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Chromium and Tungsten Pentacarbonyl Groups as Reactivity Auxiliaries in the Diels-Alder Reactions of Alkenyl Carbene Complexes with 1,3-Dienes

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Abstract: The Diels-Alder reactions of Fischer carbene complexes of the group 6 metals bearing alkenyl substituents on the carbene ligand are surveyed for 10 chromium, molybdenum, and tungsten complexes with 11 1,3-dienes. The reactions of complexes of the type $R^1CH{=}CHC(OMe){=}M(CO)_5$ (R^1 = H, CH_3 (trans), M = Cr, Mo, W) have been examined with isoprene, and it was found that the rates can be as much as 2×10^4 faster than their organic ester analogues. The regioselectivity of the cycloadditions of alkenyl carbene complexes with isoprene were also found to be significantly higher (≥91:9) than their organic esters analogues and comparable to that observed with Lewis acid mediated cycloadditions of acrylate esters with isoprene. The cycloadditions of the seven complexes of the type $R^1R^2C{=}CR^3C(OMe){=}M(CO)_5$ (R^1, R^2, R^3 = H; R^1 = CH^3, R^2, R^3 = H; R^1, R^3 = H, R^2 = CH_3 (cis and trans); R^1 = H, R^2, R^3 = CH_3; M = Cr, W) were investigated with 2,3-dimethyl-1,3-butadiene and cyclopentadiene. The reactions with cyclopentadiene were found to be stereoselective in favor of the Alder endo adduct at a level much higher than is observed for the corresponding α,β-unsaturated esters. The reaction with cyclopentadiene was also found to be stereospecific with *cis*- and *trans*-propenyl tungsten complexes where the stereochemistry about the olefin in each carbene complex was retained in the cycloadducts. The cycloadditions of six complexes of the type $R^1R^2C{=}CR^3C(OMe){=}M(CO)_5$ were also investigated with three monooxygenated dienes: 1-methoxy-, 2-methoxy-, and 1-acetoxy-1,3-butadiene. It was found that these carbene complexes display greatly enhanced reactivity compared to α,β-unsaturated esters with these dienes under either thermal or high-pressure conditions. All of the reactions of these three acyclic dienes with alkenyl carbene complexes were highly regioselective; however, like their organic ester analogues, they occurred with relatively low stereoselectivity. The endo adduct (but not the exo) from the reaction of the *trans*-propenyl chromium (but not tungsten) complex **12** with 1-methoxy-1,3-butadiene forms a methoxyl-chelated tetracarbonyl carbene complex. Several cycloadditions were examined for four complexes of the type $R^1R^2C{=}CR^3C(OMe){=}W(CO)_5$ with Danishefsky's diene and *trans,trans*-1-methoxy-2-[(trimethylsilyl)oxy]-4-ethoxy-1,3-butadiene (**27**). The reaction of the *trans*-propenyl tungsten complex with diene **27** occurs with retention of the stereochemistry in both the diene and the carbene complex. The reaction of the *cis*-propenyl tungsten complex with **27** occurs with competing isomerization to the *trans*-propenyl complex prior to cycloaddition. The chromium and tungsten cyclohexenyl complexes $C_6H_9C(OMe){=}M(CO)_5$ were found to display different chemoselectivities toward derivatives of Danishefsky's diene; the chromium complex produced divinylcyclopropanes, whereas the tungsten complex gave rise to Diels-Alder adducts. The reaction of the vinyl tungsten complex $CH_2{=}CHC(OMe){=}W(CO)_5$ with 6,6-dimethyl-6-sila-α-pyran (**28**) illustrates the advantages of rate and tolerance of sensitive organic functionality that are possible when alkenyl carbene complexes are employed as synthons in the Diels-Alder reaction. Finally, the versatility with which the metal unit can be removed from cycloadducts **43** and **44** demonstrates that alkenyl carbene complexes can serve as synthons in the Diels-Alder reaction for esters, aldehydes, ketones, methoxyallenes, 2-methoxybutadiene, and simple alkenes.

The utilization of Fischer carbene complexes in organic synthesis has been actively pursued since their discovery[2] in 1964 and has seen rapid growth in recent years.[3,4] In the 25 years of their history, a considerable number of reactions of Fischer carbene complexes have been discovered that have made possible not only the diversity of the applications in organic synthesis to which these complexes can now be employed but also the many possibilities that can still be entertained. All of the reactions of Fischer carbene complexes can be broadly divided into two classes. The first class of reactions involves those in which the metal-carbene-carbon functionality is consumed and in which new carbon-carbon bonds between the carbene ligand and an external organic functionality are made in the coordination sphere of the metal. Perhaps the reaction of most utility in organic synthesis from this class is the benzannulation reaction with acetylenes, illustrated in Scheme I.[3] This reaction was first reported[5] by Dötz in 1975 and has since been actively studied by several groups and employed in the synthesis of a number of natural products.[6] Another example from this class of reactions is the more recently discovered photoinduced reaction with imines which is finding important applications in the synthesis of β-lactams.[7] The second class of reactions of Fischer carbene complexes involve those reactions that take place on the carbene ligand and for which the metal-carbon bond of the carbene ligand remains intact. Reactions from this class have been developed more recently and have not yet been applied to natural product syntheses. Examples of reactions from this class include alkylations,[8] aldol condensations,[9] and the Diels-Alder reactions of α,β-unsaturated complexes with 1,3-dienes.[10] More recently [3 + 2] and [2 + 2] cycloadditions have been observed with α,β-unsaturated carbene complexes.[10i,j] We first reported[10a] the Diels-Alder reactions of carbene complexes in communication form in 1983, and now we describe our initial studies directed to the evaluation of the scope of the Diels-Alder reaction of alkenyl carbene complexes of the type **1** with 1,3-dienes.

The reactions of Fischer carbene complexes as well as their spectral properties can be accounted for in terms of a polarized metal-carbene carbon bond which is most conveniently expressed

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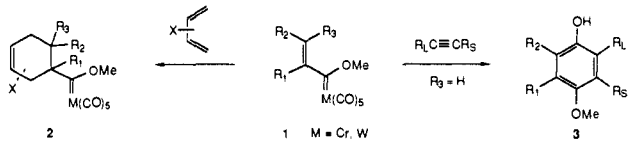
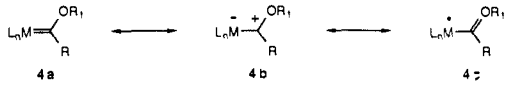
Scheme I

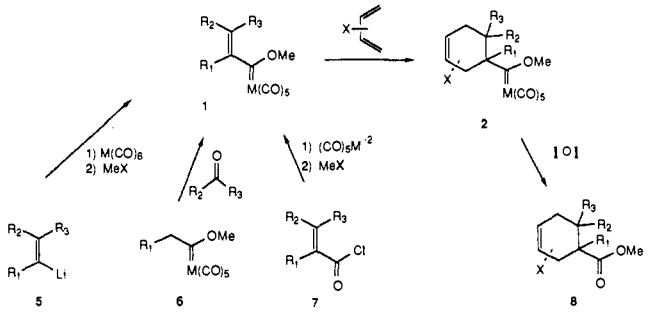


by the resonance forms **4a–c**.[3a,t1] These resonance structures reflect the same type of polarization commonly associated with esters, the closest carbon analogue of Fischer carbene complexes (i.e., $L_nM = O$). It was this parallel in the electronic structure



of esters and carbene complexes and also the parallel in reactivity between esters and carbene complexes in a number of reactions that first led us to explore the utility of alkenyl complexes as dienophiles.[3e] Although alkenyl complexes of the type **1** had been previously prepared (the parent chromium complex **9** was reported

Scheme II



in 1973[12]), their reactions with 1,3-dienes had not been previously investigated. In the preliminary communication of this work, it was not only established that alkenyl complexes can in fact participate as dienophiles in the Diels–Alder reaction but also that these Diels–Alder reactions occur with rates and regio- and stereoselectivity that are normally only associated with the Lewis-acid-catalyzed-Diels–Alder reaction of esters.[10a] We have found that this is also the case for the Diels–Alder reactions of alkynyl carbene complexes;[10b] however, this first full account will be restricted to the Diels–Alder reactions of alkenyl complexes.

The Diels–Alder reactions of activated olefins has long been established as one of the most useful and predictable reactions in organic synthesis.[13] The utility of the Diels–Alder reaction of alkenyl Fischer carbene complexes in organic synthesis will be largely dependent on three factors: (1) available methods for the preparation of the carbene complexes, (2) the synthetic advantages of the cycloaddition step involving the carbene complex, and (3) available methods for the removal of the metal subsequent to the cycloaddition. Alkenyl complexes are typically prepared by the Fischer method which involves the addition of the proper vinyl lithium to a group 6 hexacarbonyl followed by alkylation on oxygen.[t4] An alternative method that is becoming more important involves the elaboration of an existing alkyl complex of the type **6** with an aldol condensation.[9] A new method that has the virtue of allowing for the preparation of alkenyl carbene complexes from an organic starting material that is one carbon larger than vinyl halides and involves the alkylations of metal pentacarbonyl dianions.[15] This new method for the synthesis of complexes of the type **1** from the acid chloride **7** is illustrated in Scheme II. The alkenyl complexes **1** can function as α,β-unsaturated ester equivalents in the Diels–Alder reaction since one of the simplest methods for the removal of the metal from the cycloadduct **2** is oxidation to the ester **8**. This oxidative cleavage can be accom-

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Scheme III

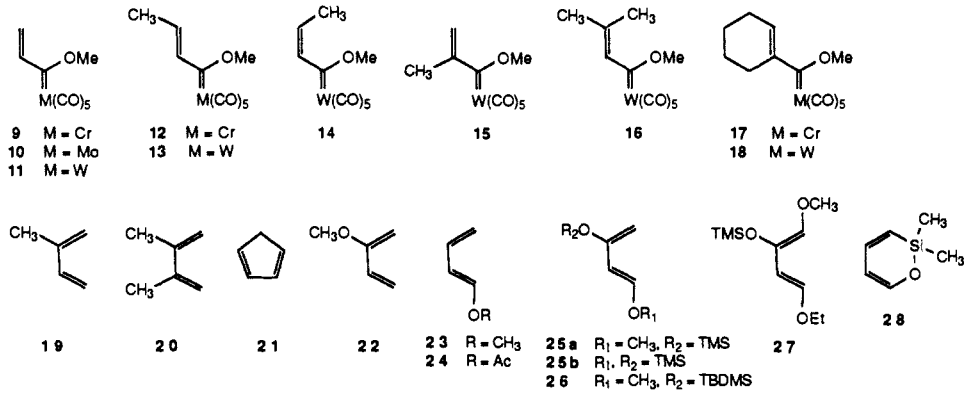
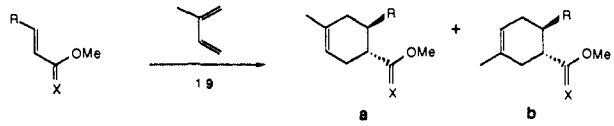


Table I. Rates and Regioselectivity of Complexes 9–13 with Isoprene



dienophile	R	X	catalyst	time	temp (°C)	% yield	a/b	rel rate[a]	adduct
29	H	O		7 mo[b]	25	54[b]	70:30[c,d]	1	**31**
29	H	O	$AlCl_3$	3 h	25	50[d]	95:5[d]	7.4×10^5[e]	**31**
9	H	$Cr(CO)_5$		3 h	25	70[f]	92:8[g]	2.1×10^4[h]	**32**
10	H	$Mo(CO)_5$		1 h	25	61[f]	94:6[g]		**33**
11	H	$W(CO)_5$		2 h	25	87[f]	91:9[g]	2.6×10^4[h]	**34**
30[i]	CH_3	O		8 h	230	–[i]	only **a**		**35**
12	CH_3	$Cr(CO)_5$		18 h	50	40	>97:3		**36**
13	CH_3	$W(CO)_5$		14 h	50	58	>97:3		**37**

[a] Ratio of rate constants. [b] Reference 20. [c] Reference 21. [d] References 22 and 23. [e] Reference 24. [f] Yield of complexes isolated by flash chromatography. [g] Determined after oxidation to the known methyl esters **31a** and **31b**. [h] Reaction followed with 0.05 M complex in benzene with 1.0 M isoprene at 25 °C; presuming a second-order reaction the rate constants are $4.9 \pm 0.4 \times 10^{-4}$ L mol^{-1} s^{-1} for **11** and $4.0 \pm 0.4 \times 10^{-4}$ L mol^{-1} s^{-1} for **9**. [i] Reaction of crotonic acid **30** with isoprene, refs 25 and 26.

plished with a variety of agents, the mildest of which is DMSO.[16] As will be discussed, the alkenyl carbene complexes of the type **1** can serve as synthons for a variety of other organic functional groups, among them allenes, aldehydes, and allyl ethers.

This work will survey the Diels–Alder reactions of the 10 chromium, molybdenum, and tungsten carbene complexes and the 11 1,3-dienes listed in Scheme III. This group of carbene complexes and 1,3-dienes were chosen such that a considerable portion of the boundaries of the synthetic scope of the Diels–Alder reactions of alkenyl carbene complexes with 1,3-dienes could be established. The carbene complexes include examples that provide a study of the effect of increasing substitution to probe the importance of sterics in the cycloadditions and also stereoisomeric complexes such that the stereospecificity of the cycloadditions can be examined. The survey of 1,3-dienes range from examples that are relatively inert to cycloadditions with simple unsaturated esters, to examples that are exceedingly reactive with ordinary dienophiles. The latter will serve to probe the efficacy of the Diels–Alder reaction of carbene complexes in the presence of highly reactive functionality on the diene, that, as we shall see in certain instances, can lead to other modes of reactivity of the metal carbene complex. The range of 1,3-dienes also includes examples that can be utilized to examine the stereoselectivity of the Diels–Alder reaction.

Cycloadditions with Isoprene, 2,3-Dimethyl-1,3-butadiene, and Cyclopentadiene

Unless otherwise specified, all of the Diels–Alder reactions in Tables I–III were conducted by simply dissolving the alkenyl complex in a slight excess of diene and monitoring the reaction by TLC for the disappearance of the red alkenyl complex and the appearance of the yellow alkyl cycloadducts. In cases where long reaction times or heating was required, the solutions were deoxygenated and carried out under argon. It was necessary to conduct the reactions of the unsubstituted vinyl complexes **9–11** in hexane or benzene solutions to prevent polymerization. In all cases the workup of the reaction entailed simple removal of the excess diene under vacuum followed by flash chromatography on silica gel under air. All of the cycloadduct complexes proved to be relatively stable to air, and unless otherwise specified, no special precautions were required during characterization.

The results from the reactions of alkenyl complexes **9–16** with isoprene, 2,3-dimethyl-1,3-butadiene, and cyclopentadiene are summarized in Tables I–III. Wherever available, direct literature comparisons with the corresponding esters, the closest carbon analogues of Fischer carbene complexes, are also shown. One of the most striking aspects of the cycloadditions is the tremendous rate enhancement observed for the alkenyl complex compared with their ester analogues. This is clearly illustrated for the reactions of **9** and **11** with isoprene. These complexes react to completion at 25 °C in 2–3 h whereas the cycloaddition of methyl acrylate with isoprene has been observed to require 7 months at the same temperature.[20] The rates of the reactions of the chromium complex **9** and the tungsten complex **11** with isoprene were measured in benzene with an initial concentration of 0.05 M for

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(18) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293.
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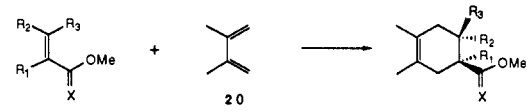
(20) Nasarov, I. N.; Titov, Y. A.; Kuznetsova, A. I. *Izv. Akad. Nauk SSSR, OKHN* **1959**, 1412.
(21) Hennis, H. E. *J. Org. Chem.* **1963**, *28*, 2570.

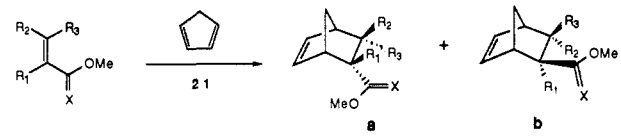
Table II. Cycloadditions with 2,3-Dimethyl-1,3-butadiene



dienophile	X	catalyst	R_1	R_2	R_3	temp (°C)	time (h)	% yield	adduct
38[a]	O		H	H	H	175	18	94[a]	**41**
29	O		H	H	H	60	24	7[b]	**42**
29	O	$AlCl_3$	H	H	H	20	5	74[c]	**42**
9	$Cr(CO)_5$		H	H	H	25	1.5	75	**43**
11	$W(CO)_5$		H	H	H	25	1.5	80	**44**
39[d]	O		H	CH_3	H	175	18	75[d]	**45**
12	$Cr(CO)_5$		H	CH_3	H	50	13	55	**64**
13	$W(CO)_5$		H	CH_3	H	50	13	57	**47**
40	O		CH_3	H	H	140	12	60[e]	**48**
15	$W(CO)_5$		CH_3	H	H	50	27	66	**49**
16	$W(CO)_5$		H	CH_3	CH_3	85	144	28	**50**

[a] Reaction of ethyl acrylate **38**, ref 27. [b] Reference 28. [c] Reference 29. [d] Reaction of ethyl crotonate **39**, ref 27. [e] Reference 30.

Table III. Cycloadditions with Cyclopentadiene **21**



dienophile	X	catalyst	R_1	R_2	R_3	temp (°C)	time	**a**/**b**	% yield	adduct
29	O		H	H	H	30	7.5 h	78:22[a]		**54**
29	O	$AlCl_3$	H	H	H	30	1 h	94:6[a]		**54**
9	$Cr(CO)_5$		H	H	H	25	3 min	94:6[b]	78	**55**
11	$W(CO)_5$		H	H	H	25	3 min	93:7[b]	93	**56**
51	O		H	CH_3	H	30	24 h	54:46[a]		**57**
51	O	$AlCl_3$	H	CH_3	H	30	0.5 h	93:7[a]		**57**
12	$Cr(CO)_5$		H	CH_3	H	25	2 h	88:12	95	**58**
13	$W(CO)_5$		H	CH_3	H	25	2 h	90:10	87	**59**
52	O		H	H	CH_3	60	13 h	54:46[c]	62	**60**
14[d]	$W(CO)_5$		H	H	CH_3	25	2.0 h	89:11	99[e]	**61**
40	O		CH_3	H	H	30	7 h	31:69[a]		**62**
40	O	$AlCl_3$	CH_3	H	H	30	1 h	60:40[a]		**62**
15	$W(CO)_5$		CH_3	H	H	25	4 h	59:41	89	**63**
53	O		H	CH_3	CH_3	140	3 weeks		29[f]	**64**
16	$W(CO)_5$		H	CH_3	CH_3	80	72 h	33:67	4	**65**

[a] Reference 31. [b] Determined by oxidation to the known methyl esters **54a** and **54b**. [c] Reference 32. [d] Contains ≤3 % trans-complex **13** by ^1H NMR. [e] Contains ≤3 % trans-endo adduct **56a** by ^1H NMR. [f] References 33 and 34.

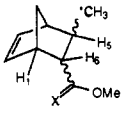
the carbene complex and 1.0 M for isoprene. The molybdenum complex **10** was too unstable to give reliable kinetic plots. From a ratio of the rate constants the rate enhancement over the reaction of isoprene with methyl acrylate is 2.1×10^4 for the chromium complex **9** and 2.6×10^4 for the tungsten complex **11**. These values are comparable to the rate enhancement observed for the corresponding aluminum chloride catalyzed reactions of methyl acrylate with isoprene.[22-24] Similar rate enhancements over ester analogues are seen at least qualitatively for all cycloadditions of carbene complexes that we have examined. The reactions of the chromium, molybdenum, and tungsten complexes **9–11** with isoprene are quite similar with the tungsten complex giving a slightly higher yield than chromium and the molybdenum complex giving a slightly higher regioselectivity. The reactions of the various methyl-substituted complexes indicated in Table II with 2,3-dimethyl-1,3-butadiene serve to further illustrate the large difference in rates of these reactions compared to their acrylate derivatives.

It is generally observed in Diels–Alder chemistry that alkyl substituents on the double bond of the dienophile result in decreased reactivity.[13] This trend is also observed for the Diels–Alder reactions of alkenyl carbene complexes. For example, the reaction of the *trans*-propenyl complexes **12** and **13** with isoprene (Table I) required heating to 50 °C whereas the same reaction with the unsubstituted complexes **9** and **11** did not require heating. Similarly, the reactions of the monomethyl-substituted complexes **12**, **13**, **14**, and **15** with 2,3-dimethyl-1,3-butadiene (Table II) and cyclopentadiene (Table III) required either elevated temperatures and/or prolonged reaction times when compared to the corresponding reactions of the unsubstituted complexes **9** and **11**. Not unexpectedly, the isobutenyl complex **16** proved to react even more sluggishly, and heating at 85 °C for several days with either 2,3-dimethyl-1,3-butadiene or cyclopentadiene allowed isolation of only low yields of cycloadducts. The complex **16** is consumed under these conditions, and it is possible that other reaction pathways are occurring although no other silica gel mobile products were observed. However, we have seen cyclopropanation side products in other reactions (vide infra).

Associated with the high reactivity of alkenyl Fischer carbene complexes is an increase in regioselectivity which was demonstrated for the reaction of **9** and **11** with isoprene (Table I). The thermal reaction of methyl acrylate with isoprene is reported to give a 70:30 mixture of para and meta regioisomers.[21-23] By contrast, the

(22) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 1121.
(23) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 872.
(24) Inukai, T.; Kojima, T. *J. Org. Chem.* **1971**, *36*, 924.
(25) M. Naef et Cie. French patent 672025. 1929; *Chem. Abstr.* **1930**, *24*, 2243.
(26) (a) Alder, K.; Vogt, W. *Justus Liebigs Ann. Chem.* **1949**, *564*, 120. (b) Alder, K.; Vogt, W. *Justus Liebigs Ann. Chem.* **1949**, *564*, 136.
(27) Monnin, J. *Helv. Chim. Acta.* **1958**, *41*, 2112.
(28) Vedejs, E.; Gadwood, R. C. *J. Org. Chem.* **1978**, *43*, 376.
(29) Inukai, T.; Kasai, M. *J. Org. Chem.* **1965**, *30*, 3567.
(30) Farmer, E. H.; Pitkethly, R. C. *J. Chem. Soc.* **1938**, 11.

