Pergamon

Tetrahedron 56 (2000) 4951–4965

TETRAHEDRON

Asymmetric Diels–Alder Reactions with Chiral Acetylenic Carbene Complexes as Dienophiles

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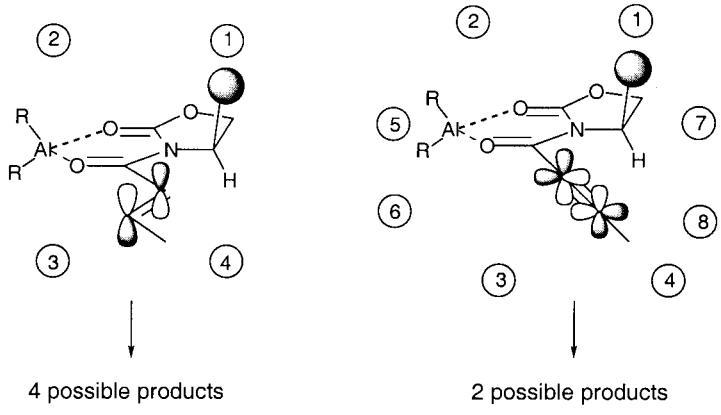
Received 6 January 2000; accepted 16 February 2000

Abstract—A new synthetic method is developed for the asymmetric Diels–Alder reactions of acetylenic dienophiles. Acetylenic Fischer carbene complexes with chiral pyrrolidines as the heteroatom stabilizing substituent were anticipated to block three of the four possible approaches of a diene and lead to selective asymmetric cycloadditions. A series of complexes of the type $(CO)_5M{=}C((C_4H_7N)CR_2OMe)$-$C{\equiv}CH$ (M=Cr, W; R=H, Me, Ph) were prepared by aminolysis of the corresponding methoxy complexes that have the terminal acetylene protected as a silane. Michael addition is completely suppressed if the alkyne is protected as a triisopropylsilyl group and after aminolylsis by 1,2-addition of a pyrrolidine the terminal alkynyl carbene complexes can be obtained predominately as *E*-isomers upon protodesilylation. The cycloadditions of the *E*-isomers (but not *Z*-isomers) of these complexes occur with significant asymmetric induction with 2-triisopropylsiloxy-1,3-pentadiene (66–73% de) but not with cyclopentadiene and α-triisopropylsiloxyvinyl cyclohexene. A model is presented to account for the observed stereoselectivities. © 2000 Published by Elsevier Science Ltd.

Introduction

Asymmetric Diels–Alder reactions with olefinic dienophiles have been investigated extensively and many excellent systems have been developed for both stoichiometric and catalytic processes.[1] However, reports of asymmetric Diels–Alder reactions with acetylenic dienophiles are rare.[2] The asymmetric induction for most Diels–Alder reactions with olefinic dienophiles is achieved by sterically blocking one side (approaches 1 or 2 vs. 3 or 4, Scheme 1) of the dienophile and electronically favoring either an *endo* or *exo* approach (2 or 3 vs. 1 or 4, Scheme 1). All four possible approaches (excluding the different approaches giving rise to regioisomers) lead to four different products. For reactions with acetylenic dienophiles, the picture is very different. Due to the presence of two orthogonal π-systems in the acetylenic dienophile, it has been suggested that both π-bonds in the acetylene may be reacting.[2a] In addition, no secondary π-orbital overlap to the carbonyl carbon is possible between the diene and dienophile, thus removing



Scheme 1.

Keywords: chiral fischer carbene complex; asymmetric Diels–Alder reaction; chromium; tungsten; acetylenic dienophile.
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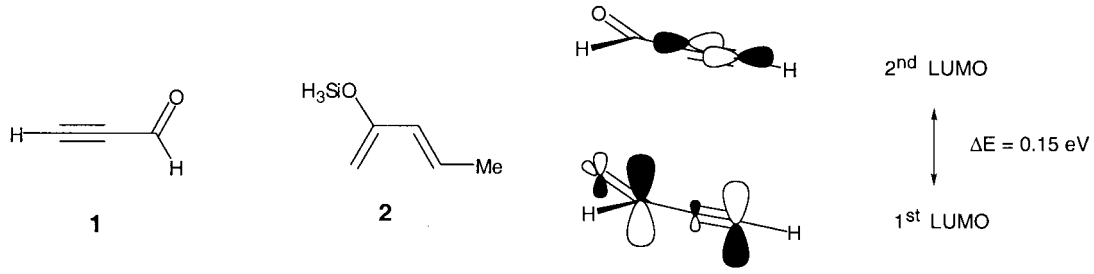
PII: S0040-4020(00)00209-X



Scheme 2.

a valuable control element for stereoselection.[3] There are eight possible directions for the diene to approach the dienophile (excluding the different approaches giving rise to regioisomers), which lead to only two different products (approaches 1, 3, 5 and 8 give one product, approaches 2, 4, 6 and 7 give the other, Scheme 1).

Design

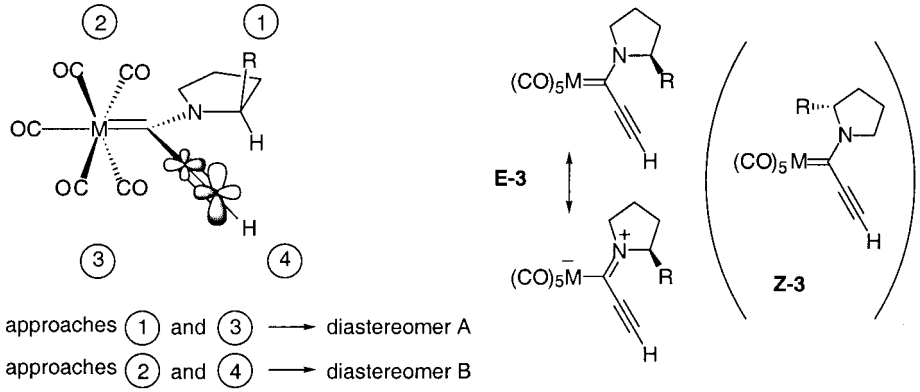
To better understand the reactivity of the two π-systems in an acetylenic dienophile, the molecular orbitals of propynal **1** and diene **2** have been calculated as model compounds with the CAChe program (Scheme 2). As one might have expected, the results suggest that the π-system in conjugation with the carbonyl group is more reactive. This implies that four of the above mentioned approaches are disfavored (5, 6, 7 and 8, Scheme 1).

Encouraged by this result, we anticipated that chiral alkynyl(amino)carbene complexes of type ***E*-3** (Scheme 3) could serve as useful acetylenic dienophiles in asymmetric Diels–Alder reactions. This expectation is based on several facts as follows: (1) terminal alkynyl(amino)carbene complexes have been made in our laboratory and found to be reactive enough to serve as dienophiles in Diels–Alder reactions,[4] (2) chiral aminocarbene complexes had been employed in a number of reactions with good asymmetric inductions,[5] (3) it has been shown that the metal pentacarbonyl fragment of Fischer carbene complexes is an effective substitute for the carbonyl group of electron poor dienophiles in Diels–Alder reactions,[6] and (4) due to the strong resonance stabilization (>25 kcal mol^{-1})[7] in aminocarbene complexes, isomerization of *E*- and *Z*-rotamers of these complexes will not be expected even at elevated temperatures. We anticipated that the large size of the metal fragment may prevent the diene from approaching from two of the remaining four possible sides (approaches 2 and 3, Scheme 3). By tuning the size of the chiral amine moiety in ***E*-3** to block approach 1, we hoped to design a system that would undergo Diels–Alder reactions with high asymmetric induction.

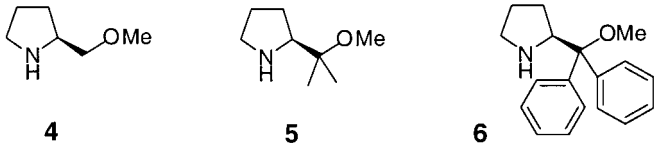
Results

Preparation and trial studies with non-chiral cyclic aminocarbene complexes

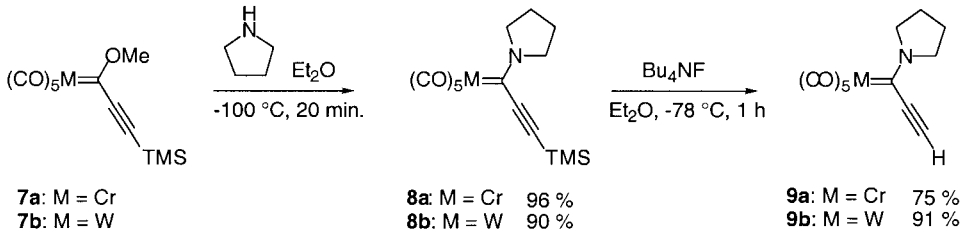
For the asymmetric Diels–Alder reactions on monosubstituted alkynyl aminocarbene complexes of type **3**, we planned to use pyrrolidines **4**, **5**, and **6** as chiral auxiliaries



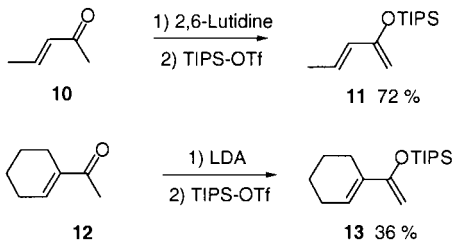
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

for the acetylenic aminocarbene complexes. Enantiomerically pure pyrrolidine **4** is commercially available, and **5** and **6** were easily synthesized in enantiomerically pure form following the route developed by Enders (Scheme 4).[8]

Prior to the preparation of chiral carbene complexes form amines **4**–**6**, we decided to prepare and evaluate the Diels–Alder activity of the achiral pyrrolidinyl complexes **9a** and **9b**. These could be prepared in excellent yield from the acetylenic methoxycarbene complexes **7**.[9] The aminolysis was performed at −100°C using one equivalent of pyrrolidine to generate the aminocarbene complexes. The protodesilylation was performed by a protocol that has previously been established (Scheme 5).[4,10]

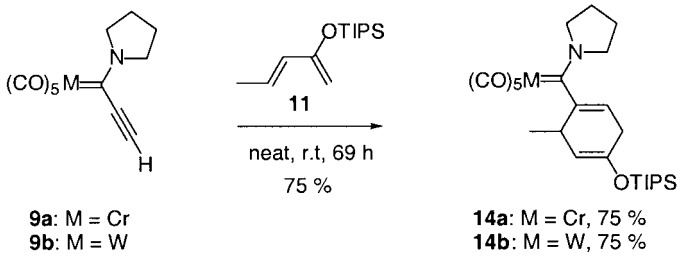
The dienes to be employed in the present study include cyclopentadiene and the acylic dienes **11** and **13**. These dienes were synthesized in analogy to the commonly used method (Scheme 6): an α,β-unsaturated ketone is deprotonated, and the enolate is subsequently trapped with triisopropylsilyl trifluoromethanesulfonate.[11]

We have previously shown that dimethylamino analogs of the unsubstituted alkynyl pyrrolidinyl **9a** and **9b** will undergo Diels–Alder reaction with cyclopentadiene at room temperature in 24 h to give good yields of the cycloadducts.[4] This is in contrast to previous attempts to conduct Diels–Alder reactions with substituted alkynyl aminocarbene complexes which failed to give the cycloadducts even at elevated temperature.[12,13] Thus, while it was expected that the tungsten and chromium complexes **9a** and **9b** should be competent dienophiles, we were nonetheless delighted to find that these complexes would both react with the diene **11** to give good yields (75%, in each case) of the desired Diels–Alder adducts **14a** and **14b** (Scheme 7).

Preparation of chiral complexes by aminolysis

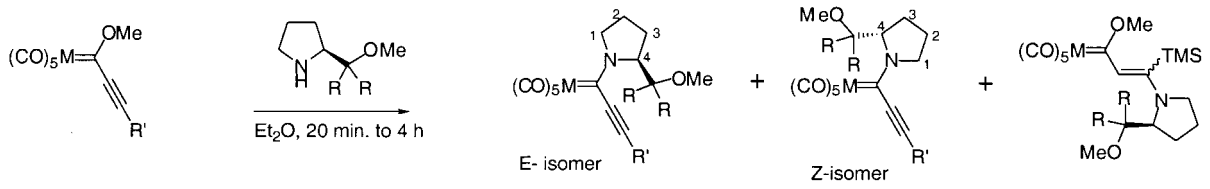
Following these trial studies, we examined the aminolysis of the trimethylsilyl and triisopropylsilylalkynyl complexes **7a**–**7d** with the with chiral amines **4**, **5** and **6**. It had been shown previously that the reaction of an amine with an alkynyl carbene complex has two competitive pathways: 1,2-addition and 1,4-addition.[14] It has been established, that the addition reaction can be directed to 1,2-addition product formation (avoiding the 1,4-addition pathway) by choosing lower reaction temperatures,[14] increasing the size of the substituent on the acetylene,[15,16] and decreasing the size of the incoming amine.[16]

The reaction is further complicated when non-C_2-symmetrical chiral amines are employed, because of the possible formation of two rotamers as products. Considering the design of our system, it is not only important to avoid 1,4-addition, but also crucial to have high selectivity for the correct rotamer of the 1,2-adduct. Reaction with the 'wrong' rotamer (as ***Z*-3**, Scheme 3) is expected to give low asymmetric induction, because the chiral moiety is on the side opposite to the acetylene group. Furthermore, it is expected that it will not be possible to thermally isomerize the 'wrong' rotamer and thus recycle it to the useful rotamer given the higher thermal barrier to rotation about the nitrogen–carbene carbon bond that has been reported for amino carbene complexes.[7] The distribution of the rotamers in the 1,2-addition is believed to be determined kinetically[17]. However, it does not appear as if there is a generally reliable method for the prediction of the kinetically favored product. If the ratio was determined only by steric factors,



Scheme 7.

