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DFT Study on the Diels−Alder Cycloaddition between Alkenyl−M(0) (M = Cr, W) Carbene Complexes and Neutral 1,3-Dienes

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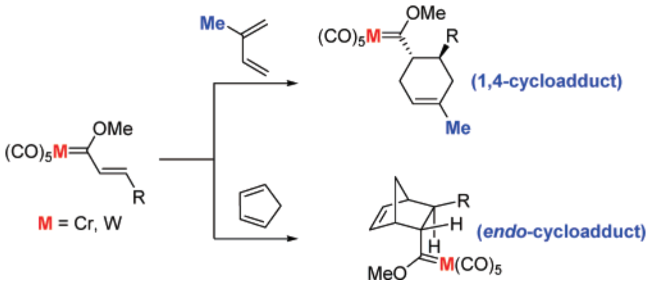
Received October 18, 2007



The thermal Diels−Alder reaction between alkenylmetal(0) Fischer carbenes and 1,3-dienes (isoprene and cyclopentadiene) has been studied computationally within the density functional theory framework. The selectivity of the [4 + 2] cycloadditions between alkenyl−group 6 (Fischer) carbene complexes and isoprene is similar to the selectivity computed for the reactions involving Lewis acid complexed acrylates. The experimentally observed complete *endo* selectivity in the [4 + 2] cycloadditions of alkenyl−group 6 (Fischer) carbene complexes with cyclopentadiene, which takes place under kinetic control, may be due in part to the presence of stabilizing secondary orbital interactions. These interactions are stronger than the analogues in the metal-free processes. The [4 + 2] cycloadditions between alkenyl−group 6 (Fischer) carbene complexes and neutral dienes occur concertedly via transition structures which are more asynchronous and less aromatic than their non-organometallic analogues, a behavior which is extensible to the reactions between Lewis acid complexed acrylates.

Introduction

Fischer-type carbene complexes experience high-yielding, unconventional transformations under mild conditions.[1] The [4 + 2] Diels−Alder cycloaddition between alkenyl or alkynyl group 6 carbene complexes and 1,3-dienes occurs smoothly and efficiently, and it has been used repeatedly in the synthesis of new organic and organometallic compounds.[2] The origin of this success is the compatibility of Fischer carbene complexes with sensitive functionalities, which are not tolerated for metal-free or Lewis acid catalyzed Diels−Alder reactions. The reaction rates, the *endo*/*exo* selectivities, and the regioselectivities of the Diels−Alder reaction involving Fischer complexes were found to be comparable to Lewis acid catalyzed reactions of their corresponding organic esters.[2d] For instance, the activating effect of the pentacarbonylchromium(0) moiety makes the reaction rate of the Diels−Alder cycloaddition between [(methoxy)(vinyl)pentacarbonyl]chromium(0) carbene and isoprene comparable to the reaction rate associated with the reaction of isoprene and methyl acrylate catalyzed by $AlCl_3$.

In this context, we recently reported[3] that in terms of the isolobal analogy model,[4] it can be concluded that alkynylalkoxymetal(0) Fischer carbene complexes act in their [3 + 2] reaction with nitrones to produce *s-trans*-2,3-dihydroisoxazole carbene complexes (Scheme 1) as organometallic analogues of organic alkyl propiolates with enhanced electrophilic character. This dipolar cycloaddition takes place via transition structures which are more asynchronous and less aromatic than their non-

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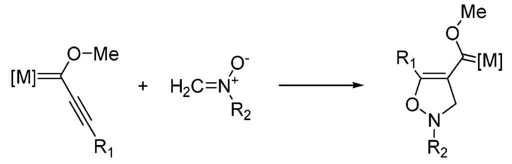
10.1021/jo702257s CCC: $40.75

SCHEME 1



organometallic analogues but similar to the transition structures obtained with Lewis acid−ester complexes. Although the latter process takes place on the carbene ligand and, therefore, the metal−carbene bond of the carbene ligand remains intact, the latter DFT study proved that the metal plays an active role in the transformation, and therefore it does not act as a mere spectator in the reaction.

We now extend those previous findings and report an extensive computational study on the mechanism of the [4 + 2] cycloaddition reaction between group 6 alkenyl (Fischer) carbene complexes and 1,3-dienes (isoprene and cyclopentadiene). This study includes the origins of the observed regioselectivities, as well as an insight in the nature of the saddle points of the processes in terms of the aromaticity of the transition states[5] and calculated synchronicities.

Computational Details

All of the calculations reported in this paper were obtained with the GAUSSIAN 03 suite of programs.[6] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[7] and the standard 6-31+G(d) basis set[8] for hydrogen, carbon, oxygen, nitrogen, chlorine, aluminum, and silicon and the Hay−Wadt small-core effective core potential (ECP) including a double-ξ valence basis set[9] for chromium and tungsten (LanL2DZ keyword). Spin−orbit corrections have been not included in the calculations involving tungsten. Zero-point vibrational energy (ZPVE) corrections were computed at the B3LYP/LANL2DZ&6-31+G(d) level and were not scaled. Reactants and cycloadducts were characterized by frequency calculations[10] and have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method.[11] Nucleus-independent chemical shifts (NICS) were evaluated by using the gauge invariant atomic orbital[12] (GIAO) approach, at the GIAO-B3LYP/LANL2DZ&6-31+G(d) level.

