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Higher-Order Cyclization Reactions of Alkenyl Fischer Carbene Complexes: A New Selective All-Carbon [8 + 2] Cyclization with 8-Methoxyheptafulvene and Computational Mechanistic Analysis

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A new higher-order cyclization reaction of alkenyl Fischer carbene complexes is described. Chromium and tungsten alkenyl Fischer carbene complexes react toward 8-methoxyheptafulvene through an all-carbon formal [8 + 2] cycloaddition reaction with complete regio- and stereoselectivity. Tetrahydroazulene compounds bearing four consecutive stereocenters are generated. The reaction mechanism is rationalized based on computational calculations. It was found that this transformation proceeds through a concerted process. The nature of the observed stereo- and regioselectivity can be attributed to both steric and electronic factors.

Introduction

Along the last three decades, alkenyl Fischer carbene complexes (FCCs) have been recognized as one of the most versatile organometallic synthons. In particular, they have demonstrated a great ability to participate in varied cyclization processes, allowing the construction of a large number of carbocyclic and heterocyclic products.[1] Fundamental cycloadditions on the carbene complex carbon-carbon double bond, such as formal [4 + 2][2] and [3 + 2][3] cycloadditions, proceed with good selectivity owing to the strong activation imposed by the metal carbene functionality over the conjugated unsaturated unit. Moreover, the presence of both functional groups makes possible the participation of FCCs in processes involving consecutive cyclizations as well as in multicomponent reactions. Recently, we have described higher order cyclization reactions of α,β–unsaturated alkoxy carbene complexes and fulvenoid systems. Thus, alkenyl FCCs were found to undergo the [6+3] cyclization reaction with carbopentafulvenes[4] and 1,4-diazapentafulvenes.[5] On the other hand, we reported that nitrogen-containing heptafulvenes, like 8-azaheptafulvenes,[6] were also reactive toward alkenyl FCC's affording heterocyclic fused cycloheptenes through formal [8+2] or [8+3] heterocyclizations, depending on the C_β substituent.[7] To explain the competition between these reactions, we suggested a stepwise mechanism for the [8+2] cyclization through a zwiterionic intermediate resulting from a 1,4-addition of the heptafulvene nitrogen atom to the activated carbon-carbon double bond (Scheme 1, eq 1). This pathway competes with a 1,2-nucleophilic attack of the nitrogen atom on the metal-carbene bond followed by a cyclization inducted by a 1,2 metal migration that finally leads to the [8 + 3] cycloadduct (Scheme 1, eq 2).

In addition, stepwise mechanisms were also suggested for [8+2] cyclizations involving alkynyl carbene complexes, either with 8-azaheptafulvenes[8] or with tropothione.[9] Similarly to alkenyl carbene complexes, the cyclization is initiated by a 1,4-nucleophilic addition from the heptafulvene heteroatom to the metal-carbene activated triple bond.

At this point, we focused on the study of the ability of substrates lacking the reactive heteroatom functionality to deliver all-carbon high-order cycloadducts. In this respect, 8-methoxy heptafulvene **2**[10] has proved to be an excellent 8π partner with electron deficient alkenes giving rise to the corresponding [8 + 2] hydroazulene adducts.[11] However, these cycloadditions suffer from poor stereoselectivity, yielding mixtures of *endo*- and *exo*- cycloadducts. Within this scenario, we report herein a smooth and concerted reaction between alkoxy alkenyl Fischer carbene complexes **1** and 8-methoxyheptafulvene **2** to provide exclusively [8+2] hydroazulene adducts in high yield and in a totally regio- and

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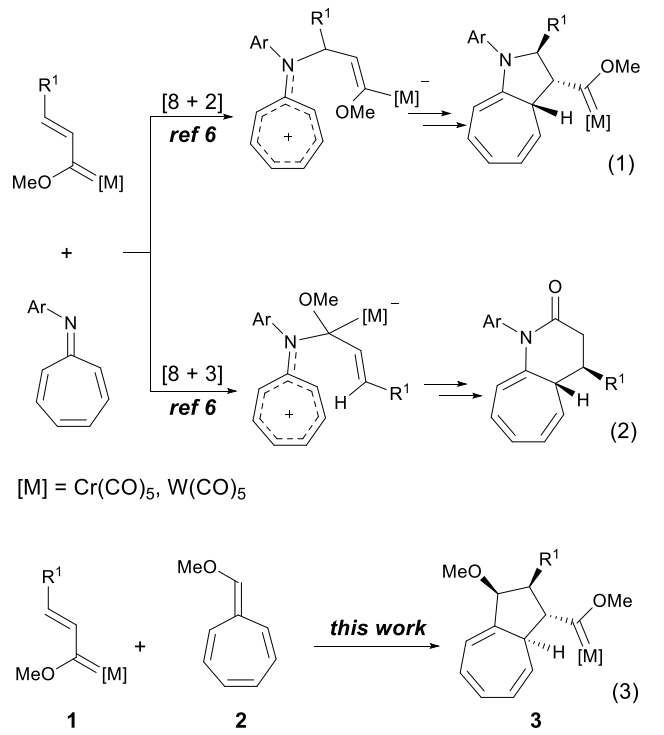
Electronic Supplementary Information (ESI) available: [^{1}H and ^{13}C NMR spectra for all compounds, X-ray data for **3e** and **5**, Cartesian coordinates and free energies for the calculated geometries]. See DOI: 10.1039/x0xx00000x

diastereoselective manner (Scheme 1, eq 3).



