Effect of Alkene Substituents on Molybdenum and Chromium Carbene Complex Mediated Cyclization Reactions

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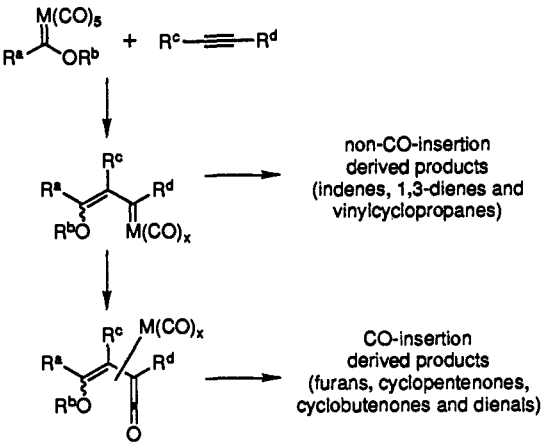
Abstract: Numerous aryl and alkenyl chromium and molybdenum carbene complexes are prepared, and their reactions with trienyne **2** are examined. With chromium as the metal, insertion of carbon monoxide occurs leading to the formation of hydroquinones. When carbene complexes of molybdenum are employed, the product distribution is highly dependent on the alkyl substituent of the carbene complex. Aryl substituted molybdenum carbene complexes produce hexahydroazulenes while alkenyl substituted molybdenum carbene complexes generate hydroquinones or cyclopentadiene derivatives. The mechanisms of these reactions with respect to the partitioning between the different reaction pathways is discussed.

The ability of group VI carbene complexes to mediate a variety of novel reaction pathways has been firmly established.[1] Of particular utility are their reactions with substituted alkynes which can lead to the production of a diverse array of structures (see Scheme 1). In general, these reactions can be grouped into those that involve the incorporation of carbon monoxide and those that do not. Products derived from carbon monoxide insertion pathways include hydroquinones (the Dötz reaction),[2] furans,[3] cyclopentenones,[4,5] cyclobutanones,[3d] cylobutenones,[3a,6] and dienals.[7] Products derived from pathways that do not involve the insertion of carbon monoxide include indenes,[3a,6d,8] cyclopentafurans,[9] cyclopentadienes,[10] and 1,3-dienes[8,11] as well as

Scheme 1



vinylcyclopropanes and derivatives thereof.[12] Though mechanisms for the formation of each of these products can be presented, the factors that determine which pathway is followed are still poorly understood.

Recently we described the direct preparation of the hexahydroazulene skeleton via the reaction of 1,3-dien-8-ynes with a molybdenum carbene complex (see eq 1).[12g] This reaction involves a non-carbon monoxide insertion pathway through which a divinylcyclopropane intermediate is produced. Subsequent [3.3]-sigmatropic rearrangement gives the 1,4-cycloheptadiene product. In connection with the application of this reaction to the synthesis of a variety of natural product frameworks, the influence of additional functionality on this reaction pathway is currently being explored. Of particular interest is the inclusion of olefinic

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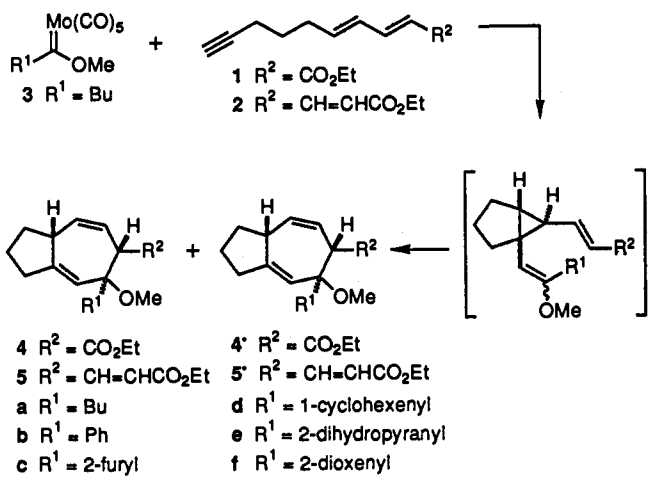
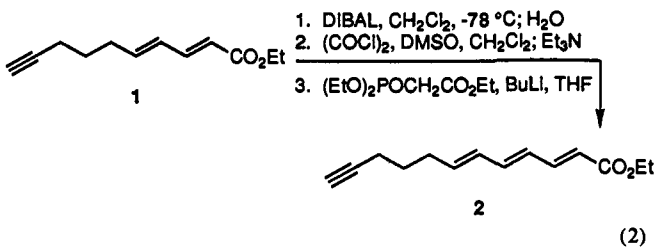
functionality at the R^1 and R^2 positions (see eq 1). In our initial studies, R^1 was consistently a simple alkyl group.[12g] The effect of various alkenyl and aryl R^1 substituents on this reaction and their impact on the partitioning between carbon monoxide-insertion and non-carbon monoxide-insertion pathways is discussed herein.



(1)

Results

Trienyne **2** was employed as the standard substrate in these investigations. Dienyne **1**, readily available in two steps from 5-hexyn-1-ol,[12g] was converted to trienyne **2** by a conventional reduction, oxidation, olefination sequence in 64% overall yield. The requisite molybdenum and chromium carbene complexes were prepared using conventional procedures, details of which are presented in the Experimental Section.

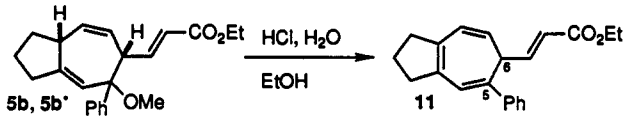


(2)

Previously we have demonstrated that dienyne **1**, upon treatment with butylmethoxymolybdenum carbene complex **3**, gives hexahydroazulenes **4** and **4'** in 87% yield as a 4.8:1 mixture of diastereomers.[12g] The reaction of complex **3** with trienyne **2** occurred similarly to give hexahydroazulene **5a** in 66% yield as a single diastereomer (see Table 1, entry 1).

As expected, the analogous butyl chromium carbene complex, **6** (Table 1, entry 2), gave a mixture of carbon monoxide insertion products of which we were able to identify and characterize dienal **7** (17%) and cyclopentenones **8a** (14%) and **9** (10%). Upon standing in chloroform, cyclopentenone **8a** isomerized to the conjugated isomer, **8b**. The formation of dienals[7] and cyclopentenones[4] has been reported previously. It is important to note that the hexahydroazulene products, **5a** and **5a'**, were not detected as products of this reaction.

Treatment of **2** with molybdenum carbene complex **10**, bearing a phenyl group in place of the butyl substituent (Table 1, entry 3), produced a 2:1 mixture of hexahydroazulenes **5b** and **5b'** in 50% yield. As these isomers were difficult to separate, **5b** and **5b'** were converted to cycloheptatriene **11** by treatment with dilute HCl in ethanol at room temperature for 4 h. Cycloheptatriene **11** was the sole isomer obtained from this transformation. If both C_5 and C_6 of **11** are sp^2 hybridized, as they would be in five of the other six possible cycloheptatriene isomers, there would be severe steric interactions between the phenyl group and the propenoate substituent. The analogous phenyl chromium carbene complex, **12**, followed the expected Dötz reaction pathway to give, following oxidation, benzoquinone **13** in 25% yield (Table 1, entry 4).



(3)

Furyl molybdenum complex **14** (Table 1, entry 5) gave hexahydroazulene **5c** as a single diastereomer in 42% yield. No Dötz reaction or other carbon monoxide insertion derived products were isolated. Furyl chromium complex **15** (Table 1, entry 6) gave the anticipated Dötz reaction product, benzofuran **16**, in 52% yield and hexahydroazulene **5c'** in 10% yield. It is important to note that **5c'** is a different diastereomer than **5c**, which was obtained as the sole hexahydroazulene diastereomer from cyclization of molybdenum complex **15**.

The effect of solvent and reaction conditions on the reactivity of carbene complexes **14** and **15** was briefly investigated in connection with studies of the reactivity of dienyne **1**. Complex **15** gave the carbon monoxide insertion product **18** as the only isolable product in both benzene and THF, though the yield was significantly better in benzene (Table 2, entries 1 and 2). In contrast, the reaction of molybdenum complex **14** with **1** was dramatically different in benzene and THF. In benzene, both carbon monoxide insertion and non-carbon monoxide insertion pathways were operative, giving approximately equal amounts of the hexahydroazulene and hydroquinone products (Table 2, entries 3–5) while in THF, there was almost exclusive formation of non-carbon monoxide insertion products with only trace amounts of carbon monoxide insertion (entry 9). Also significant in the reaction of **1** with **14** is that a 1:2 mixture of **17** and **17'** was obtained in benzene, while **17** was the only isomer observed in THF. The reaction of **1** with **14** in 1,4-dioxane produced virtually the same results as observed in THF (entries 10 and 11).

Although temperature did not significantly influence the overall yield, it did effect the time required for the reaction to go to completion. In benzene, the reaction took 56 h at 25 °C (entry 3), 4 h at 70 °C (entry 4), and 2 h at 100 °C (entry 5). In THF, the same trend was observed. After 4 h at 55 °C, 12% of **17** was isolated with 47% of **1** recovered (entry 6). At 67 °C, after 20 min 10% of **17** was isolated with 50% of **1** recovered (entry 7), while after 2 h the reaction was complete with **17** isolated in 40% yield and all starting material consumed (entry 8). When the temperature was increased from 67 to 100 °C, the reaction was complete in 1.5–2 h with **17** produced in 42% yield. A 2-h time period was generally used as our standard reaction time.

The effect of concentration on closely related reactions has been examined previously.[13] Reaction conditions were optimized for production of the desired hexahydroazulenes with the best yields obtained at concentrations in the range of 1–10 mM. At higher concentrations the isolated yields were significantly lower, but no new products were obtained. The reactions reported in Table 1 were all performed at concentrations in the range of 2–10 mM. In general, the reactions in Table 1 involving chromium carbene complexes were done in benzene at 70 °C, while the reactions of molybdenum carbene complexes were performed in THF at 70–100 °C.

The above results with aryl molybdenum carbene complexes demonstrate that the desired cyclopropanation pathway is favored when R^1 is equal to phenyl or furyl. However, with substituted vinyl substituents at the R^1 position, the reaction pathway changed quite dramatically. Molybdenum vinylsilane complex **19** and

(13) Lund, K. P. Ph. D. Dissertation, UCSD, 1992.

Table 1. Reactions of Carbene Complexes with Trienyne 2[b]

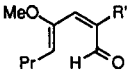
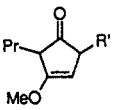
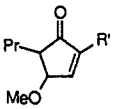
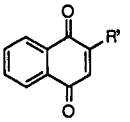
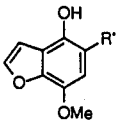
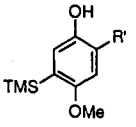
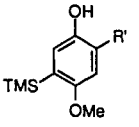
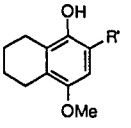
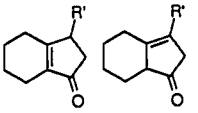
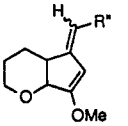
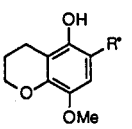
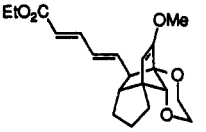
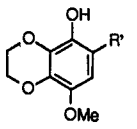
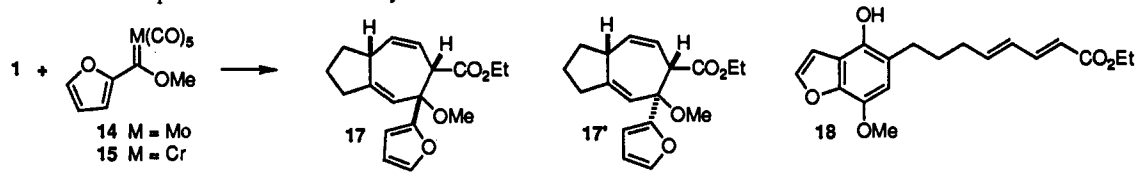
entry	carbene complex	R^1	M	cyclopropane-derived product	carbon monoxide insertion product(s)	cyclopentadiene-derived product
1	**3**	Bu	Mo	**5a** 66%	 **7** 17 %	
2	**6**	Bu	Cr		 **8a** 14%  **9** 10%	
3	**10**		Mo	**5b,5b'** (2:1) 50%		
4	**12**		Cr		 **13** 25 %	
5	**14**		Mo	**5c** 42%		
6	**15**		Cr	**5c'** 10%	 **16** 52 %	
7	**19**		Mo		 **20** 30 %[a]	
8	**21**		Cr		 **20** 46 %	
9	**22**		Mo		 **23** 24 %	 **24a,b** 35 %
10	**25**		Cr	**5d'** 3%	**23** 53%	
11	**26**		Mo			
12	**28**		Cr	**5e'** 3%	 **29** 41 %	**27** 34 %

Table 1. (Continued)

entry	carbene complex	R^1	M	cyclopropane-derived product	carbon monoxide insertion product(s)	cyclopentadiene-derived product
13	**30**		Mo			 31 72 %
14	**32**		Cr	**5f'** 3%	 33 38 %	

[a] 44% yield based on recovered starting material. [b] R' = $(CH_2)_3CH{=}CHCH{=}CHCH{=}CHCO_2Et$, R'' = $(CH_2)_2CH{=}CHCH{=}CHCH{=}CHCO_2Et$.

Table 2. Reactions of Complexes 14 and 15 with Enyne 1



entry	complex	equiv of complex	solvent	temperature	time	17 (%)	17' (%)	18 (%)	1 (%) recovered
1	**15**	1.1	benzene	70 °C	2 h			37	
2	**15**	1.1	THF	100 °C[a]	2 h			10	
3	**14**	1.1	benzene	25 °C	56 h	8	17	19	
4	**14**	2.1	benzene	70 °C	4 h	8	16	12	
5	**14**	1.1	benzene	100 °C[a]	2 h	5	10	17	
6	**14**	1.1	THF	55 °C	4 h	12		trace	47
7	**14**	1.1	THF	67 °C	20 min	10			50
8	**14**	1.1	THF	67 °C	2 h	40			
9	**14**	1.1	THF	100 °C[a]	2 h	42		trace	
10	**14**	1.1	1,4-dioxane	102 °C	2 h	34		trace	
11	**14**	1.1	1,4-dioxane	102 °C[a]	2 h	34		trace	

[a] Sealed vial conditions.

cyclohexenyl molybdenum complex **22** did not give the anticipated hexahydroazulene products. Instead, **19** produced hydroquinone **20** in 44% yield (Table 1, entry 7), while complex **22** gave hydroquinone **23** in 24% yield and a 3:1 mixture of cyclopentenone derivatives **24a** and **24b** in 35% yield (Table 1, entry 9). From the reactions of both **19** and **22**, the anticipated cyclopropanation derived hexahydroazulene products, or products derived therefrom, were not detected.