The synchronicity[13,14] of the reactions was quantified by using a previously described approach.[15] For a given concerted reaction, "synchronicity" is defined as[16]

$$S_{\mathrm{y}} = 1 - \frac{\sum_{i=1}^{n} \frac{|\delta B_{\mathrm{i}} - \delta B_{\mathrm{AV}}|}{\delta B_{\mathrm{AV}}}}{2n - 2}$$

where n is the number of bonds directly involved in the reaction (in this case, $n = 6$) and δB_i stands for the relative variation of

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a given bond index B_i at the transition state (TS), according to the following formula

$$\delta B_i = \frac{B_i^{TS} - \mathrm{B}_i^{R}}{B_i^{P} - B_i^{R}}$$

where the superscripts R and P refer to the reactants and the product, respectively. The average value of δB_i, denoted as δB_{AV} is therefore

$$\delta B_{\mathrm{AV}} = n^{-1} \sum_{i=1}^{n} \delta B_{\mathrm{i}}$$

The Wiberg bond indices[17] B_i and donor−acceptor interactions have been computed using the natural bond orbital (NBO)[18] method. The energies associated with these two-electron interactions have been computed according to the following equation

$$\Delta E^{(2)}_{\phi\phi^*} = -\, n_{\phi} \frac{\langle \phi^* | \hat{F} |\, \phi \rangle^2}{\epsilon_{\phi}{}^* - \epsilon_{\Phi}}$$

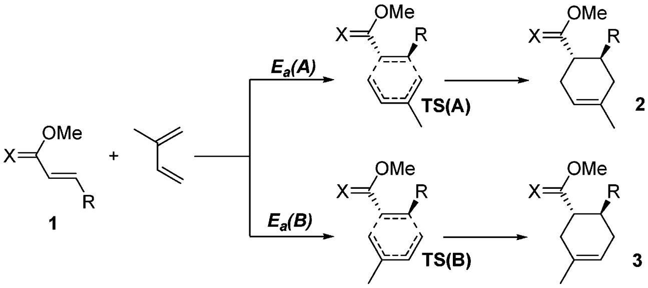
where $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled natural bond orbitals having ϵ_ϕ y $\epsilon_\phi{}^*$ and energies, respectively; n_ϕ stands for the occupation number of the filled orbital.

In the present report, we only examine two-electron processes. Therefore, we have considered neither biradical nor di-ion steps.

Results and Discussion

DFT calculations (B3LYP/LANL2DZ&6-31+G(d)) were carried out starting with the *anti*-form of alkenylmetal(0) Fischer carbene complexes **1** (an orientation where the methyl group of the methoxy substituent is directed toward the metal fragment) which is the most stable conformation in the gas phase and in the solid state.[19] The regiochemistry of the reaction of these complexes and isoprene was studied first. The [4 + 2] cycloaddition reaction between isoprene and Fischer carbenes may lead to two regioisomeric cyclohexenyl−carbene complexes, **2** through pathway A, and **3** through pathway B, respectively (Scheme 2).

SCHEME 2



Data compiled in Table 1 demonstrate the high regioselectivity of the reaction, which forms cycloadducts **2** almost exclusively. Compounds **2** have the pentacarbonylmetal fragment and the methyl group of the isoprene in a 1,4-relative disposition and should be formed through the pathway A (Scheme 2). Since the reaction energy differences (ΔE_{R}) between paths A and B in Scheme **2** are negligible in all cases (Table 1), the observed regioselectivity must be of kinetic origin. This becomes clear from the higher energy barrier required for the formation of cycloadduct **3** through the pathway B in Scheme 2 (Table 1). These results are in very good agreement with the **2**/**3** ratio experimentally observed by Wulff and coworkers.[2d] This is also true for the higher regioselectivities observed for group 6 Fischer carbene complexes (ΔE_{a}(A−B) $\approx$ 1.5 kcal/mol) compared to the corresponding organic esters (ca. 0.7 kcal/mol), as well as for the experimentally observed reaction rate enhancement (ca. 2×10^4) by the pentacarbonylmetal(0) moiety compared to the corresponding organic ester analogues.[2d] Interestingly, we found higher energy barriers for methyl substituted compounds (entries 3, 4, and 9) compared to the corresponding hydrogen substituted compounds (entries 1, 2, and 7, respectively). This results in the higher temperature required for the cycloaddition of complexes **1c**,**d** (50 °C) and ester **1i** (230 °C) compared to complexes **1a**,**b** (25 °C) and ester **1g** (25 °C).[20] Therefore, we predict that the [4 + 2] reaction of $\mathrm{SiH_3}$ and phenyl-substituted complexes **1e**,**f** with isoprene would require a high temperature on the basis of their high reaction barriers (see entries 5 and 6 in Table 1, respectively). Finally, no systematic difference was observed between isostructural chromium (Table 1, entries 1 and 3) and tungsten complexes (Table 1, entries 2 and 4).