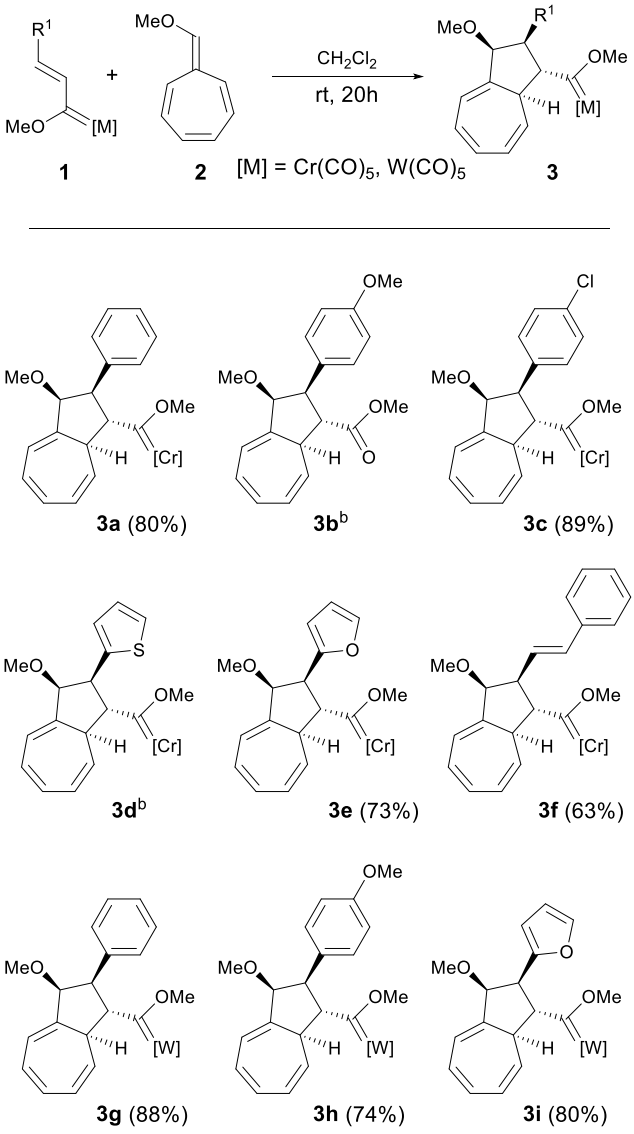
Scheme 1. Higher-Order Cycloaddition Reactions of Alkenyl FCCs **1** and Heptafulvenes.

Results and discussion

Experimental results.

We selected first alkoxy alkenyl carbene complexes of chromium in their reaction with methoxyheptafulvene. Thus, a solution of carbene complexes **1a-f** in dichloromethane were reacted with 1-methoxyheptafulvene **2** (1:3 molar ratio) at room temperature for 20 hours (Table 1). After solvent removal, the crude was purified through a column chromatography (silica gel; hexanes/CH_2Cl_2, 2:1) to give tetrahydroazulenyl chromium carbene complexes **3a-f**, in high yield. The reaction ⁻a formal [8+2] carbocyclization⁻ proceeds with formation of four contiguous stereocenters with complete regio and diastereoselectivity. Additionally, tungsten (0) alkenyl carbene complexes **1g-i** were also used under the same reaction conditions leading to the corresponding tungsten carbene adducts **3g-i**. No significant differences were observed in terms of selectivity and reaction yields related to their chromium counterparts.

Table 1. [8+2] Cyclization adducts from carbene complexes **1a-i** and 8-methoxyfulvene **2**.[a]



[a] Yields after chromatographic column purification

[b] Carbene cycloadduct could not be isolated and was directly oxidized (See, Table 2).

The tetrahydroazulene structure of complexes **3** and the relative position of the substituents were determined by ^1H and ^{13}C NMR spectroscopic data. Moreover, the relative stereochemistry of the four consecutive stereogenic centers was unambiguously determined by an X-ray analysis of a monocrystal of **3e** (R^1 = 2-furyl) grown from a hexane/chloroform mixture (Figure 1).[12]

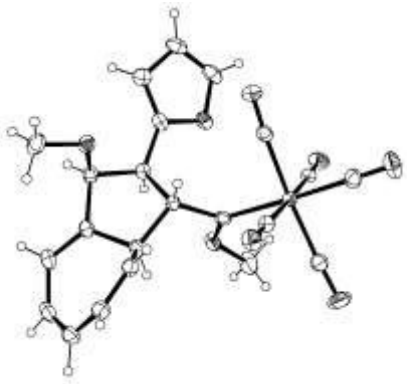
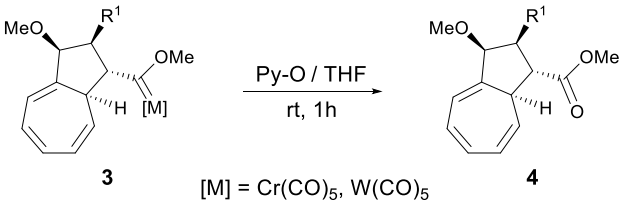


Fig 1. X-ray crystal structure for compound **3e**. Thermal ellipsoids at the 50% probability level.

The scope of the reaction for the different C_β substituents of alkenyl carbene complex **1** is illustrated in Table 1. Thus, the reaction works well for metal carbene complexes containing aryl groups with different electronic properties. In addition to the presence of a phenyl ring (**3a,3g**), tetrahydroazulene complexes were also accessed with electron-donating (**3b,3h**) or electron-withdrawing groups (**3c**) at the 7-position. Additionally, 2-thienyl (**3d**) and 2-furyl (**3e,i**) heterocyclic units can also be incorporated. Moreover, the participation of the dienyl carbene complex **1f** (R^1 = *trans*-cinnamyl) allows for the access to the corresponding cycloadduct **3f** that features an effective functionalization at the 7-position. Unfortunatelly, chromium and tungsten alkenyl Fischer carbene complexes **1** bearing an alkyl substituent at the β-position failed in their reaction with compound **2**, and unidentifiable mixtures of products were obtained.

Chromium carbene complexes **3b** and **3d** could not be purified since they are partially oxidized when subjected to column chromatography. Subsequently, the crude adducts **3b,d** were oxidatively demetallated by treatment with pyridine oxide in tetrahydrofuran, to furnish hydroazulene esters **4b,d**. (Table 2). Additionally, chromium carbene complexes **3a,c** and also tungsten complexes **3g,h** were in turn subjected to the same oxidative conditions to form the corresponding tetrahydroazulenes **4a–c**. In all cases tetrahydroazulenes **4** were obtained in high yield and without epimerization.

Table 2. Demetallation of Chromium and Tungsten Carbene Complexes **3**.



