = 180 Hz), 73.5 (s, $(CH_3)_3C$), 66.4 (d, $^2J_{CF}$ = 25 Hz), 27.3 (s); MS *m/e* 123 ($PhCHFCH_2^+$), 109 ($PhCHF^+$). Anal. Calcd for $C_{12}H_{17}FO$: C, 73.47; H, 8.67. Found: C, 73.69; H, 8.90. The more polar fraction proved to be 1-fluoro-1-phenyl-3-cyanopropane (**3**), oil, 15% yield: IR 2248 cm^{-1}; ^{1}H NMR (ppm) 7.45–7.24 (5 H, m), 5.59 (1 H, ddd, J_1 = 48 Hz, J_2 = 8 Hz, J_3 = 4 Hz), 2.52 (2 H, dd, J_1 = 15 Hz, J_2 = 9 Hz), 2.28–2.10 (2 H, m); ^{19}F NMR −180.1 ppm (m); ^{13}C NMR (ppm) 136–125 (C_{arom}), 118 (*C*N), 92.05 (d, $^1J_{CF}$ = 172 Hz), 32.7 (d, $^2J_{CF}$ = 26 Hz), 13.2 (s); MS *m/e* 163 (M^+), 143 [$(M - HF)^+$], 109 ($PhCHF^+$). Anal. Calcd for $C_{10}H_{10}FN$: C, 73.62; H, 6.13; N, 8.59; F, 11.66. Found: C, 73.36; H, 6.37; N, 8.42; F, 12.09.

Reaction of *tert*-Butyl Hypofluorite with 1,1-Diphenylethene (4), When 1.8 g of **4** (10 mmol) was reacted with 50 mmol of *tert*-butyl hypofluorite, the less polar compound isolated by chromatography proved to be 1-fluoro-1,1-diphenyl-2-*tert*-butoxyethane (**5**), oil, 70% yield: ^{1}H NMR (ppm) 7.45–7.26 (10 H, m), 3.99 (2 H, d, J = 20 Hz), 1.14 (9 H, s); ^{19}F NMR −152.0 ppm (t, J = 20 Hz); MS *m/e* 252 [$(M - HF)^+$], 195 [$(M - HF - (CH_3)_3C)^+$], 185 (Ph_2CF^+). The compound tends to decompose at room temperature, and no analytically pure sample could be obtained. The more polar fraction proved to be 1-fluoro-1,1-diphenyl-3-cyanopropane (**6**), mp 48 °C, 15% yield: IR 2246 cm^{-1}; ^{1}H NMR (ppm) 7.40–7.27 (10 H, m), 2.86–2.69 (2 H, m), 2.37 (2 H, M); ^{19}F NMR −152 ppm (t, J = 22.5 Hz); MS *m/e* 239 (M^+), 219 [$(M - HF)^+$], 185 (Ph_2CF^+). Anal. Calcd for $C_{16}H_{14}FN$: C, 80.33; H, 5.85; Found: C, 79.87; H, 5.50.

Reaction of *tert*-Butyl Hypofluorite with *trans*-1-Phenyl-1-propene (7), When 0.6 g of **7** (5 mmol) was reacted with the oxidizing solution containing 50 mmol of *tert*-butyl hypofluorite, the only compound isolated by chromatography proved to be 1-fluoro-1-phenyl-2-*tert*-butoxypropane (**8**), oil, 80% yield (60% conversion). This adduct, however, is a 3:1 mixture of the corresponding erythro and threo isomers. For the erythro isomer: ^{1}H NMR (ppm) 7.36–7.27 (5 H, m), 5.24 (1 H, dd, J_1 = 47 Hz, J_2 = 4.5 Hz), 3.85 (1 H, m), 1.1 (9 H, s), 0.96 (3 H, d, J = 8 Hz); ^{19}F NMR −190.5 ppm (dd, J_1 = 47 Hz, J_2 = 16 Hz); ^{13}C NMR (ppm) 128–126 (C_{arom}), 96.6 (d, $^1J_{CF}$ = 192 Hz), 73.8 (s, (CH_3C), 70.6 (d, $^2J_{CF}$ = 25 Hz), 28 (s), 18 (*C*H_3CH, s); MS *m/e* 190 [$(M - HF)^+$], 133 [$(M - Ph)^+$], 109 ($PhCHF^+$). Anal. Calcd for $C_{13}H_{19}FO$: C, 74.29; H, 9.05; F, 9.05. Found: C, 74.09; H, 9.08; F, 8.64. For the minor threo isomer: ^{1}H NMR (ppm) 5.19 (1 H, dd, J_1 = 46 Hz, J_2 = 6 Hz); ^{19}F NMR −182.3 ppm (dd, J_1 = 46 Hz, J_2 = 13 Hz); ^{13}C NMR (ppm) 95.5 (d, $^1J_{CF}$ = 185 Hz), 69.4 (d, $^2J_{CF}$ = 25 Hz), 19.6 (CH_3CH, s).

Reaction of *tert*-Butyl Hypofluorite with Acenaphthylene (9), When 1.5 g of **9** (10 mmol) was reacted with the oxidizing solution containing 50 mmol of *tert*-butyl hypofluorite, the only product isolated by chromatography proved to be *threo*-1-fluoro-2-*tert*-butoxyacenaphthene (**10**), oil, 90% yield (60% conversion); ^{1}H NMR (ppm) 7.79–7.37 (6 H, m), 6.2 (1 H, dd, J_1 = 54 Hz, J_2 = 1.5 Hz), 5.54 (1 H, dd, J_1 = 22 Hz, J_2 = 1.5 Hz), 1.45 (9 H, s); ^{19}F NMR −173.7 ppm (dd, J_1 = 54 Hz, J_2 = 22 Hz); ^{13}C NMR (ppm) 128–120 (C_{arom}), 102.6 (d, $^1J_{CF}$ = 182 Hz), 80.7 (d, $^2J_{CF}$ = 26 Hz), 75.1 (s, $(CH_3)_3C$, 28.5 (s); MS *m/e* 244 (M^+), 187 [$(M - (CH_3)_3C)^+$]. Anal. Calcd for $C_{16}H_{17}FO$: C, 78.69; H, 6.97; F, 7.79. Found: C, 78.13; H, 6.41; F, 7.60.

Acknowledgment. We thank Professor Kazuo Nakamoto for helpful discussions of the infrared spectrum of *tert*-butyl hypofluorite. The Israeli authors wish to acknowledge the financial support of the USA–Israel Binational Science Foundation (BSF), Jerusalem, Israel, under Grant No. 89-00079. The research at Argonne was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under Contract W-31-109-Eng-38.

Metal-Promoted Higher-Order Cycloaddition Reactions. Stereochemical, Regiochemical, and Mechanistic Aspects of the [6π + 4π] Reaction

James H. Rigby,* Humy S. Ateeq, Nelly R. Charles, Stephane V. Cuisiat, Mark D. Ferguson, James A. Henshilwood, A. Chris Krueger, Cyprian O. Ogbu, Kevin M. Short, and M. J. Heeg[†]

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received August 24, 1992*

Abstract: Transition-metal-promoted higher-order cycloaddition reactions are described. (η^6-1,3,5-Cycloheptatriene)tricarbonylchromium(0) and various substituted derivatives undergo photochemically or thermally initiated [6π + 4π] cycloaddition with a range of substituted butadiene partners. Electron-rich and electron-deficient dienes participate equally well in the transformation, and in every case examined only the endo diastereomer was produced. The reaction displays little regioselectivity for 2- and 3-substituted cycloheptatriene complexes; however, most yields of products exceed 85%. Chiral auxiliaries appended to the diene partner can provide very good stereoinduction in the resultant bicyclo[4.4.1]undecane adducts. Tropone and 1-substituted tropone complexes also undergo photoinduced cycloadditions with hydrocarbon dienes but not with oxygen-substituted partners. Azepine and thiepin 1,1-dioxide complexes engage dienes to provide high yields of the corresponding heterocyclic adducts. Molybdenum- and tungsten-based complexes are inferior to Cr(0) complexes as 6π partners in the [6 + 4] cycloaddition, and tungsten has been totally ineffective for promoting the cycloadditions studied to date. Possible mechanistic schemes are presented, and the implications of each are discussed with regard to the scope and limitations of the cycloaddition reaction. Optimization of the reaction conditions on the basis of the aspects of these mechanisms is also outlined. The [6 + 4] cycloaddition of cycloheptatrienechromium(0) complexes can also be effected by heating in various ether solvents, and the cycloadducts produced in this fashion are identical in all respects with those prepared photochemically. The [6 + 4] reaction can also be carried out with modest efficiency employing only catalytic quantities of chromium(0) catalysts.

Introduction

The application of so-called higher-order cycloaddition reactions (i.e., those involving 6π + 4π, 4π + 4π, and 6π + 2π combinations (Figure 1)) to problems in organic synthesis has been of relatively limited scope, although most known examples of these transformations exhibit many features that are considered attractive from a synthetic perspective.[1] In general, higher-order cycloaddition reactions proceed with very high levels of predictable stereoselectivity and can accommodate substantial functionalization in the participating addends. Furthermore, these processes are in-

---

[†] Address inquiries regarding X-ray structures to this author.

(1) For recent reviews of higher-order cycloaddition chemistry as applied to synthesis, see: (a) Hosomi, A.; Tominaga, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 593–615. (b) Rigby, J. H. *Ibid.*; Vol. 5, pp 617–643. (c) Wender, P. A.; Siggel, L.; Nuss, J. M. *Ibid.*; Vol. 5, pp 645–673.

0002-7863/93/1515-1382$04.00/0

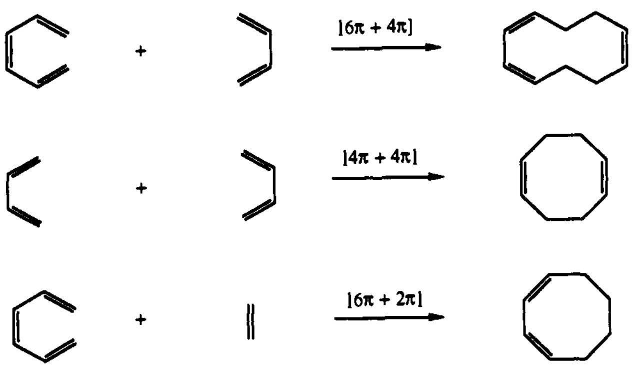
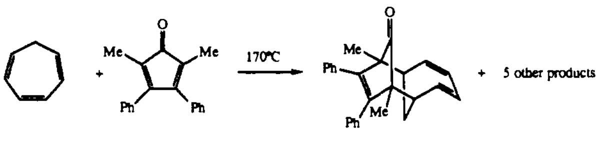


Figure 1. Generalized examples of typical higher-order cycloaddition reactions.

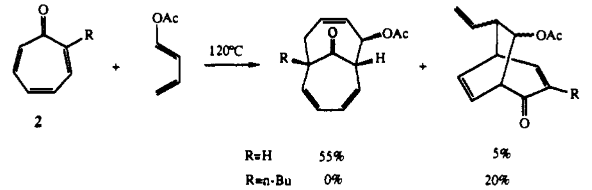
variably characterized by an attendant rapid increase in molecular complexity. In spite of these important attributes, this chemistry has attracted little attention for synthetic applications because of low chemical yields stemming from a general absence of periselectivity. The interaction of the extended π-arrays that distinguishes these processes usually gives rise to multiple, competitive reaction pathways that result in a plethora of products. The thermal reaction of cycloheptatriene with 2,5-dimethyl-3,4-diphenylcyclopentadienone illustrates this phenomenon quite well.[2] At least six distinct products were isolated from this transformation, including the [6 + 4] adduct 1 (eq 1). Although produced

 (1)

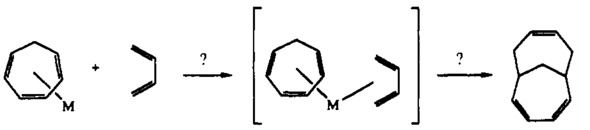
1

in only modest amounts, this higher-order adduct was formed exclusively as the exo diastereomer. This sense and degree of stereoselectivity is typical of most higher-order cycloadditions.

Tropone (2, R = H) has emerged as one of the more effective 6π participants in higher-order cycloaddition reactions.[3,4] Yields of [6 + 4] adducts in excess of 50% can often be obtained with simple diene partners; however, minor structural variations in either component[3c–e] suppress the higher-order pathway and severely restrict the synthetic utility of these transformations.[3c] Non-hydrogen substituents at bond-forming centers in the 6π component completely inhibit the higher-order pathway, as shown in eq 2.[3e]

 (2)

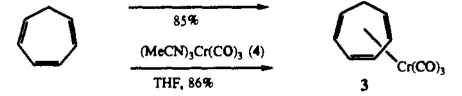
In light of the considerable synthetic potential that higher-order cycloadditions would offer with improved chemical efficiency, we embarked on a systematic examination of possible general solutions to this problem. The use of transition-metal templates represented a particularly intriguing strategy for addressing these issues. It was envisioned that an appropriate transition metal could serve to precomplex both addends, thereby rendering the reaction temporarily intramolecular in nature (eq 3). At the outset of

 (3)

this investigation, it was not at all obvious that the desired higher-order pathway would necessarily be the principal beneficiary of this tactic, since relatively little was known about the influence of metals on the course of higher-order cycloadditions at the time.

The concept of metal-promoted cycloaddition has been the subject of occasional study for a number of years. Pettit and co-workers were among the earliest investigators to recognize the potential of this approach for successfully effecting otherwise difficult conversions.[5a,b] The actual implementation of synthetically viable examples, however, has been relatively rare. In recent years a number of cycloaddition processes mediated by various transition metals have surfaced.[5] An important development in the area of higher-order cycloadditions as applied to synthesis has been the work of Wender and co-workers, who have explored the nickel-facilitated intramolecular [4π + 4π] cycloaddition reaction.[6] This chemistry has proven to be particularly effective and has been applied to a range of natural product targets. In terms of [6 + 4] cycloaddition reactions, reports of chromium(0)-mediated transformations from the Kreiter laboratory were particularly significant.[7] These investigators have demonstrated over a number of years that photochemically initiated [6 + 4] cycloadditions between a number of cyclic hydrocarbon (triene)tricarbonylchromium(0) complexes and simple diene partners could be effected in modest yields. With this fundamental precedent in hand, a thorough investigation of the cycloadditions of (η-1,3,5-cycloheptatriene)tricarbonylchromium(0) (3) and its derivatives from a synthetic perspective seemed warranted.[8]

Basic Features of the Photochemical [6 + 4] Cycloaddition Reaction. Complex 3 was conveniently prepared as a stable red-orange solid by exposing cycloheptatriene to either commercially available $Cr(CO)_6$ in refluxing diglyme[9a,b] or to $(MeCN)_3Cr(CO)_3$ (4)[9c] in refluxing THF.

 (4)

3

---

(2) Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4143.

(3) [6 + 4] cycloadditions: (a) Fujise, Y.; Saito, H.; Ito, S. *Tetrahedron Lett.* **1976**, 1117. (b) Garst, M. E.; Roberts, V. A.; Prussin, C. *J. Org. Chem.* **1982**, *47*, 3969. (c) Garst, M. E.; Roberts, V. A.; Prussin, C. *Tetrahedron* **1983**, *39*, 581. (d) Garst, M. E.; Roberts, V. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 3882. (e) Rigby, J. H.; Moore, T. L.; Rege, S. *J. Org. Chem.* **1986**, *51*, 2398. (f) Ito, S.; Ohtani, H.; Narita, S.; Honma, H. *Tetrahedron Lett.* **1972**, 2223.

(4) [6 + 2] cycloadditions: (a) Feldman, K. S.; Come, J. H.; Freyer, A. J.; Kosmider, B. J.; Smith, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 1327. (b) Feldman, K. S.; Come, J. H.; Fegley, G. J.; Smith, B. D.; Parvez, M. *Tetrahedron Lett.* **1987**, *28*, 607. (c) Feldman, K. S.; Come, J. H.; Kosmider, B. J.; Smith, P. M.; Rotella, D. P.; Wu, M.-J. *J. Org. Chem.* **1989**, *54*, 592. (d) Feldman, K. S.; Wu, M.-J.; Rotella, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 8490.

(5) (a) Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562. (b) Ward, J. S.; Pettit, R. *Ibid.* **1971**, *93*, 262. For other recent examples of metal-promoted cycloadditions, see: (c) Wilson, A. M.; Waldman, T. E.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 6252. (d) Lautens, M.; Tam, W.; Edwards, L. G. *J. Org. Chem.* **1992**, *57*, 8. (e) Chaffee, K.; Sheridan, J. B.; Aistars, A. *Organometallics* **1992**, *11*, 18. (f) Fischler, I.; Grevels, F.-W.; Leitich, J.; Özkar, S. *Chem. Ber.* **1991**, *124*, 2857. (g) Kreiter, C. F.; Lehr, K.; Leyendecker, M.; Sheldrick, W. S.; Exner, R. *Ibid.* **1991**, *124*, 3. (h) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965. (i) Onoue, H.; Moritani, I.; Murahashi, S.-I. *Tetrahedron Lett.* **1973**, 121.

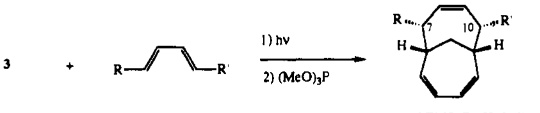
(6) (a) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. (b) Wender, P. A.; Snapper, M. L. *Tetrahedron Lett.* **1987**, *28*, 2221. (c) Wender, P. A.; Ihle, N. C. *Tetrahedron Lett.* **1987**, *28*, 2451. (d) Wender, P. A.; Ihle, N. C.; Correia, C. R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5904. (e) Wender, P. A.; Tebbe, M. J. *Synthesis* **1991**, 1089.

(7) (a) Özkar, S.; Kurz, H.; Neugebauer, D.; Kreiter, C. G. *J. Organomet. Chem.* **1978**, *160*, 115. (b) Kreiter, C. G.; Kurz, H. *Chem. Ber.* **1983**, *116*, 1494. (c) Michels, E.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *252*, C1. (d) Michels, E.; Sheldrick, W. S.; Kreiter, C. G. *Chem. Ber.* **1985**, *118*, 964. (e) Kreiter, C. G.; Michels, E. *J. Organomet. Chem.* **1986**, *312*, 59. (f) Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.

(8) For a preliminary account of this work, see: Rigby, J. H.; Ateeq, H. S. *J. Am. Chem. Soc.* **1990**, *112*, 6442.

(9) (a) Abel, E. W.; Bennett, M. A.; Burton, R.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4559. (b) Munro, J. D.; Pauson, P. L. *Ibid.* **1961**, 3475. (c) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

In a typical cycloaddition experiment, complex **3** was irradiated (450-W Canrad–Hanovia medium-pressure Hg vapor lamp, various filters) at room temperature in the presence of an excess of a given diene. The results depicted in eq 5 are typical and summarize the salient features of the process.