Hydroquinones **20** and **23** are the result of a Dötz reaction pathway involving the incorporation of carbon monoxide. In our previous studies, carbon monoxide insertion pathways had been rarely observed in reactions involving molybdenum carbene complex **3**.[7] Cyclopentenones **24a** and **24b** are thought to be produced via hydrolysis of the corresponding methoxycyclopentadiene (vide infra). This pathway to substituted cyclopentadienes has been observed by the Wulff group,[14] but literature reports of such a process have been rare.[10] It is mechanistically related to the often observed formation of indenes from aryl carbene complexes.[3a,6d,8]

The analogous chromium carbene complexes, **21** (Table 1, entry 8) and **25** (Table 1, entry 10), gave the expected Dötz reaction products **20** and **23** in 46% and 53% yield, respectively. With complex **25** (Table 1, entry 10), a small amount of a cyclopropanation derived product, hexahydroazulene **5d'** (3%), was obtained.

The reactivity of several additional substituted vinylcarbene complexes of both molybdenum and chromium was studied. Treatment of **2** with dihydropyran derived molybdenum carbene complex **26** did not give either the carbon monoxide insertion or cyclopropanation derived products. Instead, **27** was obtained in 34% yield as a 3.4:1 mixture of olefin isomers. Chromium complex **28** behaved in a fashion analogous to cyclohexenyl complex **25**, giving hydroquinone **29** in 41% yield and hexahydroazulene **5e'** in 3% yield. The 1,4-dioxene derived molybdenum carbene complex **30** gave polycyclic product **31** (see Figure 1) in 72% yield, while the analogous chromium complex, **32**, gave hydroquinone **33** in 38% yield and hexahydroazulene **5f'** in 3% yield. Tetracyclic product **31**, like **24** and **27**, is derived from a methoxycyclopentadiene intermediate. However, instead of hydrolysis to the corresponding cyclopentenone or double bond migration to the conjugated enol ether, an intramolecular Diels–Alder cycloaddition reaction has occurred. The structure of **31** was confirmed by X-ray crystallography.

Discussion

From the data presented in Table 1, two general conclusions can be made. Though an aryl group at the R^1-position allows for production of cyclopropanation-based products, an alkenyl substituent at this position causes the cyclopropanation pathway to be disfavored, instead producing either the hydroquinone or products derived from methoxycyclopentadienes. Furthermore, the ratio of hydroquinone to cyclopentadiene products appears to be linked to the nature of the substituents on the R^1-alkenyl group with electron-donating groups causing the cyclopentadiene products to be favored. Detailed analysis of these observations should shed considerable light on the mechanisms of the reactions

(14) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chang, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102–126.

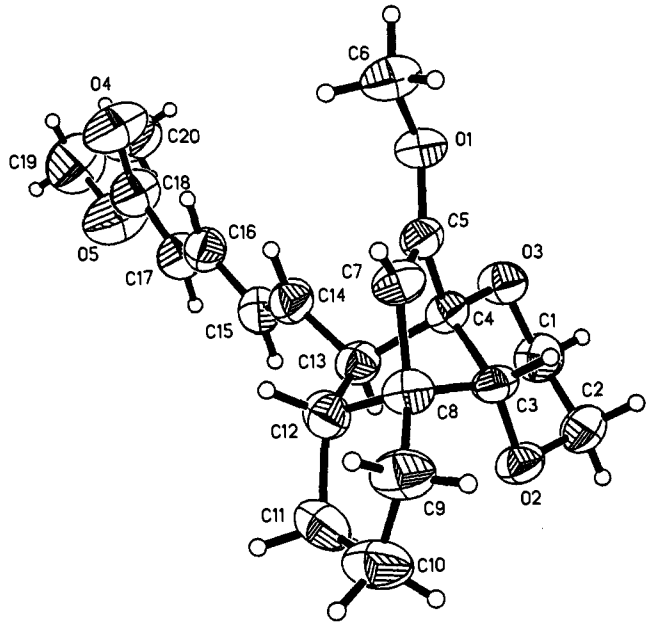


Figure 1. ORTEP diagram of **31**.

of molybdenum and chromium carbene complexes with alkynes and allow for the more accurate prediction of the outcome of future investigations.

It has been amply demonstrated that vinylcarbene complexes of chromium react with alkynes to give hydroquinones.[1,2] This reaction has been extensively investigated with respect to both its synthetic utility and mechanism.[1a,3g,6d,15] Since its discovery, several mechanisms have been proposed and subsequently refined as more detailed studies have been performed. Recently, in order to account for the dependence of the product ratio on concentration, Wulff and co-workers have suggested that coordination of a second equivalent of alkyne prior to carbon monoxide insertion is involved.[16,17]

It has generally been accepted that the Dötz reaction is initiated by loss of carbon monoxide and regioselective reaction of the coordinatively unsaturated carbene complex with an alkyne to produce η^1,η^3-vinylcarbene intermediate **35**. Coordination of a second equivalent of alkyne to **35** and transformation of the vinylcarbene ligand to η^1,η^1-coordination has been suggested by Wulff to lead to **36** with the coordinated alkyne functioning as a 2e$^-$ donor. The key step of the Wulff proposal involves the conversion of **36** to **37**, wherein the insertion of carbon monoxide occurs, while the alkyne converts from 2e$^-$ donation to 4e$^-$ donation to allow the metal to maintain a full 18e$^-$ valence shell. Isomerization of **37** to η^4-bound ketene complex **38**, with the alkyne isomerizing back to 2e$^-$ donation, followed by electrocyclic ring closure and dissociation of the alkyne, gives **39**. Subsequent keto–enol tautomerization and decomplexation completes the process. In summary, the major difference between this reaction pathway and those previously proposed is that all of the key steps involve 18e$^-$ coordinatively saturated intermediates. This is accomplished by using a second equivalent of alkyne as a transient ligand to satisfy the valence demands of the intermediate metal complexes. As we will suggest below, it appears that alkenyl substituents, when appropriately positioned, may play a role similar to that proposed by Wulff for the second equivalent of alkyne.

Our previous studies have demonstrated that alkyl molybdenum carbene complexes will react with 1,6-enynes to give vinylcyclopropanes and with 1,3-nonadien-8-ynes to give hexahydroazulenes. The general mechanism that we have presumed to be operative in these transformations is outlined in Scheme 3. The first step is identical to the first step of the Dötz reaction presented in Scheme 2. Loss of carbon monoxide and reaction with the alkyne moiety gives vinylcarbene complex **42**. As mentioned previously, the most stable form of **42** is probably the η^1,η^3-derivative, as shown. Isomerization of the vinylcarbene unit to η^1,η^1-coordination with concomitant intramolecular coordination of the tethered alkene produces intermediate **43**. From **43**, metallacyclobutane formation, to give **44**, and subsequent reductive elimination produce cyclopropane **45**. Subsequent [3.3]-sigmatropic rearrangement leads to the corresponding 1,4-cycloheptadiene. As in the Wulff mechanism for the Dötz reaction presented in Scheme 2, all of the intermediates shown in Scheme 3 maintain an 18e$^-$ environment at the metal center.

The key difference between these two processes is that with molybdenum, olefin coordination to form **43** effectively competes with the insertion of carbon monoxide, while with chromium, products resulting from the insertion of carbon monoxide, via ketene complex **46**, are generally observed (see Scheme 3). This is in part the result of the relative strength of the metal to carbon monoxide bonds which are significantly stronger when M = Cr than when M = Mo.[18] Additional factors that promote olefin coordination and, in most cases, cause the cyclopropanation pathway to be favored have been identified. Olefin coordination to the metal is primarily via d-π^* backbonding. Electron-withdrawing groups attached to the alkene lower the energy level of the π^* orbital and increase the strength of the metal–olefin bond of **43**. Additionally, due to a "reactive rotamer" or Thorpe–Ingold effect,[19] the presence of appropriate substituents on the tether between the alkyne and the alkene enhances the intramolecular coordination of the alkene, provided that the substituents themselves are incapable of intramolecular coordination to the metal.[20]

Let us now look in detail at each step of these processes when an additional alkenyl substituent is present at the R^1 position. From vinylcarbene complex **34**, loss of carbon monoxide and reaction of the coordinatively unsaturated metal center with the alkyne portion of **1** or **2** can produce a mixture of vinylcarbene complexes **47** and **48**. In general, based on the final products observed, the (*E*)-enol ether isomer, **47**, is the dominant intermediate, though in some cases significant amounts of products derived from the *Z*-isomer, **48**, are also obtained.[21]

In each isomer, the metal may coordinate to the carbon framework in several different ways. As presented in Scheme 4, the organic framework of the (*E*)-enol ether isomer can bind to the metal in an η^1,η^3-fashion, as in **47**. In the absence of additional π-bonds (vide infra), this is the expected mode of coordination. Alternatively the metal may abandon the η^3-coordination mode and coordinate to the additional π-bond originally from vinylcarbene complex **34** resulting in the metal coordinating in an η^1,η^1,η^2-fashion as shown in **47′**.[22] Interconversion between **47** and **47′** should be relatively rapid since sliding of the metal from one π-bond to a neighboring π-bond is all that is required. The

(15) For example, see: (a) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689. (b) Sivavec, T. M.; Katz, T. J.; Chinag, M. Y.; Yang, G. S.-Q. *Organometallics* **1989**, *8*, 1620. (c) Xu, Y.-C.; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269–7271. (d) Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383–8391.

(16) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293–9319.

(17) Mechanistic studies of the Dötz reaction have generally involved only chromium carbene complexes. We assume that with molybdenum the general mechanism for this transformation is not significantly different.

(18) For a discussion of CO dissociation in metal–carbene complexes, see: Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87–94.

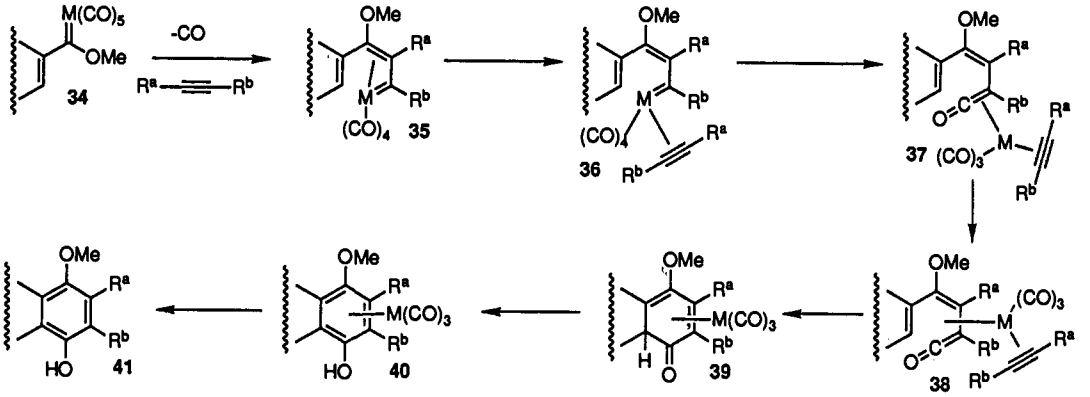
(19) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224–232 and references cited therein.

(20) Backenstrass, F., unpublished results.

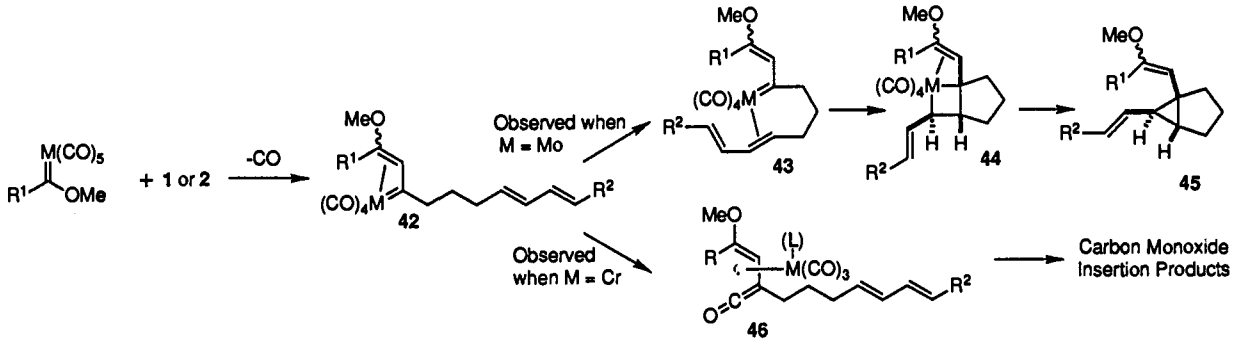
(21) The stereoselective formation of 1,4-dialkoxy-1,3-butadienes by reaction of molybdenum carbene complexes with propargyl ethers is thought to occur via the (*Z*)-enol ether isomer. See ref 11e.

(22) Loss of a second equivalent of carbon monoxide and coordination in an η^1,η^5-fashion is also possible.