Table 1. Aminolysis of carbene complexes **7a–7d**



M	R^1	Carbene complex	R	Amine	Temp (°C)	1,2-adduct	% Yield 1,2-adduct	*E*:*Z*	1,4-adduct	% Yield 1,4-adduct	Total yield
Cr	$SiMe_3$	**7a**	H	**4**	−100	**15**	94	16:1	**23**	–	94
		7a	Me	**5**	−78	**16**	15	*E* only	**24**	60	75
		7a	Me	**5**	−150	**16**	10	*E* only	**24**	64	74
	$Si(iPr)_3$	**7c**	Me	**5**	25	**17**	81	4:1	**25**	–	81
		7c	Me	**5**	−78	**17**	98	48:1	**25**	–	98
		7c	Ph	**6**	−78 to 125	**18**	–	–	**26**	–	–
W	$SiMe_3$	**7b**	H	**4**	−100	**19**	94	2:1	**27**	–	94
		7b	Me	**5**	−78	**20**	58	14:1	**28**	24	82
		7b	Me	**5**	−100	**20**	88	43:1	**28**	1	89
		7b	Ph	**6**	−78 to 25	**21**	–	–	**29**	17	17
	$Si(iPr)_3$	**7d**	Me	**5**	−78	**22**	93	7:1	**30**	–	93

we would expect that the predominate product from reaction with a chiral, non C_2-symmetrical amine would be the one where the bulky substituent is directed away from the metal pentacarbonyl moiety, thus leading to the desired *E*-isomers of **3** (Scheme 3).

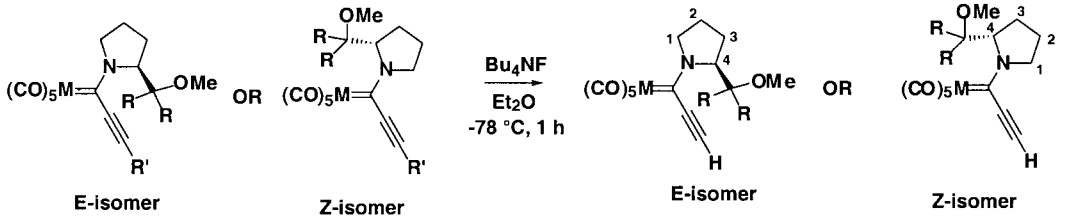
The aminolysis reactions of complexes **7** with the chiral pyrrolidine derivatives **4**, **5** and **6** were investigated at different temperatures. As indicated in Table 1, we were able to synthesize several of desired 1,2-adducts with high selectivities and high yields. All the products formed in each reaction were separable, making it possible to continue the work with pure individual *E* and *Z*-rotamers. The assignment of the *E* and *Z*-diastereomers was done by comparison of their ^1H NMR and ^{13}C NMR spectra according to the method of Fischer[13,18,19] and confirmed in one case by X-ray diffraction after a Diels–Alder reaction (vide infra). The proton and carbon atoms located in proximity to the metal pentacarbonyl are observed to appear at lower field than the those more distant from the metal.[13,18,19] We were able to observe considerable effects of reaction temperature, the size of the silyl substituent, and the size of the amine on the regio- and stereoselectivity of the aminolysis reactions.

Pyrrolidine **6** is too large to be reactive in a 1,2-addition (Table 1, entries 6 and 10), and only small amounts of a product, tentatively assigned as Michael adduct **29** was obtained. While the smallest pyrrolidine **4** does not lead to Michael adducts (Table 1, entries 1 and 7), the medium sized pyrrolidine **5** does. In the case of the trimethylsilylacetylene chromium complex **7a**, Michael addition was the major reaction pathway and occurred even at low temperature (Table 1, entries 2 and 3). However, when the triisopropyl substituted ethynyl complex **7c** was used, Michael addition was disfavored even at room temperature (Table 1, entries 4 and 5). In addition, tungsten complexes give much less Michael addition than do chromium complexes (entries 2 vs. 8).

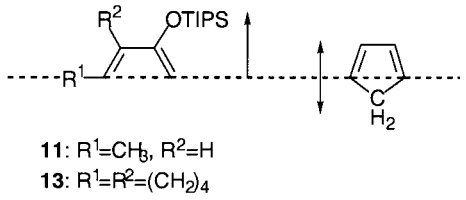
Proto-desilylation to give chiral mono-substituted alkynyl aminocarbene complexes

The pure *E* and *Z* isomers of chiral amino carbene complexes were subjected to proto-desilylation (Table 2).[4,10] No rotamer inter-conversion was detected by ^1H NMR spectroscopy in the terminal acetylenic carbene complexes (Table 2). As discussed above, the geometry of

Table 2. Proto-desilylation of alkynyl carbene complexes



Silyl alkyne complex *E*-isomer	Silyl alkyne complex *Z*-isomer	M	R′	R	Terminal alkyne complex *E*-isomer	Terminal alkyne complex *Z*-isomer	% Yield
***E*-15**		Cr	$SiMe_3$	H	***E*-31**		74
***E*-17**		Cr	$Si(iPr)_3$	Me	***E*-32**		84
***E*-19**		W	$SiMe_3$	H	***E*-33**		91
***E*-20**		W	$SiMe_3$	Me	***E*-34**		74
***E*-22**		W	$Si(iPr)_3$	Me	***E*-34**		74
	***Z*-19**	W	$SiMe_3$	H		***Z*-33**	84
	***Z*-22**	W	$Si(iPr)_3$	Me		***Z*-34**	40



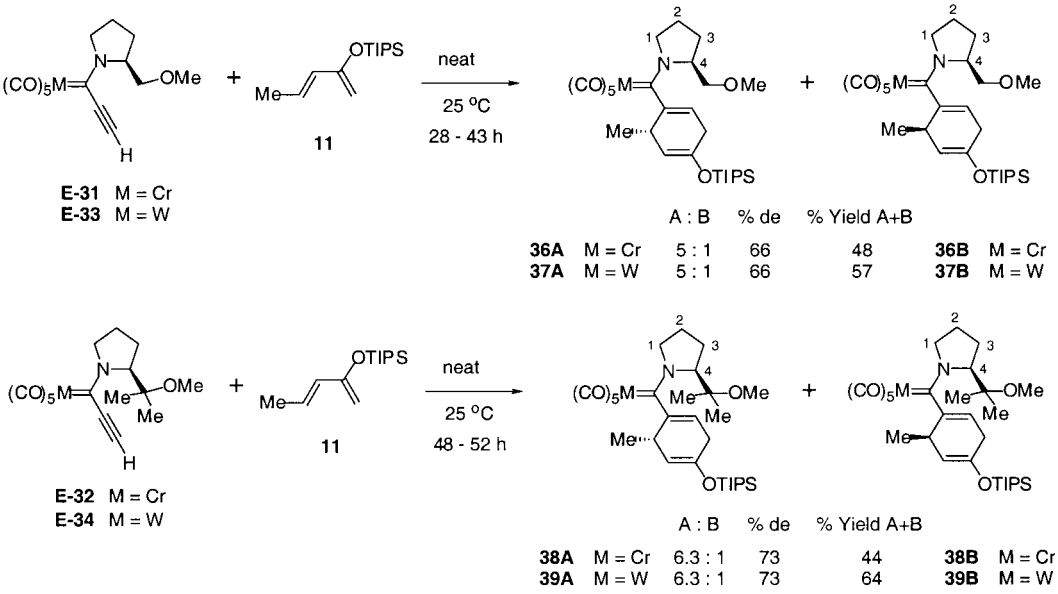
Scheme 8.

the rotamers was assigned by comparing the ^{1}H NMR and ^{13}C NMR spectra of *E*- and *Z*- complexes.

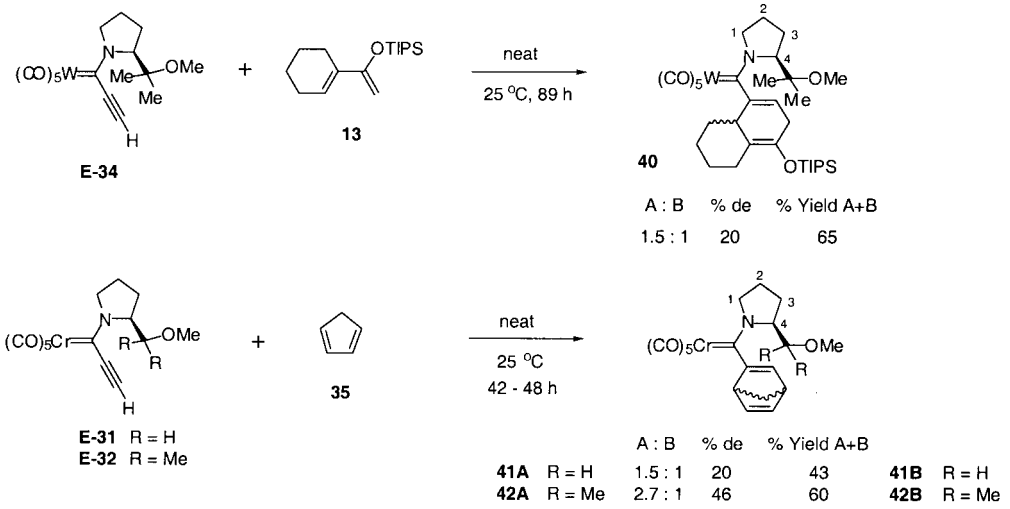
Asymmetric Diels–Alder reactions

The Diels–Alder reaction of complexes ***E*-31**, ***E*-33**, ***E*-32** and ***E*-34** with dienes **11**, **13** and cyclopentadiene were studied. We anticipated that the reactions with dienes **11** and **13** would give higher induction than those with cyclopentadiene because, as depicted in Scheme 8, the acyclic dienes **11** and **13** have a larger spatial difference between the two sides of the axis 'connecting' the two terminal sp^2 carbon atoms of the diene than does cyclopentadiene. In addition, dienes **11** and **13** are substituted in the 2 and/or 3 positions and thus should extend further into regions 1 and 4 in Scheme 3 and also should have more serious negative interactions in regions 2 and 3. Therefore, the size differentiation in the approach of an acyclic diene should be much more unambiguous and result in a higher selection between approaches 3, 4 vs. 1, 2 (Scheme 3).

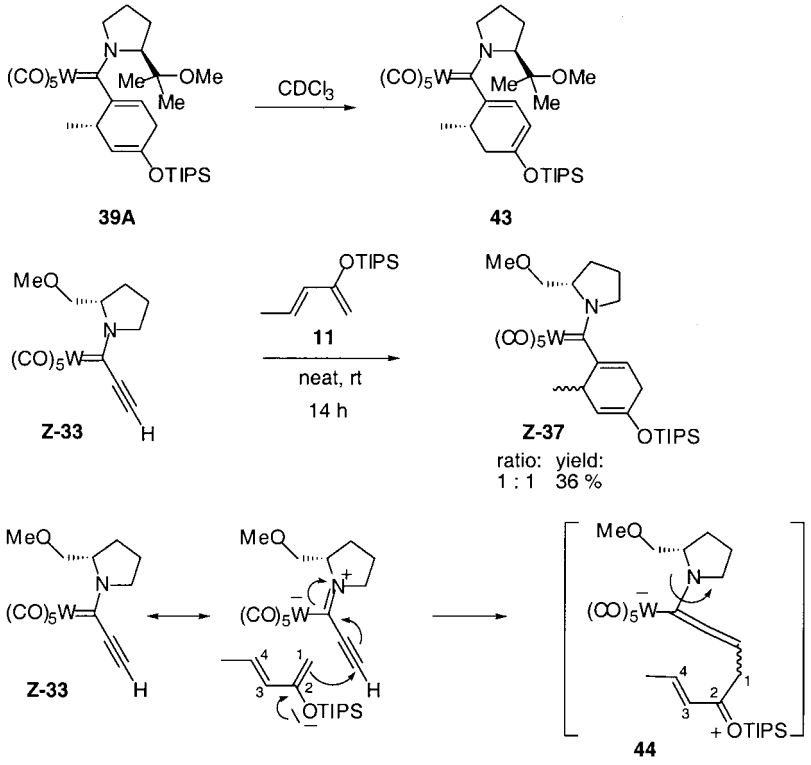
The Diels–Alder reactions were carried out in neat diene and took 2 to 4 days at room temperature. The results of the reactions of complexes ***E*-31**–***E*-34** with dienes **11**, **13** and **35** are summarized in Schemes 9 and 10. In the cases of cycloadducts **38**–**40**, the major stereoisomer (**A**) could be separated from the minor stereoisomer (**B**). In the other cases, a mixture of stereoisomers was isolated. No



Scheme 9.