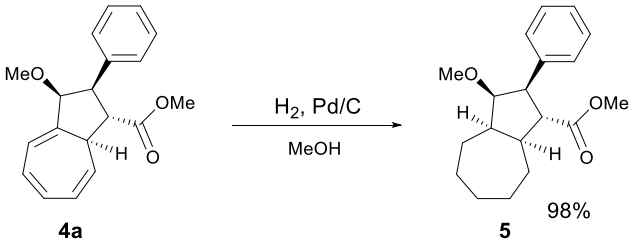
3 [M] = $Cr(CO)_5$, $W(CO)_5$ **4**

Entry	M	R^1	Product	Yield[a] (%)
1	Cr	Ph	**4a**	82
2	Cr	*p*OMe-C_6H_4	**4b**	76[b]
3	Cr	*p*Cl-C_6H_4	**4c**	89
4	Cr	2-Thienyl	**4d**	70[b]
5	W	Ph	**4a**	92
6	W	*p*MeO-C_6H_4	**4b**	75

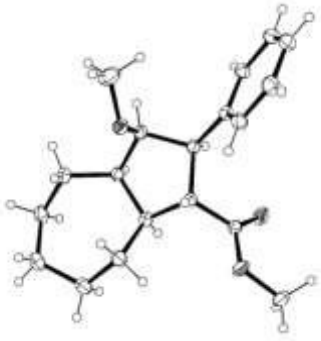
[a] Yields after column chromatographic purification.

[b] Overall yield from carbene complexes **1b**,**d**.

In order to confirm that the relative stereochemistry of all the stereocenters of **4** remained unchanged**,** compound **4a** was reduced through a catalytic hydrogenation (H_2, 1 atm, Pd/C, MeOH) to give **5** in a totally diastereoselective process (Scheme 2). An X-ray analysis of a monocrystal of **5** grown from hexanes/chloroform,[12] allowed to unambiguously stablish the relative stereochemistry of the five consecutive stereogenic centers.

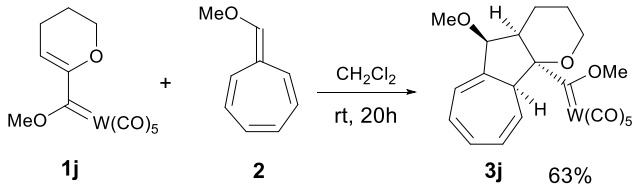


4a **5**



Scheme 2. Diatereoselective Hydrogenation of Tetrahydroazulene **4a**. X-ray crystal structure for compound **5**. Thermal ellipsoids at the 50% probability level.

In addition to the described tetrahydroazulenyl chromium and tungsten carbene complexes, we explored other substitution pattern at C_α and C_β of the alkenyl carbene complexes. Accordingly, we found that cyclic tungsten alkenyl carbene complex **1j** was effective in its reaction toward heptafulvene **2.** Thus, tungsten carbene complex **1j** was reacted with **2** under the standard reaction conditions to furnish the expected tungsten carbene cycloadduct **3j** in a 63% yield. The densely functionalized cycloadduct **3j** was formed again with complete regio- and diastereoselectivity and its structure was confirmed by NMR spectroscopic data.



Scheme 3. Reaction between Tungsten Alkenyl FCC **1j** and 8-Methoxyheptafulvene **2**.

As it has just been described, the cycloaddition reaction of alkenyl carbene complexes **1** and heptafulvene **2** displays a remarkable selectivity. In this way, the regiochemistry of the reaction is in accordance with the electronic distribution of the heptafulvene **2** and the alkenyl carbene complex **1**, and it is consistent with the selectivity found in formal [8 + 2] cycloaddition reactions of 8-methoxyheptafulvene with other electron-poor olefins.[11e] Apart from the regioselectivity of the reaction, the formation of the corresponding adducts containing four contiguous stereocenters with complete diastereoselectivity is noteworthy. Accordingly, the relative position of the substituents matches with an *exo* approach of the carbene moiety to the heptafulvene **2**, probably to avoid steric interactions with the heptafulvene ring. Moreover, the presence of the metal moiety is essential since no reaction was observed between heptafulvene **2** and methyl cinnamate even in refluxing 1,2-dichloroethane (84°C) and during prolonged reaction times. This result corroborates the activating effect of the metal moiety.

Theoretical calculations.

In order to fully understand the reaction mechanism, we decided to perform a computational study (PCM-B3PW91-D3/cc-pVDZ//B3PW91/cc-pVDZ level). Similar level of theory demonstrated to be useful in the elucidation of reaction mechanisms of cycloaddition reactions[9,13] and organometallic compounds involving reactions.[9,14] Since both chromium and tungsten carbene complexes have proved their utility in these reactions (see experimental results above), we selected chromium complexes due to their lower computational cost.

We started the theoretical study by modelling the reaction between carbene complex **1e** (R^1=2-furyl) and 8-methoxyheptafulvene **2**. As explained above, this reaction led to the formation of cycloadduct **3e** (73% yield, Table 1). For this reaction, two different reaction pathways, concerted *versus* stepwise, are possible. The energy profile for the access to adduct **3e** from **1e** and **2** is depicted in Figure 2, which gathers the computed free energies (at 298 K) in CH_2Cl_2. Although we have made a thorough revision for both pathways, it should be highlighted that only the concerted pathway was located on the potential energy surface. From **TS1** the IRC (intrinsic reaction coordinate) brings directly to **3e**. The computed value for **TS1** barrier ($\Delta G^{\ddagger}_{298}$ = 11.9 kcal/mol) is compatible with the [8+2] cycloaddition reaction of **2** and **1e** to give **3e** under the experimental reaction conditions (i.e., 20 h at room temperature).For **TS1**, distances of 1.983 and 2.845 Å (C_1–C_4 and C_3–C_5, respectively) for the two C–C forming bonds were found, which indicates that the cycloaddition takes place through a concerted mechanism associated to a highly asymmetric transition structure. This large asymmetry is in agreement with previously computed cycloadditions[9,13,15] and it should be attributed to the electron-donating effect of the methoxy group on heptafulvene **2** together with the electron-withdrawing effect of the conjugated C=Cr bond on the carbene complex **1e**. These two factors favour the C–C bond formation at one of the positions. Consistently, the Cr=C_6 bond is enlarger from 2.054 Å, at **1e**, to 2.125 Å, at **TS1**.

