High Stereoselectivity and Facial Selectivity in Diels−Alder Cycloadditions of Novel Captodative Olefins: α-Alkoxyvinyl(ethoxy)carbene Chromium Complexes with Cyclopentadienes

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A study of reactivity and selectivity of the new Fischer carbene complexes $(CO)_5Cr{=}C[C(=CHR')(OR)]OCH_2CH_3$ (**3**, R′ = H, R = CH_2CH_3; **4**, R′ = H, R = $CH_2CH_2CH_3$; **5**, R′ = H, R = $CH_2CH_2CH_2CH_3$; **6**, R′ = CH_3 (*E* and *Z*), R = CH_2CH_3) was carried out in Diels−Alder cycloadditions with cyclopentadiene (**1**) and 1,2,3,4,5-pentamethylcyclopentadiene (**7**). The cycloadditions between the α-alkoxyvinyl(ethoxy)carbene complexes **3**, **4**, and **5** with **1** were found to be highly stereoselective, favoring the *endo* adduct at a much higher level than that observed for the analogous α-alkoxy-α,*β*-unsaturated esters, whereas complex **6***E* showed low reactivity. When 1,2,3,4,5-pentamethylcyclopentadiene (**7**) was employed, the cycloadditions with α-alkoxyvinyl(ethoxy)carbene complexes **3**−**6***E* were highly *anti*/*exo* selective. The *exo* adducts form new alkoxy-chelated tetracarbonyl carbene complexes. The stereochemical assignment of the cycloadducts was supported by NOE measurements, and the chelated *exo* cycloadduct **21** was further characterized by single-crystal X-ray diffraction.

Introduction

Metal carbene complexes have been an issue of much research activity, since their discovery by E. O. Fischer in 1964.[1] In particular, the Dötz reaction,[2] a formal cycloaddition of Fischer α,*β*-unsaturated carbene complexes to alkynes, has been of increasing interest to organic chemists.[3] The report of Wulff in 1983,[4] that the vinylcarbene complexes of Fischer can be involved in Diels−Alder reaction as dienophiles, broadened even further the scope of their applications. Thus, it has been established that the Diels−Alder reactions of α,*β*-unsaturated complexes with cyclopentadiene (**1**) are stereoselective in favor of the *endo* adduct,[5] although there are some cases of *exo* selectivity[6] depending on the nature of the dienophile (conformationally *s-cis* restricted,[7] α-substituted[6c,8]) or of the dienes (furan or cyclopentadiene derivatives[9]).

Captodative olefins **2** belong to a class of dienophiles with a special interest in cycloaddition reactions, due to the interplay of electronic and steric interactions provided by the substituents geminally attached to the olefin, which display an opposite electronic effect.[10,11]

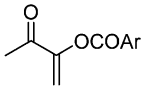

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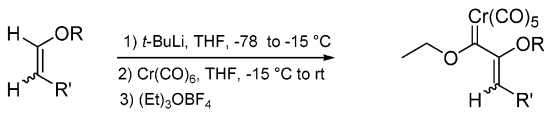
Table 1. Reaction Conditions and Yields in the Preparation of Carbene Complexes 3−6

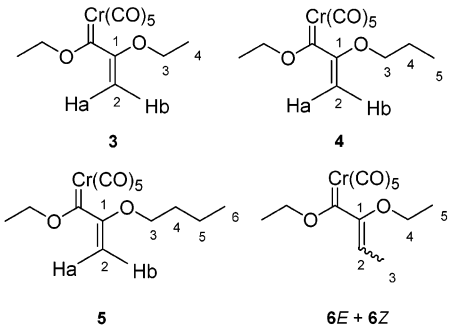


8-11 3-6

vinyl ether	R	R′	carbene (%)
8	Et	H	**3** (47)
9	Pr	H	**4** (46)
10	Bu	H	**5** (39)
11*E* + **11***Z*[b]	Et	Me	**6***E* + **6***Z* (25(*E*)/5(*Z*))[c]

[a] After column chromatography. [b] As a 1:2 mixture, respectively. [c] As a 5:1 mixture, respectively.

In this context, we describe herein the preparation of the new captodative α-alkoxyvinyl(ethoxy)carbene chromium(0) complexes **3**−**6** and the study of their behavior as dienophiles in Diels−Alder cycloadditions with cyclopentadiene (**1**) and pentamethylcyclopentadiene (**7**). It is worth noticing that this is the first time that *captodative olefins derived from metallic carbenes* are used in this type of reaction. In addition, we also carried out an evaluation of how the reactivity and stereoselectivity of the Diels−Alder cycloadditions are affected by structural modifications of the olefinic framework, such as the elongation of the α-alkoxy side chain and the presence of a methyl group in the *β*-position of the double bond.

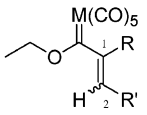


3 **4** **5** **6***E* + **6***Z*

Results and Discussion

Preparation of Complexes 3−6. The pentacarbonyl-α-alkoxyvinyl(ethoxy)carbene chromium(0) complexes **3**−**6** were prepared by the standard Fischer method,[1] to give complexes in moderate yields (Table 1). In the preparation of complexes **6***E* + **6***Z*, the ethyl-1-propenyl ether (**11**) was used as a mixture of *E*/*Z* isomers (1:2 ratio). The separation of this mixture was achieved by column chromatography on silica gel using hexane as eluent. It was possible to obtain a single crystal of complex **6***Z* and carry out the corresponding X-ray diffraction study.

Table 2. Selected ^{13}C NMR Chemical Shifts (*δ* ppm) of α-Alkoxyvinyl



3-6 (M =Cr), **12** (M = W)

carbene[a]	R	R′	C-1	C-2	$C_{carbene}$
3	OEt	H	167.0	82.0	336.4
4	OPr	H	167.2	81.5	336.5
5	OBu	H	167.2	81.5	336.3
6*E*	OEt	Me	160.1	88.8	344.9
6*Z*	OEt	Me	164.8	118.2	338.6
12[b]	Me	H	160.3	121.4	326.7

[a] Determined in $CDCl_3$. [b] Reference 5b.

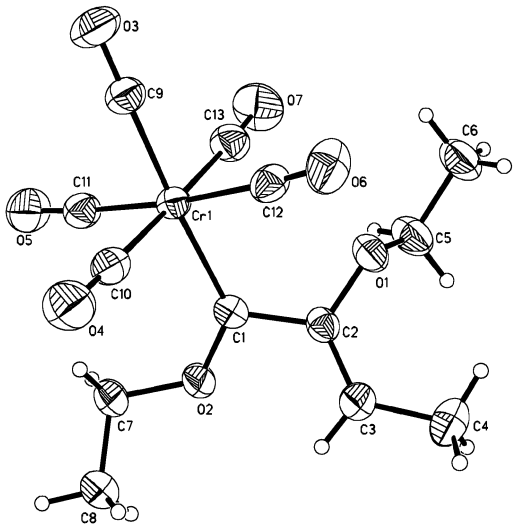


Figure 1. ORTEP diagram of $(CO)_5Cr{=}C[C(=CHCH_3)(OCH_2CH_3)]OCH_2CH_3$ (**6***Z*). Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Cr(1)−C(9) = 1.881(3), Cr(1)−C(10) = 1.894(3), Cr(1)−C(11) = 1.892(3), Cr(1)−C(12) = 1.917(3), Cr(1)−C(13) = 1.906(3), Cr(1)−C(1) = 2.062(2), C(1)−O(2) = 1.318(3), C(1)−C(2) = 1.490(3), C(2)−C(3) = 1.341(4), C(2)−O(1) = 1.377(3), C(3)−C(4) = 1.501(4), C(5)−O(1) = 1.422(3), C(5)−C(6) = 1.490(4), C(7)−O(2) = 1.461(3), C(7)−C(8) = 1.483(4).

It is interesting to notice the large difference in the ^{13}C chemical shifts of the vinylic carbons (C-2) of **6***Z* (118.2 ppm) and **6***E* (88.8 ppm), which could be ascribed to a conformational effect (Table 2). In the **6***E* isomer, the α-alkoxy group is expected to be coplanar with the delocalized system, allowing for delocalization of one of the oxygen lone pairs to the double bond and shifting the chemical shift to higher fields. In the **6***Z* isomer, the presence of the methyl *syn* to this alkoxy group prevents coplanarity, and the oxygen lone pairs are not able to produce the shielding effect on the *β*-carbon and the associated proton.