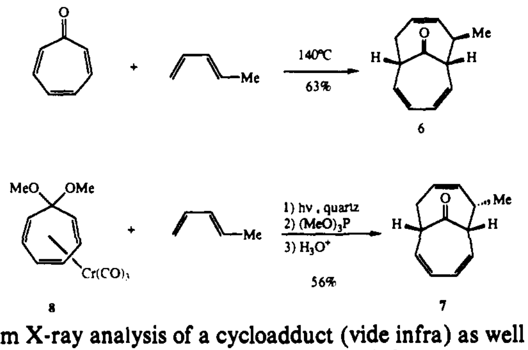


(5)

5a, R=OTMS, R'=H 86%
5b, R, R'=OAc 65%
5c, R, R'=Me 86%
5d, R=CO_2Me, R'=Me 96%
5e, R, R'=CO_2Me 89%
5f, R=CO_2Me, R'=H 83%

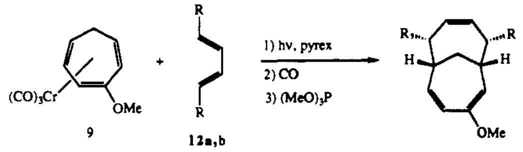
It is noteworthy that a systematic evaluation of reaction conditions, which will be detailed subsequently, resulted in dramatic improvements in the efficiency of the photochemical [6 + 4] process relative to our earlier efforts. A comparison of the yields in eq 5 with our previous results (50–70%)[8] is particularly striking. The optimum reaction conditions involve irradiation of a mixture of complex and diene through either a Pyrex or a uranium glass filter with concomitant bubbling of argon or nitrogen gas through the solution. Our initial conditions employed a quartz filter with no degassing. When electron-rich diene partners are used, yields can usually be improved by stirring the reaction mixture under a blanket of carbon monoxide *subsequent* to photolysis. The resultant cycloadduct metal complex is then decomplexed and the organic substrate isolated. The efficiency of the metal-promoted reaction can be contrasted with an attempted thermal cycloaddition of cycloheptatriene and methyl sorbate (xylene, reflux, 72 h), conducted in the absence of a metal center, in which *none* of the higher-order adduct could be identified. The same outcome occurred when a mixture of cycloheptatriene and methyl sorbate was irradiated without metal intervention,

Consideration of the reactions presented in eq 5 reveals a number of significant aspects of the chromium(0)-mediated [6 + 4] reaction, In contrast to the thermal, metal-free [6 + 4] cycloaddition, which gives the exo isomer exclusively,[1,2] only the endo diastereomer is produced in the metal-promoted version. This level of stereocomplementarity enhances the overall synthetic capabilities of the [6 + 4] cycloaddition for controlling relative stereogenicity, The stereochemical course of the metal-mediated reaction was established by comparing substituted bicyclo[4.4.1]undecanones **6**[3f] and **7**, which were derived from tropone and 7,7-dimethoxycycloheptatriene complex **8**,[10] respectively (eq 6). Additional support for this stereochemical assignment came from X-ray analysis of a cycloadduct (vide infra) as well as from the observed coupling constants (1–2 Hz) for the exo protons on C-7 and C-10, These data are consistent with the presence of endo substituents at C-7 and C-10, assuming that the bicyclic system adopts the conformation with the substituents disposed in the less hindered pseudoequatorial orientation. This is the case in the solid state, as evidenced by X-ray crystallography (vide infra).



(6)

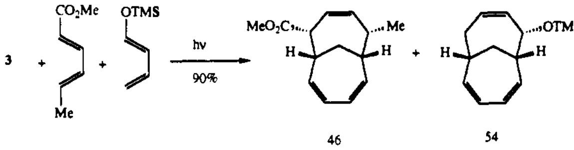
One of the more intriguing aspects of the metal-promoted reaction is the minimal impact that the electronic nature of the diene has on reaction efficiency. Note the comparable yields of most adducts in eq 5. This observation is in direct contrast to the Diels–Alder reaction, in which carefully matched participants are a prerequisite for efficient reaction, Additional examples documenting this feature are provided in eq 7 in which complex **9**,[11] bearing a methoxy substituent, reacts smoothly with relatively electron-rich 4π addends such as **12b**[12] (R = OTBDMS). The lower adduct yields obtained for both **5b** and **11** appear to be due principally to the sensitivity of the respective dienes rather than intrinsic difficulties with the transformations,



(7)

10, R=Me 90%
11, R=OTBDMS 70%

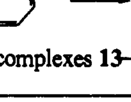
To ascertain whether any rate differences exist between the reactions of electron-rich and electron-deficient dienes with parent complex **3**, a mixture of **3**, methyl sorbate (2 equiv), and 1-((trimethylsilyl)oxy)-1,3-butadiene (2 equiv) was photolyzed under standard conditions (eq 8). A 90% yield (based on complex) of a mixture consisting of 54% of the adduct derived from the silyloxydiene and 46% of the sorbate-derived adduct emerged from this reaction. Thus, possible steric effects not withstanding, the cycloadditions of electron-rich and electron-poor dienes appear to be comparable,



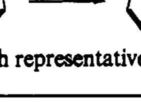
(8)

Regio- and Stereochemical Studies of Substituted Cycloheptatriene Complexes. A systematic examination of the reactions of a variety of substituted cycloheptatriene complexes should provide additional insight into the details of the metal-promoted cycloaddition process. A number of substituted complexes were known prior to our investigations and unless otherwise noted were prepared according to the procedures of Pauson and co-workers.[13,14] Certainly the most stringent test of the capabilities of the metal-mediated protocol relative to the metal-free thermal process would be the behavior of 6π partners substituted at the bond-forming centers. As noted earlier, this substitution pattern inhibited the higher-order pathway in the tropone series (eq 2).

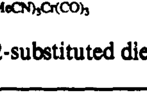
To examine this issue, 1-substituted cycloheptatriene complexes **13**,[13] **14**,[14a] and **15** were prepared; the first two by literature methodology and the latter by the sequence outlined in eq 9.[14b] The crucial step in this synthesis is the $MeCeCl_2$[15] addition to the highly enolizable carbonyl group of 2,7-dihydrotropone, Reaction of complexes **13–15** with representative 1- and 2-substituted dienes



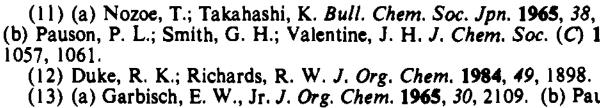
13



14



15



(9)

---

(10) Pauson, P. L.; Todd, K. H. *J. Chem. Soc. C* **1970**, 2638.

(11) (a) Nozoe, T.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 665. (b) Pauson, P. L.; Smith, G. H.; Valentine, J. H. *J. Chem. Soc.* (*C*) **1967**, 1057, 1061.

(12) Duke, R. K.; Richards, R. W. *J. Org. Chem.* **1984**, *49*, 1898.

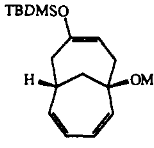
(13) (a) Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109. (b) Pauson, P. L.; Todd, K. H. *J. Chem. Soc.* (*C*) **1970**, 2315.

(14) (a) Pauson, P. L.; Todd, K. H. *J. Chem. Soc.* (*C*) **1970**, 2636. (b) For another approach to this complex, see: Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 293.

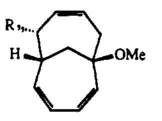
(15) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392.

provided adducts in yields ranging between 22% and 52%. Although these yields are somewhat lower than those of the parent complex, they represent a dramatic improvement over previous methodology. As a consequence, convenient access to bridgehead-substituted bicyclo[4.4.1]undecane systems is now available for the first time.[16]

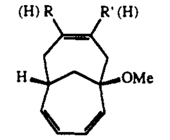
In several cases the high regioselectivity can be attributed to steric hindrance; however, a rationale for the selectivity displayed in **16** and **19** is not obvious at this time. The structural identification of these two substrates was complicated by premature partial hydrolysis of the silylenol ether to the corresponding ketone, which was not amenable to analysis by decoupling experiments.



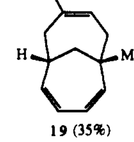
16 (52%)



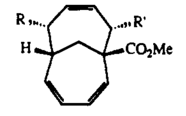
17a, R=Me (45%)
17b, R=OTMS (38%)



18a, R=Me : 18b, R'=Me (47%)
3 : 1

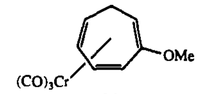


19 (35%)

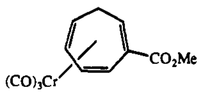


20a, R'=OTMS : 20b, R=OTMS (22%)
1 : 1

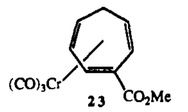
The 2- and 3-substituted cycloheptatriene complexes **21–23** as well as **9** were also prepared by literature methods[10,13b,14] and subjected to the standard photochemical reaction conditions in the presence of a variety of dienes to determine regiochemical preferences. In these cases, electronic influences should be more pronounced in the absence of significant steric effects. Although the chemical yields were generally quite high, little regiochemical discrimination was exhibited. Isomer ratios are rounded to 1:1 throughout this study when only small selectivity differences were observed. The general insensitivity to substituent electronic effects in these reactions is quite apparent and is fully consistent with the results described earlier. These trends can be contrasted with the predictable regioselectivity, although low chemical yields, displayed by the thermal cycloadditions of metal-free, substituted tropones.[3d] Adducts **28–30** were prepared to examine the effect of triene substituent location on cycloaddition efficiency with hydrocarbon dienes. It is noteworthy that cycloadducts **27** and **28** were produced in somewhat lower yields than those from the other complexes. This may reflect a number of factors, including the greater lability of complex **22** vis-à-vis the other complexes in this study.



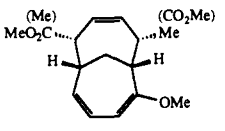
21



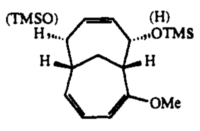
22



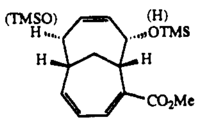
23



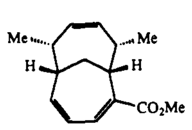
25a,b (1:1), (89%)



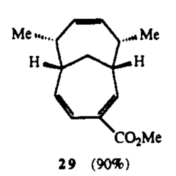
26a,b (1:1), (89%)



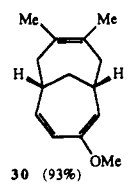
27a,b (1:1), (75%)



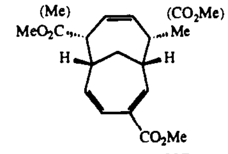
28 (74%)



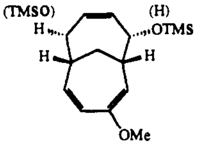
29 (90%)



30 (93%)

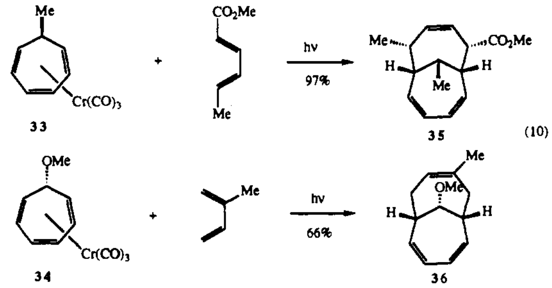


31a,b (1:1) (90%)



32a,b (1:1) (79%)

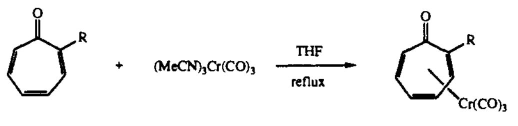
7-Substituted cycloheptatriene complexes also undergo smooth cycloaddition with numerous dienes to provide adducts possessing as many as five contiguous stereogenic centers. Control of the spatial disposition of the one-carbon bridge substituent can be exercised by selecting the appropriate 7-exo or 7-endo metal complex, either of which can be prepared selectively by methodology pioneered by Pauson.[9b,11b,13b] The readily available 7-*exo*-methyl complex **33**[9b] and the 7-*endo*-methoxy derivative **34**[9b] both undergo cycloaddition in good to excellent yields to provide adducts rich in stereochemical information. The yield of adduct **36** is somewhat depressed since quartz-filtered light was employed for this particular reaction. It has been established in other cases that irradiation under these conditions consistently provides inferior product yields.



33 35 (10)
34 36

[6 + 4] Cycloaddition Reactions of (η-2,4,6-Cycloheptatrien-1-one)tricarbonylchromium(0) (37a). The known chromium tricarbonyl complex of tropone **37a**[13b] also provides some interesting opportunities for higher-order cycloaddition reactions. The parent complex, as well as several 2-substituted species, is available in good to excellent yields employing a modification of the original Pauson procedure.[13b] It was immediately apparent that the tropone-based complexes were much more labile than the corresponding hydrocarbon-based complexes. However, the 2-alkyl-substituted species proved to be somewhat more robust than the parent **37a**.

Complexes **37a–c** were subjected to a series of cycloaddition reactions with a variety of diene partners. The results of this study are compiled in Table I. The yields for these transformations were uniformly lower than those in the corresponding cycloheptatriene series, due principally to the lability of the starting complexes. Once again, however, the metal-promoted cycloaddition protocol can be distinguished in some significant ways from the purely thermal process. Most notable is the observation that cycloaddition occurs with triene partners displaying substituents at the bond-forming centers (Table I, entries 3–5). Recall that 2-alkyl-substituted tropones failed to provide bicyclo[4.4.1]undecane products with simple dienes under thermal activation (eq 2). Also, in accord with previous observations, only the endo diastereomer was produced in each case in which a 1-substituted diene was employed (entries 1 and 3).[17] This stereochemical assignment was supported by comparing the adduct



(11)

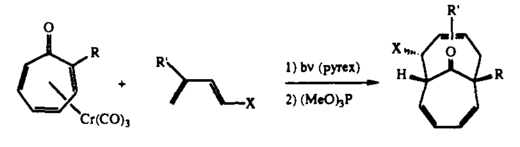
37a, R=H, 61%
37b, R=Me, 83%
37c, R=n-Bu, 79%

---

[16] The structural assignments of compounds **16–20** were made on the basis of extensive decoupling experiments. In certain instances the signals for crucial protons were partially obscured, and regiochemical assignments are tentative in these cases.

[17] The endo stereochemistry for the adduct in entry 1, Table I was established by comparison with tropone adduct 6 and adduct 7 derived from the chromium tricarbonyl complex of 7,7-dimethoxycycloheptatriene. See eq 6. This adduct was shown to be identical in all respects with compound 7.

Table I. Photochemical [6 + 4] Cycloadditions of Complexes **37a–c**

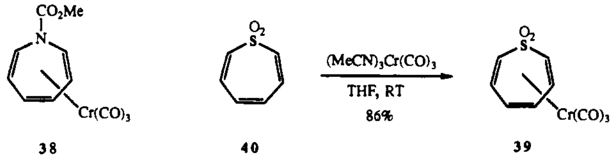


entry	R	R′	X	yield (%)
1	H	H	Me	20
2	H	Me	H	40
3	Me	H	Me	23[a,c]
4	Me	Me	H	65[b]
5	*n*-Bu	Me	H	24[b]
6	H	H	OAc	0
7	H	H	OTMS	0

[a] Isolated as a single regioisomer. [b] Isolated as an inseparable 1:1 mixture of regioisomers. [c] Regiochemistry of adduct established by decoupling experiments.

in entry 1 (Table I) with the known endo adduct **7** (eq 6). This stereocomplementarity between the metal-promoted and metal-free reactions once again emphasizes the opportunities available for controlling relative substituent stereochemistry by judicious choice of reactants and reaction conditions. It is noteworthy that no cycloaddition could be induced between any of the tropone complexes and dienes possessing oxygen functions (entries 6 and 7). These results are presumably reflective of the relative instability of these complexes compared to their hydrocarbon counterparts, Oxygen functionality of this type appears to be sufficiently nucleophilic to decomplex the starting materials in preference to cycloaddition. In contrast to our experience in the hydrocarbon series, the use of a uranium glass filter during photolysis had no substantive impact on reaction efficiency. Furthermore, the tropone-based complexes are only sparingly soluble in the customary hydrocarbon solvents used in the photochemical experiments, and the addition of a small amount of Et_2O as co-solvent was essential for complete dissolution. It is suspected that the ether solvent also contributes to the lower yields observed in these reactions. A range of other cosolvent candidates have been screened during the course of these investigations with limited success.

[6 + 4] Cycloaddition Reactions of Heterocyclic Triene Chromium Tricarbonyl Complexes. An attractive extension of the metal-promoted cycloaddition process would involve heterocycles as 6π ligands. We have found that the known *N*-(methoxycarbonyl)azepine complex **38**[18] and the previously unreported thiepin 1,1-dioxide complex **39**[19] are excellent participants in photochemically initiated [6 + 4] cycloadditions.[20] Complex **38** is available using the procedure of Kreiter and Özkar,[18] and complex **39** is available in excellent yield by treating thiepin 1,1-dioxide (**40**)[21] with $(MeCN)_3Cr(CO)_3$ at room temperature.



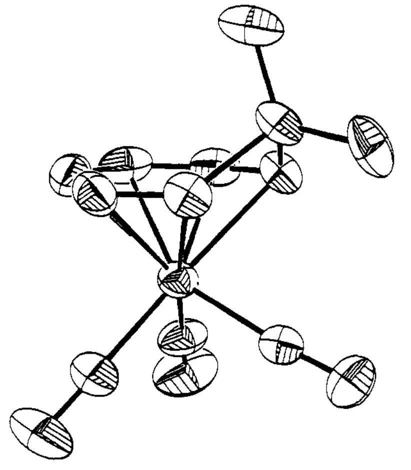


Figure 2. ORTEP drawing of complex **39**.

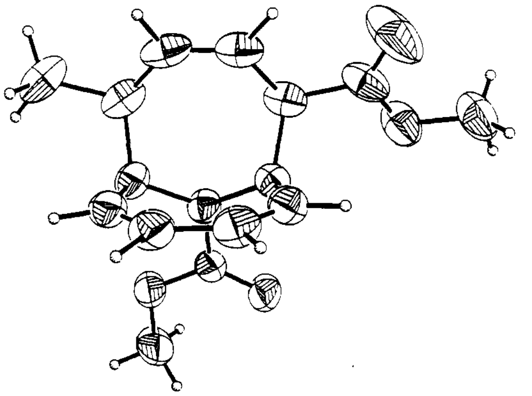
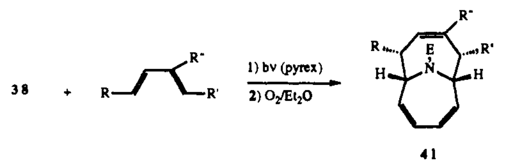


Figure 3. ORTEP drawing of cycloadduct **41d**.

Table II. [6 + 4] Cycloaddition Reactions of Complex **38**



entry	product	substituents	yield (%)
1	**41a**	R, R′ = H, R″ = OTMS	87[a]
2	**41b**	R = OAc, R′, R″ = H	75
3	**41c**	R = OTMS, R′, R″ = H	79
4	**41d**	R = Me, R′ = CO_2Me, R″ = H	83

[a] Product isolation was accompanied by some of the corresponding ketone.

To ascertain what, if any, impact the strongly electronegative SO_2 group would have on the bonding characteristics and conformation of complex **39**, an X-ray structure was obtained. The resultant ORTEP diagram is presented in Figure 2. The typical puckering of the uncomplexed atom is evident and parallels the all-carbon series in this regard,[13b,22] No unusual structural features were noted, and a cycloaddition study of both heterocyclic series was initiated.

The [6 + 4] cycloaddition reactions of azepine complex **38** are collected in Table II. As with the all-carbon examples, only products derived from an endo approach of the diene were generated, and the nature of the stereochemical course of the cycloaddition was established by a single crystal X-ray structure of compound **41d**, The ORTEP diagram is displayed in Figure 3. The anticipated pseudoequatorial disposition of the C-7 and

---

(18) Kreiter, C. G.; Özkar, S. *Z. Naturforsch.* **1977**, *32B*, 408.