Scheme 10.



Scheme 11.

inter-conversion of the rotamers was observed in the conversion of starting carbene complex to the product carbene complex in the cycloaddition.

The assignment of the stereochemistry of the products was complicated in some cases because the major isomers of the Diels–Alder reaction underwent double bond isomerization to complexes of type **43** in $CDCl_3$ in the NMR tube. We followed the double bond isomerization of complex **39A** in the NMR tube and assigned structure **43** by ^{1}H NMR, COSEY, and ^{13}C NMR spectra (Scheme 11). Interestingly, the corresponding minor stereoisomer **39B** was not observed to undergo double bond isomerization.

The relative stereochemistry of the chiral center formed in the Diels–Alder reaction was assigned by X-ray crystallographic analysis of the major diastereomer **38A** (Fig. 1). The stereochemistry observed is consistent with what we expected from our design, namely the approach of the diene through quadrant 4 (Scheme 3). Additionally, the X-ray structure determination confirmed our NMR assignments about the nitrogen-carbene carbon bond: the bulky substituent of the pyrrolidine moiety points away from the metal fragment.

Control experiments

Two control experiments were performed. It was shown that the product ratio did not reflect a thermodynamic product distribution. A sample of the Diels–Alder product enriched with the minor isomer (**38A/38B**=1.5:1) was subjected to the same reaction conditions (Scheme 11). After stirring 4 days with excess diene **11** and 25°C it was found that the products had not equilibrated to reflect the ratio in the actual Diels–Alder reaction (**38A/38B**=6.3:1), but remained the same (**38A/38B**=1.5:1). This indicates that the Diels–Alder reaction is not reversible under these reaction conditions.

In the second control experiment (Scheme 11), we tested our assumption that the *Z*-rotamers of the unsubstituted alkynyl carbene complexes, which have the chiral substituent pointing towards the metal fragment, would not be effective in asymmetric induction. Rotamer ***Z*-33** was subjected to the Diels–Alder reaction with diene **11** and indeed, the ratio of diastereomers in the product ***Z*-37** was determined to be 1:1.

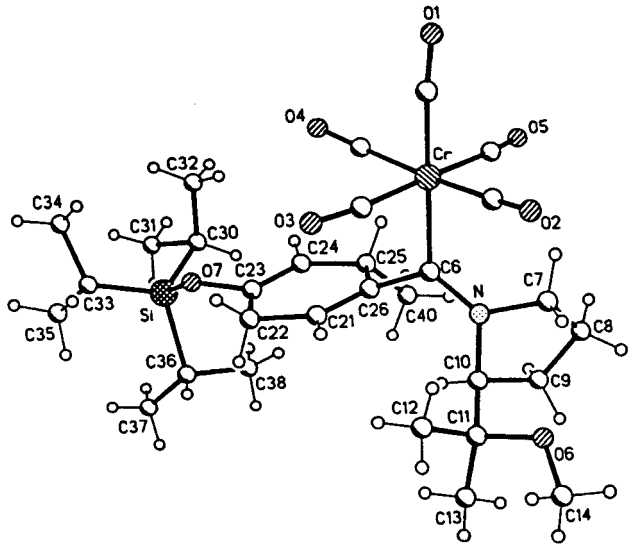


Figure 1. ORTEP picture of major isomer **38A**.

This is a clear indication that the *Z*-isomers of these complexes are not effective for chiral Diels–Alder reactions as was predicted by the model in Scheme 3.

Discussion

The results described above reveal that the Diels–Alder reactions of complexes ***E*-31**–***E*-34** with dienes **11**, **13** and cyclopentadiene proceed to give asymmetric inductions roughly in accord with the model presented in Scheme 3. The optimal complex in terms of yield and induction in the tungsten dimethylmethoxylmethylpyrrolidine complex ***E*-34**. Its reaction with diene **11** gives the cycloadduct **39** in 73% yield and 76% diastereoselectivity. Furthermore, the stereoisomeric products **39A** and **39B** are separable, and therefore the cycloadduct **39A** is available in enantiomerically pure form.

The influence of the metal was expected to be twofold. Due to the greater stability of tungsten unsubstituted alkynyl aminocarbene complexes, it was expected that their reactions would give higher yields than their chromium analogs. This was observed for the reactions of complexes ***E*-31**–***E*-34** with diene **11** (Scheme 9). Furthermore, due to the larger size of tungsten and the resulting longer bond length to the carbene carbon, it was expected that the tungsten carbene complexes would be sterically less congested. Therefore, the stereoselectivity in their reactions was expected to be lower than in the reactions of their chromium counterparts. However, it was found that the carbene complexes from both metals gave the same diastereomeric ratios. It is not clear why this expectation was not realized, but in other Diels–Alder reactions where differences in stereoselectivity between the two metals has been seen the differences have been small.[6]

It has been shown above that the outcome of both the regio- and the stereoselectivity in the Diels–Alder reactions were predicted correctly from the model in Scheme 3. The direction of induction in these reactions was determined via the X-ray structure determination of major isomer of **38**. The structure determination reveals that the major isomer has the stereochemistry indicated in **38A** and the formation of this isomer as the major product is consistent with a favored approach of the diene through quadrant 4 (Scheme 3 and Fig. 2, view A). Another factor anticipated to affect the stereoselectivity is the size of the chiral auxiliary. In all

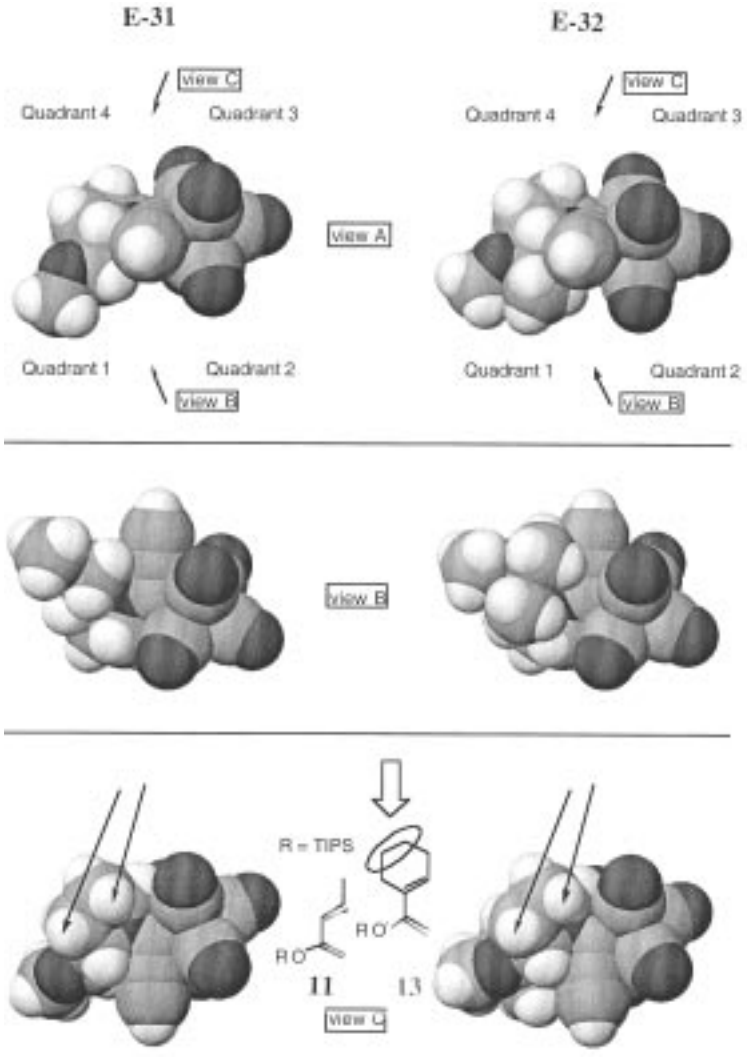


Figure 2. Space filling models of minimized structures of complexes ***E*-31** and ***E*-32**.

cases in which the chiral aminocarbene complex is derived from the more bulky pyrrolidine **5** (complexes ***E*-32** and ***E*-34**, Scheme 9), the diastereoselectivities obtained are higher than in the cases of aminocarbene complexes derived from pyrrolidine **4** (complexes ***E*-31** and ***E*-33**, Scheme 9). This observation is in good agreement with the design outlined in Scheme 3. The model indicates that approach of the diene through quadrant 1 should be more impeded in the case of the dimethyl substituted complex ***E*-32** than in the case of the less bulky complex ***E*-31** (Fig. 2, view B). The data suggest that while the phenyl group was too large to incorporate into the pyrrolidine in the carbene complex, the induction does increase with the size of the substituent R (Table 1). Perhaps other groups larger than methyl (or methoxy) would lead to increase inductions over those of complex ***E*-32** and ***E*-34** in Scheme 9.

The topology of the diene is also important in determining the stereoselectivity. The Diels–Alder reactions of cyclopentadiene and diene **13** was observed to give quite low asymmetric induction (Scheme 10). The result of the reactions with cyclopentadiene can be explained by the spatial properties of the diene illustrated in Scheme 8. The reason for the low induction in the reaction with diene **13** relative to diene **11** is less obvious. However considering the space filling models of quadrants 3 and 4 (Fig. 2, view A and C), it becomes apparent that the methylene groups of the pyrrolidine moiety are spatially demanding. The pyrrolidine methylenes would be expected to have little effect on the approach of diene **11**. Its approach to the acetylenic moiety in the dienophile is most favored through quadrant 4 as the methyl substituent on the diene can be accommodated between the pyrrolidine (marked in Fig. 2, view C with →) and the metal carbonyl moiety while the diene moiety containing the large triisopropylsilyoxy group in the 2-position would not be expected to interact with the pyrrolidine ring. However, the situation is quite different for diene **13**. The model indicates that the interaction between the methylene groups of the pyrrolidine moiety in the carbene complex (marked in Fig. 2, view C with →) and the methylene groups of the cyclohexyl moiety of diene **13** (marked in Fig. 2, view C with ⇒) should be significant in the approach from quadrant 4. This unfavorable situation makes an approach of diene **13** to the carbene complex from quadrant 3 more likely.

Our design is based on the assumption that the Diels–Alder reaction proceeds via a concerted mechanism rather than a stepwise mechanism involving formal Michael addition followed by intra-molecular trapping. No experiments to probe this point have been done to date. The only comment that can be made at this time is that the Diels–Alder reaction of complex ***Z*-33** with diene **11** (Scheme 11) proceeds to give the product ***Z*-37** without loss of stereochemistry about the nitrogen-carbene carbon bond. It seems plausible that in a stepwise mechanism, once intermediate **44** is formed, the amine would rotate to release steric compression (Scheme 11). However, this argument is only valid if the rotation occurs faster than the intra-molecular trapping step. In order to answer this question more conclusively, further experiments are planned to address this issue.

The results described in this work show that chiral pyrrolidinyl carbene complexes can be used as chiral synthons for the Diels–Alder reactions of acetylenic dienophiles. The Diels–Alder products could serve as building blocks in organic synthesis since a variety of methods are available to oxidatively cleave the metal fragment[20] to produce the corresponding aldehydes and amides. In a recent report, it has been demonstrated that aminocarbene complexes can be reduced to amines in a procedure employing triflic acid and $NaBH_4$.[21] In addition, since the Diels–Alder products furnish alkenyl aminocarbene complexes, it was recognized that their transformation in a benzannulation reaction would lead to synthetically interesting products.

Experimental

General information

Unless otherwise indicated all common reagents and solvents were used as obtained from commercial suppliers without further purification. Tetrahydrofuran (THF) and diethylether were distilled from sodium/benzophenone; methylene chloride was distilled from calcium hydride prior to use. All reactions were carried out under either an argon or nitrogen atmosphere. Flash chromatography was carried out on Merck silica gel grade 60, 230–400 mesh, 60 Å. Elemental analyses were performed by Galbraith Laboratories in Knoxville, Tennessee.