This hypothesis was confirmed by the X-ray structure of isomer **6***Z* (Figure 1), in which the α-alkoxy group is out of the plane of the conjugated system (torsion angle C(5)−O(1)−C(2)−C3) of 76.4°) with respect to the double bond, and the X-ray structure of the tungsten analogue

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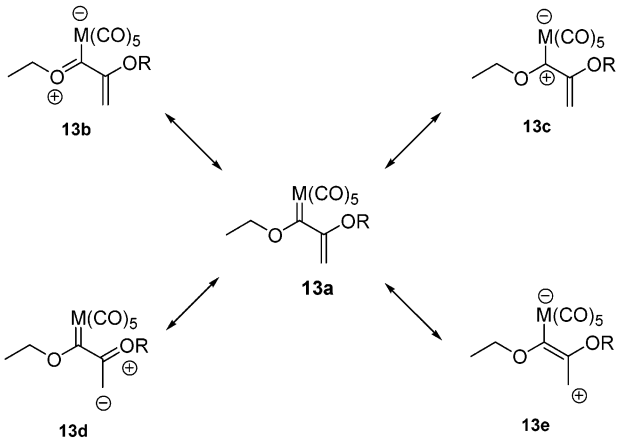
Scheme 1. Resonance Structures 13a−d



of **4**,[12] in which there is no methyl group at C-3, and the α-alkoxy moiety is almost coplanar with the delocalized system (torsion angle C(5)−O(1)−C(2)−C(3) of 27.5°). The presence of the methyl at C-3 in **6***Z* and the twisting of the alkoxy group at C-2 also prevent the carbenic bond from being coplanar with the double bond (torsion angle Cr−C(1)−C(2)−C(3) of 147.8°), which, in turn, can also affect the ^{13}C NMR chemical shift at C-2. In contrast, the torsion angle W−C(1)−C(2)−C(3) in **4** is 172.7°, making the pentacarbonyl chromium moiety a stronger electron-withdrawing group with respect to the double bond. As further proof of the above, Table 2 includes ^{13}C NMR data of the isopropenyl carbene of tungsten **12**,[5b] where the α-substituent is a methyl group. In this molecule, there is no electron donation to carbon C-2, and the corresponding chemical shift is similar to that of **6***Z*.

The purpose of varying the length of the α-alkoxy substituent was to evaluate the steric effect of this substituent on the course of the cycloaddition reaction. It is necessary to mention that we tried to synthesize other vinyl carbenes, such as the *tert*-butyloxy and benzyloxy derivatives, to introduce a larger steric effect; however, our attempts to prepare these complexes were unsuccessful.

In accord with Wulff,[5b] the high reactivity of alkenylcarbene complexes as dienophiles correlates with the electrophilicity of the carbene carbon, expressed by the resonance structures **13a**−**c** (Scheme 1), which control most of the reactivity pattern of these complexes. It was uncertain, however, whether the introduction of the α-alkoxy group would make complexes **3**-**6** reactive enough as dienophiles in Diels−Alder cycloadditions. Mesomeric electron donation from the alkoxy group (**13d**) might make the system less susceptible to a [4+2] cycloaddition under *normal electron demand*, despite the fact that the metal fragment [(CO)$_5$Cr] is activating the alkene (**13e**, Scheme 1).

If the contribution of the resonance structure **13d** is important in these complexes, it would be anticipated that the presence of the α-alkoxy group leads to a decrease in reactivity toward dienes such as cyclopentadiene (**1**) and pentamethylcyclopentadiene (**7**). The former hypothesis would be supported by the chemical shifts of the vinyl carbons shown in Table 2, in which a shielding effect is exhibited by carbon C-2 in comparison with complexes **6***Z* and **12**.[5b]

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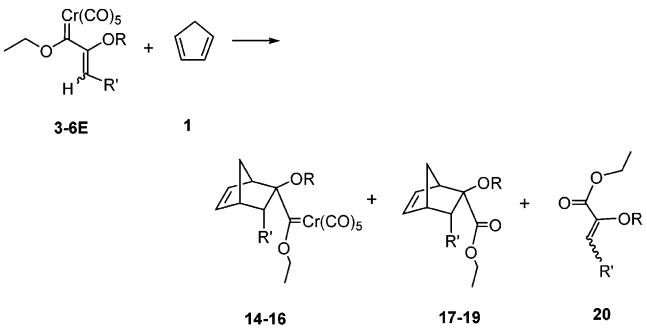
Table 3. Reaction Conditions and Yields in the Diels−Alder Additions of Carbenes 3−6 to 1



carbene	R	R′	time (h)[a]	adduct (%)[b]	ester (%)
3	Et	H	2.5	**14** (35)	**17** (8[c])
4	Pr	H	3.0	**15** (33)	**18** (7[c])
5	Bu	H	4.0	**16** (32)	**19** (7[c])
6*E*	Et	Me	20.0		**20** (65[b])

[a] At room temperature. [b] After column chromatography. [c] Estimated from the ^{1}H NMR spectra of the crude reaction mixtures.

Cycloaddition with Cyclopentadiene (1). The α-alkoxyvinyl(ethoxy)carbene chromium(0) complexes **3**−**6***E* were evaluated in terms of reactivity and stereoselectivity toward cyclopentadiene (**1**) in Diels−Alder reactions. Thus, when a large excess (40 molar equiv) of **1** reacted with α-ethoxyvinyl(ethoxy)carbene complex **3** (25 °C, 2.5 h), only the *endo* cycloadduct **14** was obtained in moderate yield (35%), as judged from ^{1}H NMR analysis (300 MHz) of the crude reaction mixture. Ester **17** was also detected in the reaction mixture (Table 3), which probably originated from oxidation of the *endo* adduct **14**.

A similar behavior was observed in the reaction of the homologous complexes **4** and **5** with cyclopentadiene (**1**), since cycloadducts **15** and **16** were obtained as a single *endo* isomer, in 33% and 32% yield, respectively (Table 3). The moderate yields are in part due to the oxidation of the adducts to the corresponding esters **18** and **19** under the reaction conditions, or in the purification by column chromatography. As shown in Table 3, the reactivity and selectivity of carbenes **4** and **5** are similar to those found for carbene **3**, suggesting an almost negligible effect of the length of the electron-donating group at the transition state. However, the presence of a methyl group in the *β*-position in carbene **6***E* produced a large effect, inhibiting addition to **1** under the same experimental conditions (20 h) and providing only the oxidation ester **20**. This result is in agreement with previous reports that show deactivation of the double bond in Diels−Alder cycloadditions of *β*-substituted captodative olefins.[13] The moderate yields obtained in the reaction of carbene **3** with cyclopentadiene (**1**) were increased when the reaction was carried out at 40 °C. In this case the oxidized adduct **17** was the only product (72% yield).

It has been shown that the presence of an α-methoxy group in acrylates decreases the electron-deficient na-

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ture of the double bond conjugated to the carbonyl group, strongly diminishing their reactivity in Diels−Alder reactions.[14] For example, it has been reported that ethyl α-methoxyacrylate reacts with **1** after 20 h at 150−170 °C, to give 35% of a mixture of the corresponding *endo* and *exo* cycloadducts in a 1:1 ratio.[15] In contrast, the cycloaddition with ethyl acrylate is carried out at room temperature, furnishing an 86:14 *endo*/*exo* mixture of adducts.[16]

On the other hand, cycloaddition of **1** with pentacarbonyl α-methyl vinyl(methoxy)carbene W(0) complex (**12**) gave, after 4 h at 25 °C, 89% yield of a mixture of the corresponding *endo* and *exo* cycloadducts in 59:41 ratio.[5b] The results in Table 3 suggest that despite the presence of the α-alkoxy group in carbenes **3**−**5**, the carbene metal complex fragment greatly offsets the deactivating effect of the electron-releasing alkoxy group. This supports the idea that, from an electronic point of view, the electron-withdrawing group is the dominant factor controlling reactivity and perhaps also selectivity in Diels−Alder additions of captodative dienophiles.[17] However, the exclusive formation of the *endo* isomers in our case contrasts with the usual preference of captodative olefins for the *exo* stereoselectivity.[8,18] This is illustrated, for example, in the case of α-substituted acrylic derivatives, where the *exo* selectivity is enhanced when the size of the α-substituent is increased.[19]

It is likely that the mobility of the alkoxy group attached to the double bond in organometallic olefins **3**−**5** may decrease the repulsive van der Waals interactions with the methylene bridge of the diene when the *endo* transition state is reached. These interactions might be less significant than those generated by the bulky pentacarbonylcarbene chromium group at the *exo* transition state (Figure 2).[20]