Transition states depicted in Figure 1 show the cycloadditons of alkenylcarbene complexes **1** and isoprene to form the cycloadducts **2** occurring by a concerted pathway. Highly asynchronous transition structures were located in contrast to the transition states obtained for the analogous organic reaction which points to a strong participation of the metal in the reaction. In fact, in all cases the terminal C(alkenyl complex)−C1-(isoprene) NBO bond orders are higher (ranging from 0.48 in **TSa(A)** to 0.50 in **TSf(A)**) than the respective C(alkenyl complex)−C4(isoprene) bond orders (ranging from 0.12 in **TSa(A)** to 0.17 in **TSf(A)**, see Figure 1 for the corresponding bond distances). Thus, Fischer carbene complexes lead to transition states where the terminal C-C1 bonds are almost fully developed while the second C−C4 bonds are only emerging. The computed synchronicities are therefore quite low ($S_{\mathrm{y}} \approx 0.75$) as can be found in Table 3. Actually, these values are close to the limit between concerted and stepwise mechanisms. To the extent that these processes involve two-electron steps, and not biradical or di-ion steps, they appear concerted and asynchronous. This result contrasts with the higher synchronicities computed for the metal-free cycloadditions whose values are closer to the perfect synchronicity ($S_{\mathrm{y}} = 0.86$ for methyl acrylate and 0.90 for (*E*)-methyl but-2-enoate, see Table 3).

The [4 + 2] cycloaddition reaction between isoprene and the methyl acrylate−$\mathrm{AlCl_3}$ and (*E*)-methyl but-2-enoate−$\mathrm{AlCl_3}$

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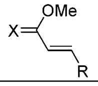
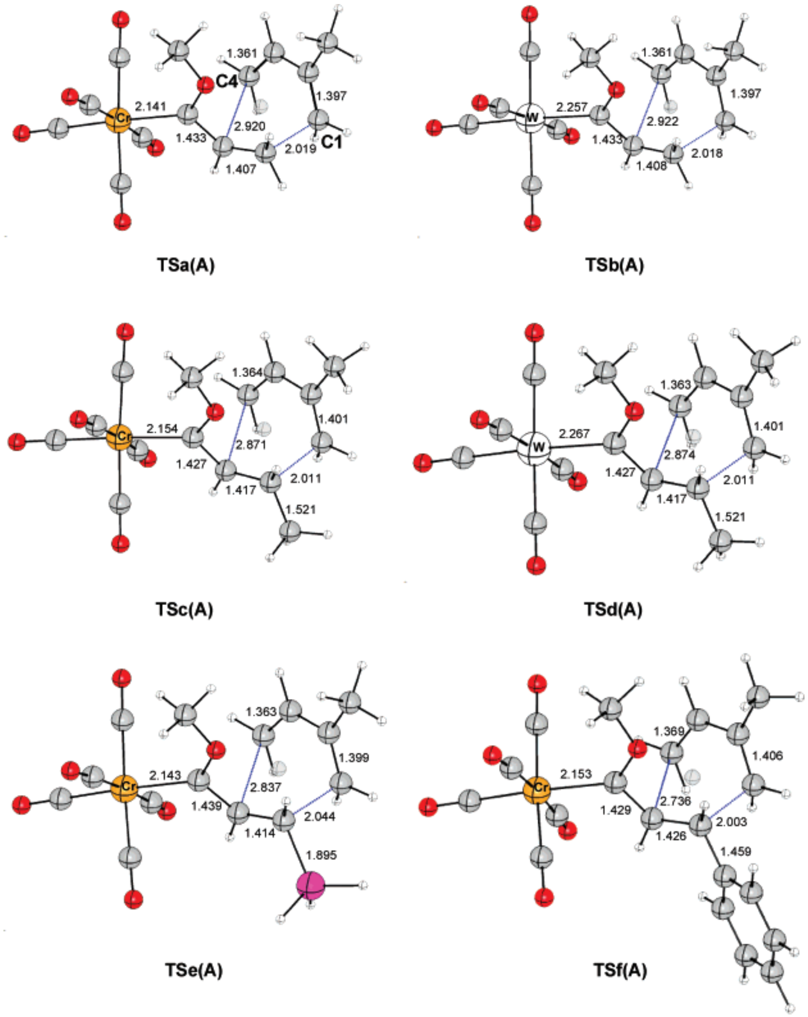
[20] The reaction between **1g** and isoprene occurs at 25 °C in 7 months in only 54% yield, which is in accord with the high computed energy barrier ($E_{\mathrm{a}} = 20.6$ kcal/mol, entry 7, Table 1). See ref 2d and: Nazarov, I. N.; Titov, Y. A.; Kuznetsova, A. I. *Izv. Akad. Nauk. SSSR, OKHN* **1959**, 1412.