Triisopropylethynyl(methoxy)carbene complexes 7c and 7d. These complexes were prepared following a procedure reported for **7a**.[9] A solution of triisopropylsilyl acetylene (2.24 mL, 10 mmol) in 80 mL diethylether was cooled to −78°C and *n*-butyllithium in hexane (6.24 mL, 10 mmol, 1.6 M) was added. After stirring for 15 min at −78°C, the cold bath was removed and the solution was allowed to warm for 15 min. This reaction mixture was transferred via canula into a slurry of chromium hexacarbonyl (2.2 g, 10 mmol) in 100 mL THF. After stirring for 1 h, the mixture was concentrated and briefly dried under high vacuum. The remaining oil was dissolved in 60 mL methylene chloride and cooled to 0°C. Methyl trifluoromethanesulfonate (1.36 mL, 12 mmol) was added to the solution. It was quenched after 15 min with sat. $NaHCO_3$ and washed with water and brine. After drying with $MgSO_4$, the solution was filtered and concentrated. The crude product was purified by column chromatography (pentane). Carbene complex **7c** (2.54 g, 6.1 mmol) was isolated as a dark red oil in 45% yield. Spectral data for **7c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (s, 3H), 1.27–1.19 (m, 3H), 1.15 (d, 18H, J=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 318.0, 225.6, 216.0, 140.0, 106.5, 65.9, 18.5, 11.2; IR (thin film) 2947–2868m, 2064s, 1997m, 1944s, 1463–1436w, 1224m, 1153m, 1063s, 882w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 416 (M^+, 17), 360 (M^+-2CO, 13), 332 (M^+-3CO, 7), 304 (M^+-4CO, 73), 276 (M^+-5CO, 94), 234 (67), 204 (12), 192 (42), 177 (5), 162 (13), 150 (25), 135 (15), 120 (16), 105 (17), 93 (12), 80 (14), 52 (100). Anal. Calcd for $C_{18}H_{24}O_6SiCr$: C, 51.91; H, 5.81. Found: C, 51.91; H, 5.86.

Carbene complex **7d** was obtained as a dark yellow–brown oily solid in 50% from $W(CO)_6$ following the above procedure. Spectral data for **7d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ

3.68 (s, 3H), 1.12 (s, 21H); ^{13}C NMR (75 MHz, C_6D_6) δ 197.5, 136.1, 106.4, 57.5, 18.8, 11.6 (C_{carb} and C_{trans}–CO were not detected, even with various delay times); IR (thin film) 2957–2866s, 2143m, 2071s, 2023m, 1992m, 1953s, 1463m, 1224m, 1169w, 1102m, 1070w, 996w, 883m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 548 (M^+, 3, ^{184}W), 492 (M^+-2CO, 2, ^{184}W), 464 (M^+-3CO, 4, ^{184}W), 448 (100), 418 (M^+-5CO, 3, ^{184}W), 279 (15), 145 (45), 117 (49), 103 (17), 89 (72), 75 (58), 55 (43).

2-(Triisopropyl)silyloxy-1,3-pentadiene 11. Commercially available 3-pentene-2-one (containing 30% 3-methyl-3-pentene-2-one, Aldrich) was purified by column chromatography (pentane:Et_2O=16:1) and concentrated on a rotary evaporator at 0°C. The ratio of pentane, Et_2O and 3-pentene-2-one was determined by ^{1}H NMR integration. This 3-pentene-2-one solution (27.9 mmol) and 2,6-lutidine (3.89 mL, 3.58 g, 33.5 mmol) were dissolved in 300 mL THF and cooled to 0°C. After addition of triisopropylsilyl triflouromethane sulfonate (6.6 mL, 7.52 g, 24.6 mmol), the solution was stirred for 30 min at 0°C and 30 min at 25°C. The reaction mixture was poured into a separation funnel containing sat. $NaHCO_3$ and pentane and then the oragnic layer washed with water and brine. After drying with $MgSO_4$ and filtration, the solution was concentrated. The crude product was filtered through a small column of NEt_3 treated silica gel and was washed with pentane. Concentration of the filtrate afforded **11** (4.26 g, 17.7 mmol) as a clear liquid. Spectral data for **11**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (dd, 1H, *J*=6.8, 15.0 Hz), 5.9 (dd, 1H, *J*=1.3, 15.3 Hz), 4.19 (s, 1H), 4.14 (s, 1H), 1.79 (d, 3H, *J*=6.7 Hz), 1.29–1.22 (m, 3H), 1.13 (d, 18H, *J*=7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 129.3, 126.2, 92.5, 18.1, 17.6, 12.9; IR (thin film) 2963–2868s, 1589m, 1465m, 1320s, 1027s, 959m, 883m cm^{-1}. Anal. calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.33; H, 11.93.

α-(Triisopropyl)silyloxyvinylcyclohexene 13. Diisopropylamine (0.77 mL, 505 mg, 4.94 mmol) was dissolved in 10 mL THF and cooled to −78°C. *n*-Butyllithium (3.15 mL, 1.6 M, 5.04 mmol) in hexane was added and after stirring for 10 min, acetylcyclohexene (0.578 mL, 558 mg, 4.5 mmol) was added dropwise over 3 min. This solution was stirred at −78°C for 10 min and triisopropylsilyl triflouromethanesulfonate (1.814 mL, 2.07 g, 6.75 mmol) was added quickly. After stirring for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 45 min. The solution was diluted with 20 mL pentane and washed with dilute $NaHCO_3$, water and brine. After drying with $MgSO_4$ and filtration, the solution was concentrated. The crude product was filtered through a small column of Et_3N treated silica gel and was washed with pentane. Concentration of the filtrate afforded **13** (2.99 g, 10.69 mmol) as a clear liquid in 36% yield. Spectral data for **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (s, 1H), 4.30 (s, 1H), 4.18 (s, 1H), 2.17–2.15 (m, 4H), 1.71–1.66 (m, 2H), 1.61–1.57 (m, 2H), 1.29–1.23 (m, 3H), 1.13 (d, 18H, *J*=7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 133.2, 125.1, 88.5, 25.5, 25.1, 22.8, 22.2, 18.1, 12.9; IR (thin film) 2964–2833s, 1590w, 1465w, 1288m, 1261m, 1089w, 1017m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 280 (M^+, 72), 237 (100), 195 (12), 167 (7), 131 (11), 115 (11), 103 (13), 87 (8), 75 (22), 59 (23). Anal. calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50. Found: C, 72.62; H, 11.73.

Trimethylsilylethynyl pyrrolidinecarbene metalpentacarbonyl complexes 8a and 8b. Methoxy carbene complex **7b**[9] (905 mg, 1.95 mmol) was dissolved in 20 mL diethyl ether and cooled to −100°C. Pyrrolidine (0.174 mL, 147.8 mg, 1.95 mmol) was added and the solution was stirred for 20 min at −100°C. The solution was poured into a separatory funnel containing water and was washed with water and brine. The aqueous phase was extracted with diethyl ether. The combined extract was dried with $MgSO_4$, filtered and concentrated. Purification by column chromatography (Et_2O/CH_2Cl_2/hexane; 1:1:10) afforded **8b** (883.8 mg, 1.76 mmol) as a yellow solid in 90% yield. Spectral data for **8b**: mp 78–80°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (t, 2H, *J*=6.3 Hz), 3.85 (t, 2H, *J*=6.2 Hz), 2.15 (m, 4H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 224.1, 204.1, 198.6 (J_{CW}=128 Hz), 131.1, 106.8, 59.9, 56.4, 25.4, −0.6; IR (thin film) 2973–2880w, 2062s, 1974 shoulder, 1939–1899s, 1493m, 1448m, 1251m, 1067m, 849m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 503 (M^+, ^{184}W), 475 (M^+-CO, 2, ^{184}W), 447 (M^+-2CO, 82, ^{184}W), 419 (M^+-3CO, 76, ^{184}W), 391 (M^+-4CO, 92, ^{184}W), 363 (M^+-5CO, 100, ^{184}W), 346 (24), 330 (33), 316 (30), 277 (32), 263 (28), 249 (13), 180 (12), 165 (3), 149 (2), 73 (2). Anal. calcd for $C_{15}H_{17}NO_5SiW$: C, 35.80; H, 3.40; N, 2.78. Found: C, 35.59; H, 3.52; N, 2.60.

Trimethylsilylacetylene pyrrolidine chromium carbene complex **8a** was made from **7a**[9] following this procedure in 96% yield. Spectral data for **8a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (t, 2H, *J*=6 Hz), 3.84 (t, 2H, *J*=6 Hz), 2.18–2.13 (m, 4H), 0.28 (s, 9H).

Ethynyl pyrrolidinecarbene metalpentacarbonyl complexes 9a and 9b. Carbene complex **8b** (200 mg, 0.398 mmol) was dissolved in 25 mL diethyl ether and cooled to −78°C. Tetrabutylammonium fluoride (0.400 mL, 1 M, 0.400 mmol) in THF was added and the solution was stirred for 1 h at −78°C. The reaction was quenched with water and washed with water and brine. After drying with $MgSO_4$ and filtration, the solution was concentrated. Purification with column chromatography (Et_2O/CH_2Cl_2/hexane, 1:1:10) afforded **9b** (156.9 mg, 0.364 mmol) as a yellow solid in 91% yield. Complex **9a** was made from **8a** following this procedure in 75% yield. Spectral data for **9b**: mp 77–79°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 1H), 4.02 (t, 2H, *J*=6 Hz), 3.87 (t, 2H, *J*=6 Hz), 2.18 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 224.4 (s), 203.9 (s), 198.4 (s), 110.0 (d, $^1J_{CH}$=254 Hz), 86.7 (d, $^2J_{>CH}$=47 Hz), 60.3 (t), 56.7 (t), 25.4 (t); IR (thin film) 3299w, 2981–2880w, 2070m, 1974shoulder, 1902s, 1498m, 1447m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 431 (M^+, 49, ^{184}W), 375 (M^+-2CO, 56, ^{184}W), 347 (M^+-3CO, 92, ^{184}W), 319 (M^+-4CO, 100, ^{184}W), 291 (M^+-5CO, 95, ^{184}W), 262 (42), 234 (29), 208 (14), 145 (13), 106 (8), 91 (11), 55 (7). Anal. calcd for $C_{12}H_9NO_5W$: C, 33.44; H, 2.10; N, 3.25; W, 42.65. Found: C, 34.22; H, 2.12; N, 3.02; W, 42.60.

Diels–Alder adducts 14a and 14b. Carbene complex **9b** (87.1 mg, 0.202 mmol) was dissolved in 0.5 mL diene **11**

and stirred for 69 h at 25°C. The reaction mixture was loaded directly onto to a silica gel column and eluted with a 1:1:10 mixture of ether, methylene chloride and hexane to afford **14b** (101.1 mg, 0.152 mmol) as a yellow solid in 75% yield. Diels–Alder adduct **14a** was obtained in 75% yield from **9a** following this procedure. Spectral data for **14b**: mp 100–103°C; ^{1}H NMR ($CDCl_3$) δ 4.93 (m, 1H), 4.47–4.44 (m, 1H), 3.99–3.92 (m, 1H), 3.64–3.55 (m, 1H), 3.47–3.37 (m, 1H), 2.92–2.77 (m, 3H), 2.68–2.56 (m, 1H), 1.31–0.87 (m, 25H of which at 1.15 (d, 21H, J=1.75 Hz)), 0.78 (d, 3H, J=7.17 Hz); ^{13}C NMR (C_6D_6, 75 MHz) δ 251.6, 203.6, 199.6, 153.7, 147.8, 110.0, 106.4, 61.7, 54.8, 34.8, 30.3, 25.0, 24.4, 20.6, 18.2, 13.0; IR (thin film) 2947–2867w, 2059m, 1967m, 1908s, 1687w, 1502w, 1452w, 1381w, 1210w, 1147w, 883w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 671 (M^+, 3, ^{184}W), 643 (M^+-CO, 9, ^{184}W), 615 (M^+-2CO, 7, ^{184}W), 585 (16, ^{184}W), 555 (M^+-4CO, 4, ^{184}W), 527 (M^+-5CO, 12, ^{184}W), 508 (2), 488 (4), 458 (4), 416 (2), 370 (1), 347 (47), 304 (6), 276 (100), 233 (17), 205 (7), 177 (9), 124 (16), 103 (14), 84 (33), 59 (37). Anal. calcd for $C_{26}H_{37}NO_6SiW$: C, 46.50; H, 5.55; N, 2.09; W, 27.38. Found: C, 46.44; H, 5.76; N, 1.61; W, 27.80.

Trimethylsilylethynyl (*S*)-methoxymethylpyrrolidine carbene complexes 15 and 19. The chromium carbene complex **7a**[9] (332.3 mg, 1 mmol) was dissolved in 10 mL diethyl ether and cooled to −100°C. (*S*)-Methoxymethylpyrrolidine **4** (0.160 mL, 149.3 mg, 1.3 mmol) was added. After stirring for 15 min, the solution was poured into a separatory funnel containing water and the organic layer was washed with water and brine. The aqueous phase was extracted with diethyl ether. The combined oragnic layer was dried with $MgSO_4$, filtered and concentrated. Purification by silica gel chromatography with a 1:1:10 mixture of ether, methylene chloride and hexanes as eluent afforded ***E*-15** (352.3 mg, 0.882 mmol) as a yellow solid in 88% yield and ***Z*-15** (21.7 mg, 0.054 mmol) as a yellow solid in 5% yield. Spectral data for ***E*-15**: mp. 62–63°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68–4.62 (m, 1H), 4.35–4.22 (m, 2H), 3.63–3.52 (m, 2H), 3.36 (s, 3H), 2.32–2.22 (m, 1H), 2.22–2.08 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 247.0 (s), 224.1 (s), 217.4 (s), 135.3 (s), 104.4 (s) 72.3 (t), 67.5 (d), 59.1 (q), 58.2 (t), 27.8 (t), 23.5 (t), −0.8 (q); IR (thin film) 2054m, 1979w, 1919s, 1448w, 846w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 415 (M^+, 7), 359 (M^+-2CO, 12), 331 (M^+-3CO, 13), 303 (M^+-4CO, 22), 275 (M^+-5CO, 100), 260 (8), 245 (6), 230 (3), 206 (4), 194 (9), 180 (23), 147 (22), 133 (7), 97 (10), 83 (12), 73 (18), 52 (11). Anal. calcd for $C_{17}H_{21}NO_6SiCr$: C, 49.15; H, 5.09; N, 3.37. Found: C, 48.95; H, 5.19; N, 3.09. Spectral data for ***Z*-15**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67–4.70 (m, 1H), 4.17–4.07 (m, 1H), 3.86–3.79 (m, 1H), 3.67–3.63 (m, 2H), 3.39 (s, 3H), 2.32–2.05 (m, 4H), 0.29 (s, 9H).