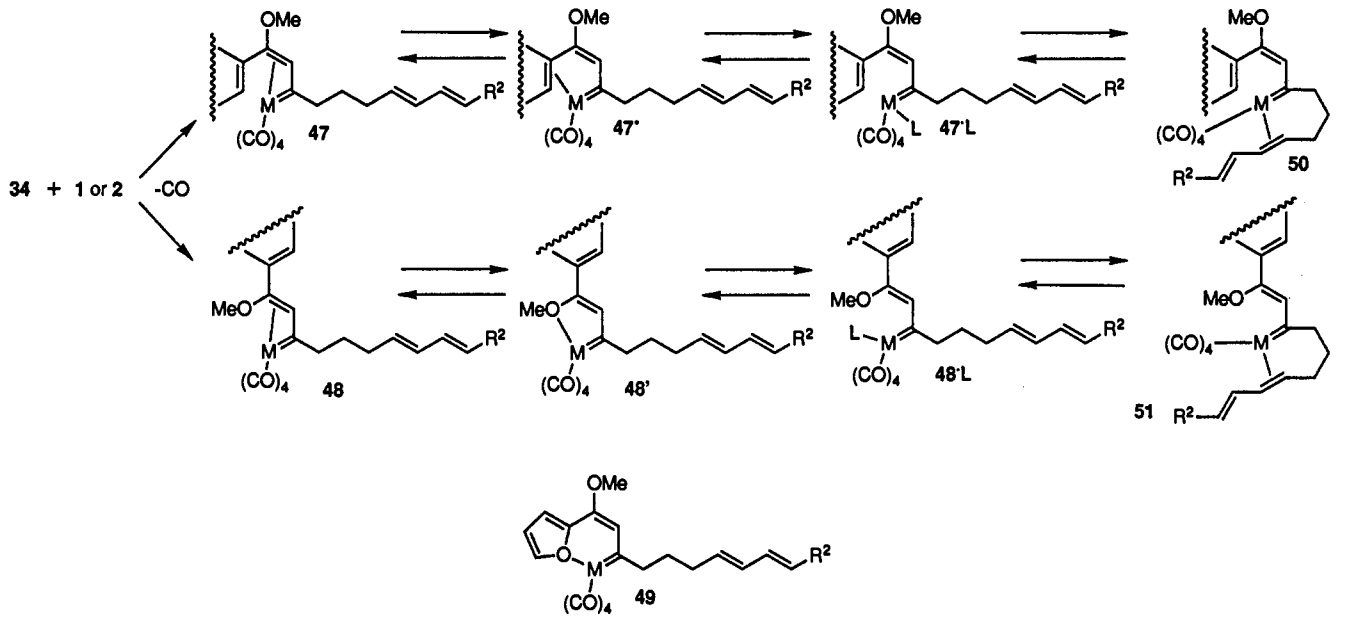
Scheme 2



Scheme 3



Scheme 4



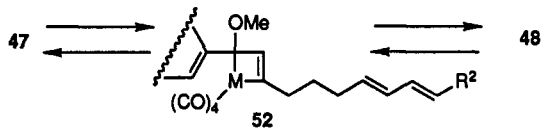
metal may also fill its labile coordination site by coordination to an ancillary ligand as shown in **47·L**. This additional ligand could be an alkyne, as suggested by Wulff,[16] or solvent. In tetrahydrofuran, coordination of the ether oxygen to the metal center is possible.[3g] In benzene η^2-coordination of the metal to the π-system of the aromatic ring is feasible but probably less likely. Other solvents may also coordinate to the metal center.[23] With furylcarbene complexes **14** and **15**, coordination of the furan oxygen, as in **49**, is also possible. The labile coordination site can also be occupied by the π-bond of the pendant alkene, as in complex **50**, through which formation of the cyclopropane derived products is believed to occur.

The (*Z*)-enol ether isomer **48** can also have the metal center coordinated to the organic ligand in several different ways. Coordination in an η^1,η^3-fashion (**48**) is again possible. Coordination to the oxygen of the methoxy group may also occur, giving complex **48′**. As with **47** and **47′**, interconversion between **48** and **48′** is expected to be relatively facile. Alkoxy coordination to coordinatively unsaturated group VI carbene complexes has been previously observed with *o*-alkoxyarylcarbene complexes[6d,16,24] and intramolecular coordination of an ether oxygen has previously been invoked to account for the high degree of stereocontrol

(23) For example, see: (a) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53–56. (b) Yang, G. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett.* **1986**, *125*, 566–568. (c) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751–6753. (d) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538–5540.

(24) Dötz, K. H. *J. Organomet. Chem.* **1987**, *334*, 57–75.

Scheme 5



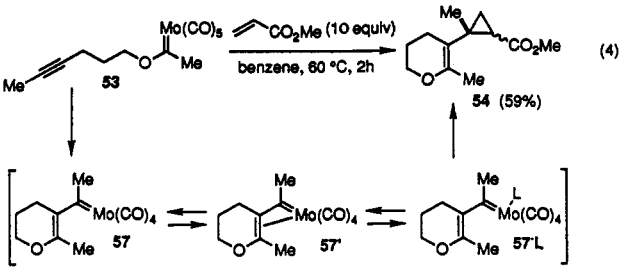
observed in the molybdenum carbene complex mediated cyclopropanation of *s-cis*-1,3-dienes.[25] As with the *E*-isomer, ancillary ligand coordination (**48·L**) and complexation to the pendant alkene (**51**) are also possible.

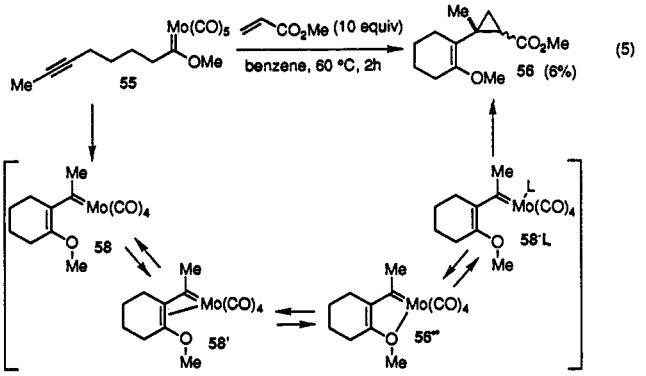
Interconversion between the *E*- and *Z*-isomers may occur. Though several pathways can be envisioned, the simplest pathway involves the intermediacy of metallacyclobutene **52** (see Scheme 5).[26] Calculations suggest that metallacyclobutene **52** is best viewed as a transition state rather than a reactive intermediate.[27]

Our previous studies of cyclizations of butyl molybdenum carbene complex **3** with enynes and dienynes demonstrated that mixtures of cyclopropanation based products are produced, with those derived from the (*E*)-enol ether isomer preferred over those derived from the *Z*-isomer in the general range of 3–5:1. The studies described herein showed a much higher propensity for products derived from the (*E*)-enol ether isomer, the only exception being phenyl molybdenum carbene complex **10**, where a 2:1 mixture of **5b** and **5b′** was isolated. The major hexahydroazulene products, **5a–f**, are generated from the (*E*)-enol ether, while the minor isomers, **5a′–f′**, are obtained from the (*Z*)-enol ether.[12g] The ability of the alkenyl substituent to coordinate to the metal, as in **47′** and **49**, is likely to cause the *E*-isomer to be favored to a greater extent than when R^1 is an alkyl substituent. The observation of a 2:1 ratio in the case of phenyl carbene complex **10** is likely a reflection of the absence of coordination of the aromatic ring to the coordinatively unsaturated metal center. Alternatively, the difference in reactivity between the (*E*)- and (*Z*)-vinylcarbene complexes may be greater with the R^1 substituents presented in Table 1 than when R^1 is a butyl group.

Previous studies suggest that coordination of the alkoxy substituent can dramatically effect the reactivity of in situ generated vinylcarbene complexes. For example, complex **53** was found to readily react with methyl acrylate to give dihydropyran derivatives **54** in 59% yield (eq 4),[12f] while complex **55** produced methoxycyclohexene derivative **56** in only 6% yield (eq 5).[12e] This difference in reactivity was suggested to be due to the different modes of coordination available at the vinylcarbene complex stage. Complex **57**, resulting from intramolecular reaction of complex **53** with the pendant alkyne, can exist in the coordinatively unsaturated η^1,η^1-form, **57**, or the coordinatively saturated η^1,η^3-form, **57′**. Coordination of methyl acrylate to **57/57′** gives **57·L** (L = methyl acrylate) and leads to **54**. Complex **58**, resulting from reaction of complex **55** with the pendant alkyne, can exist in either the coordinatively unsaturated η^1,η^1-form **58**, the coordinatively saturated η^1,η^3-form **58′**, or the oxygen-bound coordinatively saturated form **58″**. Again, coordination to methyl acrylate gives **58·L** (L = methyl acrylate) which leads to the observed products. Because of the ability of the oxygen to coordinate as in **58″**, **58** is expected to be considerably more stable than **57** and less likely to coordinate to the electron-deficient alkene of methyl acrylate.

Several of the reactions presented in Table 1 clearly indicate that the (*E*)- and (*Z*)-vinylcarbene complexes follow different reaction pathways. Summarized in Scheme 6 are the three major reaction pathways available to the (*E*)-enol ether isomer **47**.





Reaction pathways available to the (*Z*)-enol ether isomer are presented in Scheme 7.

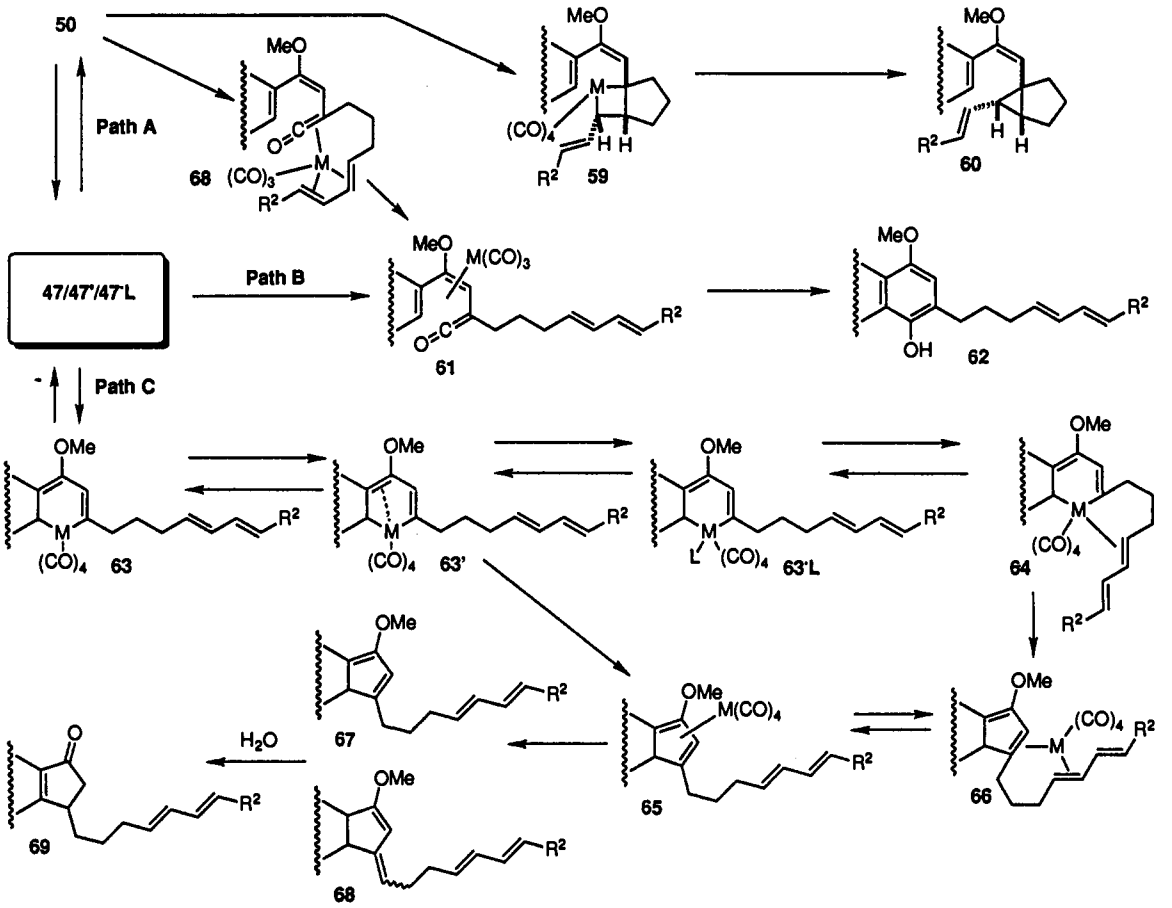
As mentioned earlier, the (*E*)-enol ether isomer can be viewed as **47**, **47′**, or **47·L**. Coordination of the tethered olefin (path A) produces **50**. Subsequent metallacyclobutane formation (**50** → **59**) and reductive elimination leads to divinylcyclopropane **60**. Insertion of carbon monoxide (path B) gives ketene complex **61**, which, after electrocyclic ring closure, keto–enol tautomerization, and decomplexation, gives hydroquinone **62**. A third possibility (path C) is electrocyclic ring closure, which is expected to most likely occur through **47′**, to give metallacyclohexadiene **63**. Complex **63**, as drawn, is coordinatively unsaturated. The metal may fill its vacant coordination site by coordination in an η^3-fashion, as in **63′**. It might also fill this site by coordination to solvent (**63·L**) or to the tethered alkene (**64**). Reductive elimination and decomplexation from **63** leads to methoxycyclopentadiene **67** through either the η^4-bound complex **65** or the η^2,η^2-bound complex **66**. Metal-mediated 1,5-hydrogen shift and subsequent decomplexation leads from **65**/**66** to **68**. Upon hydrolysis, both **67** and **68** produce cyclopentenone **69**.

It has previously been suggested that metallacyclohexadienes related to **63** may insert carbon monoxide leading to eventual formation of phenol products such as **62**.[28] This results in crossover between paths B and C of Scheme 6 at a later stage in the reaction pathway. Though we cannot discount such a pathway with our substrates, recent studies by Wulff and co-workers have suggested that with arylcarbene complexes this pathway does not occur.[16]

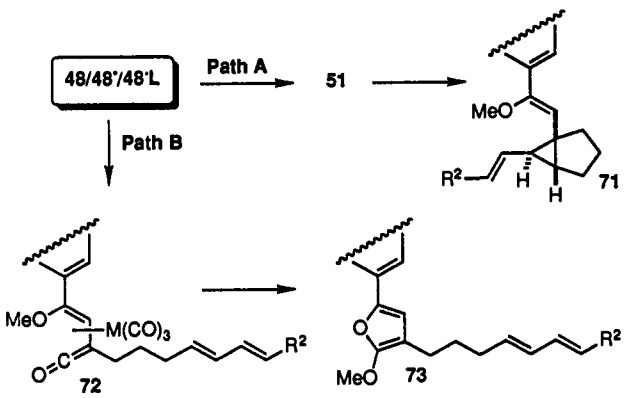
With chromium as the metal, regardless of the nature of the R^1 substituent, only products resulting from the insertion of carbon monoxide are isolated. In the absence of the additional olefin from the vinylcarbene substrate, carbon monoxide insertion products, dienal **7** and cyclopentenones **8a** and **9**, are obtained (entry 2 in Table 1).[29] When the additional olefin is present, hydroquinone formation occurs via path B. Clearly, when chromium is the metal, insertion of carbon monoxide (path B) is faster than olefin complexation (path A) or electrocyclic ring closure (path C).

