Organometallics **2005,** *24,* 3413−3421

Facial Stereoselectivity in the Diels−Alder Reactions of (Arylethynyl)ethoxycarbenes of Group 6 with 1,2,3,4,5-Pentamethylcyclopenta-1,3-diene and Unusual Rearrangement of Strained Norbornadienyl Fischer Carbene Complexes of Chromium(0)

Miguel A. Vázquez,[†] Leonor Reyes,[†] René Miranda,[‡] Juventino J. García,[§]
Hugo A. Jiménez-Vázquez,[†] Joaquín Tamariz,[†] and Francisco Delgado*[,†]

Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, IPN, Prol. Carpio y Plan de Ayala, 11340 México, D. F., México, Sección de Química Orgánica, Facultad de Estudios Superiores Cuautitlán-UNAM, Campo 1, Cuautitlán Izcalli, 54740 Edo. de México, México, Facultad de Química, Universidad Nacional Autónoma de México, 04510 México, D. F, México

Received March 4, 2005

A study of reactivity and facial selectivity in Diels−Alder reactions of the Fischer carbene complexes $(CO)_5M{=}C(C{\equiv}CC_6H_4R)OCH_2CH_3$ (**1a**, M = Cr, R = H; **1b**, M = Cr, R = *p*-OCH$_3$; **1c**, M = Cr, R = *p*-CH$_3$; **2**, M = W, R = H; **3**, M = Mo, R = H), with 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (**4**) was carried out. The cycloadditions were found to be highly π-facial stereoselective, favoring the *anti* adduct. Among these complexes, **3** was the most reactive dienophile. The stereochemical assignment of the adducts **5**−**7** was supported by NOE measurements; structures of the *anti* cycloadducts **5a** and **6** were established by single-crystal X-ray diffraction. A [4 + 2] cycloaddition/benzannulation/rearrangement cascade reaction was observed for the chromium carbene complexes **1a**−**c** with **4** under thermal conditions, resulting in the naphthofurandione derivatives **9**−**11**.

Introduction

Synthetic applications of Fischer carbene complexes have been the target of a large number of recent studies.[1] In particular, the Dötz reaction, a cycloaddition of Fischer α,β-unsaturated carbene complexes to alkynes, has attracted widespread interest in organic synthesis.[2] It is well known that alkynyl carbene complexes can be employed as dienophiles in Diels−Alder reactions; the resultant α,β-unsaturated adducts can react further either by spontaneous or thermal means to form cyclopentadienes[3,4] or by photolysis to produce phenol derivatives.[5]

Recently, we reported the reactivity and selectivity in the reaction of (α-alkoxyvinyl)ethoxycarbene complexes with 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene, which produced new alkoxy-chelated tetracarbonyl carbene complexes with a high *anti*/*exo* selectivity.[6] This study has now been extended to the reaction of the (arylethynyl)ethoxycarbene complexes **1**−**3** in Diels−Alder cycloadditions.

Herein, we describe the cycloaddition of (arylethynyl)ethoxycarbene complexes **1**−**3** with 1,2,3,4,5-pentam-

---

[†] Escuela Nacional de Ciencias Biológicas, IPN.

[‡] Facultad de Estudios Superiores Cuautitlán-UNAM.

[§] Universidad Nacional Autónoma de México.

(1) (a) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539−587. (b) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int., Ed.* **2000**, *39*, 3964−4002. (c) Wu, H. P.; Aumann, R.; Fröhlich, R.; Wegelius, E.; Saavenketo, P. *Organometallics* **2000**, *19*, 2373−2381. (d) Rudler, H.; Parlier, A.; Durand-Réville, T.; Martín-Vaca, B.; Audouin, M.; Garrier, E.; Certal, V.; Vaissermann, J. *Tetrahedron* **2000**, *56*, 5001−5027. (e) Merlic, C. A.; Burns, E. E.; Xu, D.; Chen, S. Y. *J. Am. Chem. Soc.* **1992**, *114*, 8722−8724. (f) Wang, H.; Huang, J.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 8980−8981. (g) Kagoshima, H.; Akiyama, T. *J. Am. Chem. Soc.* **2000**, *122*, 11741−11742. (h) Ghorai, B. K.; Jiang, D.; Herndon, J. W. *Org. Lett.* **2003**, *5*, 4261−4263. (i) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pérez-Priede, M. *J. Am. Chem. Soc.* **1999**, *121*, 3065−3071. (j) Barluenga, J.; Martínez, S.; Suárez-Sobrino, A. L.; Tomás, M. *J. Am. Chem. Soc.* **2002**, *124*, 5948−5949. (k) Rudler, H.; Parlier, A.; Certal, V.; Vaissermann, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3417−3419. (l) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257−1280. (m) Rawat, M.; Wulff, W. D. *Org. Lett.* **2004**, *6*, 329−332. (n) Rudler, H.; Parlier, A.; Certal, V.; Humbert, N.; Vaissermann, J. *Tetrahedron Lett.* **2002**, *43*, 5897−5899.

(2) (a) Vorogushin, A. V.; Wulff, W. D.; Hansen, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6512−6513. (b) Painter, J. E.; Quayle, P. *Tetrahedron Lett.* **1995**, *36*, 8089−8092. (c) Barluenga, J.; Aznar, F.; Palomero, M. A. *J. Org. Chem.* **2003**, *68*, 537−544. (d) Dötz, K. H.; Mittenzwey, S. *Eur. J. Org. Chem.* **2002**, *1*, 39−47. (e) Fogel, L.; Hsung, R. P.; Wulff, W. D.; Sommer, R. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 5580−5581. (f) Xu, Y. C.; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1989**, *111*, 7269−7271. (g) Flynn, B. L.; Schirmer, H.; Duetsch, M.; de Meijere, A. *J. Org. Chem.* **2001**, *66*, 1747−1754.