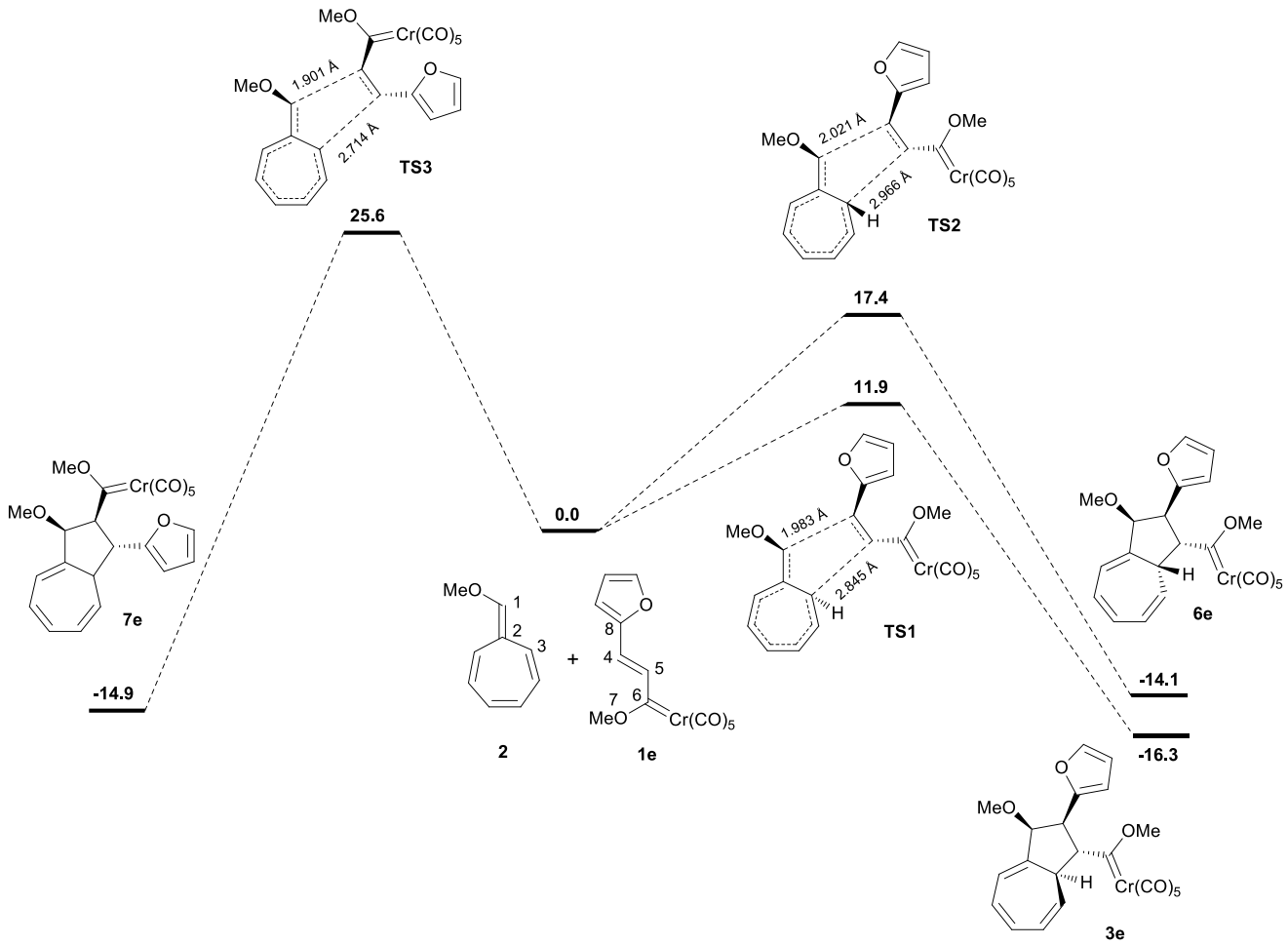


Figure 2. Computed energy diagram (PCM-B3PW91-D3/cc-pVDZ//B3PW91/cc-pVDZ level) showing possible channels for the [8+2] cycloaddition reaction between **1e** and **2**. Relative free energies (ΔG_{298}) are given in kcal/mol.

Considering that the reaction takes place with complete regio- and stereoselectivity, we have explored alternative pathways. First, starting from species **1e** and **2**, the model **6e** stereoisomer could also be obtained from an *exo*- approach. In this case, on the potential energy surface it could only be located the concerted pathway. As shown in Figure 2, according to our calculations, from **1e** and **2** it is necessary to overcome an energy barrier of $\Delta G^{\ddagger}_{298}$ = 17.4 kcal/mol, through **TS2**, to yield the structure **6e**. This barrier is 5.5 kcal/mol higher than the barrier to access to **TS1**. This gap is high enough to explain the observed stereoselectivity in favour of compound **3e**. Looking at **TS2**, it can be noticed higher distances for the two C–C forming bonds (2.021 and 2.966 Å, C_1–C_4 and C_3–C_5, respectively), compared with those of **TS1** (1.983 and 2.845 Å, C_1–C_4 and C_3–C_5, respectively), although interestingly, the Cr=C_6 distance is larger for **TS2** (2.137 Å) than for **TS1** (2.125 Å). Since electron-donating effect (methoxyheptafulvene **2**) and Cr=C_6 bond electron-withdrawing effect (carbene complex **1e**) seem to be present in both, **TS1** and **TS2**, an additional factor should determine the difference between the transition state energies. Thus, looking at structures **TS1** and **TS2**, it could be noticed that the approach between **1e** and **2** takes place along a staggered conformation in **TS1** (C_2–C_1–C_4–O_7 and C_2–C_1–C_4–C_8 dihedral angles = 104.8 and -77.5°, respectively), while the conformation is eclipsed in **TS2** (C_2–C_1–C_4–O_7 and C_2–C_1–C_4–C_8 dihedral angles = -3.1 and 172.7°, respectively). This fact allows us to explain the observed diastereoselectivity. Finally, the lower stability calculated for **6e** (ΔG_{298} = –14.1 kcal/mol), compared with **3e** (ΔG_{298} = –16.3 kcal/mol), could be attributed to the *cis*-ring fusion in the former.