Table IV. Selected Spectral Data for Endo and Exo Norbornenyl Cycloadducts



adduct	isomer	X	$J_{1,6}$ (Hz)	$J_{5,6}$ (Hz)	$\delta(*CH_3)^a$ (ppm)
54a	trans, endo	O	3.5	4.5	1.22[b]
54b	trans, exo	O	–	–	0.88[b]
58a	trans, endo	$Cr(CO)_5$	3.0	4.6	1.12
58b	trans, exo	$Cr(CO)_5$	–	–	0.87
59a	trans, endo	$W(CO)_5$	3.0	4.6	1.14
59b	trans, exo	$W(CO)_5$	–	–	0.89
61a	cis, endo	$W(CO)_5$	2.6	9.8	0.69
61b	cis, exo	$W(CO)_5$	–	–	0.93

[a] $CDCl_3$ as solvent unless otherwise noted. [b] Reference 36, CCl_4 as the solvent.

reactions of complexes **9** and **11** demonstrate greater than 90% para selectivity which again parallels the results reported for the aluminum chloride catalyzed reactions of methyl acrylate.[22,23] For the reactions of *trans*-propenyl complexes **12** and **13** only the para regioisomers could be isolated and inspection of the crude reaction mixtures by 500-MHz ^1H NMR failed to reveal the presence of any of the metal isomers. The para regiochemistry of adducts **36** and **37** was confirmed by ^1H NMR decoupling experiments which demonstrated the connectivity between the olefinic proton and the α-carbene proton, and the details are presented in the experimental section. This type of regioselectivity is not unusual for this family of reactions. Although the reaction of methyl crotonate and isoprene has not been reported, the reaction with crotonic acid has been reported not to give any of the meta isomer.[13a]

The results obtained for the reactions of complexes **9**, **11–16** with cyclopentadiene are summarized in Table III. The degree of Alder endo stereoselectivity observed for these complexes follows the same comparative trends with their ester analogues as was seen in the rates and in the regioselectivities discussed above. The alkenyl complexes show much greater endo selectivity than the reactions of the corresponding esters with cyclopentadiene under uncatalyzed reactions. For example, the red vinyl chromium complex **9** reacts with cyclopentadiene in 3 min at 25 °C to give a 78% yield of the yellow endo and exo cycloadducts **55a** and **55b** in a 94:6 ratio that is identical with the endo/exo ratio obtained for the aluminum chloride catalyzed reaction of methyl acrylate and cyclopentadiene.[31] The uncatalyzed reaction of methyl acrylate and cyclopentadiene gives a 78:22 ratio of endo and exo cycloadducts.[31] The ratio of the isomeric endo and exo carbene complex cycloadducts for both **55** and **56** was determined by oxidation of the crude mixtures obtained from the reactions of **9** and **11** with ceric ammonium nitrate and analysis by capillary GC with the aid of authentic samples of the esters **54a** and **b**. It has been observed[35] that the relative endo selectivity of substituted ester dienophiles decreases in the order of H > *trans*-β-CH_3 > α-CH_3, a trend which is also followed by complexes **9**, **11**, **12**, **13**, and **15**. This trend has been attributed to the inherent endo orienting ability of the methyl group. For alkenyl acids, *cis*-crotonic acid demonstrates even greater endo selectivity than *trans*-crotonic acid. The lower endo ratio observed for the *cis*-propenyl complex **14** represents a deviation from this trend.

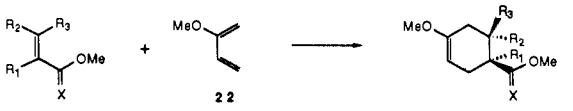
The assignments of endo and exo stereochemistry for cycloadducts **58** and **59** are based on coupling constants $J_{1,6}$ and $J_{5,6}$ (Table IV) as well as the relative chemical shifts of the aliphatic methyls (i.e., $*CH_3$). The coupling constants for the major trans-endo adducts **58a** and **59a** of $J_{1,6}$ = 3.0 Hz and $J_{5,6}$ = 4.6 Hz are nearly identical with the reported values for the corresponding trans-endo ester **54a**.[36] In addition, $J_{1,6}$ is clearly outside the range expected for the trans-exo isomer **54b** (ca. 0 Hz).[37] For norbornene ring systems it has been amply documented that signals for an endo-$*CH_3$ appear upfield in the ^1H NMR spectrum from and exo-$*CH_3$,[36,38] and this phenomenon was very helpful in identifying and quantifying (integration of signals for $*CH_3$ in ^1H NMR spectrum at 500 MHz) the minor trans-exo isomers **58b** and **59b**. A similar strategy for assigning stereochemistry was employed for cycloadducts **63**[39] and **65**.[40] The major cycloadduct from the cycloaddition of cyclopentadiene and the chromium analogue of **15** has been demonstrated to be the endo adduct by X-ray crystallography.[10d]

Given the high acidity of protons α to the carbene carbon in Fischer carbene complexes,[41] isomerization at the α-position in the norbornenyl cycloadducts was a possibility, and thereby the issue was raised as to whether the endo/exo ratios observed with cyclopentadiene were thermodynamic or kinetic values. It was found that the composition of a mixture of **56a** and **56b** enriched in the exo isomer **56b** (5.1:1.0) remained unchanged on exposure to the reaction conditions as well as upon oxidation to the corresponding esters **54** with ceric ammonium nitrate. Thus the endo/exo ratios given in Table III represent kinetic values.

The retention of stereochemistry with respect to the dienophile in Diels–Alder reactions cannot always be presupposed.[42] For the reactions of complexes **12** and **13** with all of the dienes reported in this work, formation of cis cycloadducts was not observed, attesting to the retention of stereochemical integrity about the carbene complex double-bond during the cycloaddition. In an effort to examine the stereospecificity of the Diels–Alder reactions of Fischer carbene complexes, the reactions of the *cis*- and *trans*-propenyl tungsten complexes **14** and **13** were carried out with cyclopentadiene. The *trans*-propenyl complex **13** reacts with cyclopentadiene to provide an 87% yield of the endo and exo adducts **59a** and **59b** in which the trans relationship of the methyl and the tungsten pentacarbonyl groups is maintained in both. No detectable amount of the cis isomer **14** could be observed to isomerize to the trans isomer in THF under the temperature and time for its reaction with cyclopentadiene (25 °C, 2 h), and isomerization of the cis isomer was found not to begin until heated to 70 °C for several hours. The reaction of the cis isomer **14** with cyclopentadiene produced an 89:11 mixture of the cis cycloadducts **61a** and **61b**. Thus the Diels–Alder reaction of Fischer carbene complexes is stereospecific and may occur with a concerted mechanism or with a stepwise mechanism in which the formation of the second bond is faster than interconversion of the conformers of the zwitterionic intermediate.

(31) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 2032.
(32) Parlar, H.; Baumann, R.; Korte, F. *Z. Naturforsch., B: Anorg. Chem., Org., Chem.* **1981**, *36*, 898.
(33) LeFeure, G. N.; Crawford, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 1019.
(34) Alder, K.; Roth, W. *Chem. Ber.* **1957**, *90*, 1830.
(35) Kobuke, Y.; Fueno, T.; Furukawa, J. *J. Am. Chem. Soc.* **1970**, *92*, 6548.
(36) Hoffmann, H. M. R.; Vathke, E. H. *Chem. Ber.* **1981**, *114*, 2208.
(37) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL, 1982.
(38) Jackmann, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; 229–233.
(39) The chemical shifts of the aliphatic methyls at δ 1.31 for the endo isomer **63a** and δ 1.04 for the exo isomer **63b** were correlated with the shifts for the corresponding esters reported at δ 1.10 and δ 0.92 (ref 35).
(40) Assignments were based on $J_{1,6}$ = 2.6 Hz for the endo cycloadduct **65a** and $J_{1,6}$ = 1.18 Hz for the exo cycloadduct **65b** (see ref 37).
(41) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.
(42) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Eng.* **1980**, *19*, 779.
(43) The assignment of stereochemistry for the major cis-endo isomer **61a** is based on the magnitude of $J_{1,6}$ = 2.6 Hz and $J_{5,6}$ = 9.8 Hz (Table IV), the latter of which being well within the range expected for cis–exo protons.[37] The minor cis–exo isomer **61b** is identified by the characteristic downfield shift of its ^1H NMR signal for the $*CH_3$ relative to **61a** (vide supra).
(44) Dane, E.; Schmitt, J.; Rautenstrauch, C. *Justus Liebigs Ann. Chem.* **1937**, *532*, 30.
(45) Fiesselmann, H. *Angew. Chem.* **1950**, *62*, 344.
(46) Young, S. T.; Turner, J. R.; Tarbell, D. S. *J. Org. Chem.* **1963**, *28*, 928.

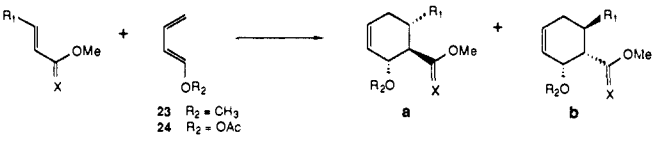
Table V. Cycloadditions with 2-Methoxy-1,3-butadiene (**22**)



dienophile	X	R_1	R_2	R_3	temp (°C)	time	% yield	adduct
31	$W(CO)_5$	H	CH_3	H	25	26 h	83	**66**
40	O	CH_3	H	H	219	23 h	60[a]	**67**
15	$W(CO)_5$	CH_3	H	H	25	26 h	76	**68**
16	$W(CO)_5$	H	CH_3	CH_3	60	8 days	20	**69**

[a] Reference 44.

Table VI. Cycloadditions with 1-Methoxy-1,3-butadiene (**23**) and 1-Acetoxy-1,3-butadiene (**24**)



dienophile	X	pressure (atm)	R_1	R_2	temp (°C)	time	**a**/**b**	% yield	adduct
9	$Cr(CO)_5$		H	CH_3	25	23 h	1.0:1.1	52[a]	**70**
29	O	15000	H	OAc	25	4 h	b only	19[b]	**71**
9	$Cr(CO)_5$		H	OAc	25	29 h	1.0:1.1	19[c]	**72**
11	$W(CO)_5$		H	OAc	25	8 days	1.0:2.8	57[a]	**73**
51	O		CH_3	CH_3	140	24 h	–	53[d]	**74**
51	O	15000	CH_3	CH_3	25	12 h		0[b]	**74**
12	$Cr(CO)_5$		CH_3	CH_3	25	26 h	1.0:1.6	82[e]	**75**
13	$W(CO)_5$		CH_3	CH_3	25	30 h	1.0:1.7	79	**76**
51	O	15000	CH_3	OAc	25	4 h		0[b]	**77**
13	$W(CO)_5$		CH_3	OAc	60	6 days	1.0:2.6	25	**78**

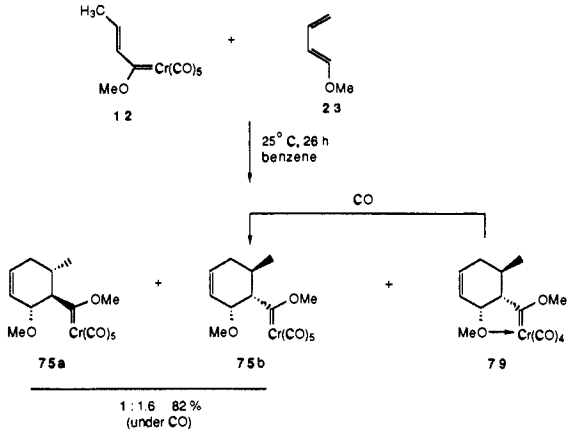
[a] Reaction conducted in benzene at 0.1 M in carbene complex with 2 equiv of diene. [b] Reference 47. [c] Reaction conducted in hexane at ~1.0 M in carbene complex with 2 equiv of diene. [d] Reference 46. [e] Reaction conducted in excess diene (10 equiv) under 1.2 atm of CO.

Cycloadditions with Monooxygenated Dienes: 1-Methoxy- and 2-Methoxy-1,3-butadienes (22 and 23) and 1-Acetoxy-1,3-butadiene (24)

The reactions of the tungsten complexes **13**, **14**, and **15** with 2-methoxy-1,3-butadiene (**22**) are summarized in Table V. Complexes **13** and **15** react with **22** at room temperature in 26 h to give high yields of cycloadducts. The more highly substituted complex **16** reacted more sluggishly than **13** or **15**, requiring heating at 60 °C over several days. Despite the low yield of **69**, this reaction is of significance since there are no examples in the literature for the reaction of 2-methoxy-1,3-butadiene with an ester of β,β-dimethylacrylic acid. In all cases only the expected para isomer was observed from the reactions of the carbene complexes in Table V.

The cycloaddition of 1-methoxy- and 1-acetoxy-1,3-butadienes **23** and **24** with the complexes **9**, **11**, **12**, and **13** all resulted in high regioselectivity, yielding in each case only the ortho regioisomer (Table VI). We have included in Table VI for comparison the results reported from the high-pressure reactions of methyl acrylate and methyl crotonate with dienes **23** and **24**.[47] The stereoselectivity for the cycloadditions of the carbene complexes listed in Table VI, however, proved to be low, providing nearly equal mixtures for the vinyl complexes **9** and allowing only a moderate excess of the endo adduct **b** for complexes **11**, **12**, and **13** (see below for discussion of assignment of stereochemistry). Related Diels–Alder reactions of 1-oxo-, 1-amino-, and 1-thio-substituted butadienes with carbon-based dienophiles are generally reported to give mixtures of stereoisomers ranging from nearly equal to highly endo selective.[48] In the reactions of the isopropenyl and isobutenyl complexes **15** and **16** with **23**, unexpectedly, only trace amounts of cycloadducts were isolated in each case. The reaction of **16** with **23** at 85 °C in 4 days produced a 7% yield of a compound **78** whose structure was assigned as the chelated endo cycloadduct that corresponds to **79**.

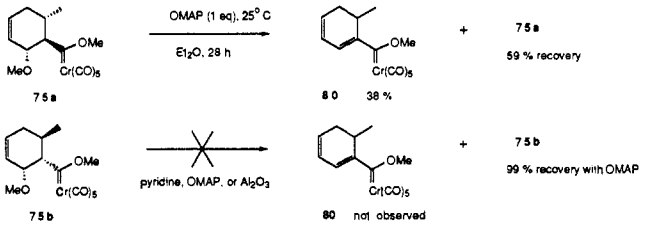
Scheme IV



The reaction of the chromium complex **12** with 1-methoxy-1,3-butadiene (**23**) was conducted in hexane solution under 1.2 atm of carbon monoxide at room temperature and gave a 1:1.6 mixture of the exo to endo adducts **75a** and **75b** (Scheme IV). In the absence of carbon monoxide, a third, red complex appeared with concomitant decrease in the amount of endo adduct **75b** formed. Heating of the latter reaction mixture at 46 °C for 21 h drove the mixture to exclusively **75a** and the same red complex which is assigned the structure of the chelated complex **79**.[49] The proton NMR spectrum of this chelate shows broad absorptions obscuring the coupling constants, precluding determination of the stereochemistry by this method.[50] The endo assignment for **79** is based on the observations that at 56 °C in THF (45 h) under

(47) Dauben, W. D.; Krabbenhoft, H. O. *J. Org. Chem.* **1977**, *42*, 282.
(48) See ref 13c and Kakushima, M. *Can. J. Chem.* **1979**, *57*, 2564.
(49) Internally chelated carbene complexes have been reported and characterized, see: ref 3c, 10d, and (a) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267. (b) Raubenheimer, H. G.; Lotz, S.; Coetzer, J. *J. Chem. Soc., Chem. Commun.* **1976**, 732.
(50) The spectrum does clearly shoow a downfield shift of the β-OMe (by 0.34 ppm relative to **74b**) which is consistent with coordination to the metal.

Scheme V



argon **75b** is converted nearly quantitatively to **79**, whereas **75a** remains unchanged under similar conditions. Furthermore, under carbon monoxide, **79** is converted exclusively to the endo isomer **75b**. The reaction of the tungsten complex **13** with 1-methoxy-1,3-butadiene exhibits no such chelate formation presumably due to the higher metal–carbonyl bond strength for tungsten compared with chromium.[51]

The Diels–Alder reactions of chromium carbene complexes with 1-alkoxy-1,3-butadienes is a potentially useful reaction for the preparation of 1-cyclohexa-1,3-dienyl carbene complexes of the type **80** which might be very useful in benzannulations reactions (Scheme V).[3,6] Interestingly, methanol could only be eliminated from the exo adduct **75a**. Elimination of methanol from **75a** could be effected by treatment with alumina or by treatment with either pyridine or 4-(dimethylamino)pyridine (DMAP), the latter base being the most effective. Treatment of the endo cycloadduct **75b** under the conditions of either of these methods for the same duration led only to the recovery of the endo adduct. The failure of the endo adduct to eliminate was surprising in view of the high acidity of the protons on carbons α to the carbene carbon in alkyl carbene complexes.[41] It is also surprising from the stereoelectronic point of view that it should be the endo and not the exo adduct that is slowest to eliminate. With the reasonable assumption that the carbene ligand and metal unit is in an equatorial position, then it would only be in the endo adduct **75b** that the methoxy and α-carbene hydrogen would have trans-diaxial relationship.

It is suspected that the failure of the endo cycloadduct **75b** to undergo elimination is due to the relative stabilities of the conformers about the carbene–carbon ipso-cyclohexyl carbon bond. On the basis of molecular models and on the solid-state structures of a number of carbene complexes,[52] it can be anticipated that the preferred orientation of the cyclohexyl ring for both the endo and exo adducts **75a** and **75b** is with the plane of the cyclohexane ring perpendicular to the plane containing the carbene carbon and its substituents. The two such conformers for both the endo and exo cycloadducts **75a** and **75b** are shown in Figure 1. From a consideration of these conformers it can be judged that relative to the exo adduct **75a**, there will be a considerable difference in the energies of the anti and syn conformers for the endo adduct **75b** due steric interaction between the metal center and the methoxyl group in the anti conformer. If in fact the syn conformer is of significantly higher population than the anti for the endo adduct **75b**, then the slow rate for the elimination of methanol can be understood since the α-hydrogen is shielded from the base by the metal center. On the basis of the steric interactions of the substituents of the cyclohexyl ring and the metal center, it is anticipated that there would be much less of an energy difference between the syn and anti conformers of the exo adduct **75a**. More rapid elimination of methanol from the exo adduct **75a** is then explained by the greater access by the base to the α-hydrogen via the anti conformer.

Cycloadditions with Danishefsky's Diene 25a, 1,3-Bis[(trimethylsilyl)oxy]-1,3-butadiene (25b), and 1-Methoxy-4-ethoxy-2-[(trimethylsilyl)oxy]-1,3-butadiene (27)

The reactions of carbene complex dienophiles with the more highly oxygenated dienes **25a**, **25b**, and **27** were investigated since they have proven to be very reactive in traditional Diels–Alder

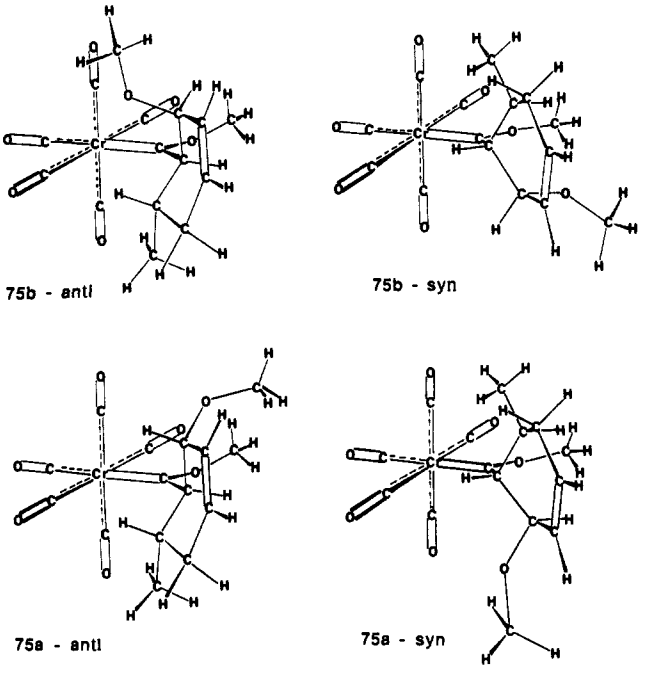
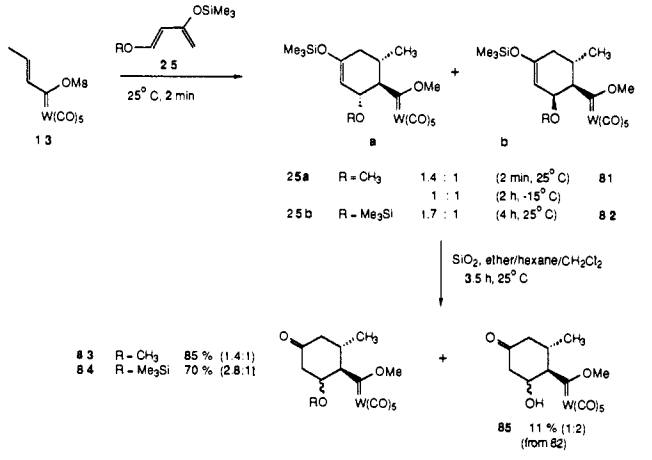


Figure 1.