(3) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565−7567. (b) Rahm, A.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1993**, *12*, 597−599. (c) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *Org. Lett.* **2002**, *4*, 3659−3662.

(4) (a) Barluenga, J. *Pure Appl. Chem.* **2002**, *74*, 1317−1325. (b) Barluenga, J.; Aznar, F.; Barluenga, S.; Fernández, M.; Martín, A.; García-Granda, S.; Piñeira-Nicolás, A. *Chem. Eur. J.* **1998**, *4*, 2280−2298. (c) Barluenga, J.; Aznar, F.; Barluenga, S.; Martín, A.; García-Granda, S.; Martín, E. *Synlett* **1998**, 473−474. (d) Barluenga, J.; Lopéz, L. A.; Martínez, S.; Tomás, M. *Synlett* **1999**, 219−221.

(5) (a) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418−7420. (b) Merlic, C. A.; Aldrich, C. C.; Albaneze-Walker, J.; Saghatelian, A. *J. Am. Chem. Soc.* **2000**, *122*, 3224−3225. (c) Merlic, C. A.; Xu, D.; Gladstone, B. G. *J. Org. Chem.* **1993**, *58*, 538−545. (d) Merlic, C. A.; You, Y.; McInnes, D. M.; Zechman, A. L.; Miller, M. M.; Deng, Q. *Tetrahedron* **2001**, *57*, 5199−5212.

(6) Vázquez. M. A.; Cessa, L.; Vega, J. L.; Miranda, R.; Herrera, R.; Jiménez-Vázquez, H. A.; Tamariz, J.; Delgado, F. *Organometallics* **2004**, *23*, 1918−1927.

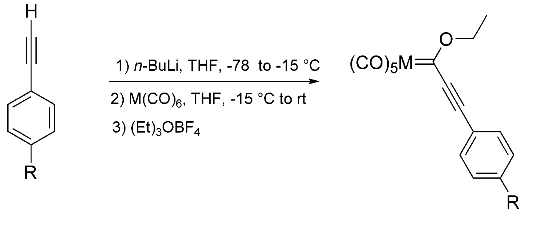
10.1021/om050159q CCC: $30.25

ethyl-1,3-cyclopentadiene (**4**) and their evaluation in terms of reactivity and facial selectivity. In addition, we report the unusual behavior in the reaction of complexes **1a**−**c** with diene **4** under thermal conditions.

Results and Discussion

The (arylethynyl)ethoxycarbene complexes **1**−**3** were prepared in moderate yields (45−86%) by the standard methodology,[4b,7] starting from the corresponding acetylenes (Scheme 1), and characterized by their ^{1}H NMR and ^{13}C NMR data.

Scheme 1



1a M = Cr, R = H
1b M = Cr, R = p-OCH$_3$
1c M = Cr, R = p-CH$_3$
2 M = W, R = H
3 M = Mo, R = H

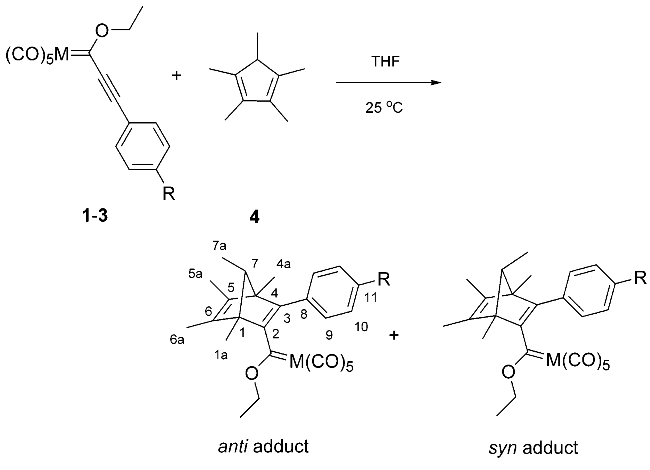
Diels−Alder Cycloadditions. The (arylethynyl)ethoxycarbene complexes **1**−**3** were evaluated in terms of reactivity and facial selectivity toward pentamethylcyclopentadiene (**4**) in Diels−Alder reactions. After screening several reaction conditions, we found that the Diels−Alder cycloaddition between **1a** and **4** could be carried out at room temperature. Thus, when **1a** reacted with **4** (25 °C), only the *anti* cycloadduct **5a** was obtained (Table 1), as judged from ^{1}H NMR (300 MHz) analysis of the crude reaction mixture.

To evaluate the effect of the substituent in the aromatic ring on the reactivity and the facial selectivity, **4** was added under identical conditions to complexes **1b**,**c**. A similar behavior was observed for the latter with respect to **1a**, since cycloadducts **5b**,**c** were obtained as a single *anti* stereoisomer, with similar yields.

However, the reaction between the (arylethynyl)ethoxycarbene complex of W(0), **2**, with **4** failed to give the [4 + 2] adduct, after 24 h at room temperature. It was necessary to raise the temperature to 50 °C for 4 h to afford complex **6** in 68% yield. In the case of the (arylethynyl)ethoxycarbene complex of Mo(0), **3**, the reaction was performed at room temperature but for a shorter reaction time (1 h) to afford the *anti* cycloadduct **7**, in fair yield (40%) (Table 1).