In addition to the rationalization of the mechanistic pathway, we have also performed a computational analysis for the regiochemistry of the process (Figure 2, left). Although **3e** and **7e** are close in energy (ΔG_{298} = –16.3 and –14.9 kcal/mol, respectively), it becomes obvious that formation of **7e** is not competitive due to the much higher activation barrier of the process ($\Delta G^{\ddagger}_{298}$ = 25.6 kcal/mol) via **TS3**, compared with that of the formation of **3e** through **TS1** ($\Delta G^{\ddagger}_{298}$ = 11.9 kcal/mol). Consistently, the **TS3** barrier prevents the transformation of starting products into **7e**. Looking at the calculated structure for **TS3**, the two C–C forming bonds exhibit distances of 1.901 and 2.714 Å (C_1–C_5 and C_3–C_4, respectively), while the Cr=C_6 bond is placed at 2.052 Å, almost identical to that of **1e** (2.054 Å). This result denotes that carbene bond is not in the proper position to be conjugated with the incipient C_1–C_5 bond. Thus,

the highest energy barrier found for **TS3** could be explained in terms of non-participation of the metal moiety in the course of the reaction.

Finally, in order to evaluate the effect of the metal in the reaction, we have carried out calculations replacing the Fischer carbene moiety by an ester group. We analyzed the reaction between 8-methoxyheptafulvene **2** and methyl (*E*)-3-(furan-2-yl)acrylate **8e**. As shown in Figure 3, the lack of the metallic fragment has a significant impact in both energy barrier and geometry of the transition state. According to our calculations, the two C–C forming bonds in **TS4** are placed at 2.727 Å (C_1–C_4) and 1.960 Å (C_3–C_5), while in **TS1** distances of 1.983 Å (C_1–C_4) and 2.845 Å and (C_3–C_5) were found, which change the order of the bond formed first. Moreover, the energy barrier to reach **TS4** should be 22.4 kcal/mol, 10.5 kcal/mol higher than that of the **TS1** analogue (11.9 kcal/mol), while the relative energy of product remains essentially the same (-16.5 kcal/mol, **9e**, *vs.* -16.3 kcal/mol, **3e**). Consequently, it is possible to conclude that the metal carbene moiety plays an essential role in the stabilization of the transition state.

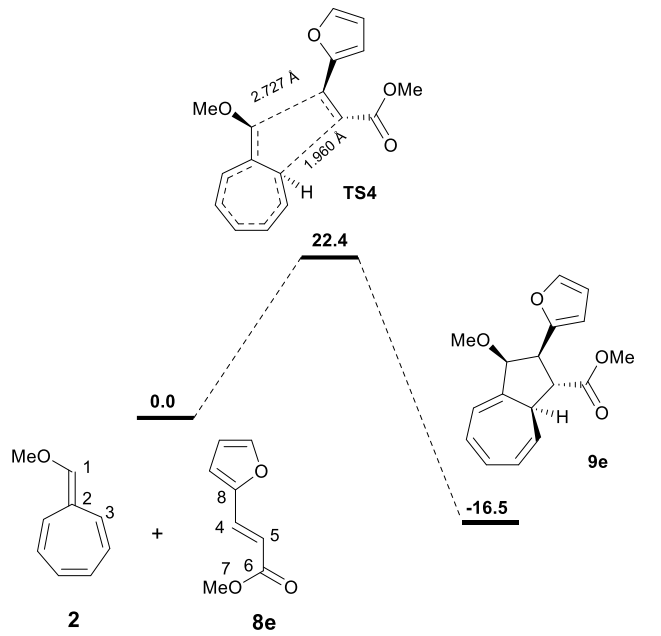


Figure 3. Computed energy diagram (PCM-B3PW91-D3/cc-pVDZ//B3PW91/cc-pVDZ level) showing the [8+2] cycloaddition reaction between **8e** and **2**. Relative free energies (ΔG_{298}) are given in kcal/mol.

Experimental

General Experimental Methods

All reactions involving air sensitive compounds were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated and purged with nitrogen. Alkenyl Fischer carbene complexes **1**[16] were prepared following described procedures. 8-Methoxyheptafulvene **2** was prepared following the procedure described below. Solvents were dried by standard methods and distilled prior to use. Flash column chromatography was carried out on silica gel 60, 230–240 mesh. NMR experiments were recorded on 300 and 400 MHz spectrometers. NMR chemical shifts are reported in ppm. ^{1}H NMR splitting pattern abbreviations are: s, singlet; d, doublet; m, multiplet; ^{13}C NMR spectra were recorded with complete proton decoupling and the multiplicities were determined by DEPT. High resolution mass spectra (HRMS) were obtained by electron ionization techniques (EI) (70 eV) with a magnetic sector analyzer or electrospray (ESI) using a TOF analyzer.

Procedure for the preparation of 8-Methoxyheptafulvene 2.

9,4 mL (15 mmol) of a butyllithium solution (hexane, 1.6 M) was added dropwise under nitrogen to 2.1 mL (15 mmol) of diisopropylamine in 15 mL THF at –40 °C. The resulting mixture was stirred for 30 min and allowed to warm to – 25 °C. Then, 831 mg (5 mmol) of 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal[17] dissolved in 5 mL of THF was added dropwise. The resulting red mixture was stirred at – 25 °C for 20 min. and then for 2h at rt. The solvent was removed in the rotatory evaporator at 50 °C bath temperature, and 20 mL of hexanes were added to the resulting crude. Then, the mixture was stirred for 1h at rt, filtered through a pad of Celite® under nitrogen and the solvent removed to get 1-methoxyfulvene **2** as a red oil (590 mg, 88%).

General procedure for the preparation of carbenes 3.

Carbene complexes **1** (0.50 mmol) and 8-methoxyheptafulvene **2** (1.5 mmol) were dissolved in CH_2Cl_2 (5 mL) and the solution was stirred at 25 °C for 20 h. Then, the solvent was removed and the crude was purified by column chromatography (silica gel: hexanes/CH_2Cl_2, 2:1) to get cycloadducts **3**.