The new adduct complexes **14**−**16** were isolated as yellow oils, and their ^{1}H and ^{13}C NMR spectra are consistent with the norbornene skeleton. In addition, they show the presence of a pentacarbonyl(ethoxy)carbene fragment and an alkoxy group. The structural assignment of the *endo* adducts was made on the basis of ^{1}H NMR chemical shifts of the protons at C-3 and decoupling experiments. It is well known that in the *endo* adducts of cyclopentadiene and activated dienophiles, the signal of the *endo* proton is shifted downfield with respect to the *exo* proton.[11,19a,c,d,21] For carbene complexes **14**−**16**, protons H-3n and H-3x appear as a doublet of doublets with an additional smaller coupling: H-3n appears between 2.18 and 1.95 ppm and H-3x between 2.06 and 1.92 ppm (J_{3x-3n} = 12.6−12.0 Hz). Decoupling experiments of adduct **14** provided additional support of the assignment of the *endo* stereochemistry of the adducts; H-3n showed a four-bond coupling (*W*-coupling) to H-7s ($J_{3n,7s}$ = 2.7 Hz), and H-3x had a three-bond coupling to H-4 (J_{3x-4} = 3.7 Hz).[22]

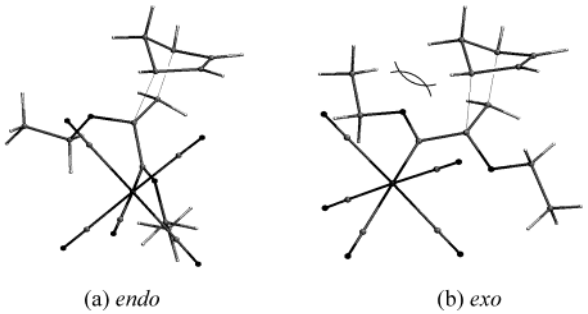

Figure 2. Proposed *endo* and *exo* transition states in the Diels−Alder reaction of cyclopentadiene (**1**) and organometallic dienophile **3**, showing steric congestion disfavoring the *exo* adduct.

The stereochemical assignment was further confirmed by treatment of complex **14** with ceric ammonium nitrate (CAN) at room temperature in acetone, to afford compound **17** in 53% yield, as a yellow oil. The ^{1}H and ^{13}C NMR spectra were consistent with the expected structure. The ^{13}C NMR spectrum of **17** showed the presence of the carbonyl ester group at 172.8 ppm. In the ^{1}H NMR spectrum, the signal of proton H-3n was observed at 1.94 ppm, shifted downfield with respect to the H-3x proton (1.75 ppm). The relative configuration at C-2 was supported by NOE experiments, where an enhancement of the signal of proton H-3x was observed when H-8 was irradiated (Figure 3).

In view of the high *endo* selectivity of the Diels−Alder reaction of carbene complexes **3**−**6***E* with **1**, we also evaluated the effect of the α-alkoxy substituents in these complexes on reactivity and facial stereoselectivity with 1,2,3,4,5-pentamethylcyclopentadiene (**7**). Thus, when the pentacarbonyl-α-ethoxyvinyl(ethoxy)carbene Cr(0) complex **3** reacted with **7** at 40 °C for 12 h, only complex **21** was obtained in 62% yield, as judged from ^{1}H NMR (300 MHz) analysis of the crude reaction mixture (Table 4).

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(20) We attempted to carry out molecular orbital calculations in order to locate the transition states of these reactions. However, even with semiempirical models (PM3) we had problems with the convergence of the wave function. We were unable to carry out any optimizations, even of the products or the carbenes themselves. The drawings that we present here (Figures 2 and 5) were made by molecular mechanics optimization using the Sybyl force field as implemented in the MacSpartan program package. The distances between C-1 and C-4 of the cyclopentadienes and C-2 and C-3 of the dienophile were fixed at 2.55 and 1.85 Å, respectively. The figures are only intended to be approximate representations of the real transition states and to show the important interactions involved in determining the stereoselectivity of these processes.
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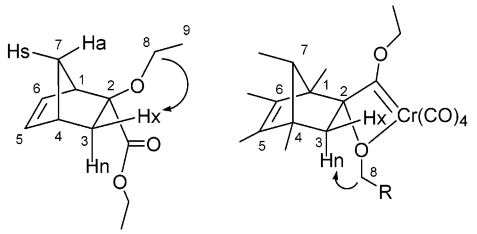
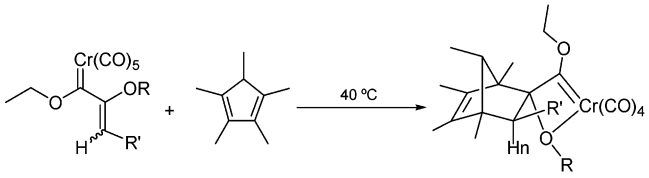


17 **21** R = Me
22 R = Et
23 R = Pr

Figure 3. NOE observed upon irradiation of protons H-8 for adducts **17** and **21**−**23**.

Table 4. Reaction Conditions and Yields in the Formation of Cycloadducts 21−24



3-6*E* **7** **21-24**

carbene	R	R′	time (h)	adduct (%)
3	Et	H	10	**21** (62)
4	Pr	H	12	**22** (60)
5	Bu	H	36	**23** (24)
6*E*	Et	Me	144	**24** (25)

The mass spectra indicate that this new complex is the result of the cycloaddition of **7** and complex **3**, with chelation between the oxygen atom of the α-ethoxy group and the metal fragment, which has lost one CO ligand. Its ^{1}H NMR spectra show the presence of one ethoxy group with two magnetically different OCH_2 protons (H-8a and H-8b), which appear as multiplets at 2.95 and 3.10 ppm. The ^{13}C NMR spectra show signals due to four nonequivalent CO groups at 217.7, 217.9, 231.0, and 231.8 ppm; the signal of $C_{carbenic}$ at 351.6 ppm; and the signal for C-8 at 68.4 ppm.[22] Chelate formation is suggested by the characteristic downfield signals of OCH_2-8 in both the ^{1}H NMR and ^{13}C NMR spectra, indicating the oxonium character of the metal-coordinated oxygen atom.

The structure of complex **21** was confirmed by an X-ray diffraction study, which showed that the *exo* adduct formed the four-membered ring system of the internal chelate (Figure 4). The oxygen atom O(1) of the α-ethoxy group occupies the sixth coordination site of the tetracarbonyl chromium fragment *cis* to the carbene ligand, resulting in a distorted octahedral coordination geometry. Due to the formation of the four-membered ring, the C(10)−Cr−O(1) angle is reduced to 64.67 (12)° and the *cis* CO groups are slightly bent away from the chelate ligand. The metallacycle thus formed is essentially planar, with the largest ring torsion angle (Cr−O(1)−C(2)−C(10)) being 7.4°. The C(10)−Cr−O(1) angle is rather small, 64.7°, while the Cr−C(10)−C(2) angle is 104.2°. The other two internal ring angles are close to 95°. The bond length between the chromium atom and the carbenic carbon is 1.947 Å, while the Cr−O(1) distance is 2.194 Å. The oxygen atom directly bonded to the carbenic carbon is sp^2 hybridized, with a C(11)−O(2)−C(10) angle of 118.8°. The high level of conjugation of O(2) with the carbenic carbon is confirmed by the

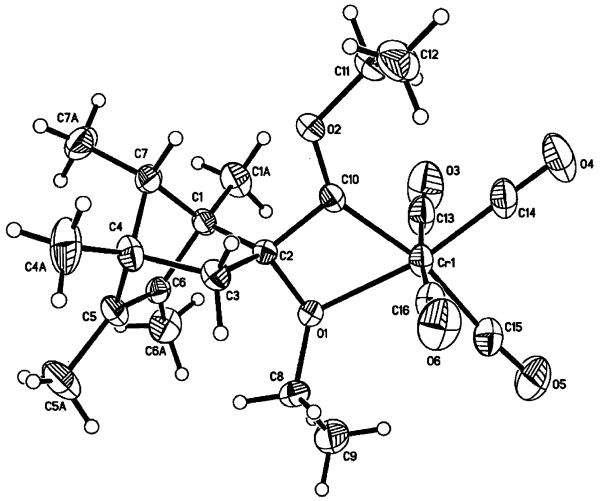


Figure 4. ORTEP diagram of (1*R**,2*R**,4*S**,7*S**)-*cis*-tetracarbonyl{2-ethoxy-1,4,5,6,7-pentamethylbicyclo[2.2.1]-hept-5-enyl(ethoxy)carbene}chromium(0) (**21**). Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Cr(1)−C(14) = 1.809(5), Cr(1)−C(15) = 1.887(5), Cr(1)−C(5) = 1.892(5), Cr(1)−C(13) = 1.903(5), Cr(1)−C(10) = 1.947(4), Cr(1)−O(1) = 2.194(2).