As shown in Table 1, the reaction time was longer for carbenes **1b**,**c** than for **1a**. This is probably due to the electron-donating effect of the substituent of the benzene ring in the former carbenes. In terms of Alder's rule, it is expected that the rate of cycloaddition is retarded by increasing the electron density at the dienophile.[8] On the other hand, it is noteworthy to see that the change in the metal atom of the carbene also affects the reactivity, since the relative rate is reduced when molybdenum is replaced by chromium or strongly reduced by tungsten. However, the *anti* selectivity observed in adducts **5**−**7** does not seem to be influenced by the change of the metal atom.

Table 1. Reaction Conditions and Yields in the Diels−Alder Cycloadditions of Alkynyl Carbene Complexes 1−3 to 4[a]



5-7

carbene	M	R	*T* (°C)	time (h)	*anti* adduct (amt, %)[b]
1a	Cr	H	25	4	**5a** (72)
1b	Cr	p-OCH$_3$	25	12	**5b** (60)
1c	Cr	p-CH$_3$	25	6	**5c** (77)
2	W	H	50	4	**6** (68)
3	Mo	H	25	1	**7** (40)

[a] All the reactions were carried out with 2 mol equiv of **4**. [b] After workup.

The new α,*β*-unsaturated carbene complexes **5**−**7** were isolated as red solids. Their ^{1}H and ^{13}C NMR spectra were consistent with the norbornadienyl skeleton, with the presence of a pentacarbonyl ethoxycarbene fragment, and the aryl group. It is noteworthy that the ^{1}H NMR analysis of the crude mixtures did not show evidence of the presence of any other isomer; hence, the cycloaddition reaction was highly *anti*-facial selective. The assignment of the structure of **7** was supported by NOE experiments, where the signals of protons H-10 (7.28 ppm), H-7 (2.42 ppm), and H-4a (1.17 ppm) were enhanced when the H-9 proton (6.87 ppm) was irradiated (Figure 1).

The *anti* stereochemistry for compounds **5a** and **6** was confirmed by X-ray crystallography (Figures 2 and 3). The X-ray structures show that both the aryl group and the [M(CO)$_5$] carbenic moiety are out of the plane of the endocyclic double bond, presenting the following consistent torsion angles: 61.73° for C(2)−C(3)−C(8)−C(9) and 60.92° for C(3)−C(2)−C(C-carbenic)−(Cr); −60.91° for C(2)−C(3)−C(8)−C(9) and −63.35° for C(3)−C(2)−C(C-carbenic)−(W). The bond lengths between the metal

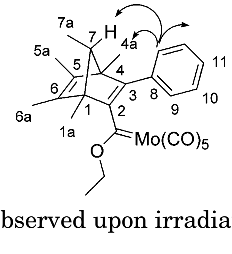


Figure 1. NOE observed upon irradiation of protons H-9 for **7**.

---

[7] Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23−C26.

[8] (a) Saver, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16−18. (b) Anh, N. T.; Canadell, E.; Eistein, O. *Tetrahedron* **1978**, *34*, 2283−2288.

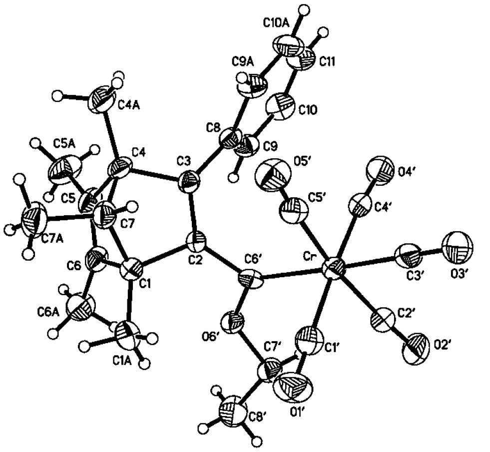


Figure 2. Molecular structure of complex **5a** with thermal ellipsoids at the 30% probability level.

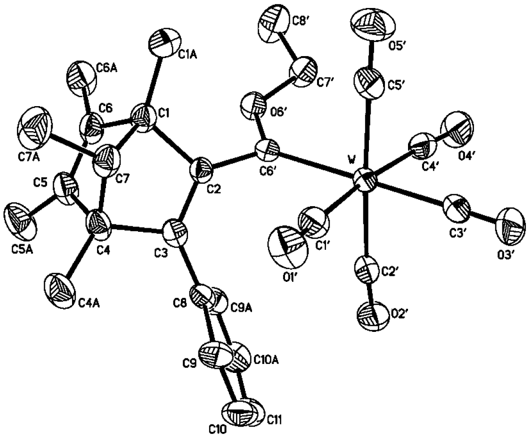


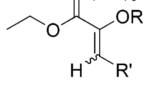
Figure 3. Molecular structure of complex **6** with thermal ellipsoids at the 30% probability level.

atoms and the carbenic carbons were 2.057 Å for chromium and 2.188 Å for tungsten, which agree with the size of the metal atom.