TABLE 1. Energy Barriers (E_a, kcal/mol)[a] and Reaction Energies (E_R, kcal/mol)[a] for the [4 + 2] Cycloaddition Reactions between Fischer Carbene Complexes 1 and Isoprene

Entry		E_a(A)[b]	E_a(B)[c]	ΔE_a(A–B)[d]	E_R(A)[e]	E_R(B)[f]	ΔE_R(A–B)[g]	exp. 2/3[h]
1	**1a**, X=Cr(CO)$_5$, R=H	16.1	17.6	-1.5	-30.2	-30.1	-0.1	92:8
2	**1b**, X= W(CO)$_5$, R=H	16.4	17.9	-1.6	-29.7	-29.7	0.0	91:9
3	**1c**, X=Cr(CO)$_5$, R=Me	21.0	22.6	-1.6	-23.8	-23.9	0.1	>97:3
4	**1d**, X= W(CO)$_5$, R=Me	21.1	22.7	-1.6	-23.8	-23.8	0.0	>97:3
5	**1e**, X= Cr(CO)$_5$, R=SiH$_3$	18.6	19.9	-1.3	-23.7	-23.7	0.0	–
6	**1f**, X= Cr(CO)$_5$, R=Ph	23.3	25.0	-1.7	-19.2	-19.2	0.0	–
7	**1g**, X=O, R=H	20.6	21.3	-0.7	-33.5	-33.5	0.0	70:30
8	**1h**, X= Cl$_3$Al–O, R=H	9.2	10.8	-1.6	-36.5	-36.4	-0.1	95:5
9	**1i**, X=O, R=Me	25.1	25.8	-0.7	-29.2	-29.2	0.0	only **2**
10	**1j**, X= Cl$_3$Al–O, R=Me	15.1	16.7	-1.6	-30.3	-30.3	0.0	–

[a] All values have been calculated at the B3LYP/LANL2DZ&6-31+G(d)+ΔZPVE level. [b] E_a(A) values computed as E_a(A) = E(**TS-pathway A**) − E(**1**) − E(**isoprene**). [c] E_a(B) values computed as E_a(B) = E(**TS-pathway B**) − E(**1**)-E(**isoprene**). [d] ΔE_a values computed as ΔE_a = E(**TS-A**) − E(**TS-B**). [e] E_R(A) values computed as E_R(A) = E(**2**) − E(**1**) − E(**isoprene**). [f] E_R(B) values computed as E_a(B) = E(**3**) − E(**1**) − E(**isoprene**). [g] ΔE_R values computed as ΔE_R = E_R(**A**) − E_R(**B**). [h] Experimental **2/3** ratio taken from ref 2d.



TSa(A) **TSb(A)**

TSc(A) **TSd(A)**

TSe(A) **TSf(A)**

FIGURE 1. Ball-and-stick representations of the TSs corresponding to the reaction of complexes **1** and the isoprene to yield cyclohexenyl−carbene complexes **2** through pathway A (see Scheme 2). All structures correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) geometries. Bond distances are given in angstroms. The dummy atoms denote the ring point of electron density. Unless otherwise stated, white, gray, red, blue, and pink colors denote hydrogen, carbon, oxygen, nitrogen, and silicon atoms, respectively.

complexes **1h** and **1j** was computed next.[2d] The energy barrier difference between the two possible pathways (Table 1, entries 8 and 10) is close to the energy difference involving the analogous Fischer carbene complexes (Table 1, entries 1−4).

TABLE 2. Energy Barriers (E_a, kcal/mol)[a] and Reaction Energies (E_R, kcal/mol)[a] for the [4 + 2] Cycloaddition Reactions between Fischer Carbene Complexes 1 and Cyclopentadiene

entry	compd	E_a (*endo*)[b]	E_a (*exo*)[c]	ΔE_a (*endo-exo*)[d]	E_R (*endo*)[e]	E_R (*exo*)[f]	ΔE_R (*endo-exo*)[g]	exptl *endo*/*exo*[h]
1	**1a**, X = Cr(CO)$_5$, R = H	16.3	17.4	−1.1	−7.3	−7.6	0.3	94:6
2	**1b**, X = W(CO)$_5$, R = H	16.7	17.6	−0.9	−6.8	−7.2	0.4	93:7
3	**1c,** X = Cr(CO)$_5$, R = Me	21.5	22.2	−0.7	−1.9	−2.4	0.6	88:12
4	**1d**, *X* = W(CO)$_5$, R = Me	21.1	22.7	−1.6	−1.6	−2.3	0.6	90:10
5	**1g**, X = O, R = H	20.7	21.1	−0.4	−10.9	−11.0	0.1	78:22
6	**1h**, X = Cl$_3$AlO, R = H	8.9	9.9	−1.0	−14.8	−14.5	−0.3	94:6
7	**1i,** X = O, R = Me	25.7	25.5	+0.2	−7.0	−6.6	−0.4	54:46
8	**1j**, X = Cl$_3$AlO, R = Me	14.9	15.5	−0.6	−8.3	−8.5	0.2	93:7