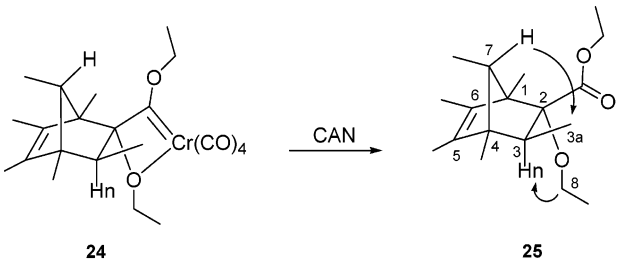
short C(10)−O(2) distance (1.314 Å) and the C(11)−O(2)−C(10)−C(2) torsion angle of 179.8°. On the other hand, the oxygen O(1) coordinated to the chromium atom is pyramidalized, with the sum of the valence angles being 337.9°.

A comparable behavior was observed in the reactions of complexes **4** and **5** with 1,2,3,4,5-pentamethylcyclopentadiene (**7**), which gave only the *exo* adducts **22** and **23** (Table 4). The more substituted complex **6***E* reacted more slowly than **3**, **4**, or **5**, requiring 144 h to yield adduct **24**. The *exo* stereoselectivity observed in adducts **21**−**24** does not seem to be affected either by elongation of the chain on the α-alkoxy group or by the presence of a methyl group in the *β*-position in complex **6***E*; only the time of reaction is affected. However, the low yields and longer reaction times employed in the cycloadditions of **5** and **6***E* might be explained in terms of the lesser stability of **5** in comparison with **3** and **4** (which is evidenced by the lower yields obtained in its preparation). In the case of **6***E*, it has been previously mentioned (vide supra) that the *β*-methyl substituent lowers the reactivity of these captodative alkenes. The longer reaction time can increase the possibility of its decomposition. A good amount of the esters derived from the oxidation of **5** and **6***E* was observed in the reaction crudes by NMR. The chelate cycloadducts **21**−**24** are quite resistant to oxidation.

The stereochemistry of the chelated adducts **22** and **23** was assigned by analogy with the ^{1}H NMR, ^{13}C NMR, and MS spectra of **21**.[22] NOE experiments carried out on **21**−**24** showed an increment of the signals of proton H-3n upon irradiation of methylene OCH_2-8 (Figure 3).

The stereochemistry of **24** was established by oxidation of the alkoxy-chelated complex with CAN (acetone, 25 °C, 3 h) to provide compound **25** in 40% yield, as a yellow oil (Scheme 2). NOESY experiments carried out for compound **25** showed an interaction of the signals of protons H-3n and Me-1a with the signal assigned to

Scheme 2. Oxidation of 24 and NOE Observed upon Irradiation of Protons H-7 and H-8 for 25



24 **25**

methylene OCH_2-8b. In addition, an observable enhancement of the signal of Me-3a was recorded upon irradiation of the signal of proton H-7.

The isolation of the chelated adducts **21**−**24** might suggest that chelation takes place in the dienophile before the cycloaddition. However, when the carbene used as starting material was heated to 40 °C under the same reaction conditions, in the absence of diene, no chelation of the α-ethoxy group to the metal was observed under these conditions, ruling out cycloaddition to the chelated species.

Diene **7** has been widely used to evaluate facial stereoselectivity with a variety of olefins.[23] Thus, in the reaction with cyclic dienophiles, such as maleic anhydride, the *anti-endo* adduct is the major stereoisomer.[24] Analogous stereoselectivity and facial selectivity were observed with the less reactive and acyclic dienophile methyl acrylate, although the *anti-exo* isomer was also isolated in a small proportion.[25] The facial selectivity has been accounted for as a result of electronic effects of the substituents on the methylene bridge of the diene.[23a,25] In accord with this model, in the presence of electron-donor groups, such as the methyl group, an *anti* preference is predicted. Nevertheless, the steric effect seems to play an important role as well.[23a,24,27] The *anti* facial selectivity of olefins **3**−**6***E* could also be controlled by the steric hindrance produced by the geminally substituted double bond and the methyl group on the methylene bridge (Figure 5).[20]

The preferred *exo* orientation of the carbene chromium complexes **3**−**6***E* with pentamethylcyclopentadiene (**7**) is unexpected, since organic dienophiles afford the opposite stereoselectivity.[23a,24]

The stereoselectivity observed in the cycloadditions of the carbene complexes **3**−**6***E* with cyclopentadiene (**1**) and pentamethylcyclopentadiene (**7**) could be explained in terms of a combination of several factors affecting the stability of the corresponding transition states: (a) the repulsive van der Waals interactions of

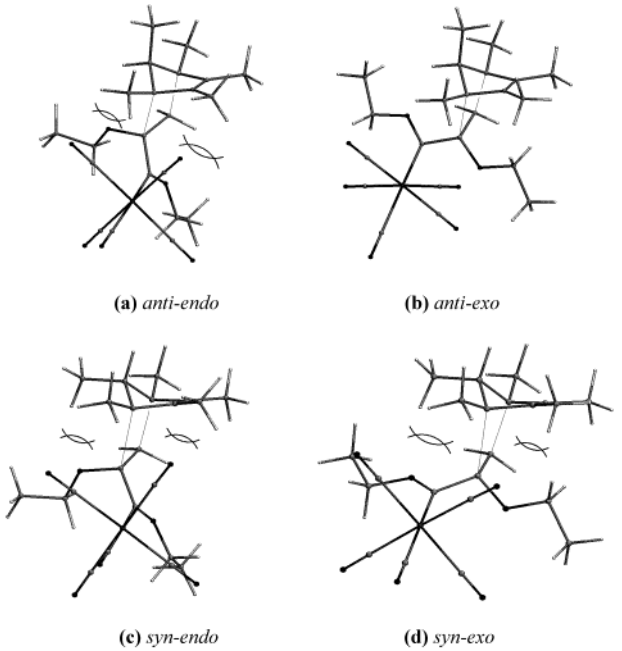


Figure 5. Proposed *endo* and *exo* transition states in the Diels−Alder reaction of pentamethylcyclopentadiene (**7**) and organometallic dienophile **3**, showing steric congestion favoring the a*nti-exo* adduct.

the pentacarbonyl chromium moiety, which is expected to be stronger in the *endo* transition states (Figure 5a,c); (b) the steric effects of the methylene bridge in both dienes and, in the case of **7**, the methyl substituents of the ring (Figures 2 and 5); (c) the known repulsive effect of the heteroatom of the α-alkoxy group, which is expected to destabilize the *exo* transition states (Figures 2 and 5);[28] (d) the presence of the methyl at C-5 in **7**, which would be expected to polarize the *anti* face of the diene, making it more electron-rich, thus favoring the *anti* transition states (Figure 5a,b vs 5c,d).

It is likely that in the cycloadditions with cyclopentadiene **1** (Figure 2) the repulsive interaction between the oxygen of the α-alkoxy group and the diene and the steric repulsion between the methylene bridge and the carbene molecule would destabilize more the *exo* transition state than the steric repulsion of the diene with the metal moiety at the *endo* transition state would. In the cycloadditions with pentamethylcyclopentadiene (**7**) (Figure 5), the *anti* transition states would be stabilized with respect to the *syn* by two factors: (i) the *anti* face would be richer in electron density, and (ii) the methyl at C-5 would offer a stronger repulsive interaction with the dienophile.[29] In addition, the *exo* transition state would be favored with respect to the *endo* because, in the latter, there is a very strong repulsive interaction between the metal moiety and the methyls of the diene, which is apparent in Figure 5a,c.

Conclusions

In summary, we described the preparation of new and stable α-alkoxyvinyl(ethoxy)carbene Cr(0) complexes **3**−**6***E*. These novel organometallic captodative olefins behave as reactive dienophiles, showing a high *endo*

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selectivity with cyclopentadiene (**1**) and an *anti*/*exo* stereofacial selectivity with pentamethylcyclopentadiene (**7**) in Diels−Alder cycloadditions. Both reactivity and selectivity may be associated with dominant electronic and steric effects, respectively, of the electron-withdrawing carbene group.