The origin of the π-facial stereoselectivity in the Diels–Alder reactions of cyclopentadienes substituted unsymmetrically at the methylene bridge has been studied experimentally and theoretically.[9] Although steric interactions seem to be a major factor in determining the π-facial selectivity, it has been less clear how relevant stereoelectronic effects are in controlling this selectivity.[10] Burnell used pentamethylcyclopentadiene (**4**) to evaluate the π-facial stereoselectivity in the reaction with dimethyl acetylenedicarboxylate, which gives an *anti*/*syn* mixture of adducts in a 76:24 ratio.[11] Even though the stereoselectivity was explained on the basis of steric hindrance, the major product is also in accord with that predicted by stereoelectronic control.[10a]

On the other hand, the *anti* selectivity is predicted by the reactivity-enhanced selectivity theory (RES) to be enhanced with the reactivity of the dienophiles. Inagaki has confirmed the dependence of the π-facial selectivities of 5-substituted cyclopentadienes on the reactivities of dienophiles in Diels–Alder reactions.[12]

Recently, we have reported the Diels–Alder reaction of (α-alkoxyvinyl)ethoxycarbene complexes (**8**) with pentamethylcyclopentadiene (**4**), which gave only the *anti*-*exo* diastereoisomer.[6] The *exo* selectivity was probably due to the strong repulsive interactions between the metal moiety and the methyl group of the diene at the *endo* transition state.



8

The *anti* stereoselectivity observed in the cycloadditions of complexes **1**–**3** with pentamethylcyclopentadiene (**4**) can be explained in terms of a combination of several factors: (a) repulsive van der Waals interactions occur between the [(CO)$_5$M] moiety and the substituted methylene bridge of the diene, which is expected to be stronger at the *syn* transition states; (b) the presence of the methyl group at C-5 in **4** would be expected to polarize the electron density toward the *anti* face of the diene, making it more electron-rich, favoring the *anti* transition states. This would be in agreement with the product predicted by the Cieplak theory.[13]

The relative reactivity among carbenes **1a** and **8** was estimated from the reaction conditions. Thus, the reaction of **4** with **8** was carried out in THF at 40 °C for 12 h, whereas the cycloaddition with **1a** was carried out in THF at 25 °C for 4 h; it is clear then that **1a** is much more reactive than **8**. In both cases the corresponding *anti* cycloadducts were obtained. These results of facial selectivity are also in agreement with the stereoelectronic effects predicted by the theory of reactivity-enhanced selectivity.[10a]

Thermal Reactions. The influence of temperature on the reaction of (arylethynyl)ethoxycarbenes **1a**–**c** with **4** was studied. In a first attempt, a mixture of the alkynylcarbene complex **1a** and diene **4** in dry THF was heated to 50 °C and the reaction was monitored by TLC until the disappearance of **1a** (12 h). After workup, an unexpected mixture of the two new naphthofurandiones **9a** (26%) and **9b** (22%) were isolated (Table 2). The structural elucidation of products **9a**,**b** was made on the basis of their spectroscopic data.

Thus, the ^{1}H NMR spectrum of **9a** showed the presence of an *ortho*-substituted benzene ring, with signals attributed to H-6 and H-9 protons at 8.00–8.05 ppm and H-7 and H-8 protons at 7.60–7.72 ppm. At 3.20 ppm, a quartet was found integrating for one proton (H-1); and four singlets and one doublet were observed at 1.65, 1.62, 1.50, 1.37, and 1.05 ppm, respectively, for five methyl groups. The ^{13}C NMR spectrum displayed

---

(9) (a) Xidos, J. D.; Poirier, R. A.; Pye, C. C.; Burnell, D. J. *J. Org. Chem.* **1998**, *63*, 105–112. (b) Ishida, M.; Kobayashi, H.; Tomohiro, S.; Wasada, H.; Inagaki, S. *Chem. Lett.* **1998**, 41–42. (c) Wellman, M. A.; Burry, L. C.; Letourneau, J. E.; Bridson, J. N.; Miller, D. O.; Burnell, D. J. *J. Org. Chem.* **1997**, *62*, 939–946. (d) Ishida, M.; Aoyama, T.; Beniya, Y.; Yamabe, S.; Kato, S.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3430–3439. (e) Macaulay, J. B.; Fallis, A. G. *J. Am. Chem. Soc.* **1990**, *112*, 1136–1144. (f) Ishida, M.; Sakamoto, M.; Hattori, H.; Shimizu, M.; Inagaki, S. *Tetrahedron Lett.* **2001**, *42*, 3471–3474. (g) Ishida, M.; Hirasawa, S.; Inagaki, S. *Tetrahedron Lett.* **2003**, *44*, 2187–2190. (h) Brown, F. K.; Houk, K. N.; Burnell, D. J.; Valenta, Z. *J. Org. Chem.* **1987**, *52*, 3050–3059.

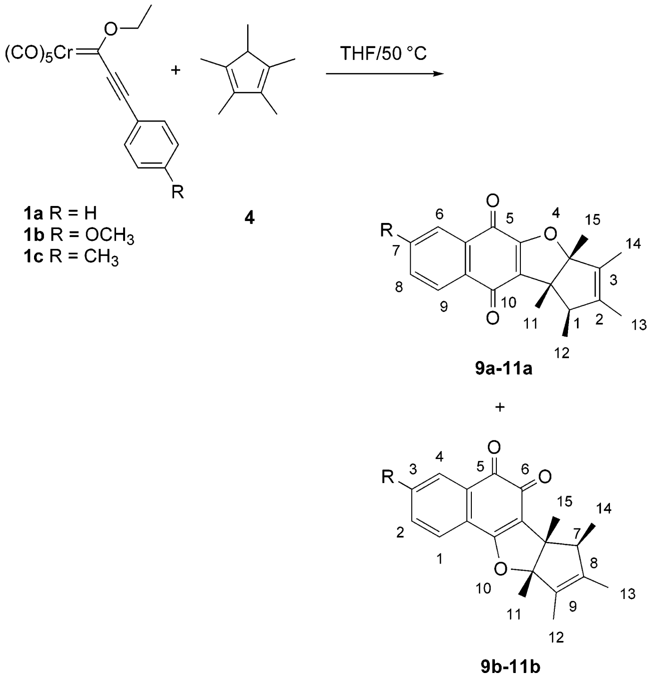
(10) (a) Halterman, R. L.; McCarthy, B. A.; McEvoy, M. A. *J. Org. Chem.* **1992**, *57*, 5585–5589. (b) Bodepudi, V. R.; le Noble, W. *J. Org. Chem.* **1991**, *56*, 2001–2006. (c) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447–8462.