(25) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 8916–8921.
(26) For a recent report of a reaction proposed to involve interconversion of vinylcarbene complexes, see: Herndon, J. W.; Zora, M.; Patel, P. P.; Chatterjee, G.; Chatterjee, G.; Matasi, J. J.; Tumer, S. U. *Tetrahedron* **1993**, *49*, 5507–5530.
(27) Hoffmann, P.; Hammerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 908–910.
(28) Casey, C. P. *React. Intermed.* **1981**, 2.
(29) For a detailed discussion of the mechanism of cyclopentenone formation, see ref 4a. The formation of **7**, **8**, and **9** involves both CO insertion and metal-mediated hydride migration. The sequence in which these steps occur has not yet been clearly delineated.

Scheme 6



Scheme 7



In the studies by Wulff and co-workers of the reaction of vinylcarbene complexes of chromium with alkynes, the dramatic concentration effect that had been observed with chromium arylcarbene complexes[16] was not detected.[14] This is likely due to the vinylcarbene intermediate preferring to complex to the additional alkene substituent, as in **47′**, rather than to an alkyne, as in **36**. Complex **47′** could then insert carbon monoxide and maintain an 18e⁻ metal coordination environment, without the need for coordination to an auxiliary ligand, by directly going to η^6-hexatrienylchromium tricarbonyl complex **61**.

In our system, wherein conjugated π-bonds are present in the alkyl side chain, the tethered olefins might also participate in the carbon monoxide insertion pathway. From **50**, insertion of carbon monoxide could give complex **70**. The polyunsaturated tether could function as a 4e⁻ donor to maintain the metal's 18e⁻ environment and play much the same role as the second equivalent of alkyne in the Wulff mechanism for the Dötz reaction.

When molybdenum carbene complexes are employed, the observed reaction pathway for the (*E*)-enol ether isomer is highly dependent upon the substituents present on the alkenyl substituent at the R^1 position. Without the additional π-bond (entry 1 in Table 1) or when the additional π-bond is part of an aromatic ring (entries 3 and 5 in Table 1), only products resulting from path A are observed. When the coordinating alkene is part of an aromatic ring, **47′** is less favorable than **50**, since **47′** would require disruption of the aromaticity. This causes path A to be favored over path B, with path C not being possible. With vinyl molybdenum carbene complexes **19**, **22**, **26**, and **30**, no products from path A were observed. Instead, only products from paths B and C were isolated. With these substrates, intermediate **47′** is more favorable and appears to be preferred over **50**.

Partitioning between paths B and C is dependent upon the electron-donating/electron-withdrawing properties of the substituents on the alkene moiety. With the electron-withdrawing trimethylsilyl substituent of complex **19**, only path B is observed (entry 7, Table 1), while the electronically neutral cyclohexenyl complex, **22**, produces products derived from both paths B and C (entry 9, Table 1). With the electron rich complexes **26** and **30**, only products from path C are observed. Similar observations have previously been made with aryl chromium complexes wherein electron donating groups on the aromatic ring cause indene formation to occur preferentially over Dötz cyclization.[16] The electron-donating groups increase the electron density at the metal center which reduces the likelihood of carbon monoxide insertion occurring.

In Wulff's studies of cyclopentadiene formation,[14] the hydroquinone to cyclopentadiene ratio was, in general, not as high as observed in the studies reported herein. Aside from relatively minor differences in the reaction conditions employed, the only major difference between these studies is the presence of the tethered diene or triene functionality in our substrates, **1** and **2**. As presented in Scheme 6, this functionality might influence the

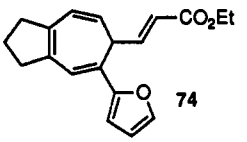
partitioning between the carbon monoxide insertion and cyclopentadiene formation pathways by intramolecularly coordinating to the metal center. If the interconversion between the vinylcarbene complex **47**/**47'**/**47**·**L** and metallacyclohexadiene **63**/**63'**/**63**·**L** is an equilibrium process, intramolecular coordination of the tethered alkene, as in **64**, may assist in the reductive elimination step to form the metal–cyclopentadiene complexes **65** and **66**.

Depending upon the substrate employed, three different products arise from complexes **65** and **66**. From cyclohexenyl complex **22**, only cyclopentenone product **69** was obtained, while dihydropyranyl complex **26** produced hydrogen shift product **68** as a mixture of isomers. The additional electron-donating substituent from the dihydropyran ring of **26** reduces d-π^* backbonding which may facilitate the hydrogen shift process via destabilization of the η^4-coordination mode for cyclopentadiene complex intermediate **65**. With a second electron-donating substituent present, as in dioxenyl complex **30**, an intramolecular Diels–Alder reaction occurs giving polycyclic product **31**.

Though only small amounts of products derived from the (*Z*)-enol ether complex **48** are observed, their isolation offers important insight into the mechanistic pathways under study. As with the *E*-isomers (Scheme 6), several distinct reaction pathways are possible for the *Z*-isomers (Scheme 7). Coordination of the tethered alkene to give **51**, followed by metallacyclobutane formation and reductive elimination, leads to cyclopropanation product **71** (Scheme 7, path A). Alternatively, insertion of carbon monoxide gives vinylketene complex **72** (path B). Often this intermediate is viewed as being an η^4-diene complex. As such, the metal is coordinatively unsaturated. The vacant coordination site can be occupied by either an additional auxiliary ligand or by the oxygen of the methoxy group. Coordination to the methoxy oxygen makes the methoxyvinylketene unit an η^5-, 6e$^-$ donor and coordinatively saturates the metal. Coordination in this η^5-fashion has been observed with vinylketene complexes derived from aminocarbene complexes.[30] Isomerization of **72** to furan **73** has been observed to occur most readily in tetrahydrofuran, and a mechanism invoking coordination of THF en route from **72** to **73** has been proposed.[3g] Because of the enol ether geometry, **72** cannot cyclize to give the hydroquinone product of the Dötz reaction. Instead, from **72**, rearrangement to furan **73** is anticipated to be the dominant pathway in THF. In our studies, reactions of chromium carbene complexes were carried out in benzene. In this solvent rearrangement of **72** to **73** is less likely.

With molybdenum as the metal, except for phenyl derivative **10**, only products derived from (*E*)-enol ether complexes were obtained. With chromium carbene complexes **15**, **25**, **28**, and **32**, Dötz cyclization, which can only occur through the (*E*)-enol ether complex, was the dominant pathway. However, small quantities of (*Z*)-enol ether derived cyclopropanation products were also isolated. This is likely due to the absence of coordination to the π-bond derived from the vinylcarbene substrate. Through complex **47'** the (*E*)-enol ether proceeds through path B of Scheme 6 to give the carbon monoxide insertion-derived products. The (*Z*)-enol ether complex, **48**, which cannot coordinate to the π-bond derived from the vinylcarbene substrate, instead coordinates to the pendant alkene, as in **51**, which leads to the observed cyclopropanation derived product. Without coordination of and subsequent reaction with the pendant alkene, carbon monoxide insertion to give **72** would be expected.

Reactivity of the Cyclopentadiene Products. Reactions of several of the molybdenum carbene complexes were found to produce substituted methoxycyclopentadiene derivatives or hydrogen shift products derived therefrom. In most cases these were isolated in modest yield as the corresponding cyclopentenones, obtained via hydrolysis of the enol ether functionality. Even



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though they all had a tethered electron-deficient alkene, only in the case of molybdenum carbene complex **30** did the methoxycyclopentadiene product undergo facile intramolecular Diels–Alder cycloaddition, producing **31** in 72% yield. Of the cyclopentadienes produced in these studies, the one derived from complex **30** bears three alkoxy substituents and is the most electron-rich. It is, therefore, the most likely to undergo facile [4 + 2] cycloaddition with the pendant electron-deficient alkene.[31] The modest isolated yields of cyclopentadienes, or derivatives thereof, may be the result of the precursor η^4-cyclopentadiene complexes going on to give η^5-cyclopentadienyl complexes. Such systems have previously been prepared by a variety of approaches but are anticipated to not be isolable using the conditions employed in the studies described herein.[32] Further investigations of this reaction are currently in progress and will be reported separately.

Conclusions

Both the metal and the nature of the aryl/alkenyl substituent of the carbene complex have a profound effect on the product distribution in this reaction. Chromium carbene complexes produce predominantly carbon monoxide insertion derived products through the (*E*)-enol ether isomer. With molybdenum complexes, when R^1 is an aryl group, cyclopropanation pathways are preferred. When R^1 is an electron-deficient alkenyl substituent, carbon monoxide insertion to form hydroquinones occurs, while when R^1 is an electron-rich alkenyl group, cyclopentadiene formation is favored. This insight should now allow us, and others, to rationally predict the outcome of related reactions.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 500 MHz or GE 300 MHz spectrometers. IR spectra were recorded on a Mattson Galaxy 2020 FT-IR spectrophotometer. Low-resolution mass spectra were recorded on a Hewlett-Packard 5970 mass-selective detector (20 eV) interfaced with a Hewlett-Packard 5890 gas chromatograph equipped with a 12 m × 0.2 mm HP-1 fused silica capillary column. High-resolution mass spectra were performed at the U.C. Riverside Mass Spectrometry Facility on a VG-ZABZFHF or VG-7070EHF mass spectrometer. Elemental analyses were performed by Oneida Laboratories, Inc. Column chromatography was performed with Fisher Scientific Florisil (100–200 mesh) or silica gel (200–425 mesh) using various ratios of ethyl acetate/hexane as eluent unless otherwise specified. All reagents were obtained from commercial suppliers and used as received unless otherwise indicated. Reactions were performed under a nitrogen atmosphere in flame-dried glassware. Benzene and tetrahydrofuran (THF) were distilled from potassium/benzophenone ketyl under a nitrogen atmosphere. Diethyl ether was distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane and acetonitrile were distilled from calcium hydride under a nitrogen atmosphere.

Ethyl (2*E*,4*E*,6*E*)-2,4,6-Dodecatrien-11-ynoate (2). To a solution of ethyl (2*E*,4*E*)-2,4-decadien-9-ynoate (**1**)[12g] (2.30 g, 11.9 mmol) in CH_2Cl_2 (120 mL) at -78 °C was added DIBAL in CH_2Cl_2 (25 mL, 25 mmol, 1.0 M). The resulting mixture was stirred at -78 °C for 20 min and then allowed to warm to 0 °C. The reaction was quenched with H_2O (3.56

(30) Anderson, B. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 8615–8617.

(31) Intramolecular Diels–Alder reactions of cyclopentadienes have been previously described. For example, see: (a) Sternbach, D. D.; Hughes, J. W.; Burdi, D. F.; Banks, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 2149–2153. (b) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 855–856. (c) Snowden, R. L. *Tetrahedron* **1986**, *42*, 3277–3290. (d) Stille, J. R.; Grubbs, R. H. *J. Org. Chem.* **1989**, *54*, 434–444. (e) Lei, B.; Fallis, A. G. *J. Am. Chem. Soc.* **1990**, *112*, 4609–4610. (f) Sternbach, D. D.; Ensinger, C. L. *J. Org. Chem.* **1990**, *55*, 2725–2736. (g) Himeda, Y.; Hiratani, K.; Hatanaka, M.; Ueda, I. *J. Chem. Soc., Chem. Commun.* **1992**, 1684–1685.

(32) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Elmsford, NY 1982; Vol. 3, pp 961–972, 1176–1203, and references cited therein.

mL) followed sequentially by 10% NaOH solution (3.56 mL) and H_2O (10.7 mL). The mixture was filtered through a glass frit and concentrated in vacuo to give crude (2*E*,4*E*)-2,4-decadien-9-yn-1-ol (1.60 g) which was taken on without further purification. ^1H NMR of crude (2*E*,4*E*)-2,4-decadien-9-yn-1-ol: (300 MHz, $CDCl_3$) δ 1.58 (pentet, J = 7.2 Hz, 2 H), 1.93 (t, J = 2.6 Hz, 1H), 2.12–2.19 (m, 4 H), 2.40 (br s, 1 H), 4.09 (d, J = 5.9 Hz, 2 H), 5.57–5.72 (m, 2 H), 5.98–6.20 (m, 2 H).

Oxalyl chloride (1.03 mL, 11.8 mmol) was dissolved in CH_2Cl_2 (60 mL) and cooled to –60 °C. DMSO (1.68 mL, 23.5 mmol) was slowly added followed, after 5 min, by (2*E*,4*E*)-2,4-decadien-9-yn-1-ol (1.60 g, 10.7 mmol). Stirring was continued for an additional 30 min at –60 °C. Triethylamine (7.75 mL, 55.6 mmol) was then added and the solution was allowed to warm to room temperature. The reaction mixture was poured into H_2O (60 mL) and extracted with CH_2Cl_2. The organic phases were combined, washed with H_2O followed by saturated NaCl solution, dried over $MgSO_4$, and concentrated to give crude (2*E*,4*E*)-2,4-decadien-9-yn-1-al (1.36 g) which was taken on without further purification. An independent sample of (2*E*,4*E*)-2,4-decadien-9-yn-1-al was purified by silica gel chromatography: ^1H NMR (500 MHz, $CDCl_3$) δ 1.70 (p, J = 7.3 Hz, 2 H), 1.98 (t, J = 2.7 Hz, 1 H), 2.23 (dt, J = 7.3, 2.7 Hz, 2 H), 2.35 (q, J = 6.8 Hz, 2 H), 6.09 (dd, J = 15.1, 7.8 Hz, 1 H), 6.25 (dt, J = 15.1, 6.8 Hz, 1 H), 6.36 (dd, J = 15.1, 10.7 Hz, 1 H), 7.07 (dd, J = 15.1, 10.7 Hz, 1 H), 9.53 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.8, 27.2, 31.9, 69.0, 83.8, 129.4, 130.4, 145.5, 152.3, 193.8; IR (CH_2Cl_2) 3304, 3034, 2947, 2820, 2745, 1680, 1642 cm^{-1}; LRMS (CI, CH_4) m/e (%) 149 (82), 131 (51), 121 (18), 119 (44), 109 (29), 108 (23), 107 (32), 105 (30), 95 (17), 93 (58), 92 (12), 91 (96), 81 (100), 80 (18), 79 (86); HRMS (EI) calcd for $C_{10}H_{13}O$ (MH^+) 149.0966, found 149.0966.