[a] All values have been calculated at the B3LYP/LANL2DZ&6-31+G(d)+ΔZPVE level. [b] E_a(*endo*) values computed as E_a(*endo*) = *E*(**TS-*endo***) − *E*(**1**) − *E*(**cyclopentadiene**). [c] E_a(*exo*) values computed as E_a(B) = *E*(**TS-*exo***) − *E*(**1**)-*E*(**cyclopentadiene**). [d] ΔE_a values computed as ΔE_a = *E*(**TS-*endo***) − *E*(**TS-*exo***). [e] E_R(A) values computed as E_R(*endo*) = *E*(**4-*endo***) − *E*(**1**) − *E*(**cyclopentadiene**). [f] E_R(*exo*) values computed as E_a(*exo*) = *E*(**4-*exo***) − *E*(**1**) − *E*(**cyclopentadiene**). [g] ΔE_R values computed as ΔE_R = E_R(***endo***) − E_R(***exo***). [h] Experimental **4-*endo*/4-*exo*** ratio taken from ref 2d.

Therefore, the regioselectivity of the cycloaddition should be also quite similar as was experimentally reported.[2d] The transition states of these reactions have geometrical features (Figure 2) resembling the transition states of the analogous [4 + 2] cycloadditions of Fischer carbene complexes (Figure 1) and isoprene. Again, in the Lewis acid catalyzed reaction, the terminal C−C1 bond is nearly developed (2.011 Å, B_{CC} = 0.48 in **TSh(A)**, and 2.009 Å, B_{CC} = 0.49 for **TSj(A)**), while the C−C4 bond is only emerging (2.873 Å, B_{CC} = 0.12 in **TSh-(A)**, and 2.810 Å, B_{CC} = 0.14 for **TSj(A)**). The computed synchronicities of these processes are also similar to the synchronicity values of their Fischer complex analogues (Table 3) and, therefore, lower than the values for the processes involving the respective metal-free organic esters **1g**,**i**.

TABLE 3. Synchronicities[a] (S_y) and Nucleus-Independent Chemical Shifts[b] (NICS, ppm) of the Reactions between Carbene Complexes 1a−e, Organic Esters 1f,j, and Isoprene or Cyclopentadiene To Produce the Cycloadducts 2 and 4-*endo*, Respectively

reaction with isoprene	S_y	NICS (TS)	reaction with cyclopentadiene	S_y	NICS (TS)
1a → **2a**	0.75	−13.57	**1a** → **4a-*endo***	0.77	−17.30
1b → **2b**	0.74	−13.08	**1b** → **4b-*endo***	0.78	−16.85
1c → **2c**	0.76	−14.00	**1c** → **4c-*endo***	0.78	−17.30
1d → **2d**	0.76	−13.53	**1d** → **4d-*endo***	0.76	−17.09
1e → **2e**	0.76	−14.51			
1f → **2f**	0.80	−14.76			
1g → **2 g**	0.86	−17.17	**1 g** → **4 g-*endo***	0.89	−21.42
1h → **2h**	0.76	−13.33	**1h** → **4h-*endo***	0.79	−18.22
1i → **2i**	0.90	−17.35	**1i** → **4i-*endo***	0.90	−21.41
1j → **2j**	0.77	−13.78	**1j** → **4j-*endo***	0.80	−18.05

[a] Computed at the B3LYP/LANL2DZ&6-31+G(d) level. [b] Computed at the GIAO-B3LYP/LANL2DZ&6-31+G(d) level.

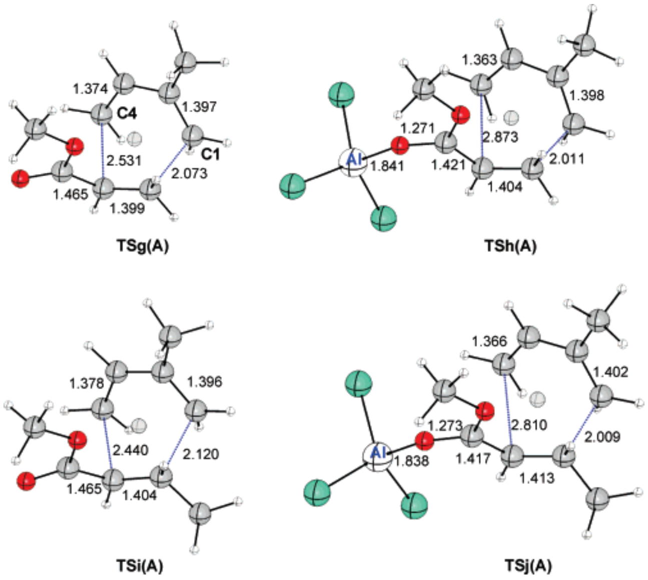
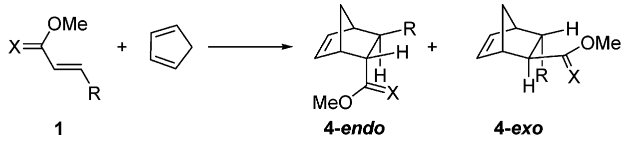