(11) Letourneau, J. E.; Wellman, M. A.; Burnell, D. J. *J. Org. Chem.* **1997**, *62*, 7272–7277.

(12) Ishida, M.; Kakita, S.; Inagaki, S. *Chem. Lett.* **1995**, 469–470.

(13) Cieplak, A. S. *Chem. Rev.* **1999**, *99*, 1337–1376.

Table 2. Formation of Naphthofurandiones 9a–11a and 9b–11b[a]



carbene	R	time (h)	product (amt, %)[b]
1a	H	12	**9a/9b** (26/22)
1b	*p*-OCH$_3$	14	**10a/10b** (22/20)
1c	*p*-CH$_3$	14.5	**11a/11b** (20/20)

[a] All trials with 2 mol equiv of **4**, in dry THF, and heating to 50 °C. [b] After workup.

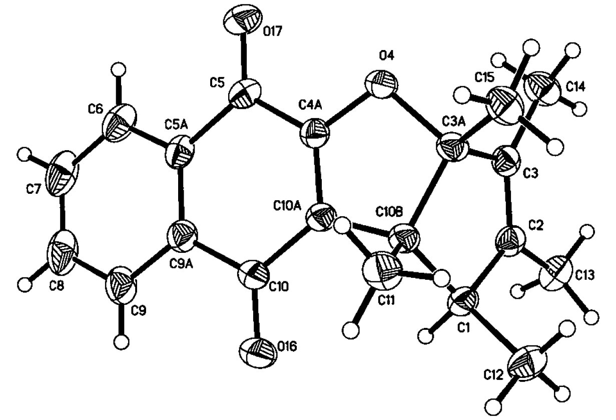


Figure 4. Molecular structure of complex **9a** with thermal ellipsoids at the 30% probability level.

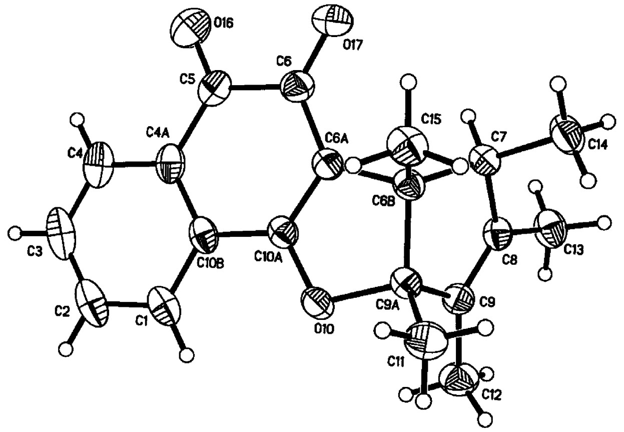


Figure 5. Molecular structure of complex **9b** with thermal ellipsoids at the 30% probability level.

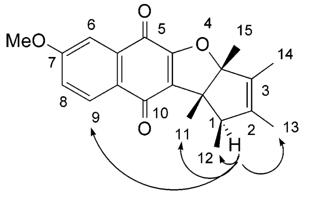


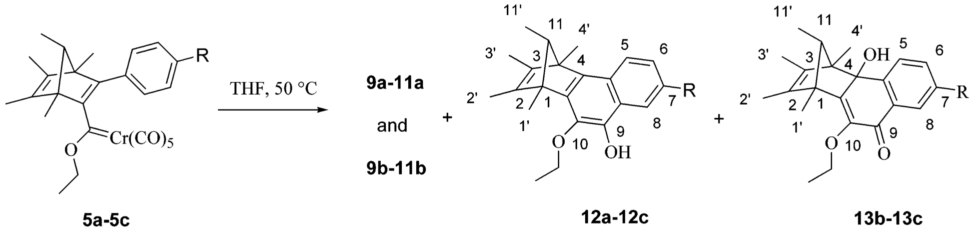
Figure 6. NOEs observed upon irradiation of proton H-4 in compound **10a**.

signals due to two carbonyl groups at 182.4 ppm (C-5) and 179.2 ppm (C-10), signals for sp^2 and for the aromatic ring at 158.0–125.7 ppm, and eight signals at 107.1, 54.2, 49.5, 19.4, 16.0, 15.9, 12.8, and 9.3 ppm for sp^3 carbon atoms. Furthermore, the HMBC spectrum of **9a** showed three-bond C–H long-range correlations between the protons at 8.00–8.05 ppm and the carbon atoms at 182.4 and 179.2 ppm, in agreement with the presence of a 1,4-naphthoquinone core. The ^{1}H NMR spectra of **9b** showed the presence of four contiguous protons in the aromatic region, with signals at 8.01 ppm (H-4), and three more protons at 7.50–7.65 ppm. The ^{13}C NMR spectra showed signals due to the two non-equivalent carbonyl groups at 182.0 ppm (C-5) and 175.0 ppm (C-6). The HMBC experiment of **9b** showed a three-bond long-range correlation between carbon C-5 (182.0 ppm) and the low-field proton H-4 at 8.03 ppm; however, carbonyl carbon C-6 at 175.0 ppm had no correlation with aromatic protons, in agreement with the presence of the 1,2-naphthofurandione nucleus. The molecular structures of **9a**,**b** were confirmed by single-crystal X-ray analyses (Figures 4 and 5).