Experimental Section

All reactions, except oxidation reactions, were carried out under nitrogen in anhydrous solvent. All glassware was either flamed under vacuum or dried in an oven prior to use. All commercially available compounds were used without further purification. Melting points are not corrected. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under N_2 atmosphere prior to use. *n*-Hexane and ethyl acetate were distilled before use. ^{1}H NMR and ^{13}C NMR experiments were performed at 300 MHz (^{1}H at 300 MHz and ^{13}C at 75.4 MHz) or 500 MHz (^{1}H at 500 MHz and ^{13}C at 125 MHz) using TMS as internal reference. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). High-resolution mass spectrometry (HRMS) was conducted under 70 eV electron impact ionization. X-ray data were collected using Mo Kα radiation (graphite crystal monochromator, λ = 71073 Å). TLC analyses were performed using silica plates and were visualized using UV (254 nm) or iodine. Cyclopentadiene (**1**) was obtained from distillation of dicyclopentadiene at atmospheric pressure and collected at 40−40.5 °C. *tert*-Butyllithium (1.7 M in hexane) was purchased.

General Procedure: Preparation of Pentacarbonyl[α-alkoxyvinyl(ethoxy)carbene]chromium(0) Complexes 3−6. To a solution of the corresponding alkyl vinyl ether (**8**−**11**) (12.49 mmol) in dry THF (25 mL) at −78 °C was cautiously added *tert*-butyllithium in hexane (7.26 mL, 1.7 M, 12.49 mmol). After stirring for 30 min at −5 °C, the mixture was transferred via cannula into a slurry of chromium hexacarbonyl (2.5 g, 11.36 mmol) in 100 mL of THF at −78 °C. After stirring for 2 h at room temperature, the solvent was removed under vacuum. The residue was dissolved in 25 mL of ethyl acetate, hexane (50 mL), and water (100 mL), and then triethyloxonium tetrafluoroborate was added in small portions (2.2 g, 11.36 mmol or until pH = 6). The organic layer instantaneously turned red. The reaction mixture was extracted with *n*-hexane. The organic layer was washed with a saturated sodium bicarbonate solution (150 mL), water (300 mL), and brine solution (150 mL) and dried over sodium sulfate. The solvent was removed under vacuum at room temperature, and final purification was carried out by chromatography on silica gel using *n*-hexane, to afford the corresponding carbene complexes **3**−**6**.

General Procedure for the Diels−Alder Reaction of Pentacarbonyl[α-alkoxyvinyl(ethoxy)carbene]chromium(0) Complexes 3, 4, 5, and 6*E* with Cyclopentadiene (1). A solution of the corresponding α-alkoxyvinyl(ethoxy)carbene complexes **3**−**6***E* (0.625 mmol) in cyclopentadiene (**1**) freshly distilled (1.65 g, 25 mmol) was deoxygenated by the freeze−thaw method (−78 to 0 °C, 3 cycles), then was allowed to warm slowly from −78 °C to room temperature. After 2.5−40 h the excess of cyclopentadiene was removed under vacuum. The residue was purified by column chromatography on silica gel using hexane/EtOAc (7:3) as eluent, to afford the corresponding cycloadducts **14**−**16**.

General Procedure for the Diels−Alder Reaction of Pentacarbonyl[α-alkoxyvinyl(ethoxy)carbene]chromium(0) Complexes 3, 4, 5, and 6*E* with 1,2,3,4,5-Pentamethylcyclopentadiene (7). A solution of the corresponding α-alkoxyvinyl(ethoxy)carbene complexes **3**−**6***E* (1.0 mmol) in 1,2,3,4,5-pentamethylcyclopentadiene (**7**) (20 mmol) was deoxygenated by the freeze−thaw method (−78 to 0 °C, 3 cycles), then the mixture was warmed at 40 °C and stirred. After 10−144 h the excess of **7** was removed under vacuum. The residue was purified by column chromatography on silica gel using hexane/EtOAc (7:3) as eluent, to afford the corresponding cycloadducts **21**−**24**.

Oxidation of the Adducts 14 and 24. A sample (0.08 g, 0.20 mmol) of chromium adduct **14** was dissolved in acetone (8 mL) and added to a solution of 0.170 g (0.31 mmol) of $(NH_4)_2Ce(NO_3)_6$ in 11 mL of dry acetone. After stirring for 1 h at room temperature, the solvent was removed; the residue was dissolved in 25 mL of water and extracted with ethyl ether (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated. After column chromatography on silica gel, 0.023 g (53%) of **17** was isolated as a yellow oil. Oxidation of **24** by the same methodology gave 0.020 g (40%) of **25** as a yellow oil.

Pentacarbonyl[α-ethoxyvinyl(ethoxy)carbene]chromium(0) (3). Following the general procedure with **8** (1.2 mL, 12.49 mmol) afforded 1.67 g (47%) of **3** as a red solid: mp 42−43 °C; IR ($CHCl_3$) 2062, 1986, 1932 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (t, J = 7.1 Hz, 3H), 1.65 (t, J = 7.1 Hz, 3H), 3.87 (q, J = 7.1 Hz, 3H), 3.88 (d, J = 2.3 Hz, 1H), 4.47 (d, J = 2.3 Hz, 1H), 5.18 (q, J = 7.1 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.3, 16.1, 65.0, 77.0, 82.0, 167.0, 216.4, 225.0, 336.4; MS (70 eV), *m*/*z* (%) 320 ($M^{+\bullet}$, 48), 292 (59), 264 (100), 236 (58), 208 (99), 180 (44); HRMS (FAB) calcd for $C_{12}H_{12}O_7Cr^{52}$ 319.9988, found (MH^+) 321.9973.

Pentacarbonyl[α-propoxyvinyl(ethoxy)carbene]chromium(0) (4). Following the general procedure with **9** (1.5 mL, 12.49 mmol) afforded 1.2 g (46%) of **4** as a red solid: mp 41−42 °C; IR ($CHCl_3$) 2063, 2019, 1982 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (t, J = 6.6 Hz, 3H), 1.68 (t, J = 7.2 Hz, 3H), 1.94 (sext., J = 6.6 Hz, 2H), 3.76 (t, J = 6.6 Hz, 2H), 3.92 (d, J = 2.3 Hz, 1H), 4.45 (d, J = 2.3 Hz, 1H), 5.18 (q, J = 7.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.8, 15.1, 22.0, 70.7, 76.9, 81.5, 167.2, 216.6, 224.8, 336.5; MS (70 eV), *m*/*z* (%) 334 ($M^{+\bullet}$, 40), 306 (37), 278 (99), 250 (71), 222 (100), 194 (51); HRMS (FAB) calcd for $C_{13}H_{14}O_7Cr^{52}$ 334.24, found (MH^+) 335.0130.

Pentacarbonyl[α-butoxyvinyl(ethoxy)carbene]chromium(0) (5). Following the general procedure with **10** (1.6 mL, 12.49 mmol) afforded 1.54 g (39%) of **5** as a red oil: IR ($CHCl_3$) 2065, 20259, 1982 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 3H), 1.48−1.57 (m, 2H), 1.66 (t, J = 7.2 Hz, 3H), 1.87 (quint., J = 7.0 Hz, 2H), 3.78 (t, J = 7.0 Hz, 2H), 3.86 (br d, J = 2.3 Hz, 1H), 4.43 (br d, J = 2.3 Hz, 1H), 5.15 (q, J = 7.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.8, 15.1, 19.4, 30.7, 68.8, 76.9, 81.5, 167.2, 216.6, 224.8, 336.3; MS (70 eV), *m*/*z* (%) 348 ($M^{+\bullet}$, 25), 320 (23), 292 (60), 264 (50), 236 (100), 208 (50); HRMS (FAB) calcd for $C_{14}H_{16}O_7Cr^{52}$ 348.0325, found (MH^+) 349.0146.