The tungsten carbene complex **19** was prepared in a similar manner from complex **7b**.[9] Upon separation of isomers ***E*-19** was obtained as a yellow solid in 60% yield and ***Z*-19** as a yellow oil in 34% yield. Spectral data for ***E*-19**: mp: 73–75°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.57–4.53 (m, 1H), 4.02–3.98 (m, 2H), 3.58–3.520 (m, 2H), 3.37 (s, 3H), 2.30–2.09 (m, 4H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.0 (s), 204.2 (s), 198.2 (s, J_{CW}=128 Hz), 131.9 (s), 106.3 (s), 76.6 (t), 72.0 (d), 66.4 (t), 60.4 (q), 28.0 (t), 23.2 (t), −0.8 (q); IR (thin film) 2964–2815w, 2061m, 1964m, 1901s, 1483m, 1446m, 1251m, 845m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 547 (M^+, 43, ^{184}W), 519 (M^+-CO, 5, ^{184}W), 491 (M^+-2CO, 78, ^{184}W), 463 (M^+-3CO, 37, ^{184}W), 435 (M^+-4CO, 9, ^{184}W), 407 (M^+-5CO, 95, ^{184}W), 392 (97, ^{184}W), 364 (30), 349 (27), 335 (25), 321 (30), 293 (42), 277 (46), 263 (33), 238 (18), 222 (5), 204 (7), 180 (7), 155 (5), 135 (6), 111 (7), 97 (15), 73 (100), 59 (4). Anal. calcd for $C_{17}H_{21}NO_6SiW$: C, 37.31; H, 3.87; N, 2.56; W, 33.59. Found: C, 37.72; H, 3.94; N, 1.91; W, 33.84. Spectral data for ***Z*-19**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61–4.52 (m, 1H), 4.07–3.96 (m, 1H), 3.81–3.70 (m, 1H), 3.62 (d, 2H, J=8 Hz), 3.37 (s, 3H), 2.29–2.07 (m, 4H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 224.3 (s), 203.7 (s), 198.5 (s, J_{CW}=128 Hz), 132.2 (s), 107.2 (s), 76.6 (t), 73.1 (d), 59.3 (q), 55.9 (t), 27.0 (t), 22.7 (t), −0.7 (q); IR (thin film) 2962–2851w, 2062m, 1976m, 1917s, 1483w, 1449w, 1260m, 847m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 547 (M^+, 24, ^{184}W), 519 (M^+-CO, 30, ^{184}W), 491 (M^+-2CO, 43, ^{184}W), 463 (M^+-3CO, 60, ^{184}W), 435 (M^+-4CO, 7, ^{184}W), 407 (M^+-5CO, 87, ^{184}W), 392 (100, ^{184}W), 363 (28), 347 (21), 321 (23), 306 (27), 265 (26), 249 (14), 224 (5), 204 (7), 182 (8), 155 (4), 120 (5), 97 (10), 83 (40), 70 (85), 55 (23). Anal. calcd for $C_{17}H_{21}NO_6SiW$: C, 37.31; H, 3.87; N, 2.56; W, 33.59. Found: C, 37.45; H, 4.20; N, 2.55; W, 34.68.

Preparation of trimethylsilylethynyl (*S*)-dimethylmethoxymethylpyrrolidine carbene complexes 16 and 20. The chromium carbene complex **7a**[9] (156 mg, 0.5 mmol) was dissolved in 5 mL diethyl ether and cooled to −78°C and then pyrrolidine **5**[8] (78.3 mg, 0.55 mmol) was added. After stirring for 2 h at −78°C, the solvent was removed and purification of the crude reaction mixture by column chromatography on silica gel (Et_2O,CH_2Cl_2, hexanes:1:1:10) afforded ***E*-16** (33.3 mg, 0.075 mmol) in 15% yield and the Michael adduct **24** (142.7 mg, 0.3 mmol) in 64% yield both as yellow solids. The same procedure at −150°C afforded ***E*-16** (21.1 mg, 0.048 mmol) in 10% yield and **24** (151.1 mg, 0.318 mmol) in 64% yield. Spectral data for ***E*-16**: mp 87–90°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68–4.66 (m, 1H), 4.40–4.35 (m, 1H), 4.21–4.15 (m, 1H), 3.18 (s, 3H), 2.27–2.24 (m, 2H), 2.04–2.00 (m, 2H), 1.22 (s, 3H), 1.14 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 247.0, 224.4, 217.4, 134.0, 105.8, 78.0 (s), 76.1 (d), 58.4 (t), 49.1 (q), 24.5, 23.1, 21.9, −0.8; IR (thin film) 2973–2957w, 2054m, 1922s cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 443 (M^+, 7), 387 (M^+-2CO, 16), 359 (M^+-3CO, 18), 331 (M^+-4CO, 36), 303 (M^+-5CO), 273 (45), 220 (33), 195 (61), 180 (64), 149 (21), 125 (16), 97 (16), 83 (15), 73 (55), 52 (18). Anal. calcd for $C_{19}H_{25}NO_6SiCr$: C, 51.46; H, 5.68; N, 3.16. Found: C, 51.42; H, 5.84; N, 2.93. Spectral data for **24**: (approx. 2:1 mixture of isomers A and B); mp 113–117°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 1H, **A**), 6.53 (s, 1H, **B**), 4.29 (s, 3H, **A**), 4.29 (s, 3H, **B**), 4.25–4.16 (m, 2H, **B**), 3.96–3.94 (m, 1H, **B**), 3.69–3.66 (m, 1H, **A**), 3.52–3.40 (m, 2H, **A**), 3.16 (s, 3H, **A**), 3.13 (s, 3H, **B**), 2.08–1.66 (m, 8H, **A**+**B**), 1.20 (s, 3H, **A**), 1.18 (s, 3H, **A**), 1.05 (s, 3H, **B**), 1.01 (s, 3H, **B**), 0.29 (s, 9H, **A**), 0.28 (s, 9H, **B**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 281.1,

279.4, 224.4 (2 peaks), 219.5 (2 peaks), 175.8, 168.3, 125.8 (2 peaks), 78.7, 77.8, 70.4, 67.7, 63.1, 62.4, 57.7, 56.0, 49.1 (2 peaks), 25.2, 24.7, 23.8, 23.6, 22.0, 21.4, 21.0, 18.3, 2.2 (2 peaks); IR (thin film) 2982–2837w, 2044m, 1963 shoulder, 1907s, 1428m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 475 (M^+, 3), 419 (M^+-2CO, 1), 391 (M^+-3CO), 363 (M^+-4CO, 13), 335 (M^+-5CO, 44), 292 (16), 252 (34), 224 (73), 194 (43), 162 (17), 141 (5), 111 (34), 89 (26), 73 (100), 52 (38).

The tungsten complex **20** was prepared in a similar manner from complex **7b**.[9] Upon separation of isomers ***E*-20** was obtained as an orange solid in 53% yield, ***Z*-20** as an orange oil in 5% yield and the Michael adduct 28 was obtained in 24% yield. The same procedure at −100°C afforded a mixture of ***E*-20**:***Z*-20** (2.6:1) (20.6 mg, 0.036 mmol) in 7% yield, pure ***Z*-20** (233.4 mg, 0.406 mmol) in 81% yield and **28** (4.2 mg, 0.007 mmol) in 1% yield. Spectral data for ***E*-20**: mp 101–104°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.59 (d, 1H, J=7.4 Hz), 4.26–4.22 (m, 1H), 4.02–3.96 (m, 1H), 3.19 (s, 3H), 2.31–2.20 (m, 2H), 2.06–1.98 (m, 2H), 1.24 (s, 3H), 1.13 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.8, 204.7, 198.6 (J_{CW}=130 Hz), 107.8, 94.0, 77.9 s, 75.0 d, 60.6 t, 49.1 q, 24.8, 22.9, 22.2, 21.9, −0.8; IR (thin film) 2979–2960w, 2062m, 1974w, 1915s, 1487w, 846w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 575 (M^+, 44, ^{184}W), 547 (M^+-CO, 3, ^{184}W), 519 (M^+-2CO, 88, ^{184}W), 491 (M^+-3CO, 6, ^{184}W), 462 (5), 437 (100), 435 (M^+-5CO, 89, ^{184}W), 420 (83), 402 (21), 364 (20), 349 (18), 331 (13), 291 (18), 277 (17), 263 (10), 249 (4), 220 (2), 180 (3), 149 (3), 83 (3), 73 (13), 55 (5). Anal. calcd for $C_{19}H_{25}NO_6SiW$: C, 39.66; H, 4.38; N, 2.43. Found: C, 39.49; H, 4.55; N, 2.16. Spectral data for ***Z*-20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.48 (d, 1H, J=8.5 Hz), 4.43–4.38 (m, 1H), 3.68–3.63 (m, 1H), 3.18 (s, 3H), 2.29–2.23 (m, 1H), 2.18–2.12 (m, 1H), 2.04–1.96 (m, 1H), 1.32 (s, 3H), 1.29 (s, 3H), 0.29 (s, 9H); IR (thin film) 2082m, 1914s cm^{-1}; MS (EI) *m/z* (% intensity) 575 (M^+, 5, ^{184}W), 547 (M^+-CO, 28, ^{184}W), 519 (M^+-2CO, 14, ^{184}W), 491 (M^+-3CO, 21, ^{184}W), 435 (M^+-5CO, 85, ^{184}W), 420 (50, ^{184}W), 404 (16), 364 (14), 349 (12), 291 (13), 277 (14), 263 (9), 249 (6), 220 (11), 197 (3), 180 (5), 155 (4), 111 (7), 89 (28), 73 (100), 55 (31). Spectral data for **28**: tentative assignment, isolated as a 2:1 mixture of two isomers **A**:**B**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (s, 1H, **A**), 6.57 (s, 1H, **B**), 4.19 (s, 3H, **B**), 4.17–4.13 (m, 1H, **A** or **B**), 4.08 (s, 3H, **A**), 3.99–3.94 (m, 1H, **A** or **B**), 3.69–3.63 (m, 1H, **A** or **B**), 3.52–3.49 (m, 1H, **A** or **B**), 3.47–3.39 (m, 1H, **A** or **B**), 3.18 (s, 3H, **A**), 3.15 (s, 3H, **B**), 2.12–1.73 (m, 8H, **A**+**B**), 1.21 (s, 3H, **A**), 1.19 (s, 3H, **A**), 1.07 (s, 3H, **B**), 1.03 (s, 3H, **B**), 0.33 (s, 9H, **B**), 0.32 (s, 9H, **A**).