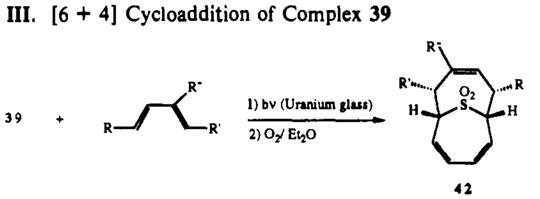
(19) To the best of our knowledge, this is the first report of the chromium complex of thiepin 1,1-dioxide; however, the corresponding iron tricarbonyl complex was recently described: Nishino, K.; Takagi, M.; Kawata, T.; Murata, I.; Inanaga, J.; Nakasuji, K. *J. Am. Chem. Soc.* **1991**, *113*, 5059.

(20) For a preliminary account of this work, see: Rigby, J. H.; Ateeq, H. S.; Krueger, A. C. *Tetrahedron Lett.* **1992**, *33*, 5873.

(21) (a) Mock, W. L. *J. Am. Chem. Soc.* **1967**, *89*, 1281. (b) Mock, W. L. *J. Chem. Soc., Chem. Commun.* **1970**, 1254. (c) Paquette, L. A.; Maiorana, S. *Ibid.* **1971**, 313.

(22) (a) Dunitz, J. D.; Pauling, P. *Helv. Chim. Acta* **1960**, *43*, 2188. (b) Baikie, P. E.; Mills, O. S. *J. Chem. Soc.* (*A*) **1968**, 2704. (c) Barrow, M. J.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1971**, 119. (d) Lõuer, M.; Simonneaux, G.; Jaouen, G. *J. Organomet. Chem.* **1979**, *164*, 235. (e) Simonneaux, G.; Jaouen, G.; Dabard, R. *Tetrahedron* **1980**, *36*, 893. For a recent discussion of the structure and bonding in (cycloheptatriene)tricarbonylchromium(0) and derivatives, see: Reynolds, S. D.; Albright, T. A. *Organometallics* **1985**, *4*, 980.

Table III. [6 + 4] Cycloaddition of Complex **39**



42

entry	product	substituents	yield (%)
1	**42a**	R, R′ = H, R″ = Me	77
2	**42b**	R = OAc, R′, R″ = H	78
3	**42c**	R = OTMS, R′, R″ = H	65 (55)[a] (42)[b]
4	**42d**	R = CO_2Me, R′, R″ = H	38
5	**42e**	R = CO_2Me, R′ = Me, R″ = H	21
6	**42f**	R, R′ = CO_2Me, R″ = H	0

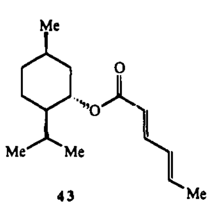
[a] Performed using a Pyrex filter. [b] Performed using a quartz filter.

C-10 substituents is clearly evident, and the characteristic insensitivity of reaction efficacy to the electronic nature of the participants is apparent once again. Restricted rotation around the carbamate N–C(O)OMe bond resulted in the doubling of many of the signals in the ^{13}C NMR of the adducts in this series, and variable temperature NMR experiments on compound **41d** revealed a coalescence temperature of approximately 68 °C. An interesting modified protocol for cycloadduct decomplexation was also instituted during these studies. The known lability of group 6 metal complexes to molecular oxygen[23] was exploited as a particularly clean method for removing the metal center from the product complexes. It is noteworthy, however, that the corresponding adduct complexes in the cycloheptatriene series were not as well behaved using this decomplexation procedure. The clean higher-order pathway followed by complex **38** can be distinguished from the behavior of metal-free azepines, which tend to participate principally as 4π or 2π partners.[24] There have been sporadic reports of metal-free azepine derivatives that cycloadd in a [6 + 4] manner with very reactive dienes; however, they invariably result in low yields of exo products.[25]

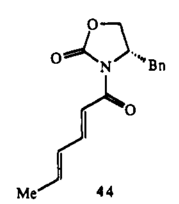
The cycloaddition chemistry of thiepin dioxide complex **39** was also explored, and the results are summarized in Table III. In general, the reactions were well behaved and proceeded in a fashion similar to those mentioned previously. However, in contrast to the hydrocarbon and azepine cases, the electronic character of the diene appears to have a moderate influence on reaction efficiency. For example, yields were uniformly lower for reactions involving electron-deficient diene partners relative to those employing electron-rich dienes (Table III, entries 4–6).

The capability of effecting metal-promoted higher-order cycloaddition reactions with highly functionalized and substituted reaction partners is a compelling argument for the potential utility of this methodology as applied to complex synthetic problems, and efforts in this direction are currently being pursued in our laboratory.

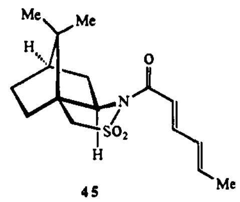
Asymmetric Induction in Metal-Promoted [6 + 4] Cycloadditions. An important contemporary issue in organic synthesis is the ability to create bonds with control of absolute stereochemistry. Several strategies can be envisioned for inducing chirality in the cycloadducts resulting from metal-promoted higher-order cycloadditions. An attractive approach that is easily implemented would append an appropriate chiral auxiliary to the diene component.[26] To assess the effectiveness of this strategy in these reactions, a series of three chiral auxiliaries were chosen for study and incorporated onto the sorbate moiety.



43



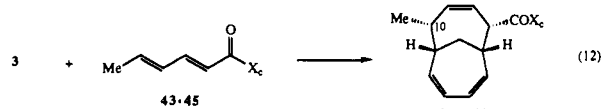
44



45

Chiral diene **43** was prepared in virtually quantitative yield from sorbic acid and (1*S*,2*R*,5*R*)-(+)-isomenthol through the agency of DCC; the known dienes **44** and **45** were available in excellent yields from (*S*)-(−)-4-benzyl-2-oxazolidinone and D-(−)-2,10-camphorsultam using the procedures of Evans[27] and Oppolzer,[28] respectively.

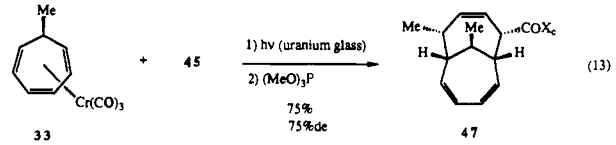
The parent complex **3** was reacted with dienes **43–45** under standard photochemical conditions to yield **46a**, **46b**, and **46c** as easily separable mixtures of diastereomers, respectively. The diastereomer ratios were assayed by integration of the prominent C-10 methyl signals in the ^1H NMR spectra of the crude diastereomeric pairs. The mixtures were then separated by chromatography, fractional crystallization, or a combination of both to provide enriched diastereomers. In each case, only the major isomer could be isolated in analytically pure form. While the monoterpene auxiliary was totally ineffective for chiral induction, adduct **46c**, obtained from the Oppolzer sultam-derivatized diene, was produced with respectable diastereoselectivity.



46a, 50% (0% de)
46b, 75% (45% de)
46c, 74% (84% de)

(12)

Substituted cycloheptatriene complexes were also briefly studied for their response to chiral induction efforts. The 7-*exo*-methylcycloheptatriene complex **33** was irradiated in the presence of chiral diene **45** to give a mixture of diastereomers **47** (75% de).



(13)

It is noteworthy that employing a diene with the antipodal sultam chiral auxiliary gave the corresponding adduct as a mixture in which the enantiomeric species was produced in 75% excess. The absolute stereochemistry of compound **47** and, by inference, **46c** was established by obtaining an X-ray structure of a derivative in the enantiomeric series.[29] The absolute stereochemistry for the major diastereomer of **46b** has not been determined at this time.

[6 + 4] Cycloadditions with Other Group 6 Metal Complexes and the Effects of Ligand Modification on Cycloaddition Efficiency. Molybdenum and tungsten complexes have also been examined as substrates in the photoinduced [6 + 4] cycloaddition process. The corresponding CHT-$Mo(CO)_3$[23] and CHT-$W(CO)_3$[30] were prepared in excellent yields by heating the hydrocarbon with either $M(CO)_6$ or $(MeCN)_3M(CO)_3$. The corresponding thiepin 1,1-dioxide complexes **48** (M = Mo) and **49** (M = W) were also prepared for the first time for this investigation. The results of this comparative study are displayed in Table IV.

---

(23) Cotton, F. A.; McCleverty, J. A.; White, J. E. *Inorg. Synth.* **1967**, *9*, 121.

(24) (a) Wiseman, J. R.; Chong, B. P. *Tetrahedron Lett.* **1969**, 1619. (b) Paquette, L. A.; Kuhla, D. E.; Barrett, J. H.; Leichter, L. M. *J. Org. Chem.* **1969**, *34*, 2888.

(25) (a) Saito, K.; Iida, S.; Mukai, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3483. (b) Harano, K.; Yasuda, M.; Ban, T.; Kanematsu, K. *J. Org. Chem.* **1980**, *45*, 4455. (c) Harano, K.; Ban, T.; Yasuda, M.; Kanematsu, K. *Tetrahedron Lett.* **1979**, 1599.

(26) The use of chiral auxiliaries for inducing asymmetry in Diels–Alder reactions is well-known: Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876.

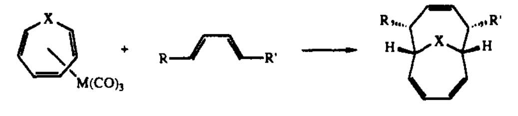
(27) (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (b) Evans, D. A.; Chapman, K. T.; Bisaha, J. *Ibid.* **1984**, *106*, 4261. (c) Martinelli, M. J. *J. Org. Chem.* **1990**, *55*, 5065.

(28) (a) Oppolzer, W.; Chapuis, C.; Bernardinelli, G. *Helv. Chim. Acta.* **1984**, *67*, 1397. (b) Oppolzer, W.; Poli, G.; Kingma, A. J.; Starkemann, C.; Bernardinelli, G. *Ibid.* **1987**, *70*, 2201.

(29) The details of this X-ray structure will be published elsewhere.

(30) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

Table IV. Comparison of Photoinduced [6 + 4] Cycloadditions of a Series of Group 6 Metal Tricarbonyl Complexes

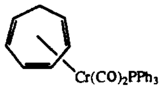


entry	X	M	diene	yield (%)
1	CH_2	Cr	R = OTMS, R' = H	86
2	CH_2	Mo	R = OTMS, R' = H	51
3	CH_2	W	R = OTMS, R' = H	0
4	CH_2	Cr	R = Me, R' = H	70
5	CH_2	Mo	R = Me, R' = H	32
6	CH_2	W	R = Me, R' = H	0
7	CH_2	Cr	R = Me, R' = CO_2Me	96
8	CH_2	Mo	R = Me, R' = CO_2Me	27
9	CH_2	W	R = Me, R' = CO_2Me	0
10	SO_2	Cr	R = OAc, R' = H	78
11	SO_2	Mo (**48**)	R = OAc, R' = H	0[a]
12	SO_2	W (**49**)	R = OAc, R' = H	0

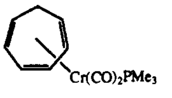
[a] Principal reaction was decomplexation of starting complex.

The superiority of Cr(0) for promoting these cycloadditions is clearly evident from the data in this table. While in most instances adducts were isolated from molybdenum-mediated reactions, the yields were uniformly lower than those for the corresponding chromium-based reactions, Perhaps the molybdenum species, which are known to be the most labile of the group 6 complexes,[31] are too easily stripped of the metal center under the reaction conditions used for cycloaddition and as a result are not efficient participants in the ring-forming process, In no instance was a cycloadduct detected from any tungsten-mediated reaction. This observation may be reflective of the metal-ligand bond strength characteristic of this complex, CHT-W(CO)$_3$ is reported to have the strongest metal-ligand bonding in the group 6 series.[32]

As a further probe of the influence of changes at or around the metal center on cycloaddition efficiency, several complexes were examined in which one of the CO ligands was replaced with a PR$_3$ group, Employing the photochemical procedure of Anderson et al.,[33] known complexes **50** and **51** were prepared in good yield.

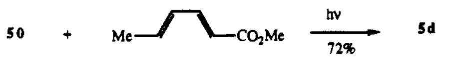


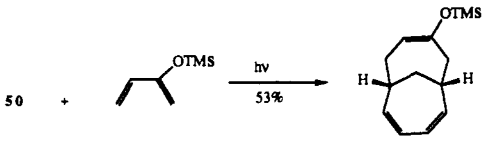
50



51

These complexes were reacted with electron-rich and electron-poor diene partners under standard photochemical conditions to provide the expected cycloadducts in modest to good yields after decomplexation, While these results are promising for future development, no attempt has been made to optimize reaction conditions.

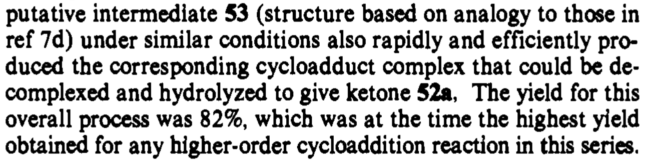




52

The results using complexes with modified coordination spheres are significant from a number of perspectives. First, they indicate that the cycloaddition process can tolerate a reasonable range of ligand types. Phosphine ligands are electronically quite distinct from carbonyls. These observations further suggest that the reaction has a potential flexibility that should be conducive to extensive modification as future situations demand. Most significantly, achieving chiral induction by surrounding the metal center with chiral phosphine ligands is now a viable option, A brief foray in this direction has been initiated. A complex in which one of the carbonyl ligands was replaced with commercially available (+)-neomenthyldiphenylphosphine was prepared and reacted with methyl sorbate. Unfortunately, no selectivity was discerned in this example; however, more extensive examination of this intriguing chiral induction strategy is currently underway.

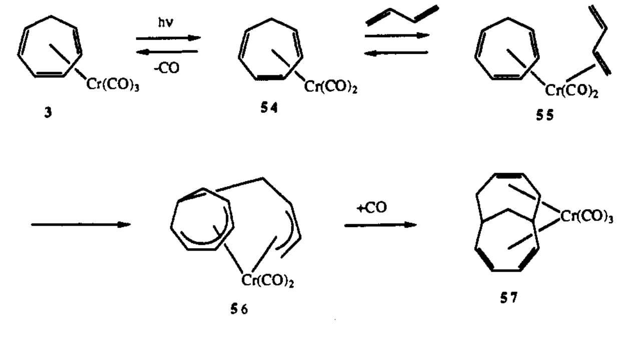
Mechanistic Considerations and Yield Optimization Studies. A particularly revealing cycloaddition experiment involved the photoinduced combination of parent complex **3** with 2-((trimethylsilyl)oxy)butadiene[34] (eq 14). Initial attempts to effect



this transformation yielded none of the anticipated bicyclo[4.4.1]undecane cycloadduct. A thermally labile, structurally ill-defined species was generated instead. Kreiter and co-workers had noted what may be analogous intermediates during their investigations on the reaction of (heptafulvene)tricarbonylchromium with certain hydrocarbon dienes.[7d] These species were observed to collapse to bicyclo[4.4.1]undecane complexes upon stirring under a blanket of carbon monoxide. Treatment of our putative intermediate **53** (structure based on analogy to those in ref 7d) under similar conditions also rapidly and efficiently produced the corresponding cycloadduct complex that could be decomplexed and hydrolyzed to give ketone **52a**, The yield for this overall process was 82%, which was at the time the highest yield obtained for any higher-order cycloaddition reaction in this series. When other cycloadditions were treated in a similar fashion, an intriguing pattern became apparent. The yields of cycloadducts from reactions involving electron-rich dienes increased by as much as 20% when exposed to excess CO after the photolysis was completed. However, a similar enhancement was not realized in reactions employing electron-deficient diene partners,

All of the evidence accumulated to date indicates that these cycloaddition reactions are stepwise in nature, and the possible intermediacy of species such as **53** was suggestive of a mechanistic profile as depicted in Scheme I. In this scenario, light-induced ejection of a CO ligand produces the coordinatively unsaturated species **54**, which can then engage the diene partner to give complex **55**. Bond reorganization would afford intermediate **56**, which must then recapture the dissociated CO and collapse to the observed cycloadduct complex **57**. Ample precedent for the initial activation step exists.[35] Indeed, Stufkens and co-workers have

Scheme I



---

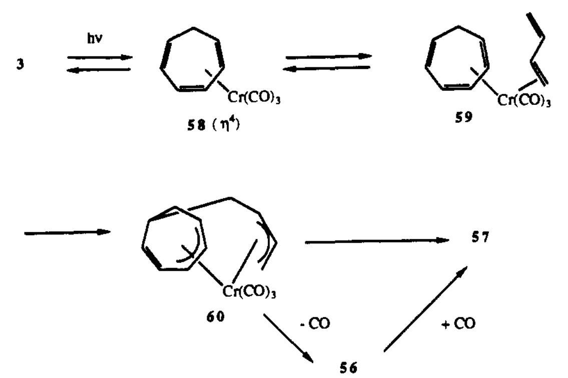
(31) (a) Strohmeier, W.; Müller, R. *Z. Phys. Chem.* **1964**, *40*, 85. (b) Pidcock, A.; Taylor, B. W. *J. Chem. Soc.* (*A*) **1967**, 877. (c) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1974**, 428.

(32) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Leung, M. L.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani Moattar, M. T. *J. Organomet. Chem.* **1977**, *142*, 321.

(33) Anderson, W. P.; Blenderman, W. G.; Drews, K. A. *J. Organomet. Chem.* **1972**, *42*, 139.

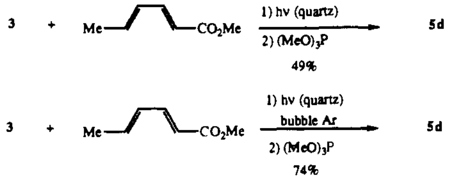
(34) Jung, M. E.; McCombs, C. A. *Org. Synth. Coll. Vol. VI* **1988**, 445.

Scheme II



demonstrated that the mechanism described in Scheme I is the likely reaction pathway for these processes in low-temperature matrices and in liquid noble gas solutions.[36] A crucial, and apparently necessary, step in this mechanism is the recapture of the dissociated CO by species **56** to produce **57** since all cycloadduct complexes isolated to date have exhibited three CO ligands bound to the metal center. Based on this scheme, we reasoned that inefficient trapping of the free CO was responsible in the main for the relatively modest yields of cycloadducts obtained in these reactions. In our early studies, the yields of cycloadducts tended to plateau at around 60–65%, and the improved yield observed for the reaction described in eq 14, wherein additional CO was made available for recapture, supports this contention.

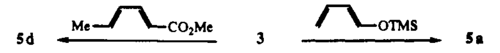
To further probe the influence of carbon monoxide availability on reaction efficiency, an experiment was performed to compare the yield under normal conditions with a situation in which the reaction is intentionally deprived of the dissociated carbonyl ligand by vigorously flushing the solution with an inert gas *during* photolysis. Yields of adducts would be expected to decrease under the latter conditions.[37] The findings are displayed in eq 15.