(*E*)-Pentacarbonyl[α-ethoxypropenyl(ethoxy)carbene]chromium(0) (6*E*) and (*Z*)-Pentacarbonyl[α-ethoxypropenyl(ethoxy)carbene]chromium(0) (6*Z*). Following the general procedure with **11***E* + **11***Z* (ratio 2:1) (1.4 mL, 12.49 mmol) afforded 0.95 g (25%) of **6***E* as a red oil and 0.18 g (5%) of **6***Z* as a red solid, mp 30−31 °C. Data of **6***E*: IR ($CHCl_3$) 2064, 1992, 1950 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, J = 7.0 Hz, 3H), 1.55 (d, J = 7.2 Hz, 3H), 1.65 (t, J = 7.0 Hz, 3H), 3.80 (q, J = 7.0 Hz, 2H), 4.30 (q, J = 7.2 Hz, 1H), 4.90 (br s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 14.2, 14.9, 63.5, 76.6, 88.8, 160.1, 216.2, 224.7, 344.9; MS (70 eV), *m*/*z* (%) 334 ($M^{+\bullet}$, 12), 306 (17), 278 (20), 250 (10), 222 (41), 194 (100), 165 (11), 150 (41), 137 (14), 96 (72), 52 (50); HRMS (FAB) calcd for $C_{13}H_{14}O_7Cr^{52}$ 334.242, found (MH^+) 335.0146. Data of **6***Z*: IR ($CHCl_3$) 2060, 1988, 1942 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3H), 1.65 (t, J = 7.0 Hz, 3H), 1.82 (d, J = 7.1 Hz, 3H), 3.70 (q, J = 7.1 Hz, 2H), 5.00 (q, J = 7.0 Hz, 2H), 5.70 (q, J = 7.1 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 15.1, 15.2, 68.0, 76.9, 118.2, 164.8, 216.7, 224.2, 338.6; MS (70 eV), *m*/*z* (%) 334 (M^+, 13), 306 (23), 278 (31), 250 (17), 222 (44), 194 (100), 96 (96), 52 (72); HRMS (FAB) calcd for $C_{13}H_{14}O_7Cr^{52}$ 334.2422, found (MH^+) 334.0131.

(1*R,2*S**,4*R**)-*endo*-Pentacarbonyl{2-ethoxybicyclo-[2.2.1]hept-5-enyl (ethoxy)carbene}chromium(0) (14).** The general procedure was followed using carbene complex **3** (0.2 g, 0.62 mmol) and **1** (1.65 g, 25 mmol) as starting materials, affording 0.084 g (35%) of **14** as a yellow oil: IR ($CHCl_3$) 2060, 1983, 1942 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 0.92 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.0 Hz, 3H), 1.44 (br d, J = 8.4, 1H), 1.83 (br d, J = 8.4, 1H), 1.92 (dd, J = 12.6, 3.3 Hz, 1H), 1.95 (dd, J = 12.6, 2.1 Hz, 1H), 2.50 (br s, 1H), 2.82−2.92 (m, 1H), 3.02 (br s, 1H), 3.08−3.18 (m, 1H), 4.47−4.56 (m, 2H), 5.58 (dd, J = 5.4, 2.7, 1H), 5.95 (dd, J = 5.4, 2.7, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.1, 15.6, 41.0, 41.2, 47.5, 49.6, 59.7, 78.3, 101.6, 132.7, 140.9, 216.8, 223.8, 362.8; MS (70 eV), *m*/*z* (%) 386 ($M^{+\bullet}$, 10), 358 (20), 330 (60), 302 (53), 274 (100), 246 (36); HRMS (FAB) calcd for $C_{17}H_{18}O_7Cr$[52] 386.3167, found (MH^+) 387.0246.

(1*R,2*S**,4*R**)-*endo*-Pentacarbonyl{2-propoxybicyclo-[2.2.1]hept-5-enyl (ethoxy)carbene}chromium(0) (15).** The general procedure was followed using carbene complex **4** (0.2 g, 0.59 mmol) and **1** (1.58 g, 23.9 mmol) as starting materials, affording 0.08 g (33%) of **15** as a yellow oil: IR ($CHCl_3$) 2059, 1983, 1935 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 3H), 1.54 (d, J = 7.75 Hz, 1H), 1.61 (sext., J = 7.1 Hz, 2H), 1.68 (t, J = 6.8 Hz, 3H), 1.92 (d, J = 7.75 Hz, 1H), 2.06 (dd, J = 12.0, 3.3 Hz, 1H), 2.15 (dd, J = 12.0, 2.7 Hz, 1H), 2.81 (br s, 1H), 2.95−3.05 (m, 1H), 3.22 (br s, 1H), 3.20−3.25 (m, 1H), 5.06 (q, J = 6.8 Hz, 2H), 5.75 (dd, J = 5.6, 2.3 Hz, 1H), 6.20 (dd, J = 5.6, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.5, 15.1, 23.4, 41.2, 41.2, 47.3, 49.3, 65.8, 78.2, 102.0, 132.6, 141.0, 216.7, 223.3, 362.8; MS (70 eV), *m*/*z* (%) 400 ($M^{+\bullet}$, 13), 372 (27), 344 (30), 316 (36), 288 (36), 260 (73), 202 (55), 176 (100); HRMS (FAB) calcd for $C_{18}H_{20}O_7Cr$[52] 400.3433, found (MH^+) 401.0646.

(1*R,2*S**,4*R**)-*endo*-Pentacarbonyl{2-butoxybicyclo-[2.2.1]hept-5-enyl (ethoxy)carbene}chromium(0) (16).** The general procedure was followed using carbene complex **5** (0.2 g, 0.57 mmol) and **1** (1.52 g, 23 mmol) as starting materials, affording 0.075 g (32%) of **16** as a yellow oil: IR ($CHCl_3$) 2060, 1983, 1942 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.35 (sext., J = 7.2 Hz, 2H), 1.62−1.53 (m, 3H), 1.68 (t, J = 7.2 Hz, 3H), 1.91 (d, J = 8.1 Hz, 1H), 2.05 (dd, J = 12.3, 3.9 Hz), 2.18 (dd, J = 12.3, 2.5 Hz), 2.81 (br s, 1H), 2.99−3.07 (m, 1H), 3.21 (br s, 1H), 3.26−3.34 (m, 1H), 5.07 (q, 2H, J = 7.2 Hz), 5.75 (dd, J = 5.3, 3.0 Hz, 1H), 6.21 (dd, J = 5.3, 3.0 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 15.1, 19.2, 32.2, 41.1, 41.6, 47.4, 49.3, 64.0, 78.2, 101.5), 132.6, 141.0, 216.8, 223.4, 362.8; MS (70 eV), *m*/*z* (%) 414 ($M^{+\bullet}$, 9), 386(22), 358 (36), 330 (38), 302 (34), 274 (100); HRMS (FAB) calcd for $C_{13}H_{14}O_7Cr$[52] 414.3699, found (MH^+) 415.0778.

(1*R,2*R**,4*S**,7*S**)-*cis*-Tetracarbonyl{2-ethoxy-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-enyl(ethoxy)carbene}-chromium(0) (21).** The general procedure was followed using carbene complex **3** (0.3 g, 0.94 mmol) and **7** (2.5 g, 18.8 mmol) as starting materials. After chromatography on silica gel, 0.25 g (62%) of **21** was obtained as a red solid, mp 123−124 °C: IR ($CHCl_3$) 2018, 1927, 1909, 1830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.47 (d, J = 6.4 Hz, 3H), 1.00 (s, 3H), 1.05 (s, 3H), 1.15 (t, J = 7.1, 3H), 1.48 (s, 3H), 1.50 (s, 3H), 1.57 (d, J = 13.7 Hz, 1H), 1.65 (t, J = 7.1 Hz, 3H), 1.89−2.05(m, 2H), 2.95−2.99 (m, 1H), 3.10−3.16 (m, 1H), 5.05 (q, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.0, 10.3, 10.5, 11.8, 14.5, 14.7, 14.8, 41.5, 52.3, 56.6, 65.3, 68.4, 76.9, 118.6, 133.3, 138.2, 217.7, 217.9, 231.0, 231.8, 351.6; MS (70 eV), *m*/*z* (%) 428.43 ($M^{+\bullet}$, 5), 400 (6), 372 (4), 344 (15), 316 (29), 232 (100). Anal. Calcd for $C_{21}H_{28}O_6Cr$:[52] C, 58.87; H, 6.59. Found: C, 58.57; H, 6.66.

(1*R,2*R**,4*S**,7*S**)-*cis*-Tetracarbonyl{2-propoxy-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-enyl(ethoxy)carbene}-chromium(0) (22).** The general procedure was followed using carbene complex **4** (0.3 g, 0.89 mmol) and **7** (2.4 g, 17.8 mmol) as starting materials. After chromatography on silica gel, 0.23 g (60%) of **22** was obtained as a red solid, mp 86−87 °C: IR ($CHCl_3$) 2013, 1922, 1893, 1848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.47 (d, J = 6.2 Hz, 3H), 0.81 (t, J = 7.4 Hz, 3H), 1.00 (s, 3H), 1.04 (s, 3H), 1.32−1.36 (m, 1H), 1.48 (s, 3H), 1.49 (s, 3H), 1.58 (d, J = 13.7 Hz, 1H), 1.65 (t, J = 7.1 Hz, 3H), 1.78−1.82 (m, 1H), 1.92−1.96 (m, 2H), 2.82−2.93 (m, 2H), 5.01 (q, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.9, 9.4, 10.2, 10.5, 11.8, 14.5, 14.8, 22.0, 41.4, 52.3, 56.7, 65.3, 74.4, 77.2, 118.9, 133.2, 138.2, 217.6, 217.9, 230.8, 231.8, 351.6; MS (70 eV), *m*/*z* (%) 442 ($M^{+\bullet}$, 4), 414 (10), 386 (8), 358 (13), 330 (29), 246 (100). Anal. Calcd for $C_{22}H_{30}O_6Cr$:[52] C, 59.72; H, 6.83. Found C, 59.05; H, 6.44.

