A comprehensive study of [2 + 2] cycloadditions and ene reactions of alkynyl chromium and tungsten carbene complexes with enol ethers and ketene acetals and of the stereochemistry of the electrocyclic ring opening of cyclobutenyl carbene complexes

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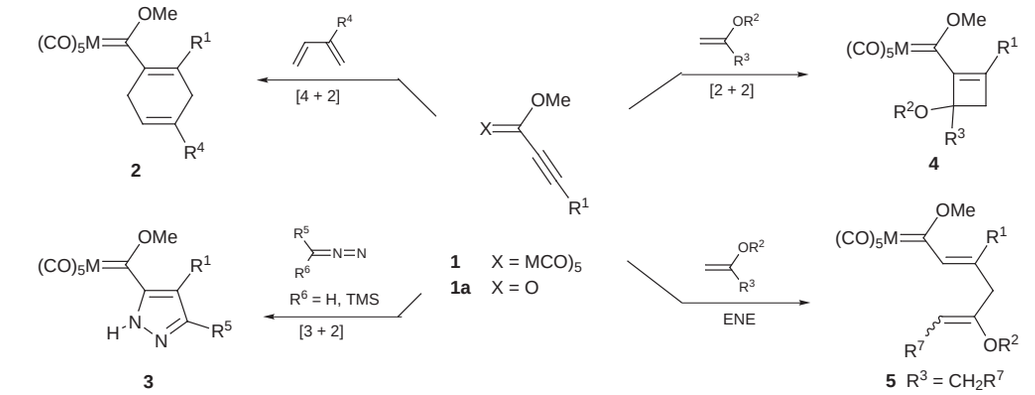
The reactions of several alkynyl carbene complexes [$(CO)_5M{=}C(OMe)C{\equiv}CR^1$, M = Cr, W, R^1 = Me, Me_3Si, Ph, i-Pr, t-Bu) with a variety of acyclic enol ethers and ketene acetals [$CH_2{=}C(OR^2)R^3$, R^2 = Et, Me, i-Bu, $SiMe_2$t-Bu, R^3 = H, Me, EtO, *p*-MeC_6H_4] are examined. These reactions occur to give [2 + 2] cycloaddition products in all cases except with $R^1 = Me_3Si$ where ene products predominate. The cyclobutenyl carbene complexes produced in the [2 + 2] cycloadditions undergo rapid electrocyclic ring-opening at room temperature when R^3 = H to give butadienyl carbene complexes as the isolated products. The reactions of the alkynyl carbene complexes with cyclic enol ethers derived from cyclohexanone and cyclopentanone are more prone to give ene products than the acyclic enol ethers. Greater proportions of ene products are seen for six- rather than five-membered ring enol ethers and for silyl rather than alkyl enol ethers and for silyl rather than carbon substituents at R^1. Only small differences are seen between chromium and tungsten complexes. The [2 + 2] cycloadditions with the *E*- and *Z*-isomers of ethyl prop-1-enyl ether are stereospecific with complexes in which R^1 = Me but not with those with $R^1 = SiMe_3$. The cyclobutenyl carbene complexes from the latter reactions with tungsten derivatives were found to undergo stereoselective electrocyclic ring-opening at 70 °C to give only *Z*,*E*-butadienyl carbene complexes which result from the conrotatory ring-opening in which the ethoxy group rotates in an outward direction. An *E*,*E*-isomer was also isolated from the thermolysis mixture; however, it was shown not to be a primary product but rather the result of an isomerization of the *Z*,*E*-butadienyl carbene complex under the reaction conditions. The stereoselectivity of the electrocyclic ring-opening of these cyclobutenyl carbene complexes was shown to be the same as that found for their corresponding cyclobutenyl esters. In one case, an interesting cine-rearrangement of a cyclobutenyl carbene complex was observed. The metal can be oxidatively removed from the cyclobutenyl carbene complexes to give the corresponding cyclobut-1-enyl esters in good yield. Thus, alkynyl carbene complexes can serve as synthons for alkynyl esters in [2 + 2] cycloadditions with enol ethers and have the attractive feature of greatly increased reaction rates. Additional synthetic interest can be associated with processes in which the [2 + 2] cycloaddition of the alkynyl carbene complex is coupled in tandem with other reactions of the carbene complex functionality in the cycloadducts. This is illustrated with Diels–Alder reactions of the butadienyl carbene complexes and cyclohexadienone annulations of a cyclobutenyl carbene complex.

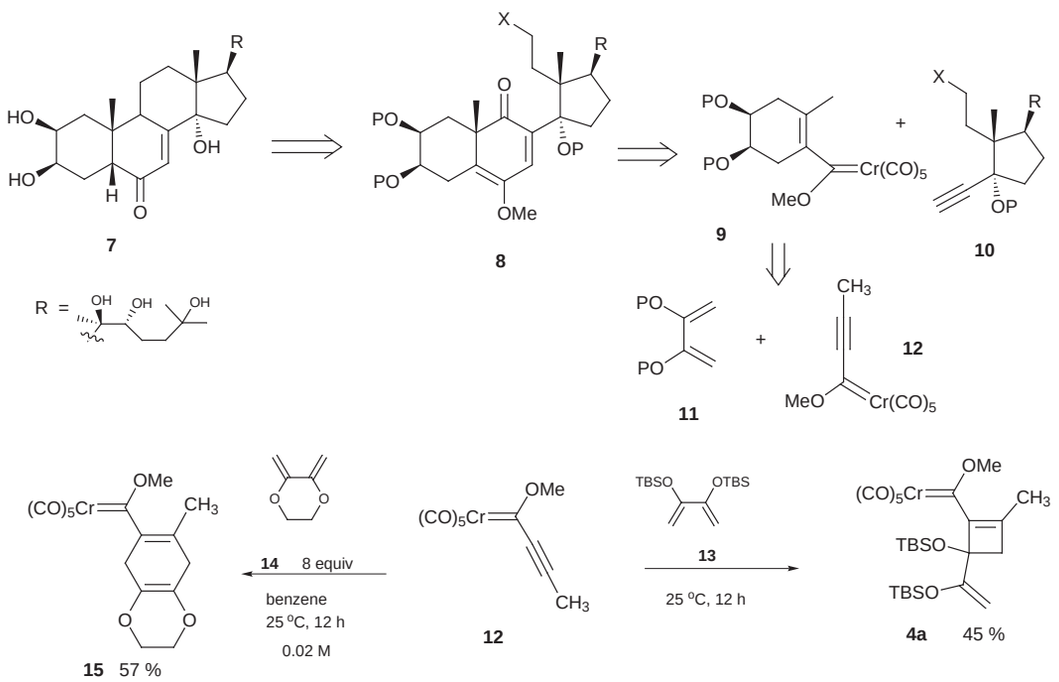
One of the aspects of the chemistry of Fischer carbene complexes that is responsible for a diverse array of reactions with applications in organic synthesis is the ability of the metal–carbene unit to electronically and sterically modify the reactivity of an organic fragment bound to the carbene carbon.[1] This has been especially realized in cycloadditions where the metal pentacarbonyl fragment of Fischer carbene complexes serves to accelerate cycloaddition reactions relative to an oxygen atom in the corresponding ester (**1** *vs.* **1a**). This was first realized in [4 + 2] cycloadditions where Diels–Alder products were obtained in the reactions of Fischer carbene complexes with 1,3-dienes for both alkenyl (not illustrated in Scheme 1) and alkynyl complexes.[2,3] The reaction rates and product selectivities have been observed to be much higher for the reaction of carbene complexes than for the corresponding esters not only for [4 + 2] cycloadditions but also for [3 + 2] cycloadditions.[4] Several years ago we reported the first examples of thermal [2 + 2] cycloadditions and ene reactions of carbene complexes from the reactions of alkynyl complexes with enol ethers and ketene acetals.[5] Since that time a number of other reports have appeared describing [2 + 2] cycloadditions of alkynyl and alkenyl carbene complexes.[6] We report here a full account of our studies on the [2 + 2] cycloadditions and ene reactions of alkynyl carbene complexes and the results of an investigation into the stereochemistry of the electrocyclic ring opening of cyclobutenyl carbene complexes that are produced from these reactions.

Introduction

The first [2 + 2] cycloaddition of Fischer carbene complexes was inadvertently observed in the course of investigating a synthesis of β-ecdysone **7**, an insect moulting hormone.[7] The retrosynthetic analysis is illustrated in Scheme 2 and features two key steps that involve carbene complexes. The first is the cyclohexadienone annulation[8] of the alkenyl complex **9** with alkyne **10** and the second is a Diels–Alder reaction of an alkynyl carbene complex with a 2,3-dioxygenated diene which



Scheme 1



Scheme 2

will serve to provide access to complex **9**. The reaction of the propynyl complex **12** with the bis-silyloxy diene **13** gave not the desired [4 + 2] cycloadduct, but rather the [2 + 2] cycloadduct **4a**. This was certainly surprising since [2 + 2] cycloadditions with dienes of this type were not known,[9] nor at the time were [2 + 2] cycloadditions of α,β-unsaturated carbene complexes. This result was also unanticipated since the transformation that would be expected to be competitive with [4 + 2] cycloadditions is cyclopropanation.[10,11] The unexpected preference for [2 + 2] over [4 + 2] cycloaddition in this reaction can be attributed to the relatively high energy of the s-*cis* conformation of the diene **13** and support for this supposition comes from the fact that the first key step in the synthesis of β-ecdysone could be accomplished by employing the diene **14** which is constrained to conformations not significantly deviant from s-*cis*.[12] The observation of **4a** from this reaction served to stimulate an investigation into the generality of the [2 + 2] cycloaddition of unsaturated carbene complexes with alkenes.

[2 + 2] Cycloadditions

The [2 + 2] cycloadditions of a variety of alkynyl carbene complexes with several different enol ethers were examined and the results are presented in Table 1. The typical procedure involves dissolving the carbene complex in an excess of the enol ether (~10 equiv.) and allowing to stir at room temperature under an argon atmosphere until the reaction is complete which typically is 2 to 24 hours. In the case of the ketene acetal (entry 14) the reaction is too exothermic to perform neat, and is carried out in a methylene chloride solution with a procedure that is essentially a titration of the alkynyl carbene complex. An indication of the rate enhancement that the chromium pentacarbonyl carbene function provides over the ester function for these [2 + 2] cycloadditions is provided by the reaction with diethyl ketene acetal. The propynyl carbene complex **12** basically reacts with ketene diethyl acetal upon mixing (entry 14), whereas the reaction of methyl propiolate with ketene diethyl acetal requires 29 hours at 40 °C despite the fact that, as a terminal alkyne, methyl propiolate should react much faster than carbene complex **12** if only steric factors were considered.[13a] The only other known thermal [2 + 2] cycloaddition of an acetylenic ester with a ketene acetal is with dimethyl acetylenedicarboxylate.[13b]

As indicated in Table 1, the [2 + 2] cycloadditions of acetylenic carbene complexes typically produce moderate to high yields of the cyclobutenyl carbene complexes **4**, but in some cases the corresponding ring-opened complexes **16** and/or **17** can be isolated. It is interesting that in all cases, the ring-opened butadienyl carbene complexes are produced as a single stereoisomer with the alkoxy group in the 1-position *syn* to the carbene carbon, which indicates that the alkoxy group rotates outward in the electrocyclic ring opening of **4**. This stereo-

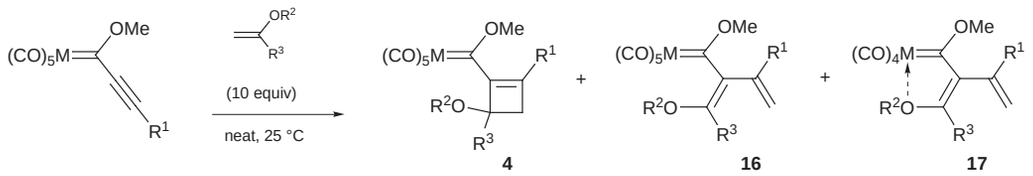


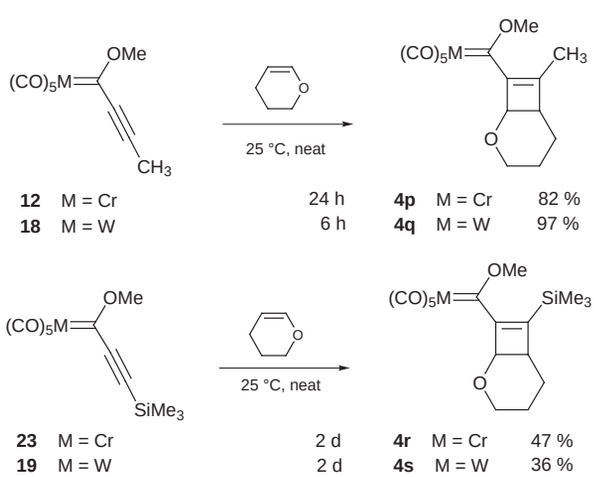
Table 1 [2 + 2] Cycloadditions with enol ethers and ketene acetals

Entry	R^2	R^3	Complex	M	R^1	Time	Product series	Isolated yield (%)[a] 4	16	17	Total yield (%)
1	Et	H	**12**	Cr	Me	29 h	**b**		29		32
2			**18**	W	Me	4 h	**c**	6	40		46
3			**19**	W	TMS	24 h	**d**		79	19	98
4	iBu	H	**18**	W	Me	18 h	**e**		54		54
5			**19**	W	TMS	48 h	**f**		51		51
6	TBS	H	**19**	W	TMS	25 h	**g**		8		8
7	Me	Me	**12**	Cr	Me	6 h	**h**	63			63
8			**18**	W	Me	2 h	**i**	82			84[b]
9			**20**	W	Ph	2 d	**j**	14[c]		34[d]	48
10			**21**	W	iPr	2 h	**k**	80			80
11			**22**	W	tBu	2 d	**l**	53			53
12	TBS	Me	**18**	W	Me	24 h	**m**	19			20
13	TBS	*p*-$CH_3C_6H_4$	**12**	Cr	Me	3 h	**n**	63			63
14	Et	EtO	**12**	Cr	Me	10 min	**o**	73			73[e]

[a] Purified yields after chromatography on silica gel. [b] A 2% yield of ene product was also obtained. [c] Characterized only by ^{1}H NMR as this complex was unstable with respect to ring-opening. [d] Obtained as a 3:1 mixture of **17j** to **16j** which was characterized as **17j** by allowing the mixture to go completely to **17j**. [e] A 0.2 M solution of **12** in CH_2Cl_2 was titrated with ketene diethyl acetal at 25 °C until all starting material was gone; complex **4o** was sensitive to silica gel but could be purified (73%) by chromatography on silica gel at −60 °C.

chemistry is confirmed by NOE studies and by the interconversion of the chelated and non-chelated complexes **16** and **17** (*vide infra*). For those complexes where R^3 is non-hydrogen, the cyclobutenyl carbene complexes are stable with respect to electrocyclic ring-opening at room temperature. With few exceptions, the ring-opened butadienyl complexes are only observed for those complexes where R^3 is hydrogen and this may be due to the lower barrier for inward rotation when R^3 is hydrogen. The electrocyclic ring opening of complexes **4h** and **4i** can be effected by heating to 75–85 °C to give the butadienyl complexes **17h** and **17i** in 55% and 43% yields, respectively.

The cyclobutenyl carbene complexes obtained from reaction with dihydropyran are significantly more stable than the related complexes indicated in Table 1. This is undoubtedly related to the fact that a concerted symmetry-allowed electrocyclic ring-opening in these bicyclic complexes would lead to an eight membered ring containing a *trans*-double bond. All of the complexes **4p**–**4s** are stable with respect to their monocyclic analogs **4a**–**4o** although the adducts derived from the trimethylsilylacetylenic complexes **23** and **19** are not formed as efficiently as those generated from the propynyl complexes **12** and **18** which lead to the isolation of **4p** and **4q** in excellent yields (Scheme 3). An even better estimation of the accelerating effect that carbene complexes have over esters in the [2 + 2] cycloaddition of alkynes with enol ethers can be gained from these reactions with dihydropyran. There are only three known examples of thermal [2 + 2] cycloadditions of acetylenic esters with enol ethers and one is the reaction of dimethyl acetylenedicarboxylate with dihydropyran.[14] Despite the fact that dimethyl acetylenedicarboxylate is doubly-activated, its reaction with dihydropyran in toluene requires 180 °C for 16 hours.[14b] As activated as these carbene complexes are, no reaction is seen at room temperature between complex **18** and either cyclohexene, hex-1-ene, vinyl acetate or allyl(trimethyl)silane.

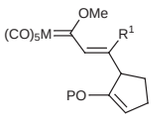
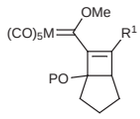
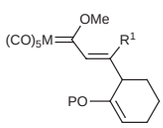
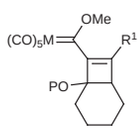


Scheme 3

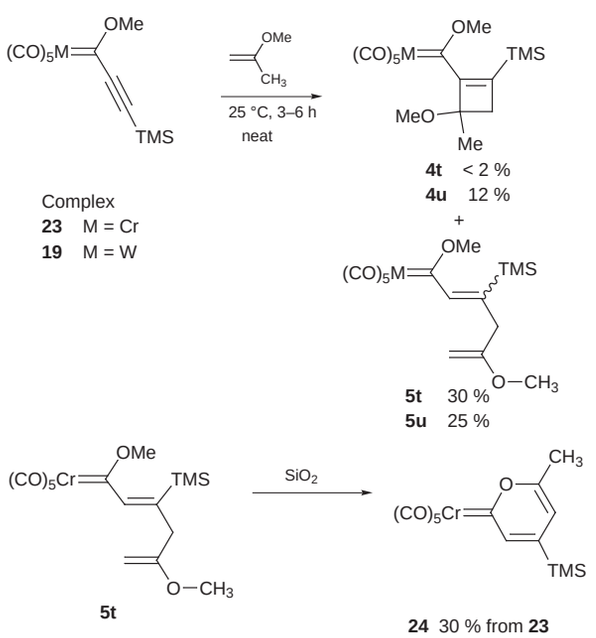
Ene reactions

The first observation of ene products from these reactions was observed for the reactions of the trimethylsilyl complexes **19** and **23** with methyl isopropenyl ether. When the red product from the reaction of the chromium complex **23** and methyl isopropenyl ether was subjected to routine purification on silica gel it was observed to close to the dark purple pyranylidene complex **24** (Scheme 4).[15] Minimizing exposure to silica gel by rapid elution provided the ene product **5t** in 30% yield. The reaction of the tungsten complex **19** was less selective for the ene product **5u** and gave some of the [2 + 2] cycloaddition product **4u** as well. The stereochemistry of the ene products **5t** and **5u** were not determined although the former seemed to be one isomer whereas the latter appeared to be a 2:1 mixture of olefin isomers. Ene products were not observed for any of the reactions

Table 2 Ene *versus* [2 + 2] cycloaddition reactions of cyclic enol ethers[a]

Enol ether	Complex	Time	Ene product[b] yield (%)	[2 + 2] Product yield (%)	Ene/[2 + 2]
					
	M = W				
25	**19** R^1 = $SiMe_3$	24 h	**29a** 39	**30a** 12	3.25
P = TBS	**18** R^1 = Me	12 h	**29b** 28	**30b** 62	0.45[c]
26	**19** R^1 = $SiMe_3$	8 h	**31a** 10	**32a** 64	0.16
P = Me	**18** R^1 = Me	1 h	**31b** 2	**32b** 87	0.02
	21 R^1 = iPr	3 h	**31c** <2	**32c** 90	<0.02
	22 R^1 = tBu	9 h	**31d** <2	**32d** 59	<0.02
	M = Cr				
	12 R^1 = Me	12 h	**31e** 4	**32e** 82	0.05
					
	M = W				
27	**19** R^1 = $SiMe_3$	48 h	**33a** 42	**34a** <3	>14.0
P = TBS	**18** R^1 = Me	12 h	**33b** 86	**34b** 10	8.8
	M = Cr				
	12 R^1 = Me	12 h	**33c** 50	**34c** <3	>16.0
	M = W				
28	**19** R^1 = $SiMe_3$	48 h	**35a** 67	**36a** <2	>33.0
P = Me	**18** R^1 = Me	48 h	**35b** 9	**36b** 60	0.15
	21 R^1 = iPr	12 h	**35c** 24	**36c** 69	0.35
	22 R^1 = tBu	7 d[d]			

[a] All reactions were carried out in neat enol ether (10–20 equiv.) at 25 °C under argon for the indicated time. All products were purified on silica gel. [b] A single double-bond isomer was obtained in each case which is assumed to be that resulting from *syn*-addition since this was shown to be the case for **35a** by NOE experiments (see Experimental section). [c] Compounds **29b** and **30b** could not be separated by silica gel chromatography. [d] Only recovered starting materials observed.

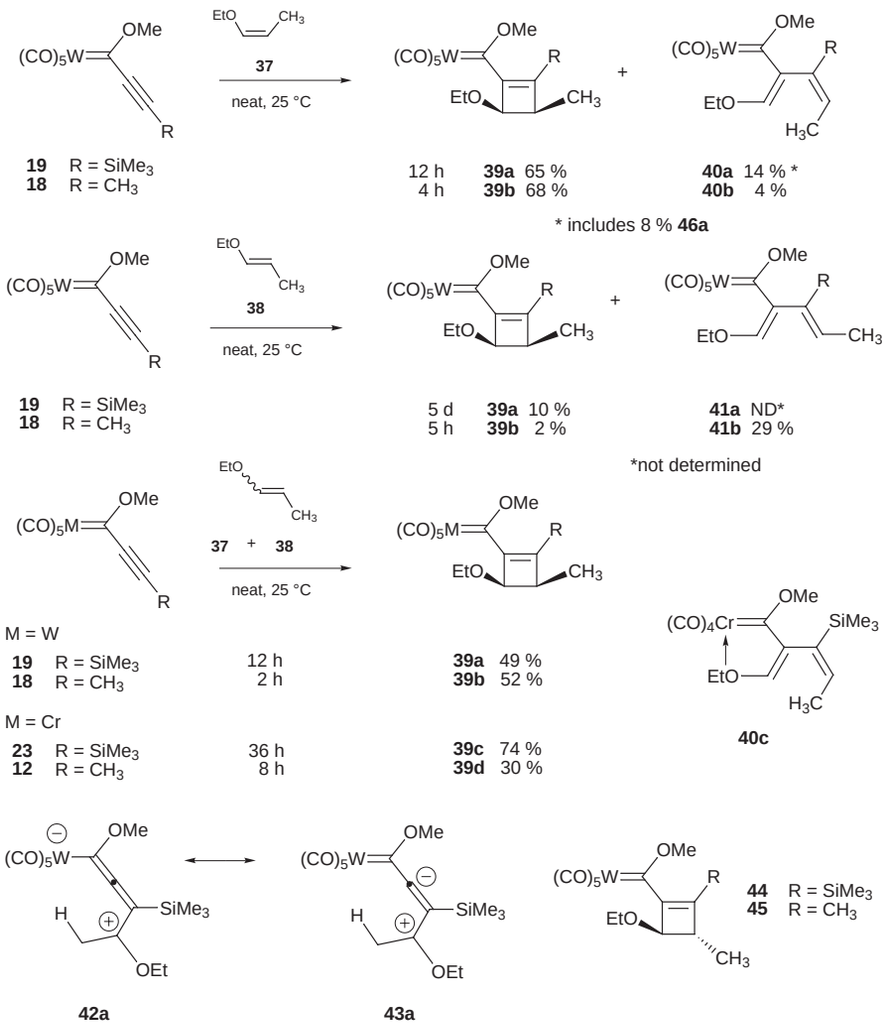


Scheme 4

in Table 1 despite the fact that this outcome was possible in six of the reactions listed (entries 7–12). Ene products were not observed with methyl isopropenyl ether for any alkynyl carbene complex where R^1 is alkyl or aryl and in fact were only observed for the silyl complexes **19** and **23**.