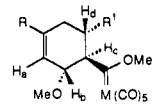
Scheme VI

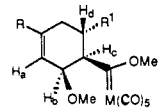


reactions.[53] Danishefsky's diene **25a**, in particular, has become a part of the standard repertoire of the synthetic organic chemist because of its utility as a preparative method for α,β-unsaturated cyclohexanones and α,β-unsaturated δ-lactones via [4 + 2] cycloadditions reactions.[54] As indicated in Scheme VI, the *trans*-propenyl complex **13** reacts *extremely rapidly* with Danishefsky's diene **25a** at room temperature. The red color of the propenyl complex **13** is dissipated within 2 min upon dissolution in **25a** to give the light yellow solution of the exo and endo cycloadducts **81a** and **81b** as a 1.4:1 mixture as determined by ^{1}H NMR on the crude reaction mixture before hydrolysis on silica gel to **83**. At −15 °C the reaction required 2 h and gave a 1:1 mixture of **81a** and **81b**, indicating that the reaction is kinetically selective for the endo product. The adducts were best isolated as their corresponding ketones (inseparable mixtures of diastereomers by flash chromatography) after hydrolysis on silica gel in 85% total yield and identical exo/endo ratios. Not unexpectedly, the reaction of **13** with the more bulky diene **25b** proceeded more sluggishly requiring 2 h at 25 °C to go completion. In this case, treatment with silica gel in hexane resulted in some cleavage of the alkoxy trimethylsilyl group to give a 70% yield of **84** (2.8:1,

(51) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87.
(52) See U. Schubert in ref 3a.
(53) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400.
(54) Danishefsky, S. J. et al. *J. Am. Chem. Soc.* **1985**, *107*, 1246, 1256, 1269, 1274, 1280, 1285.

Table VII. Coupling Constants for the 3-Cyclohexenyl Carbene Complexes **70**, **76**, and **81**





	70a	**76a**	**81a**	**70b**	**76b**	**81b**
R^1	H	CH_3	CH_3	H(d′)	CH_3	CH_3
R	H	H	$OSiMe_3$	H	H	$OSiMe_3$
M	Cr	W	W	Cr	W	W
J_{bc} (Hz)	8.8	9.0	8.3	3.2	3.8	3.6
J_{cd} (Hz)	10.0	9.0	8.3	12.2	11.1	11.4
J_{ab}(Hz)	<1	<1	1.7	~3	~4	5.4

endo/exo) as well as an 11% yield of **85** (1:2 endo/exo), for an overall endo/exo ratio of 2.1:1.[55]

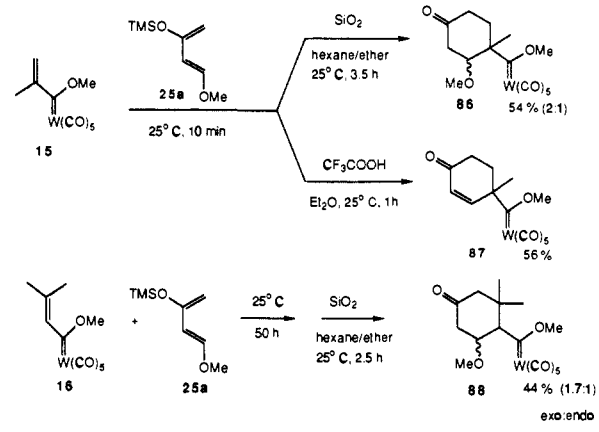
The reaction of the *trans*-propenyl tungsten complex **13** is much more reactive toward Danishefsky's diene than its corresponding ester, methyl crotonate **51**.[56] The reaction of methyl crotonate requires refluxing in toluene for 54 h and gives only a 30% total yield of adducts which consists of a 2:1 mixture of endo and exo isomers. The advantage of the Diels–Alder reaction of complex **13** over methyl crotonate **51** is thus in rate and yield, but both dienophiles are found lacking with regard to stereoselectivity. The fact that both dienophiles give a slight preference for the exo isomer is not unprecedented in the Diels–Alder reactions of acyclic dienes.[57]

When the crude mixture from the reaction of **13** with **25a** was rapidly chromatographed, small amounts of **81a** and **81b** (in addition to predominantly **83**) could be isolated and analyzed by ^{1}H NMR. The relevant coupling constants for **81a** and **81b** (Table VII) correlate very closely with the corresponding coupling constants for adducts **70** and **75** and are consistent with coupling constants reported for related cyclohexenyl systems.[47,56,58] Particularly diagnostic for differentiating between stereoisomers are J_{bc}, which is expected to have a larger value for the exo than for the endo adduct,[47,58] and J_{ab}, which is anticipated to have a larger value for the endo isomer.[56,58a] The values of J_{cd} confirm the expectation that the large carbene metal unit occupies an equatorial position in both the exo and endo cycloadducts.

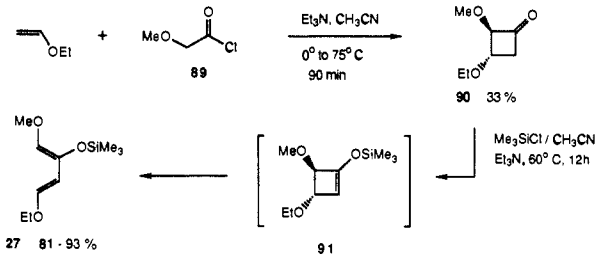
Unlike the reactions with 1-methoxy-1,3-butadiene (**23**), the reactions of the isopropenyl and isobutenyl complexes **15** and **16** gave good to moderate yields of cycloadducts with Danishefsky's diene **26a** (Scheme VII). We could not find the reaction of Danishefsky's diene with an ester of β,β-dimethylacrylic acid in the literature, but the reaction of methyl methacrylate has been reported to occur in 22 h at 95 °C to give a 65% yield of a mixture of stereoisomeric cycloadducts corresponding to **86**.[56] Hydrolysis on silica gel again proved to be the best method for isolation of the ketones **86**[59] and **88**. On attempts to hydrolyze the trimethylsilyl enol ether with concurrent elimination of the methoxy group, it was observed that the adducts of complexes **13**, **15**, and **16** were unstable toward aqueous mineral acid (0.005 N HCl in THF, 0 °C)[56] and only the adducts of **15** were stable to CF_3CO_2H.[60] The latter allowed the direct, one-pot, preparation of α,β-unsaturated ketone **87**.

We had previously determined in the reactions of the *cis*- and *trans*-propenyl tungsten complexes **13** and **14** with cyclopentadiene (Table III) that the Diels–Alder reactions of alkenyl carbene

Scheme VII



Scheme VIII



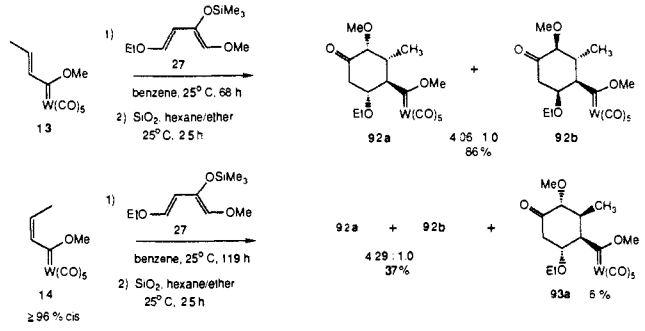
complexes are stereospecific. We thought to examine the stereoselectivity of the Diels–Alder reaction of carbene complexes with 1,4-disubstituted dienes of a given stereochemical configuration. To this end we chose the *trans,trans*-1,2,4-trisubstituted diene **27**, since it is being employed in our group in a synthesis of olivin and could be prepared by the method of Scheeren,[61] uncontaminated by any of the other possible olefin isomers. The cyclobutanone **90** was prepared by the indicated [2 + 2] cycloaddition of ethyl vinyl ether to methoxyketene. Cyclobutanone **90** can vary somewhat in stereochemistry depending on reaction conditions, but Scheeren found that for cyclobutanones of this type that in the subsequent step involving treatment with triethylamine and trimethylchlorosilane, the cyclobutanone is completely isomerized to the trans isomer before it silylated to generate the cyclobutene **91** which is not isolated but allowed to undergo a *conrotatory* ring opening to give exclusively the trans,trans isomer of **27** (Scheme VIII).

The cycloaddition of the *trans*-propenyl tungsten complex **13** with the trisubstituted diene **27** gives only two cycloadducts as determined by crude ^{1}H NMR before and after hydrolysis. Upon chromatography on silica gel, the only two organometallic products that could be isolated were the exo cycloadduct **92a** and the endo cycloadduct **92b** in a total of 86% yield. Analysis of the proton–proton couplings of the ^{1}H NMR spectral data for each adduct revealed that the stereochemical relationship of the methoxy and ethoxy groups as well as the methyl group and the carbene ligand are maintained in both the endo and exo cycloadducts. This was found not the case for the reaction of the *cis*-propenyl tungsten complex **14** with the diene **27**. The mass balance of this reaction was lower and gave as the major products the same two adducts (and in the same ratio) produced from the reaction of the *trans*-propenyl complex **13**. A third product produced from this reaction was identified by proton–proton decoupling experiments as the exo-adduct from the addition of the *cis*-propenyl complex **14** to **27** with all relative stereochemistry retained.

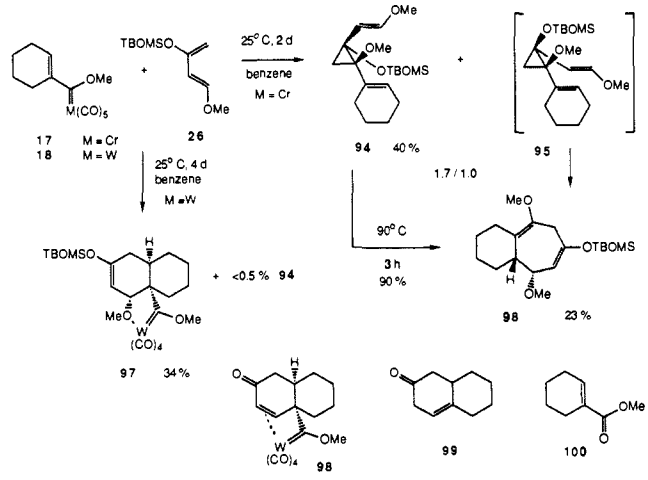
When the reaction with the *cis*-propenyl complex **14** was repeated and stopped at low conversion (22 h, ~10–20% conversion), the recovered propenyl complex was found to be a 1:1.4 mixture of the trans to cis isomers **13** and **14**. This isomerization occurs

(55) That the overall exo/endo ratio of **84** and **85** is 2.1:1 and not 1.7:1 could be due to loss of some of the polar β-hydroxy adduct **85** on silical gel.
(56) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996.
(57) See leading citations in ref 56.
(58) (a) Govesnard, J. P.; Martin, G. J.; Blain, M. *Tetrahedron* **1974**, *30*, 151. (b) Cohen, T.; Ruffner, R. J.; Shull, D. W.; Doniewski, W. M.; Ottenbrite, R. M.; Alston, P. V. *J. Org. Chem.* **1978**, *43*, 4052.
(59) The stereochemistry of the isomers of **93** have not been assigned.
(60) (a) Schubert, V.; Fischer, E. O. *Chem. Ber.* **1973**, *106*, 3882. (b) Weiss, K.; Fischer, E. O. *Chem. Ber.* **1973**, *106*, 1277.
(61) Aben, R. W.; Scheeren, H. W. *J. Chem. Soc., Perkin Trans. I* **1979**, 3132.

Scheme IX



Scheme X



only in the presence of the diene **27**, since in a control experiment no significant amount of isomerization of **14** could be detected after stirring **14** in benzene for 21 h followed by the same workup with silica gel. Failure to achieve cycloaddition with *cis*-propenyl units due to isomerization has also been observed by Evans for *N*-acyloxazolidinones.[62a] While the exact mechanism of the isomerization of **14** cannot be determined from the present data, it is likely that the trans cycloadducts **92a** and **92b** are the result of a cycloaddition of the *trans*-propenyl complex **13** and the cis cycloadduct **93a** is the result of a cycloaddition of the *cis*-propenyl complex **14** (Scheme IX). Thus, the Diels–Alder reactions of carbene complexes can also be stereoselective with highly reactive electron-rich dienes.

Competitive Diels–Alder and Cyclopropanation Reactions with the Cyclohexenyl Complexes 17 and 18

The reaction of complex **17** with diene **26** proceeded at room temperature which represents a tremendous rate acceleration over the Diels–Alder reaction of the corresponding ester **100** with the related diene **25a** which requires 30 h at 190 °C.[62b,63] However, neither of the two products from the reaction of the chromium complex **17** were Diels–Alder products. The major product was the cyclopropane **94** which was obtained in 40% yield as a single diastereomer. This product arises from the formal transfer of the carbene ligand to the most electron-rich double bond of the diene. We have recently communicated this result in a study directed to certain aspects of the mechanism of the cyclopropanation reaction.[10h] This was the first report of the cyclopropanation of a 1,3-diene by a group 6 Fischer carbene complex; however, in the last year a second report has appeared in the literature.[64] The second product isolated from the reaction of **17** and **26** was the bicyclo[5.4.0]undecane **96** in 23% yield.

The cyclopropane **94** underwent clean conversion via a Cope rearrangement to the bicyclo[5.4.0]undecane product **96** at 90 °C in 3 h. Cope rearrangements of divinylcyclopropanes have been examined, and it is usually found that the cis isomers undergo the Cope rearrangements at or below room temperature while the trans isomers have a high barrier to rearrangement.[65,66] It has been established that the trans isomers must first undergo isomerization to the cis isomer before Cope rearrangement occurs. The thermal requirement for unfunctionalized *trans*-divinylcyclopropanes can be upwards of 200 °C; however, if the cyclopropane bears substituents that can stabilize radical intermediates the thermal requirement is observed to drop significantly.[65b] On this basis, the cyclopropane **94** is assigned the trans configuration. Thus it can be deduced that the ratio of the *trans*-cyclopropane product and the Cope product from the reaction of the cyclohexenyl carbene complex **17** and Danishefsky's define is a reflection of the stereoselectivity of the cyclopropanation reaction (1.7:1.0).[67] Since the thermal rearrangement of the cyclopropane **94** is very efficient, this reaction should be useful for the preparation of highly functionalized, fused, seven-membered rings in good overall yield.

Another surprise was encountered when it was found that the tungsten complex **18** reacts with the diene **26** to give the Diels–Alder adduct **97**. The yield of the Diels–Alder reaction is only 34%, but the increased rate of this reaction compared to that of the cyclohexenyl ester **100** is quite remarkable.[62b,63] If the cycloadduct **97** is not quickly chromatographed on silica gel, then varying amounts of the hydrolyzed product **98** can be isolated which has the tungsten internally chelated to the enone double bond.[10d] It was also interesting to observe that attempted fluoride induced cleavage of the silyl enol ether function in **97** led to the formation of the decalenone **99** in 20% yield. This reaction has not yet been optimized, and we have previously speculated on a mechanism for this transformation.[10g] The reactions of the chromium and tungsten complexes **17** and **18** with diene **26** are highly chemoselective in their reactions with diene **26**. The chromium complex **17** gave no detectable amounts of the Diels–Alder product. Small amounts (<5%) of several other products were formed in the tungsten reaction. The cyclopropane **94** is absent (<0.5%) by crude ^{1}H NMR, but GCMS indicates the presence of isomers of **94** which may prove to be five-membered ring compounds and/or small amounts of **96**.

The tandem cyclopropanation/Cope sequence in Scheme X has obvious potential in natural product synthesis. A key factor in its successful implementation will be understanding the reasons for the extreme sensitivity of the nature of the metal on the product distribution and on the range of carbene complexes and dienes that can be employed, and these studies are in progress.

The observations indicated in Scheme X have particular significance to the present study with regard to the degree to which cyclopropanation competes with Diels–Alder reactions of alkenyl complexes in the general case. The data in Scheme X suggest that this should not be as serious a problem with tungsten as it is for chromium. Nevertheless, in forcing Diels–Alder reactions such as those for the *iso*-butenyl tungsten complex **16** it may very well be that cyclopropanation products are formed. In most instances the reactions of the alkenyl carbene complexes with the dienes indicated in Scheme III were carried out and screened for Diels–Alder products. All of the crude reaction mixtures were examined by TLC, and in many cases by ^{1}H NMR (where stereoisomers are formed) but it is certainly possible that cyclopropane products could have been missed. The reaction of the chromium complex **17** with diene **26** suggests cyclopropane products should be looked for in the Diels–Alder reactions of

(62) (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (b) Danishefsky, S.; Kitahara, T. *J. Org. Chem.* **1975**, *40*, 538.

(63) Danishefsky, D.; Schuda, P. F.; Kitahara, T.; Etheredge, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 6066.

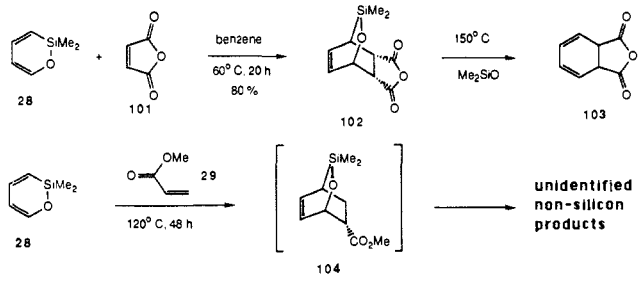
(64) Buchert, M.; Reissig, H. U. *Tetrahedron Lett.* **1988**, *29*, 2319.

(65) (a) Brown, J. M.; Golding, T.; Stofko, J. J. *J. Chem. Soc., Chem. Commun.* **1973**, 319. (b) Wender, P. A.; Filosa, M. P. *J. Org. Chem.* **1976**, *41*, 3490.

(66) (a) Ullenius, C.; Ford, P. W.; Baldwin, J. E. *J. Am. Chem. Soc.* **1972**, *94*, 5910. (b) Baldwin, J. E.; Ullenius, C. *J. Am. Chem. Soc.* **1974**, *96*, 1542.

(67) For leading citations on the stereoselectivity of cyclopropanation reaction, see: references 10g, 10h, and 62.

Scheme XI



carbene complexes, especially in those cases where the yields of the Diels–Alder adducts are not particularly high.

Cycloaddition of the Silapyran 28: A Sensitive Diene with a Limited Thermal Requirement

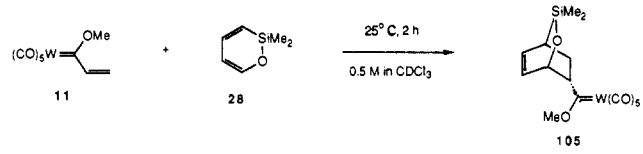
The preparation of the silapyran **28** and its Diels–Alder reaction with maleic anhydride[68] were reported several years ago. There appears to be considerable potential for the silapyran **28** in organic synthesis since cleavage of the silicon–oxygen bond in Diels–Alder adducts of the type **102** should lead to uniquely functionalized, six-membered rings. In a model study for the synthesis of pipoxide,[69] we attempted the cycloaddition of the silapyran **28** with methyl acrylate and found that it was necessary to heat this reaction to 120 °C to effect a reaction (Scheme XI). These were conditions that apparently exceeded the stability of the cycloadduct **104**, since the only products obtained were devoid of silicon as determined by GC/mass spectral analysis of the complex mixture obtained from this reaction. It was deemed likely that the adduct **104** underwent a retro-Diels–Alder reaction with extrusion of silaacetone. This was demonstrated in the thermolysis of the cycloadduct **102** at 150 °C.

In those cases where Diels–Alder reactions fail or are otherwise unsatisfactory under thermal conditions, the traditional solution is to employ Lewis acid catalysts or high pressure.[13] Since we did not have access to high-pressure equipment, we decided to examine the effects of Lewis acids on this reaction. The reaction of the silapyran **28** with methyl acrylate failed in the presence of Lewis acids ($AlCl_3$, BF_3–OEt_2, $ZnCl_2$), perhaps due to the sensitive nature of the silapyran **28** or of the cycloadduct **104**. It was actually the failure of this reaction that eventually lead us to attempt the Diels–Alder reaction of an alkenyl carbene complex.[3e] After it was determined that the Diels–Alder reactions of carbene complexes displayed great rate acceleration with simple dienes, we investigated the reaction of the vinyl tungsten complex **11** with the silapyran **28** (Scheme XII). This reaction was found to proceed with 1 equiv of the silapyran **28** at room temperature at 0.5 M in $CDCl_3$ in 2 h to give essentially a quantitative yield (by ^1H NMR) of the cycloadduct **105** as a single regio- and stereoisomer as determined by 500-MHz ^1H NMR. This reaction illustrates that in addition to the advantages of rates and regio- and stereoselectivities, the Diels–Alder reaction of alkenyl carbene complexes have the additional advantage of being much more tolerant of sensitive organic functionality than the commonly used Lewis acids.

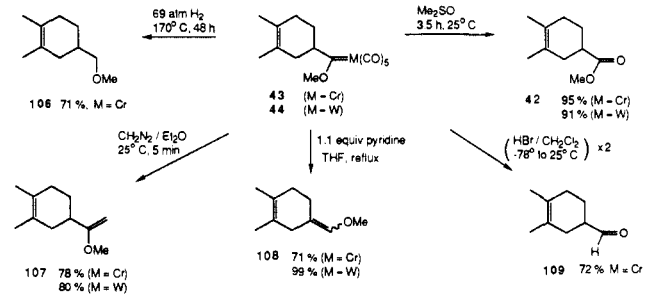
Chromium and Tungsten Pentacarbonyl Groups as Versatile Synthons

It is of course true that alkenyl carbene complexes could not be synthons of any kind unless the metal could be removed in a productive manner after the Diels–Alder reaction. Given the large body of literature on the reaction chemistry of carbene complexes, it was anticipated that the Fischer alkenyl carbene complexes could serve as synthons for a variety of organic functional groups.[3] We

Scheme XII



Scheme XIII



have examined five of these reactions for the chromium and tungsten cycloadducts **43** and **44** which demonstrate that the metal pentacarbonyl unit is indeed a potentially useful broad-ranged synthon in addition to a highly effective reactivity and selectivity auxilliary (Scheme XIII). We have previously mentioned (Scheme II) that carbene complexes can be easily oxidized to esters, and in the present case, both the chromium and tungsten adducts **43** and **44** can be oxidized to the methyl ester **42** in greater than 90% yield simply by dissolving the carbene complex in dimethyl sulfoxide[16] at room temperature and stirring for a few hours. (Dimethyl sulfide)pentacarbonylchromium is also produced in this reaction and, like dimethyl sulfoxide, is inert to most common organic functionality. The aldehyde **109** can be obtained in good yield from the reaction of complex **43** with hydrogen bromide without addition to the double bond if the conditions are controlled carefully. Aldehydes have been detected but not previously isolated from the reaction of Fischer carbene complexes and hydrogen halides.[70] The methyl vinyl ether **108** can be obtained by heating either **43** or **44** with pyridine.[71] In this case the vinyl carbene complexes **9** and **11** serve as synthons for methoxyallene in which the Diels–Alder reaction occurs selectively at the double bond in the 2-position. Carbon homologated enol ethers can be obtained from cleavage reactions with diazoalkanes.[72] The reaction of the cycloadducts **43** and **44** with diazomethane gives the enol ether **107** in which the vinyl carbene complexes have served as synthons to provide a selective cycloaddition of 2,3-dimethyl-1,3-butadiene to one of the double bonds of 2-methoxy-1,3-butadiene. The metal can be reductively removed by treatment with hydrogen,[73] where the metal center can serve to activate and deliver hydrogen allowing the double bond in **43** to survive intact. Finally, the inadvertent fluoride cleavage of the cycloadduct **97** that occurs with carbon loss to give the decalenone **99** has not been optimized or further examined. It can be realized this represents a potential for alkenyl carbene complexes to be employed as synthons for simple alkenes (cyclohexene in the present case) with 1,3-dialkoxy-1,3-dienes.