*Chromium metal carbene (**3a**).* Yield: 189 mg (0.400 mmol, 80%,); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.40 (m, 2H), 7.38–7.23 (m, 3H), 6.73–6.65 (m, 2H), 6.33–6.24 (m, 1H), 6.20–6.11 (m, 1H), 5.61–5.55 (m, 1H), 5.45–5.30 (m, 1H), 4.75 (s, 3H), 4.22–4.10 (m, 1H), 3.70–3.59 (m, 1H), 3.12 (s, 3H), 2.32–2.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 367.3 (C), 222.9 (C), 215.5 (4 x C), 140.5 (C), 137.4 (C), 131.4 (CH), 130.2 (2 x CH), 128.9 (CH), 127.9 (2 x CH), 127.4 (CH), 126.9 (CH), 124.0 (CH), 120.4 (CH), 84.9 (CH), 80.8 (CH), 67.7 (CH_3), 56.2 (CH_3), 55.2 (CH), 47.8 (CH); HRMS (EI) m/z; $[M]^+$ Calcd for $C_{24}H_{20}O_7Cr$ 472.0614; Found 472.0619.

*Chromium metal carbene (**3c**).* Yield: 225 mg (0.445 mmol, 89%); orange solid; mp: decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.32 (m, 2H); 7.30–7.21 (m, 2H), 6.69–6.57 (m, 2H), 6.26–6.19 (m, 1H), 6.10–6.01 (m, 1H), 5.58–5.46 (m, 1H), 5.31–5.18 (m, 1H), 4.73 (s, 3H), 4.10–4.01 (m, 1H), 3.62–3.51

(m, 1H), 3.09 (s, 3H), 2.24–2.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 367.0 (C), 222.9 (C), 215.6 (4 x C), 140.1 (C), 136.1 (C), 132.9 (C), 131.7 (CH), 131.0 (2 x CH), 129.0 (CH), 128.2 (2 x CH), 127.4 (CH), 124.2 (CH), 120.7 (CH), 84.8 (CH), 81.0 (CH), 67.9 (CH_3), 55.5 (CH_3), 55.3 (CH), 47.8 (CH); HRMS (EI) m/z: $[M]^+$ Calcd for $C_{24}H_{19}O_7CrCl$ 506.0224; Found 506.0229.

*Chromium metal carbene (**3e**).* Yield: 169 mg (0.366 mmol, 73%); orange solid; mp: decomposition; ^{1}H NMR (400 MHz, C_6D_6) δ 7.20–7.17 (m, 1H), 6.65–6.60 (m, 1H), 6.55–6.47 (m, 2H), 6.24–6.20 (m, 1H), 6.11–6.02 (m, 1H), 6.00–5.90 (m, 1H), 5.75–5.67 (m, 1H), 5.67–5.51 (m, 1H), 4.03 (s, 3H), 3.91 (d, J = 4.0 Hz, 1H), 3.70 (dd, J = 10.8, 7.8 Hz, 1H), 2.98 (s, 3H), 2.50–2.41 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 367.9 (C), 225.9 (4 x C), 218.3 (C), 154.2 (C), 143.1 (CH), 142.1 (C), 134.3 (CH), 131.3 (CH), 130.3 (CH), 126.7 (CH), 123.2 (CH), 113.1 (CH), 110.7 (CH), 85.8 (CH), 82.2 (CH), 69.6 (CH_3), 57.0 (CH_3), 52.7 (CH), 50.4 (CH); HRMS (EI) Calcd for $C_{22}H_{18}O_8Cr$ $[M]^+$: 462.0401; Found: 462.0405.

*Chromium metal carbene (**3f**).* Yield: 157 mg (0.315 mmol, 63 %); orange solid; mp: decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.24 (m, 5H), 6.64–6.55 (m, 3H), 6.31 (d, J = 16.0 Hz, 1H), 6.21–6.19 (m, 1H), 6.15–6.06 (m, 1H), 5.50–5.41 (m, 1H), 5.21–5.08 (m, 1H), 4.83 (s, 3H), 4.03 (d, J = 4.3 Hz, 1H), 3.72–3.68 (m, 1H), 3.12 (s, 3H), 2.37–2.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 367.8 (C); 223.2 (C), 215.8 (4 x C), 140.8 (C), 136.7 (C), 131.7 (CH), 131.5 (CH), 129.2 (2 x CH), 128.4 (CH), 127.4 (CH), 126.4 (CH), 126.1 (2 x CH), 124.2 (CH), 120.8 (CH), 85.3 (CH), 80.3 (CH), 67.6 (CH_3), 56.2 (CH_3), 55.6 (CH), 47.4 (CH); HRMS (EI) m/z: $[M]^+$ Calcd for $C_{26}H_{22}O_7Cr$ 498.0771; Found 498.0775.

*Tungsten metal carbene (**3g**).* Yield: 266 mg (0.440 mmol, 88 %); orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.40 (m, 2H), 7.37–7.22 (m, 3H), 6.72–6.54 (m, 2H), 6.26 (d, J = 5.1 Hz, 1H), 6.20–6.09 (m, 1H), 5.58 (dd, J = 9.4, 4.3 Hz, 1H), 5.30 (dd, J = 11.1, 7.8 Hz, 1H), 4.57 (s, 3H), 4.15 (d, J = 4.3 Hz, 1H), 3.70 (dd, J = 11.0, 4.3 Hz, 1H), 3.09 (s, 3H), 2.41–2.30 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 340.8 (C), 203.4 (C), 197.2 (4 x C), 140.9 (C), 138.0 (C), 132.1 (CH), 129.9 (2 x CH), 129.5 (CH), 128.5 (2 x CH), 128.0 (CH), 127.4 (CH), 124.7 (CH), 121.2 (CH), 85.4 (CH), 82.3 (CH), 70.8 (CH_3), 56.7 (CH), 55.8 (CH_3), 48.5 (CH); HRMS (ESI) m/z: $[M\text{-}4CO\text{-}3H]^+$ Calcd for $C_{20}H_{17}O_3W$ 489.0685; Found 489.0682.