Cyclic enol ethers were found to give higher yields of ene products from reactions with alkynyl carbene complexes and a summary of the results from these reactions are presented in Table 2. As was the case with acyclic enol ethers, greater proportions of the ene product were observed with alkynyl carbene complexes bearing a silyl substituent on the alkyne. For example, the reaction of the cyclohexenyl methyl ether **28** with the silyl carbene complex **19** gave only the ene product, whereas, the methyl and isopropyl complexes **18** and **21** gave predominately [2 + 2] cycloaddition products. The Lewis acid mediated reactions of acetylenic esters and alkenes are known to give mixtures of ene and [2 + 2] cycloadducts where the ratio of products has been shown to have a strong dependence on the olefin substitution pattern and on the conformation of the starting materials.[16,17] However, this effect of silicon has not been reported for the Lewis-acid mediated ene reactions of olefins with either β-silyl-substituted acetylenic esters or β-silyl-substituted alkenyl esters.

Cyclic enol ethers also show a greater tendency to give ene products than do the acyclic enol ethers. For example, the cyclohexenyl methyl ether **28** gives both ene and [2 + 2] cycloaddition products with alkynyl carbene complexes bearing alkyl groups on the alkyne whereas the same complexes with methyl propenyl ether gave only [2 + 2] cycloaddition products (Table 1, entries 8–11). Silicon substituents on the enol ether also play a role in the product distribution. The silyl enol ether **25** gives a greater proportion of ene products than does the methyl enol ether **26**. The product distribution is dependent on the ring-size of the enol ether where the six-membered ring cyclic enol ethers give a larger proportion of ene products than do the corre-



Scheme 5

sponding five-membered ring enol ethers and this effect has also been seen in the reactions of esters.[17a] From the data collected here, there does not seem to be a great effect on the nature of the metal on the distribution between ene and cycloaddition products, although this point was not specifically addressed in these studies. From the limited data in Scheme 4 and Table 2, it seems that chromium has a slightly greater preference to give ene products than tungsten. All of the ene products in Table 2 were obtained as a single stereoisomer, and are assumed to be the isomers shown resulting from *syn* addition on the basis of the stereochemistry assigned for complex **35a** by NOE experiments (see Experimental section).

Stereospecificity of the [2 + 2] cycloaddition

The nature of the effect of silicon in the alkynyl carbene complexes on the distribution between ene and [2 + 2] cycloaddition products can be judged to be electronic on the basis of the data in Table 2. The trends seen for the variations of the product distributions with the steric size of substituent R^1 of the alkynyl carbene complexes for alkyl substituents (methyl, isopropyl and *tert*-butyl) do not correlate with the trends observed for complex **19** with $R^1 = SiMe_3$ on the basis of the size of the trimethylsilyl group. The origin of the source of an electronic influence of the silicon atom on the product distribution will depend on the nature of the mechanism of these reactions. There are two extreme possibilities. Either the [2 + 2] cycloaddition occurs by a concerted mechanism and the ene products result from zwitterionic intermediates **42** and **43** which are stabilized by silicon, or the ene reaction occurs by a concerted mechanism and the [2 + 2] cycloaddition results from zwitterionic intermediates **42** and **43** that are destabilized by silicon. The former seems more likely since silicon is well known to stabilize a β-positive charge.[18] In addition, it has been found that rates of the [2 + 2] cycloadditions of complexes **18** and **20** with dihydropyran show negligible solvent dependence and taken together with the volumes of activation determined for these reactions, the best evidence to date suggests that the [2 + 2] cycloadditions of the methyl and phenyl complexes **18** and **20** occur by a non-polar concerted mechanism.[5c] This suggests that the role of the silicon is to stabilize a zwitterionic intermediate and that the ene product is formed by a two-step mechanism. In an effort to gain further experimental evidence to test these conclusions a study of the stereospecificity of these reactions was undertaken.

The issue of stereospecificity was examined with the reactions of the methyl and trimethylsilyl substituted carbene complexes **18** and **19** with *cis* and *trans* ethyl propenyl ether. Both complexes reacted with the *cis* enol ether **37** to give the *cis*-substituted cyclobutenyl carbene complexes **39** and the ring-opened dienyl carbene complexes **40**. The stereochemistry of **39a** and **39b** was assigned as *cis* on the basis of NOE experiments. NOE data were also used to assign the stereochemistry of the dienyl carbene complex **40b** as that indicated in Scheme 5 where the ethoxy group on the 1,2-double bond is *syn* to the metal and the R group (methyl) on the 3,4-double bond is *trans* to the methyl group. An unambiguous assignment of stereochemistry could not be deduced from the NOE data for **40a** and thus the stereochemistry was assumed to be the same as that determined for **40b**.

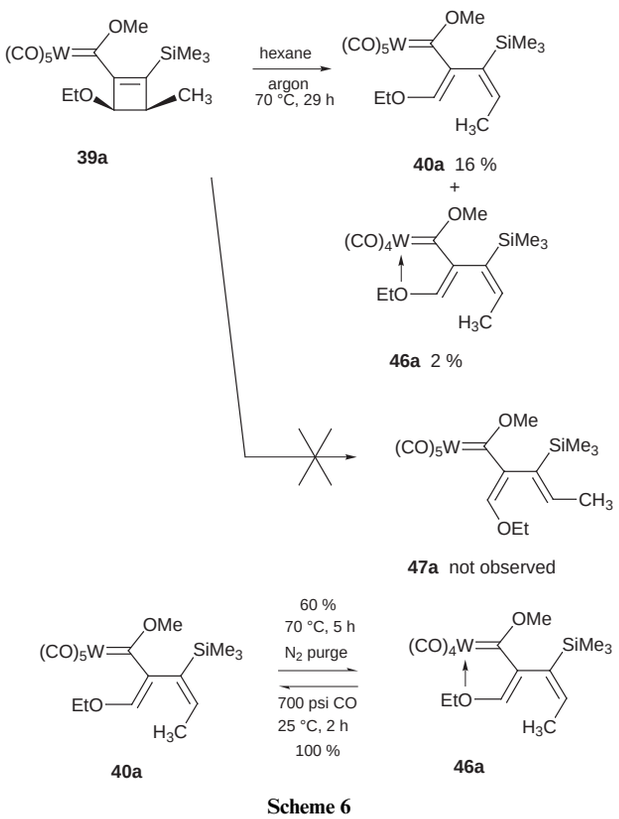
The reaction of the methyl complex **18** with the *trans* propenyl ether **38** was carried out neat in 15 equivalents of **38** at 25 °C for 5 hours and gave one predominant product that was mobile on silica gel and was the dienyl complex **41b**. Two minor products were observed (~2%) which were not characterized but one may have been the *trans*-substituted cyclobutenyl carbene complex **45**. The stereochemistry of the dienyl complex **41b** was assigned on the basis of NOE experiments as the *cis*,*trans*-isomer shown in Scheme 5. This is the stereochemistry expected for a symmetry allowed conrotatory electrocyclic ring-opening of the expected *trans*-cyclobutenyl carbene complex **45**. TLC analysis of the reaction mixture indicated the presence of a transient red compound that appeared to decompose to the dienyl complex **41b**. That the *trans* substituted cyclobutenyl carbene complex **45** would undergo electrocyclic ring opening faster than its *cis* isomer **39b** is to be expected since the transition state on the way to the olefin geometry present in the s-*cis* configuration of **41b** would lack the allylic strain present in the transition state on the way to the olefin geometry present in **40b**. The maximum amount of crossover possible to the *cis*-cyclobutenyl complex **39b** was determined to be 2% by ^{1}H NMR. Analysis of the enol ether remaining after the reaction by ^{1}H NMR indicated no detectable loss in stereochemistry had occurred with the *trans* : *cis* ratio still greater than 65 : 1.

The reaction of the trimethylsilylalkynyl complex **19** with the *trans* propenyl ethyl ether **38** was a significantly slower reaction that took five days to go to completion at room temperature. The crude reaction mixture contained a large number of products which were difficult to separate and were not characterized except for the major product (10%) which was found to have spectral data identical with the *cis* cyclobutenyl carbene complex **39a** isolated from the reaction of complex **19** with the *cis* propenyl ethyl ether **37**. This change in stereochemical relationship of the ethoxy and methyl groups must have occurred during the reaction of **19** with **38** since no loss of stereochemistry in the recovered enol ether **38** could be detected by ^{1}H NMR (*trans* : *cis* ≥ 65 : 1) and since the *trans* cyclobutenyl carbene complex **44** would be expected to undergo electrocyclic ring opening rather than isomerization. While the mass balance of these reactions are low and the outcome of these reactions can not be accounted for in complete detail, the isolation of the *cis* cyclobutenyl complex **39a** from the reaction of complex **19** with the *trans* propenyl ethyl ether **38** does indicate that this reaction is not stereospecific. This suggests that the [2 + 2] cycloaddition of the silyl substituted carbene complex **19** can occur *via* a two step mechanism that presumably would involve the zwitterionic species **42** or **43** which is stabilized by the effect of the silicon on the β-positive charge.

Stereoselectivity of the electrocyclic ring-opening of cyclobutenyl carbene complexes

It became clear that one of the reasons that the reactions of the complexes **18** and **19** with methyl propenyl ethers **37** and **38** gave low yields and/or variable product distributions was related to the fact the [2 + 2] adducts were undergoing electrocyclic ring-opening. To understand these reactions fully it was thus necessary to study the thermolysis of these cyclobutenyl carbene complexes. As a consequence of the large rate differences in the [2 + 2] cycloaddition of the *cis* and *trans* methyl propenyl ethers **37** and **38**, large quantities of the pure *cis*-cyclobutenyl adducts **39a**–**39d** could be obtained from the reaction of the commercially available mixture of *cis* and *trans* enol ethers thus obviating the need for the difficult separation of these isomers (see Experimental section). The investigation focused on the tungsten complexes **39a** and **39b** since the chromium complexes were not stable to storage with respect to ring-opening (**39c** undergoes slow electrocyclic ring-opening in the freezer).

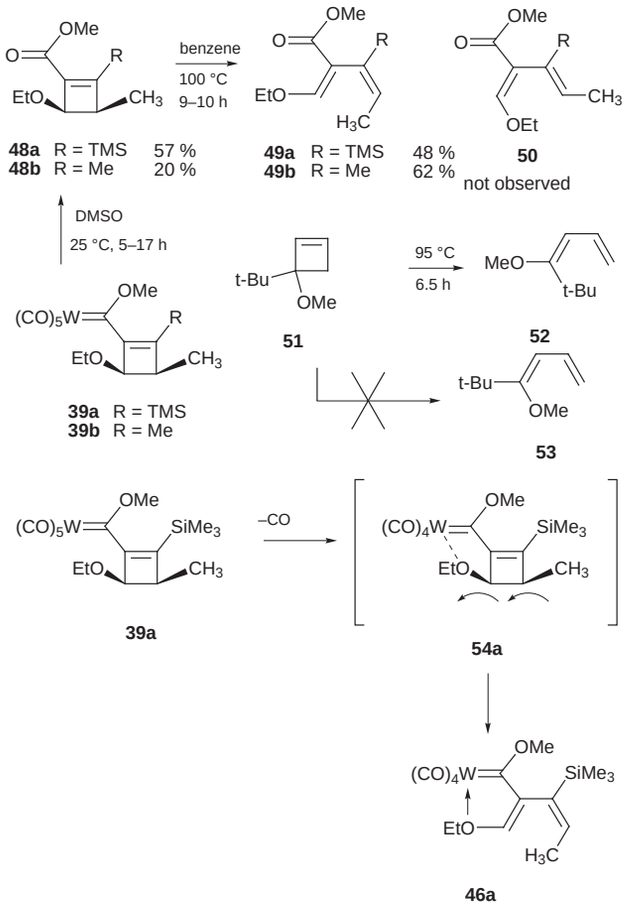
The thermolysis of the cyclobutenyl carbene complex **39a** in hexane at 70 °C under an argon atmosphere only gave two products which were mobile on silica gel. These were isolated and identified as the non-chelated and chelated *Z*,*E*-butadienyl complexes **40a** and **46a**, respectively (Scheme 6). The identity of



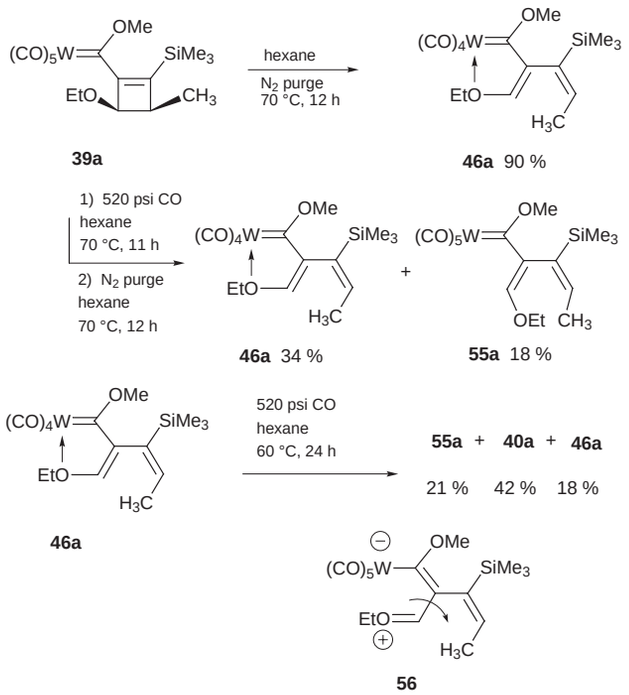
Scheme 6

the stereochemistry of the Δ^1-double bond in the two products was established when complex **40a** was heated for 5 hours at 70 °C in hexane, under a purge of nitrogen to sweep out carbon monoxide, and was found to give the chelated complex **46a** in 60% isolated yield. The chelated complex **46a** could be recycled in a quantitative fashion to complex **40a** by exposure to 700 psi of carbon monoxide at room temperature for 2 hours. The stereochemistry of the Δ^2-double bond in **40a** and **46a** was initially assigned on the basis of the expectation that the electrocyclic ring opening of **39a** would obey the Woodward–Hoffman rules and occur in a conrotatory fashion. Later the assignment was confirmed by a chemical correlation with complex **55a** whose structure was determined by X-ray diffraction. No detectable amount of the other possible conrotatory ring-opening product **47a** could be found from this reaction.

The preferential conrotatory ring-opening of an alkoxy-substituted cyclobutene that has the alkoxy group rotating in an outward manner has precedent.[19] From the work of Houk, for example, the electronic preference for the outward rotation of an alkoxy group has been shown to be strong enough to overcome the steric hindrance associated with the inward rotation of a *tert*-butyl group (cyclobutene **51**, Scheme 7). However, it has never been determined whether the presence of a strongly electron withdrawing group on the double-bond of the cyclobutene could influence the direction of the conrotatory ring-opening of an alkoxy-substituted cyclobutene. For example, the electrocyclic ring-opening of the cyclobutene **48** may be expected to give the diene **50** due to the electronic preference for alkoxy groups and ester groups to be *trans* on a double-bond.[20] To test if this would be the case, we oxidatively removed the metal in the cyclobutenyl complexes **39a** and **39b** by stirring with DMSO to give the cyclobutenyl esters **48a** and **48b**. The thermolysis of both **48a** and **48b** gave a single diastereomer of the butadiene **49**. The stereochemistry of diene **49** was deter-



Scheme 7



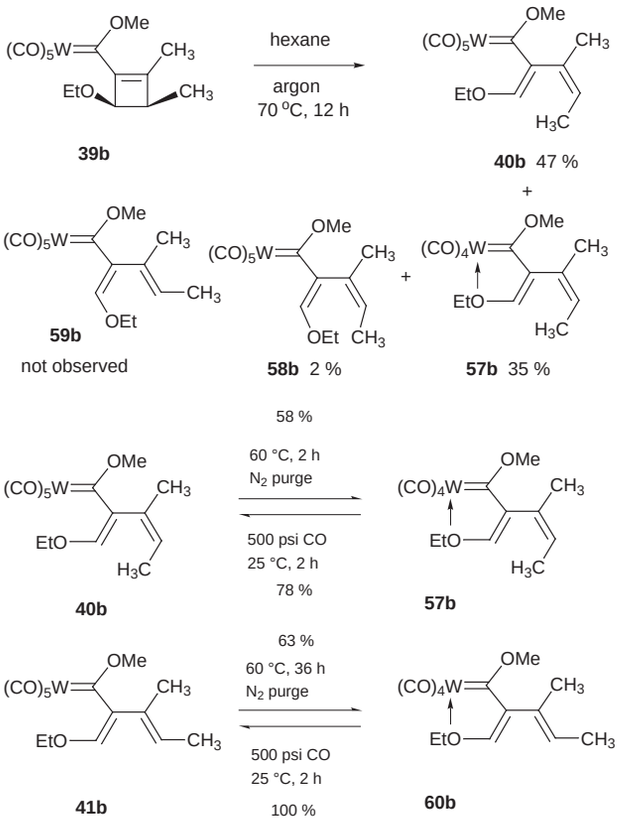
Scheme 8

mined in the case of the trimethylsilyl derivative **49a** by chemical correlation with the butadienyl carbene complex **46a**. The oxidative cleavage of **46a** was not efficient with either DMSO or with cerium(IV) (Scheme 11), but only a single silica gel mobile compound was isolated and it was found to be identical to the diene produced from the thermolysis of **48a**. These experiments reveal that neither an ester group nor a carbene complex substituent on the double-bond of **39** or **48** can offset the electronic preference for the ethoxy group to rotate outward.

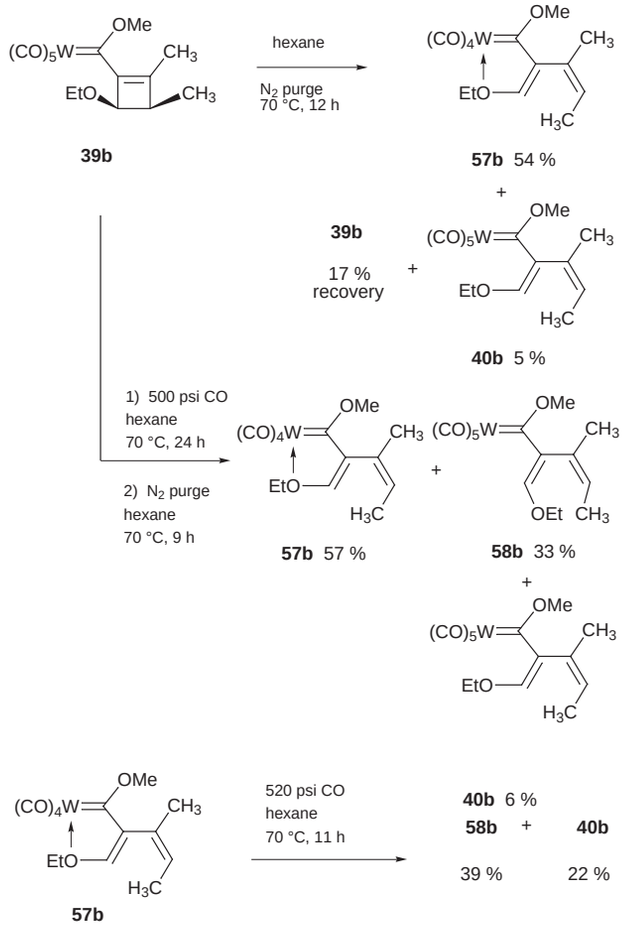
In the case of the cyclobutenyl carbene complex **39a**, there is another alternative explanation for the outward rotation of the ethoxy group. As illustrated in Scheme 7, it is possible that thermolysis of carbene complex **39a** results in an initial loss of a carbon monoxide ligand and then the open coordination site on the metal center leads to a directed electrocyclic ring-opening and the formation of the chelated dienyl complex **46a**. Return of the carbon monoxide ligand could regenerate the saturated complex **40a**. As a probe for this possibility, the thermolysis of **39a** was performed under 520 psi of carbon monoxide to maintain a saturated metal center. Indeed, as indicated in Scheme 8, a new isomer of the ring-opened carbene complex was produced under CO. The reason that the crude reaction mixture is heated under a nitrogen purge is to increase the mass balance. The mass balance for the thermolysis of **39a** under argon in a sealed flask was quite low (18%, Scheme 6). It was suspected that the reason for this was the instability of the saturated pentacarbonyl complex **40a**. Since the chelated tetracarbonyl complex **46a** was observed to be more stable than the saturated complex **40a**, the thermolysis of **39a** in hexane under a slow nitrogen purge was investigated to find that the chelated complex **46a** was produced in 90% yield. The mass balance was also improved for the thermolysis under CO but only to the extent of 52% and this may be due to loss of the saturated complex **40a** during the first phase of the process (70 °C, 11 hours). The new product from the thermolysis of **39a** under a CO atmosphere was initially assigned as the isomer **47a** (Scheme 6) since this is the other possible conrotatory ring-opened product. However, NOE experiments were not consistent with this assignment and this precipitated the determination of the structure of **55a** by X-ray diffraction. This confirmed that **55a** was the *E*,*E*-diastereomer and was quite a surprise since its formation would require that the electrocyclic ring-opening of **39a** occur in a disrotatory fashion. With the expectation that the Woodward–Hofmann rules were not violated in this reaction, we considered the possibility that **55a** was not a primary product in the thermolysis of **39a**. This was found to be the case, since when the chelated complex **46a** was heated to 60 °C in hexane for 24 hours under a CO atmosphere, a 21% yield of **55a** was produced along with a 42% yield of **40a** and the recovery of a small amount of **46a**. The selective isomerization about the Δ^1-double-bond of **46a** can be explained by the resonance structure **56** which is expected to be a significant contributor as a result of stabilization that should be accompanied by the indicated charge separation.

The thermolysis of the cyclobutenyl complex **39b** in hexane under an argon atmosphere produces three products which were isolated and identified as those shown in Scheme 9. It was shown that the two major products **40b** and **57b** both have the *Z*,*E*-configuration since they could be interconverted by the addition and extrusion of a carbon monoxide ligand. The corresponding pair of butadienyl carbene complexes **41b** and **60b**, obtained directly from the reaction of the alkynyl complex **18** with *trans*-propenyl ethyl ether **38** (Scheme 5), could also be interconverted by addition or subtraction of a CO ligand. Since the butadienyl complexes **40b** and **41b** both have a *Z*-configuration about the Δ^1-double bond, the third product **58b** from the thermolysis of **39b** must have an *E*-configuration about the Δ^1-double bond. The configuration about the Δ^2-double bond in **58b** was assigned on the basis of a comparison with the spectral data of **40b** and **41b** and with the complex **55a** whose structure was determined by X-ray diffraction.