(15)

Surprisingly, the yield improved to 74% when argon gas was bubbled vigorously through the solution during photolysis. While no effort was made to detect any CO that may have evolved during these reactions, the purging conditions were sufficient to remove at least a substantial portion of this modestly soluble gas.[38] Only trace amounts of cycloaddition products were isolated when the photolysis was executed under a blanket of CO gas. While in no way conclusive, these results are consistent with the notion that initial CO dissociation may not be a necessary step for successful cycloaddition under usual laboratory conditions. The increased yield observed may be due to removal of adventitious molecular oxygen, a gas that is known to labilize metal triene complexes in solution.[23] In light of these results, an alternative mechanism, the basic features of which were first proffered by Kreiter,[7d] may also merit consideration in certain circumstances (Scheme II).

Table V. Optimization of Cycloaddition Reaction Conditions



conditions	yield (%)	conditions	yield (%)
quartz	49	quartz	46
Ar, quartz	$74^{a,b}$	CO, quartz	56^{c}
Ar, Pyrex	84^{a}	N_2, CO, quartz	$67^{a,c}$
Ar, uranium glass	96^{a}	N_2, CO, Pyrex	$86^{a,c,d}$

[a] Inert gas was bubbled through reaction mixture during irradiation. [b] No influence was noted in reactions involving electron deficient dienes when treated with excess CO. [c] Stirring under a blanket of CO after termination of irradiation. [d] No additional yield enhancement was noted in this case using a uranium glass filter.

The principal features of this scheme are (1) all three CO ligands remain bound to the metal center throughout the reaction and (2) the requisite coordinatively unsaturated species **58** is produced by a light-induced "hapticity slippage" from η^6 to η^4 (**3** → **58**).[39] The observations in eq 14 can also be accommodated by invoking intermediate **56** in those cases involving electron-rich dienes. While the details of bond reorganizations **59** to **60** and **60** to **57** remain obscure, the integrity of the relative spatial disposition of diene substituents is maintained throughout the process, as evidenced by the clean endo selectivity observed in every cycloaddition examined to date. Furthermore, there has been no evidence for any stereochemical "leakage" in any example involving an (*E*)-diene partner. In contrast, evidence for equilibration of double-bond geometry has surfaced in reactions of (*Z*)-dienes with complex **3**. For example, *cis*-piperylene provided a low yield of a mixture of the corresponding cycloadduct diastereomers in which the quantity of product presumably derived from the (*E*)-isomer exceeded the amount of that isomer in the original starting diene.

Regardless of the details of the mechanistic pathway for these reactions, observations made during this investigation have led to modified reaction conditions that have had a profound influence on the efficiency levels that can be attained. Table V depicts the evolution of reaction optimization for typical combinations involving both electron-rich and electron-deficient diene partners. The apparent dependency of yield on the wavelength of light is noteworthy.[40] It is not clear at what stage of the step-wise process this relationship manifests itself; however, control experiments reveal that cycloadduct–metal complexes are stable for extended irradiation periods (>3 h) with uranium glass- and Pyrex-filtered light, while rapid decomposition was evident using quartz-filtered light. Systematic modifications of reaction conditions clearly have reaped substantial rewards in the form of routine cycloaddition yields in excess of 90% in many cases.

Thermal and Catalytic [6 + 4] Cycloaddition Reactions. A direct consequence of the mechanistic pathways suggested in Schemes I and II (particularly the latter) is the possibility of effecting these cycloadditions using thermal activation. Considerable precedent for thermal exchange of carbonyl ligands in the chromium(0) series is available.[41] Thermal haptotropic changes formally related to those suggested in Scheme II have also been discussed previously.[31,39,42] These considerations prompted an examination of

---

(35) (a) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401. For some recent studies on the photochemistry of polyene–M(CO)$_3$ complexes, see: (b) Astley, S. T.; Churton, M. P. V.; Hitam, R. B.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3243. (c) Bloyce, P. E.; Hooker, R. H.; Rest, A. J.; Bitterwolf, T. E.; Fitzpatrick, N. J.; Shade, J. E. *Ibid.* **1990**, 833. (d) Hooker, R. H.; Rest, A. J. *Ibid.* **1982**, 2029. (e) Hitam, R. B.; Mahmoud, K. A.; Rest, A. J. *Coord. Chem. Rev.* **1984**, *55*, 1. (f) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4800.

(36) Van Houwelingen, T.; Stufkens, D. J.; Oskam, A. *Organometallics* **1992**, *11*, 1146.

(37) Stufkens noted that product formation was suppressed if CO was allowed to escape from his reaction medium (ref 36).

(38) The solubility of carbon monoxide in toluene is 0.17 mL/mL at 20 °C: *Solubilities of Inorganic and Organic Compounds*; Stephen, H., Stephen, T., Eds.; MacMillan: New York, 1963; Vol. 1, part 2, p 1053.

(39) For discussion of other "hapticity slippages", see: (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Dixon, D. T.; Burkinshaw, P. M.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2237. (c) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (d) Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041. (e) Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 716. (f) Wey, H. G.; Butenschön, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 880. (g) Lawless, M. S.; Marynick, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 7513. (h) Arthurs, M.; Piper, C.; Morton-Blake, D. A.; Drew, M. G. B. *J. Organomet. Chem.* **1992**, *429*, 257.

(40) For recent examples of wavelength effects on CO extrusion in metal complexes, see: (a) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (b) Song, J.-S.; Bullock, R. M.; Creutz, C. *Ibid.* **1991**, *113*, 9862.

(41) (a) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154. (b) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res. (M)* **1979**, 1752. (c) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1990**, *28*, 136.

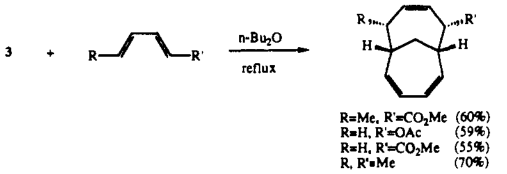
(42) (a) Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27. (b) Yagupsky, G.; Cais, M. *Inorg. Chim. Acta* **1975**, *12*, L27.

Table VI. Solvent and Temperature Effects on the Thermal [6 + 4] Cycloaddition[a]

entry	solvent	T (°C)	yield (%)
1	THF	67	0
2	isobutyl ether	122	60
3	octane	125	29[b]
4	THF/butyl ether	140	30[b]
5	*n*-butyl ether	142	60
6	diglyme	162	22

[a] All entries involved the reaction of complex **3** with methyl sorbate. [b] Performed in a sealed tube.

heat-initiated [6 + 4] cycloaddition reactions in our laboratory. Equation 16 depicts some of the results of this study,

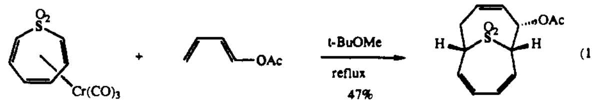


(16)

Heating the generic complex **3** with a series of electronically distinct diene partners in refluxing *n*-Bu$_2$O provided the corresponding cycloadducts in unoptimized yields in the 60% range. The products of the thermal reaction were identical in every respect to those obtained in the photochemical version (see eq 5). Significantly, they were also isolated *metal-free* in each case. Once again the electronic nature of the participants appears to have little or no impact on the course of these reactions,

A series of solvents were examined to evaluate the influence of nucleophilicity and temperature on the [6 + 4] reaction, The results are summarized in Table VI, In general, *n*-butyl ether emerged as the solvent of choice for this reaction, even though it is generally regarded as a weakly nucleophilic solvent in other ligand exchange processes,[41] It is also noteworthy that product yields with more interactive solvents such as diglyme were inferior (entry 6). A caveat to this particular result must be issued in that the low yield may be due, in part, to isolation difficulties experienced with the higher boiling solvent. In contrast to related reactions, the mixed THF/*n*-Bu$_2$O solvent system (entry 4) was also not particularly effective in these reactions.[41] Surprisingly, the noninteractive solvent octane gave rise to some modest product formation (entry 3), In light of these observations, we have generally employed *n*-Bu$_2$O as the solvent in the thermal higher-order cycloaddition reactions examined to date, although *tert*-butyl methyl ether has been an effective solvent as well. A significant observation was made when complex **3** was heated in the presence of chiral diene **45** in dibutyl ether. Adduct **46c** was isolated, displaying virtually the same level of diastereoselectivity and in the same sense as was obtained in the photochemical reaction (eq 12), This result implies that similar events are transpiring in both the thermal and light-induced versions of this process,

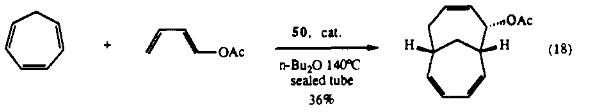
The generality of the thermal activation of metal-promoted cycloadditions has been further substantiated by the successful cycloadditions of heterocyclic 6π partners. Equation 17 shows the results of the thermally induced reaction of complex **39**. In this instance the yield was decidedly lower than that in the corresponding photochemical reaction. The lower cycloaddition efficiency in the thermal version appears to stem from the instability of the starting complex to the reaction conditions employed.



39

(17)

The direct isolation of metal-free adducts in the thermal [6 + 4] cycloadditions suggested the possibility of effecting these transformations using only a catalytic quantity of an appropriate Cr(CO)$_3$ source.[42] In view of its ease of handling and relative stability, (η^6-1,3,5-cycloheptatriene)tricarbonylchromium(0) (**3**) appeared to be the ideal candidate for serving as the Cr(CO)$_3$ catalyst, Heating a mixture of cycloheptatriene and excess 1-acetoxy-1,3-butadiene in *n*-butyl ether for 50 h at reflux in the presence of 10 mol % of complex **3** yielded about 20% of the expected cycloadduct. Extended reaction periods did not improve the conversion efficiency. A change in the color of the reaction mixture from orange-red to a dark green color accompanied the longer reactions, which is suggestive of oxidation to Cr(III) species. Careful degassing prior to heating resulted in some yield improvement.



(18)

Somewhat better results were obtained when complex **50** was employed as the catalyst. In this instance the yield of adduct was 36%. The low conversions and long reaction times that characterize these reactions are likely due to a slow turnover rate for the catalyst since the cycloadduct–metal complexes presumably produced during the catalytic cycle are known to be relatively robust in the bicyclo[4,4.1]undecane series, Consequently, the rate of cycloadduct decomplexation is correspondingly slow, Further investigations directed at circumventing these difficulties are currently underway in our laboratories.

Conclusions

Several higher-order cycloaddition reactions can be promoted by group 6 metals. The reactions can be implemented using stoichiometric amounts of cyclic triene chromium tricarbonyl complexes in combination with a variety of 4π reaction partners under photochemical or thermal activation, Furthermore, the cycloadditions can also be carried out with modest efficiency using catalytic amounts of metal. In all cases examined, the reactions proceed with clean endo stereoselectivity and efficiencies are independent of the electronic nature of the reactants.

Experimental Section

General Procedures, Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. A General Electric QE-300 NMR spectrometer was used for the 300-MHz ^{1}H NMR and 75-MHz ^{13}C NMR spectra. IR spectra were recorded on a Nicolet 30DX spectrophotometer.

Photolysis reactions were conducted using a Canrad-Hanovia medium-pressure mercury lamp operating at 450 W, which was placed in a water-cooled immersion well constructed of either quartz or Pyrex glass. A sleeve made of uranium glass available from the Houde Glass Co., Newark, NJ was also used in certain cases. Combustion analyses were performed by Midwest Microanalytical Laboratories, Indianapolis, IN.

Materials. Tetrahydrofuran was distilled from sodium–benzophenone ketyl under a nitrogen atmosphere just prior to use. Methylene chloride and acetonitrile were distilled from CaH$_2$, and hexanes (technical grade) were distilled at atmospheric pressure. Chromium, molybdenum, and tungsten hexacarbonyls (Pressure Chemical or Strem) were used without further purification.

General Procedure for the Photochemical [6 + 4] Cycloaddition of (η^6-1,3,5-Cycloheptatriene)tricarbonylchromium(0) Complexes. To a dry photochemical reaction vessel equipped with either a quartz or Pyrex glass immersion well (and a uranium glass sleeve as indicated) was added a hexanes solution (350 mL) of (η^6-1,3,5-cycloheptatriene)tricarbonylchromium(0) (**3**) (1 equiv) and the given diene (0.8–10.0 equiv). Vigorous bubbling of either Ar or N$_2$ gas was begun, and the orange-red solution was irradiated (Canrad-Hanovia 450-W medium-pressure mercury vapor lamp) with continuous bubbling until the disappearance of starting material as indicated by TLC analysis (0.5–10 h). The resultant orange solution was filtered, and the filtrate was reduced in volume to 20–50 mL. The resultant mixture was stirred with P(OMe)$_3$ (5–20 mL) at room temperature until the solution was colorless (8–10 h). The mixture was then concentrated in vacuo and purified by flash chromatography.[43]

For those cycloadditions involving electron-rich dienes, the reaction mixture was saturated with carbon monoxide and stirred under a blanket of this gas for 15 h immediately after irradiation was completed. At this

---

[43] Still. W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

point the mixture was then concentrated and decomplexed as above.

7α-((Trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (5a). Compound **5a** was prepared from (η^6-cycloheptatriene)tricarbonylchromium(0) (**3**) (310 mg, 1.36 mmol) and 1-((trimethylsilyl)oxy)-1,3-butadiene (1.21 g, 8.5 mmol) in hexanes (350 mL) by irradiation (Pyrex, 30 min). Chromatography (silica gel, hexanes/ethyl acetate, 19:1) afforded 273 mg (86%) of a colorless oil: IR (film) ν 3069, 3022, 3010, 1199, 1083; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 2.13–2.49 (m, 4 H), 2.72 (br s, 1 H), 2.82 (br s, 1 H), 4.67 (m, 1 H), 5.55 (m, 2 H), 5.84 (m, 3 H), 6.05 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.06, 31.79, 33.41, 37.46, 46.78, 75.11, 125.21, 126.18, 126.74, 134.67, 137.29, 141.14; mass spectrum *m/e* (rel intensity) 234 (5), 219 (2), 145 (2), 142 (100); HRMS calcd for $C_{14}H_{22}OSi$ 234.1440, found 234.1442. Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.45. Found: C, 72.05; H, 9.37.

7α,10α-Diacetoxy-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (5b). Compound **5b** was prepared from complex **3** (541 mg, 2.37 mmol) and 1,4-diacetoxy-1,3-butadiene (273 mg, 1.6 mmol) in hexanes (350 mL) by irradiation (quartz, 20 h). Chromatography (silica gel, petroleum ether/ethyl acetate, 19:1) provided 275 mg (65%) of a white solid: mp 123–125 °C (hexane/ethyl acetate); IR ($CDCl_3$) ν 3025, 1734, 1654, 1097; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (m, 1 H), 2.11 (s, 6 H), 2.44 (m, 1 H), 2.90 (m, 2 H), 5.47 (m, 2 H), 5.59 (m, 2 H), 5.88 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.12, 29.77, 41.69, 75.69, 127.21, 131.83, 132.83, 170.09; mass spectrum *m/e* (rel intensity) 262 (3), 203 (6), 202 (6), 170 (27), 142 (50), 128 (100); HRMS calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1208. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.91. Found: C, 68.35; H, 6.83.

7α,10α-Dimethyl-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (5c). Compound **5c** was prepared from complex **3** (0.43 g, 1.87 mmol) and (*E,E*)-2,4-hexadiene (0.86 g, 10.5 mmol) in hexanes (350 mL) by irradiation (Pyrex, 1 h). Chromatography (silica gel, pentane) afforded 0.28 g (86%) of a colorless oil: IR (film) ν 3008, 2953, 2904, 2849, 1652; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, *J* = 7.3 Hz, 6 H), 2.10–2.30 (m, 2 H), 2.55 (m, 2 H), 2.70–2.85 (m, 2 H), 5.28 (m, 2 H), 5.81 (m, 2 H), 5.91 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.32, 37.08, 37.51, 44.26, 125.78, 134.86, 137.47; mass spectrum *m/e* (rel intensity) 174 (14), 159 (3), 92 (100); HRMS calcd for $C_{13}H_{18}$ 174.1408, found 174.1410.

7α-(Methoxycarbonyl)-10α-methyl-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (5d). Compound **5d** was prepared from complex **3** (570 mg, 2.5 mmol) and methyl sorbate (284 mg, 2.25 mmol) in hexanes (320 mL) by irradiation (uranium glass sleeve, 30 min). Chromatography (silica gel, hexanes/ether, 19:1) afforded 469 mg (96%) of a colorless oil: IR (film) ν 3018, 2957, 2917, 2875, 2855, 1739, 1435; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.2 Hz, 3 H), 2.23 (m, 3 H), 2.55 (m, 1 H), 2.69 (m, 1 H), 3.20 (m, 1 H), 3.60 (m, 1 H), 3.74 (s, 3 H), 5.40 (m, 1 H), 5.78 (m, 4 H), 5.92 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.29, 36.80, 37.50, 39.97, 44.19, 48.35, 52.13, 126.07, 126.76, 128.79, 133.89, 135.04, 139.19, 174.44; mass spectrum *m/e* (rel intensity) 218 (19), 159 (10), 127 (42), 92 (100); HRMS calcd for $C_{14}H_{18}O_2$ 218.1306, found 218.1303. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.08; H, 8.21.

7α,10α-Bis(methoxycarbonyl)-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (5e). Compound **5e** was prepared from complex **3** (167 mg, 0.73 mmol) and dimethyl muconate (153 mg, 0.90 mmol) in hexanes (350 mL) by irradiation (Pyrex, 40 min). Chromatography (silica gel; hexanes/ethyl acetate, 19:1) afforded 169 mg (89%) of the adduct as a white solid: mp 62–62.5 °C (hexanes/ether); IR ($CDCl_3$) ν 3022, 1734, 1656, 1105; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (m, 2 H), 3.25 (m, 2 H), 3.54 (m, 2 H), 3.77 (s, 6 H), 5.78 (m, 4 H), 5.98 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.10, 39.68, 47.88, 52.05, 126.59, 130.18, 133.69, 173.63; mass spectrum *m/e* (rel intensity) 262 (12), 231 (9), 203 (6), 144 (4), 143 (21), 92 (100); HRMS calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1209. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.91. Found: C, 68.35; H, 7.20.

7α-(Methoxycarbonyl)-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (5f). Compound **5f** was prepared from complex **3** (0.31 g, 1.36 mmol) and methyl penta-2,4-dienoate (0.16 mL, 1.38 mmol) in hexanes (320 mL) by irradiation (uranium glass, 2 h). Chromatography (silica gel, chloroform/hexanes, 1:3) yielded 0.23 g (83%) of a colorless oil: bp (0.1 Torr) = 100 °C; IR (film) ν 3008, 2948, 2916, 1725, 1425, 1200, 1167; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (m, 2 H), 2.41 (m, 2 H), 2.74 (br s, 1 H), 3.23 (br s, 1 H), 3.59 (m, 1 H), 3.74 (s, 3 H), 5.67–5.90 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.59, 36.71, 37.65, 40.68, 48.50, 52.15, 59.08, 125.07, 126.74, 131.07, 131.78, 134.04, 138.06, 174.53; mass spectrum *m/e* (rel intensity) 204 (15), 160 (5), 145 (15), 91 (100); HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1148. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.33; H, 7.88.