Conclusion

In summary, the Diels–Alder reactions of alkenyl Fischer carbene complexes have been observed to have rates and regio- and stereoselectivities that are significantly higher than α,β-unsaturated esters (their closest organic analogues) and that are comparable to the rates and selectivities that are normally associated with the Lewis acid mediated Diels–Alder reactions of

(68) Hussman, G.; Wulff, W. D.; Barton, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1263.
(69) (a) Joshi, B. S.; Gawad, D. H.; Fuhrer, H. *Tetrahedron Lett.* **1979**, 2427. (b) Holbert, G. W.; Ganem, B.; Van Engen, D.; Clardy, J.; Borsub, K.; Chantrapromma, K.; Sadavongvivad, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1979**, 715.
(70) (a) Schubert, V.; Fiacher, E. O. *Chem. Ber.* **1973**, *106*, 3882. (b) Fischer, E. O.; Walz, S.; Kreis, G.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1651.
(71) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1973**, *107*, 3326.
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α,β-unsaturated esters. Coupled with their tolerance of organic functionality, their ease of preparation and handling, and the extensive reaction chemistry that has been developed for group 6 carbene complexes that is available for subsequent transformations of the cycloadducts, the Diels–Alder reactions of alkenyl Fischer carbene complexes promise to be of great service to synthetic organic chemistry.

Experimental Section

Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. Cycloaddition reactions were normally conducted as mixtures in neat diene (ca. 5 equiv) on a 0.3–1.0 mmol scale inside a closed round-bottom flask equipped with a threaded vacuum Teflon stopcock under an atmosphere of argon. Where noted the mixtures were deoxygenated by the freeze–thaw method (−195 to 25 °C, three cycles). All column chromatography was carried out under air by using the "flash" method as described by Still with 230–240-mesh silica gel.[52] All melting points were uncorrected.

Routine proton NMR spectra were recorded on either a Bruker 270-MHz or a DC 1000 (Chicago built) 500-MHz spectrometer in $CDCl_3$ with tetramethylsilane as internal standard unless otherwise specified. All samples of carbene complexes were filtered through a plug of Celite immediately prior to recording the spectra. The ^{13}C NMR were obtained on a Nicolet 200 spectrometer at 50.3 MHz. Infrared spectra were recorded on a Perkin-Elmer 282 spectrophotometer as neat films on NaCl unless otherwise noted. A Finnigan 1015 mass spectrometer was used to obtain low-resolution spectra. High-resolution mass spectra were carried out on a VG Analytical 7070 E mass spectrometer or were obtained from the Midwest Center for Mass Spectrometry (MCMC) and the University of Illinois. Elemental analyses were conducted by Galbraith Lab., Inc. and Micro-Tech Lab., Inc.

Preparation of Alkenyl Carbene Complexes. Preparation of Vinyl Chromium Complex 9. The preparation of the vinyl chromium complex **9** has been described by Fischer.[12] With use of method A described for the tungsten complex **11**, complex **9** can be obtained in 20–30% yield. We have not yet attempted the preparation of **9** with the improved method B described for the tungsten complex. Unlike the tungsten complex **11**, the chromium complex **9** (and the molybdenum complex **10**) is not stable as an oil but can be purified by flash chromatography with hexane if the solvent is removed (0 °C) below its melting point. This compound can be stored as a solid or better as a frozen benzene solution.

Preparation of Vinyl Molybdenum Complex 10. The complex **10** was prepared according to method A described for **11** from $Mo(CO)_6$ in 7% yield: ^1H NMR δ 4.71 (s, 3 H), 5.20 (dd, J = 10, 1 Hz, 1 H), 5.65 (dd, J = 15.5, 1 Hz, 1 H), 7.38 (dd, J = 15.5, 10 Hz, 1 H). Unlike the tungsten complex **11**, the molybdenum complex **10** (and the chromium complex **9**) is not stable as an oil but can be purified by flash chromatography with hexane if the solvent is removed (0 °C) below its melting point. This compound should be used immediately upon preparation.

Preparation of the Vinyl Tungsten Complex 11.[17a,c] Method A. Vinyl bromide (0.8 mL, 11.4 mmol) was condensed into a graduated conical test tube at −78 °C and then transferred via cannula to a 500-mL flask containing 120 mL of dry ether and a stir bar and which had been precooled to −78 °C under an argon atmosphere. A solution of *tert*-butyllithium (22.7 mmol, 1.7 M in pentane) was added dropwise to the solution of vinyl bromide, and the resulting solution was stirred for 30 min to ensure complete formation of vinyllithium. The solution of vinyllithium was transferred via cannula over a period of 20 min to a slurry of $(CO)_6W$ (5.2 g, 14.82 mmol) and 150 mL of ether and 100 mL of THF at room temperature, and after the addition the slurry was stirred for 1 h. The solvents were removed from the dark brown mixture by rotorary evaporator and then by high vacuum (0.05 mm) for 5 min. The residue was dissolved in 20 mL of methylene chloride and 100 mL of hexane, and then trimethyloxonium tetrafluoroborate (3.27 g, 25.52 mmol) was added. If when the oxonium salt is first added, a deep red color is not observed more should be added until this happens. Water (5 mL) was added dropwise to this mixture while the flask was swirled vigorously. After addition of the water, the flask was swirled for an additional 3 min and the contents then transferred to a separatory funnel. The water layer was removed, and the organic layer was filtered with vacuum through a layer of Celite covered with anhydrous sodium sulfate. The organic layer was then reduced in volume to ~70 mL by rotorary evaporator and then loaded onto a large flash chromatography column containing 200 mL of silica gel. Upon elution with hexane the product was collected as a red band (R_f = 0.41) and the volume of this fraction was reduced to 50 mL by rotorary evaporator. The remaining solvent was removed from the product at 0 °C under high vacuum (0.01 mm) to leave 1.75 g (39%) of complex **11** as a red solid (oil at 25 °C): ^1H NMR δ 4.62 (s, 3 H), 5.28 (d, J = 10.5 Hz, 1 H), 5.72 (d, J = 17 Hz, 1 H), 7.38 (dd, J = 17, 10.5 Hz); ^{13}C NMR δ 69.5 (q), 119.4 (t), 152.6 (d), 197.2 (s), 203.8 (s), 313.0 (s); IR ($CHCl_3$) 2060, 1970 br s, 1935 s cm^{-1}. Anal. Calcd for $C_9H_6O_6W$: C, 27.44; H, 1.53. Found C, 27.76; H, 1.81. Unlike the chromium and molybdenum complexes **9** and **10**, the tungsten complex **11** could be handled as an oil but was best stored as a solid (<0 °C) or as a frozen benzene solution. The yield of complex **11** can be variable and the 39% yield represents the best that has been obtained by method A. The procedure described in method B has not been tested to the same extent as method A; however, it gives much a higher yield of complex **11** (53%).

A second compound was obtained upon further elution with hexane (R_f = 0.15) as a purple solid (0.078 g, 1%) and was identified as (η^2-vinyl)(η^2-methoxyvinyl)methylenebis-(tungsten pentacarbonyl) (**125**) by comparison of its ^1H NMR with that which has previously been reported for this compound.[19,74] Complex **125**: ^1H NMR δ 3.57 (d, J = 14 Hz, 1 H), 3.58 (d, J = 9 Hz, 1 H), 4.43 (s, 3 H), 5.55 (dd, J = 14, 9 Hz, 1 H). This dinuclear product **125** was obtained in 20% yield if 1.5 equiv of $W(CO)_6$ was used.

Improved Procedure—Method B.[17a] A solution of *tert*-Butyllithium (1.7 M in pentane, 20.0 mmol) was added to an excess of vinyl bromide (1.35 mL, 19.1 mmol) in 100 mL of dry Et_2O at −78 °C. After 2 h at −78 °C the solution was transferred dropwise (slowly) via cannula to a suspension of tungsten hexacarbonyl (3.87 g, 11.0 mmol) in Et_2O (220 mL) at 0 °C. When the addition was complete, the mixture (a brown precipitate forms) was stirred for another 0.5 h at 0 °C and then transferred via cannula to a solution of methyl fluorosulfate (1.7 mL, 20.0 mmol) in methylene chloride (30 mL) at 0 °C. The resulting brown colored solution did not look any different than before transfer. After the solution was stirred at 0 °C for 30 min and at 25 °C for 30 min, the reaction was quenched by adding 10 mL of $NaHCO_3$ (saturated solution). The reaction mixture immediately turned dark red colored. Examination of the reaction by TLC (hexane solvent) showed a dark red spot at R_f = 0.41. After the solution was stirred for another 20 min, an additional 50 mL of $NaHCO_3$ solution was added, and the reaction was worked up. The dark red mixture was diluted with Et_2O. The organic layer was separated, washed with $NaHCO_3$ saturated solution (1 × 50 mL) and brine (1 × 50 mL), and dried over $MgSO_4$. The red solution was filtered through Celite and concentrated to approximately 5 mL. The dark red oil was then chromatographed (SiO_2, hexane) quickly, and the complex **11** was obtained as a dark red oil (2.10 g, 5.33 mmol, 53%) upon removal of the solvents on a rotovap and a vacuum line. The dinuclear complex **125** was isolated upon further elution with hexane in 0.6% yield (45 mg).

Preparation of the *trans*-Propenyl Chromium Complex 12. This complex was prepared according to the procedure described for isopropenyl tungsten complex **15** from *trans*-1-bromo-1-propene (>97%) that was prepared according to the procedure of Hayashi.[75] Complex **12** was obtained as a red solid in 75% yield (2.5-mmol scale) upon purification by flash chromatography with hexane: R_f = 0.23; mp 37–38 °C; ^1H NMR δ 1.88 (dd, J = 6.9, 1.1 Hz, 3 H), 4.72 (s, 3 H), 6.35 (sextet, J = 7.0 Hz, 1 H), 7.32 (dq, J = 14.7, 1.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.3, 66.5, 132.6, 146.0, 216.9, 224.0, 335.8; IR ($CDCl_3$) 2050 s, 1950 brs, 1605 s, 1440 s, 1225 s, 640 s cm^{-1}; mass spectrum, m/e (rel intensity) 276 M^+ (5), 248 (0.5), 220 (43), 192 (3), 164 (8), 136 (16), 108 (100), 80 (100), 52 (100). Anal. Calcd for $C_{10}H_8O_6Cr$: C, 43.48; H, 2.90; Cr, 18.84. Found: C, 43.62; H, 3.07; Cr, 18.49.

Preparation of the *trans*-Propenyl Tungsten Complex 13.[17c] This complex was prepared according to the procedure described for isopropenyl tungsten complex **15** from *trans*-1-bromo-1-propene (>97%) that was prepared according to the procedure of Hayashi.[75] Complex **13** was obtained as a red solid in 73% yield (5.0-mmol scale) upon purification by flash chromatography with hexane: mp 49.5–51 °C; ^1H NMR δ 1.81 (dd, J = 6.8, 1.1 Hz, 3 H), 4.56 (s, 3 H), 6.55 (sextet, J = 7.2 Hz, 1 H), 7.22 (dq, J = 13.7, 1.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.52, 69.05, 137.19, 149.30, 197.50, 203.61, 309.69; IR (neat) 2040 w, 1900 brs, 1595 s, 1430 s, 1220 s cm^{-1}; mass spectrum, m/e (rel intensity) 408 M^+ (^{184}W) (29), 380 (23), 352 (21), 324 (17), 309 (28), 296 (53), 281 (29), 268 (100), 251 (44), 237 (30), 225 (37), 210 (16); calcd for $C_{10}H_8O_6{}^{184}W$ m/e 407.9830, measured m/e 407.9822. Anal. Calcd for $C_{10}H_8O_6W$: C, 29.42; H, 1.96. Found: C, 29.37; H, 1.89.

Preparation of the *cis*-Propenyl Tungsten Complex 14. *cis*-1-Chloropropene (1.0 mL, 12.2 mmol), obtained from Wiley Organics (>97% Z), was added over 10 min to a stirred and cooled (−5 °C) suspension of freshly cut lithium wire (0.6 g, 86.5 mmol) in ether (30 mL). After 2.5 h at 25 °C the grayish solution was transferred via

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cannula into a suspension of tungsten hexacarbonyl (3.4 g, 9.76 mmol) in 100 mL of THF which turned to a yellow-brown upon addition. After stirring this solution for 3.5 h, it was transferred via cannula into a solution of methyl fluorosulfate (24.4 mmol) in 100 mL of methylene chloride and stirred for 30 min. The reaction was then quenched by addition of saturated aqueous sodium bicarbonate. The mixture was then extracted with ether, and the combined organic layers were washed with saturated brine and dried over anhydrous MgSO4. After evaporation of the solvent, the residue was redissolved in hexane and filtered through a bed of Celite to remove any unreacted $W(CO)_6$. Flash chromatography on silica gel with hexane (R_f = 0.23) gave 0.677 g (17%, 1.7 mmol) of complex **14** as a red solid: mp 48–52 °C; ^{1}H NMR δ 1.82 (d, J = 7 Hz, 3 H), 4.61 (s, 3 H), 5.54 (m, 1 H), 7.19 (br d, J = 11 Hz, 1 H); ^{13}C NMR δ 17.47, 69.64, 130.47, 147.57, 204.29, 316.87; IR ($CHCl_3$) 2068 m, 1984 sh, 1937 s, 1596 m, 1111 w, 988 w, 900 w cm^{-1}; mass spectrum, m/e (rel intensity) 408 M$^+$ (^{184}W) (25), 380 (5), 352 (35), 324 (10), 296 (40), 268 (100), 240 (40), 212 (35), 184 (20), 106 (5); Anal. Calcd for $C_{10}H_8O_6W$: C, 29.42; H, 1.96. Found: C, 29.47; H, 1.91. The *cis*-propenyl complex **14** obtained above was found to be greater than 97% the *Z* isomer by ^{1}H NMR. The *cis*-propenyl tungsten complex **14** will begin to isomerize to the trans isomer when heated at 70 °C for several hours.

Preparation of the Isopropenyl Tungsten Complex 15.[19] A 0.2 M solution of 2-bromopropene (0.25 mL, 2.81 mmol) in ether (14.1 mL) was cooled to −78 °C under an argon atmosphere. After a few minutes, 2 equiv of *tert*-butyllithium (1.7 M in pentane) was added very slowly over 10 min, and then the colorless solution was stirred for 1.5 h at −78 °C. The solution of the isopropenyllithium at −78 °C was added slowly via cannula to a 0.05 M solution of tungsten hexacarbonyl (1.09 g, 3.1 mmol) in ether at 25 °C. After 2 h at room temperature, the yellow solution of the metal acylate was transferred via cannula to a solution of methyl fluorosulfate (0.47 mL, 5.12 mmol) in 10 mL of methylene chloride at 0 °C. The resulting dark red-orange solution was stirred for 1 h at 0 °C and 0.5 h at room temperature. The reaction was quenched by adding 15 mL of saturated aqueous sodium bicarbonate. The reaction mixture was diluted with ether, and the organic layer was separated, washed with saturated aqueous sodium bicarbonate (50 mL) and brine (50 mL), and dried over magnesium sulfate. After filtration and concentration on a rotorary evaporator, the dark red oil was chromatographed on silica gel with hexane as eluent to give an 80% yield of complex **15** (0.903 g, 2.24 mmol) as a dark red oil: ^{1}H NMR δ 1.91 (s, 3 H), 4.61 (s, 3 H), 5.42 (s, 1 H), 5.49 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.05 (q, J = 119.5 Hz), 71.38 (q, J = 147.2 Hz), 121.45 (t, J = 147.8 Hz), 160.35 (s), 197.19 (s), 203.22 (s), 326.72 (s); IR 2030, 1900 brs, 1440, 1225 s cm^{-1}; mass spectrum, m/e (rel intensity) 408 M$^+$ (^{184}W) (30), 380 (24), 352 (50), 324 (31), 309 (31), 296 (100), 268 (58), 251 (45), 223 (41), 151 (32), 113 (25); calcd for $C_{10}H_8O_6{}^{184}W$ m/e 407.9830, measured m/e 407.9834. Anal. Calcd for $C_{10}H_8O_6W$: C, 29.42; H, 1.96. Found: C, 29.46; H, 1.92.

Preparation of the Isobutenyl Tungsten Complex 16. This complex was prepared according to the procedure described above for **15** from isobutenyl bromide in 55–60% yield: mp 40–41 °C; ^{1}H NMR δ 1.85 (s, 3 H), 1.89 (s, 3 H), 4.58 (s, 3 H), 7.31 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.67 (q, J = 127.8 Hz, CH_3), 28.46 (q, J = 127.5 Hz, CH_3), 69.13 (q, J = 147.2 Hz, OCH_3), 144.94 (d, J = 158.7 Hz, vinyl CH), 145.33 (s, vinyl), 197.73 (s, cis CO), 203.77 (s, trans CO), 311.36 (s, carbene carbon); IR (neat) 2050, 1975 sh, 1900 brs, 1575, 1440, 1245, 1100, 975 cm^{-1}; mass spectrum, m/e (rel intensity) 422 M$^+$ (^{184}W) (25), 394 (14), 366 (18), 338 (16), 310 (19), 295 (21), 282 (100), 278 (39), 265 (27), 252 (22), 237 (41), 222 (16), 83 (21), 55 (29); calcd for $C_{11}H_{10}O_6{}^{184}W$ m/e 421.9987, measured m/e 421.9985. Anal. Calcd for $C_{11}H_{10}O_6W$: C, 31.29; H, 2.37. Found C, 31.18; H, 2.29.

Preparation of the Cyclohexenyl Tungsten Complex 18. This complex was prepared according to the procedure described above for **15** from cyclohexenyl bromide in 52% yield (1.12 mmol) and obtained as red-orange solid: mp 34–35 °C; ^{1}H NMR δ 1.62 (m, 4 H), 2.23 (m, 2 H), 2.37 (m, 2 H), 4.61 (s, 3 H), 6.98 (br s, 1 H); ^{13}C NMR δ 21.50, 22.02, 25.07, 26.99, 69.44, 147.56, 156.05, 197.81, 203.01, 321.10; IR (neat) 3010 w, 2930 s, 2030 s, 1950 s, 1625 s, 1445 s, 1225 s, 1180 s, 985 s; mass spectrum, m/e (rel intensity) 448 M$^+$ (^{184}W) (5), 420 (25), 392 (5), 364 (5), 347 (18), 336 (20), 308 (100), 291 (30), 278 (35), 263 (60); calcd for $C_{13}H_{12}O_6{}^{184}W$ m/e 448.0143; measured m/e 448.0143.

Reactions with Isoprene. The procedure for the unsubstituted vinyl complexes **9–11** involves dissolving the complex in an excess of isoprene (~50 equiv) and stirring under air at 25 °C for 1–3 h. For the substituted alkenyl complexes **12** and **13** the reaction mixtures were deoxygenated prior to heating (see Table I). The excess diene was removed under vacuum (0.1 mm Hg) at 25 °C and the residue was chromatographed with hexane. The regioisomers of the cycloadducts **32**, **33**, and **34** could not be separated by silica gel chromatography. The spectral data for complexes **32**, **33**, and **34** were collected on the mixture, but only the data for the para isomer **a** is reported below, since it was in all cases greater than 90% of the mixture. The adducts **36** and **37** appeared by all spectroscopic techniques to be uncontaminated (≥97:3) by the meta isomer **b**.

32a: R_f = 0.33 (hexane); ^{1}H NMR δ 1.56 (m, 1 H), 1.66 (s, 3 H), 1.82 (m, 1 H), 1.96 (m, 2 H), 2.10 (m, 2 H), 4.06 (m, 1 H), 4.78 (s, 3 H), 5.39 (m, 1 H); IR ($CDCl_3$) 2050 w, 1980 w, 1935 s cm^{-1}; mass spectrum, m/e (rel intensity) 330 M$^+$ (3), 302 (2), 274 (10), 246 (15), 218 (20), 190 (90).

33a: ^{1}H NMR δ 1.35 (dq, J = 12.5, 5.5 Hz, 1 H), 1.66 (s, 3 H), 1.8–2.0 (m, 3 H), 2.05–2.15 (m, 2 H), 4.01 (tm, J = 11 Hz, 1 H), 4.67 (s, 3 H), 5.39 (m, 1 H).

34a: R_f = 0.32 (hexane); ^{1}H NMR δ 1.41 (m, 1 H), 1.65 (m, 3 H), 1.85, (m, 1 H), 1.95 (m, 2 H), 2.12 (m, 2 H), 4.04 (m, 1 H), 4.59 (s, 3 H), 5.39 (m, 1 H); IR ($CDCl_3$) 2050 w, 1975 w, 1930 s cm^{-1}; mass spectrum, m/e (rel intensity) 462 M$^+$ (^{184}W) (50), 434 (10), 406 (35), 378 (15), 350 (25).