As was the case for the thermolysis of complex **39a**, the thermolysis of **39b** under a carbon monoxide atmosphere produced an increased amount of the *E*,*E*-butadienyl carbene complex (**58b**, Scheme 10). Here also it was established that the *E*,*E*-isomer is produced from isomerization of the *Z*,*E*-isomer. Thermolysis of **57b** in hexane at 70 °C for 11 hours under an



Scheme 9

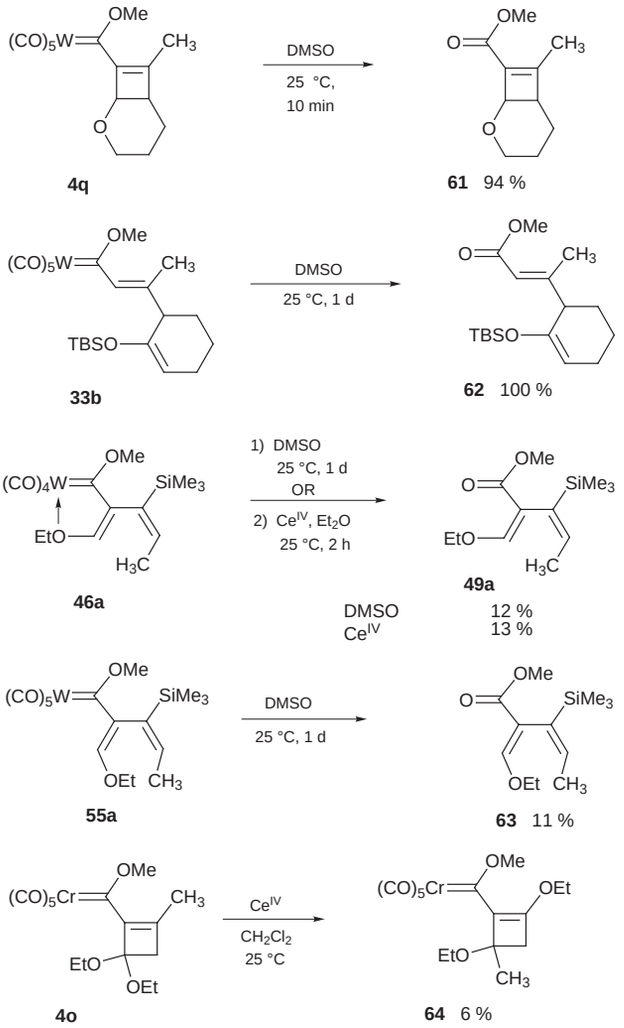


Scheme 10

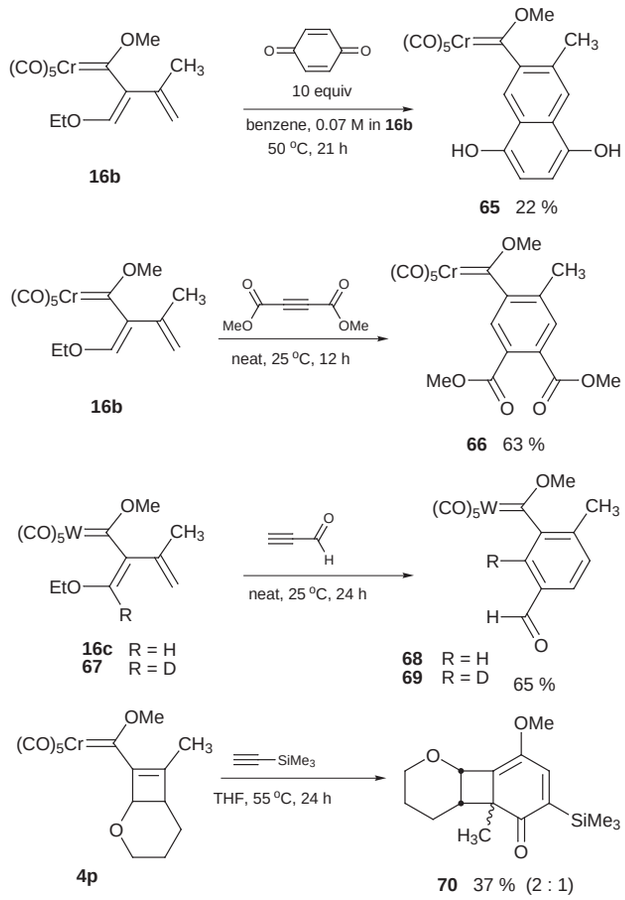
atmosphere of CO gave a 39% yield of **58b** and a 22% yield of the pentacarbonyl complex **40b**. Thus, for both the methyl- and trimethylsilyl-substituted tungsten cyclobutenyl complexes **39a** and **39b**, respectively, it was found that the electrocyclic ring-opening is stereoselectively occurring only in a conrotatory fashion and furthermore giving only the product in which the ethoxy group rotates outward.

Given the large rate acceleration noted for the [2 + 2] cycloadditions of alkynyl carbene complexes relative to their corresponding esters (**1** *vs.* **1a**, Scheme 1), these carbene complexes have value as synthons for alkynyl esters in [2 + 2] cycloadditions with enol ethers and ketene acetals. This is of course provided that the metal can be efficiently removed from the carbene complex after the cycloaddition. As illustrated in Scheme 11, the oxidative cleavage with DMSO is quite efficient in giving esters from both the [2 + 2] cycloadducts and from the ene products. The ring-opened butadienyl esters are only obtained in low yields from the oxidation of the ring-opened carbene complexes. Thus, the butadienyl esters are more readily obtained by oxidative removal of the metal prior to the electrocyclic ring-opening since it was established (Scheme 7) that the cyclobutenyl ester **48** and the cyclobutenyl carbene complex **39** both give the same stereochemistry for the electrocyclic ring-opening. This is illustrated for the butadienyl ester **49a** where oxidative removal of the metal occurs in 12% yield after the ring-opening but in 57% yield before the ring-opening (Scheme 7). Finally, it was surprising to find that one of the products from the oxidative cleavage the cyclobutenyl acetal complex **4o** was a new carbene complex. Since cine-rearrangements of cyclobutenes have been documented,[21] it was thus possible that cerium induced a 1,3-migration of the ethoxy group to give the complex **64** which would be expected to be more resistant to oxidation due to the conjugation of the enol ether function with the carbene complex. The structure of **64** was confirmed by an X-ray diffraction. This observation suggests that the effect of other metals of lower oxidizing potential be investigated with regard to effecting this interesting cine rearrangement. A cine-rearrangement of a related cyclobutenyl carbene complex has been proposed as one possible pathway for an intermolecular reaction of an ynyl carbene complex with an alkene function.[6f]

The synthetic value of the [2 + 2] cycloadditions of alkynyl carbene complexes is not limited to the ability of these complexes to serve as synthons for alkynyl esters in [2 + 2] cycloadditions as discussed above, but also their synthetic value derives from the unique overall transformations made possible by coupling of the [2 + 2] cycloadditions of carbene complexes with other reactions of carbene complexes and a few examples are presented in Scheme 12.[22] The butadienyl complexes **16b** and **16c** will undergo Diels–Alder reactions with typical dienophiles at or near room temperature. If the Diels–Alder reaction is carried out at too high a temperature, then the chelated butadienyl complex is formed which is inert to the Diels–Alder reaction. In each case shown in Scheme 12, the initial cycloadduct suffers loss of ethanol to give aromatized carbene complexes such as the interesting hydronaphthoquinone complex **65**. The issue of regiochemistry for these Diels–Alder reactions was investigated in the reaction of complex **16c** with propynal. It was not clear before this reaction was performed whether the ethoxy group on the diene **16c** would control the regiochemistry or whether the carbene complex substituent would control the regiochemistry. If the ethoxy group was in control then the product would be **68** and if the carbene complex was in control then the product would be an isomer of **68** in which the carbaldehyde group would be *para* to the carbene complex substituent. The regiochemistry of this reaction was determined by carrying out the Diels–Alder reaction with the deuterated butadienyl complex **67** which was prepared from the reaction of α-deuteroethyl vinyl ether with alkynyl complex **18** and which reacted with propynal to give **69**. Thus the ethoxy group controls the regiochemistry of this cycloaddition which suggests perhaps that in the reactive conformation, the carbene complex substituent on the diene is twisted so as not to be in the



Scheme 11



Scheme 12

plane of the s-*cis* diene. Finally, the cyclobutenyl complexes will undergo cyclohexadienone annulations with alkynes in a process that incorporates the alkyne, the carbene ligand, the α,β-unsaturated substituent of the carbene complex and a carbon monoxide ligand as illustrated by the reaction of **4p** with trimethylsilylacetylene.[8]

In summary, the [2 + 2] cycloaddition of alkynyl carbene complexes with enol ethers is an effective method for the synthesis of cyclobut-1-enyl esters and their ring opened isomers, butadien-2-yl esters. The electrocyclic ring-opening reaction that converts the former to the latter occurs in a conrotatory fashion with an outward rotation of an alkoxy group for both the esters and their corresponding carbene complexes. The cyclobut-1-enyl carbene complexes and the butadien-2-yl carbene complexes are also of synthetic value as a result of the special reactivity imparted to these fragments by the metal pentacarbonyl group as is illustrated by Diels–Alder and cyclohexadienone annulation.

Experimental

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran, ether and benzene were distilled from benzophenone ketyl under nitrogen. Dichloromethane and hexane were distilled from calcium hydride. Proton NMR data were obtained either on a University of Chicago built DS-1000 500 MHz instrument or a QE-300 MHz instrument. Carbon-13 spectral data were obtained on the QE-300 instrument at 75 MHz. Infrared spectra were taken on a Nicolet 20SX FTIR. Low-resolution mass spectra were recorded on a Finnigan 1015 mass spectrometer. High-resolution mass spectra were recorded on a VG 70-250 instrument or obtained from the Midwest Center for Mass Spectrometry in Lincoln, NE. Elemental analyses were done by Galbraith Laboratories in Knoxville, TN.

The *cis* and *trans* isomers of 1-ethoxypropene[23a] were separated by distillation using a Nester Faust spinning band distillation[23b] apparatus with a 24 inch Teflon coiled band. Potassium carbonate (5 mol%) was added to the distillation pot to prevent polymerization of the olefin. The distillation was monitored by gas chromatography (OV-101 column, 25 °C column temperature; *cis* olefin, R_t = 6.9 min: *trans* olefin, R_t = 8.3 min). Final criterion of purity was measured by ^{1}H NMR integration. The purity of the isomers was established by the ratio of the integration curve values where the integration value for any "*cis* contaminant" was measured over the region of δ 5.9–6.0 and any "*trans* contaminant" over the region of δ 6.15–6.25; spectrum noise was included in this measurement. The purity of the *cis* isomer was determined to be ≥54 : 1 (*cis* : *trans*) and that of the *trans* isomer as >65 : 1 (*trans* : *cis*).

General procedure for the reaction of silyl and alkyl enol ethers with acetylenic carbene complexes

The carbene complexes were purified by column chromatography immediately prior to use. The carbene complex (50 mg–1.0 g) was added to a round bottomed flask which has been adapted with a threaded Teflon high vacuum valve stopcock. The enol ether was then added *via* syringe in quantities to effect solvation of the complex. The mixture is then deoxygenated by the freeze–thaw method (−196 °C to 22 °C, 3 cycles) and allowed to stir at 25 °C under one atmosphere of argon. The progress of the reactions was followed by TLC unless otherwise specified. When the starting complex was consumed, the

volatiles are removed by high vacuum (0.01 mmHg) and the residue loaded directly onto a silica gel column and eluted with either hexanes or a ternary mixture of ether, methylene chloride and hexanes. All yields reported are of isolated, purified material.

The preparation of 2,3-bis(*tert*-butyldimethylsiloxy)buta-1,3-diene 13

A solution of 1.66 mL (18.92 mmol) of butane-2,3-dione and 11.0 mL (78.92 mmol) of triethylamine (dried over CaH_2) was prepared in 95 mL of anhydrous ether. After cooling to −20 °C, under argon, 10 g (37.83 mmol) of *tert*-butyldimethylsilyl triflate was added dropwise *via* cannula. Upon completion of the addition, the cold bath was removed and the solution was allowed to warm to room temperature over 1 hour. The organic layer was decanted and washed with pH = 4 buffer solution and brine and dried over Na_2SO_4. Following filtration and concentration on the rotary evaporator, the residue was chromatographed from silica gel, with hexanes to give 3.78 g (67%) of a viscous, colorless oil which was identified as diene **13** on the basis of the following spectral data: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 12H), 0.98 (s, 18H), 4.3 (br s, 2H), 4.84 (br s, 2H); Anal. calcd. for $C_{16}H_{34}O_2Si_2$: C, 61.08; H, 10.89. Found: C, 61.32; H, 10.36%.

The reaction of the propynyl chromium carbene complex 12 with 2,3-bis(siloxy)diene 13 to give 4a

A mixture of 0.289 g (0.92 mmol) of complex **12**[4a] and 0.261 g (0.92 mmol) of 2,3-bis(*tert*-butyldimethylsiloxy)buta-1,3-diene **13** reacted according to the general procedure. After stirring at 25 °C for 18 hours the reaction appeared complete by TLC. The crude mixture was placed on a silica gel column which had been pre-treated with triethylamine (TEA) and eluted with pentane. Pre-treatment consisted of preparing a slurry of silica gel and a 10% solution of TEA in hexanes and thoroughly removing the volatiles with heat under high vacuum (0.01 mmHg). By this route, complex **4a** was obtained (91 mg, 45%) as a red oil. ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 3H), 0.02 (s 3H), 0.06 (s, 3H), 0.10 (s, 3H), 0.84 (s, 9H), 0.97 (s, 9H), 2.24 (d, 1H, J = 16.2 Hz), 2.24 (s, 3H), 2.58 (d, 1H, J = 16.2 Hz), 4.16 (s, 1H), 4.24 (s, 3H), 4.84 (s, 1H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2930w, 2858w, 2058m, 1981w, 1940s, 1193w, 1166w, 1082w, 840w.

The reaction of the propynyl chromium and tungsten carbene complexes 12 and 18 with ethyl vinyl ether to give 16b and 16c

Complex 12. A mixture of 0.304 g (1.11 mmol) **12**[4a] and 0.604 g (8.88 mmol) of ethyl vinyl ether was deoxygenated according to the general procedure. After 29 hours the volatiles were removed and the residue chromatographed on silica gel using a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes as the mobile phase. A red crystalline solid was obtained (113 mg, 29%) which was identified as **16b**: ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3H, J = 7.1 Hz), 1.90 (s, 3H), 3.92 (q, 2H, J = 7.1 Hz), 4.2 (s, 3H), 4.30 (s, 1H), 4.86 (s, 1H), 5.89 (s, 1H); IR ($CHCl_3$) ν_{max}/cm^{-1} 2952m, 2926m, 2887m, 2855w, 2061s, 1990s, 1918s, 1620s, 1455w, 1390w, 1379w, 1350w, 1308w, 1101s, 968s, 888w, 604w; mass spectrum *m*/*z* (% rel. intensity) 346 M$^+$ (29), 318 (12), 290 (24), 262 (15), 234 (71), 206 (100), 191 (7), 177 (35), 162 (96), 147 (30), 132 (36), 119 (61), 103 (10), 91 (26) 80 (22), 67 (9). Anal. calcd. for $C_{14}H_{14}O_7Cr$: C, 48.56; H, 4.08. Found: C, 48.67; H, 4.06.

Complex 18. A mixture of 0.501 g (1.23 mmol) of complex **18**[4a] and 3.0 mL (31.37 mmol) of ethyl vinyl ether was reacted according to the general procedure. After four hours, the volatiles were removed and the residue was chromatographed using a 1 : 1 : 50 solvent mixture to give compound **16c** (232 mg, 40%) as a red crystalline solid: ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3H, J = 7.08 Hz), 1.89 (s, 3H), 3.91 (q, 2H, J = 7.08 Hz), 4.1–4.35 (br s, 3H), 4.39 (s, 1H), 4.86 (s, 1H), 5.90 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.05 (q, J_{CH} = 127.2 Hz), 20.04 (q, J_{CH} = 128.9 Hz), 63.5–70.0 (m), 69.70 (t, J_{CH} = 144.32 Hz), 112.75 (t, J_{CH} = 157.4 Hz), 133–135 (broad), 135.20 (s), 137.14 (d, J_{CH} = 180.1 Hz), 197.78 (s), 205.74 (s), 329.61 (s); IR ($CHCl_3$) ν_{max}/cm^{-1} 2070m, 1985w, 1939s, 1520w, 1385w, 1107w, 981w, 958w; mass spectrum *m*/*z* (% rel. intensity) 478 M$^+$ (29, ^{184}W), 450 (55), 422 (20), 394 (45), 323 (100), 295 (96), 265 (51), 238 (27), 224 (10), 210 (7), 84 (14). Anal. calcd. for $C_{14}H_{14}O_7W$: C, 35.17; H, 2.95. Found: C, 35.22; H, 2.94. Compound **4c** was obtained as a minor product during the preparation of **16c**. It was obtained in 6–17% yield, depending on the total reaction time. **4c** is a red oil. ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, J = 7.04 Hz), 1.96 (s, 3H), 2.10 (dd, 1H, J = 16.0, 1.8 Hz), 2.46 (dd, 1H, J = 16.0, 1.8 Hz), 3.5–3.62 (m, 2H), 4.55 (s, 3H), 4.86 (br s, 1H); IR ($CHCl_3$) ν_{max}/cm^{-1} 2068m, 1985w, 1937s, 1620w, 1588w, 1358m, 1105w, 1079w, 973w; mass spectrum *m*/*z* (% rel. intensity) 478 M$^+$ (24, ^{184}W), 450 (38), 422 (32), 394 (46), 367 (16), 339 (71), 324 (84), 294 (100), 266 (75), 239 (35), 215 (16), 199 (9), 183 (7), 84 (17).

The reaction of the trimethylsilylacetylene tungsten carbene complex 19 with ethyl vinyl ether to give 16d and 17d

The reaction of 0.124 g (0.27 mmol) of complex **19**[4a] with 3.0 ml of ethyl vinyl ether was carried out as described in the general procedure. After reaction for 9 hours at 25 °C, the volatiles were removed under high vacuum (0.01 mmHg) and the crude mixture was purified by flash chromatography using a 1 : 1 : 20 ternary solvent mixture to give 113 mg (79% yield) of **16d** as a red oil and 27 mg (19%) of **17d** as a brown oil. Spectral data for **17d**: ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.33 (t, 3H, J = 7.1 Hz), 4.51 (s, 3H), 4.66 (q, 2H, J = 7.1 Hz), 5.5 (d, 1H, J = 2.7 Hz), 5.6 (d, 1H, J = 2.7 Hz), 7.11 (s, 1H); IR (neat) ν_{max}/cm^{-1} 2955m, 2019s, 1905s, 1842s, 1595m, 1450m, 1236m, 1082m, 1002m, 841m. Spectral data for **16d**: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H), 1.32 (t, 3H, J = 7.1 Hz), 3.96 (q, 2H, J = 7.1 Hz), 4.30 (s, 3H), 5.23 (d, 1H, J = 1.9 Hz), 5.37 (d, 1H, J = 2.0 Hz), 6.11 (s, 1H); ^{1}H NMR (C_6D_6) δ 0.16 (s, 9H), 0.94 (t, 3H, J = 7.14 Hz), 3.37 (q, 2H, J = 7.14 Hz), 3.71 (s, 3H), 5.24 (d, 1H, J = 1.8 Hz), 5.28 (d, 1H, J = 1.8 Hz), 5.90 (s, 1H); IR (neat) ν_{max}/cm^{-1} 2955s, 2898m, 2067s, 2020s, 1984s, 1920s, 1849s, 1613s, 1582m, 1448s, 1391m, 1193m, 1088s, 963s, 845s; ^{13}C NMR ($CDCl_3$) δ −0.32 (q, J_{CH} = 119.3 Hz), 15.17 (q, J_{CH} = 126.94 Hz), 66.23 (q, J_{CH} = 148.03 Hz), 70.16 (t, J_{CH} = 144.6 Hz), 125.04 (t, J_{CH} = 155.8 Hz), 136.36 (s), 142.32 (d, J_{CH} = 178.0 Hz), 144.05 (s), 198.06 (t, J_{CW} = 63.8 Hz), 205.35 (s), 325.55 (s). Anal. calcd. for $C_{16}H_{20}O_7SiW$: C, 35.84; H, 3.76. Found: C, 35.68; H, 3.70.

Reaction of the propynyl tungsten carbene complex 18 with isobutyl vinyl ether to give 16e

The reaction of 0.143 g (0.353 mmol) of complex **18**[4a] and 0.5 mL (3.83 mmol) of isobutyl vinyl ether was carried out according to the general procedure for 18 hours at 25 °C. The major product was purified by chromatography on silica gel using a 1 : 1 : 50 solvent mixture to give 95.7 mg (54%) of a red oil which was tentatively identified as **16e**: ^{1}H NMR ($CDCl_3$) δ 0.93 (d, 6H, J = 6.7 Hz), 1.89 (s, 3H), 1.8–2.0 (m, 1H), 3.60–3.65 (m, 2H), 4.18–4.38 (br s, 3H), 4.40 (s, 1H), 4.87 (s, 1H), 5.87 (s, 1H).

Reaction of the trimethylsilylacetylene tungsten carbene complex 19 with isobutyl vinyl ether to give 16f

A mixture of 0.127 g (0.274 mmol) of **19**[4a] and 0.80 mL (6.13 mmol) of isobutyl vinyl ether was reacted according to the general procedure. After 24 hours at 25 °C, the reaction appears ≈50% complete. After 36 hours, the reaction was judged complete and the volatiles were removed under vacuum (0.01

mmHg) and the residue eluted from silica gel with hexanes. A single red band was collected to give 78.3 mg (51%) of a compound tenatively assigned as **16f**: ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9H), 0.95 (d, 6H, J = 6.7 Hz), 2.14–2.4 (m, 1H), 3.64 (d, 2H, J = 6.6 Hz), 4.31 (s, 3H), 5.21 (d, 1H, J = 1.5 Hz), 5.37 (d, 1H, J = 1.9 Hz), 5.99 (s, 1H).

Reaction of the trimethylsilylacetylene tungsten carbene complex 19 with *tert*-butyldimethylsiloxyethene to give 16g

A sample (0.196 g, 0.42 mmol) of complex **19**[4a] was combined neat with 2.96 g (18.7 mmol) of *tert*-butyldimethylsiloxyethene and reacted under the conditions described in the general procedure. After 25 hours, the volatiles were removed and the residue chromatographed from silica gel, using hexanes as the eluent to give 80 mg of starting complex **19**. A single red band was collected (21 mg, 8%, 13% based on recovered starting complex) and identified as **16g**: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.22 (s, 9H), 0.93 (s, 9H), 4.2–4.4 (br s, 3H), 5.18 (s, 1H), 5.39 (s, 1H), 6.09 (s, 1H); IR (neat) ν_{max}/cm^{-1} 2955m, 2932m, 2861m, 2069s, 1984m, 1928s, 1605m, 1472w, 1434w, 1364w, 1253m, 1235m, 1192m, 1152m, 1082m, 964w, 861m, 832m, 785w, 724.