The (arylethynyl)ethoxycarbenes **1b**,**c** also showed reactivity similar to that of **1a** toward **4** under the reaction conditions above depicted in Table 2. The product mixtures **10a/10b** and **11a/11b** were characterized on the basis of their spectroscopic analysis. The ^{1}H and ^{13}C NMR spectra of **10a** and **11a** were similar to those of **9a**, except for the presence of the methoxy group in **10a** and the methyl group in **11a** at the naphthofurandione moieties. For compound **10a**, the presence of the methoxy group was revealed by the observation of a signal in the ^{13}C NMR spectrum at 163.2 ppm corresponding to the quaternary carbon C-7 and of a singlet at 3.95 ppm in the ^{1}H NMR spectrum. NOE experiments carried out on **10a** showed increases in the signals of the protons H-13, H-12, and H-11 and that of the aromatic proton H-9 upon irradiation of H-1 (Figure 6).

When the (arylnorbornadienyl)ethoxycarbene complex **5a** was heated to 50 °C in dry THF, the naphthofurandione derivatives **9a**,**b** were formed in 35% and 33% yields, respectively (Scheme 2). A similar behavior was observed for the homologous complexes **5b**,**c**, since the cycloadduct mixtures **10a/10b** and **11a/11b** were obtained in 22% and 20% yields (1:1 ratios), confirming that complexes **5a**–**c** are active precursors to the new organic products. It is worth noting that the products of benzannelation **12a**–**c** were detected from the crude reaction mixture by ^{1}H NMR (300 MHz) analysis and the oxidized products **13b**,**c** were isolated in low yields from the corresponding reaction mixtures; however, only traces of products **9**–**11** were observed in the spectra of the crude reaction mixtures.

Scheme 2

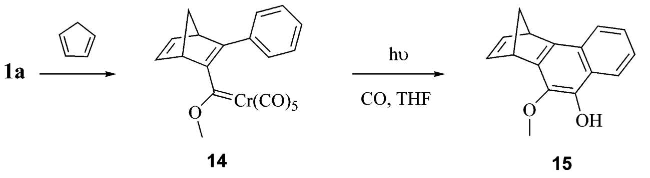


A single-crystal determination for compound **13b** allowed us to confirm its molecular structure (Figure 7). The formation of compounds **13a**–**c** could be due to the presence of traces of O_2 in the reaction mixture or exposure to air during the workup. Therefore, it is likely that the compounds **9**–**11** were completely formed during the workup process, which consisted of fast purification by column chromatography over silica gel.

These results proved that the (arylethynyl)ethoxycarbenes **1a**–**c** undergo cascade reactions with pentamethylcyclopentadiene (**4**) under thermal conditions. Initially, the [4 + 2] cycloaddition affords the *anti* adducts **5a**–**c**, which undergo a carbonyl insertion, thus furnishing **12a**–**c**. The subsequent oxidation of the benzannulation adducts **12** leads to **13**, and rearrangement of the adducts **13** affords the naphthofurandiones **9**–**11**.

Merlic[5a] has reported that the photolysis of the norbornenyl complex **14**, obtained from the Diels–Alder reaction between **1a** and cyclopentadiene, leads to the *o*-alkoxy phenol **15** via electrocyclization and aromatization of a chromium-complexed dienylketene (Scheme 3). On the other hand, the thermal reaction of **14** produced small amounts of the annulated product **15**, while with other substrates little or no benzannulation was observed. Furthermore, there was no evidence that **15** underwent the rearrangement reaction that we observed.

Scheme 3



The higher reactivity of the (arylnorbornadienyl)ethoxycarbene complexes **5a**–**c**, in comparison with carbenes such as **14**, that leads to successive carbonyl insertion, electrocyclization, aromatization, oxidation, and ring transposition under thermal conditions, could be explained in terms of several factors affecting the stability of the corresponding cycloadducts. The higher strain of the pentamethylnorbornadienyl moiety, the α,β-unsaturation that constrained the ring in **5a**–**c**, and the *cis* stereochemistry of the aryl group and the pentacarbonyl chromium moiety would favor the benzannelation reaction; this is in agreement with Merlic.[1d,5a] The steric effects of the methyl substituents and an increment of the ring strain, in cycloadducts **12a**–**c**, make the oxidation and rearrangement reactions possible. These results point out that, in addition to ring strain, steric hindrance seems to play an important role and may be required for the cascade reactions to proceed in acceptable yields.