7α-Methyl-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-trien-11-one (7). A solution of (η^6-7,7-dimethoxy-1,3,5-cycloheptatriene)tricarbonylchromium(0)[10] (273 mg, 0.947 mmol) and piperylene (6.14 g, 90.1 mmol) in hexanes (350 mL) was irradiated (quartz) for 16.5 h. The reaction mixture was then concentrated to approximately 20 mL in vacuo and allowed to stir with $P(OMe)_3$ (10 mL) for 20 h. Removal of volatiles in vacuo followed by purification via flash chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) provided the cycloadduct (153 mg, 73%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.4 Hz, 3 H), 2.19 (m, 1 H), 2.37 (m, 1 H), 2.56 (m, 1 H), 2.75 (m, 1 H), 2.91 (m, 1 H), 3.19 (s, 3 H), 3.24 (s, 3 H), 5.50 (m, 1 H), 5.60 (m, 1 H), 5.61 (m, 2 H), 5.73 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.78, 25.87, 30.67, 43.54, 47.39, 47.80, 50.75, 103.03, 125.26, 126.18, 127.61, 128.90, 130.51, 138.66; HRMS calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1460.

A solution of the dimethoxy ketal cycloadduct (49 mg, 0.22 mmol) and a crystal of *p*-TsOH in acetone (3 mL) was allowed to stir for 1.25 h at room temperature. The reaction mixture was concentrated to 1 mL, diluted with diethyl ether, and washed with 5% aqueous sodium bicarbonate solution (20 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. Chromatography (silica gel; petroleum ether/ethyl acetate, 50:1) provided the product (30 mg, 77%) as a colorless oil: IR ($CDCl_3$) ν 3027, 1692, 1652; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (d, *J* = 7.2 Hz, 3 H), 2.31 (m, 1 H), 2.53 (m, 1 H), 2.71 (m, 1 H), 3.38 (m, 1 H), 3.53 (m, 1 H), 5.46–5.67 (m, 3 H), 5.76–5.92 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.51, 27.24, 34.56, 56.57, 63.20, 125.04, 125.58, 125.80, 127.14, 128.79, 138.21, 208.24; mass spectrum *m/e* (rel intensity) 174 (25), 159 (14), 107 (100); HRMS calcd for $C_{12}H_{14}O$ 174.1045, found 174.1042. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 7.99.

7α,10α-Dimethyl-3-methoxy-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (10). Employing the general procedure for electron-rich dienes outlined above, this compound was prepared from complex **9**[11] (736 mg, 2.85 mmol) and (*E,E*)-2,4-hexadiene (281 mg, 3.42 mmol) by irradiation (Pyrex, 2 h). Chromatography (silica gel, hexanes/ethyl acetate, 20:1) afforded 522 mg (90%) of the product as a colorless oil: IR (neat) ν 3006, 2950, 2865, 1696, 1654, 1450, 1266, 1006; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (d, *J* = 7.2 Hz, 3 H), 1.21 (d, *J* = 7.2 Hz, 3 H), 2.13 (dt, *J* = 13.8, 3.6 Hz, 1 H), 2.24 (dt, *J* = 13.8, 3.6 Hz, 1 H), 2.45–2.52 (m, 2 H), 2.69–2.75 (m, 2 H), 3.48 (s, 3 H), 4.98 (d, *J* = 7.2 Hz, 1 H), 5.24 (s, 2 H), 5.72 (dd, *J* = 12.6, 2.4 Hz, 1 H), 5.88 (dd, *J* = 12.6, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.27, 21.37, 37.51, 37.66, 37.79, 39.42, 43.51, 54.39, 101.94, 127.70, 134.14, 137.11, 137.66, 153.51; mass spectrum *m/e* (rel intensity) 204 (27), 122 (100), 107 (24), 91 (15); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1510.

7α,10α-Bis((*tert*-butyldimethylsilyl)oxy)-3-methoxy-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (11). Compound **11** was prepared using the general procedure for electron-rich dienes from complex **9** (127 mg, 0.49 mmol) and (*E,E*)-1,4-bis((*tert*-butyldimethylsilyl)oxy)butadiene[12] (170 mg, 0.54 mmol) by irradiation (Pyrex) for 4 h. Chromatography (silica gel, hexanes) provided the product (149 mg, 70%) as a white solid: mp 61–62 °C (hexanes); IR ($CHCl_3$) ν 3021, 2922, 2848, 1644, 1465, 1152, 1092; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 6 H), 0.08 (s, 6 H), 0.90 (s, 9 H), 0.91 (s, 9 H), 2.06 (dt, *J* = 14.1, 3.0 Hz, 1 H), 2.21 (dt, *J* = 14.7, 1.8 Hz, 1 H), 2.62–2.70 (m, 2 H), 3.48 (s, 3 H), 4.42 (d, *J* = 9.3 Hz, 2 H), 5.05 (dd, *J* = 7.2, 1.5 Hz, 1 H), 5.41 (s, 2 H), 5.76 (dd, *J* = 12.9, 2.4 Hz, 1 H), 5.93 (dd, *J* = 12.6, 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.85, −4.90, 18.03, 25.62, 25.78, 31.09, 41.16, 45.12, 54.34, 74.61, 74.73, 101.40, 128.27, 133.16, 135.31, 136.09, 153.64; mass spectrum *m/e* (rel intensity) 436 (2), 379 (5), 314 (100), 122 (7); HRMS calcd for $C_{24}H_{44}O_3Si_2$ 436.2829, found 436.2824.

(η^6-1-Methylcyclohepta-1,3,5-triene)tricarbonylchromium(0) (15). A solution of 1-methoxycycloheptatriene[13a] (10.0 g, 0.082 mol) in methanol (200 mL) was added dropwise to a cooled solution (ice bath) of concentrated aqueous hydrochloric acid (50 mL) and water (50 mL). The ice bath was removed after 30 min, and the reaction mixture was allowed to stir at room temperature for 1.5 h. The reaction mixture was then diluted with water (350 mL) and extracted with methylene chloride (3 × 400 mL). The organic phase was washed with saturated aqueous sodium bicarbonate solution (2 × 500 mL) and saturated aqueous sodium chloride solution (100 mL) and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo, and chromatography (silica gel, hexanes/ethyl acetate, 20:1) provided 2.9 g (33%) of product, which was immediately carried on to the next step.

Cerium trichloride heptahydrate (12.7 g, 0.0338 mol) was dried at 200 °C for 2 h under vacuum and then suspended in dry THF (100 mL). The vigorously stirred suspension was cooled to −78 °C, and methyllithium (25 mL of a 1.35 M solution in diethyl ether) was added dropwise to the solution. After the solution was stirred for 1 h at this temperature, dihydrotropone (1.96 g, 0.0181 mol) in dry THF (50 mL) was added dropwise to the reaction mixture. After the mixture was stirred an additional 1 h at −78 °C, the reaction was quenched with saturated aqueous ammonium chloride solution and allowed to warm to room temperature. This mixture was extracted with diethyl ether (3 × 150 mL), and the combined extracts were washed with saturated aqueous sodium bicarbonate solution (1 × 100 mL) and saturated aqueous sodium chloride solution (1 × 100 mL) and dried over anhydrous sodium sulfate. The solution was concentrated in vacuo, and chromatography (silica gel, hexanes/ethyl acetate, 5:1) provided 0.99 g (44%) of product as a colorless oil, which was carried on to the next step.

To a solution of 1-methylcyclohepta-3,5-dien-1-ol (0.366 g, 2.94 mmol) in freshly distilled pyridine (12 mL) was added thionyl chloride (0.4 g, 3.36 mmol). The resultant mixture was heated at reflux for 45 min, allowed to cool to room temperature, and diluted with pentane (150 mL). This mixture was washed consecutively with water (2 × 100 mL), saturated aqueous copper sulfate solution (2 × 100 mL), saturated aqueous sodium bicarbonate solution (2 × 100 mL), and saturated aqueous sodium chloride solution (1 × 100 mL) and then dried over anhydrous magnesium sulfate. The solvent was removed by distillation at ambient pressure to provide crude 1-methylcycloheptatriene (0.286 g), which was taken onto the next step without further purification.

Chromium hexacarbonyl (0.58 g, 2.63 mmol) and freshly distilled acetonitrile (15 mL) were heated at reflux in a flame-dried flask for 15 h. After the mixture was cooled to room temperature, the excess acetonitrile was removed under vacuum to give tris(acetonitrile)tricarbonylchromium(0) as a yellow pyrophoric solid. To this material was added dry THF (15 mL) and 1-methylcycloheptatriene (0.28 g, 2.63 mmol), and the mixture was heated at reflux for 2 h. After the solvent was removed in vacuo and chromatography was performed (silica gel, petroleum ether/diethyl ether, 50:1), 0.134 g (36%) of an orange oil was obtained: IR ($CDCl_3$) ν 2845, 1975, 1909, 1876, 1669, 1606, 1524; ^1H NMR (300 MHz, $CDCl_3$) δ 1.87 (dd, J = 14, 2 Hz, 1 H), 1.96 (s, 3 H), 2.68 (dd, J = 13.4, 9.35 Hz, 1 H), 3.22 (dt, J = 11.2, 2.4 Hz, 1 H), 4.61 (d, J = 6.5 Hz, 1 H), 4.89 (t, J = 7.8 Hz, 1 H), 5.90 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.86, 29.60, 52.48, 75.34, 96.38, 97.81, 98.91, 100.31; mass spectrum *m/e* (rel intensity) 242 (16), 186 (11), 158 (48), 143 (11); HRMS calcd for $C_{11}H_{10}O_3Cr$ 242.0040, found 242.0035.

8-((*tert*-Butyldimethylsilyl)oxy)-1β-methoxy-(6*H*β)-bicyclo[4,4.1]-undeca-2,4,8-triene (16). Compound **16** was prepared employing the general procedure for electron-rich dienes from complex **13**[13] (206 mg, 0.80 mmol) and 2-((*tert*-butyldimethylsilyl)oxy)butadiene (280 mg, 1.53 mmol) in hexanes (300 mL) by irradiation (Pyrex, 2 h). Chromatography (silica gel, hexanes) provided 127 mg (52%) of a colorless oil: bp (3 Torr) = 120 °C; IR ($CDCl_3$) ν 3067, 2897, 1663, 1467, 1190, 1058; ^1H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 6 H), 0.89 (s, 9 H), 1.95 (dt, J = 13.1, 3 Hz, 1 H), 2.12 (dd, J = 15.5, 6 Hz, 1 H), 2.26 (ddd, J = 14.7, 9.4, 2 Hz, 1 H), 2.48 (dd, J = 15, 5.6 Hz, 1 H), 2.55 (dt, J = 13.1, 2.5 Hz, 1 H), 2.70–2.78 (m, 2 H), 3.29 (s, 3 H), 4.50 (dd, J = 9.4, 6.5 Hz, 1 H), 5.59 (dd, J = 13.1, 3.7 Hz, 1 H), 5.75 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.58, −4.16, 18.09, 25.82, 35.59, 37.95, 38.53, 39.27, 50.53, 76.83, 100.42, 124.79, 125.71, 137.34, 138.89, 155.68; mass spectrum *m/e* (rel intensity) 306 (3), 134 (6), 122 (100); HRMS calcd for $C_{18}H_{30}O_2Si$ 306.2017, found 306.2015. Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.86. Found: C, 70.39; H, 9.76.

1β-Methoxy-7α-methyl-(6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (17a). Compound **17a** was prepared using the procedure for electron-rich dienes from complex **13** (0.5 g, 1.95 mmol) and piperylene (10 mL) in hexanes (300 mL) by irradiation (quartz, 2 h). Chromatography (silica gel, hexanes/ethyl acetate, 20:1) afforded 0.167 g (45%) of a colorless oil: bp (0.6 Torr) = 80 °C; IR ($CDCl_3$) ν 3020, 2964, 2936, 2880, 1617, 1069; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, J = 7.3 Hz, 3 H), 2.05 (d, J = 13 Hz, 1 H), 2.37 (m, 1 H), 2.50 (m, 1 H), 2.62 (m, 2 H), 2.75 (dt, J = 5, 2.5 Hz, 1 H), 3.28 (s, 3 H), 5.40–5.55 (m, 2 H), 5.70–5.80 (m, 3 H), 5.91 (dd, J = 11, 6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.78, 36.71, 38.75, 39.63, 42.86, 50.09, 75.72, 124.98, 125.61, 125.90, 135.14, 138.60, 140.05; mass spectrum *m/e* (rel intensity) 190 (7), 122 (100), 107 (27); HRMS calcd for $C_{13}H_{18}O$ 190.1352, found 190.1357. Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 82.06; H, 9.36.

1β-Methoxy-7α-((trimethylsilyl)oxy)-(6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (17b). Compound **17b** was prepared using the general procedure for electron-rich dienes from complex **13** (0.428 g, 1.66 mmol) and 1-((trimethylsilyl)oxy)butadiene (0.365 g, 2.56 mmol) in hexanes (300 mL) by irradiation (quartz, 4.5 h). Chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) afforded 0.124 g (38%) of an oil: bp (1 Torr) = 120 °C; IR ($CDCl_3$) ν 3030, 2960, 2828, 1253, 1064; ^1H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 2.05 (d, J = 13.3 Hz, 1 H), 2.45 (m, 2 H), 2.59 (ddd, J = 13.4, 4.0, 2.5 Hz, 1 H) 2.72 (m, 1 H), 3.26 (s, 3 H), 4.65 (d, J = 2.8 Hz, 1 H), 5.42 (m, 1 H), 5.55 (dd, J = 11.2, 1.8 Hz, 1 H), 5.65 (dt, J = 11, 2.6 Hz, 1 H), 5.80 (m, 2 H), 6.05 (dd, J = 11, 6.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.18, 36.51, 38.90, 44.92, 50.24, 74.45, 75.71, 123.29, 125.51, 126.17, 135.10, 138.29, 141.49; mass spectrum *m/e* (rel intensity) 264 (0.3), 232 (11), 174 (11), 159 (15), 142 (28), 122 (100); HRMS calcd for $C_{15}H_{24}O_2Si$ 264.1550, found 264.1545. Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.14. Found: C, 68.58; H, 8.61.

1β-Methoxy-8-methyl-(6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (18a) and 1β-Methoxy-9-methyl-(6*H*β)-bicyclo[4,4.1]undeca-2,4,8-triene (18b). Compounds **18a** and **18b** were prepared from complex **13** (175 mg, 0.68 mmol) and isoprene (681 mg, 10 mmol) in hexanes (300 mL) by irradiation (Pyrex, 2 h). Chromatography (silica gel, hexanes/diethyl ether, 20:1) provided 45.5 mg (35%) of **18a** and 15 mg (12%) of **18b**.

18a: colorless oil; IR (film) ν 2958, 2921, 2849, 1642, 1252, 1087; ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 3 H), 1.98–2.09 (m, 2 H), 2.29 (ddd, J = 13.8, 9.0, 2.4 Hz, 1 H), 2.50–2.61 (m, 3 H), 2.68–2.73 (m, 1 H), 3.27 (s, 3 H), 5.20–5.26 (m, 1 H), 5.55 (dd, J = 13.2, 2.0 Hz, 1 H), 5.67–5.81 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.68, 35.94, 36.37, 39.11, 39.34, 50.24, 76.91, 120.85, 124.01, 125.32, 137.04, 138.51, 140.74; mass spectrum *m/e* (rel intensity) 190 (9), 158 (9), 143 (17), 122 (100); HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1360.

18b: colorless oil; IR (film) ν 2977, 2803, 1633, 1371, 1090; ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 3 H), 2.01–2.08 (m, 1 H), 2.13–2.21 (m, 1 H), 2.25 (ddd, J = 8.4, 6.0, 1.2 Hz, 1 H), 2.37–2.44 (m, 1 H), 2.53–2.58 (m, 1 H), 2.73 (br s, 1 H), 2.77 (dd, J = 13.6, 1.6 Hz, 1 H), 3.26 (s, 3 H), 5.38 (m, 1 H), 5.60–5.86 (m, 4 H); ^{13}C NMR (75 HMz, $CDCl_3$) δ 26.87, 29.21, 31.37, 39.42, 44.16, 50.18, 76.90, 120.80, 125.26, 125.67, 137.39, 138.09, 140.75; mass spectrum *m/e* (rel intensity) 190 (13), 143 (7), 122 (100); HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1352.

8-((*tert*-Butyltrimethylsilyl)oxy)-1β-methyl-(6*H*β)-bicyclo[4.4.1]-undeca-2,4,8-triene (19). Compound **19** was prepared using the general procedure for electron-rich dienes from complex **15** (0.227 g, 0.937 mmol) and 2-((*tert*-butyldimethylsilyl)oxy)butadiene (0.17 g, 0.94 mmol) in hexanes (300 mL) by irradiation (Pyrex, 3 h). Chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) provided 0.095 g (35%) of a pale yellow oil: IR ($CDCl_3$) ν 2957, 2929, 2857, 1662, 1471; ^1H NMR (300 MHz, $CDCl_3$) δ 0.077 (s, 6 H), 0.89 (s, 9 H), 1.08 (s, 3 H), 1.85 (dt, J = 13.5, 2.1 Hz, 1 H), 2.03 (m, 1 H), 2.10 (dd, J = 9, 1.5 Hz, 1 H), 2.17 (ddt, J = 13.2, 4, 1.5 Hz, 1 H), 2.25 (dd, J = 14.7, 5.4 Hz, 1 H), 2.65 (m, 1 H), 2.75 (m, 1 H), 4.56 (m, 1 H), 5.46 (d, J = 11.4 Hz, 1 H), 5.70 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.82, −4.38, 25.60, 32.71, 36.75, 38.55, 38.62, 39.91, 43.93, 103.48, 123.15, 124.95, 137.05, 142.91, 154.64; mass spectrum *m/e* (rel intensity) 290 (15), 176 (12), 127 (21); HRMS calcd for $C_{18}H_{30}OSi$ 290.2068, found 290.2065.

1β-(Methoxycarbonyl)-7α-((trimethylsilyl)oxy)-(6*H*β)-bicyclo-[4,4,1]undeca-2,4,8-triene (20a) and 1β-(Methoxycarbonyl)-10α-((trimethylsilyl)oxy)-(6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (20b). Compounds **20a** and **20b** were prepared using the general procedure for electron-rich dienes from complex **14**[14a] (0.284 g, 0.993 mmol) and 1-((trimethylsilyl)oxy)-1,3-butadiene (0.41 g, 2.88 mmol) in hexanes (300 mL) by irradiation (Pyrex, 2 h). Chromatography (silica gel, petroleum ether/ethyl acetate, 80:1) afforded 0.064 g (22%) of an inseparable mixture consisting of equal portions of **20a** and **20b**: IR ($CDCl_3$) ν 3030, 2964, 1722, 1649, 1616, 1085; ^1H NMR (300 MHz, $CDCl_3$) δ 0.074 (s, 4.5 H), 0.13 (s, 4.5 H), 1.25 (m, 2 H), 2.25–2.60 (m, 7 H), 2.66 (m, 1 H), 2.80 (m, 1 H), 3.71 (s, 1.5 H), 3.73 (s, 1.5 H), 4.70 (d, J = 7.8 Hz, 0.5 H), 5.00 (t, J = 2.5 Hz, 0.5 H), 5.50–6.20 (m, 6 H); mass spectrum *m/e* (rel intensity) 292 (1), 143 (51), 142 (94), 127 (10); HRMS calcd for $C_{16}H_{24}O_3Si$ 292.1499, found 292.1495.