*Tungsten metal carbene (**3h**).* Yield: 235 mg (0.371 mmol, 74 %); orange solid; mp: decomposition; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.70–652 (m, 2H), 6.24 (d, J = 5.2 Hz, 1H), 6.18–6.08 (m, 1H), 5.55 (dd, J = 9.4, 4.3 Hz, 1H), 5.30–5.19 (m, 1H), 4.57 (s, 3H), 4.09 (d, J = 4.4 Hz, 1H), 3.81 (s, 3H), 3.64 (dd, J = 11.0, 4.3 Hz, 1H), 3.09 (s, 3H), 2.40–2.30 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 341.3 (C), 203.4 (C), 197.2 (4 x C), 159.0 (C), 141.0 (C), 132.1 (CH), 130.9 (2 x CH), 130.0 (C), 129.5 (CH), 128.0 (CH), 124.7 (CH), 121.1 (CH), 113.9 (2 x CH), 85.5 (CH), 82.6 (CH), 70.7 (CH_3), 56.1 (CH_3), 55.8 (CH_3), 55.6 (CH), 48.4 (CH); HRMS (ESI) m/z: $[M\text{-}CO\text{-}3H]^+$ Calcd for $C_{24}H_{19}O_7W$ 603.0640; Found 603.0635.

*Tungsten metal carbene (**3i**).* Yield: 235 mg (0,400 mmol, 80 %); orange solid; mp: decomposition; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.70–6.53 (m, 2H), 6.38–6.29 (m, 2H), 6.25 (d, J = 5.4 Hz, 1H), 6.16–6.06 (m, 1H), 5.51 (dd, J = 9.5, 4.4 Hz, 1H), 5.18 (dd, J = 8.9, 5.4 Hz, 1H), 4.65 (s, 3H), 4.21 (d, J = 3.1 Hz, 1H), 3.77 (dd, J = 10.9, 3.2 Hz, 1H), 3.13 (s, 3H), 2.35–2.25 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 339.0 (C), 203.6 (C), 197.3 (4 x C), 152.2 (C), 141.4 (CH), 139.9 (C), 132.3 (CH), 129.4 (CH), 127.8 (CH), 124.7 (CH), 121.4 (CH), 110.8 (CH), 108.2 (CH), 84.1 (CH), 81.3 (CH), 70.8 (CH_3), 55.7 (CH_3), 50.0 (CH), 48.2 (CH) HRMS (EI) m/z; $[M]^+$ Calcd for $C_{22}H_{18}O_8W$ 594.0511; Found 594.0519.

*Tungsten metal carbene (**3j**).* Yield: 184 mg (0.315 mmol, 63%); orange solid; mp: decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, J = 11.0, 6.0 Hz, 1H); 6.59 (dd, J = 11.0, 5.8 Hz, 1H), 6.42–6.39 (m, 1H), 6.15 (dd, J = 9.0, 6.1 Hz, 1H), 5.02 (d, J = 9.0 Hz, 1H), 4.91 (s, 3H), 4.47–4.42 (m, 1H), 4.02–3.91 (m, 1H), 3.51–3.45 (m, 1H), 3.30 (s, 3H), 2.62–2.58 (m, 1H), 2.26–2.23 (m, 1H), 2.11–1.90 (m, 2H), 1.60–1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 339.1 (C), 192.8 (C), 189.4 (4 x C), 129.6 (C), 123.9 (CH), 122.2 (CH), 118.8 (CH), 112.5 (CH), 107.0 (CH), 90.4 (C), 75.0 (CH), 64.0 (CH_3), 59.3 (CH_2), 48.9 (CH_3), 46.7 (CH), 35.4 (CH), 13.8 (CH_2), 12.9 (CH_2); HRMS (EI) m/z; $[M]^+$ Calcd for $C_{21}H_{20}O_8W$ 584.0668; Found 584.0671.

General procedure for the preparation of esters 4.

Metal carbenes **3** (0.3 mmol) were dissolved in 3 mL THF and pyridine oxide (0,9 mmol) was added. The solution was stirred at rt for 30 min and water (10 mL) was added, the resulting mixture was extracted with diethyl ether (3 x 5 mL). After solvent removal and crude purification (silica gel; hexanes/ethyl acetate, 10:1) esters **4** were obtained.

*(1R,2R,3S,8aR/1S,2S,3R,8aS)-Methyl 3-methoxy-2-phenyl-1,2,3,8a-tetrahydroazulene-1-carboxylate **(4a).*** Yield: 73 mg (0.247 mmol, 82%) from **3a** or 82 mg (0.277 mmol, 92%) from **3g**; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58–7.18 (m, 5H), 6.66–6.48 (m, 2H), 6.27 (d, J = 5.2 Hz, 1H), 6.18–6.07 (m, 1H), 5.38 (dd, J = 9.5, 4.0 Hz, 1H), 4.12–4.04 (m, 1H), 3.72–3.65 (m, 2H), 3.63 (s, 3H), 3.04 (s, 3H), 2.78–2.69 (m, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 175.0 (C), 140.8 (C), 137.2 (C), 131.7 (CH), 129.2 (CH), 129.1 (2 x CH), 128.1 (2 x CH), 127.8 (CH), 126.9 (CH), 125.1 (CH), 121.9 (CH), 84.8 (CH), 55.4 (CH_3), 54.6 (CH), 52.9 (CH), 51.9 (CH_3), 46.4 (CH); HRMS (EI) m/z $[M]^+$ Calcd for $C_{19}H_{20}O_3$ 296.1412; Found 296.1409; Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.26; H, 6.98.

*(1R,2R,3S,8aR/1S,2S,3R,8aS)-Methyl 3-methoxy-2-(4-methoxyphenyl)-1,2,3,8a-tetrahydroazulene-1-carboxylate (**4b**).* Yield: 125 mg (0.383 mmol, 76%) overall from 0,5 mmol **1b** or 73 mg (0.224 mmol, 75%) from **3h**; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.65–6.47 (m, 2H), 6.25 (d, *J* = 5.3 Hz, 1H), 6.16–6.06 (m, 1H), 5.35 (dd, J = 9.6, 4.0 Hz, 1H), 4.04–3.98 (m, 1H), 3.82 (s,

3H), 3.61 (s, 3H), 3.65–3.56 (m, 2H), 3.04 (s, 3H), 2.76–2.66 (m, 1H).; ^{13}C NMR (75 MHz, C_6D_6); δ 175.0 (C), 158.5 (C), 140.9 (C), 131.7 (CH), 130.1 (2 x CH), 129.5 (C), 129.2 (CH), 127.8 (CH), 125.1 (CH), 121.9 (CH), 113.5 (2 x CH), 84.7 (CH), 55.4 (CH_3), 55.2 (CH_3), 54.0 (CH), 53.4 (CH), 51.9 (CH_3), 46.3 (CH); HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{22}O_4$ 326.1518; Found 326.1521. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.12; H, 6.99.