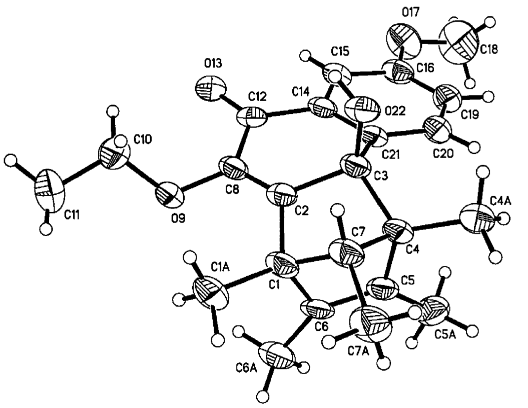


Figure 7. Molecular structure of complex **13b** with thermal ellipsoids at the 30% probability level.

A proposed mechanism for these cascade reactions is shown in Scheme 4. The Diels–Alder reaction of **1a**–**c** with **4** produces the carbene complexes **5a**–**c**; removal of a CO ligand from complexes **5a**–**c** can occur, generating the chromium-complexed dienylketene **I**,[5] which is trapped by the aryl ring to yield **12a**–**c**. The latter undergo oxidation to yield the reactive compounds **13a**–**c** and ring opening to yield the cation intermediate **II**, which may be in equilibrium with **III**–**V**. The cyclization of **IV** should lead to the naphthofuran-5,10-diones **9a**–**11a**, whereas intermediate **V** would afford the naphthofuran-5,6-diones **9b**–**11b**.

These results indicate that the pathway leading to the naphthofurandiones **9**–**11** could be related to that proposed by Nair.[14a] He has reported that ceric(IV) ammonium nitrate (CAN) reacts with 2-hydroxyquinone and cyclopentadiene to produce naphthofurandiones analogous to **9**–**11**, presumably through the cation intermediate **II**. This unexpected reaction is particularly fascinating, because the thermal reactions of carbene complexes **1a**–**c** with diene **4** have provided a straightforward route to the highly substituted naphthofurandiones **9**–**11** via a tandem Diels–Alder/benzannulation/rearrangement reaction. These types of reactions are highly relevant, since there are a number of biologically active natural products that contain a naphthofurandione framework.[14]

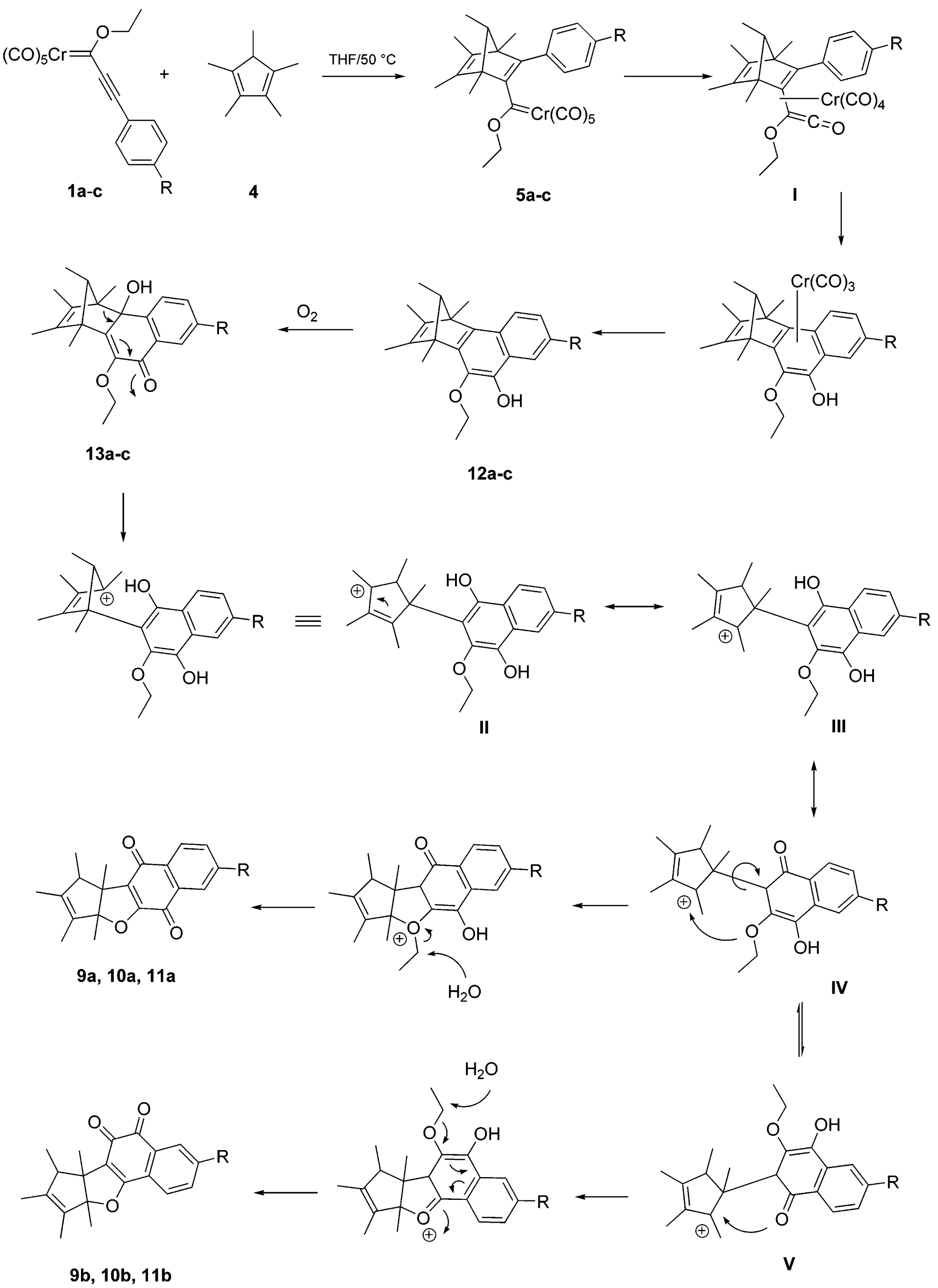
Conclusions

In summary, we report Diels–Alder reactions of (arylethynyl)ethoxycarbene complexes of metals of group