The reaction of the propynyl chromium and tungsten carbene complexes 12 and 18 with 2-methoxypropene to give 4h and 4i

Complex 18. A neat mixture of 0.508 g (1.25 mmol) of complex **18**[4a] in 4.0 mL (41.77 mmol) of 2-methoxypropene was deoxygenated and reacted according to the general procedure. After 3 hours the volatiles were removed and the residue was eluted from a silica gel column using a 1 : 1 : 20 ternary solvent mixture. The two principal colored bands were collected and identified by their spectral data as **5i** and **4i**. Complex **5i**: 13 mg, 2.1%, red oil; ^{1}H NMR ($CDCl_3$) δ 1.86 (d, 3H, J = 0.5 Hz), 2.83 (s, 2H), 3.54 (s, 3H), 3.98 (d, 1H, J = 2.0 Hz), 4.05 (d, 1H, J = 2.2 Hz), 4.59 (s, 3H), 7.29 (br s, 1H); mass spectrum *m*/*z* (% rel. intensity) 478 M$^+$ (39, ^{184}W), 422 (68), 392 (24), 364 (18), 336 (100), 321 (42), 306 (54), 291 (71), 279 (50), 265 (47), 250 (40), 224 (33), 210 (18), 167 (13), 153 (19), 123 (19), 105 (37), 91 (78), 77 (37). Complex **4i**: 490 mg, 82%, red solid: ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3H), 2.11 (d, 1H, J = 16.3 Hz), 2.32 (s, 3H), 2.56 (d, 1H, J = 16.3 Hz), 3.13 (s, 3H), 4.54 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 19.22 (q, J_{CH} = 133 Hz), 24.16 (q, J_{CH} = 133 Hz), 43.0 (t, J_{CH} = 138 Hz), 51.79 (q, J_{CH} = 133 Hz), 68.65 (q, J_{CH} = 148 Hz), 80.50 (s), 157.35 (s), 162.44 (s), 197.6 (s), 202.92 (s), 305.27 (s); IR ($CHCl_3$) ν_{max}/cm^{-1} 3345br m, 2954w, 2927w, 2872w, 2859w, 2066w, 2980w, 1939s, 1708w, 1617w, 1592w, 1572w, 1358s, 1103w, 976w, 889w, 595w; mass spectrum *m*/*z* (% rel. intensity) 478 M$^+$ (21, ^{184}W), 450 (35), 422 (26), 392 (9), 366 (32), 321 (100), 293 (89), 265 (33), 249 (26), 223 (16), 147 (8), 123 (14), 105 (5), 91 (15), 79 (8), 67 (7). Anal. calcd. for $C_{14}H_{14}O_7W$: C, 35.17; H, 2.95. Found: C, 35.20; H, 2.99. R_f = 0.26 (1 : 1 : 10, ether : methylene chloride : hexanes).

Complex 12. This reaction was performed as described above for complex **18** on 0.262 g (0.96 mmol) of **12**[4a] in 6.0 mL (62.6 mmol) of 2-methoxypropene. After 12 hours, the volatiles were removed and the residue chromatographed on silica gel with a 1 : 1 : 10 solvent mixture to give 210 mg (63%) of **4h** as a red crystalline solid: ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3H), 2.21 (d, 1H, J = 15.9 Hz), 2.42 (s, 3H), 2.66 (d, 1H, J = 15.9 Hz), 3.1 (s, 3H), 4.70 (s, 3H); ^{13}C NMR (C_6D_6) δ 19.78 (q, J_{CH} = 127.5 Hz), 25.19 (q, J_{CH} = 125.9 Hz), 43.55 (t, J_{CH} = 137.2 Hz), 52.32 (q, J_{CH} = 140.8 Hz), 66.88 (q, J_{CH} = 147.9 Hz), 81.55 (s), 156.46 (s), 161.67 (s), 218.31 (s), 225.14 (s), 333.62 (s). IR (CH_2Cl_2) ν_{max}/cm^{-1} 2058w, 1981w, 1940s; mass spectrum *m*/*z* (% rel. intensity) 346 M$^+$ (11), 318 (16), 290 (20), 262 (32), 234 (90), 206 (100), 191 (20), 176 (27), 163 (46), 146 (61), 133 (39), 105 (18), 91 (38), 82 (25), 67 (8). Anal. calcd. for $C_{14}H_{14}O_7Cr$: C, 48.56; H, 4.08. Found: C, 48.65; H, 4.03.

Thermally induced electrocyclic ring opening of chromium and tungsten cyclobutenyl carbene complexes 4h and 4i to give the dienyl complexes 17h and 17i

Thermolysis of 4h. A 0.06 M solution of 0.123 g (0.36 mmol) of complex **4h** in 6 mL C_6H_6 was deoxygenated as described in the general procedure and was heated under argon. The reaction was monitored by TLC and was heated at 45 °C for 3 hours, 60 °C for 12 hours and finally at 85 °C for 8 hours. At this time, the crude ^{1}H NMR indicated the presence of one dienyl complex. The solvent was removed under high vacuum (0.01 mmHg) and the residue was purified by flash chromatography using a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes as the eluent. The dienyl complex **17h** was obtained as a brown solid in 55% yield (82 mg). A second brown band was collected to give compound **71** (5 mg, 3.4% yield) whose structure has not been assigned but whose data indicate it is an isomer of **17h**. Complex **17h**: ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3H), 2.18 (s, 3H), 4.18 (s, 3H), 4.62 (d, 1H, J = 0.9 Hz), 4.66 (s, 3H), 5.15 (d, 1H, J = 0.9 Hz); IR ($CHCl_3$) ν_{max}/cm^{-1} 2014m, 1918s, 1846m, 1603w; mass spectrum *m*/*z* (% rel. intensity) 318 M$^+$ (43), 290 (10), 262 (16), 234 (67), 206 (95), 191 (13), 176 (18), 163 (100), 144 (13), 133 (78), 123 (23), 105 (20), 91 (23), 83 (24), 77 (11), 67 (13). Compound **71**: ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H), 2.31 (s, 3H), 3.24 (s, 1H), 3.77 (s, 3H), 4.25 (s, 1H), 4.36 (s, 3H); IR ($CHCl_3$) ν_{max}/cm^{-1} 2009s, 1917s, 1870m, 1602w, 1579w, 987w; mass spectrum *m*/*z* (% rel. intensity) 318 M$^+$ (37), 290 (10), 262 (15), 234 (46), 206 (77), 176 (15), 163 (100), 133 (63), 119 (20), 105 (18), 91 (22), 83 (17).

Thermolysis of 4i. The thermolysis of 0.259 g (0.54 mmol) of complex **4i** was carrried out as described for **4h** above. After 24 hours at 50 °C and then 24 hours at 75 °C the reaction mixture was loaded onto a chromatography column and upon elution with a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes complex **17i** was isolated as a brown solid in 43% yield (111 mg): ^{1}H NMR ($CDCl_3$) δ 1.78–1.79 (m, 3H), 2.19 (s, 3H), 4.49 (s, 6H), 4.64 (m, 1H), 5.16 (m, 1H); ^{1}H NMR (C_6D_6) δ 1.12 (s, 3H), 1.60 (d, 3H, J = 1.1 Hz), 3.42 (s, 3H), 4.20 (s, 3H), 4.44–4.45 (m, 1H), 4.95–4.96 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.49 (q, J_{CH} = 130.25 Hz), 23.69 (q, J_{CH} = 129.3 Hz), 68.42 (q, J_{CH} = 149.4 Hz), 69.34 (q, J_{CH} = 146.9 Hz), 117.33 (t, J_{CH} = 156.2 Hz), 138.80 (s), 139.86 (s), 173.68 (s), 201.86 (s), 216.14 (s), 219.64 (s), 312.38 (s); IR ($CHCl_3$) ν_{max}/cm^{-1} 2018m, 1917s, 1845m, 1612w, 1454w, 1358m, 983w, 895w; mass spectrum calcd. for $C_{13}H_{14}O_6{}^{186}W$ *m*/*z* 452.0333, measured 452.0348.

The reaction of the phenylacetylene tungsten carbene complex 20 with 2-methoxypropene to give 4j and 17j

A mixture of 0.158 g (0.337 mmol) of 1-methoxy-3-phenylprop-2-ynylidene(pentacarbonyl)tungsten(0) **20**[23] in 1.5 mL (15.66 mmol) of 2-methoxypropene was allowed to react under the conditions described in the general procedure. After 24 hours at 25 °C, the volatiles were removed and the residue was chromatographed on silica gel using a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes as the eluent. Many compounds were formed in the reaction but only the three major bands were collected. In order of elution the first band (28.3 mg) was determined to be a mixture of **4j** and **16j**. The second band (29.1 mg) was found to be a mixture of **16j** and **17j**. The third band was found to be a pure fraction of **17j** (37.3 mg, 22%). Compounds **4j** and **16j** were difficult to further purify since slow conversion of **4j** to **16j** and of **16j** to **17j** was observed. The presence of **4j** was indicated by methyl singlets at δ = 1.68, 3.32 and 4.52 and doublets (J = 1.2 Hz) at δ = 5.09 and 5.63. The presence of **16j** was indicated by methyl singlets at δ = 1.96, 3.76 and 4.32 and doublets (J = 13.7 Hz) at δ = 2.59 and 2.97. The first fraction is nearly pure **4j** and the yield is estimated to be 14%. The yield of **16j** was not estimated but upon standing it gave an additional 12% of **17j**. Chelated com-

plex **17j**: R_f(1 : 1 : 10, ether : methylene chloride : hexanes) = 0.42; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H), 4.37 (s, 3H), 4.57 (s, 3H), 5.02 (s, 1H), 5.89 (s, 1H), 7.2–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.74 (q, J_{CH} = 129.9 Hz), 68.66 (q, J_{CH} = 150.1 Hz), 69.30 (q, J_{CH} = 147.1 Hz), 116.95 (t, J_{CH} = 158.2 Hz), 125.45 (d, J_{CH} = 158.1 Hz), 127.99 (d, J_{CH} = 160.4 Hz), 128.54 (d, J_{CH} = 160.2 Hz), 136.77 (s), 138.53 (s), 141.79 (s), 175.30 (s), 201.80 (s), 215.99 (s), 219.62 (s), 311.69 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2018m, 1976w, 1911s, 1843m. Anal. calcd. for $C_{18}H_{16}O_6W$: C, 42.21; H, 3.15. Found: C, 42.75; H, 3.23.

Preparation of 1-methoxy-4-methylpent-2-ynylidene(pentacarbonyl)tungsten(0) 21

A solution of 1.7 mL (16.6 mmol) of isopropylacetylene in 100 mL THF under argon was cooled to −78 °C and 10.0 mL (1.6 M in hexane, 16.0 mmol) of *n*-butyllithium was added dropwise. The mixture was stirred for 20 minutes at −78 °C and then allowed to warm to 0 °C over 30 minutes. At this time, the formation of the metal acylate was assumed to be complete and the solution was transferred (*via* cannula) to a suspension of 6.21 g (17.6 mmol) of $(CO)_6W$ in 300 mL THF. After the addition was complete, the resulting solution was allowed to stir at room temperature for an additional hour. The solvent was then removed by rotary evaporation, and the residue was taken up in 300 mL CH_2Cl_2. The methylene chloride solution was cooled to 0 °C and 3.5 g (23.66 mmol) of $(CH_3)_3OBF_4$ and 1.0 mL water was added. The ice bath was removed and the suspension was allowed to come to room temperature over 20 minutes. At this time, the solution had turned to a dark burgundy color and was diluted with 300 mL of ether and quenched by extraction with liberal amounts of water (approximately 500 mL) and brine (approximately 500 mL). After drying over $MgSO_4$ and filtration through Celite, the volatiles were removed on the rotary evaporator and the residue was chromatographed on silica gel with hexanes as eluent to give 3.614 g (52%) of a dark red-black oil which was identified as **21**. Spectral data for **21**: ^{1}H NMR ($CDCl_3$) δ 1.33 (d, 6H, J = 6.9 Hz), 2.97–3.03 (m, 1H), 4.26 (br s, 3H); ^{13}C NMR ($CDCl_3$) δ 21.70 (q, J_{CH} = 129.2 Hz), 23.16 (d), 66.30 (br m), 90.5 (br s), 143.0 (br s), 197.44 (t, J_{CW} = 63.4 Hz), 205.68 (s), 291.4 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2069m, 1945s; mass spectrum *m*/*z* calcd. for $C_{12}H_{10}O_6{}^{186}W$ 436.0020, measured 436.0010. Anal. calcd. for $C_{12}H_{10}O_6W$: C, 33.21; H, 2.32. Found: C, 33.40; H, 2.36.

The reaction of the isopropylalkynyl tungsten carbene complex 21 with 2-methoxypropene to give 4k

The reaction of 0.649 g (1.49 mmol) of complex **21** with 3.0 mL (31.33 mmol) of 2-methoxypropene was carried out according to the general procedure. The reaction appeared complete by TLC after 6 hours. After the volatiles were removed the residue was chromatographed on silica gel using a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes as the eluent. Two major products were obtained and identified by their spectral data as, in order of their elution, the ene product **5k** (31 mg, 4.1%, unstable red oil) and the [2 + 2] cycloadduct **4k** (602 mg, 80%, red solid). Spectral data for **5k**: ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 6H, J = 6.9 Hz), 2.84 (s, 2H), 3.26–3.38 (m, 1H), 3.55 (s, 3H), 4.02 (d, 1H, J = 2.2 Hz), 4.12 (d, 1H, J = 2.0 Hz), 4.50 (s, 3H), 7.08 (br s, 1H). Spectral data for **4k**: ^{1}H NMR ($CDCl_3$) δ 1.09 (d, 3H, J = 6.8 Hz), 1.16 (d, 3H, J = 6.8 Hz), 1.49 (s, 3H), 2.11 (d, 1H, J = 16.1 Hz), 2.48 (d, 1H, J = 16.1 Hz), 3.11 (s, 3H), 3.54–3.64 (m, 1H), 4.52 (s, 3H); mass spectrum *m*/*z* (% rel. intensity) 506 M^+ (20, ^{184}W), 478 (18, ^{184}W), 450 (5, ^{184}W), 422 (7, ^{184}W), 394 (20, ^{184}W), 366 (79, ^{184}W), 349 (82), 321 (40), 289 (40), 249 (43), 224 (17), 182 (1), 151 (25), 105 (10), 83 (100).

The preparation of 1-methoxy-4,4-dimethylpent-2-ynylidene-(pentacarbonyl)tungsten(0) 22

This complex was prepared on an 11 mmol scale in 45% yield by the procedure described above for the isopropylalkynyl complex **21**. Spectral data for **22**: ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9H), 4.26 (s, 3H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2069m, 1945s, 1097w; mass spectrum *m*/*z* (% rel. intensity) 448 M^+ (100, ^{184}W), 392 (50, ^{184}W), 364 (74, ^{184}W), 336 (81, ^{184}W), 308 (83, ^{184}W), 291 (32), 261 (70), 247 (31), 222 (25), 208 (9), 184 (2), 146 (1), 124 (3). Anal. calcd. for $C_{13}H_{12}O_6W$: C, 34.85; H, 2.70. Found: C, 34.89; H, 2.78.

The reaction of the *tert*-butylalkynyl tungsten carbene complex 22 with 2-methoxypropene to give 4l

The reaction of 0.518 g (1.16 mmol) of complex **22** with 3.0 mL (31.33 mmol) of 2-methoxypropene was performed neat according to the general procedure. After 48 hours, the majority of the starting complex had been consumed and the volatiles were removed and the residue was chromatographed on silica gel using a 1 : 1 : 20 mixture of ether : methylene chloride : hexanes as the eluent. Many compounds were formed in this reaction which remain unidentified; however, there was no evidence by ^{1}H NMR of ene product presence in any fraction taken from the column. The major product was obtained as a red solid (208.5 mg, 53%) and was identified as the [2 + 2] cycloadduct **4l**: ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.55 (s, 3H), 2.19 (br d, 1H, J = 13.4 Hz), 2.48 (d, 1H, J = 13.4 Hz), 3.26 (s, 3H), 4.44–4.55 (br s, 3H); ^{13}C NMR ($CDCl_3$) δ 22.17 (q, J_{CH} = 125.9 Hz), 28.20 (q, J_{CH} = 126.0 Hz), 33.59 (s), 37.96 (t, J_{CH} = 135.0 Hz), 51.53 (q, J_{CH} = 141.5 Hz), 68.22 (br m), 80.78 (br s), 146.42 (br s), 155.18 (br s), 197.51 (t, J_{CW} = 62.2 Hz), 204.42 (t, J_{CW} = 53.2 Hz), 321.26 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2069s, 1988w, 1943s; mass spectrum *m*/*z* (% rel. intensity) 520 M^+ (6, ^{184}W), 492 (17, ^{184}W), 464 (7, ^{184}W), 436 (4, ^{184}W), 408 (20, ^{184}W), 380 (62, ^{184}W), 363 (65), 335 (29), 307 (20), 291 (21), 277 (19), 263 (18), 249 (13), 224 (6), 197 (5), 181 (20), 165 (11), 149 (23), 133 (45), 107 (79), 91 (100). Anal. calcd. for $C_{17}H_{20}O_7W$: C, 39.25; H, 3.88. Found: C, 39.38; H, 3.71.

Reaction of the propynyl tungsten carbene complex 18 with 2-*tert*-butyldimethylsiloxypropene to give 4m

The tungsten carbene complex **18**[4a] was combined with 2-*tert*-butyldimethylsiloxypropene either neat or as a 0.2 M solution in CH_2Cl_2 (0.189 g, 0.47 mmol **18** and 0.665 g, 3.86 mmol enol ether) and reacted according to the general procedure. After 24 hours at 25 °C, the volatiles were removed and the residue was chromatographed on silica gel using a 1 : 1 : 50 mixture of ether : methylene chloride: hexanes as the mobile phase to give **4m** as a red solid (70 mg, 19%). Spectral data for **4m**: R_f = 0.4 (1 : 1 : 50, ether : methylene chloride : hexanes); ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 3H), 0.04 (s, 3H), 0.84 (s, 9H), 1.48 (s, 3H), 2.31 (s, 3H), 2.25–2.35 (m, 1H), 2.40 (d, 1H, J = 16.9 Hz), 4.53 (s, 3H); ^{13}C NMR ($CDCl_3$) δ −3.31 (m), −2.92 (m), 17.91 (s), 19.41 (q, J_{CH} = 142.7 Hz), 25.58 (q, J_{CH} = 129.0 Hz), 27.52 (q, J_{CH} = 127.4 Hz), 49.26 (t, J_{CH} = 135.2 Hz), 68.32 (q, J_{CH} = 142.7 Hz), 159.02 (s), 161.29 (s), 197.56 (s), 202.90 (s), 306.03 (s) (methine C of *tert*-butyl group not located); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2929w, 2857w, 2066m, 1979w, 1936s, 1609w, 1138w, 827w; mass spectrum *m*/*z* (% rel. intensity) 578 M^+ (10, ^{184}W), 522 (12, ^{184}W), 494 (1, ^{184}W), 466 (6, ^{184}W), 438 (30, ^{184}W), 423 (20), 380 (7), 350 (30), 322 (15), 292 (11), 266 (8), 235 (4), 182 (4), 149 (3), 105 (4), 89 (4), 73 (100); Anal. calcd. for $C_{19}H_{26}O_7SiW$: C, 39.46; H, 4.52. Found: C, 40.03; H, 4.19.

The reaction of the propynyl chromium carbene complex 12 with the *tert*-butyldimethylsilyl enol ether of *p*-methylacetophenone to give 4n

Preparation of 1-(*tert*-butyldimethylsiloxy)-1-*p*-tolylethene. A solution of 4.0 mL (29.96 mmol) of *p*-methylacetophenone and 6.3 mL (45.2 mmol) of triethylamine was prepared in 75 mL anhydrous ether and cooled to 0 °C. To this was added 8.8 mL (38.32 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate dropwise. The mixture was allowed to come to room

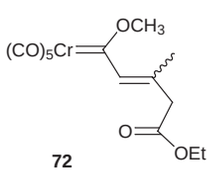
temperature over 10 minutes. Work-up consisted of extracting into ether and washing with water, brine and drying over $MgSO_4$. Filtration and removal of the volatiles using a rotary evaporator and then high vacuum (0.01 mmHg) gave the desired enol ether: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.20 (s, 9H), 2.34 (s, 3H), 4.36 (d, 1H, J = 1.5 Hz), 4.83 (d, 1H, J = 1.5 Hz), 7.12 (d, 2H, J = 8.1 Hz), 7.49 (d, 2H, J = 8.2 Hz).

Reaction of 1-(*tert*-butyldimethylsiloxy)-1-*p*-tolylethene with complex 12. A sample of complex **12**[4a] (0.431 g, 1.57 mmol) was combined with sufficient enol ether to effect solution and the reaction performed according to the general procedure. After 3 hours at 25 °C, the olefin was removed under high vacuum (0.01 mmHg) and the residue was purified using flash chromatography with hexanes as the mobile phase. The starting material was recovered (124 mg, 29%) and the major products were isolated to give 516 mg of **4n** as a red oil (63% yield, 88% based on recovered starting material): ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 3H), 0.11 (s, 3H), 0.96 (s, 9H), 2.33 (s, 3H), 2.64 (s, 3H), 2.70 (d, 1H, J = 15.0 Hz), 2.83 (d, 1H, J = 15.0 Hz), 4.45 (s, 3H), 7.08 (d, 2H, J = 8.2 Hz), 7.16 (d, 2H, J = 8.2 Hz); mass spectrum (% rel. intensity) 522 M^+ (2, ^{184}W), 494 (1, ^{184}W), 466 (5, ^{184}W), 438 (27, ^{184}W), 410 (10, ^{184}W), 382 (100, ^{184}W), 363 (21), 330 (23), 315 (41), 283 (17), 259 (5), 218 (19), 199 (29), 161 (10), 126 (44), 108 (8), 89 (21), 73 (94). Anal. calcd. for $C_{25}H_{30}O_7SiCr$: C, 57.46; H, 6.19. Found: C, 57.80; H, 5.89.

The reaction of the propynyl chromium carbene complex 12 with ketene diethyl acetal to give 4o

A sample of complex **12**[4a] (1.08 g, 3.98 mmol) was placed in a round bottom flask and 7 mL of CH_2Cl_2 was added. The solution was deoxygenated as described in the general procedure. Under a blanket of Ar, ketene diethyl acetal was added neat dropwise. Immediately after the final addition of acetal, the TLC showed complete consumption of the starting complex. The volatiles were removed under high vacuum (0.01 mmHg) and the crude residue was purified by flash chromatography under argon at −60 °C using pentane as the eluent to give 1.13 g (2.91 mmol) of **4o** as a red oil in 73% yield. Spectral data for **4o**: ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 6H, J = 7.0 Hz), 2.03 (s, 3H), 2.60 (s, 2H), 3.30–3.40 (m, 2H), 3.55–3.65 (m, 2H), 4.53 (s, 3H). ^{1}H decoupled ^{13}C NMR ($CDCl_3$) δ 16.27 (s), 44.74 (s), 60.92 (s), 66.96 (s), 104.58 (s), 154.48 (s), 217.37 (s), 225.76 (s), 342.34 (s).