2-Methoxy-7α-(methoxycarbonyl)-10α-methyl-(1*H*β,6*H*β)-bicyclo-[4,4,1]undeca-2,4,8-triene (25a) and 2-Methoxy-10α-(methoxycarbonyl)-7α-methyl-(1*H*β,6*H*β)-bicyclo[4,4.1]undeca-2,4,8-triene (25b). Compounds **25a** and **25b** were prepared from complex **21**[10,13b] (0.151 g, 0.585 mmol) and methyl sorbate (0.10 g, 0.792 mmol) in hexanes (300 mL) by irradiation (Pyrex, 1 h). Chromatography (silica gel, hexanes/ethyl acetate, 40:1) afforded two products in a total of 89% yield.

25a (0.058 g, 40%): oil; bp (0.5 Torr) = 90 °C; IR ($CDCl_3$) ν 3017, 2964, 1735, 1649, 1623, 1018; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, J = 7.2 Hz, 3 H), 2.30 (m, 2 H), 2.43 (m, 1 H), 2.62 (ddd, J = 9.6, 4.7, 2.3 Hz, 1 H), 3.24 (t, J = 1.7 Hz, 1 H), 3.41 (s, 3 H), 3.52 (dt, J = 7.6, 2.3 Hz, 1 H), 3.73 (s, 3 H), 4.92 (d, J = 8 Hz, 1 H), 5.45 (ddd, J = 10.7, 5.0, 2.3 Hz, 1 H), 5.65 (m, 2 H), 6.03 (ddd, J = 11.0, 5.3, 2.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.04, 34.77, 37.86, 42.29, 43.22, 47.04, 51.81, 54.57, 97.22, 122.76, 127.39, 127.87, 139.08, 162.14, 174.11; mass spectrum *m/e* (rel intensity) 248 (17), 122 (100), 107 (20); HRMS calcd for $C_{15}H_{20}O_3$ 248.1407, found 248.1412. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.11. Found: C, 72.64; H, 8.21.

25b (0.071 g, 49%): oil; bp (0.5 Torr) = 90 °C; IR ($CDCl_3$) ν 3017, 2964, 1735, 1649, 1623, 1430, 1018; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, J = 7.2 Hz, 3 H), 2.28 (m, 2 H), 2.56 (br s, 1 H), 2.75 (m, 1 H), 3.48 (s, 3 H), 3.61 (m, 1 H), 3.75 (s, 3 H), 4.91 (d, J = 9 Hz, 1 H), 5.48 (m, 2 H), 5.72 (m, 1 H), 5.90 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.94, 34.29, 36.87, 38.29, 45.83, 48.31, 52.01, 54.16, 96.13, 123.67, 126.63, 129.22, 137.99, 164.10, 174.31; mass spectrum *m/e* (rel intensity) 248 (17), 122 (100), 107 (20); HRMS calcd for $C_{15}H_{20}O_3$ 248.1407, found 248.1412.

2-Methoxy-10α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (26a) and 2-Methoxy-7α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (26b). Compounds **26a** and **26b** were prepared using the general procedure for electron-rich dienes from complex **21** (0.089 g, 0.344 mmol) and 1-((trimethylsilyl)oxy)butadiene (0.20 g, 1.40 mmol) in hexanes (300 mL) by irradiation (Pyrex, 30 min). Chromatography (silica gel, carbon tetrachloride/chloroform, 7:3) provided two compounds in a total yield of 89%.

26a (0.049 g, 53%): oil; bp (0.16 Torr) = 90 °C; IR ($CDCl_3$) ν 3004, 2964, 1656, 1616, 1476, 1164; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 9 H), 2.07 (br s, 2 H), 2.24 (br s, 2 H), 2.53 (s, 1 H), 2.70 (s, 1 H), 3.42 (s, 3 H), 4.60 (s, 1 H), 4.80 (d, *J* = 8.5 Hz, 1 H), 5.35 (dd, *J* = 11.8, 6.5 Hz, 1 H), 5.45 (m, 2 H), 5.59 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.21, 31.29, 32.12, 35.82, 48.41, 54.74, 74.05, 96.81, 122.35, 127.21, 130.03, 140.03, 162.90; mass spectrum *m/e* (rel intensity) 264 (17), 142 (57), 122 (100); HRMS calcd for $C_{15}H_{24}O_2Si$ 264.1540, found 264.1545. Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.14. Found: C, 67.82; H, 9.01.

26b (0.033 g, 36%): IR ($CDCl_3$) ν 3004, 2964, 1656, 1616, 1164; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.138 (s, 9 H), 2.25 (m, 3 H), 2.66 (m, 3 H), 3.52 (s, 3 H), 4.58 (d, *J* = 2.5 Hz, 1 H), 4.90 (dd, *J* = 4.0, 3.7 Hz, 1 H), 5.60 (m, 2 H), 5.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.25, 30.08, 30.94, 39.25, 44.59, 54.25, 75.03, 95.58, 122.77, 125.30, 127.14, 141.23, 164.11; mass spectrum *m/e* (rel intensity) 264 (17), 142 (57), 122 (100); HRMS calcd for $C_{15}H_{24}O_2Si$ 264.1540, found 264.1545.

2-(Methoxycarbonyl)-10α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (27a) and 2-(Methoxycarbonyl)-7α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (27b). Compounds **27a** and **27b** were prepared using the general procedure for electron-rich dienes from complex **22** (0.29 g, 1.01 mmol) and 1-((trimethylsilyl)oxy)-1,3-butadiene (0.22 g, 1.54 mmol) in hexanes (300 mL) by irradiation (Pyrex, 1.5 h). Chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) afforded two products in a total yield of 75%.

27a (0.11 g, 37.5%): oil; bp (0.35 Torr) = 80 °C; IR ($CDCl_3$) ν 3033, 2951, 1704, 1640, 1606, 1089; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.084 (s, 9 H), 2.00 (m, 1 H), 2.30 (m, 1 H), 2.45 (m, 1 H), 2.80 (m, 1 H), 3.60 (m, 1 H), 3.71 (s, 3 H), 4.60 (m, 1 H), 5.40 (m, 1 H), 5.53 (d, *J* = 11.3 Hz, 1 H), 5.80 (dd, *J* = 11.8, 7.9 Hz, 1 H), 6.80 (d, *J* = 7.9 Hz, 1 H); mass spectrum *m/e* (rel intensity) 292 (2), 223 (5), 142 (100); HRMS calcd for $C_{15}H_{24}O_3Si$ 292.1490, found 292.1494.

27b (0.11 g, 37.5%): IR ($CDCl_3$) ν 3033, 2951, 1704, 1640, 1606, 1089; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.141 (s, 9 H), 2.00 (dd, *J* = 11.3, 1.5 Hz, 1 H), 2.25 (m, 1 H), 2.35 (t, *J* = 3.0 Hz, 1 H), 2.60 (m, 1 H), 2.90 (m, 1 H), 3.30 (br s, 1 H), 3.75 (s, 3 H), 4.50 (m, 1 H), 5.50 (m, 2 H), 6.00 (dd, *J* = 11.8, 8.2 Hz, 1 H), 6.35 (dd, *J* = 11.8, 6.75 Hz, 1 H), 7.11 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.18, 31.16, 32.68, 35.71, 46.93, 52.01, 75.07, 124.89, 126.89, 135.03, 136.45, 141.30, 142.80, 168.62; mass spectrum *m/e* (rel intensity) 292 (2), 223 (5), 142 (100); HRMS calcd for $C_{16}H_{24}O_3Si$ 292.1490, found 292.1494. Anal. Calcd for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27. Found: C, 66.18; H, 8.35.

7α,10α-Dimethyl-2-(methoxycarbonyl)-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-triene (28). Compound **28** was prepared from complex **22** (0.20 g, 0.71 mmol) and (*E,E*)-2,4-hexadiene (0.37 g, 4.38 mmol) in hexanes (300 mL) by irradiation (Pyrex, 30 min). Chromatography (silica gel, hexanes/ethyl acetate, 5:1) afforded 0.122 g (74%) of a white solid: mp 38–40 °C (hexanes); IR ($CHCl_3$) ν 3006, 2950, 2805, 1703, 1598, 1260, 1041; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (d, *J* = 7.5 Hz, 3 H), 1.23 (d, *J* = 7.2 Hz, 3 H), 1.95 (dt, *J* = 14.1, 3.6 Hz, 1 H), 2.33 (dt, *J* = 13.8, 3.3 Hz, 1 H), 2.34 (br s, 1 H), 2.81 (m, 1 H), 3.38 (br s, 1 H), 3.74 (s, 3 H), 5.15 (ddd, *J* = 10.5, 4.8, 2.1 Hz, 1 H), 5.26 (ddd, *J* = 10.5, 4.8, 2.1 Hz, 1 H), 5.92 (dd, *J* = 11.7, 8.1 Hz, 1 H), 6.18 (dd, *J* = 11.7, 6.9 Hz, 1 H), 6.97 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.07, 21.66, 35.69, 37.45, 37.55, 41.01, 44.31, 51.81, 124.53, 134.40, 135.68, 137.05, 137.82, 141.60, 170.47; mass spectrum *m/e* (rel intensity) 232 (8), 150 (19), 119 (15); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1460. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.60; H, 8.68. Found: C, 77.78; H, 8.49.

7α,10α-Dimethyl-3-(methoxycarbonyl)-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (29). Compound **29** was prepared from complex **23**[14a] (0.769 g, 2.69 mmol) and (*E,E*)-2,4-hexadiene (0.67 g, 8.15 mmol) in hexanes (300 mL) by irradiation (Pyrex, 30 min). Chromatography (silica gel, hexanes/ethyl acetate, 5:1) afforded 0.560 g (90%) of a white solid: mp 45–46 °C (hexanes); IR ($CHCl_3$) ν 3009, 2849, 1711, 1605, 1046; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (d, *J* = 7.2 Hz, 3 H), 1.24 (d, *J* = 7.5 Hz, 3 H), 2.12 (dt, *J* = 13.8, 3.6 Hz, 1 H), 2.15–2.21 (m, 2 H), 2.52 (br s, 1 H), 2.64–2.86 (m, 3 H), 3.72 (s, 3 H), 5.20 (s, 1 H), 5.98 (dd, *J* = 12.6, 7.2 Hz, 1 H), 6.42 (d, *J* = 12.6 Hz, 1 H), 7.20 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.24, 36.24, 37.36, 37.82, 43.59, 43.67, 51.92, 123.46, 129.77, 135.46, 136.72, 137.80, 144.79, 168.59; mass spectrum *m/e* (rel intensity) 232 (18), 150 (23), 149 (15), 119 (23); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1463.

8,9-Dimethyl-3-methoxy-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (30). Compound **30** was prepared from complex **9**[13b] (0.576 g, 2.23 mmol) and 2,3-dimethyl-1,3-butadiene (0.225 g, 2.73 mmol) in hexanes (300 mL) by irradiation (Pyrex, 1 h). Chromatography (silica gel, hexanes/ethyl acetate, 10:1) afforded 0.398 g (93%) of a colorless oil: IR (film) ν 3021, 2915, 1647, 1231, 1013; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 6 H), 1.94–2.16 (m, 4 H), 2.67 (br s, 2 H), 2.71 (br s, 2 H), 3.47 (s, 3 H), 4.88 (d, *J* = 6.9 Hz, 1 H), 5.66 (dd, *J* = 12.3, 2.4 Hz, 1 H), 5.77 (dd, *J* = 12.3, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.28, 22.50, 33.06, 36.84, 37.14, 39.34, 40.63, 54.32, 104.53, 126.56, 129.81, 130.27, 135.87, 153.24; mass spectrum *m/e* (rel intensity) 204 (29), 122 (100), 110 (45); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1514.

3,7α-Bis(methoxycarbonyl)-10α-methyl-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (31a) and 3,10α-Bis(methoxycarbonyl)-7α-methyl-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (31b). Compounds **31a** and **31b** were prepared from complex **23** (0.382 g, 1.33 mmol) and methyl sorbate (0.5 g, 3.96 mmol) in hexanes (300 mL) by irradiation (Pyrex, 30 min). Chromatography (silica gel, hexanes/ethyl acetate, 40:1) afforded two products in a total yield of 90%.

31a (0.183 g, 49.5%): oil; bp (2.5 Torr) = 130 °C; IR ($CDCl_3$) ν 2980, 1700, 1440, 1220; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.0 Hz, 3 H), 2.22 (m, 1 H), 2.27 (m, 1 H), 2.70 (m, 1 H), 2.80 (m, 1 H), 3.25 (m, 1 H), 3.60 (m, 1 H), 3.75 (s, 3 H), 3.78 (s, 3 H), 5.37 (ddd, *J* = 11.4, 5.3, 2.1 Hz, 1 H), 5.78 (ddd, *J* = 10.8, 5.4, 2.1 Hz, 1 H), 5.85 (dd, *J* = 12.4, 6.8 Hz, 1 H), 6.47 (d, *J* = 12.1 Hz, 1 H), 7.30 (d, *J* = 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.18, 35.88, 37.75, 39.18, 43.47, 48.05, 52.13, 124.31, 129.26, 129.89, 134.46, 138.37, 144.76, 168.44, 173.99; mass spectrum *m/e* (rel intensity) 276 (2), 261 (1), 245 (3), 217 (3), 205 (1), 150 (20); HRMS calcd for $C_{16}H_{20}O_4$ 276.1368, found 276.1362. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.29. Found: C, 69.62; H, 7.35.

31b (0.15 g, 40.5%): IR ($CDCl_3$) ν 1700; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, *J* = 7.0 Hz, 3 H), 2.20 (m, 1 H), 2.70 (m, 1 H), 3.40 (br s, 1 H), 3.58 (m, 1 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 5.40 (m, 1 H), 5.75 (m, 1 H), 6.10 (m, 1 H), 6.38 (d, *J* = 12.0 Hz, 1 H), 7.00 (d, *J* = 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.29, 36.00, 37.38, 39.03, 43.57, 48.17, 52.24, 123.88, 128.29, 130.72, 135.75, 139.75, 143.26, 168.63, 174.11; mass spectrum *m/e* (rel intensity) 276 (2), 261 (1), 245 (3), 217 (3), 150 (20); HRMS calcd for $C_{16}H_{20}O_4$ 276.1368, found 276.1362. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.29. Found: C, 69.52; H, 7.31.

3-Methoxy-7α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (32a) and 3-Methoxy-10α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (32b). Compounds **32a** and **32b** were prepared using the general procedure for electron-rich dienes from complex **9** (0.184 g, 0.71 mmol) and 1-((trimethylsilyl)oxy)-1,3-butadiene (0.35 g, 2.26 mmol) in hexanes (300 mL) by irradiation (quartz, 1 h). Chromatography (silica gel, hexanes/ethyl acetate, 90:1) provided 0.149 g (79%) of an inseparable mixture of regioisomers in a ratio of 1:1: bp (0.85 Torr) = 95 °C; IR ($CDCl_3$) ν 3041, 2959, 2836, 1655, 1441, 1081; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.130 (s, 9 H), 0.134 (s, 9 H), 2.15 (m, 4 H), 2.35 (m, 4 H), 2.71 (m, 4 H), 3.44 (s, 3 H), 3.48 (s, 3 H), 4.57 (d, *J* = 2.7 Hz, 1 H), 4.65 (d, *J* = 2.7 Hz, 1 H), 4.85 (dd, *J* = 5.8, 1.6 Hz, 1 H), 5.08 (m, 1 H), 5.50 (m, 4 H), 5.72 (m, 3 H), 5.95 (m, 1 H); mass spectrum *m/e* (rel intensity) 264 (8), 249 (8), 142 (18), 122 (100). Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.12; H, 9.14. Found: C, 68.54; H, 9.01.

10α,11β-Dimethyl-7α-(methoxycarbonyl)-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (35). Compound **35** was prepared from complex **33**[11b] (1.23 g, 5.25 mmol) and methyl sorbate (0.631, 5.0 mmol) in hexanes (320 mL) by irradiation (uranium glass, 3 h). Chromatography (silica gel, hexanes/diethyl ether; 95:5) afforded 1.12 g (97%) of a colorless oil: bp (0.54 Torr) = 66 °C; IR ($CDCl_3$) ν 3019, 1730, 1641; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (d, *J* = 7.2 Hz, 3 H), 1.24 (d, *J* = 7.3 Hz, 3 H), 2.20 (m, 1 H), 2.35 (m, 1 H), 2.54 (m, 1 H), 2.99 (m, 1 H), 3.45 (m, 1 H), 3.75 (s, 3 H), 5.35 (m, 1 H), 5.60 (m, 1 H), 5.79 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.41, 21.63, 38.18, 41.51, 45.69, 48.85, 50.43, 52.11, 126.76, 127.44, 127.97, 131.15, 132.45, 138.22, 174.34; mass spectrum *m/e* (rel intensity) 232 (16), 173 (4), 158 (2); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1465. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.67. Found: C, 77.66; H, 8.74.

11α-Methoxy-8-methyl-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (36). Compound **36** was prepared from complex **34**[11b,13b] (0.18 g, 0.70

mmol) and isoprene (0.24 g, 3.5 mmol) in hexanes (350 mmL) by irradiation (quartz, 2 h). Chromatography (silica gel, petroleum ether/EtOAc, 20:1) provided 87 mg (66%) of a colorless oil: bp (0.62 Torr) = 65 °C; IR ($CDCl_3$) ν 3015, 1642, 1171, 1098; ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.76 (dd, J = 13.8, 4.7 Hz, 1 H), 1.95 (m, 1 H), 2.87 (m, 3 H), 3.09 (m, 1 H), 3.38 (s, 3 H), 3.81 (m, 1 H), 5.26 (m, 1 H), 5.55 (m, 2 H), 5.68 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 26.00, 27.22, 30.45, 41.94, 42.33, 56.35, 82.55, 125.04, 125.36, 130.88, 132.21, 139.88; mass spectrum m/e (rel intensity) 190 (8), 175 (1), 159 (9), 158 (59), 144 (9), 143 (74); HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1353. Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 81.99; H, 9.64.

(η^6-2-Methylcyclohepta-2,4,6-trien-1-one)tricarbonylchromium(0) (37b). A flame-dried 250-mL round-bottomed flask equipped with a reflux condenser and nitrogen inlet was charged with chromium hexacarbonyl (0.916 g, 4.2 mmol) and freshly distilled acetonitrile (50 mL). The mixture was refluxed (15 h) and cooled to room temperature, and the solvent removed in vacuo. A solution of 2-methyltropone (0.25 g, 2.1 mmol) in THF (30 mL) was added to the resultant yellow solid under a blanket of nitrogen, and the solution was refluxed for 20 min. At this time the solution was cooled and carefully passed through a plug of silica gel to remove any inorganic residue, and the resultant filtrate was concentrated in vacuo. Chromatography (silica gel, hexanes/ethyl acetate, 1:1) provided 0.44 g (83%) of an orange-red solid: mp 76–78 °C (hexanes); IR (Nujol) ν 1988, 1937, 1906, 1585, 637; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3 H), 5.00 (d, J = 9.9 Hz, 1 H), 5.76 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.96, 88.96, 95.66, 96.22, 101.24, 102.09, 106.92, 175.80, 227.85; mass spectrum m/e (rel intensity) 256 (11), 228 (5), 200 (9), 172 (64), 120 (35); HRMS calcd for $C_{11}H_8O_4Cr$ 255.9828, found 255.9833. Anal. Calcd for $C_{11}H_8O_4Cr$: C, 51.57; H, 3.15. Found: C, 51.49; H, 3.14.