Triisopropylsilylethynyl (*S*)-dimethylmethoxymethyl-pyrrolidine carbene complexes 17 and 22. A solution of chromium complex **7c** (208 mg, 0.500 mmol) in 5 mL diethyl ether was cooled to −78°C and pyrrolidine **5**[8] (86 mg, 0.600 mmol) was added. After 2 h, TLC indicated that the reaction was not complete. Additional **5** (15 mg, 0.105 mmol) was added and the reaction was complete after an additional 45 min. After concentration, the residue was loaded onto a silica gel column and eluted with a 1:30 mixture of ether and pentane to two red–orange oils, ***E*-17** (253.3 mg, 0.480 mmol) in 96% yield and ***Z*-17** (6.3 mg, 0.012 mmol) in 2% yield. The same reaction run at room temperature gave ***E*-17** (171.3 mg, 0.325 mmol) in 65% yield and ***Z*-17** (42.6 mg, 0.081 mmol) in 16% yield after isolation. Spectral data for ***E*-17**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (d, 1H, J=6.4 Hz), 4.44–4.38 (m, 1H), 4.24–4.16 (m, 1H), 3.17 (s, 3H), 2.24–2.19 (m, 2H), 2.04–1.97 (m, 2H), 1.56 (s, 3H), 1.25 (s, 3H), 1.14–1.04 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 246.8(s), 224.3(s), 217.4(s), 129.8(s), 107.7(s), 77.9(s), 76.3(d), 58.6(t), 49.4(q), 24.5(t), 23.1(t), 21.7(2q), 18.6(q), 11.3(d); IR (thin film) 2997–2841m, 2054m, 1977w, 1926s, 1717m, 1472m, 1445w, 1231w, 1083w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 527 (M^+, 2), 471 (M^+-2CO, 5), 456 (13), 443 (M^+-3CO, 5), 415 (M^+-4CO, 8), 387 (M^+-5CO, 92), 355 (17), 335 (7), 304 (16), 279 (79), 264 (100), 231 (6), 209 (7), 194 (5), 175 (12), 153 (15), 139 (8), 111 (16), 97 (8), 83 (13), 73 (23), 59 (7). Anal. calcd for $C_{25}H_{37}NO_6SiCr$: C, 56.91; H, 7.07; N, 2.65; Cr, 9.85. Found: C, 56.95; H, 7.28; N, 2.60; Cr, 10.53. Spectral data for ***Z*-17**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.58 (d, 1H, J=6.4 Hz), 4.49–4.43 (m, 1H), 3.68–3.62 (m, 1H), 3.20 (s, 3H), 2.18–1.92 (m, 4H), 1.28 (s, 3H), 1.22 (s, 3H), 1.18–1.04 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 244.8, 223.8, 217.8, 107.6, 77.8, 76.9, 57.2, 48.93, 24.3, 23.4, 21.1, 21.0, 18.6, 11.2 (one of the acetylenic C's could not be detected); IR (thin film) 2992–2867w, 2054m, 1977w, 1920s, 1476–1448w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 527 (M^+, 1), 471 (M^+-2CO, 2), 456 (3), 443 (M^+-3CO, 2), 415 (M^+-4CO, 2), 387 (39), 355 (6), 304 (7), 279 (100), 262 (8), 237 (9), 209 (10), 175 (6), 139 (7), 111 (13), 96 (8), 73 (68), 59 (18). Anal. calcd for $C_{25}H_{37}NO_6SiCr$: C, 65.91; H, 7.07; N, 2.65. Found: C, 56.73; H, 7.07; N, 2.48.

The tungsten carbene complex **22** was prepared in a similar manner from **7d**. Separation of the isomers gave ***E*-22** in 58% yield as an orange oil and ***Z*-22** in 26% yield as an orange oil. Spectral data for ***E*-22**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (d, 1H, J=7.7 Hz), 4.28–4.20 (m, 1H), 4.04–3.95 (m, 1H), 3.16 (s, 3H), 2.29–2.13 (m, 2H), 2.06–1.92 (m, 2H), 1.23 (s, 3H), 1.14 (s, 3H), 1.18–1.06 (m, 3×1H), 1.10–1.08 (m, 6×3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.5 (s), 204.4 (s), 198.7 (s), 126.6 (s), 109.5 (s), 77.8 (s), 75.2 (d), 60.8 (t), 49.0 (q), 24.7 (t), 22.8 (t), 21.9 (q), 21.6 (q), 18.6 (q), 11.3 (d); IR (thin film) 2945m, 2892w, 2868m, 2061m, 1974m, 1918s, 1482m, 1444w, 1131w, 1683m, 1046w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 659 (M^+, 2, ^{184}W), 631 (M^+-CO, 7, ^{184}W), 603 (M^+-2CO, 5, ^{184}W), 575 (M^+-3CO, 8, ^{184}W), 519 (M^+-5CO, 15, ^{184}W), 502 (12), 475 (4), 448 (5), 432 (4), 415 (2), 392 (2), 362 (3), 328 (4), 303 (5), 264 (10), 182 (3), 139 (11), 111 (13), 96 (12), 70 (100), 59 (23). Anal. calcd for $C_{25}H_{37}NO_6SiW$: C, 45.53; H, 5.65; N, 2.12. Found: C, 45.63; H, 5.86; N, 2.10. Spectral data for ***Z*-22**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (d, 1H, J=6.7 Hz), 4.48–4.37 (m, 1H), 3.68–3.57 (m, 1H), 3.18 (s, 3H), 2.29–2.21 (m, 1H), 2.21–2.12 (m, 1H), 2.06–1.96 (m, 2H), 1.26 (s, 3H), 1.25 (s, 3H), 1.24–1.09 (m, 3×1H, 6×3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 224.4 (s), 203.6 (s), 199.0 (s), 127.3 (s), 109.5 (s), 78.4 (d), 55.6 (t), 48.9 (q), 24.1 (t), 23.3 (t), 21.1 (q), 20.6 (q), 18.8 (q), 11.2 (d), one C-atom under $CDCl_3$ peak; ^{13}C NMR (75 MHz, C_6D_6) δ 224.9 (s), 203.4 (s), 199.0 (s), 110.2 (s), 78.6 (d), 77.7 (s), 56.0 (t), 48.5 (q), 24.2 (t), 23.3 (t), 20.8 (q), 20.5 (q), 18.8 (q), 11.5 (d), one C-atom under

C_6D_6 peak; IR (thin film) 2945m, 2893w, 2867m, 2062s, 1974m, 1919s, 1473m, 1448w, 1208w, 1131w, 1083m, 1045w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 659 (M^+, 3, ^{184}W), 631 (M^+-CO, 27, ^{184}W), 603 (M^+-2CO, 11, ^{184}W), 575 (M^+-3CO, 29, ^{184}W), 547 (M^+-4CO, 2, ^{184}W), 519 (M^+-5CO, 56, ^{184}W), 502 (37,,W), 475 (16), 433 (13), 391 (7), 361 (8), 327 (11), 304 (12), 264 (15), 238 (3), 203 (3), 182 (3), 139 (12), 111 (13), 96 (15), 70 (100), 59 (44). Anal. calcd for $C_{25}H_{37}NO_6SiW$: C, 45.53; H, 5.65; N, 2.12. Found: C, 45.41; H, 5.76; N, 2.52.

Preparation of complexes 31–34 by protodesilylation: chromium complex *E*-31. The chromium carbene complex ***E*-15** (139.8 mg, 0.35 mmol) was dissolved in 20 mL diethyl ether and cooled to −78°C. Tetrabutylammonium fluoride (0.350 mL, 1 M, 0.35 mmol) in THF was added and the solution was stirred for 1 h at −78°C. The reaction was quenched with water and washed with water and brine. After drying with $MgSO_4$ and filtration, the solution was concentrated. Purification by column chromatography on silica gel (Et_2O/CH_2Cl_2/hexanes, 1:1:10) afforded ***E*-31** (89.4 mg, 0.26 mmol) as a yellow solid in 74% yield. Spectral data for ***E*-31**: mp 39–41°C, ^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (s, 1H), 4.67 (m, 1H), 4.24–4.22 (m, 2H), 3.59 (d,2H, J=5.6 Hz), 3.36 (s, 3H), 2.33–2.14 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 247.5, 223.8, 217.2, 114.5, 84.3, 72.6, 67.9, 59.3, 58.6, 27.7, 23.5; IR (thin film) 3298m, 2988–2834m, 2056s, 1979shoulder, 1911s, 1482m, 1449m, 1120w, 654m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 343 (M^+, 27), 315 (M^+-CO, 3), 287 (M^+-2CO, 45), 259 (M^+-3CO, 22), 231 (M^+-4CO, 73),220 (83), 203 (M^+-5CO, 100), 188 (22), 173 (24), 158 (14), 147 (47), 133 (18), 119 (49), 108 (87), 92 (13), 80 (100), 70 (100). Anal. calcd for $C_{14}H_{13}NO_6Cr$: C, 48.99; H, 3.82; N, 4.08. Found: C, 46.79; H, 4.40; N, 4.08.

Tungsten complex **E**-*33*. Yellow solid, 91% yield from ***E*-19**. Spectral data for ***E*-33**: mp: 40–42°C; ^1H NMR (300 MHz, $CDCl_3$) δ 5.56 (s, 1H), 4.59–4.57 (m, 1H), 4.02 (m, 2H), 3.58 (d, 2H, J=5.2 Hz), 3.35 (s, 3H), 2.26–2.09 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.3 (s), 204.0 (s), 198.4 (s, J_{CW}=128 Hz), 111.2 (d, $^1J_{CH}$=265 Hz), 86.2 (d, $^2J_{>CH}$=52 Hz), 72.3 (t), 66.7 (d), 60.8 (t), 59.3 (q), 28.0 (t), 23.2 (t); IR (thin film) 3298w, 2979–2837w, 2063m, 1977shoulder, 1904s, 1486w cm^{-1}; MS (EI) *m/z* (% intensity) 475 (M^+, 47, ^{184}W), 447 (M^+-CO, 4, ^{184}W), 419 (M^+-2CO, 28, ^{184}W), 391 (M^+-3CO, 48, ^{184}W), 363 (M^+-4CO, 58, ^{184}W), 335 (M^+-5CO, 100, ^{184}W), 278 (27), 237 (18), 211 (9), 168 (6), 145 (4), 120 (3), 96 (3), 70 (22). Anal. calcd for $C_{14}H_{13}NO_6W$: C, 35.39; H, 2.76; N, 2.95; W, 38.70. Found: C, 34.58; H, 2.95; N, 2.88; W, 38.88.

Tungsten complex **Z**-*33*. Yellow solid, 84% yield from ***Z*-19**. Spectral data for ***Z*-33**: mp 46–49°C; ^1H (500 MHz, $CDCl_3$) δ 5.55 (s, 1H), 4.62–4.56 (m, 1H), 4.05–3.98 (m, 2H), 3.66–3.62 (m, 2H), 3.38 (s, 3H), 2.31–2.08 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 224.5 (s), 203.4 (s), 198.3 (s), 111.3 (d), 87.7 (d), 73.1 (t), 69.9 (d), 59.3 (q), 56.3 (t), 27.1 (t), 22.7 (t); IR (thin film) 3296w, 2992–2837w, 2064m, 1977 shoulder, 1907s, 1485w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 475 (M^+, 40, ^{184}W), 447 (M^+-CO, 7, ^{184}W), 419 (M^+-2CO, 25, ^{184}W), 391 (M^+-3CO, 51, ^{184}W), 363 (M^+-4CO, 55, ^{184}W), 335 (M^+-5CO, 100, ^{184}W), 291 (24), 265 (23), 237 (15), 209 (7), 168 (7), 145 (3), 120 (1), 69 (15). Anal. calcd for $C_{14}H_{13}NO_6W$: C, 35.39; H, 2.76; N, 2.95; Found: C, 35.03; H, 2.99; N, 3.07.

Chromium complex **E**-*32*. Yellow solid, 84% yield from ***E*-17**. Spectral data for ***E*-32**: mp: 78–82°C (decomp); ^1H NMR (400 MHz, $CDCl_3$) δ 5.74 (s, 1H), 4.66 (m, 1H), 4.42–4.35 (m, 1H), 4.27–4.13 (m, 1H), 3.16 (s, 3H), 2.25–2.18 (m, 2H), 2.05–1.92 (m, 2H), 1.19 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 247.6, 224.2, 217.2, 113.5 (d, $^1J_{CH}$=256 Hz), 85.6 (d, $^2J_{>CH}$=49 Hz), 80.0 (s), 76.4 (d), 58.9 (t), 49.1 (q), 24.6, 23.2, 21.9, 21.8; IR (thin film) 3307w, 2988–2776w, 2054m, 1973m, 1920s, 1496m, 1082m cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 371 (M^+, 23), 315 (M^+-2CO, 17), 287 (M^+-3CO, 13), 259 (M^+-4CO, 26), 231 (M^+-5CO, 90), 220 (100), 199 (25), 175 (11), 164 (13), 148 (26), 136 (15), 119 (13), 100(65), 80 (87), 73 (33), 52 (97). Anal. calcd for $C_{16}H_{17}NO_6Cr$: C, 51.76; H, 4.61; N, 3.77. Found: C, 51.93; H, 4.86; N, 3.63.

Tungsten complex **E**-*34*. Yellow solid, 74% yield from ***E*-20** and 74% from ***E*-22** Spectral data for ***E*-34**: mp 88–97°C (decomp.); ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 9 (d, 1H, J=7.6 Hz); 4.25–4.21 (m, 1H), 4.04–3.98 (m, 1H), 3.16 (s, 3H), 2.26–2.20 (m, 2H), 2.01–1.96 (m, 2H), 1.20 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 226.7 (s), 204.5 (s), 199.1 (sd, J_{WC}=127.8 Hz), 110.7 (s), 87.7 (s), 77.9 (s), 75.6 (d), 61.4 (t), 48.8 (q), 24.6 (t), 22.8 (t), 22.1 (q), 21.3 (q); IR (thin film): 3298w, 3023–2800w, 2083m, 1978w, 1897s, 1881s, 1496m, 1085w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 503 (M^+, 47, ^{184}W), 475 (M^+-CO, 4, ^{184}W), 447 (M^+-2CO, 57, ^{184}W), 419 (M^+-3CO, 13, ^{184}W), 391 (M^+-4CO, 4, ^{184}W), 363 (M^+-5CO, 100, ^{184}W), 331 (27), 292 (29), 263 (21), 237 (17), 209 (8), 181 (6), 149 (5), 110 (7), 96 (8), 73 (94), 55 (47). Anal. calcd for $C_{16}H_{17}NO_6W$: C, 38.19; H, 3.41; N, 2.78. Found: C, 38.27; H, 3.42; N, 2.71.