To a solution of triethyl phosphonoacetate (1.9 mL, 9.2 mmol, 96% tech.) in THF (25 mL) at –78 °C was added BuLi (1.60 M in hexanes, 6.3 mL, 10.1 mmol). After 5 min, a solution of (2*E*,4*E*)-2,4-decadien-9-yn-1-al (1.36 g, 9.2 mmol) in THF (5 mL) was added, stirred for 15 min at –78 °C and allowed to warm to room temperature. After addition of H_2O (50 mL) and extraction with Et_2O, the combined organics were dried over $MgSO_4$ and chromatographed on silica gel (1% ethyl acetate/hexane) to give ethyl (2*E*,4*E*,6*E*)-2,4,6-dodecadien-11-ynoate **2** (1.65 g, 82%, 64% overall) and approximately 4% of a mixture of olefin isomers. **2**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.29 (t, J = 7.3 Hz, 3 H), 1.65 (p, J = 7.3 Hz, 2 H), 1.96 (t, J = 2.4 Hz, 1 H), 2.20 (td, J = 6.8, 2.4 Hz, 2 H), 2.27 (q, J = 7.3 Hz, 2 H), 4.19 (q, J = 7.3 Hz, 2 H), 5.84 (d, J = 15.1 Hz, 1 H), 5.89 (dt, J = 14.6, 7.3 Hz, 1 H), 6.17 (dd, J = 15.1, 10.8 Hz, 1 H), 6.22 (dd, J = 15.1, 11.7 Hz, 1 H), 6.52 (dd, J = 15.1, 10.8 Hz, 1 H), 7.28 (dd, J = 15.1, 10.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 17.8, 27.6, 31.7, 60.2, 68.7, 83.9, 120.3, 128.2, 130.7, 138.7, 140.7, 144.6, 167.1; IR (CH_2Cl_2) 3308, 2984, 2939, 2909, 2250, 1701, 1618 cm^{-1}; LRMS m/e (%) 218 (M^+, 13), 173 (14), 171 (17), 145 (23), 144 (32), 143 (14), 129 (24), 117 (39), 105 (55), 91 (100), 79 (47), 77 (64), 65 (26); HRMS (EI) calcd for $C_{14}H_{18}O_2$ (M^+) 218.1307, found 218.1301.

Ethyl (*E*)-(5α,6α,8aβ)-3-(5-Butyl-5-methoxy-1,2,3,5,6,8a-hexahydroazulenyl)propenoate (5a). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in benzene (92 mL) was added complex **3**[33] (92.4 mg, 0.275 mmol). The reaction was heated at 70 °C for 40 min, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on Florisil (2% ethyl acetate/hexane) to give **5a** (48.0 mg, 66%): ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.1 Hz, 3 H), 1.21–1.30 (m, 7 H containing 1.28 (t, J = 7.1 Hz, 3 H)), 1.47–1.57 (m, 3 H), 1.64–1.68 (m, 1 H), 1.69–1.74 (m, 1 H), 2.04–2.08 (m, 1 H), 2.38–2.42 (m, 2 H), 3.14–3.18 (m, 1 H), 3.21 (s, 3 H), 3.41 (t, J = 6.6 Hz, 1 H), 4.18 (q, J = 7.3 Hz, 2 H), 5.32 (br s, 1 H), 5.43 (ddd, J = 10.3, 6.4, 2.4 Hz, 1 H), 5.66 (dd, J = 10.3, 1.5 Hz, 1 H), 5.82 (d, J = 15.6 Hz, 1 H) 7.10 (dd, J = 15.6, 8.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$ at 60 °C) δ 14.0, 14.3, 23.1, 24.7, 26.0, 34.8, 35.0, 36.6, 42.4, 47.8, 51.0, 60.1, 79.2, 122.6, 124.5, 128.3, 133.8, 147.2, 149.0, 166.6; IR (CH_2Cl_2) 2958, 2938, 2871, 2827, 1711, 1646 cm^{-1}; LRMS m/e (%) 319 (9), 318 (M^+, 38), 289 (37), 261 (66), 215 (50), 187 (68), 155 (62), 131 (74), 129 (73), 128 (61), 117 (56), 115 (72), 91 (100), 77 (49); HRMS (EI) calcd for $C_{20}H_{30}O_3$ (M^+) 318.2195, found 318.2195. The stereochemistry assigned to the 5α, 6α, and 8aβ positions was based on comparison to previously reported ethyl (5α,6α,8aβ)-(5-butyl-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)carboxylate.[12g] In addition, irradiation of the methoxy signal at δ 3.21 showed no enhancement of the 8aβ signal at δ 3.14–3.18 or the 6α signal at δ 3.41.

(33) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529–2532.

Ethyl (2*E*,4*E*,6*E*,11*Z*,13*Z*)-11-Formyl-13-methoxy-2,4,6,11,13-heptadecapentaenoate (7), Ethyl (2*E*,4*E*,6*E*)-10-(3-Methoxy-2-propylcyclopent-3-en-1-on-5-yl)-2,4,6-decatrienoate (8a), Ethyl (2*E*,4*E*,6*E*)-10-(3-Methoxy-2-propylcyclopent-2-en-1-on-5-yl)-2,4,6-decatrienoate (8b), and Ethyl (2*E*,4*E*,6*E*)-10-(4-Methoxy-5-propylcyclopent-2-en-1-on-2-yl)-2,4,6-decatrienoate (9). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in benzene (92 mL) was added complex **6**[34] (74.0 mg, 0.252 mmol). The reaction was heated at 70 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel (gradient elution; 5–10% ethyl acetate/hexane) to give **7** (13.5 mg, 17%), **8a** (11.2 mg, 14%), and **9** (8.0 mg, 10%). Upon standing in $CDCl_3$, **8a** isomerized to **8b** over a 24-h period. **7**: ^1H NMR (300 MHz, C_6D_6) δ 0.82 (t, J = 7.4 Hz, 3 H), 1.00 (t, J = 7.2 Hz, 3 H), 1.24 (sextet, J = 7.4 Hz, 2 H), 1.57 (p, J = 7.7 Hz, 2 H), 1.98–2.09 (m, 4 H), 2.60 (t, J = 7.7 Hz, 2 H), 3.13 (s, 3 H), 4.07 (q, J = 7.2 Hz, 2 H), 5.00 (t, J = 7.6 Hz, 1 H), 5.60 (dt, J = 15.3, 7.3 Hz, 1 H), 5.85–5.94 (m, 3 H containing 5.92 (d, J = 15.4 Hz, 1H)), 6.03 (s, 1 H), 6.14 (dd, J = 15.1, 10.8 Hz, 1 H), 7.49 (dd, J = 15.4, 11.2 Hz, 1 H), 9.28 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 14.3, 22.5, 23.9, 28.1, 28.4, 33.1, 59.8, 60.2, 120.1, 127.9, 129.7, 130.2, 139.9, 140.6, 141.1, 144.8, 145.9, 154.1, 167.2, 195.2; IR ($CDCl_3$) 3053, 3023, 2983, 2962, 2935, 2873, 2839, 1697, 1681, 1618 cm^{-1}; LRMS m/e (%) 346 (M^+, 3), 317 (5), 179 (8), 169 (15), 168 (88), 154 (13), 105 (59), 91 (100), 79 (66), 77 (67); HRMS (EI) calcd for $C_{21}H_{30}O_4$ (M^+) 346.2144, found 346.2137. **8a**: ^1H NMR (500 MHz, C_6D_6) δ 0.83 (t, J = 7.3 Hz, 3 H), 1.01 (t, J = 7.3 Hz, 3 H), 1.25–1.32 (m, 2 H), 1.33–1.50 (m, 3 H), 1.57–1.63 (m, 1 H), 1.67–1.74 (m, 1 H), 1.78–1.84 (m, 1 H), 1.90 (q, J = 7.3 Hz, 2H), 2.79–2.84 (m, 2 H), 3.19 (s, 3 H), 4.08 (q, J = 7.3 Hz, 2 H), 4.42 (br s, 1 H), 5.54 (dt, J = 14.2, 6.8 Hz, 1 H), 5.86–5.95 (m, 3 H, containing 5.89 (dt, J = 15.1, 11.2 Hz, 1 H) and 5.94 (d, J = 15.6 Hz, 1 H)), 6.16 (dd, J = 14.8, 11.0 Hz, 1 H), 7.52 (dd, J = 15.4, 11.4 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.31, 14.35, 19.6, 26.5, 31.2, 31.9, 33.2, 51.8, 52.0, 55.0, 60.1, 95.1, 121.0, 128.5, 130.6, 139.2, 140.9, 144.8, 159.8, 166.7, 215.9; IR (CH_2Cl_2) 3021, 2961, 2935, 2874, 2861, 1743, 1701, 1639, 1618 cm^{-1}; LRMS m/e (%) 347 (3), 346 (M^+, 11), 180 (11), 179 (11), 167 (33), 154 (100), 125 (25), 105 (19), 91 (54), 79 (30). **8b**: ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, J = 7.3 Hz, 3 H), 1.27–1.51 (m, 8 H, containing 1.29 (t, J = 7.1 Hz, 3 H)), 1.39 (sextet, J = 7.3 Hz, 2 H), 1.48 (p, J = 7.6 Hz, 2 H)), 1.82–1.89 (m, 1 H), 2.07 (t, J = 7.3 Hz, 2 H), 2.14–2.19 (m, 2 H), 2.27 (d, J = 17.1 Hz, 1 H), 2.40–2.45 (m, 1 H), 2.81 (dd, J = 17.1, 6.4 Hz, 1 H), 3.92 (s, 3 H), 4.19 (q, J = 7.1 Hz, 2 H), 5.83 (d, J = 15.1 Hz, 1 H), 5.90 (dt, J = 15.1, 7.1 Hz, 1 H), 6.13 (dd, J = 14.6, 10.7 Hz, 1H), 6.21 (dd, J = 14.6, 11.2 Hz, 1 H), 6.50 (dd, J = 15.1, 10.7 Hz, 1 H), 7.28 (dd, J = 15.1, 11.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.3, 21.2, 23.2, 26.6, 31.1, 31.3, 32.9, 44.5, 56.3, 60.2, 120.0, 120.2, 128.1, 130.2, 139.6, 140.9, 144.7, 167.2, 183.2, 206.9; IR (CH_2Cl_2) 2960, 2934, 2871, 2862, 1704, 1619, 1461, 1366 cm^{-1}; LRMS m/e (%) 346 (M^+, 5), 167 (23), 154 (100), 125 (17), 105 (7), 91 (21), 79 (15); HRMS (EI) calcd for $C_{21}H_{30}O_4$ (M^+) 346.2144, found 346.2141. **9**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.1 Hz, 3 H), 1.29 (t, J = 7.1 Hz, 3 H), 1.40–1.48 (m, 3 H), 1.57–1.65 (m, 2 H), 1.74–1.78 (m, 1 H), 2.14–2.23 (m, 4 H), 2.27–2.30 (m, 1 H), 3.44 (s, 3 H), 4.14 (br s, 1 H), 4.20 (q, J = 7.1 Hz, 2 H), 5.84 (d, J = 15.3 Hz, 1 H), 5.89 (dt, J = 15.1, 7.3 Hz, 1 H), 6.14 (dd, J = 15.1, 10.7 Hz, 1 H), 6.23 (dd, J = 14.8, 11.3 Hz, 1 H), 6.51 (dd, J = 14.8, 10.7 Hz, 1 H), 7.18 (br s, 1 H), 7.28 (dd, J = 15.1, 11.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 14.3, 20.5, 24.3, 26.7, 31.8, 32.5, 52.3, 56.8, 60.2, 83.2, 120.3, 128.3, 130.5, 139.1, 140.8, 144.6, 147.3, 151.7, 167.2, 207.8; IR (CH_2Cl_2) 2960, 2934, 2873, 1705, 1618 cm^{-1}; LRMS m/e (%) 346 (M^+, 5), 300 (11), 225 (10), 178 (26), 161 (11), 149 (19), 139 (47), 137 (15), 133 (41), 132 (55), 131 (34), 105 (100), 91 (77), 79 (52), 77 (46); HRMS (EI) calcd for $C_{21}H_{30}O_4$ (M^+) 346.2144, found 346.2142.

Ethyl (*E*)-(5α,6α,8aβ)-3-(5-Phenyl-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)propenoate (5b), Ethyl (*E*)-(5α,6β,8aα)-3-(5-Phenyl-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)propenoate (5b′), and Ethyl (*E*)-3-(5-Phenyl-1,2,3,6-tetrahydroazulen-6-yl)propenoate (11). To a solution of **2** (50.0 mg, 0.229 mmol) in THF (92 mL) was added complex **10**[35] (98.0 mg, 0.275 mmol). The reaction was heated at reflux for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel (gradient elution; 1–3% ethyl acetate/hexane) to give a 2:1 mixture of **5b** and **5b′** (39.0 mg, 50%). This mixture was treated with HCl (0.5 mL, 0.1 M) and ethanol (5 mL) at 25 °C for 4 h. After extraction with 2% ethyl acetate and

(34) Prepared by the procedure reported for molybdenum complex **3**. See ref 33.