*(1R,2R,3S,8aR/1S,2S,3R,8aS)-Methyl 2-(4-chlorophenyl)-3-methoxy-1,2,3,8a-tetrahydroazulene-1-carboxylate (**4c**).* Yield: 88 mg (0.267 mmol, 89%); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.30 (m, 4H); 6.62–6.50 (m, 2H), 6.28–6.19 (m, 1H), 6.13–6.06 (m, 1H), 5.41–5.36 (m, 1H), 4.08–4.00 (m, 1H), 3.65–3.58 (m, 2H), 3.57 (s, 3H), 3.14 (s, 3H), 2.74–2.67 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 167.7 (C), 133.4 (C), 128.8 (C), 125.7 (C), 124.8 (CH), 124.4 (2 x CH), 123.4 (CH), 121.2 (2 x CH), 119.9 (CH), 118.2 (CH), 115.1 (CH), 77.9 (CH), 48.3 (CH_3), 47.0 (CH_3), 46.2 (CH), 45.0 (CH), 39.1 (CH); HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{19}O_3Cl$ 330.1023; Found 330.1021.

*(1R,2S,3S,8aR/1S,2R,3R,8aS)-Methyl 3-methoxy-2-(thiophen-2-yl)-1,2,3,8a-tetrahydroazulene-1-carboxylate (**4d**).* Yield: 105 mg, (0.350 mmol, 70%) overall from 0,5 mmol **1d**; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 1H); 7.12–6.90 (m, 2H), 6.61–6.50 (m, 2H), 6.29–6.18 (m, 1H), 6.12–6.08 (m, 1H), 5.36–5.23 (m, 1H), 4.12–4.02 (m, 1H), 3.95 (dd, J = 11.8, 4.2 Hz, 1H), 3.66 (s, 3H), 3.49 (dd, J = 11.8, 8.8 Hz, 1H), 3.12 (s, 3H), 2.71–2.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 174.7 (C), 140.3 (C), 139.9 (C), 131.8 (CH), 129.1 (CH), 127.6 (CH), 126.2 (CH), 126.1 (CH), 125.1 (CH), 125.0 (CH), 121.8 (CH), 84.1 (CH), 55.8 (CH_3), 55.3 (CH_3), 51.9 (CH), 50.1 (CH), 46.3 (CH), HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}O_3S$ 302.0977; Found: 302.0974.

Preparation of compound 5

To a solution of 59 mg of ester **4a** (0.2 mmol) in methanol (2 mL), 21 mg of 5 wt. % Pd/C (5 mol%) was added. The mixture was stirred at rt in a H_2 atmosphere (1 atm) for 1 h. The solvent was removed and the crude was purified by column chromatography (silica gel; hexanes/ethyl acetate, 10:1) to get 60 mg of compound **5** (98% yield)

*(1R,2R,3R,8aS/1S,2S,3S,8aR)-Methyl 3-methoxy-2-phenyldecahydroazulene-1-carboxylate (**5**).* Yield: 59 mg (0.195 mmol, 98%); white solid; mp: decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.13 (m, 5H); 3.62 (s, 3H), 3.52–3.48 (m, 1H), 3.41–3.32 (m, 1H), 3.17–3.09 (m, 1H), 2.93 (s, 3H), 2.58–2.47 (m, 1H), 2.40–2.31 (m, 1H), 2.11–1.68 (m, 6H), 1.45–1.21 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 176.3 (C), 138.5 (C), 128.4 (2 x CH), 127.9 (2 x CH), 126.3 (CH), 90.4 (CH), 60.4 (CH), 54.2 (CH_3), 54.1 (CH_3), 51.6 (CH), 49.0 (CH), 47.7 (CH), 32.2 (CH_2), 31.4 (CH_2), 30.5 (CH_2), 28.5 (CH_2), 26.5 (CH_2), HRMS (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{26}O_3$: 302.1882; Found 302.1883. Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.45; H, 8.67. Found: C, 75.12; H, 8.98.

Computational details.

All calculations were carried out using the Gaussian 03 and Gaussian 09 program packages.[18] Because DFT methods combine the importance of including electron correlation effects and the possibility of dealing with large systems, ground-state molecular geometries were optimized within the B3PW91/cc-pVDZ level. Geometry was fully optimized without any symmetry constraint for all model compounds. Optimized structures were characterized as minima or saddle points by frequency calculations, which also allowed to obtain the ZPE and thermal corrections. Gibbs free energies have been obtained from thermochemical analyses for T = 298 K. In order to fully prove the relevance of the transition structures we also computed the IRC (intrinsic reaction coordinate) connecting the critical points to confirm that the TS really relate the minima. Finally, single point calculations on the optimized structures were performed including the solvents effects of dichloromethane by the Polarizable Continuum Model (PCM)[19] and the dispersion effect by means of the Grimme's dispersion with the original D3 damping function.[20] This level is denoted as PCM-B3PW91-D3/cc-pVDZ//B3PW91/cc-pVDZ.

Conclusions

In summary, we have described a new higher-order cyclization reaction for alkenyl Fischer carbene complexes with fulvenoid substrates. Chromium and tungsten alkenyl carbene complexes react with 8-methoxyheptafulvene exclusively through an all-carbon [8 + 2] cyclization, with complete regio- and stereoselectivity. This work can be also regarded as a selective entry to hydroazulenes bearing four consecutive stereocenters. Theoretical calculations performed in order to rationalize the obtained results, indicate that this transformation proceeds through a concerted reaction mechanism. This result differs from stepwise reactions of alkenyl carbenes complexes with fulvene substrates containing a reactive heteroatom functionality. Calculations also indicate that the metal plays a key role in the activation of the cycloaddition reaction. Finally, it is concluded that the nature of the observed stereo- and regioselectivity can be attributed to both steric and electronic factors.

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A new selective and concerted all-carbon [8 + 2] cycloaddition of alkenyl Fischer carbene complexes with 8-methoxyheptafulvene is described