(η^6-2-*n*-Butylcyclohepta-2,4,6-trien-1-one)tricarbonylchromium(0) (37c). To solid tris(acetonitrile)tricarbonylchromium(0) prepared from $Cr(CO)_6$ (2.7 g, 12.3 mmol) was added 2-*n*-butylcyclohepta-2,4,6-trien-1-one (1.1 g, 6.8 mmol) in THF (50 mL), and the mixture refluxed for 30 min. Chromatography (silica gel, hexanes/ethyl acetate, 1:1) afforded 1.6 g (79%) of an orange-red solid: mp 72.5–73.5 °C (hexanes); IR (film) ν 1995, 1935 (br), 1603, 640; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (m, 3 H), 1.46 (m, 3 H), 1.71 (m, 1 H), 2.16 (m, 1 H), 2.74 (m, 1 H), 4.96 (d, J = 10.5 Hz, 1 H), 5.68 (m, 1 H), 5.78 (br s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.69, 22.62, 33.12, 34.76, 88.93, 95.95, 96.07, 100.82, 101.83, 111.84, 175.69, 227.96; mass spectrum m/e (rel intensity) 298 (10), 270 (4), 242 (10), 214 (100), 162 (24); HRMS calcd for $C_{14}H_{14}O_4Cr$ 298.0297, found 298.0300. Anal. Calcd for $C_{14}H_{14}O_4Cr$: C, 56.38; H, 4.73. Found: C, 56.30; H, 4.76.

7α-Methyl-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one (Table I, entry 1). This compound was prepared from complex **37a**[13b] (0.5 g, 2.06 mmol) and 1,3-pentadiene (2 mL, 20 mmol) in hexanes (300 mL) by irradiation (Pyrex, 2.5 h). Chromatography (silica gel, hexanes/ethyl acetate, 20:1) afforded 72 mg (20%) of a pale yellow oil: IR ($CDCl_3$) ν 3027, 1692, 1652; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (d, J = 7.2 Hz, 3 H), 2.31 (m, 1 H), 2.52 (m, 1 H), 2.70 (m, 1 H), 3.37 (m, 1 H), 3.53 (m, 1 H), 5.56 (m, 3 H), 5.83 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.50, 27.22, 34.56, 56.58, 63.21, 125.05, 125.60, 125.82, 127.17, 128.81, 138.22, 208.23; mass spectrum m/e (rel intensity) 174 (25), 159 (14), 107 (100); HRMS calcd for $C_{12}H_{14}O$ 174.1045, found 174.1042. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 7.99.

8-Methyl-(1*H*β,6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one (Table I, entry 2). This compound was prepared from complex **37a** (0.5 g, 2.06 mmol) and isoprene (2 mL, 21 mmol) in hexanes (300 mL) by irradiation (Pyrex, 2.5 h). Chromatography (silica gel, hexanes/EtOAc, 20:1) provided 145 mg (40%) of a colorless oil which was identical in all regards with authentic material.[3f]

1β,7α-Dimethyl-(6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one (Table I, entry 3). This compound was prepared from complex **37b** (0.425 g, 1.66 mmol) and 1,3-pentadiene (1.7 mL, 17 mmol) in hexanes (300 mL) by irradiation (Pyrex, 7 h). Chromatography (silica gel, hexanes) afforded 73 mg (23%) of a pale yellow oil: bp (0.54 Torr = 52 °C; IR (film) ν 2964, 1702, 1456, 1370, 1257, 1032; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (d, J = 7.5 Hz, 3 H), 1.34 (s, 3 H), 1.94 (dd, J = 15.3, 7.7 Hz, 1 H), 2.80 (m, 2 H), 3.37 (m, 1 H), 5.34 (d, J = 10.8 Hz, 1 H), 5.53 (dd, J = 11.4, 3.6 Hz, 1 H), 5.72 (m, 1 H), 5.82 (dd, J = 11.2, 4.4 Hz, 1 H), 5.93 (dd, J = 10.8, 6.6 Hz, 1 H), 6.02 (ddd, J = 11.2, 6.4, 1.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.30, 24.39, 32.21, 36.56, 56.27, 60.63, 125.34, 125.89, 127.08, 128.11, 133.88, 136.86, 206.95; mass spectrum m/e (rel intensity) 188 (22), 173 (32), 160 (28), 145 (72), 121 (66); HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1206.

1β,8-Dimethyl-(6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one and 1β,9-Dimethyl-(6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one (Table I, entry 4). These compounds were prepared from complex **37b** (0.4 g, 1.56 mmol) and isoprene (1.6 mL, 16 mmol) in hexanes (300 mL) by irradiation (Pyrex, 10 h). Chromatography (silica gel, hexanes) provided 191 mg (65%) of an inseparable 1:1 mixture of two regioisomers: bp (5.5 Torr) = 60 °C; IR (film) ν 2924, 1702, 1450, 713; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 3 H), 1.70 (d, J = 12.9 Hz, 3 H), 1.86 (m, 1 H), 2.49 (m, 2 H), 2.87 (m, 1 H), 3.55 (m, 1 H), 5.43 (m, 1 H), 5.51 (m, 1 H), 5.61 (m, 1 H), 5.97 (m, 2 H); mass spectrum m/e (rel intensity) 188 (18), 173 (35), 160 (30); HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1196.

1β-*n*-Butyl-8-methyl-(6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one and 1β-*n*-Butyl-9-methyl-(6*H*β)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one (Table I, entry 5). These compounds were prepared from complex **37c** (0.385 g, 1.29 mmol) and isoprene (2.7 mL, 27 mmol) in hexanes (300 mL) by irradiation (Pyrex, 7 h). Chromatography (silica gel, hexanes) provided 71 mg (24%) of an inseparable 1:1 mixture of regioisomers: bp (0.5 Torr) = 70 °C; IR (film) ν 2957, 1702, 1450, 1377; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (m, 3 H), 1.15 (m, 2 H), 1.30 (m, 2 H), 1.56 (m, 1 H), 1.68 (s, 1.5 H), 1.69 (s, 1.5 H), 1.87 (m, 1 H), 2.04 (m, 1 H), 2.31 (m, 1 H), 2.59 (m, 2 H), 3.59 (m, 1 H), 5.44 (m, 2 H), 5.66 (m, 1 H), 6.08 (m, 2 H); mass spectrum m/e (rel intensity) 230 (22), 173 (36), 145 (36), 133 (100); HRMS calcd for $C_{16}H_{22}O$ 230.1670, found 230.1665. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.58; H, 9.52.

(η^6-Thiepin 1,1-dioxo)tricarbonylchromium(0) (39). Tris(acetonitrile)tricarbonylchromium(0)[9c] [from $Cr(CO)_6$ (2.05 g, 9.28 mmol)] and thiepin 1,1-dioxide[21] (0.67 g, 4.64 mmol) were stirred with THF (75 mL) under nitrogen at room temperature for 12 h. The solvent was then removed in vacuo, and chromatography (silica gel, hexanes/EtOAc, 1:1) afforded 1.11 g (86%) of a red solid: mp 173–174 °C dec; IR (Nujol) ν 3074, 3041, 2017, 1986, 1946, 1302, 1142, 1122; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (d, J = 8.4 Hz, 2 H), 5.66 (m, 2 H), 6.00 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.76, 93.19, 99.91, 226.04; mass spectrum m/e (rel intensity) 278 (5), 222 (12), 194 (70), 78 (100); HRMS calcd for $C_9H_6O_5SCr$ 277.9341, found 277.9337. Anal. Calcd for $C_9H_6O_5SCr$: C, 38.89; H, 2.18. Found: C, 38.72; H, 2.05.

11-(Methoxycarbonyl)-8-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-11-azabicyclo[4.4.1]undeca-2,4,8-triene (41a). Compound **41a** was prepared from complex **38** (0.47 g, 1.62 mmol) and 2-((trimethylsilyl)oxy)-1,3-butadiene (0.34 g, 2.38 mmol) in hexanes/Et_2O (70:1) (300 mL) by irradiation (Pyrex, 30 min). Decomplexation was achieved by suspending the adduct in diethyl ether (25 mL), purging it with oxygen, and stirring the resultant solution under a blanket of oxygen for 36 h. Chromatography (silica gel, hexanes/ethyl acetate, 4:1) provided two compounds.

41a (91 mg, 19%) (exists as N-(CO)OMe rotamers): IR ($CDCl_3$) ν 3024, 1681; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 2.25–2.47 (m, 3 H), 2.71 (m, 1 H), 3.65 (s, 3 H), 4.75 (m, 1 H), 4.95 (m, 0.5 H), 5.10 (m, 0.5 H), 5.17 (m, 0.5 H), 5.34 (m, 0.5 H), 5.78 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.10, 28.76, 28.86, 37.98, 52.34, 52.47, 52.82, 54.26, 54.42, 102.39, 102.76, 124.03, 124.09, 124.42, 124.53, 136.03, 136.68, 136.71, 137.47, 156.85; mass spectrum m/e (rel intensity) 293 (5) 278 (0.5), 204 (0.2), 151 (100); HRMS calcd for $C_{15}H_{23}NO_3Si$ 293.1447, found 293.1451.

Ketone from **41a** (150 mg, 68%) (exists as N–(CO)OMe rotamers): IR ($CDCl_3$) ν 3026, 1697, 1644; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (m, 2 H), 2.50 (m, 2 H), 2.80 (m, 2 H), 3.66 (s, 3 H), 5.01 (m, 0.5 H), 5.24 (m, 1 H), 5.46 (m, 0.5 H), 5.85 (m, 3 H), 6.04 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.32, 26.36, 40.50, 40.70, 46.65, 46.84, 52.21, 52.50, 53.10, 55.68, 55.95, 124.15, 124.53, 125.11, 125.50, 134.87, 135.49, 136.00, 136.61, 156.23, 156.41, 209.21, 209.30; mass spectrum m/e (rel intensity) 221 (100), 206 (2), 190 (2), 162 (10); HRMS calcd for $C_{12}H_{15}NO_3$ 221.1051, found 221.1051.

7α-Acetoxy-11-(methoxycarbonyl)-(1*H*β,6*H*β)-11-azabicyclo[4.4.1]undeca-2,4,8-triene (41b). Compound **41b** was prepared from complex **38** (0.30 g, 1.04 mmol) and 1-acetoxy-1,3-butadiene (E/Z mixture, 0.3 g, 2.7 mmol) in hexanes/Et_2O (70:1) (350 mL) by irradiation (Pyrex, 1 h). The product was decomplexed as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 9:1) afforded 0.21 g (75%) of a viscous oil that exists as a mixture of N–(CO)OMe rotamers: IR ($CDCl_3$) ν 3027, 1738, 1689, 1044; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 3 H), 2.52 (m, 2 H), 3.68 (s, 3 H), 5.11 (m, 0.5 H), 5.21 (m, 0.5 H), 5.31 (m, 0.5 H), 5.40 (m, 0.5 H), 5.65 (m, 2 H), 5.70–6.00 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.08, 31.07, 31.24, 53.31, 53.91, 54.15, 57.46, 57.57, 73.52, 73.69, 124.52, 124.78, 126.23, 126.56, 127.56, 128.21, 131.36, 132.20, 134.47, 135.28, 135.44, 136.10, 156.82, 169.85; mass spectrum m/e (rel intensity) 263 (3), 204 (4), 203 (10), 188 (1), 151 (100); HRMS calcd for $C_{14}H_{17}NO_4$ 263.1157, found 263.1160.

11-(Methoxycarbonyl)-7α-((trimethylsilyl)oxy)-(1*H*β,6*H*β)-11-azabicyclo[4.4.1]undeca-2,4,8-triene (41c). Compound **41c** was prepared from complex **38** (0.34 g, 1.15 mmol) and (E)-1-((trimethylsilyl)oxy)-1,3-butadiene (0.32 g, 2.28 mmol) in hexanes/Et_2O (70:1) (350 mL) by irradiation (Pyrex, 1 h). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 4:1) provided 0.27 g

(79%) of a colorless oil that exists as a mixture of N–(CO)OMe rotamers: IR ($CDCl_3$) ν 3024, 1684, 1088, 1039; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 2.49 (m, 2 H), 3.71 (s, 3 H), 4.60 (m, 1 H), 5.08 (m, 1 H), 5.30 (m, 1 H), 5.65 (m, 2 H), 5.76 (m, 3 H), 6.05 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.11, 31.28, 53.13, 53.85, 60.82, 61.20, 72.47, 72.91, 124.91, 125.32, 125.73, 125.82, 126.35, 132.49, 133.59, 134.99, 135.52, 140.04, 140.36, 156.79; mass spectrum *m/e* (rel intensity) 293 (0.5), 278 (0.3), 151 (100); HRMS calcd for $C_{15}H_{23}NO_3Si$ 293.1447, found 293.1453. Anal. Calcd for $C_{15}H_{23}NO_3Si$: C, 61.39; H, 7.90; N, 4.77. Found: C, 61.52; H, 7.84; N, 4.74.

7α,11-Bis(methoxycarbonyl)-10α-methyl-(1*H*β,6*H*β)-11-azabicyclo[4.4,1]undeca-2,4,8-triene (41d). Compound **41d** was prepared from complex **38** (0.27 g, 0.95 mmol) and methyl sorbate (0.15 g, 1.15 mmol) in hexanes/Et_2O (70:1) (350 mL) by irradiation (Pyrex, 1 h). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/diethyl ether, 4:1) afforded 0.22 g (83%) of white crystals that exist as a mixture of N–(CO)OMe rotamers: mp 84–86 °C (hexanes–diethyl ether, 4:1); IR ($CDCl_3$) ν 3031, 1737, 1694, 1097; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (d, J = 7.3 Hz, 3 H), 2.83 (m, 1 H), 3.72 (s, 3 H), 3.79 (s, 3 H), 4.96 (m, 0.5 H), 5.18 (m, 0.5 H), 5.58 (m, 1 H), 5.76 (m, 4 H), 5.95 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.99, 37.47, 37.70, 48.28, 52.41, 53.28, 55.86, 59.76, 60.11, 125.22, 125.48, 125.62, 125.89, 128.37, 128.95, 132.01, 132.18, 132.56, 132.99, 137.68, 138.27, 156.80, 172.27; mass spectrum *m/e* (rel intensity) 277 (7), 246 (3), 218 (0.8), 151 (100); HRMS calcd for $C_{15}H_{19}NO_4$ 277.1313, found 277.1309. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.26; H, 6.97; N, 5.23.

8-Methyl-(1*H*β,6*H*β)-11-thiabicyclo[4.4.1]undeca-2,4,8-triene 11,11-Dioxide (42a). Compound **42a** was prepared from complex **39** (0.15 g, 0.54 mmol) and isoprene (1.6 mL, 16 mmol) in hexanes/CH_2Cl_2 (1:1) (350 mL) by irradiation (uranium glass, 30 min). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 2:1) provided 87 mg (77%) of a white solid: mp 147–148 °C (hexanes/diethyl ether); IR (Nujol) ν 3028, 1659, 1286, 1211, 1108; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, 3 H), 2.33 (m, 1 H), 2.54 (m, 1 H), 2.95 (m, 1 H), 3.14 (d, J = 15.4 Hz, 1 H), 3.82 (d, J = 5.2 Hz, 2 H), 5.47 (m, 3 H), 5.92 (m, 2 H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.30, 31.68, 64.55, 65.14, 122.25, 123.28, 123.45, 127.76, 127.79, 138.98; mass spectrum *m/e* (rel intensity) 210 (0.6), 145 (34), 91 (100); HRMS calcd for $C_{11}H_{14}O_2S$ 210.0714, found 210.0710. Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.89; H, 6.72. Found: C, 62.85; H, 6.78.

7α-Acetoxy-(1*H*β,6*H*β)-11-thiabicyclo[4,4,1]undeca-2,4,8-triene 11,11-Dioxide (42b), Compound **42b** was prepared from complex **39** (0.15 g, 0.54 mmol) and 1-acetoxy-1,3-butadiene (*E*/*Z* isomer mixture, 0.64 mL, 5.4 mmol) in hexanes/CH_2Cl_2 (1:1) (350 mL) by irradiation (uranium glass, 50 min). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 2:1) afforded 108 mg (78%) of a white solid: mp 151–152 °C (hexanes/diethyl ether); IR (Nujol) ν 3049, 1725, 1645, 1292, 1219, 1113; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 2.68 (m, 1 H), 2.98 (m, 1 H), 3.84 (m, 1 H), 4.06 (m, 1 H), 5.56 (m, 3 H), 5.74 (m, 1 H), 5.99 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.86, 26.30, 64.53, 68.73, 70.08, 120.31, 123.22, 126.22, 127.90, 129.42, 135.14, 169.36; mass spectrum *m/e* (rel intensity) 255 (M + H, 25), 254 (M^+ 7), 212 (26), 195 (45); HRMS calcd for $C_{12}H_{15}O_4S$ (M + H) 255.0690, found 255.0694. Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.73; H, 5.56. Found: C, 56.49; H, 5.58.

7α-((Trimethylsilyl)oxy)-(1*H*β,6*H*β)-11-thiabicyclo[4.4,1]undeca-2,4,8-triene 11,11-Dioxide (42c). Compound **42c** was prepared from complex **39** (0.167 g, 0.6 mmol) and 1-((trimethylsilyl)oxy)-1,3-butadiene (1 mL, 6.0 mmol) in hexanes/CH_2Cl_2 (1:1) (350 mL) by irradiation (uranium glass, 1 h). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 2:1) afforded 110 mg (65%) of a white solid: mp 139–142 °C (hexanes/diethyl ether); IR (Nujol) ν 3042, 1304, 1257, 1118; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 2.62 (m, 1 H), 2.88 (m, 1 H), 3.76 (m, 1 H), 3.88 (m, 1 H), 5.07 (br s, 1 H), 5.47 (dd, J = 9.0, 7.0 Hz, 1 H), 5.66 (m, 3 H), 5.95 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.23, 26.10, 64.03, 68.73, 72.49, 121.30, 122.64, 124.42, 128.09, 128.43, 140.15; mass spectrum *m/e* (rel intensity) 284 (4), 142 (60), 73 (100); HRMS calcd for $C_{13}H_{20}O_3SSi$ 284.0902, found 284.0906.

7α-(Methoxycarbonyl)-(1*H*β,6*H*β)-11-thiabicyclo[4,4,1]undeca-2,4,8-triene 11,11-Dioxide (42d), Compound **42d** was prepared from complex **39** (0.13 g, 0.47 mmol) and methyl penta-2,4-dienoate (0.54 mL, 4.7 mmol) in hexanes/CH_2Cl_2 (1:1) (350 mL) by irradiation (uranium glass, 30 min). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 2:1) afforded 45 mg (38%) of a white solid: mp 121–122 °C (hexanes/Et_2O); IR (Nujol) ν 3041, 3029, 1722, 1649, 1430, 1290, 1254; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.68 (m, 1 H), 2.95 (dd, J = 15.6, 5.4 Hz, 1 H), 3.81 (s, 3 H), 3.85 (m, 1 H), 4.14 (d, J = 5.5 Hz, 1 H), 4.43 (m, 1 H), 5.53 (m, 2 H), 5.94 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.41, 43.14, 53.04, 64.59, 66.48, 121.15, 123.23, 127.86, 128.92, 129.65, 130.49, 171.25; mass spectrum *m/e* (rel intensity) 254 (0.3), 223 (4), 190 (18), 158 (19), 131 (100); HRMS calcd for $C_{12}H_{14}O_4S$ 254.0612, (M – OMe) 223.0429, found 223.0431. Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.73; H, 5.56. Found: C, 56.44; H, 5.57.