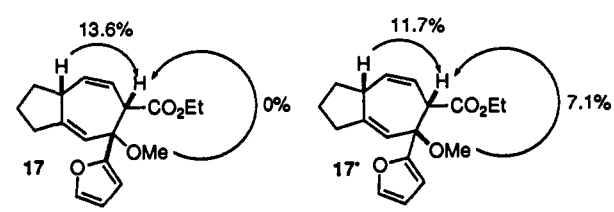
(35) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445–2456.

hexane, the combined organics were dried over $MgSO_4$, concentrated in vacuo and purified by chromatography on silica gel to give **11** (35 mg, 99%; 49% from trienyne **2**). **5b and 5b'**: ^{1}H NMR (500 MHz, C_6D_6) major isomer (**5b**): δ 0.92 (t, J = 7.1 Hz, 3 H), 1.14–1.26 (m, 2 H), 1.39–1.45 (m, 1 H), 1.64–1.68 (m, 1 H), 2.13–2.21 (m, 2 H), 2.72–2.80 (m, 1 H), 2.96 (s, 3 H), 3.74 (t, J = 6.4 Hz, 1 H), 3.99 (q, J = 7.3 Hz, 2 H), 5.36–5.42 (m, 2 H), 5.65 (s, 1 H), 5.92 (d, J = 15.6 Hz, 1 H), 7.05–7.10 (m, 2 H), 7.17–7.21 (m, 1 H), 7.46–7.48 (m, 2 H), 7.59 (dd, J = 15.6, 7.3 Hz, 1 H), minor isomer (**5b'**): δ 0.93 (t, J = 7.2 Hz, 3 H), 1.24–1.32 (m, 2 H), 1.46–1.49 (m, 1 H), 1.77–1.81 (m, 1 H), 2.13–2.21 (m, 2 H), 3.08–3.20 (m, 1 H), 3.17 (s, 3 H), 3.97 (q, J = 7.1 Hz, 2 H), 4.00 (t, J = 7.3 Hz, 1 H), 5.09 (ddd, J = 9.5, 6.1, 2.9 Hz, 1 H), 5.36-5.42 (m, 1 H), 5.63 (dt, J = 11.2, 2.0 Hz, 1 H), 5.98 (d, J = 15.6 Hz, 1 H), 7.05–7.10 (m, 2 H), 7.17–7.21 (m, 1 H), 7.43 (dd, J = 15.6, 7.3 Hz, 1 H), 7.62–7.64 (m, 2 H); ^{13}C NMR (125 MHz, C_6D_6) (mixture of **5b** and **5b'**) δ 14.2, 14.3, 23.0, 24.89, 24.94, 31.9, 34.5, 34.8, 34.9, 35.2, 41.5, 50.1, 50.9, 59.98, 60.0, 80.5, 123.1, 123.3, 123.4, 124.4, 127.42, 127.45, 127.49, 127.6, 127.9, 128.06, 128.11, 128.29, 128.35, 129.3, 136.3, 142.3, 147.9, 149.0, 166.1, 166.2; IR (CH_2Cl_2) (mixture) 3022, 2979, 2955, 2903, 2869, 2826, 1716, 1682, 1650 cm^{-1}; LRMS (mixture) m/e (%) 339 (12), 338 (M^+, 49), 306 (11), 265 (13), 233 (32), 232 (20), 218 (17), 204 (18), 178 (20), 165 (25), 121 (67), 105 (100), 91 (75), 77 (83); HRMS (EI) (mixture) calcd for $C_{22}H_{26}O_3$ (M^+) 338.1882, found 338.1891. **11**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 3 H), 1.84–1.97 (m, 2 H), 2.71 (apparent t, J = 7 Hz, 4 H), 4.13 (q, J = 7.3 Hz, 2 H), 4.20 (br t, J = 6.8 Hz, 1 H), 5.48 (t, J = 9.3 Hz, 1 H), 5.78 (dd, J = 15.6, 2.0 Hz, 1 H), 6.32 (d, J = 9.8 Hz, 1 H), 6.51 (s, 1 H), 6.76 (dd, J = 15.6, 5.4 Hz, 1 H), 7.26–7.28 (m, 1 H), 7.32–7.34 (m, 2 H), 7.40–7.42 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 23.1, 36.7, 37.1, 44.5, 60.1, 119.3, 119.9, 124.2, 127.27, 127.31, 127.5, 128.4, 131.8, 140.6, 140.8, 142.0, 146.0, 166.8; IR ($CDCl_3$) 2983, 2959, 2940, 2872, 2844, 1706, 1645, 1602 cm^{-1}; LRMS m/e (%) 307 (6), 306 (M^+, 23), 277 (10), 260 (35), 259 (30), 233 (38), 232 (37), 231 (100), 218 (34), 217 (25), 215 (29), 205 (34), 204 (27), 203 (46), 202 (41), 193 (56), 191 (38), 189 (27), 178 (42), 165 (35), 152 (21); HRMS (EI) calcd for $C_{21}H_{22}O_2$ (M^+) 306.1620, found 306.1628.

Ethyl (2*E*,4*E*,6*E*)-10-(1,4-Naphthoquinon-2-yl)-2,4,6-decatrienoate (13). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in THF (1.1 mL) was added complex **12**[35] (39.0 mg, 0.126 mmol). The reaction was heated at 45 °C for 24 h with an additional equivalent of carbene added after 18 h. After 24 h, the reaction was exposed to air, cooled to room temperature, and concentrated in vacuo. The residue was diluted with diethyl ether (5 mL), poured into a 0.5 M solution of $(NH_4)_2Ce(NO_3)_6$ in 0.1 N aqueous HNO_3 (4 mL), and stirred for 30 min. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organics were extracted with brine, dried over $MgSO_4$, concentrated in vacuo, and chromatographed on silica gel to give **13** (20.0 mg, 25%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, J = 7.3 Hz, 3 H), 1.72 (p, J = 7.3 Hz, 2 H), 2.26 (q, J = 7.3 Hz, 2 H), 2.58 (t, J = 7.3 Hz, 2 H), 4.19 (q, J = 7.3 Hz, 2 H), 5.84 (d, J = 15.1 Hz, 1 H), 5.91 (dt, J = 15.1, 6.8 Hz, 1 H), 6.16 (dd, J = 15.1, 10.7 Hz, 1 H), 6.21 (dd, J = 14.6, 11.2 Hz, 1 H), 6.50 (dd, J = 14.6, 10.7 Hz, 1 H), 6.79 (s, 1 H), 7.27 (dd, J = 15.1, 11.2 Hz, 1 H), 7.72–7.73 (m, 2 H), 8.05–8.10 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 27.3, 29.1, 32.5, 60.2, 120.4, 126.0, 126.6, 128.4, 130.8, 132.1, 132.2, 133.6, 133.7, 134.9, 138.6, 140.6, 144.5, 151.3, 167.1, 185.07, 185.11; IR ($CDCl_3$) 2984, 2958, 2954, 2935, 1703, 1664, 1619, 1596 cm^{-1}; LRMS m/e (%) 351 (3), 350 (M^+, 11), 305 (4), 304 (5), 198 (15), 197 (34), 173 (30), 172 (55); HRMS (EI) calcd for $C_{22}H_{22}O_4$ (M^+) 350.1518, found 350.1535.

((2-Furyl)methoxymethylene)pentacarbonylmolybdenum(0) (14). To a solution of furan (660 μL, 9.09 mmol) and TMEDA (1.37 mL, 9.09 mmol) in diethyl ether (15 mL) at 0 °C was added BuLi (1.60 M in hexanes, 5.68 mL, 9.09 mmol) over a 10-min period. After stirring for 1 h, the resulting solution of 2-furyllithium was added to a suspension of molybdenum hexacarbonyl (2.40 g, 9.09 mmol) in THF (15 mL) over a period of 10 min with vigorous stirring. The resulting reddish brown solution was stirred at 0 °C for 2 h and then concentrated by rotary evaporation. The residue was dissolved in deoxygenated water (10 mL) and filtered through Celite. A deoxygenated, saturated aqueous solution of tetramethylammonium bromide (4.19 g, 27.3 mmol) was added, resulting in the immediate formation of an orange precipitate. The flask was cooled to 0 °C after being purged with nitrogen and allowed to stand for 30 min. The orange solid was collected by vacuum filtration and dried under high vacuum for several hours. The product was dissolved in CH_2Cl_2 and filtered through Celite. Crystallization was induced by the addition of heptane followed by concentration and cooling to give [tetramethylammonium][(2-furyl)oxidomethylene]pentacarbonylmolybdenum(0) in 2 crops (2.17 g, 59%). This salt (2.17 g, 5.36 mmol) was then dissolved in CH_2Cl_2 and treated with $CF_3SO_3CH_3$ (0.79 mL, 6.97 mmol) at 0 °C, and the resulting dark red solution stirred for 30 min. Concentration in vacuo and purification by flash chromatography on silica gel (hexane) gave **14** as a red solid (1.56 g, 84%, 50% overall yield): ^{1}H NMR (500 MHz, C_6D_6) δ 3.96 (s, 3 H), 5.76 (dd, J = 3.4, 1.5 Hz, 1 H), 6.60 (d, J = 3.4 Hz, 1 H), 6.92 (br s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 67.2, 113.0, 114.3, 150.4, 164.6, 206.5, 213.6, 303.1; IR (CH_2Cl_2) 2069, 1990, 1946, 1448, 1439 cm^{-1}.

Ethyl (*E*)-(5α,6α,8aβ)-3-(5-(2-Furyl)-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)propenoate (5c). To a solution of **2** (47.0 mg, 0.216 mmol) in 1,4-dioxane (90 mL) was added complex **14** (82.3 mg, 0.238 mmol). The reaction was heated at reflux for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on Florisil to give **5c** (30.0 mg, 41%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.93 (t, J = 7.2 Hz, 3 H), 1.11–1.15 (m, 2 H), 1.38–1.40 (m, 1 H), 1.58–1.62 (m, 1 H), 2.08–2.21 (m, 2 H), 2.75–2.80 (m, 1 H), 2.91 (s, 3 H), 4.00 (q, J = 7.3 Hz, 2 H), 4.08 (br t, J = 7.3 Hz, 1 H), 5.25 (dd, J = 11.7, 2.4 Hz, 1 H), 5.32 (ddd, J = 11.7, 7.3, 2.4 Hz, 1 H), 5.68 (s, 1 H), 6.03 (dd, J = 2.9, 2.0 Hz, 1 H), 6.08 (d, J = 15.6 Hz, 1 H), 6.19 (d, J = 3.4 Hz, 1 H), 7.10 (br s, 1 H), 7.63 (dd, J = 15.6, 7.3 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.3, 24.6, 34.4, 35.2, 44.7, 49.2, 50.9, 60.0, 79.3, 109.9, 110.6, 122.9, 123.3, 126.0, 131.3, 142.5, 147.4, 148.5, 154.1, 166.3; IR (C_6D_6) 3053, 2958, 2940, 2907, 2889, 2870, 1710, 1647 cm^{-1}; LRMS m/e (%) 329 (4), 328 (M^+, 18), 296 (7), 255 (14), 223 (34), 222 (20), 221 (18), 195 (22), 165 (45), 152 (33), 129 (38), 128 (58), 115 (75), 111 (43), 95 (100), 91 (62), 77 (49), 55 (26). During transport to the U.C. Riverside Mass Spectrometry Facility, **5c** eliminated methanol to give cycloheptatriene **73**.[36] HRMS of **73** (EI) calcd for $C_{19}H_{20}O_3$ (M^+) 296.1412, found 296.1427. Stereochemistry at the 5α, 6α, and 8aβ positions was assigned by comparison to **17**. NOE studies were performed on **17** and the corresponding (5α,6β,8aα) isomer, **17'**, with the results shown below. Additionally, irradiation of the methoxy signal of **5c** at δ 2.91 showed no enhancement of the 8aβ signal at δ 2.75–2.80 or the 6α signal at δ 4.08.



Ethyl (2*E*,4*E*,6*E*)-10-(4-Hydroxy-7-methoxy-2,3-benzofuran-6-yl)-2,4,6-decatrienoate (16) and Ethyl (*E*)-(5α,6β,8aα)-3-(5-(2-Furyl)-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)propenoate (5c'). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in benzene (92 mL) was added complex **15**[37] (83.0 mg, 0.275 mmol). The reaction was heated at 70 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **16** (38.0 mg, 52%) and **5c'** (7.3 mg, 10%). **16**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, J = 7.3 Hz, 3 H), 1.76 (p, J = 6.8 Hz, 2 H), 2.21 (q, J = 7.2 Hz, 2 H), 2.68 (t, J = 6.8 Hz, 2 H), 3.95 (s, 3 H), 4.20 (q, J = 7.3 Hz, 2 H), 5.37 (s, 1 H), 5.83 (d, J = 15.1 Hz, 1 H), 5.94 (dt, J = 14.6, 6.8 Hz, 1 H), 6.15 (dd, J = 15.1, 10.7 Hz, 1 H), 6.19 (dd, J = 15.1, 11.2 Hz, 1 H), 6.50 (dd, J = 14.6, 10.7 Hz, 1 H), 6.55 (s, 1 H), 6.82 (s, 1 H), 7.28 (dd, J = 15.1, 11.2 Hz, 1 H), 7.52 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 29.3, 29.7, 32.5, 56.7, 60.3, 103.6, 109.1, 119.0, 120.0, 120.6, 127.9, 130.2, 139.5, 140.0, 140.2, 141.1, 143.7, 144.1, 144.9, 167.5; IR ($CDCl_3$) 3604, 3021, 2982, 2938, 2860, 2844, 1694, 1617, 1490 cm^{-1}; LRMS m/e (%) 357 (2), 356 (M^+, 9), 178 (16), 177 (100), 133 (12), 105 (13), 91 (21), 77 (13); HRMS (EI) calcd for $C_{21}H_{24}O_5$ (M^+) 356.1624, found 356.1609. **5c'**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.88 (t, J = 7.1 Hz, 3 H), 1.22–1.26 (m, 2 H), 1.41–1.44 (m, 1 H), 1.75–1.82 (m, 1 H), 2.18–2.22 (m, 2 H), 3.01 (s, 3 H), 3.27–3.31 (m, 1 H), 3.93 (q, J = 7.1 Hz, 2 H), 3.98–4.05 (m, 1 H), 5.34 (ddd, J = 11.3, 6.0, 2.9 Hz, 1 H), 5.56 (dt, J = 11.3, 2.0 Hz, 1 H), 5.71 (q, J = 2.6 Hz, 1 H), 5.99 (dd, J = 15.7, 1.2 Hz, 1 H), 6.00 (dd, J = 3.3, 1.8 Hz, 1 H), 6.16 (d, J = 3.3 Hz, 1 H), 7.04 (d, J = 1.8 Hz, 1 H), 7.28 (dd,

(36) Confirmed by ^{1}H NMR.