The identity of the above cycloadducts was confirmed and the isomeric composition determined by conversion to a mixture of the known methyl esters **31a,b**. In separate reactions the pure carbene complexes were mixed with excess isoprene and stirred until reaction was complete. The entire reaction mixture was then oxidized by adding a solution of $(NH_4)_2Ce(NO_3)_6$ (3 equiv) in acetone and stirring for 10 min. The mixture was diluted with ether, washed with water, dried with sodium sulfate, and concentrated. The resulting mixture of methyl esters **31a** and **31b** had identical retention times (16.7 min and 15.9 min, respectively) by gas chromatography (12 M × 0.2 mm carbowax 20 M fused silica capillary column at 50 °C) and a ^{1}H NMR (500 MHz) spectrum identical with that of an authentic mixture of the esters prepared by the reaction of methyl acrylate and isoprene.[21-24] Assuming equal response factors for the two isomers gives the reported ratio of 70:30 for the authentic esters.[21-23] The ratios for the Diels–Alder reactions of the carbene complexes from GC are thus 92:8 (Cr), 94:6 (Mo), and 91:9 (W).

The rate of these reactions was monitored by following the disappearance of the vinyl carbene complex by injecting aliquots on a Waters HPLC (Radial-Pak B) with a 254-nm UV detector. The solutions were 0.05 M in complex and 1.0 M in isoprene in benzene with benzene as internal standard and presuming a second-order reaction the rate constants are (4.9 ± 0.4) × 10^{-4} l mol^{-1} s^{-1} for **11** and (4.0 ± 0.4) × 10^{-4} l mol^{-1} s^{-1} for **9**.

36a: ^{1}H NMR δ 0.89 (d, J = 6.3 Hz, 3 H), 1.64 (s, 3 H), 1.64–1.80 (m, 2 H), 1.89–1.98 (m, 2 H), 2.26 (br d, J = 16.4 Hz, 1 H), 3.94 (dt, J = 10.6, 4.4 Hz, 1 H), 4.82 (s, 3 H), 5.34 (br d, J = 3.4 Hz, 1 H); IR (Nujol) 2050, 1980 sh, 1940 cm^{-1}; mass spectrum, m/e (rel intensity) 344 M$^+$ (2), 316 (1), 288 (4) 260 (9), 232 (14), 204 (41), 172 (23), 157 (24), 120 (10), 105 (30), 91 (15), 52 (100); calcd for $C_{15}H_{16}O_6{}^{52}Cr$ m/e 344.0351, measured m/e 344.0357.

37a: mp 63–64 °C; ^{1}H NMR δ 0.93 (d, J = 6.4 Hz, 3 H), 1.64 (s, 3 H), 1.72–1.78 (m, 2 H), 1.92–2.02 (m, 2 H), 2.25 (br d, J = 16.3 Hz, 1 H), 3.92 (td, J = 10.5, 4.5 Hz; collapses to a dd with J = 10.5, 10.5 Hz upon $h\nu$ at δ 2.25, 1 H), 4.63 (s, 3 H), 5.36 (br d, J = 3.7 Hz; collapses to a broad s upon $h\nu$ at δ 2.25, 1 H); IR (Nujol) 2050, 1980 sh, 1920 s cm^{-1}; mass spectrum, m/e (rel intensity) 476 M$^+$ (^{184}W) (14), 448 (6), 420 (18), 392 (16), 364 (14), 346 (92), 336 (11), 318 (100), 304 (23) 289 (49), 266 (14), 107 (33), 91 (54), 77 (25), 67 (23); calcd for $C_{15}H_{16}O_6{}^{184}W$ m/e 476.0457, measured m/e 476.0466. Anal. Calcd for $C_{15}H_{16}O_6W$: C, 37.83; H, 3.36. Found: C, 37.82; H, 3.42.

Reactions with 2,3-Dimethylbutadiene. The general procedure for the substituted vinyl carbene complexes **12**, **13**, **15**, and **16** involves dissolving the complex in an excess of 2,3-dimethylbutadiene (~50 equiv), deoxygenating the mixture, and heating (see Table II for temperature and time). For the unsubstituted complexes **9** and **11** the reactions were conducted in the presence of air at room temperature in benzene (0.05 M, 30 equiv of diene). The excess diene was removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with hexane to give pure cycloadducts.

43: ^{1}H NMR δ 1.29 (m, 1 H), 1.62 (s, 6 H), 1.80 (m, 1 H), 1.96 (m, 2 H), 2.10 (m, 2 H), 4.13 (m, 1 H), 4.78 (s, 3 H); IR ($CHCl_3$) 2060 w, 1980 w, 1940 s cm^{-1}; mass spectrum, m/e (rel intensity) 344 M$^+$ (4), 316 (2), 288 (10), 260 (15), 232 (20), 204 (70). Anal. Calcd for $C_{15}H_{16}O_6Cr$: C, 52.33; H, 4.68; Cr 15.10. Found: C, 52.38; H, 4.90; Cr, 14.85.

44: ^{1}H NMR δ 1.37 (ddd, J = 22, 11, 5 Hz, 1 H), 1.62 (s, 6 H), 1.83 (m, 1 H), 1.98 (m, 3 H), 2.11 (m, 1 H), 4.10 (m, 1 H), 4.60 (s, 3 H); IR ($CHCl_3$) 2070 w, 1980 w, 1935 s cm^{-1}; mass spectrum, m/e (rel intensity) 474 M$^+$ (^{182}W) (10); calcd for $C_{15}H_{16}O_6{}^{182}W$ m/e 474.0430, measured m/e 474.0441.

46: mp 80–81 °C dec; ^{1}H NMR δ 0.87 (d, J = 6.0 Hz, 3 H), 1.59 (s, 6 H), 1.72–1.92 (m, 4 H), 2.12 (br d, J = 16.2 Hz, 1 H), 4.00 (td,

J = 10.4, 4.4 Hz, 1 H), 4.82 (s, 3 H); IR (Nujol) 2050, 1975, 1935 s, 1900 cm^{-1}; mass spectrum, m/e (rel intensity) 358 M$^+$ (3), 330 (1), 302 (4), 274 (9), 246 (17), 218 (40), 186 (28), 171 (28), 119 (18), 105 (21), 91 (13), 52 (100); calcd for $C_{16}H_{18}O_6{}^{52}Cr$ m/e 358.0508, measured m/e 358.0507. Anal. Calcd for $C_{16}H_{18}O_6Cr$: C, 53.63; H, 5.03. Found: C, 53.59; H, 5.08.

47: mp 95–96 °C ^{1}H NMR δ 0.91 (d, J = 6.3 Hz, 3 H), 1.59 (s, 6 H), 1.75–1.82 (m, 2 H), 1.90–1.99 (m, 2 H), 2.10 (br dd, J = 15.7, 4 Hz, 1 H), 3.98 (td, J = 10.6, 4.6 Hz, 1 H), 4.64 (s, 3 H); IR (Nujol) 2060, 1975, 1925 s cm^{-1}; mass spectrum, m/e (rel intensity) 490 M$^+$ (^{184}W) (19), 464 (5), 434 (19), 406 (35), 376 (17), 360 (79), 348 (21), 332 (100), 318 (25), 302 (42), 121 (32), 105 (37), 91 (32) 55 (25); calcd for $C_{16}H_{18}O_6{}^{184}W$ m/e 490.0613, measured m/e 490.0619. Anal. Calcd for $C_{16}H_{18}O_6W$: C, 39.19; H, 3.67. Found: C, 39.20; H, 3.68.

49: mp 56–57 °C; ^{1}H NMR δ 1.11 (s, 3 H), 1.60 (s, 3 H), 1.62 (s, 3 H), 1.80–2.08 (m, 5 H), 2.47 (d, J = 16.7 Hz, 1 H), 4.71 (s, 3 H); IR (Nujol) 2050, 1970, 1920 s cm^{-1}; mass spectrum, m/e (rel intensity) 490 M$^+$ (^{184}W) (8), 462 (7), 434 (17), 406 (13), 376 (11), 360 (76), 332 (100), 303 (36), 121 (47), 105 (54), 91 (44), 79 (32), 55 (33); calcd for $C_{16}H_{18}O_6{}^{184}W$ m/e 490.0613, measured 490.0614. Anal. Calcd for $C_{16}H_{18}O_6W$: C, 39.19; H, 3.67. Found: C, 39.15; H, 3.65.

50: mp 94–95 °C; ^{1}H NMR δ 0.92 (s, 3 H), 1.00 (s, 3 H), 1.58 (s, 3 H), 1.59 (s, 3 H), 1.60 (br d, J = 14 Hz, 1 H), 1.82 (m, 1 H), 1.94 (br d, J = 17.2 Hz, 1 H), 2.10 (br dd, J = 17.4, 4.5 Hz, 1 H), 4.22 (dd, J = 9.20, 5.5 Hz, 1 H), 4.60 (s, 3 H); IR (Nujol) 2050, 1965, 1935 s, 1900 s cm^{-1}; mass spectrum, m/e (rel intensity) 504 M$^+$ (^{184}W) (17), 476 (6), 448 (18), 420 (33), 392 (7), 364 (44), 347 (42), 334 (30), 320 (100), 313 (34), 304 (23), 135 (31), 119 (21), 105 (30), 91 (33), 77 (24), 55 (27); calcd for $C_{17}H_{20}O_6{}^{184}W$ m/e 504.0770, measured m/e 504.0773. Anal. Calcd for $C_{17}H_{20}O_6W$: C, 40.49; H, 3.97. Found: C, 40.92; H, 4.02.

Reactions with Cyclopentadiene. The procedure for the unsaturated vinyl complexes **9** and **11** involves addition of freshly distilled cyclopentadiene (100 equiv) to a solution of the carbene complex in benzene (0.11 M) and stirring for 3 min at 25 °C. For the substituted complexes **12**, **13**, **14**, **15**, and **16** the reactions were conducted in excess, neat cyclopentadiene after deoxygenation by the freeze–thaw method (see Table III for reaction temperatures and times). The excess diene was removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with hexane. The endo and exo cycloadducts with cyclopentadiene could not be separated by column chromatography, and thus the spectral data for each cycloadduct were collected on the mixture of endo and exo cycloadducts. The spectral data are presented only for the endo cycloadduct **a** in those cases where the endo/exo selectivity is ≥85:15.

55a: ^{1}H NMR δ 1.31 (m, 1 H), 1.46 (br s, 2 H), 1.88 (m, 1 H), 2.94 (br s, 1 H), 3.43 (br s, 1 H), 4.69 (br s, 4 H), 5.69 (br s, 1 H), 6.15 (br s, 1 H); IR ($CDCl_3$) 2040, 1970, 1930 s cm^{-1}; mass spectrum, m/e (rel intensity) 328 M$^+$ (3), 300 (3), 272 (8), 244 (8), 216 (15), 188 (53).

56a: ^{1}H NMR δ 1.35 (ddd, J = 12, 5, 2 Hz, collapses to a broad d with J = 12 Hz upon $h\nu$ at δ = 4.47, 1 H), 1.42 (m, 2 H), 1.85 (ddd, J = 11, 8, 4 Hz, collapses to a dd with J = 8, 4 Hz upon $h\nu$ at δ = 1.35 and to a dd with J = 1 and 4 Hz upon $h\nu$ at δ = 4.47, 1 H), 2.94 (br s, 1 H), 3.45 (br s, 1 H), 4.47 (m, collapses to dd with J = 8 and 5 Hz upon $h\nu$ at δ = 3.41, 1 H), 4.50 (s, 3 H), 5.69 (dd, J = 5, 2.5 Hz, collapses to a d with J = 5 Hz upon $h\nu$ at δ = 3.45, 1 H), 6.14 (dd, J = 5, 2.5 Hz, collapses to a d with J = 5 Hz upon $h\nu$ at δ = 2.94, 1 H); IR ($CHCl_3$) 2065, 1980, 1935 s cm^{-1}.

The identity of the above cycloadducts was confirmed, and the isomeric composition was determined by conversion to a mixture of the known methyl esters **54a,b**. In separate reactions the pure carbene complexes **9** and **11** were mixed with excess cyclopentadiene in benzene as described above and stirred until the reaction was complete. The entire reaction mixture was oxidized by adding a solution of $(NH_4)_2Ce(NO_3)_6$ (3 equiv) in acetone and stirring for 10 min. The mixture was diluted with ether, washed with water, dried with sodium sulfate, and stripped of solvents. The resulting mixture of methyl esters **54a,b** had identical retention times (5.1 and 4.3 min, respectively) by gas chromatography ($^1/_8$ in. × 6 in. FAPP on Chromosorb H, A.W., 110 °C) and a ^{1}H NMR (500 MHz) spectrum identical with that of an authentic mixture of the esters prepared by the reaction of methyl acrylate and cyclopentadiene. Assuming equal response factors for the two isomers, the spectrum gives the reported ratio of 78:22 for the authentic esters.[31] The ratios for the Diels–Alder reactions of the complexes from GC are thus 94:6 (Cr) and 93:7 (W).

Attempts at equilibrating the tungsten endo and exo complexes **56a** and **56b** were made with sodium methoxide in methanol. a 13.3:1 mixture of the tungsten complexes **56a** and **56b** was dissolved in methanol-d_4, and a catalytic amount of sodium methoxide was added. After 1.5 h the ratio had decreased to 5.8:1.0; however, the α proton at δ = 4.47 had been completely exchanged. Prolonged treatment of a separate sample with sodium methoxide in methanol for 48 h gave a low recovery (~10%) of a 1.0:5.9 mixture of **56a** and **56b**, which was enriched in the endo isomer **56b**: ^{1}H NMR ($CDCl_3$), δ = 1.2–1.6 (m, 4 H), 2.90 (bs. 1 H), 2.95 (bs, 1 H), 3.90 (m, 1 H), 4.61 (s, 3 H), 6.16 (m, 1 H), 6.20 (m, 1 H). This ratio was determined by integration of the methoxyl protons. The isomeric composition of this enriched mixture was not altered by exposure to the reaction conditions nor by oxidation to the methyl esters as described above. Thus the ratios of endo adducts a to exo adducts b in Table III represent kinetic values.

58a: mp 50–65 °C; dec; ^{1}H NMR δ 1.12 (d, J = 7.0 Hz, 3 H), 1.42 (dd, J = 8.6, 1.7 Hz, 1 H), 1.68 (br d, J = 8.6 Hz, 1 H), 1.74 (m, 1 H), 2.47 (br s, 1 H), 3.33 (br s, 1 H), 4.25 (dd, J = 3.0, 4.6 Hz, collapses to a d with J = 4.5 Hz upon $h\nu$ at δ = 3.33, 1 H), 4.65 (s, 3 H), 5.62 (dd, J = 2.7, 5.5 Hz, 1 H), 6.24 (dd, J = 3.2, 5.4 Hz, 1 H); IR (Nujol) 2050, 1880 brs cm^{-1}; mass spectrum, m/e (rel intensity) 342 M$^+$ (2), 314 (2), 286 (5), 258 (5), 230 (13), 202 (34), 148 (23), 136 (32), 117 (17), 93 (11), 82 (13), 66 (10), 52 (100); calcd for $C_{15}H_{14}O_6{}^{52}Cr$ m/e 342.0195, measured m/e 342.0194. Anal. Calcd for $C_{15}H_{14}O_6Cr$: C, 52.63; H, 4.09. Found: C, 52.51; H, 4.15.

59a: ^{1}H NMR δ 1.13 (d, J = 6.9 Hz, 3 H), 1.42 (dd, J = 8.6, 1.6 Hz, 1 H), 1.69 (br d, J = 8.6 Hz, 1 H), 1.77 (m, 1 H), 2.51 (br s, 1 H), 3.35 (br s, 1 H), 4.18 (dd, J = 4.6, 3.0 Hz, 1 H), 4.49 (s, 3 H), 5.66 (dd, J = 5.6, 2.8 Hz, 1 H), 6.24 (dd, J = 5.5, 3.3 Hz, 1 H); IR (Nujol) 2050, 1975, 1930 s, 1895 s cm^{-1}; mass spectrum, m/e (rel intensity) 474 M$^+$ (^{184}W) (20), 446 (20), 418 (24), 408 (28), 390 (13), 380 (44), 362 (23), 354 (51), 334 (50), 326 (63), 319 (99), 304 (71), 296 (58), 289 (73), 266 (100), 251 (46), 240 (36), 223 (35), 143 (20), 119 (22), 91 (33), 77 (35), 66 (70); calcd for $C_{15}H_{14}O_6{}^{184}W$ m/e 474.0300, measured m/e 474.0307. Anal. Calcd for $C_{15}H_{14}O_6W$: C, 37.99; H, 2.95. Found: C, 38.19; H, 2.97.

61a: ^{1}H NMR δ 0.69 (d, J = 7.2 Hz, 3 H), 1.42 (m, 2 H), 2.71 (br s, 1 H), 2.91 (m, 1 H), 2.99 (br s, 1 H), 4.53 (s, 3 H), 4.94 (dd, J = 2.6, 9.8 Hz, 1 H), 6.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.4, 42.7, 49.1, 49.8, 50.5, 70.3, 77.3, 133.4, 136.1, 198.1, 204.1, 342.7; IR (Nujol) 2050, 1920 br s cm^{-1}; mass spectrum, m/e (rel intensity) 476 (281), 474 (30), 446 (8), 418 (20), 408 (10), 380 (15), 352 (55), 314 (85), 304 (53), 289 (44), 268 (100), 251 (37), 238 (35), 223 (35), 119 (42).

63a and 63b. The following spectral data represents a mixture of both endo and exo cycloadducts (absorptions assignable to the major adduct indicated by asterisk): ^{1}H NMR δ 1.04 (s, 3 H), 1.05 (br d, J = 9 Hz, 1 H), 1.23 (dd, J = 12.0, 2.5 Hz, 1 H), 1.31* (s, 3 H), 1.45 (m, 2 H), 1.59 (d, J = 8.8 Hz, 1 H), 2.00 (dd, J = 12.1, 3.5 Hz, 1 H), 2.73 (dd, J = 12.2, 2.5 Hz, 1 H), 2.76 (dd, J = 12.4, 4.2 Hz, 1 H), 2.83 (br s, 1 H), 2.89 (br s, 1 H), 2.92 (br s, 1 H), 3.44 (br s, 1 H), 4.64* (s, 3 H), 4.70 (s, 3 H), 5.90 (dd, J = 5.5, 2.6 Hz, 1 H), 6.06 (dd, J = 5.5, 2.9 Hz, 1 H), 6.11 (m, 1 H), 6.30 (dd, J = 5.5, 2.9 Hz, 1 H); IR (Nujol) 2050, 1900 br s cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_6W$: C, 37.99; H, 2.95. Found: C, 37.92; H, 2.96.

65a and 65b. The following spectral data represent a miture of both endo and exo cycloadducts (absorptions assignable to the major adduct indicated by asterisk): ^{1}H NMR δ 0.74 (s, 3 H), 1.02* (s, 3 H), 1.18* (s, 3 H), 1.37 (m, 2 H), 1.46 (s, 3 H), 1.76 (d, J = 8.7 Hz, 1 H), 2.00* (d, J = 8.84 Hz, 1 H), 2.27* (br s, 1 H), 2.35 (br s, 1 H), 2.68* (br s, 1 H), 3.05 (br s, 1 H), 3.92* (d, J = 1.2 Hz, 1 H), 4.53 (s, 3 H), 4.64* (s, 3 H), 4.77 (d, J = 2.6 Hz, 1 H), 5.91 (m, 1 H), 6.20 (m, 2 H), 6.25 (dd, J = 3.1, 5.4 Hz, 1 H); IR (Nujol) 2050, 1925 br s cm^{-1}.

Reactions with 2-Methoxy-1,3-butadiene. The general procedure involves dissolving the vinyl carbene complexes **13**, **15**, and **16** in excess 2-methoxy-1,3-butadiene, deoxygenating, and allowing to react under the conditions indicated in Table V. The excess diene was removed under vacuum (0.1 mmHg) at 25 °C and the residue was chromatographed using a 1:1:10 Et_2O–CH_2Cl_2–hexane solvent mixture for cycloadducts **66** and **68** and a 1:1:30 Et_2O–CH_2Cl_2–hexane mixture for **69**.

66: ^{1}H NMR δ 0.95 (d, J = 6.2 Hz, 3 H), 1.80–1.95 (m, 2 H), 2.04–2.09 (m, 2 H), 2.35 (td, J = 15.9, 5.0 Hz, collapses to dd with J = 5.7, 15.9 Hz upon $h\nu$ at δ 3.94, 1 H), 3.49 (s, 3 H), 3.94 (td, J = 10.6, 4.6 Hz, collapses to t with J = 10.6 Hz upon $h\nu$ at δ 2.35, 1 H), 4.57 (brd, J = 5.7 Hz, collapses to a br s upon $h\nu$ at δ 3.94, 1 H), 4.64 (s, 3 H); IR 2920, 2050 sh, 1910 s, 1710, 1440, 1225 cm^{-1}; mass spectrum, m/e (rel intensity) 492 M$^+$ (^{184}W) (6), 464 (14), 436 (12), 408 (6), 380 (2), 362 (100), 334 (35), 305 (16), 125 (11), 91 (12), 77 (13); calcd for $C_{15}H_{16}O_7{}^{184}W$ m/e 492.0405, measured m/e 492.0388. Anal. Calcd for $C_{15}H_{16}O_7W$: C, 36.60; H, 3.25. Found: C, 36.39; H, 3.20.