(1*R,2*R**,4*S**,7*S**)-*cis*-Tetracarbonyl{2-buthoxy-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-enyl(ethoxy)carbene}-chromium(0) (23).** The general procedure was followed using carbene complex **5** (0.3 g, 0.86 mmol) and **7** (2.4 g, 17.8 mmol), as starting materials. After chromatography on silica gel, 0.01 g (24%) of **23** was obtained as a red solid, mp 63−64 °C: IR (KBr) 2017, 1909, 1875 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.47 (d, J = 6.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 1.01 (s, 3H), 1.04 (s, 3H), 1.15−1.40 (m, 2H), 1.48 (s, 3H), 1.49 (s, 3H), 1.57 (d, J = 13.7 Hz, 1H), 1.65 (t, J = 7.1 Hz, 3H), 1.75−1.85 (m, 1H), 1.93−1.98 (m, 2H), 2.82−2.90 (m, 1H), 2.92−3.05 (m, 1H), 5.01 (q, J = 7.1 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 7.0, 10.3, 10.6, 12.0, 13.9, 14.6, 14.9, 18.7, 29.7, 41.8, 52.3, 56.7, 65.3, 73.1, 77.2, 118.8, 133.2, 138.1, 217.6, 217.9, 230.8, 231.9, 351.6; MS (70 eV), *m*/*z* (%) 456 ($M^{+\bullet}$, 6), 428 (13), 400 (12), 372 (18), 342 (29), 246 (100). Anal. Calcd for $C_{23}H_{32}O_6Cr$:[52] C, 60.51; H, 7.07. Found: C, 61.35; H, 7.55.

(1*R,2*R**,3*S*,4*R**,7*S**)-*cis*-Tetracarbonyl{2-ethoxy-1,3,4,5,6,7-hexamethylbicyclo[2.2.1]hept-5-enyl(ethoxy)-carbene}chromium(0) (24).** The general procedure was followed using carbene complex **6***E* (0.3 g, 0.89 mmol) and **7** (2.4 g, 17.8 mmol) as starting materials. After chromatography on silica gel, 0.01 g (25%) of **24** was obtained as a red solid, mp 82−83 °C, yield (0.01 g, 25%): IR ($CHCl_3$) 2012, 1922, 1893, 1848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.48 (d, J = 6.4 Hz, 3H), 0.88 (s, 1H), 1.03 (s, 3H), 1.06 (d, J = 7.2, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.49 (s, 3H), 1.52 (s, 3H), 1.69 (t, J = 7.1 Hz, 3H), 2.10 (q, J = 6.4 Hz, 1H), 2.37 (q, J = 7.2 Hz, 1H), 3.00−3.11 (m, 1H), 3.18−3.27 (m, 1H), 5.03 (q, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.0, 10.0, 10.9 11.5, 11.7, 13.6, 14.7, 15.0, 44.2, 52.4, 54.6, 64.0, 67.4, 77.3, 120.4, 133.0, 139.1, 217.8, 219.7, 230.7, 231.5, 353.9; MS (70 eV), *m*/*z* (%) 442 (M^+, 4), 414 (10), 386 (8), 358 (13), 330 (29), 246 (100). Anal. Calcd for $C_{22}H_{30}O_6Cr$:[52] C, 59.72; H, 6.83. Found: C, 60.24; H, 7.22.

(1*R,2*S**,4*R**)-*endo*-2-Ethoxybicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Ethyl Ester (17).** A sample (0.08 g, 0.20 mmol) of chromium adduct **14** was dissolved in acetone (8 mL) and added to a solution of 0.170 g (0.31 mmol) of $(NH_4)_2Ce(NO_3)_6$ in 11 mL of dry acetone. After stirring for 1 h at room temperature, the solvent was removed, and the residue was dissolved in 25 mL of water and extracted with ethyl ether (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated, giving 0.023 g (53%) of **17** as a yellow oil: IR ($CDCl_3$) 2978.0, 1733.9, 1446.5, 1261.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (t, J = 7.0 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.60−1.68 (m, 1H), 1.75 (dd, J = 12.4, 3.6 Hz, 1H), 1.92 (d, J = 8.4 Hz, 1H), 1.94 (dd, J = 12.4, 3.0 Hz, 1H), 2.90 (br s, 1H), 3.11 (br s, 1H), 3.38−3.53 (m, 2H), 4.18−4.27 (m, 2H), 5.91 (dd, J = 5.6, 2.8 Hz, 1H), 6.33 (dd, J = 5.6, 2.8 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.3, 16.6, 38.0, 42.4, 48.6, 51.2, 61.6, 62.0, 89.3, 133.1, 142.0, 172.8. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 67.34; H, 8.52.

(1*R,2*R**,3*S**,4*R**,7*S**)-2-Ethoxy-1,3,4,5,6,7-hexamethylbicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Ethyl Ester (25).** Following the method of preparation of **17**, using carbene complex **24** (0.75 g, 1.69 mmol), afforded 0.020 g (40%) of **25** as a yellow oil: IR ($CHCl_3$) 2929, 2875, 1726, 1448, 1377, 1226, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.50 (d, J = 6.5 Hz, 3H), 0.89 (s, 3H), 0.98 (d, J = 7.6 Hz, 3H), 0.99 (s, 3H), 1.03 (t, J = 6.9 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.53 (q, J = 1.1 Hz, 1H), 1.56 (q, J = 1.1 Hz, 1H), 1.67 (q, J = 7.6 Hz, 1H), 2.39 (q,

Table 5. Crystal Structure Determination of 6*Z* and 21

	6*Z*	**21**
formula	$C_{13}H_{14}CrO_7$	$C_{21}H_{28}CrO_6$
fw	334.24	428.43
cryst syst	monoclinic	orthorhombic
temp (K)	293(2)	293(2)
space group	$P2(1)/n$	$P2_12_12_1$
a (Å)	7.2783(6)	9.7402(11)
b (Å)	11.9761(9)	12.8326(10)
c (Å)	18.4008(14)	17.981(2)
α (deg)	90	90
β (deg)	90.753(2)	90
γ (deg)	90	90
V (Å^3)	1603.8(2)	2247.4(4)
Z	4	4
D_{calcd} (mg/cm^3)	1.384	1.266
abs coeff (mm^{-1})	0.740	0.540
cryst size (mm)	0.5 × 0.4 × 0.3	0.3 × 0.5 × 0.8
θ range (deg)	2.03−23.26	1.95−24.0
no. of data collected	10 229	2668
no. of indep reflns	2301 [R(int) = 0.0586]	2485 [R(int) = 0.0303]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	2301/0/194	2485/0/254
goodness of fit on F_o^2	1.059	1.047
R indices ($F_o > 4\sigma(F_o)$)	R1 = 0.0363, wR2 = 0.0912	R1 = 0.0343, wR2 = 0.0882
R indices (all data)	R1 = 0.0434, wR2 = 0.0964	R1 = 0.0413, wR2 = 0.0932
largest diff peak and hole (e Å^3)	0.205 and −0.200	0.226 and −0.268

Table 6. Bond Lengths (Å) and Angles (deg) for 6*Z*

Bond Distances			
Cr(1)−C(9)	1.881(3)	Cr(1)−C(11)	1.892(3)
Cr(1)−C(10)	1.894(3)	Cr(1)−C(13)	1.906(3)
Cr(1)−C(12)	1.917(3)	Cr(1)−C(1)	2.062(2)
C(1)−O(2)	1.318(3)	C(1)−C(2)	1.490(3)
C(2)−C(3)	1.341(4)	C(2)−O(1)	1.377(3)
C(3)−C(4)	1.501(4)	C(5)−O(1)	1.422(3)
C(5)−C(6)	1.490(4)	C(7)−O(2)	1.461(3)
C(7)−C(8)	1.483(4)	C(9)−O(3)	1.147(3)
C(10)−O(4)	1.140(3)	C(11)−O(5)	1.147(3)
C(12)−O(6)	1.137(3)	C(13)−O(7)	1.143(3)