(37) Prepared by the procedure described above for the preparation of molybdenum complex **14**.

J = 15.7, 7.9 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.2, 24.8, 35.0, 35.1, 42.6, 50.0, 50.5, 60.0, 78.2, 109.7, 110.1, 118.7, 123.2, 127.2, 127.7, 132.8, 142.4, 147.6, 155.7, 166.1; IR (C_6D_6) 2941, 2904, 2870, 2824, 1711, 1648, 1618 cm^{-1}; LRMS m/e (%) 329 (4), 328 (M^+, 18), 296 (12), 255 (16), 223 (50), 221 (31), 195 (31), 165 (56), 152 (38), 129 (38), 128 (56), 115 (69), 111 (59), 95 (100), 91 (57), 77 (47), 55 (31). Stereochemistry at the 5α, 6β, and 8aα positions was assigned by comparison to **17′**.

(((1-(Trimethylsilyl)ethenyl)methoxymethylene)pentacarbonylmolybdenum(0) (19). To a solution of (1-bromovinyl)trimethylsilane (500 mg, 2.79 mmol) in THF (6.0 mL) at −78 °C was added *s*-BuLi (1.30 M in cyclohexane, 2.36 mL, 3.07 mmol). After 30 min the vinyllithium solution was warmed to 0 °C and added via cannula to a slurry of molybdenum hexacarbonyl (0.737 g, 2.79 mmol) in diethyl ether (6.0 mL) at 0 °C. After 1 h, $CF_3SO_3CH_3$ (0.38 mL, 3.34 mmol) was added, and the resulting red solution was stirred for 15 min and warmed to room temperature. Saturated $NaHCO_3$ solution and saturated NaCl solution were sequentially added, and the organic phase was separated. The aqueous phase was extracted twice with hexane, and the combined organics were dried over $MgSO_4$, concentrated in vacuo, and purified by chromatography on silica gel (hexane) to give **19** as a red oil (287 mg, 27%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.00 (s, 9 H), 3.48 (s, 3 H), 5.23 (br s, 1 H), 5.64 (br s, 1 H); IR (C_6D_6) 2956, 2069, 1982, 1947, 1447, 1232 cm^{-1}.

Ethyl (2*E*,4*E*,6*E*)-10-(1-Hydroxy-4-methoxy-3-(trimethylsilyl)phen-6-yl)-2,4,6-decatrienoate (20) from Complex 19. To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in THF (20 mL) was added complex **19** (86.6 mg, 0.229 mmol). The reaction was heated in a sealed vial at 100 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **21** (26.0 mg, 30%). Trienyne **2** (17.0 mg) was recovered in 34% yield.

20 from 21. To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in benzene (92 mL) was added complex **21**[38] (84.0 mg, 0.252 mmol). The reaction was heated at 70 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **20** (41.0 mg, 46%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.24 (s, 9 H), 1.29 (t, J = 7.3 Hz, 3 H), 1.76 (p, J = 7.3 Hz, 2 H), 2.23 (q, J = 7.3 Hz, 2 H), 2.61 (t, J = 7.3 Hz, 2 H), 3.75 (s, 3 H), 4.20 (q, J = 7.3 Hz, 2 H), 4.46 (s, 1 H), 5.84 (d, J = 15.1 Hz, 1 H), 5.96 (dt, J = 15.1, 6.8 Hz, 1 H), 6.17 (dd, J = 15.1, 10.7 Hz, 1 H), 6.21 (dd, J = 15.1, 11.2 Hz, 1 H), 6.53 (dd, J = 14.7, 10.8 Hz, 1 H), 6.59 (s, 1 H), 6.75 (s, 1 H), 7.30 (dd, J = 15.1, 11.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.0, 14.3, 29.0, 30.0, 32.7, 55.8, 60.2, 112.0, 120.1, 121.6, 126.6, 128.0, 129.9, 130.2, 139.9, 141.1, 144.8, 147.1, 158.5, 167.3; IR ($CDCl_3$) 3692, 3604, 3020, 2955, 2940, 2905, 2860, 1702, 1641, 1616 cm^{-1}; LRMS m/e (%) 390 (7), 389 (25), 388 (M^+, 73), 373 (16), 343 (13), 342 (25), 249 (12), 210 (22), 209 (100), 193 (23), 191 (13), 179 (15), 177 (21), 165 (9), 164 (14), 163 (9), 135 (13), 133 (62), 105 (47), 91 (32); HRMS (EI) calcd for $C_{22}H_{32}O_4Si$ (M^+) 388.2070, found 388.2054.

((1-Cyclohexenyl)methoxymethylene)pentacarbonylmolybdenum(0) (22). To a solution of cyclohexanone 2,4,6-triisopropylbenzenesulfonylhydrazone[39] (2.00 g, 5.28 mmol) in tetrahydrofuran (20 mL) at −78 °C was added *t*-BuLi (1.70 M in pentane, 6.21 mL, 10.6 mmol). After 2 h, the red solution was warmed to 0 °C and added to a suspension of molybdenum hexacarbonyl (1.39 g, 5.28 mmol) in diethyl ether (20 mL) at 0 °C. After 25 min, $CF_3SO_3CH_3$ (0.90 mL, 7.92 mmol) was added, and the reaction mixture was slowly warmed to room temperature. After 15 min saturated $NaHCO_3$ solution and saturated NaCl solution were added, and the organic phase separated. The aqueous phase was extracted twice with hexane, and the combined organics were dried over $MgSO_4$, concentrated in vacuo, and purified by chromatography on silica gel (hexane) to give **22** as a red oil (1.09 g, 57%): ^{1}H NMR (300 MHz, C_6D_6) δ 1.17–1.33 (m, 4 H), 1.88–1.97 (m, 4 H), 3.99 (s, 3 H), 7.06 (br s, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 21.6, 22.1, 24.8, 27.0, 68.1, 149.9, 155.0, 206.8, 213.6, 336.3.

Ethyl (2*E*,4*E*,6*E*)-10-(1-Hydroxy-4-methoxy-5,6,7,8-tetrahydronaphthalen-2-yl)-2,4,6-decatrienoate (23), Ethyl (2*E*,4*E*,6*E*)-10-(4,5,6,7-Tetrahydroindan-1-on-3-yl)-2,4,6-decatrienoate (24a), and Ethyl (2*E*,4*E*,6*E*)10-(2,4,5,6,7,7a-Hexahydroinden-1-on-3-yl)-2,4,6-decatrienoate (24b). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in THF (92 mL) was added complex **22** (90.8 mg, 0.252 mmol). The reaction was heated at 67 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **23** (20.0 mg, 24%) as well as **24a** and a minor isomer, believed to be **24b**, as an inseparable 3:1 mixture (26.0 mg, 35%). ^{1}H and ^{13}C NMR data are reported for **24a** only. **23**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.00 (t, J = 7.1 Hz, 3 H), 1.49–1.56 (m, 4 H), 1.75 (p, J = 7.5 Hz, 2 H), 2.07 (q, J = 7.3 Hz, 2 H), 2.26 (t, J = 5.5 Hz, 2 H), 2.63 (t, J = 7.5 Hz, 2 H), 2.81 (t, J = 5.5 Hz, 2 H), 3.47 (s, 3 H), 4.07 (q, J = 7.1 Hz, 2 H), 4.08 (s, 1 H), 5.65 (dt, J = 15.1, 7.0 Hz, 1 H), 5.88–5.96 (m, 3 H containing 5.92 (d, J = 15.3 Hz, 1 H)), 6.17 (dd, J = 15.0, 10.7 Hz, 1 H), 6.44 (s, 1 H), 7.51 (dd, J = 15.3, 11.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.1, 22.3, 23.2, 23.4, 29.2, 29.9, 32.7, 55.7, 60.2, 108.9, 120.1, 124.19, 124.24, 124.8, 127.9, 130.2, 140.0, 141.1, 144.8, 145.0, 151.0, 167.2; IR ($CDCl_3$) 3589, 3234, 2982, 2935, 2859, 2837, 1711, 1618 cm^{-1}; LRMS m/e (%) 371 (2), 370 (M^+, 8), 192 (17), 191 (100), 133 (12), 105 (13), 91 (20), 77 (9); HRMS (EI) calcd for $C_{23}H_{30}O_4$ (M^+) 370.2144, found 370.2159. Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.07; H, 8.05. **24**: ^{1}H NMR (500 MHz, $CDCl_3$) (**24a** only) δ 1.20–1.34 (m, 5 H, containing 1.29 (t, J = 7.1 Hz, 3 H), 1.42 (p, J = 7.8 Hz, 2 H), 1.52–1.62 (m, 2 H), 1.65–1.78 (m, 4 H), 2.03 (dd, J = 18.6, 1.5 Hz, 1 H), 2.09–2.24 (m, 3 H), 2.36–2.47 (m, 1 H), 2.52 (dd, J = 18.6, 6.4 Hz, 1 H), 2.66–2.70 (m, 1 H), 4.20 (q, J = 7.3 Hz, 2 H), 5.85 (d, J = 15.1 Hz, 1 H), 5.88 (dt, J = 14.7, 7.3 Hz, 1 H), 6.14 (dd, J = 15.1, 10.7 Hz, 1 H), 6.22 (dd, J = 15.1, 11.2 Hz, 1 H), 6.51 (dd, J = 14.9, 11.0 Hz, 1 H), 7.29 (dd, J = 15.1, 10.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) (**24a** only) δ 14.3, 19.9, 21.6, 22.1, 26.4, 26.5, 32.2, 32.9, 40.9, 41.6, 60.2, 120.3, 128.2, 130.4, 138.3, 140.7, 144.6, 167.1, 176.0, 208.0; IR ($CDCl_3$) (mixture) 2935, 1690, 1641, 1618 cm^{-1}; LRMS, EI, m/e (%) (mixture) 329 (2), 328 (M^+, 9), 282 (9), 254 (9), 200 (8), 175 (12), 161 (17), 149 (25), 136 (21), 133 (24), 119 (23), 107 (34), 105 (38), 91 (100), 79 (71), 77 (51), 67 (22); HRMS (EI) (mixture) calcd for $C_{21}H_{28}O_3$ 328.2038, found 328.2042.

23 and Ethyl (*E*)-(5α,6β,8aα)-3-(5-(1-Cyclohexenyl)-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)propenoate (5d′). To a solution of trienyne **2** (60.0 mg, 0.275 mmol) in benzene (110 mL) was added complex **25**[40] (96.0 mg, 0.302 mmol). The reaction was heated at 70 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **23** (54.0 mg, 53%) and impure **5d′** (2.4 mg, <3%). The structure and stereochemistry of **5d′** were assigned based on comparison to ^{1}H NMR data of structurally related compounds.

Ethyl (2*E*,4*E*,6*E*)-10-(7-Methoxy-6,7-didehydro-5-cyclopentapyranylidenyl)-2,4,6-decatrienoate (27). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in THF (92 mL) was added complex **26**[41] (125 mg, 0.344 mmol). The reaction mixture was heated at 67 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **27** as a 3.4:1 mixture of isomers (26.5 mg, 34%): ^{1}H NMR (500 MHz, C_6D_6) major isomer δ 1.00 (t, J = 7.1 Hz, 3 H), 1.14–1.20 (m, 1 H), 1.39–1.48 (m, 1 H), 1.52–1.59 (m, 1 H), 1.69–1.75 (m, 1 H), 2.12 (dt, J = 14.6, 7.3 Hz, 2 H), 2.20 (dt, J = 14.6, 7.3 Hz, 2 H), 2.47 (dt, J = 11.7, 5.9 Hz, 1 H), 3.24 (s, 3 H), 3.29 (ddd, J = 10.2, 7.8, 2.4 Hz, 1 H), 3.63 (dt, J = 11.0, 5.4 Hz, 1 H), 4.07 (q, J = 7.3 Hz, 2 H), 4.30 (d, J = 6.4 Hz, 1 H), 4.88 (t, J = 7.1 Hz, 1 H), 5.91–6.00 (m, 3 H, containing 5.92 (d, J = 15.1 Hz, 1 H)), 6.18 (dd, J = 15.1, 10.7 Hz, 1 H), 7.51 (dd, J = 15.1, 11.2 Hz, 1 H); minor isomer δ 1.01 (t, J = 7.1 Hz, 3 H), 1.29–1.35 (m, 1 H), 1.76–1.82 (m, 1 H), 2.67 (dt, J = 15.6, 6.8 Hz, 1 H), 3.22 (s, 3 H), 3.56 (ddd, J = 8.8, 5.9, 2.4 Hz, 1 H), 4.08 (q, J = 7.3 Hz, 2 H), 4.76 (d, J = 6.8 Hz, 1 H), 5.04 (t, J = 7.1 Hz, 1 H), 5.05 (s, 1 H), other signals obscured by major isomer; ^{13}C NMR (125 MHz, C_6D_6) δ 14.3, 22.0, 23.6, 28.7, 34.0, 39.9, 56.7, 60.1, 63.4, 77.4, 100.5, 108.6, 113.7, 120.9, 128.5, 130.7, 139.4, 141.0, 143.6, 144.8, 166.7; IR (C_6D_6) 2977, 2938, 2871, 2851, 1714, 1614, 1462 cm^{-1}; LRMS (EI) m/e (%) 342 (M^+ − 2, 0.1), 341 (0.5), 154 (35), 126 (43), 125 (56), 110 (14), 109 (100), 108 (11), 98 (7), 97 (33), 84 (19), 82 (16), 81 (92).

Ethyl (2*E*,4*E*,6*E*)-10-(5-Hydroxy-8-methoxy-3,4-dihydro-2*H*-benzopyran-6-yl)-2,4,6-decatrienoate (29) and Ethyl (*E*)-(5α,6β,8aα)-3-(5-(3,4-Dihydro-(2*H*)-pyran-1-yl)-5-methoxy-1,2,3,5,6,8a-hexahydroazulen-6-yl)propenoate (5e′). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in benzene (92 mL) was added complex **28**[40] (88.0 mg, 0.275 mmol). The

(38) Prepared by the procedure described above for the preparation of molybdenum complex **19**.