FIGURE 2. Ball-and-stick representations of corresponding TSs of the [4 + 2] cycloadditions of methyl acrylate **1g** and methyl acrylate−AlCl$_3$ complex **1h** and (*E*)-methyl but-2-enoate **1i** and (*E*)-methyl but-2-enoate−AlCl$_3$ complex **1j** with isoprene through pathway A, respectively. All structures correspond to fully optimized B3LYP/6-31+G(d) geometries. Bond distances are given in angstroms. The dummy atoms denote the ring point of electron density. See Figure 1 caption for additional details.

SCHEME 3



In order to study the *exo-endo* selectivity in the Diels−Alder cycloaddition involving alkenyl Fischer carbenes and cyclic dienes, the reaction of complexes **1** and cyclopentadiene was studied. Now, two possible stereoisomers may be formed, **4-*exo*** and **4-*endo*** (Scheme 3). Data in Table 2 show that alkenyl carbene complexes have a higher *endo*-stereoselectivity than the uncatalyzed reactions of the corresponding esters. This may be ascribed again to the higher computed reaction barrier differences between the *endo-exo* pathways (ΔE_a(*endo-exo*) ranging from −0.7 kcal/mol in **1c** to −1.6 kcal/mol in **1d**) compared to the ΔE_a(*endo-exo*) of metal-free processes (entries 5 and 7, Table 2). The results in Table 2 fully match the experimental values. Moreover, the stereoselectivity of the process involving alkenyl−carbene complexes and Lewis acid mediated cycloadditions is comparable because of the rather similar calculated ΔE_a(*endo-exo*) values. For instance, the experimental *endo-exo* ratio found for the reaction between methyl acrylate−AlCl$_3$ complex **1h** and cyclopentadiene (94:6, entry 6) is identical to the ratio of the corresponding Fischer carbenes **1a**,**b** as well as the computed ΔE_a(*endo-exo*) values.

Figure 3 shows the transition states associated to the formation of the *endo*-cycloadducts from Fischer carbene complexes **1a−d** and Lewis acid complexes **1h**,**j** with cyclopentadiene. Again, a concerted reaction pathway was found for these transformations, and asynchronous transition structures were also located. In all cases, the terminal C(alkenyl complex)−C1(cyclopentadiene) NBO bond orders are higher (ranging from 0.48 in **TSa(*endo*)** to 0.51 in **TSd(*endo*)**) than the respective C(alkenyl complex)−