Bond Angles			
C(9)−Cr(1)−C(11)	87.78(12)	C(9)−Cr(1)−C(10)	89.13(12)
C(11)−Cr(1)−C(10)	90.97(12)	C(9)−Cr(1)−C(13)	89.42(13)
C(11)−Cr(1)−C(13)	89.11(12)	C(10)−Cr(1)−C(13)	178.54(12)
C(9)−Cr(1)−C(12)	86.69(11)	C(11)−Cr(1)−C(12)	174.47(11)
C(10)−Cr(1)−C(12)	89.16(12)	C(13)−Cr(1)−C(12)	90.62(12)
C(9)−Cr(1)−C(1)	175.92(10)	C(11)−Cr(1)−C(1)	96.20(10)
C(10)−Cr(1)−C(1)	91.69(10)	C(13)−Cr(1)−C(1)	89.75(11)
C(12)−Cr(1)−C(1)	89.32(10)	O(2)−C(1)−C(2)	106.2(2)
O(2)−C(1)−Cr(1)	130.38(17)	C(2)−C(1)−Cr(1)	123.23(16)
C(3)−C(2)−O(1)	121.0(2)	C(3)−C(2)−C(1)	122.3(2)
O(1)−C(2)−C(1)	115.8(2)	C(2)−C(3)−C(4)	127.0(3)
O(1)−C(5)−C(6)	109.0(2)	O(2)−C(7)−C(8)	107.5(2)
O(3)−C(9)−Cr(1)	179.3(3)	O(4)−C(10)−Cr(1)	178.2(2)
O(5)−C(11)−Cr(1)	175.6(2)	O(6)−C(12)−Cr(1)	175.6(2)
O(7)−C(13)−Cr(1)	176.7(3)	C(2)−O(1)−C(5)	115.6(18)
C(1)−O(2)−C(7)	124.2(2)		

J = 6.5 Hz, 1H), 3.20−3.28 (m, 1H), 3.57−3.63 (m, 1H), 4.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.2, 9.7, 11.3, 12.0, 12.4, 14.4, 15.2, 16.2, 46.9, 52.8, 53.9, 60.1, 61.7, 62.3, 95.6, 134.3, 136.4, 174.0. Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.22; H, 9.98.

X-ray Structure Study of 6*Z* and 21. Single crystals were obtained by slow evaporation of a concentrated $CHCl_3$/*n*-hexane (2:8) solution of **6*Z*** (red solid) and from a $CHCl_3$ solution of **21** (red solid). These were mounted on glass fibers. Crystallographic measurement for **6*Z*** was performed on a Bruker 6000 CCD area detector difractometer, and for **21** on a Siemens P4 diffractometer using Mo Kα radiation (graphite crystal monochromator, λ = 0.71073 Å) and at room temperature. Unit cell parameters along with data collection and refinement details for compound **6*Z*** are listed in Table 5. The structure was solved by Patterson methods using SHELXS 97-2.[30] Least-squares refinement based on F^2 was carried out by the full-matrix method of SHELXL 97-2.[31] All non-hydrogen atoms were refined with anisotropic thermal parameters. Location of hydrogen atoms was generated geometrically and included in the refinement with an isotropic fixed thermal parameter using a "riding" model. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[32] Selected bond lengths and angles of the complex **6*Z*** are listed in Table 6; molecular structure drawings were generated using ORTEP3 for Windows.[33] Three standard reflections for **21** were monitored periodically; they showed no change during data collection. Unit cell parameters were obtained from least-squares refinement of 26 reflections in the range 2° < 2θ < 20°.

Table 7. Bond lengths (Å) and angle (deg) for 21

Bond Distances			
Cr(1)−C(14)	1.809(5)	Cr(1)−C(15)	1.887(5)
Cr(1)−C(5)	1.892(5)	Cr(1)−C(13)	1.903(5)
Cr(1)−C(10)	1.947(4)	Cr(1)−O(1)	2.194(2)
O(1)−C(8)	1.444(4)	O(1)−C(2)	1.482(4)
O(2)−C(10)	1.314(4)	O(2)−C(11)	1.453(4)
C(10)−C(2)	1.510(5)	O(6)−C(5)	1.148(5)
C(6)−C(5)	1.338(5)	C(6)−C(6A)	1.495(5)
C(6)−C(1)	1.524(5)	C(2)−C(3)	1.544(5)
C(2)−C(1)	1.568(5)	O(3)−C(13)	1.141(5)
C(1)−C(1A)	1.518(5)	C(1)−C(7)	1.545(5)
C(5)−C(5A)	1.500(5)	C(5)−C(4)	1.512(6)
C(4)−C(4A)	1.530(6)	C(4)−C(7)	1.540(6)
C(16)−C(3)	1.557(6)	C(7)−C(7A)	1.526(6)
O(4)−C(14)	1.171(6)	C(8)−C(9)	1.516(6)
C(11)−C(12)	1.479(6)	O(5)−C(15)	1.151(5)

Bond Angles			
C(14)−Cr(1)−C(15)	89.6(2)	C(14)−Cr(1)−C(5)	86.7(2)
C(15)−Cr(1)−C(5)	89.7(2)	C(14)−Cr(1)−C(13)	89.7(2)
C(15)−Cr(1)−C(13)	90.9(2)	C(5)−Cr(1)−C(13)	173.4(2)
C(14)−Cr(1)−C(10)	103.5(2)	C(15)−Cr(1)−C(10)	166.6(2)
C(5)−Cr(1)−C(10)	88.5(2)	C(13)−Cr(1)−C(10)	92.4(2)
C(14)−Cr(1)−O(1)	168.2(2)	C(15)−Cr(1)−O(1)	102.2(2)
C(5)−Cr(1)−O(1)	92.90(14)	C(13)−Cr(1)−O(1)	93.4(2)
C(10)−Cr(1)−O(1)	64.67(12)	C(8)−O(1)−C(2)	120.3(3)
C(8)−O(1)−Cr(1)	123.2(2)	C(2)−O(1)−Cr(1)	94.4(2)
C(10)−O(2)−C(11)	118.8(3)	O(2)−C(10)−C(2)	112.5(3)
O(2)−C(10)−Cr(1)	143.2(3)	C(2)−C(10)−Cr(1)	104.2(2)
C(5)−C(6)−C(6A)	128.8(4)	C(5)−C(6)−C(1)	107.5(3)
C(6A)−C(6)−C(1)	123.6(3)	O(1)−C(2)−C(10)	96.1(2)
O(1)−C(2)−C(3)	117.0(3)	C(10)−C(2)−C(3)	113.6(3)
O(1)−C(2)−C(1)	110.8(3)	C(10)−C(2)−C(1)	116.8(3)
C(3)−C(2)−C(1)	103.1(3)	C(1A)−C(1)−C(6)	116.2(3)
C(1A)−C(1)−C(7)	118.3(4)	C(6)−C(1)−C(7)	100.5(3)
C(1A)−C(1)−C(2)	114.6(3)	C(6)−C(1)−C(2)	105.3(3)
C(7)−C(1)−C(2)	99.6(3)	C(20)−C(5)−C(5A)	129.3(4)
C(6)−C(5)−C(4)	107.4(3)	C(5A)−C(5)−C(4)	123.1(4)
C(5)−C(4)−C(4A)	117.9(4)	C(5)−C(4)−C(7)	101.3(3)
C(4A)−C(4)−C(7)	117.4(4)	C(5)−C(4)−C(3)	105.5(3)
C(4A)−C(4)−C(3)	112.2(4)	C(7)−C(4)−C(3)	100.2(3)
O(6)−C(16)−Cr(1)	175.6(4)	C(7A)−C(7)−C(4)	115.8(4)
C(7A)−C(7)−C(1)	114.9(4)	C(4)−C(7)−C(1)	93.6(3)
O(3)−C(13)−Cr(1)	174.6(5)	O(4)−C(7)−Cr(1)	178.8(5)
C(2)−C(3)−C(4)	103.0(3)	O(1)−C(8)−C(9)	108.4(4)
O(2)−C(11)−C(12)	110.4(3)	O(5)−C(15)−Cr(1)	175.8(4)

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Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and their atomic coordinates refined. Unit weights were used in the refinement. Structures were solved using the SHELXTL[34] program on a personal computer. Selected bond lengths and angles of complex **21** are listed in Table 7.

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Supporting Information Available: Tables of ^{1}H, ^{13}C NMR and data for **3**, **4**, **5**, **6**, **14**, **15**, **16**, **19**, **21**, **22**, **23**, **24**, and **25**. Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic parameters for **6***Z* and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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