If complex **4o** is exposed to silica gel at 25 °C two organometallic complexes are produced which have been tentatively identified as the stereoisomers of **72**. The ratio of diastereomers



72

by ^{1}H NMR is initially 1.6 : 1.0 but upon standing in the freezer overnight this ratio inverts. Initial major isomer: ^{1}H NMR ($CDCl_3$) δ 1.2–1.4 (m, 3H), 1.86 (s, 3H), 3.09 (s, 2H), 4.1–4.25 (m, 2H), 4.71 (s, 3H), 7.12 (s, 1H); Initial minor isomer: ^{1}H NMR ($CDCl_3$) δ 1.2–1.4 (m, 3H), 1.99 (s, 3H), 3.14 (s, 2H), 4.1–4.25 (m, 2H), 4.77 (s, 3H), 7.35 (s, 1H).

The reaction of the propynyl chromium and tungsten carbene complexes 12 and 18 with dihydropyran to give 4p and 4q

Reaction of complex 12. A sample of complex **12**[4a] (0.425 g, 1.55 mmol) and 4.0 mL (43.8 mmol) of 3,4-dihydro-2*H*-pyran were combined neat and reacted according to the general procedure. After 24 hours the volatiles were removed under high vacuum (0.01 mmHg) and the residue was chromatographed with a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes as the eluent to give **4p** as a bright red oil (455 mg, 82%). Spectral data for **4p**: ^{1}H NMR (C_6D_6) δ 1.0–1.4 (m, 4H), 1.6 (br s, 3H), 2.05–2.2 (m, 1H), 3.4–3.55 (m, 1H), 3.55–3.7 (m, 1H), 4.0–4.2 (br s, 3H), 4.85–5.0 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 16.35 (q, J_{CH} = 127 Hz), 20.49 (m), 21.89 (m), 40.98 (d, J_{CH} = 139.4 Hz), 61.96 (t, J_{CH} = 144 Hz), 65.92 (q, J_{CH} = 147 Hz), 71.88 (d, J_{CH} = 159.8), 153.17 (s), 216.53 (s), 223.75 (s), 332.88 (s) (1 vinyl C not located); ^{13}C NMR (C_6D_6) δ 16.99 (q, J_{CH} = 127.5 Hz), 21.94 (t, J_{CH} = 127.2 Hz), 23.21 (t, J_{CH} = 132.3 Hz), 42.06 (d, J_{CH} = 139.8 Hz), 63.1 (t, J_{CH} = 144.7 Hz), 66.5 (q, J_{CH} = 147.4 Hz), 73.2 (d, J_{CH} = 159.3 Hz), 155.01 (s), 156.87 (s), 218.12 (s), 225.32 (s), 334.17 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2059w, 1982w, 1941s; mass spectrum *m*/*z* (% rel. intensity) 358 M^+ (19), 330 (3), 302 (19), 274 (28), 246 (78), 218 (100), 203 (3), 186 (13), 173 (8), 158 (25), 134 (26), 119 (12), 108 (15), 91 (29), 80 (32), 67 (5). Anal. calcd. for $C_{15}H_{14}O_7Cr$: C, 50.29; H, 3.94. Found: C, 50.20; H, 4.02.

Reaction of complex 18. The reaction of **18**[4a] (0.44 mmol) with dihydro-2*H*-pyran was carried in the same manner as the corresponding reaction of complex **12** described above to give **4q** in 97% yield. Spectral data for **4q**: ^{1}H NMR ($CDCl_3$) δ 1.5–1.8 (m, 3H), 1.95–2.10 (m, 1H), 1.99 (s, 3H), 2.55–2.65 (m, 1H), 3.65–3.75 (m, 1H), 3.75–3.85 (m, 1H), 4.58 (s, 3H), 4.98–4.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 16.65 (q, J_{CH} = 127.7 Hz), 20.5 (t, J_{CH} = 128.9 Hz), 21.57 (t, J_{CH} = 128.9 Hz), 41.56 (d, J_{CH} = 138.8 Hz), 61.80 (t, J_{CH} = 144.1 Hz), 68.36 (q, J_{CH} = 146.9 Hz), 72.01 (d, J_{CH} = 159.6 Hz), 155.83 (s), 159.35 (s), 197.33 (s), 203.08 (s), 305.61 (s); mass spectrum *m*/*z* (% rel. intensity) 492 M^+ (30, ^{186}W), 464 (52, ^{186}W), 436 (85, ^{186}W), 404 (45), 380 (55, ^{186}W), 352 (68, ^{186}W), 320 (96), 303 (68), 292 (100); *m*/*z* calcd. for $C_{15}H_{14}O_7{}^{184}W$ 490.0249, measured 490.0243. Anal. calcd. for $C_{15}H_{14}O_7W$: C, 36.76; H, 2.88. Found: C, 36.63; H, 2.88.

The reaction of the trimethylsilylalkynyl chromium and tungsten carbene complexes 23 and 19 with dihydropyran to give 4r and 4s

Reaction of 23. The reaction of 0.287 g (0.87 mmol) **23**[4a] and 0.582 g (6.92 mmol) of 3,4-dihydro-2*H*-pyran was carried out according to the general procedure. After stirring for 2 days at 25 °C the reaction was judged complete by TLC. The volatiles were removed by high vacuum (0.01 mmHg) and the residue was chromatographed using a 1 : 1 : 20 mixture of ether : methylene chloride : hexanes as the eluent to give **4r** as a red oil (170 mg, 47%). ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 1.5–1.7 (m, 3H), 2.04–2.12 (m, 1H), 2.82–2.90 (m, 1H), 3.68–3.82 (m, 2H), 4.77 (s, 3H), 5.26 (d, 1H, 4.28 Hz); ^{13}C NMR ($CDCl_3$) δ −1.58 (q, J_{CH} = 120.0 Hz), 20.78 (t, J_{CH} = 127.9 Hz), 24.20 (t, J_{CH} = 128.9 Hz), 40.53 (d, J_{CH} = 138.3 Hz), 62.38 (t, J_{CH} = 145.4 Hz), 65.85 (m, J_{CH} = 148.0 Hz), 74.35 (d, J_{CH} = 157.0 Hz), 156.31 (s), 169.61 (s), 216.18 (s), 223.87 (s), 337.25 (s); mass spectrum *m*/*z* (% rel. intensity) 416 M^+ (18), 388 (1), 360 (14), 332 (26), 304 (97), 276 (100), 244 (19), 220 (26), 192 (32), 164 (17), 149 (24), 126 (44), 97 (20), 83 (56), 73 (47). Anal. calcd. for $C_{17}H_{20}O_7SiCr$: C, 49.03; H, 4.80. Found: C, 48.43; H, 4.80.

Reaction of 19. The reaction of complex **19**[4a] was carried out on 1.15 mmol according to the procedure described above for **23** to give **4s** as a red solid (0.414 mmol, 22%). Spectral data for **19**: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 1.55–1.72 (m, 3H), 2.05–2.15 (m, 1H), 2.75–2.82 (m, 1H), 3.66–3.82 (m, 2H), 4.89 (s, 3H), 5.19 (d, 1H, J = 4.3 Hz); mass spectrum *m*/*z* (% rel. intensity) 548 M^+ (16, ^{184}W), 519 (3), 492 (7, ^{184}W), 464 (35, ^{184}W), 436 (10, ^{184}W), 408 (100, ^{184}W), 380 (58), 363 (18), 323 (23), 307 (14), 277 (14), 249 (7), 224 (3), 207 (2), 179 (1), 161 (1), 135 (2), 109 (2), 73 (54). Anal. calcd. for $C_{17}H_{20}O_7WSi$: C, 37.24; H, 3.68. Found: C, 37.39; H, 3.61.

The reaction of the trimethylsilylalkynyl chromium and tungsten carbene complexes 23 and 19 with 2-methoxypropene

Reaction of complex 23. A mixture of 0.363 g (1.09 mmol)

of complex **23**[4a] and 1 mL (10.44 mmol) of 2-methoxypropene was deoxygenated and allowed to react under argon according to the general procedure. After 8 hours the volatiles were removed under high vacuum (0.01 mmHg) and to the residue was added 25 mL of hexanes and approximately 1 g of silica gel. The slurry was stirred open to air until only a red-purple spot remained by TLC. The mixture was filtered through Celite to remove the solids. Upon removal of the volatiles and purification by flash chromatography, using hexanes as the eluent, 116 mg of **24** was obtained for a 30% overall yield. Complex **24**: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 2.63 (s, 3H), 6.60 (s, 1H), 8.09 (s, 1H); ^{1}H decoupled ^{13}C NMR ($CDCl_3$) δ −2.31, 20.95, 116.16, 143.79, 148.20, 175.60, 217.97, 224.34, 280.29; IR ($CHCl_3$) ν_{max}/cm^{-1} 3707w, 3603w, 2054m, 1935s, 1602s; mass spectrum *m*/*z* (% rel. intensity) 358 M^+ (11), 302 (1), 274 (3), 246 (19), 218 (100), 203 (3), 188 (2), 173 (2), 151 (3), 73 (5). Anal. calcd. for $C_{14}H_{14}O_6SiCr$: C, 46.92; H, 3.94. Found: C, 46.81; H, 3.82.

When care is taken to minimize exposure to silica gel (*i.e.*, the crude reaction mixture is filtered quickly through silica gel) intermediate **5t** can be isolated and characterized: ^{1}H NMR. ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 3.01 (s, 2H), 3.55 (s, 3H), 3.90 (d, 1H, J = 1.5 Hz), 4.05 (d, 1H, J = 1.5 Hz), 4.77 (s, 3H), 7.84 (s, 1H). Anal. calcd. for $C_{16}H_{20}O_7SiCr$: C, 47.52; H, 4.98. Found: C, 47.56; H, 4.98.

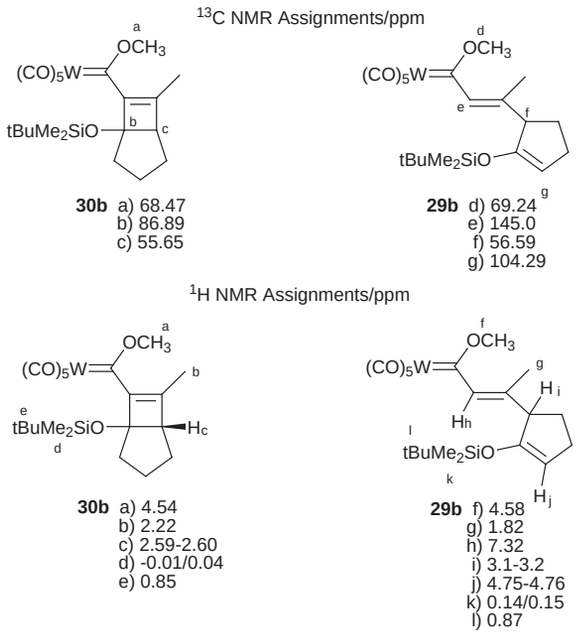
Reaction of complex 19. This reaction was carried out as described above for complex **23** to give two products that were not fully characterized. After 3 hours, separation of the products by silica gel chromatography with a 1:1:50 mixture of ether:methylene chloride:hexanes gave two major fractions. The minor fraction was obtained as a red oil and was tentatively assigned as the [2 + 2] cycloadduct **4u** (12%): **4u**: ^{1}H NMR (C_6D_6) δ −0.03 (s, 9H), 1.54 (s, 3H), 2.03 (d, 1H, J = 13.5 Hz), 2.37 (d, 1H, J = 13.5 Hz), 3.14 (s, 3H), 4.95 (s, 3H). The major fraction (25%) appears to be a 2:1 mixture of diastereomers of the ene product **5u** on the basis of the ^{1}H NMR spectrum which changed slowly with time giving additional compounds. The following partial ^{1}H NMR spectral data were extracted from the spectrum of the mixture. (**5u**/major): ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 2.18 (s, 1H), 3.52 (s, 3H), 4.55 (s, 3H), 7.72 (s, 1H). (**5u**/minor): ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 2.94 (s, 2H), 3.18 (s, 3H), 4.58 (s, 3H), 7.64 (s, 1H).

The reaction of the trimethylsilylalkynyl tungsten carbene complex 19 with the silyl enol ether 25 to give 29a and 30a

The reaction of 0.189 g (0.41 mmol) of complex **19**[4a] and 0.448 g (2.26 mmol) of 1-(*tert*-butyldimethylsiloxy)cyclopentene was carried out neat according to the general procedure. After 1 day, the volatiles were removed and the residue was chromatographed on silica gel with hexanes. Two major organometallic products were obtained and characterized. In order of elution, **30a** was obtained (33 mg, 12.4%) as a red oil and **29a** was obtained as a red solid (0.105 g, 39%). Spectral data for **30a**: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 3H), 0.08 (s, 12H), 0.90 (s, 9H), 1.5–1.6 (m, 4H), 1.7–1.8 (br m, 1H), 2.4 (d of m, 1H), 2.75 (d, 1H, J = 6.1 Hz), 4.55 (s, 3H); ^{13}C NMR ($CDCl_3$) δ −3.00 (q, J_{CH} = 118.7 Hz), −2.87 (q, J_{CH} = 118.4 Hz), −1.14 (q, J_{CH} = 120.0 Hz), 18.09 (s), 23.53 (t, J_{CH} = 132.7 Hz), 25.69 (q, J_{CH} = 119.3 Hz), 25.99 (t, J_{CH} = 131.4 Hz), 36.14 (t, J_{CH} = 129.2 Hz), 54.07 (d, J_{CH} = 145.7 Hz), 68.23 (q, J_{CH} = 147.5 Hz), 90.83 (s), 150.53 (s), 172.40 (s), 197.26 (t, J_{CW} = 63.2 Hz), 203.97 (s), 313.50 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2930w, 2857w, 2069m, 1987w, 1941s, 1212w, 1005w, 841w; mass spectrum *m*/*z* (% rel. intensity) 662 M^+ (16, ^{184}W), 606 (5, ^{184}W), 548 (1), 522 (34, ^{184}W), 464 (42), 434 (3), 408 (100), 380 (19), 354 (5), 324 (10), 277 (3), 249 (1), 198 (1), 141 (2); Anal. calcd. for $C_{23}H_{34}O_7Si_2W$: C, 41.70; H, 5.17. Found: C, 42.23; H, 5.43. R_f(hexanes) = 0.32. Spectral data for **29a**: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.13 (s, 3H), 0.15 (s, 3H), 0.86 (s, 9H), 2.2–2.4 (m, 4H), 3.3–3.35 (m, 1H), 4.55 (s, 3H), 4.82 (br s, 1H), 7.68 (br s, 1H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 3681w, 2858w, 2067m, 1982w, 1940s, 1643w, 1607w, 1088w, 845w; mass spectrum *m*/*z* (% rel. intensity) 662 M^+ (84, ^{184}W), 606 (25), 578 (55), 562 (16), 550 (30), 535 (21), 520 (100), 505 (48), 477 (30), 465 (29), 453 (10), 408 (30), 375 (15), 326 (10), 303 (8), 270 (10), 238 (4), 207 (4), 147 (6). Anal. calcd. for $C_{23}H_{34}O_7Si_2W$: C, 41.70; H, 5.17. Found: C, 41.78; H, 5.21. R_f(hexanes) = 0.23.

The reaction of the propynyl tungsten carbene complex 18 with the silyl enol ether 25 to give 29b and 30b

The reaction was run according to the general procedure (212 mg, 0.52 mmol complex **18,** 912 mg, 4.60 mmol 1-(*tert*-butyldimethylsiloxy)cyclopentene). After 12 hours, the volatiles were removed and the residue was chromatographed on silica gel using a 1:1:50 mixture of ether:methylene chloride:hexanes as the mobile phase. The [2 + 2] cycloaddition and ene products were not separable and were obtained together as a red oil in 90% yield (285 mg) as a 2.2:1 mixture of **30b** to **29b**. The following spectral data were collected on the mixture:



^{1}H NMR ($CDCl_3$) δ −0.01 (s, H_d), 0.04 (s, H_d), 0.14 (s, H_k), 0.15 (s, H_k), 0.85 (s, H_e), 0.87 (s, H_l), 1.15–1.3 (m), 1.35–1.45 (m), 1.48–1.61 (m), 1.66–1.79 (m), 1.82 (s, H_g), 2.05–2.1 (m), 2.2 (m, H_b), 2.59–2.60 (H_c), 3.1–3.2 (m, H_i), 4.54 (s, H_a), 4.58 (s, H_f), 4.75–4.76 (m, H_j), 7.32 (s, H_h); ^{13}C NMR ($CDCl_3$) δ −3.44 (q, J_{CH} = 118.7 Hz), −3.10 (q, J_{CH} = 118.9 Hz), 16.42 (q, J_{CH} = 127.6 Hz), 17.95, 23.27 (t, J_{CH} = 129.9 Hz), 23.87 (s), 25.64 (q, J_{CH} = 125.7 Hz), 27.63 (m), 28.19 (m), 35.21 (t, J_{CH} = 127.6 Hz), 55.65 (d, J_{CH} = 144.8 Hz, C_c), 56.59 (d, J_{CH} = 132.4 Hz, C_f), 68.47 (q, J_{CH} = 169.5 Hz, C_a), 69.24 (m, C_d), 86.89 (C_b), 104.29 (d, J_{CH} = 161 Hz, C_g), 145.0 (d, J_{CH} = 158.7 Hz, C_e), 149.32 (s), 154.34 (s), 155.42 (s), 163.27 (s), 197.77 (s), 203.16 (s), 305.83 (s); IR (CCl_4) 2952w, 2065s, 1977w, 1939s cm^{-1}; IR (neat) ν_{max}/cm^{-1} 2955s, 2858s, 2362w, 2065s, 1978s, 1601s, 1520s, 1449s, 1228s, 838s, 775s; mass spectrum (CI) *m*/*z* (% rel. intensity) 604 M^+ (15, ^{184}W), 577 (3), 548 (12), 520 (2), 486 (20), 458 (11), 402 (5), 374 (2), 353 (19), 346 (23), 294 (34), 281 (100), 235 (10), 163 (11), 133 (44). Anal. calcd. for $C_{21}H_{28}O_7SiW$: C, 41.73; H, 4.67. Found: C, 41.66; H, 4.73.

The reaction of the trimethylsilylalkynyl tungsten carbene complex 19 with 1-methoxycyclopentene 26 to give 31a and 32a

The reaction of 0.114 g (0.25 mmol) of complex **19**[4a] and 0.901 g

(9.18 mmol) of 2-methoxycyclopentene was performed according to the general procedure. After 8 hours at 25 °C, the reaction was stopped and the products separated on silica gel with a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes as the mobile phase. The two principle products obtained were, in order of elution, the ene product **31a** as a red oil (14 mg, 10%) and the cycloadduct **32a** as a red solid (89 mg, 64%). Spectral data for **31a**: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9H), 2.2–2.4 (m, 4H), 3.4–3.5 (m, 1H), 3.61 (s, 3H), 4.56 (s, 3H), 4.76 (br s, 1H), 7.65 (s, 1H); R_f (1 : 1 : 10, ether : methylene chloride : hexanes) = 0.40. Spectral data for **32a**: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 1.45–1.57 (m, 3H), 1.65–1.75 (m, 1H), 1.75–1.85 (m, 1H), 2.21 (d of m, 1H), 2.85–2.87 (m, 1H), 3.27 (s, 3H), 4.56 (s, 3H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2069m, 1986w, 1941s; *m*/*z* calcd. for $C_{18}H_{22}O_7Si^{186}W$ 564.0678, measured 564.0684. Anal. calcd. for $C_{18}H_{22}O_7SiW$: C, 38.44; H, 3.94. Found: C, 38.68; H, 4.07. R_f (1 : 1 : 10, ether : methylene chloride : hexanes) = 0.26.

The reaction of the propynyl tungsten and chromium carbene complexes 18 and 12 with 1-methoxycyclopentene to give 32b and 32e

Reaction of complex 18. A neat mixture of 0.164 g (0.41 mmol) of **18**[4a] and 0.903 g (92 mmol) of 1-methoxycyclopentene was prepared and allowed to react as described in the general procedure. After 1 hour at 25 °C, the reaction was stopped and the two major products were purified on silica gel with a 1 : 1 : 20 mixture of ether : CH_2Cl_2 : hexanes to give, in order of elution, **31b** (3.3 mg, 1.6%) as a red oil and **32b** (0.178 g, 87%) as a red solid. Spectral data for **31b**: ^{1}H NMR ($CDCl_3$) δ 1.70–1.78 (m, 1H), 2.20–2.28 (m, 1H), 2.28–2.41 (m, 2H), 3.2–3.24 (m, 1H), 3.60 (s, 3H), 4.59 (s, 3H), 4.71 (m, 1H), 7.27 (br s, 1H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2873w, 2065m, 1977w, 1934s. Spectral data for **32b**: ^{1}H NMR ($CDCl_3$) δ 1.25–1.38 (m, 1H), 1.42–1.55 (m, 2H), 1.58–1.65 (m, 1H), 1.7–1.8 (m, 1H), 2.05–2.12 (m, 1H), 2.23 (s, 3H), 2.80–2.85 (br d, 1H, J = 7.1 Hz), 3.17 (s, 3H), 4.53 (s, 3H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2066m, 1979w, 1938s; ^{13}C NMR ($CDCl_3$) δ 15.94 (q, J_{CH} = 128.4 Hz), 23.13 (t, J_{CH} = 125.8 Hz), 23.64 (t, J_{CH} = 130.2 Hz), 32.06 (t, J_{CH} = 128.4 Hz), 50.36 (d, J_{CH} = 145.8 Hz), 53.50 (q, J_{CH} = 141.7 Hz), 68.78 (q, J_{CH} = 146.4 Hz), 92.41 (s), 153.46 (s), 163.54 (s), 197.57 (t, J_{CW} = 63.1 Hz), 202.93 (s), 305.28 (s). Anal. calcd. for $C_{16}H_{16}O_7W$: C, 38.12; H, 3.20. Found: C, 38.31; H, 3.21.

Reaction of complex 12. The reaction was performed (12 hours) and the products purified as described for the same reaction of **18** (0.246 g, 0.90 mmol **12**[4a] and 3.32 g, 34.3 mmol 1-methoxycyclopentene). In order of elution, the two major products were **31e** (13 mg, 4%) and **32e** (274 mg, 82%). Spectral data for **31e**: ^{1}H NMR ($CDCl_3$) δ 1.7–1.79 (m, 2H), 1.80 (s, 3H), 2.2–2.4 (m, 3H), 3.2–3.5 (m, 1H), 3.59 (s, 3H), 4.70 (s, 3H), 7.19 (br s, 1H); mass spectrum *m*/*z* (% rel. intensity) 372 M^+ (5), 316 (5), 288 (25), 260 (27), 232 (100), 217 (22), 198 (50), 180 (69), 168 (42), 147 (66), 133 (29), 117 (38), 105 (37), 91 (51), 80 (67), 69 (43). Spectral data for **32e**: ^{1}H NMR ($CDCl_3$) δ 1.24–1.36 (m, 1H), 1.4–1.55 (m, 2H), 1.6–1.65 (m, 1H), 1.7–1.78 (m, 1H), 2.0–2.08 (m, 1H), 2.35 (s, 3H), 2.91 (d, 1H, J = 7.06 Hz), 3.14 (s, 3H), 4.71 (s, 3H); IR (CCl_4) ν_{max}/cm^{-1} 2057s, 1980w, 1940s, 1452w, 665m, 648w; mass spectrum *m*/*z* (% rel. intensity) 372 M^+ (10), 344 (8), 316 (22), 288 (18), 260 (61), 232 (100), 217 (22), 202 (12), 187 (18), 168 (29), 131 (17), 105 (18), 91 (21), 80 (19), 67 (5). Anal. calcd. for $C_{16}H_{16}O_7Cr$: C, 51.62; H, 4.33. Found: C, 52.33; H, 4.56. R_f = 0.42 (1 : 1 : 4, ether : methylene chloride : hexanes).