Tungsten complex **Z**-*34*. Yellow oil, 40% yield from ***Z*-22**. Spectral data for ***Z*-34**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.50 (s, 1H), 4.51 (d, 1H, J=6.8 Hz), 4.44–4.38 (m, 1H), 3.70–3.63 (m, 1H), 3.16 (s, 3H), 2.28–2.23 (m, 1H), 2.16–2.12 (m, 1H), 2.03–1.94 (m, 2H), 1.26 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 225.1 (s), 203.5 (s), 198.9 (s), 110.6 (d), 87.2 (s), 77.5 (d), 56.0 (t), 48.9 (q), 24.1 (t), 23.2 (t), 21.1 (q), 20.7 (q); IR (thin film) 3299w, 2950–2850w, 2083m, 1976m, 1905s, 1487m, 1446w, 1082w cm^{-1}.

Diels–Alder reactions of the (*S*)-methoxymethylpyrrolidine carbene complexes *E*-31 and *E*-33 with siloxy diene 11.

Cycloadduct ***36***. The chromium carbene complex ***E*-31** (570.1 mg, 1.67 mmol) was dissolved in 1.5 mL diene **11** and stirred for 28 h at room temperature. The crude reaction mixture was directly loaded onto a silica gel column and eluted with a 20:1 mixture of hexane and ether to give carbene complex **36** (467.3 mg, 0.802 mmol) as a yellow oil 48% yield. This product was obtained as a 5:1 mixture of diastereomers and the major isomer was assigned as A on the basis of a comparison of the NMR data with **38A**. The following spectral data was obtained on the mixture of isomers and the NMR data for **36A** was extracted from

the spectrum of the mixture. Spectral data for **36A**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (s, 1H), 4.86 (s, 1H), 4.36–4.33 (m, 1H), 4.16–4.12 (m, 1H), 3.72–3.71 (m, 1H), 3.39 (d, 1H, J=6.1 Hz), 3.33 (s, 3H), 2.95–2.89 (m, 1H), 2.78–2.73 (m, 1H), 2.30–2.26 (m, 1H), 2.18–2.10 (m, 2H), 1.92–1.88 (m, 1H), 1.22–1.61 (m, 3H), 1.11 (d, 18H, J=6.5 Hz), 0.94 (d, 3H, J=7.2 Hz); ^{13}C NMR (C_6D_6, 75 MHz) δ 273.0, 224.4, 218.9, 151.8, 147.7, 110.4, 106.5, 73.2, 66.6, 59.3, 58.8, 34.0, 30.2, 26.8, 21.7, 20.2, 18.2, 13.0; IR (thin film) 2960–2868w, 2050m, 1967m, 1915s, 1688w, 1491–1456w, 1211m, 884w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 527 (M^+-2CO, 36), 495 (3), 471 (M^+-4CO, 17), 443 (M^+-5CO, 100), 413 (24), 391 (92), 346 (87), 330 (18), 277 (100), 235 (32), 218 (18), 197 (22), 165 (100), 135 (91), 105 (92), 75 (100). Anal. calcd for $C_{28}H_{41}NO_7SiCr$: C, 57.62; H, 7.08; N, 2.40; Cr, 8.91. Found: C, 55.76; H, 7.86; N, 2.37; Cr, 9.17. The methoxy singlet of the minor isomer **36B** is at δ=3.30 ppm.

*Cycloadduct **37***. The tungsten carbene complex ***E*-33** (98.2 mg, 0.207 mmol) was dissolved in 0.5 mL diene **11** and stirred for 43 h at room temperature. The crude reaction mixture was directly loaded onto a silica gel column and eluted with a 1:1:20 mixture of ether, methylene chloride and hexanes to give carbene complex **37** (84.0 mg, 0.117 mmol) as a yellow oil 57% in yield. This product was obtained as a 5:1 mixture of diastereomers and the major isomer was assigned as A on the basis of a comparison of the NMR data with **38A**. The following spectral data was obtained on the mixture of isomers and the NMR data for **37A** was extracted from the spectrum of the mixture. Spectral data for **37A**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.02 (m, 1H), 4.87 (m, 1H), 4.34–4.29 (m, 1H), 4.11–4.01 (m, 2H), 3.77–3.72 (m, 1H), 3.42–3.39 (m, 2H), 3.34 (s, 3H), 2.98–2.91 (m, 1H), 2.82–2.73 (m, 1H), 2.30–2.12 (m, 3H), 1.95–1.87 (m, 1H), 1.22–1.07 (m, 21H), 0.95 (d, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 254.7, 203.8, 199.1 (J_{CW}=128 Hz), 151.9, 147.5, 111.1, 106.5, 73.3 t, 65.2 d, 61.2 t, 59.2 q, 33.8, 29.9, 27.1, 21.7, 20.0, 17.9, 12.6; IR (thin film) 2945–2868w, 2059m, 1967m, 1910s, 1686w, 1492w, 1455m, 1210m, 884w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 687 (M^+-CO, 35, ^{184}W), 659 (M^+-2CO, 31 ^{184}W), 631 (M^+-3CO, 43, ^{184}W), 603 (M^+-4CO, 8, ^{184}W), 601 (11), 575 (M^+-5CO, 47, ^{184}W), 560 (57), 519 (8), 488 (20), 458 (20), 416 (15), 391 (100), 346 (100), 278 (100), 218 (75), 157 (55), 103 (90), 87 (82), 73 (98), 59 (100). Anal. calcd for $C_{28}H_{41}NO_7SiW$: C, 47.00; H, 5.77; H, 1.96; W, 25.69. Found: C, 46.54; H, 5.92; N, 1.55; W, 17.94. The methoxy singlet of the minor isomer **37B** is at δ=3.30 ppm.

Diels–Alder reactions of the (*S*)-dimethylmethoxymethylpyrrolidine carbene complexes *E*-32 and *E*-34 with siloxy diene 11.

*Cycloadduct **38***. The chromium carbene complex ***E*-32** (515.1 mg, 1.387 mmol) was dissolved in 1.5 mL diene **11** and stirred at room temperature for 52 h. The products were purified by directly loading the crude reaction mixture on a silica gel column and elution with a 20:1 mixture of pentane and ether. The first fraction was found to be a 4:1 mixture of **38A** and **38B** (256.2 mg, 0.419 mmol, 30% yield) and was obtained as a yellow oil. The second fraction provided a pure sample of **38A** (122.5 mg, 0.200 mmol) as a yellow solid in 14% yield. Repurification of the mixed fraction by a second silica gel column gave 20.9 mg of pure **38B** for spectral analysis. Spectral data for **38A**: mp: 69–72°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.84 (s, 1H), 4.37–4.21 (m, 2H), 4.08 (d, 1H), 3.60–3.53 (m, 1H), 3.20 (s, 3H), 2.96–2.87 (m, 1H), 2.82–2.73 (m, 1H), 2.23–2.12 (m, 2H), 2.02–1.93 (m, 1H), 1.93–1.82 (m, 1H), 1.25–1.03 (m, 21H), 1.21 (s, 3H), 1.13 (s, 3H), 0.88 (d, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 274.0, 224.4, 218.7, 151.3, 147.8, 112.6, 106.7, 76.7, 74.5, 60.9, 48.7, 34.1, 30.5, 24.2, 22.4, 22.2, 21.5, 20.6, 18.2, 13.4; IR (thin film) 2945–2868w, 2049m, 1966w, 1941s, 1488w, 1465w, 1383w, 1206m, 1081w, 884w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 555 (M^+-2CO, 6), 471 (M^+-5CO, 20), 437 (5), 418 (4), 402 (4), 346 (37), 324 (8), 277 (100), 193 (67), 161 (18), 131 (30), 103 (28), 87 (15), 75 (42), 59 (41). Spectral data for **38B**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (t, 1H, J=3.6 Hz), 4.80 (d, 1H, J=2.9 Hz), 4.33–4.26 (m, 1H), 4.18–4.08 (m, 1H), 3.91 (d, 1H, J=8.2 Hz), 3.19 (s, 3H), 3.08–3.03 (m, 1H), 2.76–2.71 (m, 1H), 2.57–2.54 (m, 1H), 2.22–2.17 (m, 2H), 1.99–1.95 (m, 1H), 1.87–1.83 (m, 1H), 1.29 (d, 3H, J=7.3 Hz), 1.28 (s, 3H), 1.17 (s, 3H), 1.11 (d, 18H, J=6.8 Hz), 1.22–1.01 (m, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 280.0, 224.1, 218.5, 153.2, 148.8, 120.5, 107.4, 77.4, 74.5, 61.0, 48.7, 36.3, 30.2, 24.5, 23.4, 22.9, 22.1, 21.7, 18.1, 13.0; IR (thin film) 29.45–2868m, 2050m, 1968w, 1918s, 1465w, 1450w, 1207w, 883w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 555 (M^+-2CO, 7), 496 (3), 471 (M^+-5CO), 453 (9), 435 (7), 419 (7), 404 (15), 388 (6), 362 (9), 346 (39), 330 (8), 309 (3), 277 (73), 241 (33), 231 (83), 197 (100), 177 (15), 161 (23), 131 (56), 103 (58), 87 (28), 75 (87), 59 (71).

*Cycloadduct **39***. The tungsten carbene complex ***E*-34** (157.1 mg, 0.312 mmol) was stirred with 1 mL of diene **11** in 1 mL diethyl ether for 48 h at room temperature. The resulting mixture was concentrated and separation of the isomers by silica gel column chromatography (pentane: diethyl ether=20:1) led to **39B** (20.1 mg, 0.027 mmol) from the first fraction in 9% yield and **39A** (127.3 mg, 0.171 mmol) from the second fraction in 55% yield. Both complexes are bright yellow oils. Spectral data for **39A**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22 (m, 1H), 4.82 (d, 1H, J=2.4 Hz), 4.33–4.25 (m, 1H), 4.12–4.03 (m, 1H), 4.01 (d, 1H, J=7.8 Hz), 3.59 (bq, 1H, J=7.3 Hz), 3.17 (s, 3H), 2.91 (ddd, 1H, J=22 Hz, J=7.4 Hz, J=4.0 Hz), 2.19–2.05 (m, 2H), 1.98–1.87 (m, 1H), 1.87–1.76 (m, 1H), 1.16 (s, 3H), 1.09 (s, 3H), 1.17–1.10 (m, 3×1H), 1.06 (d, 6×3H, J=6.4 Hz), 0.84 (d, 3H, J=7.3 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ 225.4 (s), 204.1 (s), 199.8 (s), 151.7 (s), 148.0 (s), 113.7 (d), 106.7 (d), 76.5 (s), 73.4 (d), 63.0 (t), 48.7 (q), 34.3 (d), 24.4 (t), 22.6 (q), 21.9 (t), 21.5 (q), 20.5 (q), 18.2 (q), 13.0 (d); IR (thin film) 2962–2868m, 2058s, 1966m, 1905s, 1689w, 1491–1445m, 1206m 1081w, 884w cm^{-1}; mass spectrum (EI) *m/z* (% intensity) 743 (M^+, 0.3, ^{184}W), 715 (M^+-CO, 4, ^{184}W, 687 (M^+-2CO, 1, ^{184}W), 659 (M^+-3CO, 3, ^{184}W), 603 (M^+-5CO, 4, ^{184}W), 584 (2), 545 (11, ^{184}W), 517 (2), 487 (2), 457 (2), 419 (10), 387 (15), 346 (100), 325 (5), 303 (6), 278 (100), 235 (25), 191 (26), 165 (20), 124 (100), 105 (66), 73 (100), 59 (100). Anal. calcd for $C_{30}H_{45}NO_7SiW$: C, 48.46; H, 6.10; N, 1.88; W, 24.72. Found: C, 48.51; H, 6.11; N, 1.45; W,

24.43. Spectral data for **39B**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (t, 1H, J=3.7 Hz), 4.78 (dd, 1H, J=2.7 Hz, J=1.2 Hz), 4.17–4.00 (m, 2H), 3.84 (d, 1H, J=7.9 Hz), 3.15 (s, 3H), 3.16–3.05 (m, 1H), 273 (t, 1H, J=5.0 Hz), 2.59–2.50 (m, 1H), 2.27–2.11 (m, 2H), 1.99–1.76 (m, 2H), 1.29 (d, 3H, J=6.9 Hz), 1.11–1.01 (m, 3×1H), 1.06 (d, 6×3H, J=6.6 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ 261.2 (s), 204.0 (s), 199.9 (s), 153.2 (s), 148.8 (s), 121.6 (d), 107.2 (d), 77.2 (s), 73.5 (d), 63.2 (t), 48.7 (q), 36.0 (d), 30.8 (t), 24.7 (t), 24.0 (q), 22.7 (t), 22.3 (q), 21.6 (q), 18.1 (q), 12.9 (d); IR (thin film) 2946m, 2893w, 2868m, 2059s, 1967m, 1917s, 1687w, 1466m, 1449m, 1382w, 1239w, 1207m, 1163w, 1082m, 884w cm^{-1}.