68: mp 40–42 °C; ^{1}H NMR δ 1.12 (s, 3 H), 1.56 (m, 1 H), 2.00–2.10 (m, 3 H), 2.20 (br dd, J = 16.5, 3.5 Hz, collapses to d with J = 16.5 Hz upon $h\nu$ at δ 4.59 and to a br s upon $h\nu$ at δ 2.88, 1 H), 2.88 (br d, J = 16.5 Hz, 1 H), 3.49 (s, 3 H), 4.59 (m, collapses to d with J = 3.6 Hz upon $h\nu$ at δ 2.88, 1 H), 4.73 (s, 3 H); IR (Nujol) 2050, 1900 s cm^{-1}; mass spectrum, m/e (rel intensity) 492 M$^+$ (^{184}W) (2), 464 (22), 436

(21), 408 (4), 380 (6), 362 (100), 332 (89), 321 (15), 304 (29), 291 (12), 277 (15), 266 (11), 239 (10), 137 (13), 123 (28), 109 (17), 91 (43), 77 (34); calcd for $C_{15}H_{16}O_7{}^{184}W$ *m/e* 492.0405, measured *m/e* 492.0401. Anal. Calcd for $C_{15}H_{16}O_7W$: C, 36.60; H, 3.25. Found: C, 36.65; H, 3.33.

69: ^1H NMR δ 1.00 (s, 3 H), 1.03 (s, 3 H), 1.81 (d, J = 16.6 Hz, 1 H), 1.95 (m, 1 H), 2.00 (d, J = 16.6 Hz, 1 H), 2.33 (td, J = 17, 5.5 Hz, 1 H), 3.50 (s, 3 H), 4.16 (dd, J = 7.5, 6.1 Hz, 1 H), 4.50 (brs, 1 H), 4.60 (s, 3 H); IR (Nujol) 2050, 1990, 1900 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 506 M^+ (^{184}W) (8), 478 (20), 450 (15), 422 (21), 394 (6), 366 (33), 349 (44), 336 (22), 322 (42), 317 (22), 305 (23), 293 (21), 276 (15), 135 (18), 123 (27), 105 (30), 91 (100), 79 (25); calcd for $C_{16}H_{18}O_7{}^{184}W$ *m/e* 506.0562, measured *m/e* 506.0570.

Reaction of 9 with 1-Methoxy-1,3-butadiene. A solution of vinyl carbene complex **9** (0.1 M) and 1-methoxy-1,3-butadiene (2 equiv) in benzene was deoxygenated and then stirred at 25 °C for 23 h. All volatiles were removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with a 1:1:10 Et_2O–CH_2Cl_2–hexane solvent mixture to give two yellow bands with R_f = 0.47 for **70a** and R_f = 0.35 for **70b**. Complex **70a** and **70b** were obtained in a 1.0:1.1 ratio in a total of 52% yield. Spectral data for **70a**: ^1H NMR δ 1.25–1.35 (m, 1 H), 1.80–1.90 (m, 1 H), 2.00–2.25 (m, 2 H), 3.25 (s, 3 H), 4.08 (br d, J = 8.8 Hz, 1 H), 4.21 (br t, J = 10 Hz, 1 H), 4.82 (s, 3 H), 5.73 (br s, 2 H); IR 2050, 1915 brs cm^{-1}. Spectral data for **70b**: mp 67–70 °C; ^1H NMR δ 1.55 (m, 1 H), 1.82 (ddd, J = 17.6, 12.5, 5.2 Hz, 1 H), 1.97 (m, 1 H), 2.12 (br d, J = 18.4 Hz, 1 H), 3.24 (s, 3 H), 4.12 (dt, J = 12.2, 3.2 Hz, 1 H), 4.20 (br t, J = ~3 Hz, 1 H), 4.81 (s, 3 H), 5.82 (m, 1 H), 5.96 (m, 1 H); IR (Nujol) 2050, 1940 br s cm^{-1}; mass spectrum, *m/e* (rel intensity) 346 M^+ (1), 318 (14), 290 (21), 262 (10), 234 (95), 174 (71), 161 (54), 144 (68), 128 (73), 114 (41), 91 (72), 79 (51), 69 (100); calcd for $C_{14}H_{14}O_7Cr$ *m/e* 346.0144, measured *m/e* 346.0138. Anal. Calcd for $C_{14}H_{14}O_7Cr$: C, 48.60; H, 4.08. Found: C, 48.59; H, 4.36.

Reaction of 9 with 1-Acetoxy-1,3-butadiene. A solution of complex **9** (0.853 g, 3.26 mmol) and 1-acetoxy-1,3-butadiene (0.80 mL, 6.74 mmol) in 1.0 mL of hexane was deoxygenated by the freeze–thaw method (−193 to 25 °C, three cycles) and allowed to stir under argon at room temperature for 29 h. The reaction mixture was triturated with ether, and the soluble portion was stripped of solvents by rotary evaporator. The residue was chromatographed on silica gel with a 1:1:10 mixture of Et_2O–CH_2Cl_2–hexane as eluent. The exo adduct **72a** was obtained as an orange oil (R_f = 0.22) in 9% yield (0.106 g, 0.28 mmol) and the endo adduct **72b** was obtained as a bright yellow solid (R_f = 0.19) in 10% yield (0.119 g, 0.32 mmol). Spectral data for **72a**: ^1H NMR δ 1.39 (qd, J = 12, 5.5 Hz, 1 H), 1.90 (m, 1 H), 1.99 (s, 3 H), 2.04–2.25 (m, 2 H), 4.30 (m, 1 H), 4.81 (s, 3 H), 5.54 (br t, J = 10.8 Hz, 1 H), 5.62 (br s, 1 H), 5.97 (m, 1 H); IR (Nujol) 2050, 1910 s, 1725 cm^{-1}; mass spectrum, *m/e* (rel intensity) 374 M^+ (60), 369 (48), 290 (16), 262 (50), 234 (48), 231 (62), 202 (32), 142 (55), 111 (95), 91 (45), 69 (100); calcd for $C_{15}H_{14}O_8Cr$: *m/e* 374.0093, measured *m/e* 374.0088. Spectral data for **72b**: ^1H NMR δ 1.62 (m, 1 H), 1.80 (qd, J = 12, 5.6 Hz, 1 H), 2.00 (s, 3 H), 2.10 (m, 1 H), 2.19 (m, 1 H), 4.31 (td, J = 12.1, 2.7 Hz, 1 H), 4.74 (s, 3 H), 5.59 (s, 1 H), 5.77 (m, 1 H), 5.98 (m, 1 H); IR (Nujol) 2050, 1935 s, 1900, 1725, 1225 cm^{-1}; mass spectrum *m/e* (rel intensity) 374 M^+ (2), 346 (5), 343 (5), 318 (10), 317 (14), 291 (5), 290 (20), 262 (12), 234 (51), 220 (10), 202 (66), 191 (22), 189 (7), 175 (20), 158 (10), 123 (8), 91 (100), 79 (39), 67 (27); calcd for $C_{15}H_{14}O_8Cr$ *m/e* 374.0093, measured *m/e* 374.0121.

Reaction of 11 with 1-Acetoxy-1,3-butadiene. A solution of vinyl carbene complex **11** (0.1 M) and 1-acetoxy-1,3-butadiene (2.8 equiv) in benzene was deoxygenated and then stirred at 25 °C for 8 days. All volatiles were removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with a 1:1:10 Et_2O–CH_2Cl_2–hexane solvent mixture. The spectral data listed below represent a mixture of endo and exo cycloadducts. Assignments of endo and exo adducts **73a** and **73b** were made by comparison with chemical shifts of acetyl methyl in the exo and endo adducts **78a** and **78b**. The following data were collected for **73a** and **73b**: ^1H NMR δ 1.65–1.70 (m), 1.8–1.95 (m), 2.00 (s, major isomer), 2.01 (s), 2.03–2.25 (m), 4.18 (td, J = 12.3, 2.9 Hz, major isomer), 4.30 (tm, minor isomer), 4.56 (s, major isomer), 4.62 (s), 5.53–5.65 (m), 5.77–5.87 (m), 5.95–6.03 (m); IR (Nugol) 2075, 1935 cm^{-1}.

Reactions of 12 with 1-Methoxy-1,3-butadiene. The vinyl carbene complex 12 was dissolved in excess 1-methoxy-1,3-butadiene (10 equiv), and the mixture was deoxygenated. The vessel was then charged with CO gas (approximately 1.2 atm, with the system open to a CO inflated rubber balloon) and allowed to react at 25 °C for 26 h. The excess diene was removed under vacuum (0.1 mmHg at 25 °C, and chromatography with a 1:1:10 Et_2O–CH_2Cl_2–hexane solvent mixture gave two yellow bands with R_f = 0.53 for **75a** and R_f = 0.33 for **75b**. Collection of the bands gave a 32% yield of **75a** and a 50% yield of **75b**. Spectral data for **75a**: ^1H NMR δ 0.91 (d, J = 6.4 Hz, 3 H), 1.85–2.03 (m, 3 H), 3.24 (s, 3 H), 3.86 (br d, J = 8.7 Hz, 1 H), 4.19 (br t, J = 9.3 Hz, 1 H), 4.88 (s, 3 H), 5.68–5.74 (m, 2 H); IR 2050, 1915 brs cm^{-1}; mass spectrum, *m/e* (rel intensity) 360 M^+ (1), 332 (11), 304 (13), 276 (15), 272 (18), 248 (66), 220 (100), 205 (5), 189 (6), 175 (26), 158 (79), 137 (5), 123 (81), 105 (3), 91 (32), 84 (30), 77 (24); calcd for $C_{15}H_{16}O_7Cr$ *m/e* 360.0301, measured *m/e* 360.0329. Spectral data for **75b**: mp 39–41 °C; ^1H NMR δ 0.86 (d, J = 6.2 Hz, 3 H), 1.71 (br dd, J = 18.2, 10.6 Hz, 1 H), 2.10–2.20 (m, 2 H), 3.23 (s, 3 H), 4.07–4.12 (m, 2 H, appears as a dd with J = 10.9, 3.9 Hz at δ 4.06 and a m at δ 4.12 in benzene-d_6), 4.87 (s, 3 H), 5.86 (m, 1 H), 5.95 (m, 1 H); IR (Nujol) 2060, 1945 br s cm^{-1}; mass spectrum, *m/e* (rel intensity) 360 M^+ (2), 332 (48), 304 (8), 276 (15), 248 (38), 220 (8), 188 (15), 175 (38), 158 (20), 145 (20), 128 (38), 92 (45), 75 (40), 52 (100); calcd for $C_{15}H_{16}O_7Cr$ *m/e* 360.0301, measured *m/e* 360.0329. Anal. Calcd for $C_{15}H_{16}O_7Cr$: C, 50.04; H, 4.48. Found: C, 49.79; H, 4.73.

When the same reaction is conducted in the absence of CO a third, red, complex, **79**, is obtained with this spectral data: R_f = 0.44; mp 73–75 °C, ^1H NMR ($CDCl_3$ with very broad absorptions at 25 °C, very little change on heating to 80 °C in benzene-d_6) δ 0.91 (br d, $J \approx 6$ Hz, 3 H), 1.7–1.8 (br m, 1 H), 2.1–2.4 (br m, 2 H), 3.55–3.65 (br s, 1 H), 3.57 (br s, 3 H), 4.5–4.6 (br s, 1 H), 4.72 (br s, 3 H), 5.95–6.00 (br m, 1 H), 6.15–6.20 (br m, 1 H); IR (Nujol) 2010, 1930, 1910 s, 1855 cm^{-1}; mass spectrum, *m/e* (rel intensity) 332 M^+ (16), 304 (19), 276 (24), 248 (70), 220 (49), 175 (60), 158 (57), 123 (51), 105 (50), 93 (82), 91 (92), 84 (100); calcd for $C_{14}H_{16}O_6Cr$ *m/e* 332.0351, measured *m/e* 332.0342. Anal. Calcd for $C_{14}H_{16}O_6$ Cr: C, 50.60; H, 4.82. Found: C, 50.33; H, 5.04.

The assignment of the stereochemistry of the chelated adduct **79** was made as endo on the basis of the following experiments. When a deoxygenated THF solution of the nonchelated endo adduct **75b** was heated at 56 °C for 45 h a 79% yield of **79** was obtained along with a 17% recovery of **75b**. The nonchelated exo adduct **75a** was recovered in 96% yield when heated in deoxygenated THF at 47 °C for 48 h. Furthermore, when a degassed THF solution of the chelated adduct **79** was exposed to an atmosphere of carbon monoxide (under a balloon) for 42 h at 25 °C a 1.5:1 mixture of **79** and the endo adduct **75b** was produced and the presence of the exo adduct **75a** could not be detected.

Base-Induced Elimination of Methanol from the Exo Cycloadduct 75a. The exo cycloadduct **75a** (97.5 mg, 0.27 mmol) was combined with 10 mL of anhydrous ether, 14.5 mg (0.27 mmol) of sodium methoxide, and 4 mL of CH_2Cl_2 in a side-armed flask. The mixture was degassed by the freeze–thaw method and then stirred at 25 °C. No reaction was observed by TLC after stirring for 17 h. To the mixture was added 33 mg (0.27 mmol) of DMAP and stirring continued at 25 °C. The red elimination product **80** appeared by TLC within 3 h. After 28 h the reaction mixture was transferred with ether to a separatory funnel where the organic phase was washed three times with 15-mL portions of 1 M HCl and twice with brine. The organic phase was dried over $MgSO_4$ and filtered. The residue was chromatographed with a 1:1:10 mixture of CH_2Cl_2–Et_2O–hexane on silica gel. The elimination product **80** (R_f = 0.79) was obtained in 38% yield (34 mg, 0.10 mmol) along with a 59% recovery of the exo cycloadduct **75a** (58 mg, 0.16 mmol, R_f = 0.63). An unidentified yellow band was also obtained (14 mg, R_f = 0.33) which only displayed resonances due to DMAP in the ^1H NMR. Optimal conditions for the elimination of methanol from the exo adduct **75a** have not been found, although elimination could be affected by treatment with alumina but in lower yields. Spectral data for **80**: ^1H NMR ($CDCl_3$) δ 0.93 (d, J = 7.1 Hz, 3 H), 2.13–2.22 (m, 1 H), 2.44–2.55 (m, 1 H), 2.84–2.93 (m, 1 H), 4.74 (s, 3 H), 6.12–6.19 (m, 1 H), 6.21–6.27 (m, 1 H, 6.96 (d, J = 5.9 Hz, 1 H); IR ($CHCl_3$) 2927 s, 2855 s, 2056 m, 1939 s, 1103 w, 1001 w, 982 w cm^{-1}.

A side-by-side comparison of the rate of elimination of methanol with DMAP was examined for the endo and exo cycloadducts **75b** and **75a**. A solution of 274 mg of **75b** (0.76 mmol) in 15 mL of dry ether under a nitrogen atmosphere was treated with 92.8 mg (0.76 mmol) of DMAP. After stirring at 25 °C for 1 h only the starting material was present by TLC analysis, and the color of the initially orange solution remained unchanged. After employing the workup described above, removal of solvents left 272 mg of **75b** (99% recovery) which by ^1H NMR did not contain any of the eliminated product **80**. In a similar experiment, a solution of 136 mg of the exo cycloadduct **75a** (0.38 mmol) in 10 mL of ether under nitrogen was treated with 46.4 mg (0.38 mmol) of DMAP. The initially orange solution of **75a** became red within 10 min at 25 °C. After 1 h, the reaction was worked up as described above. Chromatography of the crude residue, as described above, gave an 18% yield (22 mg, 0.067 mmol) of the elimination product **80** as a red oil. Further elution produced a 68% recovery (94 mg, 0.26 mmol) of the exo adduct **75a**.

Reaction of 13 with 1-Methoxy-1,3-butadiene. The vinyl carbene

complex **13** was dissolved in 10 equiv of 1-methoxy-1,3-butadiene, deoxygenated, and allowed to react at 25 °C for 30 h. The excess diene was removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with a 1:1:10 (Et_2O–CH_2Cl_2–hexane) solvent mixture to give two separable yellow bands with R_f = 0.38 for **76a** and R_f = 0.25 for **76b** in a 1.0:1.7 ratio in a total of 79% yield. Spectral data for **76a**: ^1H NMR δ 0.96 (d, J = 6.4 Hz, 3 H), 1.85–2.03 (m, 3 H), 3.26 (s, 3 H), 3.92 (br d, J = 8.9 Hz, collapses to a br s upon $h\nu$ at δ 4.16, no change in coupling pattern upon $h\nu$ at δ 1.85–2.03 as well as δ 5.72, 1 H), 4.16 (br t, J = 9.7, collapses to d with J = 9.0 Hz upon $h\nu$ at 1.85–2.03, collapses to d with J = 9.0 Hz upon $h\nu$ at 3.92, no change in coupling pattern upon $h\nu$ at δ 5.72, 1 H), 4.69 (s, 3 H), 5.72 (m, 2 H); IR (Nujol) 2060, 1980, 1925 br s cm^{-1}; mass spectrum, m/e (rel intensity) 492 M^+ (^{184}W) (8), 464 (33), 436 (19), 408 (18), 380 (17), 361 (86), 352 (49), 332 (77), 314 (33), 305 (53), 301 (60), 291 (34), 275 (31), 249 (22), 238 (22), 224 (20), 137 (85), 123 (43), 105 (44), 91 (100), 77 (80); calcd for $C_{15}H_{16}O_7{}^{184}W$ m/e 492.0406, measured m/e 492.0409. Spectral data for **76b**: mp 72–74 °C; ^1H NMR δ 0.90 (d, J = 6.4 Hz, 3 H), 1.71 (ddd, J = 18.2, 10.4, 1.4 Hz, 1 H), 2.13–2.24 (m, 2 H), 3.24 (s, 3 H), 4.05 (dd, J = 3.8, 11.1 Hz, collapses to a d with J = 11 Hz upon $h\nu$ at δ 4.11, collapses to a d with J = 3.8 Hz upon $h\nu$ at δ 2.13–2.24, 1H), 4.11 (br t, $J \approx 4$ Hz, no change in coupling pattern upon $h\nu$ at δ 2.13–2.24, 1 H), 4.71 (s, 3 H), 5.87 (m, collapses to d with J = 9.9 Hz upon $h\nu$ at δ 4.11, 1 H), 5.94 (m, 1 H); IR (Nujol) 2060, 1925 brs cm^{-1}; mass spectrum, m/e (rel intensity) 464 M – CO (^{184}W) (40), 436 (14), 408 (30), 380 (3), 352 (76), 337 (21), 314 (79), 307 100), 298 (78), 289 (45), 258 (38), 238 (20), 224 (12), 91 (89), 77 (61); calcd for $C_{15}H_{17}O_7{}^{184}W$ (CI, CH_4, $^{m+}$ + 1) m/e 493.0484, measured m/e 493.0473. Anal. Calcd for $C_{15}H_{16}O_7W$: C, 36.60; H, 3.25. Found: C, 36.63; H, 3.20.

Reactions of 13 with 1-Acetoxy-1,3-butadiene. A solution of vinyl complex **13** (0.25 M) and 20 equiv of 1-acetoxy-1,3-butadiene (~1:2 mixture of cis–trans isomers) in benzene was deoxygenated and then stirred at 60 °C for 6 days. All volatiles were removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with a 1:1:4 (Et_2O–CH_2Cl_2–hexane) solvent mixture. The spectral data listed below represent a mixture of endo and exo cycloadducts **78a** and **78b**. (Assignments of endo and exo adducts were made by comparison with chemical shifts of the aliphatic CH_3 (d) in exo and endo adducts **78a** and **78b**): ^1H NMR δ 0.94 (d, J = 6.2 Hz, major isomer), 1.01 (d, J = 6.4 Hz), 1.77–2.30 (m), 2.00 (s, major isomer), 2.03 (s), 4.23 (m), 4.60 (s, major isomer), 4.68 (s), 5.49 (br d, J = 9.1 Hz), 5.76 (m), 5.96 (m); IR 2060, 1910 br s, 1730, 1225 cm^{-1}.

Reactions of 16 with 1-Methoxy-1,3-butadiene. The vinyl carbene complex **16** was dissolved in an excess of 1-methoxy-1,3-butadiene (10 equiv), and the mixture was deoxygenated. TLC analysis after heating at 60 °C for 5 days revealed the presence of **16** and two yellow bands. The mixture was heated an additional 4 days at 85 °C resulting in the disappearance of the yellow bands and the appearance of a single red band. The excess diene was removed under vacuum (0.1 mmHg) at 25 °C, and the residue was chromatographed with a 1:1:10 (Et_2O–CH_2Cl_2–hexane) solvent mixture. The red band (R_f = 0.27) was collected to give a 7% yield of a compound **124** that was identified as the endo cycloadduct with a chelated methoxyl as in **79**. Spectral data for **124**: ^1H NMR δ 0.63 (s, 3 H), 1.10 (s, 3 H), 2.19 (s, 1 H), 2.61 (dd, J = 17.1, 2.7 Hz, 1 H), 2.76 (d, J = 17.1 Hz, 1 H), 3.43 (s, 3 H), 4.20 (s, 1 H), 4.34 (s, 3 H), 4.80 (d of m, J = 8.9, 1 H), 5.48 (br d, J = 8.9 Hz, 1 H); IR (Nujol) 2020 m, 1935 s, 1910 s, 1860 s cm^{-1}; mass spectrum, (rel intensity) 478 M^+ (^{184}W) (22), 422 (8), 366 (42), 323 (38), 314 (67), 305 (48), 299 (44), 236 (41), 162 (80), 151 (100), 133 (54), 113 (78); calcd for $C_{15}H_{18}O_6{}^{184}W$ m/e 478.0611, measured m/e 478.0572.