Attempted conversion of cyclobutenyl carbene complex 32e to the corresponding ene product 31e

Complex **32e** was examined for its thermal stability with respect to retro-cycloaddition and ene product formation. A sample of 0.059 g (0.164 mmol) of **32e** was placed in 3.2 mL of THF and the solution was deoxygenated according to the general procedure. This solution was heated to 50 °C under argon and monitored periodically by TLC. After 4 days there appeared some signs of decomposition (origin material on TLC) but no new organometallic compounds were indicated. After a total of 11 days, the volatiles were removed and a ^{1}H NMR spectrum of the crude material was obtained. Only complex **32e** appeared in the spectrum.

The reaction of the isopropylalkynyl tungsten carbene complex 21 with 1-methoxycyclopentene to give 32c

A sample of 0.769 g (1.77 mmol) of complex **21** was combined neat with 2.176 g (22.17 mmol) of 1-methoxycyclopentene **26** and deoxygenated according to the general procedure. After 3 hours, **21** had been completely consumed and the solution was bright red. The volatiles were removed and the residue was chromatographed on silica gel using a 1 : 1 : 10 solvent mixture (ether : methylene chloride : hexanes) as the mobile phase. Two principal bands were collected and identified by their spectral data. In order of elution, the first was obtained as an unstable red oil and identified as the ene product **31c** (27.7 mg, <2.9%) and the second was a red solid which was identified as **22c** (847.7 mg, 90%). Spectral data for **31c**: IR (CH_2Cl_2) ν_{max}/cm^{-1} 2066m, 1978w, 1936s; mass spectrum: *m*/*z* calcd. for $C_{18}H_{20}O_7{}^{184}W$ 532.0719, measured 532.0726. Anal. calcd. for $C_{18}H_{20}O_7W$: C, 40.62; H, 3.79. Found: C, 40.54; H, 4.04. R_f(1 : 1 : 10, ether : methylene chloride : hexanes) = 0.51. Spectral data for **32c**: ^{1}H NMR ($CDCl_3$) δ 1.18 (d, 3H, J = 7.1 Hz), 1.22 (d, 3H, J = 6.6 Hz), 1.4–1.6 (m, 3H), 1.7–1.8 (m, 2H), 2.15–2.22 (m, 1H), 2.94–2.98 (m, 1H), 3.17 (s, 3H), 3.54 (septet, 1H, J = 6.9 Hz), 4.54 (s, 3H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 3607–3620w, 2066m, 1980w, 1938s; mass spectrum: *m*/*z* calcd. for $C_{18}H_{20}O_7{}^{184}W$ 532.0719, measured 532.0731. Anal. calcd. for $C_{18}H_{20}O_7W$: C, 40.62; H, 3.79. Found: C, 41.18; H, 4.01. R_f(1 : 1 : 10, ether : methylene chloride : hexanes) = 0.18.

The reaction of the *tert*-butylacetylene tungsten carbene complex 22 with 1-methoxycyclopentene to give 32d

The reaction of complex **22** (0.320 g, 0.71 mmol) and 1.4 g (14.27 mmol) of 1-methoxycyclopentene was carried out as described in the general procedure. After 9 days, the cycloadduct **32d** was isolated in 59% yield (230 mg) after purification on silica gel with a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes along with 11 mg of recovered **22**. No evidence for ene product formation could be found. Spectral data for **32d**: ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 9H), 1.45–2.05 (br m, 6H), 2.90 (br d, 1H), 3.28 (s, 3H), 4.53 (br s, 3H); ^{13}C NMR ($CDCl_3$) δ 23.94 (t, J_{CH} = 134.1 Hz), 26.46 (t, J_{CH} = 134.1 Hz), 29.03 (q, J_{CH} = 126.7 Hz), 29.61 (m), 34.42 (s), 47.62 (d, J_{CH} = 145.0 Hz), 52.42 (q, J_{CH} = 141.5 Hz), 68.15 (q, J_{CH} = 153.5 Hz), 91.68 (s), 150.37 (s), 152.31 (s), 197.33 (t, J_{CW} = 63.5 Hz), 204.23 (s), 319.07 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2900–3100w, 2070s, 1992m, 1954s, 1935s; mass spectrum *m*/*z* (% rel. intensity) 546 M^+ (7, ^{184}W), 518 (13, ^{184}W), 490 (9, ^{184}W), 462 (2, ^{184}W), 434 (6, ^{184}W), 406 (100, ^{184}W), 389 (8), 363 (18), 315 (10), 289 (7), 263 (7), 224 (2), 180 (3), 112 (3), 91 (5). Anal. calcd. for $C_{19}H_{22}O_7W$: C, 41.78; H, 4.06. Found: C, 41.83; H, 4.10. R_f(1 : 1 : 20, ether : methylene chloride : hexanes) = 0.25.

The reaction of the trimethylsilylalkynyl tungsten carbene complex 19 with the silyl enol ether 27 to give 33a

The reaction of 0.186 g (0.40 mmol) of complex **19**[4a] and 0.61 g (2.89 mmol) of 1-(*tert*-butyldimethylsiloxy)cyclohexene were reacted according to general procedure for 42 hours and elution of the reaction mixture from silica gel with hexanes gave one organometallic product as a red oil which was identified as **33a** (114 mg, 42%). Spectral data for **33a**: ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.10 (s, 9H), 0.82 (s, 9H), 1.35–2.1 (br m,

6H), 3.0–3.1 (m, 1H), 4.54 (s, 3H), 5.0–5.1 (m, 1H), 7.78 (s, 1H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2930w, 2067m, 1982w, 1939s, 1607w, 1111w, 850w; mass spectrum (CI) *m/z* (% rel. intensity) 677 $(M + 1)^+$ (16, ^{184}W), 649 (1, ^{184}W), 593 (2, ^{184}W), 565 (1, ^{184}W), 537 (1, ^{184}W), 353 (100), 329 (8), 277 (9), 239 (6), 181 (7). Anal. calcd. for $C_{24}H_{36}O_7Si_2W$ C, 42.61; H, 5.36. Found: C, 42.66; H, 5.36. R_f(hexanes) = 0.16.

The reaction of propynyl tungsten and chromium carbene complexes 18 and 12 with the silyl enol ether 27 to give 33b, 34b and 33c

Reaction of complex 18. A solution of 0.202 g (0.50 mmol) of **18**[4a] in excess enol ether **27** (0.5 mL) was deoxygenated and allowed to react according to the general procedure. After 17 hours, the reaction was stopped and the two major products were purified by gravity chromatography on silica gel with hexanes as eluent to give 31 mg (10%) of **34b** as a red solid and 264 mg (86%) of **33b** as a red oil. Spectral data for **34b**: ^{1}H NMR (C_6D_6) δ 0.01 (s, 3H), 0.04 (s, 3H), 0.94 (s, 9H), 1.2–1.3 (m, 4H), 1.35–1.45 (m, 1H), 1.45–1.55 (m, 1H), 1.7–1.8 (m, 2H), 1.98 (d, 3H, J = 1.6 Hz), 2.2–2.3 (m, 3H), 3.94 (s, 3H); ^{13}C NMR (C_6D_6) δ 1.93 (q, J_{CH} = 123.5 Hz), 1.53 (q, J_{CH} = 123.5 Hz), 18.18 (q, J_{CH} = 127.1 Hz), 19.42 (t, J_{CH} = 123.5 Hz), 19.67 (t, J_{CH} = 123.5 Hz), 22.57 (t, J_{CH} = 126.9 Hz), 27.09 (q, J_{CH} = 124.9 Hz), 34.52 (t, J_{CH} = 128.4 Hz), 53.85 (d, J_{CH} = 140.9 Hz), 69.30 (q, J_{CH} = 147.3 Hz), 79.22 (s), 159.91 (s), 168.33 (s), 199.34 (t, J_{CW} = 48.6 Hz), 204.55 (t, J_{CW} = 48.6 Hz), 306.6 (s) (quaternary C of *tert*-butyl group not located); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2929–2856w, 2065m, 1978w, 1936; mass spectrum *m/z* (% rel. intensity) 618 M$^+$ (31, ^{184}W), 562 (17, ^{184}W), 534 (8, ^{184}W), 506 (10, ^{184}W), 478 (94, ^{184}W), 464 (28), 404 (15), 376 (5), 352 (94), 322 (27), 292 (19), 268 (16), 118 (100). R_f(hexanes) = 0.29. Spectral data for **33b**: ^{1}H NMR (C_6D_6) δ 0.10 (s, 6H), 0.91 (s, 9H), 1.2–1.35 (m, 1H), 1.35–1.48 (m, 1H), 1.48–1.58 (m, 1H), 1.58–1.65 (m, 1H), 1.68 (s, 3H), 1.85–2.05 (m, 2H), 2.6–2.7 (m, 1H), 3.93 (s, 3H), 4.99 (m, 1H), 7.51 (s, 1H); ^{13}C NMR δ 17.96 (m), 19.03 (q, J_{CH} = 126.2 Hz), 20.54 (t, J_{CH}= 128.3 Hz), 23.95 (t, J_{CH} = 127.1 Hz), 25.49 (q, J_{CH} = 123.8 Hz), 29.04 (t, J_{CH} = 131.1 Hz), 51.61 (d, J_{CH} = 128.4 Hz), 69.11 (q, J_{CH} = 147.5 Hz), 106.11 (d, J_{CH} = 152.9 Hz), 146.06 (d, J_{CH} = 158.6 Hz), 149.26 (s), 150.76 (s), 197.77 (s), 203.9 (s), 311.58 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2065m, 1978w, 1935s; mass spectrum *m/z* (% rel. intensity) 618 M$^+$ (19, ^{184}W), 562 (9, ^{184}W), 506 (7, ^{184}W), 478 (50, ^{184}W), 447 (4), 422 (14), 388 (8), 352 (5), 329 (5), 298 (4), 268 (10), 237 (4), 209 (2), 179 (3), 151 (3), 131 (4), 89 (13), 73 (100). Anal. calcd. for $C_{22}H_{30}O_7WSi$: C, 42.73; H, 4.89. Found: C, 42.64; H, 4.79. R_f = 0.23 (hexanes).

Reaction of complex 12. The reaction of complex **12**[4a] (0.271 g, 0.99 mmol) with **27** (0.900 g, 4.24 mmol) was carried out (12 h) and the products purified in the same manner described for complex **18** above. Only the ene product **33c** was obtained from this reaction as a red solid in 49.6% yield (238 mg). Spectral data for **33c**: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 6H), 0.84 (s, 9H), 1.43–1.75 (m, 4H), 1.8 (s, 3H), 2.0–2.12 (m, 2H), 2.15–2.85 (m, 1H), 4.68 (s, 3H), 4.96–5.02 (m, 1H), 7.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 4.75 (q, J_{CH} = 119.1 Hz), 4.53 (q, J_{CH} = 118.1 Hz), 18.01 (s), 18.41 (q, J_{CH} = 124.2 Hz), 20.51 (t, J_{CH} = 123.5 Hz), 23.99 (t, J_{CH} = 127.5 Hz), 25.54 (q, J_{CH} = 119.7 Hz), 29.18 (t, J_{CH} = 123.5 Hz), 50.90 (d, J_{CH} = 130.1 Hz), 66.16 (q, J_{CH} = 147.6 Hz), 106.23 (d, J_{CH} = 153.6 Hz), 142.5 (d, J_{CH} = 157.0 Hz), 144.9 (s), 149.40 (s), 216.84 (s), 224.16 (s), 339.80 (s); IR (CCl_4) ν_{max}/cm^{-1} 2978w, 2939w, 2859w, 2057s, 1980w, 1942s, 1121w; CI mass spectrum *m/z* (% rel. intensity) 487 (40), 486 M$^+$ (51), 459 (12), 458 (28), 430 (4), 402 (19), 374 (6), 346 (70), 311 (100), 295 (71), 253 (45), 235 (19), 221 (19), 205 (4), 193 (3), 181 (4), 163 (12), 149 (8), 133 (23). Anal. calcd. for $C_{22}H_{30}O_7SiCr$: C, 54.31; H, 6.21. Found: C, 54.78; H, 5.47. R_f (hexanes) = 0.1.

The reaction of the propynyl tungsten carbene complex 19 with 1-methoxycyclohexene 28 to give 35a

A mixture of 0.123 g (0.27 mmol) of complex **19**[4a] and 0.900 g (8.02 mmol) of 1-methoxycyclohexene was allowed to react according to the general procedure. After 2 days, the major product was purified on a silica gel column with a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes. The ene product **35a** was obtained (102 mg, 67%) as a red oil. Less than 2% yield of the [2 + 2] cycloadduct was formed in this reaction. Spectral data for: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.45–1.57 (m, 3H), 1.78–1.88 (m, 1H), 2.00–2.16 (m, 2H), 3.12 (m, 1H), 3.49 (s, 3H), 4.56 (s, 3H), 4.88 (t, 1H, J = 3.8 Hz), 7.65 (br s, 1H). This compound was formed as a single diastereomer which was assigned as the *Z*-isomer on the basis of the following NOE data: Irradiation at δ 3.49 (OCH_3) resulted in a 1.3% enhancement at δ 7.65 (vinyl) and a 9% enhancement at δ 4.88 (vinyl); irradiation at δ 3.12 (methine) resulted in a 6.4% enhancement at δ 7.65 (vinyl) and a 4.5% enhancement at δ 3.49 (OCH_3); irradiation at δ 7.65 (vinyl) resulted in a 4.7% enhancement at δ 3.12 (methine).

The reaction of the propynyl tungsten carbene complex 18 with 1-methoxycyclohexene to give 35b and 36b

The reaction of 0.136 g (0.34 mmol) of complex **18**[4a] and 3.5 g (31.2 mmol) 1-methoxycyclohexene was performed according to the general procedure. After 2 days, the two major products were purified on silica gel with a 1 : 1 : 20 mixture of ether : methylene chloride : hexanes to give **35b** (16 mg, 9%) as a red oil and a 60% yield (104 mg) of **36b**. Spectral data for **35b**: ^{1}H NMR ($CDCl_3$) δ 1.5–1.55 (m, 1H), 1.57–1.63 (m, 1H), 1.63–1.7 (m, 1H), 1.8–1.86 (m, 1H), 1.87 (s, 3H), 2.05–2.2 (m, 2H), 2.85 (br t, 1H, J = 5.8 Hz), 3.48 (s, 3H), 4.58 (s, 3H), 4.88 (t, 1H, J = 3.9 Hz), 7.31 (br s, 1H); mass spectrum: *m/z* calcd. for $C_{17}H_{18}O_7{}^{184}W$ 518.0562, measured 518.0565. Spectral data for **36b**: ^{1}H NMR ($CDCl_3$) δ 1.3–1.45 (m, 2H), 1.46–1.59 (m, 2H), 1.65–1.73 (m, 1H), 1.73–1.83 (m, 1H), 1.83–1.93 (m, 2H), 2.30 (d, 3H, J = 1.5 Hz), 2.66 (br m, 1H), 3.14 (s, 3H), 4.52 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 16.75 (q, J_{CH} = 127.8 Hz), 18.18 (t, J_{CH} = 126.5 Hz), 18.37 (t, J_{CH} = 126.5 Hz), 21.26 (t, J_{CH} = 126.7 Hz), 30.07 (t, J_{CH} = 127.8 Hz), 46.00 (d, J_{CH} = 138.6 Hz), 51.31 (q, J_{CH} = 141.6 Hz), 68.68 (q, J_{CH} = 146.5 Hz), 82.31 (s), 155.98 (s), 167.08 (s), 197.59 (t, J_{CW} = 63.5 Hz), 202.90 (s), 304.84 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2066m, 1978w, 1937s; mass spectrum: *m/z* calcd. for $C_{17}H_{18}O_7{}^{184}W$ 518.0562, measured 518.0567. Anal. calcd. for $C_{17}H_{18}O_7W$: C, 39.40; H, 3.50. Found: C, 39.24; H, 3.73.

The reaction of the isopropylacetylene tungsten carbene complex 21 with 1-methoxycyclohexene to give 35c and 36c

The reaction of 0.466 g (1.07 mmol) of complex **21** and 1.616 g (14.4 mmol) of 1-methoxycyclohexene was performed neat according to the the general procedure. After 12 hours, the volatiles were removed and the residue was placed on a silica gel column and eluted first with hexanes and then with a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes to give the two principal products in pure form. They were, in order of elution, the ene product **35c** (0.139 g, 24%, red oil) and the cycloaddition product **36c** (405 mg, 69%, red solid). Spectral data for **35c**: ^{1}H NMR ($CDCl_3$) δ 1.07 (d, 6H, J = 6.8 Hz), 1.5–1.55 (m, 1H), 1.6–1.66 (m, 1H), 1.68–1.78 (m, 1H), 1.88–1.95 (m, 1H), 2.06–2.15 (m, 1H), 2.15–2.25 (m, 1H), 3.00 (septet, 1H, J = 6.9 Hz), 3.05–3.1 (m, 1H), 3.45 (s, 3H), 4.58 (s, 3H), 4.85–4.9 (m, 1H), 7.05–7.1 (br s, 1H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2770–3000w, 2066m, 1971w, 1936s, 1568w; mass spectrum: *m/z* calcd. for $C_{19}H_{22}O_7{}^{184}W$ 546.0875, measured 546.0886. Anal. calcd. for $C_{19}H_{22}O_7W$: C, 41.78; H, 4.06. Found: C, 43.93; H, 4.58. Spectral data for **36c**: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 3H, J = 7.0 Hz), 1.24 (d, 3H, J = 7.0 Hz), 1.45–1.52 (m, 4H), 1.65–1.75 (m,

1H), 1.78–1.88 (m, 2H), 1.9–1.98 (m, 1H), 2.78 (m, 1H), 3.14 (s, 3H), 3.64 (septet, 1H, J = 6.8 Hz), 4.53 (s, 3H); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2066m, 1979w, 1937s, 1589w; mass spectrum: *m/z* calcd. for $C_{19}H_{22}O_7{}^{186}W$ 548.0908, measured 548.0910. Anal. calcd. for $C_{19}H_{22}O_7W$: C, 41.78; H, 4.06. Found: C, 41.95; H, 4.11.

The reaction of the trimethylsilylalkynyl tungsten carbene complex 19 with *cis*-1-ethoxypropene to give 39a and 40a

A mixture of 0.382 g (0.823 mmol) of complex **19**[4a] and 0.90 mL (9.42 mmol) of *cis*-1-ethoxypropene (≥54:1, *Z*:*E*) were combined and deoxygenated according to the general procedure. After 12 hours, the reaction was judged complete by TLC and the ^{1}H NMR spectrum of the crude reaction mixture did not indicate any isomerized olefin. The volatiles were removed under vacuum (0.001 mmHg) and the residue was chromatographed on silica gel using a 1:1:50 mixture of ether:methylene chloride:hexanes as the eluent. Five bands were collected in addition to the material from a wash of the column with ether. The following compounds could be identified: **39a** (0.288 g, 65%), **40a** (25.4 mg, 6%) and **46a** (34 mg, 8%). The stereochemistry of **39a** was assigned as *cis* on the basis of NOE data. The stereochemistry assignment about the C3–C4 double bond of **40a** and **46a** was assigned as *E* by assuming that **39a** was undergoing a conrotatory ring opening. This was later confirmed by chemical correlation with complex **55a** (see text). Spectral data for **39a**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 1.19 (d, 3H, J = 6.7 Hz), 1.24 (t, 3H, J = 7.0 Hz), 2.92 (dq, 1H, J = 3.8, 6.7 Hz), 3.25–3.34 (m, 1H), 3.38–3.45 (m, 1H), 4.55 (s, 3H), 5.01 (d, 1H, J = 3.8 Hz); ^{1}H NMR (C_6D_6) δ −0.01 (s, 9H), 1.12 (d, 3H, J = 6.9 Hz), 1.16 (t, 3H, J = 6.9 Hz), 2.60–2.68 (m, 1H), 3.25–3.34 (m, 1H), 3.38–3.45 (m, 1H), 3.88 (s, 3H), 4.96 (d, 1H, J = 3.7 Hz); NOE data: *hv* at δ = 5.01 results in 4% and 12% enhancements at δ = 1.19 and 2.92, respectively; *hv* at δ = 3.29 resulted in 4% enhancement at δ = 5.01, *hv* at δ = 3.41 resulted in 5% enhancement at δ = 1.19, *hv* at δ = 2.92 results in 8% and 1% enhancements at δ = 5.01 and 1.19, respectively, *hv* at δ = 1.19 resulted in 6% and 5% enhancements at δ = 3.41 and 2.92, respectively; ^{13}C NMR ($CDCl_3$) δ −1.54, 14.02, 15.03, 43.25, 64.36, 68.20, 79.40, 161.00, 171.00, 197.01, 204.10, 310.00; mass spectrum *m/z* (% rel. intensity) 550 M$^+$ (23, ^{184}W), 522 (5), 494 (24), 464 (26), 410 (100), 380 (77), 365 (28), 73 (95); IR (neat) ν_{max}/cm^{-1} 2986–2869w, 2068vs, 1987s, 1920vs, 1444m, 1221m, 1125m, 841m; red solid, mp 57–58 °C. Spectral data for **40a** (R_f = 0.28, 1/1/50); ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.47 (t, 3H, J = 7.1 Hz), 1.61 (d, 3H, J = 6.4 Hz), 4.20 (q, 2H, J = 7.1 Hz), 4.44 (s, 3H), 6.00 (q, 1H, J = 6.4 Hz), 6.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.00, 16.00, 17.00, 69.00, 72.50, 135.00, 139.00, 143.00, 160.00, 199.90, 203.00, 302.50; IR (neat) ν_{max}/cm^{-1} 2977–2870s, 2062vs, 2018s, 1912vs, 1582s, 1448s, 1217s, 1167–1099s, 839s; red solid, mp 25 °C. Spectral data for **46a** (R_f = 0.09, 1/1/50); ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.51 (d, 3H, J = 7.1 Hz), 1.55 (t, 3H, J = 7.3 Hz), 4.51 (s, 3H), 4.66 (q, 2H, J = 7.1 Hz), 6.15 (q, 1H, J = 7.3 Hz), 6.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −0.97, 15.86, 17.27, 70.16, 81.88, 134.22, 137.88, 140.65, 163.26, 201.79, 216.49, 220.51, 315.12); IR (neat) ν_{max}/cm^{-1} 2964w, 2018s, 1899vs, 1836s, 1608w, 1467m, 1280s, 1109m, 856m; mass spectrum *m/z* (% rel. intensity) 522 M$^+$ (22, ^{184}W), 492 (19), 449 (8), 419 (30), 407 (7), 393 (14), 365 (33), 265 (27), 73 (100); black solid, mp 25 °C.