7α-(Methoxycarbonyl)-10α-methyl-(1*H*β,6*H*β)-11-thiabicyclo[4,4,1]undeca-2,4,8-triene 11,11-Dioxide (42e). Compound **42e** was prepared from complex **39** (0.166 g, 0.597 mmol) and methyl sorbate (0.817 g, 6.48 mmol) in hexanes/CH_2Cl_2 (1:1) (350 mL) by irradiation (uranium glass, 70 min). Decomplexation was achieved as for **41a**, and chromatography (silica gel, hexanes/ethyl acetate, 2:1) afforded 33 mg (21%) of a white solid: mp 61–62 °C (hexanes/Et_2O); IR (Nujol) ν 3028, 1731, 1651, 1618, 1452, 1432, 1312, 1172, 1113; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (d, J = 7.2 Hz, 3 H), 3.27 (m, 1 H), 3.63 (m, 1 H), 3.81 (s, 3 H), 4.14 (d, J = 6.2 Hz, 1 H), 4.39 (m, 1 H), 5.57 (m, 3 H), 5.86 (m, 1 H), 5.96 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.43, 32.62, 43.27, 53.06, 65.62, 70.71, 120.95, 121.19, 127.96, 128.82, 128.98, 137.22, 171.20; mass spectrum *m/e* (rel intensity) 268 (0.7), 237 (5), 204 (20), 145 (100); HRMS calcd for $C_{13}H_{16}O_4S$, 268.0769, (M – OMe) 237.0585, found 237.0581.

[1*S*-(1β,2α,5α)]-5-Methyl-2-(1-methylethyl)cyclohexyl 2,4-Hexadienoate (43), To sorbic acid (1.12 g, 10 mmol) in dichloromethane (10 mL) were added 4-(dimethylamino)pyridine (0.122 g, 1.0 mmol), [1*S*-(1β,2α,5α)]-5-methyl-2-(1-methylethyl)cyclohexanol (1.72 g, 11 mmol), and the resultant solution was cooled to 5 °C. 1,3-Dicyclohexylcarbodiimide (2.06 g, 10 mmol) was added, and the mixture was warmed to room temperature and stirred at that temperature for 3 h. The reaction mixture was then washed with 5% aqueous hydrochloric acid solution (5 mL) and saturated aqueous sodium bicarbonate solution (5 mL) and dried over anhydrous magnesium sulfate. Chromatography (silica gel, dichloromethane) provided 2.48 g (99%) of a colorless oil: bp (7 Torr) = 137 °C; $[\alpha]^{24.5}{}_D = +16.14°$ (c = 0.01, $CHCl_3$); IR (film) ν 2964, 2871, 1702, 1643, 1616, 1141; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, J = 7.4 Hz, 3 H), 0.91 (m, 6 H), 1.53 (m, 8 H), 1.82 (d, J = 6.9 Hz, 3 H), 5.08 (m, 1 H), 5.75 (d, J = 15 Hz, 1 H), 6.12 (m, 2 H), 7.20 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.40, 18.83, 20.01, 21.29, 26.85, 27.65, 30.03, 35.95, 45.91, 72.13, 120.00, 130.04, 138.89, 144.83, 167.10; mass spectrum *m/e* (rel intensity) 138 (54), 123 (12), 113 (11), 95 (100); HRMS calcd for $C_{16}H_{26}O_2$ 250.1932, (M – $C_6H_6O_2$) 138.1408, found 138.1407.

7α-((([1*S*-(1β,2α,5α)]-5-Methyl-2-(1-methylethyl)cyclohexyl)oxy)carbonyl)-10α-methyl-(1*H*β,6*H*β)-bicyclo[4.4,1]undeca-2,4,8-triene (46a), Compound **46a** was prepared from complex **3** (1.71 g, 7.50 mmol) and diene **43** (0.925 g, 5.0 mmol) in hexanes (320 mL) by irradiation (quartz, 3.5 h). Chromatography (silica gel, hexanes/diethyl ether, 9:1) afforded 0.86 g (50%) (0% de) of a colorless oil: IR (film) ν 3016, 2959, 1729, 1462, 1190, 709; ^{1}H NMR (300 Hz, $CDCl_3$) δ 0.82 (d, J = 10.2 Hz, 3 H), 0.93 (m, 6 H), 1.22 (d, J = 9.5 Hz, 3 H), 1.36 (m, 2 H), 1.52 (m, 6 H), 1.76 (m, 1 H), 1.87 (m, 1 H), 2.21 (m, 1 H), 2.28 (m, 1 H), 2.54 (m, 1 H), 2.69 (m, 1 H), 3.20 (m, 1 H), 3.58 (m, 1 H), 5.19 (m, 1 H), 5.41 (m, 1 H), 5.82 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.02, 20.63, 20.89, 21.02, 21.32, 26.36, 27.72, 30.07, 35.92, 36.90, 37.57, 40.18, 40.27, 44.29, 45.83, 48.69, 48.78, 72.21, 126.08, 126.67, 129.21, 134.05, 135.03, 138.84, 173.28; mass spectrum *m/e* (rel intensity) 342 (2) 204 (45), 138 (25); HRMS calcd for $C_{23}H_{32}O_2$ 342.2559, found 342.2563.

7α-((4*S*-4-(Phenylmethyl)-2-oxooxazolidin-3-yl)carbonyl)-10α-methyl-(1*H*β,6*H*β)-bicyclo[4.4,1]undeca-2,4,8-triene (46b). Compound **46b** was prepared from complex **3** (0.25 g, 1.1 mmol) and diene **44**[27c] (0.27 g, 1.0 mmol) in hexanes (320 mL) by irradiation (Pyrex, 2 h). Chromatography (silica gel, hexanes/diethyl ether, 1:1) afforded 0.27 g (75%) (45% de) of a white solid. Recrystallization (hexanes) gave only the major diastereomer: mp 158–159 °C (hexanes); $[\alpha]^{25.0}{}_D = +110.16°$ (c = 0.0133, $CHCl_3$); IR ($CDCl_3$) ν 3022, 2964, 2918, 2877, 1777, 1699, 1384, 1209; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (d, J = 7.2 Hz, 3 H), 2.22 (m, 1 H), 2.57 (m, 2 H), 2.80 (m, 2 H), 3.36 (dd, J = 16.2, 3.3 Hz, 1 H), 3.66 (dd, J = 12.3, 10.8 Hz, 1 H), 4.21 (m, 2 H), 4.76 (m, 1 H), 4.88 (m, 1 H), 5.42 (m, 1 H), 5.66 (m, 1 H), 5.91 (m, 4 H), 7.31 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.32, 36.58, 37.46, 38.34, 40.62, 44.14, 47.35, 55.46, 66.38, 125.93, 127.37, 127.54, 127.69, 129.14, 129.53, 132.95, 135.44, 139.27; mass spectrum *m/e* (rel intensity) 363 (19), 272 (36), 186 (31), 144 (18), 95 (100); HRMS calcd for $C_{23}H_{25}NO_3$ 363.1834, found 363.1830.

7α-(([3a*S*-(3aα,6α,7aβ)]-Hexahydro-8,8-dimethyl-2,2-dioxo-3*H*-3a,6-methano-2,1-benzoisothiazolyl)carbonyl)-10α-methyl-(1*H*β,6*H*β)-bicyclo[4,4,1]undeca-2,4,8-triene (46c). Compound **46c** was prepared from complex **3** (0.25 g, 1.1 mmol) and diene **45**[28b] (0.309 g, 1 mmol) in hexanes (320 mL) by irradiation (uranium glass, 4 h). Chromatography (silica gel, chloroform/carbon tetrachloride, 1:1) afforded 0.297 g (74%) (84% de) of a white solid. Recrystallization (hexanes) provided only the major diastereomer: mp 207–208 °C (hexanes); $[\alpha]^{25.0}{}_D = -123.41°$ ($c = 0.003$, $CHCl_3$); IR ($CDCl_3$) ν 3016, 2976, 2905, 1699, 1480, 791; ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (s, 3 H), 1.16 (s, 3 H), 1.20 (d, J = 7.2 Hz, 3 H), 1.40 (m, 2 H), 1.89 (m, 3 H), 2.12 (m, 3 H), 2.47 (m, 1 H), 2.58 (m, 1 H), 2.80 (m, 1 H), 3.02 (m, 1 H), 3.48 (d, J = 3.3 Hz, 2 H), 3.93 (m, 1 H), 4.21 (m, 1 H), 5.37 (m, 1 H), 5.52 (m, 1 H), 5.84 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.00, 20.95, 21.28, 26.62, 32.84, 36.46, 37.54, 38.74, 41.49, 44.09, 44.62, 47.94, 48.50, 49.64, 53.23, 65.22, 125.87, 127.19, 127.34, 132.66, 135.46, 139.10, 173.12; mass spectrum *m/e* (rel intensity) 401 (57), 310 (78), 187 (18), 159 (20), 135 (66); HRMS calcd for $C_{23}H_{31}NO_3S$ 401.2025, found 401.2028. Anal. Calcd for $C_{23}H_{31}NO_3S$: C, 68.86; H, 7.79. Found: C, 68.75; H, 7.81.

7α-(([3a*S*-(3aα,6α,7aβ)]-Hexahydro-8,8-dimethyl-2,2-dioxo-3*H*-3a,6-methano-2,1-benzoisothiazolyl)carbonyl)-10α,11β-dimethyl-(1$H\beta$,6$H\beta$)-bicyclo[4.4.1]undeca-2,4,8-triene (47). Compound **47** was prepared from complex **33**[11b] (0.433 g, 1.79 mmol) and diene **45** (0.464 g, 1.5 mmol) in hexanes (320 mL) by irradiation (uranium glass, 3.5 h). Chromatography (silica gel, hexanes/diethyl ether, 7:3) afforded 0.464 g (74%) (75% de) of a white solid. Recrystallization (hexanes/ethyl acetate, 9:1) provided only the major diastereomer: mp 200.5–201.5 °C; $[\alpha]^{25.0}{}_D = -150.54°$ ($c = 0.076$, $CHCl_3$); IR ($CDCl_3$) ν 3012, 2964, 2877, 1697, 1331, 789; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (d, J = 6.9 Hz, 3 H), 0.98 (s, 3 H), 1.18 (s, 3 H), 1.22 (d, J = 7.2 Hz, 3 H), 1.40 (m, 2 H), 1.90 (m, 3 H), 2.09 (m, 2 H), 2.37 (m, 2 H), 2.65 (t, J = 6.3 Hz, 1 H), 2.81 (m, 1 H), 3.48 (d, J = 4.2 Hz, 2 H), 3.93 (m, 1 H), 4.05 (m, 1 H), 5.36 (m, 2 H), 5.79 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.99, 20.81, 21.41, 21.83, 26.62, 32.83, 38.32, 38.73, 40.94, 44.65, 47.12, 47.94, 48.50, 50.08, 50.27, 53.23, 65.21, 126.52, 126.56, 127.79, 129.92, 132.81, 138.16, 173.09; mass spectrum *m/e* (rel intensity) 415 (24), 310 (44), 201 (6), 135 (50); HRMS calcd for $C_{24}H_{33}NO_3S$ 415.2181, found 415.2186. Anal. Calcd for $C_{24}H_{33}NO_3S$: C, 69.36; H, 8.00; N, 3.37. Found: C, 69.47; H, 8.19; N, 3.46.

(η^6-Thiepin 1,1-dioxo)tricarbonylmolybdenum(0) (48). Hexacarbonylmolybdenum (0.557 g, 2.11 mmol) and thiepin 1,1-dioxide (0.100 g, 0.70 mmol) were heated under reflux in dry tetrahydrofuran (50 mL) for 5.5 h. The solvent was evaporated, and the residue was purified by chromatography using diethyl ether as eluant to yield 0.131 g (57%) of a red-orange solid: mp 149–151 °C dec; IR (Nujol) ν 3082, 3050, 2030, 1970, 1937, 1340, 1303, 1145, 1115; ^1H NMR (300 MHz, $CDCl_3$) δ 4.97 (d, J = 8.3 Hz, 2 H), 5.52 (m, 2 H), 6.01 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.7, 91.1, 98.4, 212.7; MS *m/e* (rel intensity) 324 (8), 296 (4), 268 (5), 142 (3), 78 (100), 64 (16); HRMS calcd for $C_9H_6O_5SMo$ 323.8991, found 323.8997. Anal. Calcd for $C_9H_6O_5SMo$: C, 33.56; H, 1.88. Found: C, 33.43; H, 1.95.

(η^6-Thiepin 1,1-dioxo)tricarbonyltungsten(0) (49). Tris(acetonitrile)tricarbonyltungsten [from $W(CO)_6$ (3.00 g, 8.53 mmol)] and thiepin 1,1-dioxide (0.188 g, 1.32 mmol) were heated under reflux in dry tetrahydrofuran (75 mL) for 25 h. The solvent was evaporated, and the residue was purified by chromatography using 2:1 hexanes/EtOAc as eluant to yield 0.197 g (37%) of a red solid: mp 173–176 °C dec; IR (Nujol) ν 3074, 3050, 2027, 1961, 1922, 1337, 1304, 1144, 1115; ^1H NMR (300 MHz, $CDCl_3$) δ 4.96 (d, J = 8.2 Hz, 2 H), 5.46 (m, 2 H), 6.00 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.2, 87.8, 95.0, 202.6; MS *m/e* (rel intensity) 410 (16), 382 (4), 326 (0.2), 142 (0.4), 78 (100), 64 (14); HRMS calcd for $C_9H_6O_5SW$ 409.9446, found 409.9451. Anal. Calcd for $C_9H_6O_5SW$: C, 26.36; H, 1.48. Found: C, 26.44; H, 1.54.

Bicyclo[4,4.1]undeca-2,4-dien-8-one (52a). Compound **52a** was prepared employing the general procedure for electron-rich dienes from complex **3** (0.468 g, 2.05 mmol) and 2-((trimethylsilyl)oxy)-1,3-butadiene (0.436 g, 3.06 mmol) in pentane (350 mL) by irradiation (quartz, 4 h). Treatment of the crude adduct with 5% aqueous hydrochloric acid solution (5 mL) at room temperature (3 h) followed by dilution with diethyl ether (20 mL), washing this solution with saturated aqueous sodium bicarbonate solution (3 × 25 mL), and drying with anhydrous sodium sulfate provided the crude ketone. Chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) afforded 0.27 g (82%) of a white solid: mp 46–46.5 °C (hexanes); IR ($CDCl_3$) ν 3019, 1695, 1646; ^1H NMR (300 MHz, $CDCl_3$) δ 1.80–2.82 (m, 8 H), 2.89 (m, 1 H), 3.02 (m, 1 H), 5.69–5.92 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.48, 35.54, 37.23, 39.93, 40.11, 47.22, 125.22, 126.04, 136.21, 136.92, 214.13; mass spectrum *m/e* (rel intensity) 162 (64), 91 (100); HRMS calcd for $C_{11}H_{14}O$ 162.1045, found 162.1047. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.39; H, 8.69.

General Procedure for the Thermal [6 + 4] Cycloaddition of (η^6-1,3,5-Cycloheptatriene)tricarbonylchromium(0) Complexes. To a flame-dried flask were added complex **3** (1 equiv), the diene (1.5 equiv), and freshly distilled (from lithium aluminum hydride) *n*-butyl ether (12 mL). The resultant solution was degassed using the freeze–pump–thaw technique[44] and then refluxed for 12–48 h. After cooling, the green suspension was filtered through a plug of Celite. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography.

7α-Acetoxy-(1$H\beta$,6$H\beta$)-bicyclo[4.4.1]undeca-2,4,8-triene. This compound was prepared from complex **3** (0.105 g, 0.46 mmol) and 1-acetoxy-1,3-butadiene (0.2 mL, 1.7 mmol) in *n*-butyl ether (10 mL) by heating at 140 °C for 48 h. Chromatography (silica gel, chloroform/hexanes; 10:1) afforded 0.055 g (59%) of an oil that was identical in all respects to the material produced photochemically.[8]

7α-(Methoxycarbonyl)-10α-methyl-(1$H\beta$,6$H\beta$)-bicyclo[4,4,1]undeca-2,4,8-triene. This compound was prepared from complex **3** (0.27 g, 1.1 mmol) and methyl sorbate (0.19 g, 1.5 mmol) in *n*-butyl ether (12 mL) by heating at 140 °C for 44 h. Chromatography (silica gel, hexanes/diethyl ether, 9:1) afforded 0.156 g (60%) of a colorless oil that was identical in all respects with compound **5d**.

7α,10α-Dimethyl-(1$H\beta$,6$H\beta$)-bicyclo[4,4,1]undeca-2,4,8-triene. This compound was prepared from complex **3** (0.154 g, 0.67 mmol) and (*E*,*E*)-2,4-hexadiene (1.5 mL, 13 mmol) in *n*-butyl ether (10 mL). Chromatography (silica gel, pentane) afforded 0.115 g (98%) of a colorless oil containing a small quantity of hydrocarbon impurities but otherwise identical in all respects with **5c**.

7α-(Methoxycarbonyl)-(1$H\beta$,6$H\beta$)-bicyclo[4.4.1]undeca-2,4,8-triene. This compound was prepared from complex **3** (0.1 g, 0.45 mmol) and methyl penta-2,4-dienoate (0.15 mL, 1.29 mmol) in *n*-butyl ether (2.5 mL) by heating at 140 °C for 48 h. Chromatography (silica gel, chloroform/hexanes, 1:8) afforded 0.05 g (55%) of an oil that was identical in all respects to **5f**.

7α-Acetoxy-(1$H\beta$,6$H\beta$)-11-thiabicyclo[4,4.1]undeca-2,4,8-triene 11,11-Dioxide (Thermal route). This compound was prepared from complex **39** (0.08 g, 0.29 mmol) and 1-acetoxy-1,3-butadiene (0.34 mL, 2.88 mmol) in *tert*-butyl methyl ether (10 mL) by heating at 110 °C for 40 h. Chromatography (silica gel, hexanes/ethyl acetate, 2:1) provided 34 mg (47%) of a white solid identical in all regards to compound **42b**.

7α-Acetoxy-(1$H\beta$,6$H\beta$)-bicyclo[4.4.1]undeca-2,4,8-triene via a Catalytic Reaction. To an oven-dried pressure tube were sequentially added (cycloheptatriene)dicarbonyl(triphenylphosphine)chromium (**50**) (0.0306 g, 0.07 mmol), cycloheptatriene (90% purity, 0.03 mL, 0.26 mmol), 1-acetoxy-1,3-butadiene (0.15 mL), 1.26 mmol), and finally freshly distilled (from $LiAlH_4$) *n*-butyl ether (1.5 mL). The contents were degassed by the freeze–pump–thaw technique,[44] sealed under vacuum, and then heated to 140 °C for 18 h. During this period the initially red-purple solution had turned into a dark green suspension. After cooling, the suspension was filtered through Celite, which was rinsed with extra portions of ethyl ether. The filtrate was evaporated in vacuo to give a light yellow oil. Flash column chromatography (silica gel, chloroform hexanes; 10:1) provided 0.0238 g (36%) of a colorless oil which was identical in all respects with the material produced photochemically.[8]

Acknowledgment. We are pleased to acknowledge support of this investigation by the National Institutes of Health through Grant GM-30771.

Supplementary Material Available: Tables of experimental details and positional parameters of the X-ray analyses of **39** and **41d** (18 pages); observed and calculated structure factors for **39** and **41d** (38 pages). Ordering information is given on any current masthead page.

---

(44) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1988; p 19.