(39) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147–154.

(40) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293–2295.

(41) Prepared according to ref 14 except methylation was accomplished with $CF_3SO_3CH_3$. Complex **26** was stored as a deoxygenated solution in benzene at −5 °C.

reaction was heated at 70 °C for 1.5 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **29** (35.0 mg, 41%) and **5e'** (2.5 mg, ca. 95% pure, <3%). **29**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.00 (t, J = 7.1 Hz, 3 H), 1.44 (m, 2 H), 1.67 (p, J = 7.4 Hz, 2 H), 2.03 (q, J = 7.3 Hz, 2 H), 2.27 (t, J = 6.6 Hz, 2 H), 2.52 (t, J = 7.4 Hz, 2 H), 3,59 (s, 3 H), 3.75 (t, J = 5.1 Hz, 2 H), 4.07 (q, J = 7.1 Hz, 2 H), 4.45 (s, 1 H), 5.63 (dt, J = 15.1, 6.8 Hz, 1 H), 5.88–5.97 (m, 2 H containing 5.92 (d, J = 15.3 Hz, 1 H)), 6.17 (dd, J = 15.1, 10.6 Hz, 1 H), 6.55 (s, 1 H), 7.50 (dd, J = 15.3, 11.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 19.6, 21.6, 29.30, 29.32, 32.5, 56.4, 60.2, 66.0, 110.8, 117.4, 120.2, 128.0, 128.3, 130.3, 139.8, 140.9, 142.2, 143.2, 144.7, 145.0, 167.2; IR (CH_2Cl_2) 3598, 2980, 2938, 2878, 2861, 1703, 1618, 1491, 1466 cm^{-1}; LRMS m/e (%) 373 (3), 372 (M^+, 13), 194 (13), 193 (100), 180 (5), 179 (5), 165 (10), 105 (8), 91 (17), 79 (10), 77 (11); HRMS (EI) calcd for $C_{22}H_{28}O_5$ (M^+) 372.1937, found 372.1952. **5e'**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.94 (t, J = 7.1 Hz, 3 H), 1.23–1.45 (m, 5 H), 1.74–1.79 (m, 3 H), 2.19–2.23 (m, 2 H), 3.17 (s, 3 H), 3.28–3.29 (m, 1 H), 3.64–3.71 (m, 2 H), 3.78–3.80 (m, 1 H), 4.02 (q, J = 7.1 Hz, 2 H), 4.94 (t, J = 3.8 Hz, 1 H), 5.41 (ddd, J = 11.0, 5.9, 2.9 Hz, 1 H), 5.60 (dt, J = 11.0, 2.1 Hz, 1 H), 5.69 (q, J = 2.6 Hz, 1 H), 6.10 (dd, J = 15.7, 1.3 Hz, 1 H), 7.52 (dd, J = 15.7, 7.7 Hz, 1 H); LRMS m/e (%) 345 (8), 344 (M^+, 33), 313 (8), 312 (10), 239 (32).

((1,4-Dioxen-2-yl)methoxymethylene)pentacarbonylmolybdenum(0) (30). To a solution of 1,4-dioxene (0.50 mL, 5.96 mmol) in tetrahydrofuran (8.0 mL) at −20 °C was added *t*-BuLi (1.70 M in pentane, 3.86 mL, 6.56 mmol), and the solution stirred for 1 h. After warming to 0 °C, the vinyllithium solution was transferred via cannula to a suspension of molybdenum hexacarbonyl (1.57 g, 5.96 mmol) in tetrahydrofuran (10 mL) at 0 °C, and the resulting red solution stirred at room temperature for 1 h. The volatiles were removed by concentration in vacuo. The residue was dissolved in diethyl ether (10 mL), purged with nitrogen, chilled to 0 °C, and treated with $CF_3SO_3CH_3$ (810 μL, 7.15 mmol). After 2 h saturated $NaHCO_3$ solution and saturated NaCl solution were sequentially added, and the organic phase separated. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography on silica gel (hexane) gave **30** as a red solid (1.20 g, 62%): ^{1}H NMR (500 MHz, C_6D_6) δ 3.20 (dt J = 6.4, 3.9 Hz, 2 H), 3.37 (dt, J = 6.6, 3.4 Hz, 2 H), 3.93 (s, 3 H), 6.83 (s, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 63.1, 65.5, 66.7, 133.5, 147.5, 207.0, 214.8, 315.0; IR (CH_2Cl_2) 2988, 2951, 2881, 2066, 1988, 1947, 1937, 1579, 1439, 1370 cm^{-1}.

Ethyl (2*E*,4*E*)-5-(13-Methoxy-8,11-dioxotetracyclo[5.5.2.0^{1,5}.0^{7,12}]-tetradec-13-en-6-yl)-2,4-pentadienoate (31). To a solution of trienyne **2** (109 mg, 0.500 mmol) in THF (150 mL) was added complex **30** (193 mg, 0.600 mmol). The reaction was heated at 67 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **31** (124 mg, 72%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.98 (t, J = 7.3 Hz, 3 H), 1.52–1.58 (m, 1 H), 1.64–1.71 (m, 2 H), 1.76–1.89 (m, 2 H), 1.92–2.05 (m, 2 H), 2.94 (s, 1 H), 3.10 (s, 3 H), 3.12 (m, 1 H), 3.26 (m, 2 H), 3.48–3.50 (m, 1 H), 3.72–3.78 (m, 1 H), 4.05 (q, J = 7.3 Hz, 2 H), 4.40 (s, 1 H), 5.92 (d, J = 15.1 Hz, 1 H), 5.98 (dd, J = 15.1, 8.3 Hz, 1 H), 6.17 (dd, J = 15.1, 10.7 Hz, 1 H), 7.54 (dd, J = 15.1, 10.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 25.2, 27.1, 28.9, 42.3, 55.8, 56.5, 57.6, 60.1, 60.8, 66.4, 88.8, 89.5, 100.0, 119.4, 129.4, 144.4, 144.9, 158.4, 167.2; IR (CH_2Cl_2) 2961, 2935, 2902, 2872, 1712, 1638, 1605, 1460, 1447, 1367 cm^{-1}; LRMS m/e (%) 347 (5), 346 (M^+, 20), 317 (10), 315 (8), 273 (10), 167 (100); HRMS (EI) calcd for $C_{20}H_{26}O_5$ (M^+) 346.1780, found 346.1788. Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.20; H, 7.55. Found: C, 68.63; H, 7.48.

Crystals of **31** were grown by vapor diffusion of hexane into a solution of **31** in ethyl acetate at room temperature. Data were collected at 23 °C on a Siemans R3m/V automated four-circle diffractometer equipped with a graphite crystal monochromator employing the Wyckoff method. The structure of **31** was solved by direct methods (SHELXTL PLUS) and refined by the full-matrix least-squares method with scattering factors taken from Cromer and Waber.[42] A summary of crystallographic data is given in Table 2. The cell parameters were obtained from reflections in the range $3.0° < 2\theta < 50.0°$. A systematic search of a full hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the centrosymmetric space group $P\bar{1}$. Three standard reflections were monitored after every 197 reflections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in ideal positions by using the Riding model with fixed isotropic U. Final positional parameters are given in Table 3. Selected bond lengths and angles are provided in Tables 4 and 5.

(42) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

Table 5. Bond Lengths (Å) and Bond Angles (deg) for **31**

Bond Lengths			
O(1)–C(5)	1.345(7)	O(1)–C(6)	1.424(6)
O(2)–C(2)	1.422(5)	O(2)–C(3)	1.431(5)
O(3)–C(1)	1.435(6)	O(3)–C(4)	1.416(5)
O(4)–C(18)	1.195(8)	O(5)–C(18)	1.351(9)
O(5)–C(19)	1.456(12)	C(1)–C(2)	1.545(9)
C(3)–C(4)	1.527(8)	C(3)–C(8)	1.539(5)
C(4)–C(5)	1.505(6)	C(4)–C(13)	1.583(6)
C(5)–C(7)	1.341(8)	C(7)–C(8)	1.524(7)
C(8)–C(9)	1.517(9)	C(8)–C(12)	1.565(8)
C(9)–C(10)	1.525(9)	C(10)–C(11)	1.532(11)
C(11)–C(12)	1.553(9)	C(12)–C(13)	1.555(8)
C(13)–C(14)	1.491(9)	C(14)–C(15)	1.333(8)
C(15)–C(16)	1.441(9)	C(16)–C(17)	1.330(9)
C(17)–C(18)	1.464(11)	C(19)–C(20)	1.438(12)
Bond Angles			
C(5)–O(1)–C(6)	114.3(4)	C(15)–C(16)–C(17)	125.3(5)
C(1)–O(3)–C(4)	109.9(4)	O(4)–C(18)–O(5)	122.7(7)
O(3)–C(1)–C(2)	112.5(4)	O(5)–C(18)–C(17)	110.9(5)
O(2)–C(3)–C(4)	109.9(4)	C(2)–O(2)–C(3)	106.0(3)
C(4)–C(3)–C(8)	94.1(4)	C(18)–O(5)–C(19)	118.4(6)
O(3)–C(4)–C(5)	116.0(4)	O(2)–C(2)–C(1)	111.9(4)
O(3)–C(4)–C(13)	116.0(4)	O(2)–C(3)–C(8)	119.2(4)
C(5)–C(4)–C(13)	107.9(3)	O(3)–C(4)–C(3)	114.2(3)
O(1)–C(5)–C(7)	133.0(4)	C(3)–C(4)–C(5)	98.4(4)
C(5)–C(7)–C(8)	107.2(4)	C(3)–C(4)–C(13)	102.1(4)
C(3)–C(8)–C(9)	120.1(5)	O(1)–C(5)–C(4)	119.5(4)
C(3)–C(8)–C(12)	102.6(4)	C(4)–C(5)–C(7)	107.5(4)
C(9)–C(8)–C(12)	105.0(4)	C(3)–C(8)–C(7)	97.0(4)
C(9)–C(10)–C(11)	107.7(6)	C(7)–C(8)–C(9)	123.3(4)
C(8)–C(12)–C(11)	103.4(5)	C(7)–C(8)–C(12)	106.6(5)
C(11)–C(12)–C(13)	119.9(4)	C(8)–C(9)–C(10)	103.3(5)
C(4)–C(13)–C(14)	112.3(4)	C(10)–C(11)–C(12)	106.5(5)
C(13)–C(14)–C(15)	125.7(5)	C(8)–C(12)–C(13)	103.6(4)
C(4)–C(13)–C(12)	101.7(4)	C(16)–C(17)–C(18)	121.9(5)
C(12)–C(13)–C(14)	116.8(4)	O(4)–C(18)–C(17)	126.4(7)
C(14)–C(15)–C(16)	124.2(5)	O(5)–C(19)–C(20)	108.8(7)

Ethyl (2*E*,4*E*,6*E*)-10-(5-Hydroxy-8-methoxy-1,4-benzodioxan-6-yl)-2,4,6-decatrienoate (33) and Ethyl (*E*)-(5α,6β,8aα)-3-(5-(2-(1,4-Dioxenyl))-5-methoxy-1,2,3,5,6,8a-hexahydroazulenyl)propenoate (5f'). To a solution of trienyne **2** (50.0 mg, 0.229 mmol) in benzene (92 mL) was added complex **32**[40] (89.0 mg, 0.275 mmol). The reaction was heated at 70 °C for 2 h, cooled to room temperature, concentrated in vacuo to approximately 1 mL, and immediately chromatographed on silica gel to give **31** (33.0 mg, 38%) and **5f'** (2.1 mg, 3%). **33**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (t, J = 7.3 Hz, 3 H), 1.72 (p, J = 7.3 Hz, 2 H), 2.20 (q, J = 7.0 Hz, 2 H), 2.58 (t, J = 7.3 Hz, 2 H), 3.81 (s, 3 H), 4.19 (q, J = 7.3 Hz, 2 H), 4.30 (s, 4 H), 5.01 (s, 1 H), 5.83 (d, J = 15.6 Hz, 1 H), 5.96 (dt, J = 14.6, 7.3 Hz, 1 H), 6.16 (dd, J = 15.1, 10.7 Hz, 1 H), 6.20 (dd, J = 14.6, 11.2 Hz, 1 H), 6.24 (s, 1 H), 6.53 (dd, J = 14.6, 10.7 Hz, 1 H), 7.29 (dd, J = 15.1, 11.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 29.2, 29.3, 32.6, 56.5, 60.2, 64.3, 64.6, 104.8, 118.5, 120.0, 127.8, 130.0, 131.7, 136.9, 140.3, 141.1, 141.6, 144.8, 167.2; IR ($CDCl_3$) 3557, 3021, 2985, 2936, 2878, 2861, 1699, 1617 cm^{-1}; LRMS m/e (%) 374 (M^+, 8), 196 (15), 195 (100), 181 (9); HRMS (EI) calcd for $C_{21}H_{26}O_6$ (M^+) 374.1729, found 374.1715. **5f'**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.95 (t, J = 7.1 Hz, 3 H), 1.19–1.27 (m, 2 H), 1.38–1.47 (m, 1 H), 1.72–1.81 (m, 1 H), 2.10–2.15 (m, 2 H), 3.13 (s, 3 H), 3.13–3.16 (m, 1 H), 3.43–3.51 (m, 4 H), 3.85–3.87 (m, 1 H), 4.02 (q, J = 7.1 Hz, 2 H), 5.36 (q, J = 2.3 Hz, 1 H), 5.43 (ddd, J = 10.9, 6.0, 2.9 Hz, 1 H), 5.60 (dt, J = 10.9, 2.2 Hz, 1 H), 6.12 (dd, J = 15.7, 1.4 Hz, 1 H), 6.24 (s, 1 H), 7.60 (dd, J = 15.7, 7.6 Hz, 1 H); LRMS m/e (%) 346 (M^+, 14), 315 (10), 314 (11), 241 (36).

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Supplementary Material Available: Table 3 (crystallographic data for **31**), Table 4 (atomic coordinates and equivalent isotropic displacement coefficients for **31**), and ^{1}H and ^{13}C NMR spectra for **2**, **5a**, **5c**, **5f'**, **7**, **8a**, **9**, **13**, **13**, **20**, **23**, **24a,b**, **30**, and **31** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.