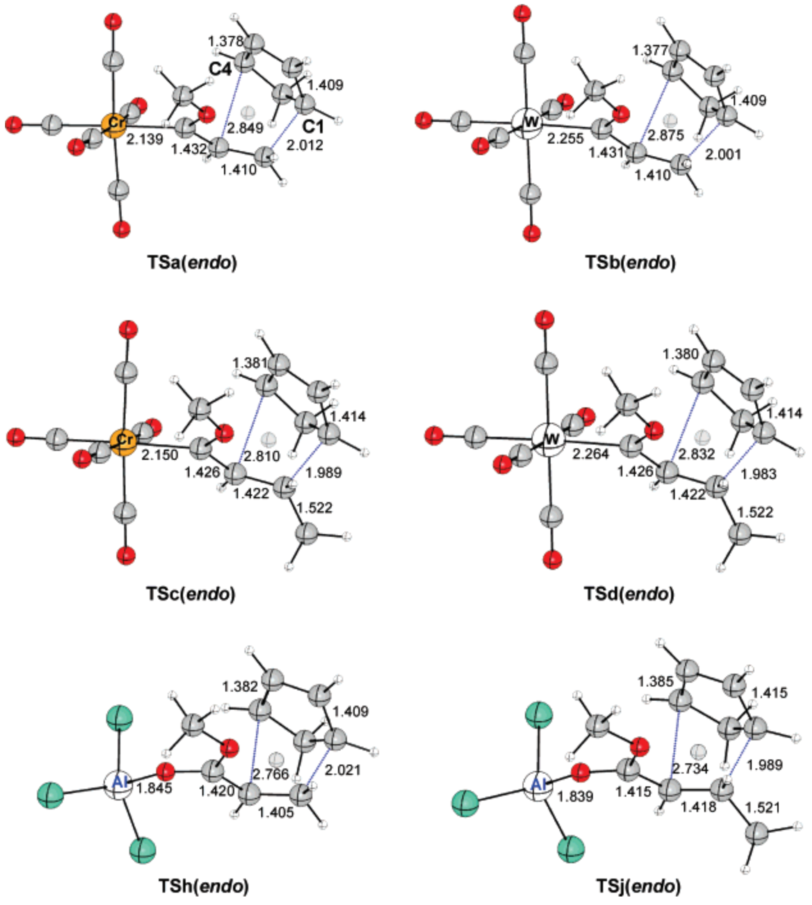


FIGURE 3. Ball-and-stick representations of the TSs corresponding to the reaction of complexes **1** and cyclopentadiene to yield cycloadducts **4-*endo***. All structures correspond to fully optimized B3LYP/LANL2DZ&6-31+G(d) geometries. Bond distances are given in angstroms. The dummy atoms denote the ring point of electron density. See Figure 1 caption for additional details.

C4(cyclopentadiene) bond orders (ranging from 0.12 in **TSa-(*endo*)** to 0.14 in **TSc(*endo*)**, see Figure 3 for the corresponding bond distances). The results collected in this work clearly show that alkenyl−group 6 (Fischer) carbene complexes react with dienes through transition states approaching the limit between concerted and stepwise mechanisms. This is clear from the fact that the terminal C−C4 bond is almost fully developed in the transition state, while the second C−C1 bond is only emerging. Similar geometric features were found for the transition states associated with the cycloadditions involving $AlCl_3$ complexes **1h**,**j**. As a consequence, the computed synchronicities of both types of complexes are low and similar ($S_y = 0.76-0.80$, Table 3). This result contrasts with the higher synchronicities computed for the metal-free cycloadditions whose values are close to the perfect synchronicity ($S_y = 0.90$).

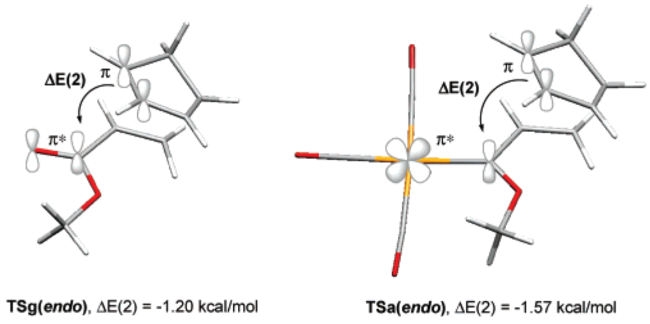


FIGURE 4. Two-electron interactions and associated second-order perturbation energies, $\Delta E^{(2)}$, in transition states **TSg(*endo*)** and **TSa-(*endo*).**

The existence of secondary orbital interactions (SOI) in the *endo*-transition states has been proposed to be an important factor in the observed *endo*-selectivity of Diels−Alder cycloadditions.[21] Thus, the natural bonding analysis on **TSg(*endo*)**, which corresponds to the transition state of the reaction of cyclopentadiene and methyl acrylate, shows a stabilizing two-electron interaction between the localized π-C═C (cyclopentadiene) and the π^*-C═O (methyl acrylate) orbitals. The associated second-order perturbation energy ($\Delta E^{(2)}$) is -1.2 kcal/mol (Figure 4). The analogous NBO analysis on **TSa(*endo*)** for the cycloaddition of carbene complex **1a** shows a similar two-electron interaction between the localized π-C═C (cyclopentadiene) and the π^*-Cr═$C_{carbene}$ orbitals, with a higher second-order energy ($\Delta E^{(2)} = -1.6$ kcal/mol). The stronger secondary interaction observed on **TSa(*endo*)** may be invoked as responsible, at least in part, for the higher (nearly complete) *endo*-selectivity encountered in the processes involving alkoxy-Fischer type carbene complexes compared to metal-free cycloadditions.

From the above data, it can be concluded that the pentacarbonyl-metal moiety in a group 6 (Fischer) carbene complex is equivalent to the coordination of a Lewis acid to the organic moiety in the [4 + 2] cycloadditions with 1,3-dienes. To support

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this conclusion, the energies of the frontier orbitals of the carbene complex **1c**, its organic ester analogue methyl but-2-enoate **1i**, the methyl but-2-enoate-$AlCl_3$ complex **1j**, and cyclopentadiene were computed (Figure 5). The most favorable HOMO (diene)–LUMO (dienophile) interaction occurs for the Lewis acid catalyzed reaction of methyl but-2-enoate, leading to the computed lowest reaction barrier value. The energy difference of the frontier orbitals for carbene **1c** and cyclopentadiene is only 0.64 eV higher than the energy gap of methyl but-2-enoate–$AlCl_3$ complex and cyclopentadiene. Therefore, the calculated trend of the HOMO–LUMO energy differences is metal-free > Fischer carbene > $AlCl_3$ complex, and it may be used to systematize the computed energy barriers, which follow a similar trend (see Table 2, entries 3, 7, and 8).