Reaction of 13 with 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (25a). The vinyl complex **13** was dissolved in a slight excess of diene **25a** (5 equiv) and stirred under air at 25 °C for 2–3 min. All volatiles were removed under vacuum (0.1 mmHg) at 25 °C over 1 h, and the residue was dissolved in a suspension of silica gel (150–200-fold excess by weight) and a 1:1:20 mixture of Et_2O–CH_2Cl_2–hexane and allowed to stand under air for 3.5 h. The mixture was filtered through a bed of Celite, and all solvent was removed. Chromatography with a 1:1:4 to 1:1:2 Et_2O–CH_2Cl_2–hexane solvent mixture gave an 85% yield of **83** as an inseparable 1:1.4 mixture of endo and exo cycloadducts (R_f = 0.31 with 1:1:2). The spectral data listed below represent a mixture of endo and exo cycloadducts: ^1H NMR δ 0.96 (d), 1.05 (d, major isomer), 1.95–2.08 (m), 2.17 (t, J = 14 Hz), 2.27 (d of m), 2.34–2.43 (m), 2.48 (dd, J = 2.9, 14.7 Hz), 2.64 (seven line m), 2.78 (d of m), 3.19 (s), 3.50 (ddd, J = 4.4, 9.0, 9.9 Hz), 4.09 (d of m), 4.20 (br d, J = 11 Hz), 4.32 (dd, J = 9.1, 9.9 Hz), 4.68 (s, major isomer), 4.69 (s); IR (Nujol) 2050, 1910 br s, 1705 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_8W$: C, 35.44, H, 3.15. Found: C, 35.31; H, 3.03.

In a separate experiment direct flash chromatography before hydrolysis using a 1:1:20 Et_2O–CH_2Cl_2–hexane solvent mixture allowed isolation of at least some of **81a** (R_f = 0.39, 18%) and **81b** (R_f = 0.25, 8%) for characterization. Further elution with a 1:1:2 solvent mixture gave another 48% of the hydrolyzed product **83**. Spectral data for **81a**: ^1H NMR δ 0.21 (s, 9 H), 0.96 (d, J = 6.5 Hz, 3 H), 1.92 (br d, J = 6.8, 2 H), 2.00 (m, 1 H), 3.20 (s, 3 H), 4.00 (dd, J = 8.3, 1.7 Hz, collapses to d with J = 8.3 Hz upon $h\nu$ at δ 4.90, no change in coupling pattern upon $h\nu$ at δ 1.92–2.00, 1 H), 4.07 (br t, J = 8.3 Hz, collapses to d with J = 8.3 Hz upon $h\nu$ at δ 1.92–2.00, no change in coupling pattern upon $h\nu$ at δ 4.90, 1 H), 4.67 (s, 3 H), 4.90 (br s, 1 H); IR (neat) 2060, 1905 br s cm^{-1}; mass spectrum, m/e (rel intensity) 580 M^+ (^{184}W) (0.4), 552 (3), 524 (1), 496 (1), 468 (1), 440 (7), 420 (15), 395 (13), 339 (13), 261.6 (100), 182 (16), 167 (20), 73 (72); calcd for $C_{17}H_{24}O_7Si^{186}W$ m/e 554.0835, measured m/e 554.0863. Spectral data for **81b**: 0.22 (s, 9 H), 0.89 (d, J = 6.4 Hz, 3 H), 1.77 (dd, J = 11.0, 17.6, Hz, collapses to d with J = 17.6 Hz upon $h\nu$ at δ 2.34, 1 H), 2.07 (dd, J = 5.6, 17.6 Hz, collapses to d with J = 17.6 Hz upon $h\nu$ at δ 2.34, 1 H), 2.34 (seven line m, 1 H), 3.19 (s, 3 H), 3.97 (dd, J = 3.6, 11.4 Hz, collapses to a d with J = 3.6 Hz upon $h\nu$ at δ 2.34, collapses to a d with J = 11 Hz upon $h\nu$ at δ 4.24, no change in coupling pattern upon $h\nu$ at δ 5.13, 1 H), 4.24 (br t, J = 4.5 Hz, collapses to d with J = 3.5 Hz upon $h\nu$ at δ 5.13, no change in coupling pattern upon $h\nu$ at δ 2.24, 1 H), 4.69 (s, 3 H), 5.13 (d, J = 5.4 Hz, 1 H); IR (neat) 2060, 1910 br s cm^{-1}; mass spectrum, m/e (rel intensity) 552 M^+ – CO (^{184}W) (26) 520 (13), 492 (10), 464 (17), 440 (30), 395 (42), 338 (62), 313 (44), 182 (65), 167 (63), 151 (15), 113 (43), 89 (31), 73 (100); calcd for $C_{17}H_{24}O_7Si^{184}W$ m/e 552.0801, measured m/e 552.0774.

Reaction 13 with 1,3-Bis[(trimethylsilyl)oxy]-1,3-butadiene (25b). The vinyl complex **13** was dissolved in a slight excess of diene **25b**[59] (5 equiv, 6:1 mixture of E–Z) and stirred (under air) at 25 °C for 4 h. All volatiles were removed under vacuum (0.1 mmHg) at 25 °C over 1 h. The ^1H NMR spectrum of the crude reaction mixture indicated a 1.7:1 mixture of exo and endo isomers with assignments made by comparison with chemical shifts of the aliphatic CH_3 (d) in **81a** and **81b**. The residue was dissolved in a suspension of silica gel (150–200-fold excess by weight) and hexane and allowed to stand under air for 4 h. The mixture was filtered through a bed of Celite, and all solvent was removed. Chromatography with a 1:1:4 solvent mixture gave a 70% yield of **84** as an inseparable 2.8:1 mixture of exo and endo cycloadducts (R_f = 0.13). The spectral data listed below represent a mixture of endo and exo (major) cycloadducts: ^1H NMR δ 0.055 (s), 0.95 (d, J = 6.6 Hz, endo adduct) 1.06 (d, J = 6.6 Hz, exo adduct), 1.91 (m), 2.03 (dd, J = 13.0, 14.4 Hz), 2.16 (t, J = 14 Hz) 2.26 (d of m), 2.35 (d of m), 2.44–2.61 (m), 2.69 (seven-line m), 4.00 (td, J = 10.2, 5.1 Hz, exo adduct) 4.22 (d, J = 11.1 Hz, endo adduct), 4.37 (t, J = 10.0 Hz, exo adduct), 4.61 (d of m, endo adduct), 4.67 (s, endo adduct) 4.70 (s, exo adduct); IR (neat) 2060, 1900 br s, 1700 cm^{-1}. Anal. Calcd for $C_{17}H_{22}O_8SiW$: C, 36.05; H, 3.89. Found: C, 35.80; H, 3.82.

Further elution with 2:1:1 (Et_2O–CH_2Cl_2–hexane) solvent mixture allowed isolation of 11% of **85** as a 1:2 mixture of exo and endo adducts. Spectral data of the mixture: ^1H NMR δ 1.02 (d, J = 6.6 Hz, endo adduct), 1.07 (d, J = 6.6 Hz, exo adduct), 1.63 (br s) 1.90 (br s), 1.95–2.69 (m), 4.03 (six-line m, exo adduct), 4.30 (t, J = 9.8 Hz, exo adduct), 4.34 (d, J = 11.3 Hz, endo adduct), 4.55 (br s, endo adduct), 4.71 (s, overlapping endo and exo adduct); IR (neat) 2420 br, 2060, 1920 br s, 1705 cm^{-1}.

Reaction of 15 with 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (25a). The vinyl complex **15** was dissolved in a slight excess of diene **25a** (10 equiv) and stirred at 25 °C for 10 min. All volatiles were then removed under vacuum (0.1 mmHg) at 25 °C over 1 h. The residue was dissolved in a 30:1 mixture of Et_2O–CF_3COOH and stirred under air at 25 °C for 1 h. This was filtered through a bed of Celite, extracted several times with a saturated, aqueous solution of $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was chromatographed with a 1:1:4 (Et_2O–CH_2Cl_2–hexane) solvent mixture to give a 56% yield of **87** (R_f = 0.12): ^1H NMR δ 1.34 (s, 3 H), 1.91–1.95 (m, 1 H), 2.27–2.34 (m, 1 H), 2.43–2.49 (m, 2 H), 4.74 (s, 3 H), 6.09 (d, J = 10.2 Hz, 1 H), 7.23 (d, J = 10.2 Hz, 1 H); IR (Nujol) 2050, 1890 br s, 1660 cm^{-1}; mass spectrum, m/e (rel intensity) 476 M^+ (^{184}W) (4), 448 (33), 420 (16), 392 (53), 362 (64), 347 (90), 308 (34), 105 (100); calcd for $C_{14}H_{12}O_7{}^{184}W$ m/e 476.0092, measured m/e 476.0077.

In a separate experiment, hydrolysis of the reaction mixture on silica gel as described for the reaction of **13** with **25a** gave a 2:1 mixture of cycloadducts **86**. Chromatography with a 1:1:4 (Et_2O–CH_2Cl_2–hexane) solvent mixture allowed isolation of some of each isomer; however, the determination of the stereochemistry of each could not be made. Spectral data for the minor adduct (R_f = 0.17): ^1H NMR δ 1.50 (s, 3 H), 2.00 (m, 1 H), 2.14 (m, 1 H), 2.25 (m, 1 H), 2.36 (m, 1 H), 2.45 (m, 1 H),

2.59 (ddd, J = 14.8, 7.4, 1.1 Hz, 1 H), 3.31 (s, 3 H), 4.20 (dd, J = 6.9, 3.7 Hz, 1 H), 4.81 (s, 3 H), IR 2060, 1900 s, 1710 cm^{-1}. Spectral data for the major adduct (R_f = 0.13): ^{1}H NMR δ 1.25 (s, 3 H), 2.31 (m, 1 H), 2.46–2.51 (m, 3 H), 2.68–2.78 (m, 2 H), 3.18 (s, 3 H), 4.18 (br s, 1 H), 4.78 (s, 3 H). IR (neat) 2060, 1900 s, 1710 cm^{-1}.

Reaction of 16 with 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (25a). The vinyl complex **16** was dissolved in a slight excess of diene **25a** (5 equiv), and the mixture was deoxygenated. This was then stirred at 25 °C for 50 h. All volatiles were removed under vacuum (0.1 mmHg), and the residue was dissolved in a suspension of silica gel (150–200-fold excess by weight) in hexane and allowed to stand under air for 2.5 h. The mixture was filtered through a bed of Celite, and all solvent was removed. Chromatography with a 1:1:10 to 1:1:4 (Et_2O–CH_2Cl_2–hexane) solvent mixture gave two yellow bands with R_f = 0.23 (1:1:4, 28%) for exo adduct **88a** and R_f = 0.18 (1:1:4, 16%) for endo adduct **88b**. Spectral data for **88b**: ^{1}H NMR δ 1.00 (s, 3 H), 1.11 (s, 3 H), 1.97 (d, J = 14.6 Hz, 1 H), 2.51 (dd, J = 14.3, 10.4 Hz, 1 H), 2.53 (d, J = 14.6 Hz, 1 H), 2.75 (dd, J = 14.4, 5.6 Hz, 1 H), 3.26 (s, 3 H), 3.89 (td, J = 10.4, 5.7 Hz, 1 H), 4.73 (s, 3 H), 4.91 (d, J = 5.8 Hz, 1 H); IR (Nujol), 2060, 1980, 1915 br s, 1700 cm^{-1}. Spectral data for **88a**: mp 80–100 °C dec; ^{1}H NMR δ 0.89 (s, 3 H), 1.19 (s, 3 H), 2.09 (d, J = 14 Hz, 1 H), 2.36 (d, J = 14 Hz, 1 H), 2.39 (dd, J = 14.1, 8.9 Hz, 1 H), 2.80 (ddd, J = 14.1, 5.1, 1.1 Hz, 1 H), 3.22 (s, 3 H), 3.74 (ddd, J = 8.9, 8.9, 5.1 Hz, 1 H), 4.68 (d, J = 8.9 Hz, 1 H), 4.72 (s, 3 H); IR (Nujol) 2060, 1980 sh, 1900, 1700 cm^{-1}; mass spectrum, m/e (rel intensity) 522 M$^+$ (^{184}W) (1), 494 (15), 466 (13), 438 (2), 410 (15), 382 (10), 367 (14), 337 (18), 314 (18), 299 (27), 167 (100), 125 (55), 119 (40), 105 (39), 91 (28), 84 (69); calcd for $C_{16}H_{18}O_8{}^{184}W$ m/e 522.0511, measured m/e 522.0504. Anal. Calcd for $C_{16}H_{18}O_8W$: C, 36.86; H, 3.45. Found: C, 36.88; H, 3.42.

Preparation of 1-Methoxy-2-ethoxycyclobutanone (90). This compound was prepared according to the procedure described for related cyclobutanones.[61] In a three-necked, round-bottom flask equipped with an overhead stirrer and reflux condenser were placed 350 mL of CH_3CN (3.75 M), 149 mL (1.56 mol, 1.44 equiv) of ethyl vinyl ether, and 198 mL (1.42 mol, 1.08 equiv) of triethylamine. The solution was cooled with an ice–water bath and 120 mL (1.31 mmol, 1 equiv) of α-methoxyacetyl chloride was added dropwise over 15 min. The mixture was placed in a 75 °C oil bath and stirred for 105 min. The volatiles were then removed via short-path distillation (20 mmHg). To the remaining yellow slurry was added 200 mL of anhydrous ether, and the mixture was filtered through Celite. The brown solution was concentrated on a rotary evaporator, and the residue was distilled at 0.1 mmHg using a short path (bp 37–52 °C) to give 60.122 g (417 mmol, 33% yield) of **90** as a colorless liquid. The first fractions contain only *trans*-cyclobutanone, while the later ones contain varying amounts of *cis*-cyclobutanone as a minor product. All fractions were used in the subsequent step. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27 (t, J = 7 Hz, 3 H), 2.93–2.76 (m, 2 H), 3.51 (s, 3 H), 3.53–3.65 (m, 2 H), 4.09–4.13 (m, 1 H), 4.52 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.0, 45.4, 58.2, 65.9, 70.2, 94.6, 203.3; mass spectrum, m/e (rel intensity) 144 M$^+$ (1), 102 (29), 87 (7), 74 (100), 73 (6), 59 (25); calcd for $C_7H_{12}O_3$ m/e 144.0786, measured 144.0787; IR (salt plate) 2979 m, 2935 m, 2896 m, 1789 s, 1374 w, 1204 m, 1123 s cm^{-1}.

Preparation of 1-Methoxy-2-siloxy-4-ethoxy-1,3-butadiene (27). This compound was prepared according to a procedure described for related 1,3-dienes.[61] To a solution of 8.00 g (55.5 mmol) of cyclobutanone **90** in 40 mL of CH_3CN was added 23.2 mL (166.6 mmol, 3 equiv) of triethylamine and 9.9 mL (77.8 mmol, 1.4 equiv) of TMSCl after which the mixture warmed to 60 °C and stirred overnight. The volatiles were removed on a rotory evaporator, and anhydrous ether was added. The solution was then filtered through Celite, concentrated, and distilled under vacuum (55–60 °C at 0.25 mmHg and 43–48 °C at 0.08 mmHg) to give 10.93 g (93% yield) of **27** as a colorless oil. Other runs have varied from 81–93% yield. Spectral data for **27**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.20 (s, 9 H), 1.27 (t, 3 H, J = 7.0 Hz), 3.53 (s, 3 H), 3.74 (q, J = 7.0 Hz, 2 H), 5.21 (d, J = 12.2 Hz, 1 H), 5.47 (s, 1 H), 6.51 (d, J = 12.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.20, 14.7, 56.3, 65.3, 101.5, 103.5, 132.8, 145.3; IR (salt plate) 2979 m, 2960 m, 1623 s, 1355 m, 1251 s, 1170 s, 1120 s, 1017 s, 848 s cm^{-1}; mass spectrum, m/e (rel intensity) 216 M$^+$ (5), 201 (5), 189 (3), 157 (5), 133 (50), 99 (8), 89 (12), 73 (100). Anal. Calcd for $C_{10}H_{20}O_3Si$: C, 55.52 H, 9.32. Found: C, 55.65; H, 8.90.

Reaction of the *trans*-Propenyl Carbene Complex 13 with 1-Methoxy-2-siloxy-4-ethoxy-1,3-butadiene (27). The diene **27** (0.4008 g, 1.85 mmol) and carbene complex **13** (0.4677 g, 1.15 mmol) were combined and diluted with 1.4 mL of benzene that had been distilled from sodium benzophenone ketyl and stirred under argon for 68 h, after which time the volatiles were removed on the rotory evaporator, and the residue was dissolved in about 15 mL of a 1:1:50 of mixture of ether, dichloromethane, and hexane. To this mixture was added 5 g of silica gel, and the solution was stirred for 2.5 h. The silica gel was filtered off, and the solution was concentrated on a rotory evaporator. Column chromatography on 200 mL of silica gel using a 1:1:4 mixture of ether, methylene chloride, and hexane gave two organometallic products identified as the exo and endo Diels–Alder adducts **92a** and **92b** on the basis of proton–proton decoupling experiments. Exo adduct **92a**: 0.4365 g (0.79 mmol, 69% yield); orange solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.1 (m, 6 H), 1.80, (m, collapses to dd, J = 11.2, 2.2 Hz, when δ = 1.1 is decoupled, 1 H), 2.63 (dd, J = 12, 4.4 Hz, 1 H), 2.84 (dd, J = 12, 11.5 Hz, 1 H), 3.15 (m, 2 H), 3.30 (s, 3 H), 3.5 (m, 2 H), 4.66 (s, 3 H), 4.75 (m, collapses to a broad doublet, J = 11 Hz, when δ = 3.5 is decoupled, collapses to broad doublet, J = 9.5 Hz, when δ = 1.8 is decoupled, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.6, 15.1, 37.6, 43.4, 57.8, 64.8, 70.3, 73.1, 80.7, 87.1, 197.3, 204.3, 208.5, 345.3; IR ($CHCl_3$) 2073 s, 1989 s, 1936 s, 1723 m cm^{-1}; mass spectrum, m/e (rel intensity) 552 M$^+$ (^{184}W) (2), 524 (4), 496 (10), 468 (2), 440 (10), 412 (4), 395 (10), 367 (10), 311 (10), 279 (10), 248 (10), 182 (10), 166 (20), 152 (70), 137 (20), 123 (100). Anal. Calcd for $C_{17}H_{20}O_9W$: C, 36.98; H, 3.65. Found: C, 37.10; H, 3.76. Endo adduct **91b**: 0.109 g (0.197 mmol, 17% yield); orange solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.05 (m, 6 H), 2.55 (dd, J = 14.0, 1.4 Hz, 1 H), 2.65 (m, collapses to a dd, J = 11.2, 11.2 Hz, when δ = 1.05 is decoupled, collapses to a dq, J = 11.3, 6.3 Hz, when δ = 3.4 is decoupled, 1 H), 2.80 (dd, J = 14.0, 3.5 Hz, 1 H), 3.10 (m, 1 H), 3.35 (d, J = 11 Hz, 1 H), 3.45 (s, 3 H), 3.50 (m, 1 H), 4.16 (br s, collapses to an apparent t, J = 2 Hz, when δ = 4.3 is decoupled, 1 H), 4.29 (dd, J = 11.5, 1.6 Hz, 1 H), 4.66 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.1, 17.0, 36.9, 44.3, 59.2, 64.9, 70.9, 75.2, 79.5, 88.0, 197.2, 202.2, 205.4, 334.2; IR ($CHCl_3$) 2070 s, 1981 m, 1938 s, 1732 m cm^{-1}; mass spectrum, m/e (rel intensity) 552 M$^+$ (^{184}W) (2), 524 (31), 496 (5), 468 (2), 440 (5), 412 (8), 397 (8), 369 (27), 311 (43), 279 (25), 248 (10), 105 (100), 93 (48), 91 (44), 77 (37). Anal. Calcd for $C_{17}H_{20}O_9W$: C, 36.98; H, 3.65. Found: C, 36.27; H, 3.85.

Reaction of the *cis*-Propenyl Carbene Complex 14 with 1-Methoxy-2-siloxy-4-ethoxy-1,3-butadiene 27. The diene **27** (0.109 g, 0.505 mmol) and carbene complex **14** (0.1637 g, 0.351 mmol, ≥96% cis by ^{1}H NMR) were combined and diluted with 2.0 mL of benzene that had been distilled from sodium benzophenone ketyl and stirred under argon for 48 h at 25 °C. At this point the reaction appeared not to be proceeding, and an additional 1.25 equiv of diene was added. The reaction was found to have gone to completion after a total of 119 h at 25 °C, and then the reaction was stopped and worked up according to the procedure described for the *trans*-propenyl complex **13** with diene **27**. Chromatography on silica gel gave three organometallic compounds two of which were identified as the cycloadducts **92a** (30%) and **92b** (7%) by comparison of their spectral data with those of the same adducts obtained from the reaction of the *trans*-propenyl complex **13**. The third was a new cycloadduct that was identified as the cis–exo cycloadduct **93a** and obtained in 6% yield as a yellow solid: mp 87–90 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.73 (d, J = 7.4 Hz, 3 H), 1.10 (t, J = 7.0 Hz, 3 H), 2.58 (dd, J = 12.7, 4.4 Hz, 1 H), 2.66 (m, 1 H), 2.74 (dd, J = 12.7, 9.05 Hz, 1 H), 3.25 (m, 1 H), 3.34 (d, J = 4.5 Hz, 1 H), 3.38 (s, 3 H), 3.52 (m, 1 H), 3.92 (sextet, 1 H), 4.68 (s, 3 H), 4.98 (dd, J = 8.7, 3.8 Hz, collapses to a doublet, J = 8.7 Hz when δ = 2.6 decoupled, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.9, 15.8, 35.9, 43.6, 58.2, 65.0, 70.0, 74.2, 75.4, 87.7, 197.4, 203.7, 208.6, 341.0; IR ($CHCl_3$) 2072 s, 1989 s, 1936 s, 1723 m, 1099 w, 978 cm^{-1}; mass spectrum, m/e (rel intensity) 524 M$^+$ – CO (^{184}W) (5), 496 (30), 468 (25), 440 (20), 412 (10), 339 (60), 311 (45), 281 (50), 185 (100), 129 (70), 105 (95); calcd for $C_{16}H_{20}O_8{}^{184}W$ m/e 524.0670, measured m/e 524.0665.

In a second run of this reaction carried out on the same scale and with the same concentrations, the reaction was stopped after 22 h and subjected to the same work-up procedure. From the crude ^{1}H NMR it was determined that both the *cis*- and the *trans*-propenyl complexes **14** and **13** were present as a 10:7 mixture. In a control experiment, a solution of the *cis*-propenyl complex **14** in benzene was stirred for 21 h at 25 °C under argon, and then submitted to the same work-up procedure (silica gel, 6 h). Analysis by ^{1}H NMR revealed that the *cis*-propenyl complex **14** had isomerized to only the slightest extent (**14**:**13** = 94:6, versus 96:4 for the starting **14**).