The reaction of the propynyl tungsten carbene complex 18 with *cis*-1-ethoxypropene to give 39b and 40b

The reaction of 0.202 g (0.497 mmol) of complex **18**[4a] and 0.5 mL (5.24 mmol) of *cis*-1-ethoxypropene (≥54:1, *Z*:*E*) was carried out according to the the general procedure. After four hours at 25 °C, the reaction was judged complete by TLC. The ^{1}H NMR spectrum of the crude reaction mixture failed to detect any isomerized olefin. The volatiles were removed under vacuum (0.01 mmHg) and the residue chromatographed on silica gel using a 1:1:20 mixture of ether:methylene chloride:hexanes as the eluent to give 9 mg (4%) of dienyl complex **40b** and 0.162 g (68%) of **39b**. The stereochemical assignments of **39b** and **40b** were made on the basis of NOE experiments. Spectral data for **40b**: red solid, mp 25 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.39 (t, 3H, J = 7.1 Hz), 1.59 (d, 3H, J = 6.9 Hz), 1.77 (s, 3H), 4.05 (q, 2H, J = 7.1 Hz), 4.46 (s, 3H), 5.41 (q, 1H, J = 6.9 Hz), 6.20 (s, 1H); NOE data: *hv* at δ = 1.77 results in 4, 8 and 2% enhancements at δ = 6.20, 5.41 and 4.46, respectively, *hv* at δ = 5.41 results in 3, 2 and 4% enhancements at δ = 4.46, 4.05 and 1.77, *hv* at δ = 1.59 results in 7 and 3% enhancements at δ = 5.41 and 6.20, respectively, *hv* at δ = 6.20 results in 4, 8, 4 and 4% enhancements at δ = 4.46, 4.05, 1.77 and 1.59, respectively; mass spectrum *m/z* (% rel. intensity) M$^+$ 492 (20, ^{184}W), 464 (54), 436 (45), 408 (8), 391 (40), 350 (61), 307 (100), 291 (41), 278 (65), 91 (30); IR (neat) ν_{max}/cm^{-1} 2952m, 2066vs, 1929vs, 1590s, 1449s, 1249s, 1197s, 1109s. Spectral data for **39b**: ^{1}H NMR ($CDCl_3$) δ 1.16 (d, 3H, J = 7.18 Hz), 1.26 (m, 3H), 1.89 (s, 3H), 2.64–2.72 (m, 1H), 3.46–3.59 (m, 1H), 3.59–3.66 (m, 1H), 4.56 (s, 3H), 4.83–4.84 (m, 1H); NOE data; *hv* at δ = 4.83 results in 11% enhancement at δ = 2.68, *hv* at δ = 2.68 results in 7% enhancement at δ = 4.83, *hv* at δ = 1.16 results in 30% enhancement at δ = 2.68; ^{13}C NMR ($CDCl_3$) δ 11.36 (q, J_{CH} = 127.8 Hz), 15.00 (q, J_{CH} = 125.6 Hz), 15.78 (q, J_{CH} = 127.6 Hz), 43.68 (d, J_{CH} = 136.4 Hz), 64.72 (t, J_{CH} = 140.5 Hz), 68.33 (q, J_{CH} = 146.7 Hz), 77.85 (m), 154.14 (s), 158.5 (s), 197.43 (t, J_{CW} = 63.4 Hz), 203.18 (s), 307.06 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 3681w, 2067m, 1982w, 1937s, 1586w; mass spectrum *m/z* (% rel. intensity) 492 M$^+$ (40, ^{184}W), 464 (75, ^{184}W), 436 (76, ^{184}W), 408 (18, ^{184}W), 380 (6, ^{184}W), 352 (100, ^{184}W), 321 (76), 310 (72), 291 (55), 276 (38), 250 (38), 250 (38), 223 (14), 186 (2), 160 (1), 123 (5), 105 (14), 91 (22). Anal. calcd. for $C_{15}H_{16}O_7W$: C, 36.61; H, 3.28. Found: C, 36.94; H, 3.26. R_f(1:1:20, ether:methylene chloride:hexanes) = 0.17.

The reaction of the trimethylsilylalkynyl tungsten carbene complex 19 with *trans*-1-ethoxypropene to give 39a

A mixture of 1.114 g (2.40 mmol) of complex **19**[4a] and 1.6 mL (16.75 mmol) of *trans*-1-ethoxypropene (≥65:1, *E*:*Z*) was deoxygenated and reacted according to the general procedure. After stirring for five days at 25 °C, TLC indicated that very little **19** remained and no detectable amount of olefin isomerization could be detected by ^{1}H NMR. The volatiles were removed under vacuum (0.01 mmHg) and the resulting residue was composed of at least seven compounds as indicated by TLC. Column chromatography on silica gel using a 1:1:10 mixture of ether:methylene chloride:hexanes as the mobile phase allowed only the major product to be obtained in pure form. The major product was identified as the *cis*-cycloadduct **39a** (141.4 mg, 10%) on the basis that its ^{1}H NMR and IR spectra were identical to those of the [2 + 2] cycloadduct obtained from the reaction of **19** and *cis*-1-ethoxypropene described above. The next three most significant fractions (11.4 mg, 10.5 mg and 18.3 mg) were not pure and were obtained in very small amounts. ^{1}H NMR analysis revealed that they consisted of a complex mixture of unidentified compounds.

The reaction of the propynyl tungsten carbene complex 18 with *trans*-1-ethoxypropene to give 41b. Studies on the chelation of 41b and the dechelation of 60b

The reaction of 0.254 g (0.625 mmol) of complex **18**[4a] and 0.9 mL (9.42 mmol) of *trans*-1-ethoxypropene (≥65:1, *E*:*Z*) was conducted according to the the general procedure. After 5 hours, the reaction appeared complete by TLC and the ^{1}H NMR spectrum of the crude reaction mixture failed to detect the presence of any isomerized olefin. The volatiles were removed under vacuum (0.01 mmHg) and the residue was chromatographed on silica gel using a 1:1:20 mixture of

ether : methylene chloride : hexanes as the eluent to give three fractions. One was identified as the dienyl complex **41b** which was formed as the major product and obtained as a red solid (0.088 g, 29%). The other two were brownish orange fractions which by ^{1}H NMR contained additional **41b** and two minor compounds which were less than 10% of the weight of **41b**. These compounds were not characterized but one may have been the *trans*-cyclobutenyl complex **45**. The *cis*-cyclobutenyl complex **39b** could not be detected but if formed would have been less than 2% yield. Spectral data for **41b**: mp 29–30 °C (decomp.); (R_f = 0.35, 1/1/20); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, J = 7.1 Hz), 1.67 (d, 3H, J = 6.8 Hz), 1.74 (s, 3H), 3.87 (q, 2H, J = 7.1 Hz), 4.20 (br s, 3H), 4.88 (q, 1H, J = 6.8 Hz), 5.75 (s, 1H); NOE data: *hv* at δ = 1.74 results in 4 and 1% enhancements at δ = 5.75 and 4.20, respectively, *hv* at δ = 1.67 results in 5% enhancement at δ = 4.88, *hv* at δ = 4.88 results in 2, 3, 2, 3, 3 and 3% enhancements at δ = 5.75, 4.20, 3.87, 1.74, 1.67 and 1.25, respectively, *hv* at δ = 5.75 results in 2, 2, 5, 3, 2 and 5% enhancements at δ = 4.88, 4.20, 3.87, 1.74, 1.67 and 1.25, respectively; ^{13}C NMR ($CDCl_3$) δ 13.99, 14.44, 15.82, 70.11, 78.56, 124.04, 129.14, 135.56, 159.11, 198.60, 206.32, 329.57); IR (neat) ν_{max}/cm^{-1} 2954–2855m, 2067s, 1927vs, 1609w, 1242m, 1141w, 909w, 734m; mass spectrum *m*/*z* (% rel. intensity) M^+ 492 (5, ^{184}W), 464 (5, ^{184}W), 436 (13, ^{184}W), 408 (12, ^{184}W), 380 (9, ^{184}W), 352 (24, ^{184}W), 309 (21), 279 (22), 97 (61), 85 (63).

Chelation of 41b. A sample of 79 mg carbene complex **41b** (0.16 mmol) was dissolved in 20 mL of hexane in a round bottomed flask with a side opening. The solution was heated at 60 °C for 36 h while a constant slow stream of nitrogen was passed through the solution *via* the side opening. A condensor was used to condense the solvent although several 5 mL portions of hexane were added to maintain the solution volume. Separation of the components of the reaction mixture on silica gel gave 30 mg of recovered **41b** and 29 mg chelated carbene complex **60b** as a black solid in 63% yield based on unrecovered starting material. Spectral data for **60b**: mp 25 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.54 (t, 3H, J = 7.1 Hz), 1.67 (d, 3H, J = 6.7 Hz), 1.73 (s, 3H), 3.89 (q, 2H, J = 7.1 Hz), 4.24 (br, 3H), 4.90 (q, 1H, J = 6.8 Hz), 5.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.27, 15.93, 17.79, 70.52, 78.16, 126.07, 128.09, 143.17, 165.53, 201.88, 216.39, 220.34, 315.53; IR (neat) ν_{max}/cm^{-1} 2954–2852m, 2018vs, 1898vs,, 1837vs, 1609w, 1450w, 1243m, 1197w, 1099w; mass spectrum *m*/*z* (% rel. intensity) M^+ 464 (15, ^{184}W), 434 (12), 350 (15), 307 (35), 278 (23), 184 (68), 155 (71), 123 (100), 95 (62).

Dechelation of 60b. A solution of 52 mg carbene complex **60b** (0.112 mmol) in 20 mL of hexane was added to a high-pressure Parr reactor. The reactor and contents was purged with nitrogen and then the reactor was charged with 500 psi† of carbon monoxide. The mixture was stirred at 60 °C for 2 h and then after release of CO pressure and removal of solvent, 54 mg carbene complex **41b** was obtained as a red solid in quantitative yield.

The reaction of the trimethylsilylalkynyl chromium and tungsten carbene complexes 23 and 19 with a mixture of *cis* and *trans*-ethoxypropene to give 39c and 39a

Complex **23**[4a] (0.267 g, 0.80 mmol) was reacted according to the general procedure with 1-ethoxypropene (1.0 mL, 10.47 mmol, *cis*/*trans* 3/1). After 36 hours, the volatiles were removed and following purification by flash chromatography using a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes, as the eluent, **39c** was obtained as a red oil (248 mg, 74%). Spectral data for **39c**: ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 9H), 1.05–1.20 (br m, 6H), 2.65–2.75 (m, 1H), 3.2–3.32 (m, 1H), 3.32–3.50 (m, 1H), 4.99 (s, 3H), 4.95–5.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −1.58 (q, J_{CH} = 119.5 Hz), 14.40 (q, J_{CH} = 126.8 Hz), 15.07 (q, J_{CH} = 125.5 Hz), 42.81 (d, J_{CH} = 135.7 Hz), 64.58 (t, J_{CH} = 140.9 Hz), 65.78 (q, J_{CH} = 147.4 Hz), 79.80 (d, J_{CH} = 151.3 Hz), 155.06 (s), 167.58 (s), 216.20 (s), 223.79 (s), 338.99 (s); mass spectrum *m*/*z* (% rel. intensity) 418 M^+ (11), 390 (1), 362 (19), 334 (18), 306 (73), 278 (74), 263 (2), 249 (5), 234 (35), 219 (22), 204 (100), 189 (14), 163 (10), 149 (16), 126 (24), 109 (4), 97 (11), 89 (11), 73 (32). Anal. calcd. for $C_{17}H_{22}O_7SiCr$: C, 48.80; H, 5.30. Found: C, 49.04; H, 5.36. Upon storage in the freezer, **39c** undergoes electrocyclic ring opening with loss of CO to form the 1,3-dienyl complex **40c**. Spectral data for **40c**: ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 1.51 (t, 3H, J = 7.1 Hz), 1.57 (d, 3H, J = 6.5 Hz), 4.44 (q, 2H, J = 7.0 Hz), 4.69 (s, 3H), 6.12 (q, 1H, J = 6.5 Hz), 6.71 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.64 (q, J_{CH} = 118.9 Hz), 14.98 (m), 16.46 (m), 67.64 (q, J_{CH} = 147.3 Hz), 78.59 (m), 132.49 (s), 134.10 (s), 139.56 (d, J_{CH} = 152.3 Hz), 163.16 (d, J_{CH} = 185 Hz), 213.74 (s), 231.24 (s), 232.30 (s), 334.25 (s). Anal. calcd. for $C_{16}H_{22}O_6CrSi$: C, 49.22; H, 5.68. Found: C, 49.31; H, 5.63.

To 2.13 g trimethylsilylalkynyl carbene complex **19**[4a] (4.59 mmol) was added 5 mL of ethyl propenyl ether (large excess, *cis*/*trans* = 3/1). The mixture was allowed to react according to the general procedure for 12 h at 25 °C. Without workup, the crude was chromatographed to give 1.23 g of pure *cis*-cyclobutenyl complex **39a** in 49% yield as red crystals (eluent: ether : dichloromethane : hexane = 1 : 1 : 50, R_f = 0.15).

The reaction of the propynyl chromium and tungsten carbene complexes 12 and 18 with a mixture of *cis* and *trans*-ethoxypropene to give 39d and 39b

A sample of 0.582 g (2.12 mmol) of complex **12**[4a] and 1.8 mL (18.85 mmol) of 1-ethoxypropene (*cis*/*trans* 3/1) was reacted according to the general procedure. After 8 hours, the volatiles were removed and the residue chromatographed on silica gel using a 1 : 1 : 50 mixture of ether : methylene chloride : hexanes as the eluent to give 0.232 g (30%) of a red oil which was identified as the pure cycloadduct **39d**: ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 3H, J = 7.0 Hz), 1.25 (t, 3H, J = 7.0 Hz), 1.91 (s, 3H), 2.75–2.85 (m, 1H), 3.5–3.6 (m, 2H), 4.71 (s, 3H), 4.87–4.88 (m, 1H). Anal. calcd. for $C_{15}H_{16}O_7Cr$: C, 50.01; H, 4.48. Found: C, 49.67; H, 4.48.

The reaction of 0.380 g (0.93 mmol) of complex **18**[4a] and 6.0 mL (62.8 mmol) of 1-ethoxypropene (*cis*/*trans* 3/1) was carried out according to the general procedure. After 2 hours, the volatiles were removed and the residue was chromatographed on silica gel using a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes as eluent to purify the major product which was identified as the *cis*-cyclobutenyl complex **39b** (231 mg, 52%) by comparison of its spectral data with those of the compound obtained from the reaction of complex **18** with *cis*-1-ethoxyprop-1-ene as described above.

The thermal electrocyclic ring opening of the cyclobutenyl carbene complex 39a and the interconversion of 40a and 46a

Under CO pressure. A sample of carbene complex **39a** (219 mg, 0.398 mmol) was dissolved in 20 mL ether in a high-pressure Parr reactor. The reactor and contents were purged with nitrogen and then filled with CO at 520 psi. The mixture was stirred at 70 °C for 11 h. The pressure of the reactor was released and the contents transferred to a round bottom flask with a side-arm and which was equipped with a condensor. The solution was brought to reflux under a slow purge of nitrogen for 12 h during which time several 5 mL portions of hexane were added to maintain volume. The major product was isolated by chromatography on silica gel to give a 34% yield (70 mg) of the chelated complex **46a** which was identical to the product obtained from the reaction of complex **19** with *cis*-1-ethoxypropene described above. The only other significant

† 1 psi = 6.895 × 10^3 Pa.

product isolated from this reaction was the chelated dienyl complex **55a** which was obtained in 18% yield (40 mg) as an orange solid ($R_f = 0.33$, 1/1/50). The structure of this product was confirmed by X-ray diffraction (*vide infra*). Spectral data for **55a**: mp 52.8–53.4 °C; ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9H), 1.37 (t, 3H, $J = 7.1$ Hz), 1.43 (d, 3H, $J = 6.4$ Hz), 4.27 (q, 2H, $J = 7.1$ Hz), 4.45 (s, 3H), 5.94 (q, 1H, $J = 6.4$ Hz), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −0.64, 16.22, 16.99, 68.97, 72.82, 136.87, 138.31, 141.10, 175.31, 199.27, 202.44, 299.72; mass spectrum *m*/*z* (% rel. intensity) M^+ 550 (10), 522 (3), 494 (10), 449 (5), 419 (9), 407 (5), 393 (4), 169 (18), 73 (100); IR (neat) ν_{max}/cm^{-1} 2955m, 2062s, 1910s, 1584m, 1240m, 1193s, 1105m, 825m.

Under nitrogen stream. A sample of 90 mg carbene complex **39a** (0.164 mmol) was dissolved in 20 mL of hexane and heated under a nitrogen purge at 70 °C for 18 h as described above in the second step of the CO experiment. After removal of solvent, the ^{1}H NMR spectrum of the crude reaction mixture indicated only the presence of the chelated complex **46a**. After purification by silica gel chromatography, **46a** was obtained in 90% yield (77 mg).

Sealed under argon. A sample of 0.91 g carbene complex **39a** (1.65 mmol) was dissolved in 100 mL hexane and deoxygenated by the freeze–thaw method (−196 to 22 °C, 3 cycles) in a flask described in the general procedure. 1 atm of argon was introduced at 22 °C, the flask was sealed with the threaded stopcock and heated at 70 °C for 12 h. Starting material was still present. A rapid filtration on silica gel gave 0.55 g of a mixture of products which was dissolved in 20 mL hexane and heated under the same conditions at 70 °C for 17 h. Purification of the products by silica gel chromatography gave 0.15 g (16%) of complex **40a** and 13 mg (2%) of chelated complex **46a**.

Dechelation of 46a. A solution of 114 mg of carbene complex **46a** (0.218 mmol) in 20 mL ether was introduced into a high-pressure Parr reactor. The reactor and contents were purged with nitrogen and then filled with CO at 700 psi. The mixture was stirred at room temperature for 2 h followed by slow release of CO. After removal of solvent, carbene complex **40a** was obtained as a red solid in quantitative yield (120 mg).

Chelation of 40a. A sample of 242 mg carbene complex **40a** (0.44 mmol) was heated at 70 °C for 5 h under a nitrogen stream under the conditions described above for complex **39a**. Purification of the product by silica gel chromatography gave the chelated carbene complex **46a** as a black solid in 60% yield (135 mg).

Thermolysis of 46a under CO. A solution of 250 mg carbene complex **46a** (0.454 mmol) in 20 mL of hexane was added to a high-pressure Parr reactor. The reactor and contents were purged with nitrogen and then filled with CO at 500 psi. The mixture was stirred at 60 °C for 24 h. After release of CO and removal of solvent, isolation of the products by silica gel chromatography gave 55 mg (21%) of carbene complex **55a**, 110 mg (42%) of complex **40a** and 44 mg (18%) of complex **46a**.

Structure determination of chelated complex 55a

Crystal data for $C_{17}H_{22}O_7SiW$: FW = 550.3, monoclinic, $P2_1/c$, $a = 9.779(3)$, $b = 14.243(4)$, $c = 15.510(5)$ Å, $\beta = 99.04(3)°$, $V = 2270.9(17)$ Å^3, $Z = 4$, μ(Mo-Kα) = 55.02 cm^{-1}, 4808 data collected (max $2\theta = 54°$), 2556 observed from 4458 independent reflections. $R(F) = 5.61\%$ and $R(wF) = 6.74\%$. Max/min residual electron density = 1.27 and −1.90 e Å^{-3}. The methyl groups of the trimethylsilyl group are rotationally disordered about the Si–C(8) vector. Full resolution of this disorder was impossible. SHELXTL (4.2) software was used for refinement (G. Sheldrick, Siemens XRD, Madison, WI).‡

Oxidation of the cyclobutenyl carbene complexes 39a and 39b to give the cyclobutenyl esters 48a and 48b

A sample of 0.216 g carbene complex **39b** (0.439 mmol) was dissolved in 2 mL freshly distilled DMSO and stirred at room temperature for 5 h. The reaction mixture was diluted with 100 mL pentane and washed with water (3 × 5 mL). After removal of solvent, silica gel chromatography provided 16.3 mg of **48b** as a slightly yellow oil in 20% yield ($R_f = 0.01$, 1:1:20, ether:CH_2Cl_2:hexane). Spectral data for **48b**: ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 3H, $J = 7.0$ Hz), 1.22 (t, 3H, $J = 6.9$ Hz), 1.98 (s, 3H), 2.82 (br s, 1H), 3.50–3.59 (m, 1H), 3.60–3.68 (m, 1H), 3.70 (s, 3H), 4.42 (br s, 1H).

The oxidation of 0.25 g carbene complex **39a** (0.452 mmol) was carried out in 2 mL freshly distilled DMSO at room temperature for 17 h. The crude reaction mixture was directly loaded onto a silica gel column and 62.5 mg of **48a** was obtained as a colorless oil in 57% yield ($R_f = 0.02$, 1:1:30, ether:CH_2Cl_2:hexane). Spectral data for **48a**: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.14 (d, 3H, $J = 7.0$ Hz), 1.17 (t, 3H, $J = 7.0$ Hz), 2.96 (dq, 1H, $J = 3.9$, 7.0 Hz), 3.57 (dq, 1H, $J = 13.0$, 7.0 Hz), 3.67 (dq, 1H, $J = 13.0$, 7.0 Hz), 3.70 (s, 3H), 4.47 (d, 1H, $J = 3.9$ Hz); ^{13}C NMR ($CDCl_3$) δ −1.07, 14.93 16.00, 45.15, 51.67, 65.90, 78.13, 143.80, 164.03, 176.00; IR (neat) ν_{max}/cm^{-1} 2956–2897s, 2040m, 1911s, 1862m, 1720s, 1220s, 1099s, 842vs; mass spectrum *m*/*z* (% rel. intensity) M^+ 242 (7), 227 (100), 211 (18), 197 (45), 183 (20), 167 (30), 109 (62), 89 (87), 73 (100).

Electrocyclic ring opening of the cyclobutenyl esters 48a and 48b

The thermolysis of 16.3 mg of ester **48b** was performed in 5 mL of benzene at 100 °C for 10 h. This led to the formation of a single diastereomer of the ring opened product which was purified on a short silica gel column with ether as eluent to give 10 mg of **49b** in 62% yield. Spectral data for **49b**: ^{1}H NMR ($CDCl_3$) δ 2.18 (t, 3H, $J = 7.1$ Hz), 2.21 (d, 3H, $J = 6.8$ Hz), 2.65 (s, 3H), 4.54 (s, 3H), 4.87 (q, 2H, $J = 7.1$ Hz), 6.32 (q, 1H, $J = 6.8$ Hz), 7.23 (s, 1H).

The thermolysis of ester **48a** (52 mg, 0.215 mmol) was carried out in the same manner. A single diastereomer of the ring opened product was obtained which was purifed in the same manner as **49b** to give a 48% yield (25 mg) of a product which was identified as the dienyl complex **49a** as a colorless oil. The stereochemistry of **49a** was assigned as *Z*,*Z* on the basis of the fact that the oxidation of the *Z*,*Z*-dienyl carbene complex **46a** gave a single compound which was found to have identical spectral data to **49a**. Spectral data for **49a**: ^{1}H NMR ($CDCl_3$) δ 0.064 (s, 9H), 1.3 (t, 3H, $J = 7.1$ Hz), 1.70 (d, 3H, $J = 6.5$ Hz), 3.68 (s, 3H), 4.03 (q, 2H, $J = 7.1$ Hz), 6.09 (q, 1H, $J = 6.4$ Hz), 6.16 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −0.75, 16.04, 16.51, 51.65, 71.14, 108.78, 138.88, 140.05, 155.42, 166.80; IR (neat) ν_{max}/cm^{-1} 2982–2854m, 1912m, 1698s, 1609s, 1435s, 1246s, 1183s, 1120s, 838s; mass spectrum *m*/*z* (% rel. intensity) M^+ 242 (54), 227 (100), 211 (57), 197 (55), 167 (43), 109 (78), 89 (87), 73 (100).