Structure determination of Diels–Alder adduct 38A. A weakly diffracting thin yellow–brown plate was mounted on a glass fiber and the unit-cell parameters determined from the angular settings of 25 reflections. From these data and systematic absences in the diffraction data, the space group was uniquely assigned. A semi-empirical correlation for absorption was required to compensate for the 20% variation in transmission seen in azimuthal scans. The structure was solved using an automated Patterson routine. Limitations in the number of data available allowed anisotropic refinement of only the Cr, Si, N and O atoms. Hydrogen atoms were treated as idealized, updated contribution. A Roger's handedness test showed that the reported coordinates are preferred (ν=1.2(3)).

Crystal data for $C_{30}H_{45}CrNO_7Si$: f.w.=611.8, orthorhombic, $P2_12_12_1$, a=8.385(3), b=9.329(4), c=43.126(5) Å, V=3374(17) Å^3, Z=4, 2133 data collected; 1332 observed from 2133 independent reflections. $R(F)$=9.61% and $R(wF)$=12.31%. SHELXTL (4.2) software was used for refinement (G. Sheldrick, Siemens XRD, Madison, WI). Lists of the atomic coordinates, thermal parameters, bond distances and bond angles have been deposited with the Cambridge Crystallographic Database, Cambridge, England.

Diels–Alder reaction of the (*S*)-dimethylmethoxymethylpyrrolidine carbene complexes *E*-34 with siloxy diene 13. The tungsten carbene complex ***E*-34** (323.4 mg, 0.322 mmol) was dissolved in 1 mL diene **13** and stirred for 89 h at room temperature. The resultant crude reaction mixture was loaded directly onto a silica gel column chromatography and eluted with a 20:1 mixture of hexane and ether. Cycloadduct **40B** (66.3 mg, 0.085 mmol) was obtained from the first fraction in 26% yield as a sticky foam and **40A** (96.3 mg, 0.123 mmol) was obtained from the second fraction in 38% yield as a yellow solid. Spectral data for **40A**: mp 108–116°C decomp, ^{1}H (500 MHz, $CDCl_3$) δ 5.18–5.15 (m 1H), 4.32–4.26 (m, 1H), 4.09–4.01 (m, 2H), 3.37–3.28 (m, 2H), 3.16 (s, 3H), 3.07–3.01 (m, 1H), 3.01–2.91 (m, 1H), 2.86–2.77 (m, 1H), 2.14–2.07 (m, 4H), 1.98–1.88 (m, 2H), 1.82–1.67 (m, 4H), 1.16 (s, 3H), 1.10–1.02 (m, 24H); ^{13}C NMR (125 MHz, C_6D_6) δ 255.1, 204.0, 200.0, 151.2, 139.2, 114.7, 112.8, 76.4, 73.3, 62.9, 48.7, 42.4, 33.1, 30.7, 27.0, 26.8, 26.6, 24.6, 22.7, 21.8, 21.6, 18.2, 13.5; IR (thin film) 2942–2866w, 2058m, 1966w, 1912s cm^{-1}; mass spectrum (EI) m/z (% intensity) 783 (M+, 0.4, ^{184}W), 755 (M$^+$−CO, 1, ^{184}W), 699 (M$^+$−3CO, 1, ^{184}W), 643 (M+, 5CO, 0.6, ^{184}W), 585 (2), 459 (7), 434 (3), 386 (32), 359 (17), 317 (75), 280 (15), 237 (40), 187 (14), 131 (42), 103 (25), 70 (100), 55 (10). Anal. calcd for $C_{33}H_{49}NO_7SiW$: C, 50.58; H, 6.30; N, 1.79. Found: C, 52.48; H, 6.71; N, 1.40. Spectral data for **40B**: ^{1}H (500 MHz, $CDCl_3$) δ 5.50 (t, 1H, J=3.4 Hz), 4.17–4.09 (m, 1H), 4.04–3.98 (m, 1H), 3.87 (d, 1H, J=8.2 Hz), 3.15 (s, 3H), 3.20–3.11 (m, 1H), 3.05–2.99 (m, 1H), 2.86–2.77 (m, 1H), 2.35–2.14 and 2.00–1.78 and 1.74–1.55 and 1.49–1.40 (m, 10H), 1.13–1.03 (m, 27H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 261.7 (s), 204.2 (s), 199.3 (s), 151.5 (s), 138.7 (s), 120.6 (d), 115.2 (s), 77.2 (s), 73.3 (d), 62.9 (t), 49.1 (q), 44.2 (d), 35.8 (t), 30.9 (t), 27.7 (t), 26.5 (t), 26.4 (t), 24.9 (t), 22.8 (t), 22.4 (q), 21.9 (q), 18.0 (q), 12.2 (d); IR (thin film) 2942–2866w, 2058m, 1966w, 1914s, 1448w cm^{-1}; mass spectrum (EI) m/z (% intensity) 783 (M$^+$, 0.04, ^{184}W), 755 (M$^+$−CO, 0.18, ^{184}W), 727 (M$^+$−2CO, 0.51, ^{184}W), 699 (M$^+$−3CO, 0.19, ^{184}W), 643 (M$^+$−5CO, 0.26, ^{184}W), 628 (0.24), 585 (3), 493 (3), 434 (3), 386 (32), 359 (6), 317 (100), 275 (24), 230 (26), 187 (7), 131 (27), 103 (19), 70 (100), 55 (10).

Diels–Alder reaction of the (*S*)-methoxymethylpyrrolidine carbene complexes *E*-31 with cyclopentadiene. The chromium carbene complex ***E*-31** (74 mg, 0.216 mmol) was dissolved in 0.5 mL cyclopentadiene (freshly cracked from its dimer). The solution was stirred for 48 h at room temperature and then concentrated. The residue was loaded onto a silica gel column and eluted with a 1:1:10 mixture of ether, methylene chloride and hexanes to give carbene complex **41** (37.7 mg, 0.092 mmol) as a yellow oil in 43% yield as a mixture of isomers (**A/B**=15:1). Spectral data for **41**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91–6.79 (m, 4H, **A**+**B**), 5.74 (broad d, 1H, J=2.2 Hz, **A**), 5.67 (broad s, 1H, **B**), 4.25–4.08 (m, **A**+**B**), 3.73 (m, 2H, **A**+**B**), 3.59 (d, 2H, J=19.0 Hz, **A**+**B**), 3.35–3.18 (m, **A**+**B**), 3.35 (s, 3H, **A**), 3.27 (s, 3H, **B**), 2.30–1.56 (m, **A**+**B**); ^{13}C NMR (75 MHz, C_6D_6) δ 269.4, 268.4, 223.8, 223.5, 218.4, 218.3, 164.8, 164.4, 143.6, 142.9, 141.3, 124.9, 122.1, 122.0, 72.3, 72.1, 71.9, 65.4, 64.3, 59.0, 58.7, 55.3, 55.2, 50.8, 50.6, 27.0, 22.1, 21.8, four carbon atoms from mixture not identified; IR (thin film) 2985–2874w, 2051m, 2007w, 1969m, 1907s, 1483w, 1415w, 1300w, 1121w cm^{-1}; mass spectrum (EI) m/z (% intensity) 381 (M$^+$−CO, 32), 353 (M$^+$−2CO, 100), 325 (M$^+$−3CO, 18), 321 (26), 297 (52), 269 (100), 230 (87), 203 (35), 148 (100), 117 (93), 80 (60). Anal. calcd for $C_{19}H_{19}NO_6Cr$: C, 55.75; H, 4.68; N, 3.42; Cr, 12.70. Found: C, 55.51; H, 4.86; N, 3.08; Cr, 13.05.

Diels–Alder reaction of the (*S*)-dimethylmethoxymethylpyrrolidine carbene complexes *E*-32 with cyclopentadiene.

The chromium carbene complex ***E*-32** (55.7 mg, 0.15 mmol) was dissolved in 0.4 mL cyclopentadiene (freshly cracked from its dimer). The solution was stirred for 42 h at room temperature and then concentrated. The residue was loaded onto a silica gel column and eluted with a 1:1:10 mixture of ether, methylene chloride and hexanes to give carbene complex **42** (39.4 mg, 0.090 mmol) as a yellow oil in 60% yield as a mixture of isomers (**A/B**=2.7:1). Spectral data for **42**: ^{1}H (500 MHz) δ 6.82 (broad s, 2H, **A**), 6.71 (broad s, 2H, **B**), 6.0 (broad s, **A**+**B**), 4.44 (broad s, 1H, **B**), 4.34 (m, 1H, **A**), 4.19 (m, 2H, **A**), 3.97 (m, 2H, **B**), 3.70 (m), 3.54–3.36 (broad m),

3.18 (s, 3H, **A**), 3.14 (s, 3H, **B**), 2.37–1.70 (3m, 8H, **A**+**B**), 1.15 (s, 3H, **A**), 1.09 (s, 3H, **A**), 1.01 (broad s, 6H, **B**); ^{13}C NMR (75 MHz, C_6D_6) δ 269.1, 224.3, 224.1, 218.6, 166.6, 166.0, 144.2, 141.4, 141.2, 77.1, 76.8, 74.7, 73.3, 72.6, 59.9, 56.1, 56.0, 55.3, 51.2, 50.9, 48.7, 24.5, 24.2, 22.8, 22.1, 21.4 (10 C atoms of mixture not identified, partially due to solvent peak); ^{13}C NMR (75 MHz, $CDCl_3$) δ 268.8, 223.9, 223.7, 217.9, 166.1, 165.5, 143.9, 143.7, 141.2, 140.9, 128.0, 127.4, 76.7, 74.9, 74.4, 72.5, 72.4, 72.2, 59.6, 55.7, 54.9, 50.8, 50.5, 49.0, 48.9, 24.5, 24.2, 22.7, 21.7, 21.5, 21.0 (4 C atoms not detected); IR (thin film) 2983–2835w, 2050m, 2005w, 1969w, 1909s, 1479w, 1448w cm^{-1}; mass spectrum (EI) *m*/*z* (% intensity) 409 (M^+-CO, 7), 381 (M^+-2CO, 32), 353 (M^+-3CO, 2), 325 (M^+-4CO, 14), 311 (3), 297 (100), 265 (25), 252 (6), 237 (12), 225 (10), 214 (15), 189 (47), 169 (27), 148 (72), 119 (100), 103 (7), 91 (23), 73 (43), 65 (12).

Isomerization of Cycloadduct 39A. A sample of **39A** in $CDCl_3$ was left in the NMR tube overnight. A new compound was formed was assigned the structure of the double-bond isomer **43** on the basis of the following spectral data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33–5.25 (m, 2H), 4.38–4.30 (m, 2H), 4.22 (d, 1H, 7.7 Hz) 4.10–4.00 (m, 1H), 3.16 (s, 3H), 2.27–2.07 (m, 4H), 1.98–1.80 (m, 2H), 1.15 (s, 3H), 1.08–1.2 (m, 3H, 6×3H), 0.89 (d, 2H, 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 256.2 (s), 204.0 (s), 199.0 (s), 153.1 (s), 144.8 (s), 115.9 (d), 101.5 (d), 76.9 (s), 73.4 (d), 62.2 (t), 49.0 (q), 38.8 (t), 34.5 (d), 24.6 (t), 22.7 (q), 22.3 (t), 22.1 (q), 17.9 (q), 16.9 (q), 12.5 (d).

Diels–Alder reaction of the (*S*)-methoxymethylpyrrolidine carbene complexes *Z*-33 with siloxy diene 11. Carbene complex ***Z*-33** (100.0 mg, 0.211 mmol) was stirred with 0.5 mL diene **11** for 14 h at room temperature. The resulting mixture was loaded directly onto a silica gel column and eluted with a 1:1:20 mixture of ether, methylene chloride and hexanes to give ***Z*-37A** and ***Z*-37B** as a 1:1 mixture (54.2 mg, 0.076 mmol) in 36% yield. Spectral data for mixture of ***Z*-37A** and ***Z*-37B**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88–4.78 (m, 4H), 4.63–4.55 (m, 2H), 4.36–4.30 (m, 1H), 4.01–3.96 (m, 1H), 3.91–3.79 (m, 3H), 3.69–3.62 (m, 4H) 3.42 (s, 3H), 3.36 (m, 3H), 2.99–2.85 (m, 2H), 2.82–2.70 (m, 2H), 2.31–2.05 (m, 6H), 2.01–1.78 (m, 2H), 1.23–1.16 (m, 6H), 1.13–1.05 (m, 36H), 0.98 (d, 3H, J=7.3 Hz), 0.95 (d, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ 252.5, 250.5, 203.7, 203.3, 200.1, 199.8, 154.7, 154.0, 147.8, 110.9, 108.6, 106.3, 106.0, 74.9, 74.3, 69.8, 69.4, 58.9, 58.8, 55.7, 53.9, 35.1, 35.0, 30.3, 30.1, 26.6, 25.8, 23.6, 23.1, 20.4, 18.2, 13.0 (4 C atoms not detected); IR (thin film) 2945–2868w, 2059m, 1967w, 1912s, 1687w, 1494w, 1463w, 1210m, 837w cm^{-1}.

Acknowledgements

This work was supported by a grant from the National Institute of Health (PHS-GM 33589).

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