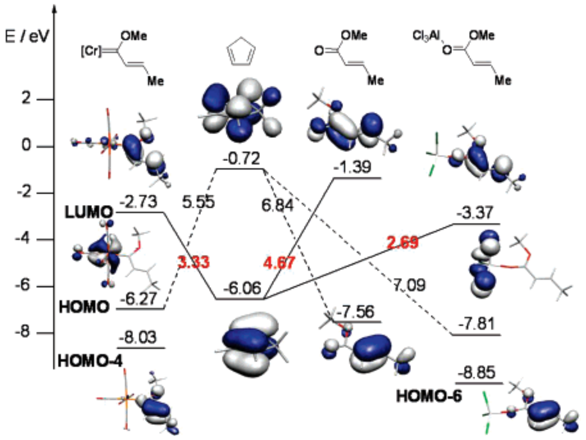

FIGURE 5. Frontier orbitals energies of cyclopentadiene and dienophiles **1c**,**i**,**j**. All values (in eV) were computed at the B3LYP/LANL2DZ&6-31+G(d) level of theory.

To complete this study, the effect of the metal moiety in the aromaticity postulated for the standard [4 + 2] cycloaddition[5] was finally addressed. The magnetic properties of the corresponding transition structures were computed using the nucleus-independent chemical shifts (NICS) values.[22] Given the strongly unsymmetrical character of our cyclic systems, we needed to define the inner points of these systems unambiguously. We proposed[3,5b,c,23] that the *in-plane* aromaticity can be estimated by the calculation of the NICS values inside the transient cyclic atomic array at the (3,+1) ring critical point of the electron density, as defined by Bader,[24] due to its high sensitivity to diamagnetic effects and its unambiguous character. The position of the ring critical points of the different saddle points is indicated in Figures 1–3, and the NICS values at these points are reported in Table 3.

All transition structures involving Fischer carbene complexes exhibit high negative NICS values (ca. −14.0 ppm for the reaction with isoprene and ca. −17.0 ppm for the reaction with cyclopentadiene), which should be attributed to strong diamagnetic shielding due to a strong aromatic character of these TSs. Interestingly, the calculated NICS values for the processes involving metal–carbene complexes are less negative than the computed values for the corresponding organic counterparts **1g**,**i** (ca. −17.2 ppm in the cycloaddition with isoprene and ca. −21.4 ppm in the cycloaddition with cyclopentadiene). Therefore, the metal moiety reduces the aromaticity of the [4 + 2] reaction. Moreover, if we assume that bonding equalization and, in transition structures, synchronicity characterize aromatic structures,[25] it is not surprising that the NICS values obtained for the Fischer carbene complexes are lower that those found for standard [4 + 2] cycloadditions between organic acrylates and 1,3-dienes. As expected, the computed data show that both NICS and synchronicity values of the reaction involving the $AlCl_3$–complexes **1h**,**j** are quite similar to those involving Fischer carbene complexes in their reactions with isoprene or cyclopentadiene (Table 3). These latter results provide further support to the aforementioned statement that the pentacarbonylmetal fragment acts as a Lewis acid for the organic moiety in this kind of cycloadditions.

Conclusions

From the computational study reported in this paper, the following conclusions can be drawn: (i) The [4 + 2] cycloadditions between alkenyl–group 6 (Fischer) carbene complexes and isoprene are completely regioselective, favoring the cycloadduct having the pentacarbonylmetal and the methyl group in 1,4-relative disposition. This selectivity is similar to the computed for the reactions between Lewis acid complexed acrylates. (ii) The complete *endo*-selectivity observed in the analogous reactions of alkenyl–group 6 (Fischer) carbene complexes with cyclopentadiene, which takes place under kinetic control, may be due in part to the presence of stabilizing secondary orbital interactions. These interactions are stronger than the analogues in the metal-free processes. (iii) The [4 + 2] cycloadditions between alkenyl–group 6 (Fischer) carbene complexes and neutral dienes occur concertedly via transition structures which are more asynchronous and less aromatic than their non-organometallic analogues, a behavior which is extensible to the reactions involving Lewis acid complexed acrylates.

Acknowledgment. Support for this work under Grant No. CTQ2007-67730-C02-01/BQU (to M.A.S.), CTQ2004-0681/BQU (to F.P.C.) from the Ministerio de Ciencia y Tecnología (Spain), and the Euskal Herriko Unibertsitatea (9/UPV 00040.215-13548/2001) (to F.P.C.) are gratefully acknowledged. The SGI/IZO-SGIker UPV/EHU (supported by the National Program for the Promotion of Human Resources within the National Plan of Scientific Research, Development and Innovation-Fondo Social Europeo, MCyT and Basque Government) is gratefully acknowledged for generous allocation of computational resources. I.F. is a Ramón y Cajal fellow.

Supporting Information Available: Cartesian coordinates (in Å) and total energies (in au, noncorrected zero-point vibrational energies included) of all the stationary points discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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