Reaction of (Cyclohexenylmethoxymethylene)pentacarbonylchromium (17) and TBDMS-1,3-diene 26. The dark red oil carbene complex **17** (700 mg, 2.21 mmol; purified by column chromatography) is dissolved in 2.1 mL of benzene (undistilled Aldrich Gold Label stored over 3A molecular sieves) and 2.0 mL of diene **26** is added, and the reaction mixture is deoxygenated by the freeze–thaw method. The dark red mixture is stirred for 48 h at room temperature under an argon atmosphere. The dark brown reaction is diluted with hexane and filtered through celite. The filtrate is concentrated, and a ^{1}H NMR spectrum shows mostly **94** and **96** present along with some minor products in the

crude reaction mixture. A 63:37 mixture of the isomers **94** and **96** was isolated by chromatography on silica gel with a 1:1:10 mixture of ether–methylene chloride–hexane and obtained as a clear colorless oil (475 mg, 1.4 mmol, 63% total yield). The cyclopropane **96** was isolated pure after further chromatography (R_f = 0.31, 1:1:10 solvent system); however, a pure sample of **94** is best obtained by thermolysis of purified **94**. The following data were obtained for cyclopropane **106**: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 6 H), 0.82 (s, 9 H), 0.83 (d, 1 H, J = 6.8 Hz), 1.07 (d, 1 H, J = 6.6 Hz), 1.54–1.64 (m, 4 H), 1.95–2.2 (m, 4 H), 3.06 (s, 3 H), 3.54 (s, 3 H), 4.92 (d, 1 H, J = 12.7 Hz), 5.65 (s, 1 H), 6.50 (d, 1 H, J = 12.7 Hz); ^{13}C NMR ($CDCl_3$) δ −3.87 (q, J = 119 Hz), −3.16 (q, J = 119 Hz), 17.87 (s), 20.94 (t, J = 157 Hz), 22.53 (t, J = 130 Hz), 22.69 (t, J = 130 Hz), 25.23 (t, J = 150 Hz), 25.62 (q, J = 135 Hz), 25.79 (t, J = 130 Hz), 53.24 (q, J = 142 Hz), 55.90 (q, J = 143 Hz), 61.48 (s), 71.65 (s), 103.32 (d, J = 163 Hz), 127.15 (d, J = 153 Hz), 133.1 (s), 149.11 (d, J = 181 Hz); IR (neat) 2929 s, 2857 m, 1654 m, 1161 m, 1124 s, 835 m, 776 m cm^{-1}. Anal. Calcd for $C_{19}H_{34}O_3Si$: C, 67.41; H, 10.12. Found: C, 67.48; H, 10.08. See below for the data for Cope product **96**.

Formation of Cope Product 96. The purified divinyl cyclopropane **94** (50 mg, 148 mmol) was dissolved in 2 mL of benzene and heated for 3 h at 90 °C. The solvent was stripped off on a rotorary evaporator and then under high vacuum to give a clear light yellow oil. The yield is quantitative by ^{1}H NMR, but after silica gel chromatography 45 mg (0.133 mmol, 90%) of **96** was isolated as a clear colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.171 (s, 3 H), 0.176 (s, 3 H), 0.93 (s, 9 H), 1.17–1.55 (m, 4 H), 1.47–1.55 (m, 1 H), 1.71–1.87 (m, 3 H), 2.25–2.3 (m, 1 H), 2.45–2.55 (m, 1 H), 2.92 (d, 1 H, J = 12.9 Hz), 3.32 (s, 3 H), 3.4 (s, 3 H), 4.1 (br s, 1 H), 4.76 (d, 1 H, J = 5.3 Hz); ^{13}C NMR ($CDCl_3$) δ −4.61 (q, J = 119 Hz), −4.42 (q, J = 119 Hz), 17.94 (s), 25.65 (q, J = 130 Hz), 26.64 (t, J = 122 Hz), 27.05 (t, J = 120 Hz), 28.45 (t, J = 140 Hz), 29.12 (t, J = 126 Hz), 35.71 (t, J = 120 Hz), 45.36 (d, J = 123 Hz), 56.53 (q, J = 143 Hz), 57.51 (q, J = 142 Hz), 78.27 (d, J = 141 Hz), 107.07 (d, J = 160 Hz), 125.79 (s), 142.68 (s), 150.85 (s); IR (neat) 2954 s, 2929 s, 2856 s, 1668 s, 1258 m, 1179 m, 1117 s, 1100 s, 930 s, 835 s, 780 s, cm^{-1}; mass spectrum, m/e (rel intensity) 338 M$^+$ (15), 323 (52), 306 (22), 281 (28), 249 (18), 109 (60), 85 (100), 73 (51).

Reaction of the Cyclohexenyl Tungsten 18 with 1,3-Diene 26. Freshly purified cyclohexenyl methoxy tungsten carbene complex **18** (400 mg, 0.89 mmol) was dissolved in 1.2 mL of benzene, and 1.1 mL of diene **26** was added. The dark red mixture was deoxygenated by the freeze–thaw method and stirred for 2 days at room temperature under argon. The yield of **97** was determined to be 34% in the crude reaction mixture by ^{1}H NMR with triphenylmethane as an internal standard. Purification of **97** by silica gel chromatography was possible but was complicated by its concomitant hydrolysis to **98** (and the β-methoxy keto precursor to **98**) and by the presence of several side products derived from the diene **26** which coeluted with **97**. Chromatographic purification of **97** was done on silica gel that had been deoxygenated and with eluted with a 1:1:20 mixture of ether–methylene chloride–hexane that had been spraged with argon. Three passes through a silica gel column with flash techniques provided pure **97** (R_f = 0.40) as a red crystalline solid in 22% yield. ^{1}H NMR (benzene-d_6) δ 0.15 (s, 3 H), 0.17 (s, 3 H), 0.83–91 (m, 1 H), 0.95 (m, 3 H), 0.95 (s, 9 H), 1.09–1.13 (m, 1 H), 1.30–1.36 (m, 2 H), 1.41 (m, 1 H), 1.59 (d, 1 H, J = 12.5 Hz), 1.91 (m, 1 H), 2.07 (d, 1 H, J = 12 Hz), 3.2 (s, 3 H), 4.04 (s, 1 H), 4.17 (s, 3 H), 4.61 (s, 1 H); ^{13}C NMR (benzene-d_6) δ −4.24 (q, J = 119 Hz), −3.86 (q, J = 119 Hz), 18.14 (s), 22.37 (t, J = 125 Hz), 25.66 (q, J = 125 Hz), 25.70 (t, J = 125 Hz), 29.84 (t, J = 126 Hz), 33.0 (d, J = 125 Hz), 34.78 (t, J = 127 Hz), 35.96 (d, J = 132 Hz), 66.0 (s), 67.06 (q, J = 145 Hz), 70.48 (q, J = 148 Hz), 86.63 (d, J = 148 Hz), 97.41 (d, J = 153 Hz), 155.62 (s), 205.23 (s), 205.92 (s), 214.1 (s), 221.63 (s), 348.4 (s); IR (neat) 2934 m, 2017 s, 1912 s, 1906 s, 1832 s, 1664 m, 1451 m, 1246 s, 1224 m, 926 m, 893 m, 853 m, 840 m cm^{-1}; Anal. Calcd for $C_{23}H_{34}O_7SiW$: C, 43.54; H, 5.40. Found: C, 43.88; H, 5.78.

Further elution provides a second compound, enone complex **98** (R_f = 0.30), which is not as sensitive as **97** and which can be separated from the diene side products by two additional passes through silica gel and obtained as a red solid (32.3 mg, 0.066 mmol, 5.5%): mp 147–9 °C dec; ^{1}H NMR (benzene-d_6) δ 0.65–0.85 (m, 2 H), 0.85–1.15 (m, 4 H), 1.2–1.35 (m, 2 H), 1.46 (d, 1 H, J = 13.13 Hz), 1.8 (d, 1 H, J = 17.95 Hz), 2.25 (dd, 1 H, J = 5.7, 20.8 Hz), 3.51 (s, 3 H), 3.90 (d, 1 H, J = 7.6 Hz), 5.07 (d, 1 H, 7.76 Hz); ^{13}C NMR (benzene-d_6) δ 21.86 (t, J = 126 Hz), 26.09 (t, J = 121 Hz), 27.38 (t, J = 127 Hz), 29.7 (t, J = 122 Hz), 38.38 (d, J = 137 Hz), 39.54 (t, J = 125 Hz), 64.02 (s), 67.27 (q, J = 147 Hz), 79.35 (d, J = 166.2 Hz), 83.9 (d, J = 159.6 Hz), 198.2 (s), 204.2 (s), 204.4 (s), 211.5 (s), 214.8 (s), 327.7 (s); IR (neat) 2950 w, 2040.7 s, 1946 s, 1893 s, 1665 m, 1300 m cm^{-1}; Anal. Calcd for $C_{16}H_{16}O_6W$: C, 39.37; H, 3.30. Found: C, 39.37; H, 3.24.

This reaction was carried out under 1400 psi of carbon monoxide with the other conditions the same, and it was found that the yield of **97** was essentially unchanged (33%) as determined by a ^{1}H NMR yield on the crude reaction mixture.

Formation of Decal-4-en-2-one (99). The Diels–Alder adduct **97** was dissolved in 3 mL each of THF and methylene chloride. In an effort to cleave the silicon group and generate the enone complex **98**, 0.49 mL of 1 M tetra-*n*-butylammonium fluoride in THF was added. The reaction mixture immediately turned from orange to light yellow, and TLC indicated that no starting material was left. The reaction mixture was dissolved in ether, washed with 2 × 10 mL of saturated aqueous NaHCO and 2 × 10 mL of saturated brine, and then dried over $MgSO_4$. The ether extract was filtered and concentrated, and TLC indicated the presence of only an organic product (R_f = 0.16). Purification of this product by chromatography on silica gel with a 1:1:10 mixture of ether–methylene chloride–hexane gave 15 mg (0.1 mmol, 20%) of decalenone **99** as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.1–1.4 (m, 3 H), 1.65–1.85 (m, 2 H), 1.85–1.9 (m, 1 H), 2.0 (m, 1 H), 2.2–2.35 (m, 2 H), 2.45 (s, 1 H), 2.56 (m, 1 H), 2.7–2.8 (m, 1 H), 2.9 (m, 1 H), 5.3 (s, 1 H); IR (neat) 2927 s, 2854 m, 1719 s, 1446 w; mass spectrum, m/e (rel intensity) 150 M$^+$ (50), 108 (100), 93 (55), 79 (63).

Reaction of the Vinyl Tungsten Complex 11 with the Silapyran 28. This reaction was followed by ^{1}H NMR on a $CDCl_3$ solution that was 0.5 M in complex **11** and 1.5 M in silapyran **28**.[68] After 2 h a quantitative conversion to the cycloadduct **105** was indicated, and the following data were recorded for **105**: yellow solid; mp 92–94 °C (ether–hexane); ^{1}H NMR δ 0.02 (s, 3 H), 0.30 (s, 3 H), 1.42 (ddd, 1 H, J = 12, 8.5, 4 Hz, collapses to dd upon $h\nu$ at δ = 4.75, J = 12, 4 Hz, collapses to dd upon $h\nu$ at δ = 1.95, J = 12, 8.5 Hz), 1.95 (m, 1 H, collapses to dd upon $h\nu$ at δ = 2.28, J = 4, 7.5 Hz), 2.28 (dt, 1 H, J = 11, 3 Hz, collapses to broad d upon $h\nu$ at δ = 1.42, J = 10 Hz, collapses to dd upon $h\nu$ at δ = 1.95, J = 10, 12 Hz), 4.50 (s, 4 H), 4.75 (dt, 1 H, J = 9, 2 Hz, collapses to broad d upon $h\nu$ at δ = 1.42, J = 10 Hz, collapses to broad d upon $h\nu$ at δ = 2.28, J = 8.5 Hz), 6.20 (dd, 1 H, J = 5, 8.5 Hz; collapses to d upon $h\nu$ at δ = 4.50, J = 8.5 Hz; collapses to d upon $h\nu$ = 6.38, J = 5 Hz), 6.38 (brd t, 1 H, J = 8 Hz, collapses to d upon $h\nu$ at δ = 6.20, J = 7.5 Hz, collapses to d upon $h\nu$ at δ = 1.95, J = 8.5 Hz); mass spectrum, m/e (rel intensity) 510 (2), 492 M$^+$ − CO (^{184}W) (2), 482 (2), 464 (2), 436 (1), 426 (4), 408 (2), 398 (6), 380 (5), 57 (100).

Oxidation of 43 and 44 with Dimethyl Sulfoxide. A small sample (0.136 g, .40 mmol) of the chromium cycloadduct **43** was dissolved in DMSO and stirred at room temperature for 35 h. The entire mixture was loaded onto a flash chromatography column and eluted with a mixture of ether, methylene chloride, and hexane (1:1:10) to give 0.063 g (0.38 mmol, 95%) of the ester **42**. The following spectral data were obtained for **42**: ^{1}H NMR ($CDCl_3$) δ 1.6 (s, 3 H), 1.62 (s, 3 H), 1.65 (m, 1 H), 1.9–2.25 (m, 5 H), 2.53 (m, 1 H), 3.67 (s, 3 H); IR ($CHCl_3$) 2900 m, 1720 s, 1430 m, 1375 w, 1310 w cm^{-1}; mass spectrum, m/e (rel intensity) 168 M$^+$ (17), 153 (1), 137 (3), 136 (5), 125 (2), 121 (2), 109 (55), 108 (100). The spectral data were found to be identical with those from an authentic sample prepared from the reaction of methyl acrylate and 2,3-dimethyl-1,3-butadiene. A similar oxidation of the tungsten complex **44** gave a 91% yield of **42**.

Reaction of Cycloadduct 43 with Hydrogen Bromide. A solution of 0.121 g (0.352 mmol) of chromium complex **43** in 450 mL of methylene chloride was purged with nitrogen for 10 min. The solution was cooled to −78 °C, and 1 equiv of HBr in methylene chloride was added. The solution was warmed up to −35 °C and stirred for 20 min, after which it was brought up to room temperature. Since TLC indicated the presence of starting material together with product, the solution was cooled down to −78 °C, and the above procedure was repeated. After the solution was warmed to room temperature, TLC indicated no starting material. The solution was diluted with ether and washed with H_2O. The aqueous layer was extracted with ether. All organic layers were combined, dried with $MgSO_4$, and concentrated. Flash chromatography with a mixture of ether, methylene chloride, and hexane (1:1:20) gave 0.035 g (0.253 mmol, 72%) of the aldehyde **109**: ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3 H), 1.65 (s, 3 H), 1.9–2.2 (m, 6 H), 2.45 (s, 1 H), 9.66 (s, 1 H); IR ($CHCl_3$) u 2900 s, 1710 s cm^{-1}. These spectral data were found to be identical with those of an authentic sample prepared by the reaction of acrolein and 2,3-dimethyl-1,3-butadiene. A 27% yield of the ester **42** was also obtained from this reaction. The yield of this ester could not be significantly minimized by careful degassing of the reaction mixture with three freeze–thaw cycles (−196 °C to 25 °C) or by changing the concentration.

Reaction of Complexs 43 and 44 with Pyridine. To a solution of 0.246 g (0.517 mmol) of the tungsten complex **44** in 15 mL of THF was added 0.042 mL (1.1 equiv) of pyridine. The solution was refluxed under nitrogen until the starting material was gone (5 h). The volatiles were removed, and the residue was flash chromatographed with a mixture of ether, methylene chloride and hexane (1:1:20) to give 0.078 g (99%) of

the enol ether **108** as a 5:3 mixture of cis and trans isomers (**108a**:**108b**). Enol ether **108a**: ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 6 H), 2.01 (m, 2 H), 2.09 (t, 2 H, J = 6.3 Hz), 2.70 (s, 2 H), 3.54 (s, 3 H), 5.78 (s, 1 H). Enol ether **108b**: ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 6 H), 2.01 (m, 2 H), 2.33 (t, 2 H, J = 6.3 Hz), 2.47 (s, 2 H), 3.53 (s, 3 H), 5.87 (s, 1 H); IR ($CHCl_3$), (mixture of **108a** and **108b**) 2480 w, 2400 m, 2330 w, 1120 s, 1100 m, and 900 s cm^{-1}. The identity of the enol ethers was confirmed upon acid hydrolysis of the mixture to give a single compound which had an ^{1}H NMR spectrum identical to that for the aldehyde **109**. A similar treatment of the chromium complex **43** gave a 71% yield of **108**.

Reaction of 43 and 44 with Diazomethane. Diazomethane was generated in ether at 0 °C by shaking *N*-methyl-*N*-nitrosourea with 40% aqueous KOH. A large excess of diazomethane was prepared (10 equiv) and added to a solution of 0.138 g (0.401 mmol) of the chromium complex **43** in 10 mL of ether containing 0.32 mL (10 equiv) of pyridine. After 15 min at room temperature the reaction was complete and the excess diazomethane was swept with a stream of nitrogen into an acetic acid trap. The solvents were removed, and the residue was flash chromatographed on silica gel with a mixture of ether, methylene chloride, and hexane (1:1:20) to give 0.0522 g (0.314 mmol, 78%) of the enol ether **107**: ^{1}H NMR ($CDCl_3$) δ 1.50 (m, 1 H), 1.61 (s, 6 H), 1.85 (m, 1 H), 1.9-2.1 (m, 4 H), 2.25 (m, 1 H), 3.54 (s, 3 H), 3.84 (s, 1 H), 3.87 (s, 1 H); mass spectrum, *m/e* (rel intensity) 166 M$^+$ (11), 151 (18), 119 (22), 91 (29), 67 (32), 43 (100). The identity of **107** was confirmed upon acid hydrolysis to give a compound which had a ^{1}H NMR identical with that of the cycloadduct of methyl vinyl ketone and 2,3-dimethyl-1,3-butadiene. A similar reaction of the tungsten complex **44** gave an 80% yield of **107**.

Reaction of 43 with Hydrogen. A solution of 0.190 g (0.551 mmol) of the chromium complex **43** in 25 mL of hexane was deoxygenated with three freeze-thaw cycles (-190 °C to 25 °C), filled with argon, transferred to a Parr bomb, and then heated at 160 °C for 2.6 days under 1000 psi of hydrogen. The resulting mixture was filtered through Celite, concentrated, and flash chromatographed with a mixture of ether, methylene chloride and hexane (1:1:30) to give a 71% of the methyl ether **106**. Spectral data for **106**: ^{1}H NMR ($CDCl_3$) δ 1.2 (m, 1 H), 1.6 (s, 6 H), 1.65-2.1 (m, 6 H), 3.24 (dd, 2 H, J = 1.7 Hz, 6.6 Hz), 3.34 (s, 3 H); IR ($CHCl_3$) 2900 s, 1445 m, 1380 m, 1105 s, 950; mass spectrum, *m/e* (rel intensity) 154 M$^+$ (5), 123 (3), 122 (28), 121 (10), 107 (10). The identity of the ether **106** was confirmed by an independent synthesis. The Diels-Alder adduct of acrolein and 2,3-dimethyl-1,3-butadiene was reduced with sodium borohydride. The resulting alcohol was methylated with potassium hydride and methane fluorosulfonate to give a compound that had an identical ^{1}H NMR spectrum and GC retention time as the ether **106**. A second product (18% GC yield) was also obtained from the reaction of **43** with hydrogen and may correspond to the further reduction of the double bond in **106**. Although the reaction conditions were sufficient for complete conversion of **43**, no attempt was made to optimize the conditions for **106**.

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Communications to the Editor

Supramolecular Transport of Metal Complexes. Chiroselective Membrane Transport of Metal Amine Complexes by a Polyether Ionophore, Lasalocid A

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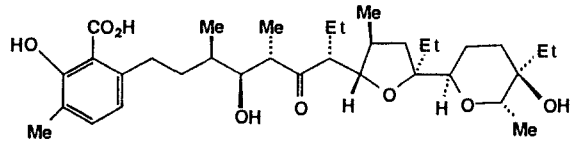
Lasalocid A (**1**) is a naturally occurring carboxylic ionophore that has been demonstrated to assist the transport of metal ions as well as amine cations across hydrophobic membranes.[1-3] It has been proposed for such systems that the anionic form of the antibiotic forms a complex with the cation to be transported such that the adduct has a hydrophobic exterior. More recently, outer-sphere complexes of lasalocid A and a number of metal ammine complexes have been isolated.[4,5] The X-ray structure of one such species, $[Co(NH_3)_6]$·(lasalocid A)$_3$], shows that three lasalocid anions in cyclic conformations (maintained by intraligand hydrogen bonds) surround the cobalt species such that the overall geometry is approximately spherical. As a consequence of its hydrophobic outer surface, the species is soluble in nonpolar solvents such as chloroform. The lasalocid A/cobalt ammine complex interactions involve a network of hydrogen bonds. These investigations parallel other recent studies[6,7] documenting related



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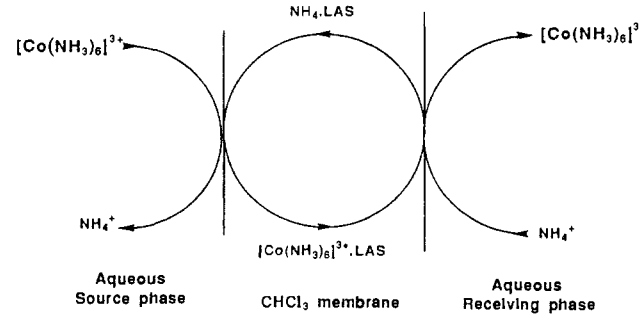

Figure 1. Lasalocid A anion (LAS) mediated transport of $[Co(NH_3)_6]^{3+}$ across a $CHCl_3$ membrane coupled to an NH_4^+ countergradient.

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