The thermal electrocyclic ring opening of the cyclobutenyl carbene complex 39b and the interconversion of 40b and 57b

Under CO pressure. Carbene complex **39b** (195 mg, 0.396

‡ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/270.

mmol) was dissolved in 50 mL hexane in a high-pressure Parr reactor. The reactor and contents were purged with nitrogen and then filled with CO at 500 psi and then heated at 70 °C for 24 h. After release of the CO pressure, the mixture was transferred from the reactor into a round bottom flask with a side-arm and equipped with a reflux condensor. The solution was brought to reflux under a slow purge of nitrogen for 12 h during which time several 5 mL portions of hexane were added to maintain volume. The three major products were purified by silica gel chromatography to give 64 mg complex **58b** as an orange solid in 33% yield (R_f = 0.30, 1/1/30), 106 mg of chelated complex **57b** in 57% yield and 13 mg complex **40b** in 6% yield. Spectral data for **58b**: Yellow crystals, mp 54–55 °C; ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 3H, J = 6.3 Hz), 1.44 (t, 3H, J = 7.1 Hz), 1.71 (s, 3H), 4.32 (q, 2H, J = 7.1 Hz), 4.52 (s, 3H), 5.41 (q, 1H, J = 6.3 Hz), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.52, 16.22, 23.96, 30.40, 73.10, 122.91, 123.70, 131.32, 141.48, 199.20, 202.48, 301.39; IR (CH_2Cl_2) ν_{max}/cm^{-1} 3054m, 2986m, 2928w, 2062m, 1927s, 1422m, 1265s, 1201m, 895m, 720br s; mass spectrum *m*/*z* (% rel. intensity) M^+ 492 (10, ^{184}W), 464 (10), 436 (14), 391 (8), 350 (23), 307 (21), 97 (75), 83 (73), 71 (100).

Under nitrogen stream. Carbene complex **39b** (164 mg, 0.334 mmol) was dissolved in 15 mL of hexane and heated at 70 °C for 12 h under a slow stream of nitrogen as described above in the second step of the CO experiment. The three major products were purified by silica gel chromatography to give 84 mg chelated complex **57b** in 54% yield, 5.5 mg complex **40b** in 5% yield and 24.8 mg of starting material **39b** in 17% recovery.

Sealed under argon. A sample of 90 mg carbene complex **39b** (0.183 mmol) was dissolved in 10 mL hexane and deoxygenated by the freeze–thaw method (−196 to 22 °C, 3 cycles) in a flask described in the general procedure. 1 atm of argon was introduced at 22 °C, the flask was sealed with the threaded stopcock and heated at 70 °C for 12.5 h. Purification of the products by chromatography on silica gel gave a mixture of complexes **40b** and **58b** (47% and 2%, respectively) and 30 mg complex **57b** in 35% yield.

Dechelation of 57b. A sample of 66.1 mg carbene complex **57b** (0.122 mmol) was dissolved in 50 mL hexane and transferred to a high pressure Parr reactor. The reactor and contents were purged with nitrogen and then filled with CO at 500 psi and then stirred at room temperature for 2 h. After release of the CO pressure and removal of solvent, the residue was loaded on a silica gel column to give 54.6 mg of carbene complex **40b** as a red solid in 78% yield (R_f = 0.53, 1/1/10).

Chelation of 40b. Carbene complex **40b** (54 mg) was dissolved in 50 mL of hexane and heated at 60 °C for 2 h under a slow stream of nitrogen as described above in the second step of the CO experiment. Purification of the product by silica gel chromatography gave 30 mg chelated carbene complex **57b** as a black solid in 58% yield (R_f = 0.21, 1/1/20). Spectral data for **57b**: mp 25 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.46 (d, 3H, J = 6.6 Hz), 1.55 (t, 3H, J = 7.0 Hz), 1.79 (s, 3H), 4.54 (s, 3H), 4.67 (q, 2H, J = 7.0 Hz), 5.54 (q, 1H, J = 6.6 Hz), 7.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.80, 15.89, 25.67, 70.48, 82.16, 126.27, 127.80, 138.16, 165.34, 198.80, 216.30, 220.35, 315.49); IR (neat) ν_{max}/cm^{-1} 2927m, 2066s, 1909vs, 1847s, 1588m, 1450m, 1238m, 1196m, 1108m; mass spectrum *m*/*z* (% rel. intensity) M^+ 464 (100, ^{184}W), 434 (49), 407 (5), 391 (25), 361 (35), 307 (85), 278 (63), 258 (39), 129 (32), 91 (27), 70 (15).

Thermolysis of 57b under CO. Carbene complex **57b** (97 mg, 0.209 mmol) was dissolved in 10 mL of hexane in a high-pressure Parr reactor. The reactor and contents were purged with nitrogen and then filled with CO at 500 psi. The mixture was stirred at 70 °C for 28 h. The two major products were the carbene complex **57b** (39 mg, 39%, orange solid) and the complex **40b** (23 mg, 22% yield).

Oxidation of carbene complex 4q to give the 7-methyl-2-oxabicyclo[4.2.0]oct-7-ene-8-carboxylate 61

A sample of 0.175 g (0.36 mmol) of complex **4q** was placed in a round bottom flask and 1.5 mL of DMSO was added as the minimum amount to effect solvation. After 10 minutes all of the complex had completely dissolved and the solution had become bright yellow. The reaction was complete by TLC and the mixture was placed neat on a silica gel column and eluted with a 1:1:4 mixture of ether:methylene chloride:hexanes. This gave 62 mg (94%) of a colorless oil which was identified as the methyl ester **61**. Spectral data for **61**: ^{1}H NMR ($CDCl_3$) δ 1.42–1.52 (m, 1H), 1.52–1.62 (m, 1H), 1.62–1.7 (m, 1H), 1.85–1.95 (m, 1H), 1.99 (s, 3H), 2.6–2.7 (m, 1H), 3.58–3.65 (m, 1H), 3.68 (s, 3H), 3.7–3.8 (m, 1H), 4.51 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.45 (q, J_{CH} = 130.9 Hz), 20.04 (t, J_{CH} = 129.6 Hz), 21.42 (t, J_{CH} = 133.5 Hz), 42.35 (d, J_{CH} = 137.2 Hz), 50.97 (q, J_{CH} = 145.0 Hz), 61.88 (t, J_{CH} = 146.1 Hz), 69.64 (d, J_{CH} = 159.7 Hz), 132.66 (s), 162.78 (s), 166.41 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2945–2873m, 1711s, 1659m, 1378w, 1098m, 1065m, 1048; mass spectrum *m*/*z* (% rel. intensity) 182 M^+ (25), 153 (100), 139 (13), 123 (48), 109 (18), 95 (22), 79 (21), 67 (21), *m*/*z* calcd. for $C_{10}H_{14}O_3$ 182.0943, measured 182.0937. Anal. calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.36; H, 7.56.

Oxidation of the ene adduct 33b to give the methyl ester 62

The carbene complex **33b** (134.5 mg, 0.218 mmol) was dissolved in 1.5 mL of freshly distilled DMSO and stirred at room temperature for 24 h. The product was purified by silica gel chromatography to give 68 mg of the ester **62** as a colorless oil in quantitative yield (R_f = 0.71, 1/1/2). Spectral data for **62**: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6H), 0.86 (s, 9H), 1.42–1.55 (m, 1H), 1.58–1.66 (m, 2H), 1.74–1.82 (m, 1H), 2.00–2.10 (m, 2H), 2.26 (s, 3H), 2.86–2.90 (m, 1H), 3.68 (s, 3H), 4.95 (t, 1H, J = 3.5 Hz), 5.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −3.94, 17.55, 18.64, 20.92, 24.68, 26.24, 29.30, 51.28, 51.43, 106.39, 117.49, 150.00, 162.40, 168.00; IR (neat) ν_{max}/cm^{-1} 2950–2858s, 2062s, 1931vs, 1721s, 1646s, 1154s, 839s; mass spectrum *m*/*z* (% rel. intensity) M^+ 310 (15), 279 (13), 253 (100), 221 (16), 193 (10), 179 (10), 119 (8), 89 (92), 73 (57).

Oxidation of the chelated dienyl carbene complex 46a to give the methyl ester 49a

Carbene complex **46a** (282 mg, 0.54 mmol) was dissolved in 2 mL DMSO and stirred at room temperature for 24 h. The only two products from this reaction that were mobile on silica gel were starting material (38 mg) and the dienyl ester **49a** (13 mg, 12% yield, R_f = 0.12, 1/1/10). No significant enhancement in yield was observed when an ether solution of complex **46a** (106 mg, 0.203 mmol) was oxidized with 3 mL of 0.5 M aqueous cerium ammonium nitrate at room temperature for 2 h. The crude reaction mixture was diluted with ether and washed with water and brine. Purification by silica gel chromatography gave 6.6 mg of **49a** as a colorless oil in 13% yield. In each case, only a single diastereomer of the dienyl ester was obtained. The spectral data of **49a** was identical with those of the compound obtained from the thermally induced ring-opening of the cyclobutenone **48a**.

Oxidation of the *E*,*E*-dienyl carbene complex 55a to give the methyl ester 63

Carbene complex **55a** (70 mg, 0.127 mmol) was dissolved in 1 mL DMSO and stirred at room temperature for 24 h. The major product of the reaction was purified by chromatography on silica gel to give 3.5 mg of **63** as a colorless oil in 11% yield (R_f = 0.12, 1/1/10). Spectral data for **63**: ^{1}H NMR ($CDCl_3$)

δ 0.06 (s, 9H), 1.23 (t, 3H, J = 7.0 Hz), 1.61 (d, 3H, J = 6.4 Hz), 3.68 (s, 3H), 4.02 (q, 2H, J = 6.4 Hz), 6.08 (q, 1H, J = 6.4 Hz), 7.37 (s, 1H); IR (neat) ν_{max}/cm^{-1} 2954–2854s, 1709s, 1629m, 1245s, 1208s, 1098s, 1022m, 839s; mass spectrum *m*/*z* (% rel. intensity) M$^+$ 242 (6), 227 (100), 211 (6), 197 (10), 167 (14), 109 (17), 89 (49), 73 (63).

Cerium(IV) mediated cine rearrangement of the cyclobutenyl carbene complex 4o

A solution of 1.083 g (3.95 mmol) of complex **12**[4a] in 7 mL of methylene chloride was deoxygenated by the freeze–thaw method. Ketene diethyl acetal (618 mg, 5.32 mmol) was added dropwise at room temperature. After the additon of the final aliquot of acetal, the solution was treated with excess Ce^{IV} as a 1 M aqueous ammonium nitrate solution. A TLC taken immediately following addition indicated the presence of many organic products and a new surviving organometallic compound. The organic layer was separated and stripped of solvent under high vacuum (0.01 mmHg) and the residue was eluted from a silica gel column using a 1 : 1 : 4 mixture of ether : methylene chloride : hexanes as the mobile phase. The organometallic compound was isolated to give 96 mg (6% yield) of a bright red solid which was identified as the rearranged cyclobutenyl carbene complex **64**. The structure of complex **64** was confirmed by X-ray diffraction (*vide infra*). Spectral data for **64**: R_f(1 : 1 : 4, ether : methylene chloride : hexanes) = 0.19; ^{1}H NMR ($CDCl_3$) δ 1.16 (m, 3H), 1.50 (m, 3H), 1.57 (s, 3H), 2.58 (d, 1H, J = 16.1 Hz), 2.85 (d, 1H, J = 16.1 Hz), 3.1–3.22 (m, 1H), 3.25–3.35 (m, 1H), 4.2–4.35 (m, 2H), 4.61 (s, 3H); NOE: *hv* at δ = 1.16 gives doublets at δ = 3.16 (J = 10 Hz) and δ = 3.30 (J = 10 Hz); *hv* at δ = 4.28 gives a singlet at δ = 1.50; ^{13}C NMR ($CDCl_3$) δ 15.12, 15.78, 24.22, 41.40, 59.08, 62.49, 68.38, 71.79, 131.81, 170.58, 217.27, 224.07, 313.88; IR ($CHCl_3$) ν_{max}/cm^{-1} 2080s, 1995m, 1610s, 1405w, 1375w, 1020w.

Structure determination of the cyclobutenyl complex 64

Chunky red crystals of **64** ($C_{16}H_{18}CrO_8$) formed from hexane in space group $P2_1/c$ with a = 16.453(3) Å, b = 6.598(1) Å, c = 17.277(3) Å and β = 93.13(1)° for Z = 4 and a calculated density of 1.384 g cm^{-3} and a calculated absorption coefficient of 54.43 cm^{-1}. An automatic four circle diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å) was used to measure 2782 potential diffraction peaks of which 2124 were observed ($I \geqslant 3\sigma I$). The data were corrected empirically for absorption. Application of a multi-solution tangent formula approach to phase solution gave an initial model for the structure[24] which was subsequently refined with least-squares and Fourier methods. Hydrogens were added with isotropic temperature factors 1.2 times that of the attached atoms and constrained to 'ride' with this atom. The function $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/(\sigma F_o)^2$ was minimized with full-matrix least-squares to give an unweighed residual of 0.045.‡

The Diels–Alder reaction of the dienyl chromium carbene complex 16b with benzoquinone to give the naphthalene carbene complex 65

Complex **16b** (0.100 g, 0.29 mmol) was combined with 0.309 g (2.86 mmol) of benzoquinone in 4.0 mL of benzene. The resulting mixture was deoxygenated as described in the general procedure. The flask was sealed under one atmosphere of argon at 25 °C and heated to 50 °C for 21 h. TLC suggested that two organometallic products were produced in this reaction. The solvent was removed under high vacuum (0.01 mmHg) and the residue was extracted into ether and filtered through Celite. After removal of the volatiles, the major product was purified by flash chromatography on silica gel using a 1 : 1 : 4 mixture of ether : methylene chloride : hexanes as eluent to give 26.0 mg (22% yield) of **65** as a red solid. Spectral data for **65**: ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H), 2.73 (s, 1H), 3.95 (s, 1H), 4.3–4.8 (br s, 3H), 6.96 (br s, 2H), 7.57 (br s, 1H), 7.89 (br s, 1H); IR ($CHCl_3$) ν_{max}/cm^{-1} 3412br w, 3269w, 1954s, 1672m, 1610w, 1595w, 1572w, 1358m, 1323w, 1056w, 988w, 976w; mass spectrum *m*/*z* (% rel. intensity) 408 M$^+$ (16), 294 (11), 281 (8), 269 (7), 243 (6), 231 (11), 199 (9), 181 (15), 169 (12), 149 (14), 131 (22), 119 (25), 100 (8), 84 (39).

The Diels–Alder reaction of the dienyl chromium carbene complex 16b with dimethyl acetylenedicarboxylate to give the carbene complex 66

The reaction of 0.103 g (0.30 mmol) of complex **16b** with 2 mL (2.31 g, 16.27 mmol) of distilled dimethyl acetylenedicarboxylate was carried out as described above for the reaction of this complex with benzoquinone. The reaction was complete in 12 h at 25 °C. The entire reaction mixture was loaded directly on a silica gel column and eluted with a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes. Collection of the prominent bright red band gave 83 mg (63% yield) of aromatized cycloadduct **66**. Spectral data for **66**: ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 4.2–4.6 (br s, 3H), 7.24 (s, 1H), 7.50 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.66 (q, J_{CH} = 128.9 Hz), 52.77 (q, J_{CH} = 147.7 Hz), 65.8–68.2 (m), 121.81 (d, J_{CH} = 153.7 Hz), 129.20 (s), 130.39, 130.86, 131.34 (d, J_{CH} = 162.9 Hz), 131.69 (s), 166.88 (s), 167.67 (s), 215.34 (s), 223.63 (s), 354.90 (s); mass spectrum *m*/*z* (% rel. intensity) 442 M$^+$ (7), 414 (9), 386 (5), 358 (3), 330 (50), 302 (100), 287 (3), 259 (26), 235 (32), 214 (31), 203 (82), 171 (8), 143 (10), 108 (7), 89 (8), 80 (16). Anal. calcd. for $C_{18}H_{14}O_{10}Cr$: C, 48.88; H, 3.19. Found: C, 49.30; H, 3.29.

The preparation of 1-methoxy-3-methyl-2-(1-deutero-1-ethoxymethylene)but-3-en-1-ylidene(pentacarbonyl)tungsten(0) 67

A sample of 0.536 g (1.32 mmol) of complex **18**[4a] and 2.0 mL (excess) of 1-deutero-1-ethoxyethene were combined and reacted according to the general procedure. After 24 hours, all of the starting material had been consumed and there appeared to be two major red compounds by TLC which were assumed to be **67** and its ring-closed isomer. After a total of 48 hours, there appeared only one major component by TLC. The volatiles were removed under vacuum (0.01 mmHg) and the residue was chromatographed on silica gel using a 1 : 1 : 20 mixture of ether : methylene chloride : hexanes to give 0.326 g (52%) of a red solid which was identified as **67**: ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3H, J = 7.0 Hz), 2.0 (s, 3H), 3.92 (q, 2H, J = 7.0 Hz), 4.25 (br s, 3H), 4.38 (s, 1H), 4.88 (s, 1H). This spectrum is similar to that taken of the fully protiated complex **16c** except that the adsorption at δ = 5.90 is greatly diminished. Integration of this adsorption indicates that dienyl complex **67** is 85% deuterated at the 1-position.

The Diels–Alder reaction of deuterated dienyl tungsten carbene complex 67 with propynal to give 69

A mixture of 0.103 g (0.215 mmol) of complex **67** and 0.266 g (4.92 mmol) of propynal was deoxygenated according to the general procedure. After stirring for 23 hours at room temperature under an argon atmosphere very little starting complex could be detected by TLC and the reaction was worked-up at this time in an effort to prevent side reactions from occurring. The volatiles were removed under vacuum (0.01 mmHg) and the residue was chromatographed on silica gel using a 1 : 1 : 20 mixture of ether : methylene chloride : hexanes. Four colored bands were isolated of which the major component was identified as the aryl carbene complex **69** (67.4 mg, 65%). The coupling constant of the aryl protons was found to be 7.9 Hz and thus the regiochemistry of the cycloaddition must be that indicated in structure **69**: Spectral data for **69**: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 4.55–4.9 (br s, 3H), 7.32 (d, 1H, J = 7.8 Hz), 7.68

(d, 1H, J = 7.8 Hz), 9.95 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.32 (q, J_{CH} = 125.8 Hz), 68.74 (s), 122–125 (m), 129.13 (d, J_{CH} = 162.0 Hz), 131.49 (d, J_{CH} = 160.5 Hz), 133.67 (d, J^2_{CH} = 24.58 Hz), 134.47 (s), 191.10 (d, J_{CH} = 175.0 Hz), 196.41 (t, J_{CW} = 62.2 Hz), 203.60 (s), 329.52 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2074m, 1948s, 1699w; mass spectrum m/z (% rel. intensity) 489 M^+ (35, ^{184}W), 461 (52, ^{184}W), 433 (45, ^{184}W), 405 (58, ^{184}W), 377 (25, ^{184}W), 362 (25), 349 (58, ^{184}W), 317 (50), 304 (85), 274 (55), 249 (30), 151 (35), 131 (38), 116 (45), 69 (100); m/z calcd. for $C_{15}H_9DO_7{}^{186}W$ 489.0031, measured 489.0052.

Cyclohexadienone annulation of the chromium carbene complex 4p with trimethylsilylacetylene

A mixture of 0.129 g (0.359 mmol) of complex **4p** and 100 μL of TMS acetylene in 1.8 mL THF was deoxygenated by the freeze–thaw method as described in the general procedure. The flask was sealed at 25 °C under 1 atm of argon and heated to 55 °C. After 24 hours at 55 °C, a trace amount of starting complex could be detected by TLC. Heating was resumed for an additional 6 hours whereupon the reaction was judged complete. The volatiles were removed under vacuum (0.01 mmHg) and the residue was taken up in 30 mL of hexanes. The solution was allowed to oxidize in air overnight. At this time the solution had become green and a precipitate had formed. Following filtration through Celite and removal of the volatiles on the rotary evaporator, a crude yellow oil was obtained. Analysis of this material indicated one compound by TLC and two compounds by ^{1}H NMR. The crude mixture was chromatographed on silica gel using a 1 : 1 : 10 mixture of ether : methylene chloride : hexanes as the eluent to give 39.2 mg (37%) of a yellow oil which was identified as a 2.2/1.0 mixture of diastereomers of the dienone **70**. Spectral data for **70**: ^{1}H NMR ($CDCl_3$) major isomer, δ 0.15 (s, 9H), 1.0–1.1 (m, 1H), 1.33 (s, 3H), 1.38–1.45 (m, 1H), 1.76–1.92 (m, 1H), 2.08–2.18 (m, 1H), 2.38–2.45 (m, 1H), 3.44–3.5 (m, 1H), 3.68–3.75 (m, 1H), 3.81 (s, 3H), 5.09 (d, 1H, J = 7.2 Hz), 6.84 (s, 1H); minor isomer, δ 0.144 (s, 9H), 0.78–0.90 (m, 1H), 1.38–1.45 (m, 1H), 1.46–1.52 (m, 1H), 1.55 (s, 3H), 1.85–2.02 (m, 1H), 2.38–2.45 (m, 1H), 3.25–3.32 (m, 1H), 3.79 (s, 3H), 3.86–3.92 (m, 1H), 4.74 (d, 1H, J = 5.3 Hz), 6.73 (s, 1H); ^{13}C NMR ($CDCl_3$) major isomer, δ −1.49 (q, J_{CH} = 118.7 Hz), 22.61 (t, J_{CH} = 129.1 Hz), 23.45 (q, J_{CH} = 127.4 Hz), 24.11 (t, J_{CH} = 130.4 Hz), 37.91 (d, J_{CH} = 141.8 Hz), 50.47 (s), 58.51 (q, J_{CH} = 144.2 Hz), 63.34 (t, J_{CH} = 146.3 Hz), 71.83 (d, J_{CH} = 157.2 Hz), 125.58 (s), 140.01 (s), 144.7 (s), 148.30 (m), 209.81 (s); minor isomer, δ −1.62 (q, J_{CH} = 119.9 Hz), 18.36 (q, J_{CH} = 130.5 Hz), 19.45 (t, J_{CH} = 125.4 Hz), 22.61 (t, J_{CH} = 125.7 Hz), 33.74 (d, J_{CH} = 135.0 Hz), 55.39 (s), 57.78 (q, J_{CH} = 144.4 Hz), 64.28 (t, J_{CH} = 144.2 Hz), 74.13 (d, J_{CH} = 152.6 Hz), 119.08 (s), 142.23 (s), 144.56 (s), 146.50 (m), 212.80 (s); IR (CH_2Cl_2) ν_{max}/cm^{-1} 2928–2860m, 1754w, 1655s, 1548w, 1466w, 1387w, 1361w, 1342m, 1127m, 1045m, 844s. Anal. calcd. for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27. Found: C, 66.00; H, 8.48.

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