---

[14] (a) Nair, V.; Treesa, P. M.; Maliakal, D.; Rath, N. P. *Tetrahedron* **2001**, *57*, 7705–7710. (b) Lee, Y. R.; Kim, B. S.; Jung, Y, U.; Koh, W. S.; Cha, J. S.; Kim, N. W. *Synth. Commun.* **2002**, *32*, 3099–3105. (c) Ohta, Y.; Doe, M.; Morimoto, Y.; Kinoshita, T. J. *Heterocycl. Chem.* **2000**, *37*, 731–734. (d) Ito, C.; Katsuno, S.; Kondo, Y.; Tan, H. T–W.; Furukawa, H. *Chem. Pharm. Bull.* **2000**, *48*, 339–343.

Scheme 4



6 (**1**−**3**) with 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene that produce the new (arylnorbornadienyl)ethoxycarbene complexes **5**−**7** with *anti*-stereofacial selectivity. Our results show that the molybdenum complex reacts more quickly than the homologous chromium and tungsten complexes in these reactions. Additionally, the thermal reaction of complexes **1**−**3** with **4** takes place in an unprecedented manner, through consecutive Diels−Alder/benzannulation/rearrangement reactions, yielding 5,10- and 5,6-naphthofurandione derivatives **9**−**11**. This is, as far as we know, the first time that such thermal behavior has been observed. Experimental and theoretical studies to elucidate the mechanism and to extend the scope of these reactions to the tungsten and molybdenum carbenes are in progress.

Experimental Section

All 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. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under an N_2 atmosphere prior to use. *n*-Hexane and ethyl acetate were distilled before use. Melting points (uncorrected) were determinated with an Electrothermal capillary melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury (300 MHz) instrument, in $CDCl_3$ or acetone-d_6 as solvents and 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, $\lambda = 0.710\ 73$ Å). TLC analyses were performed using silica plates and were visualized using UV (254 nm) or iodine.

General Procedure for the Preparation of the Pentacarbonyl (Arylethynyl)ethoxycarbene Complexes 1−3. A solution of the corresponding arylacetylenes (9.09 mmol) in dry THF (10 mL) at −78 °C was cautiously added to *n*-butyllithium (9.09 mmol, 1.7 M in hexane). After it was stirred for 30 min at −5 °C, the suspension was transferred via cannula to a suspension of $M(CO)_6$ (9.09 mmol) in THF (100 mL) at −78 °C. After 2 h at room temperature, the solution was cooled to −5 °C and then triethyloxonium tetrafluoroborate was added in small portions (2.2 g, 9.09 mmol or until pH 6) and stirred for 30 min, and then the solvent was removed under vacuum. The residue was dissolved in a saturated sodium bicarbonate solution (150 mL). The reaction mixture was extracted with *n*-hexane, washed with a brine solution (150 mL) and water (300 mL), and dried over sodium sulfate, and the solvent was removed under vacuum at room temperature. Purification was carried out by flash chromatography on silica gel using *n*-hexane as eluent, to afford the corresponding carbene complexes **1**−**3**.

Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium(0) (1a). Following the general procedure, complex **1a** was prepared and isolated as a dark purple solid in 60% yield: mp 61−62 °C; FT-IR ν_{max} 2066, 1946 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 4.77 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 7.43−7.62 (m, 5H, Ph); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.9 (OCH_2CH_3), 75.8 (OCH_2CH_3), 92.2 (C≡), 117.9 (C, Ph), 128.8 (CH, Ph), 132.8 (CH, Ph), 136.7 (≡CPh), 142.8 (CH, Ph), 216.4 (CO *cis*), 225.7 (CO *trans*), 313.9 (Cr=C); EIMS (70 eV; *m*/*z* (%)) 350 (M$^+$, 58), 322 (6), 294 (100), 266 (38), 238 (29), 210 (44); HRMS (EI) calcd for $C_{16}H_{10}O_6{}^{52}Cr$ 349.9882, found 349.9871. Anal. Calcd for $C_{16}H_{10}O_6{}^{52}Cr$ (350.24): C, 54.87; H, 2.88. Found: C, 54.67; H, 2.58.

Pentacarbonyl[1-ethoxy-3-(*p*-methoxyphenyl)-2-propyn-1-ylidene]chromium(0) (1b). Following the general procedure, complex **1b** was prepared and isolated as a dark purple solid in 86% yield: mp 54−55 °C; FT-IR ν_{max} 2064, 1946 cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 1.58 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 3.96 (s, 3H, OCH_3), 4.90 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 7.16 (d, *J* = 9 Hz, 2H, system AA′, *p*-$OCH_3(C_6H_4)$), 7.66 (d, *J* = 9 Hz, 2H, system BB′, *p*-$OCH_3(C_6H_4)$); ^{13}C NMR (75.4 MHz, $(CD_3)_2CO$) δ 14.5 (OCH_2CH_3), 55.5 (OCH_3), 76.9 (OCH_2CH_3), 94.0 (C≡), 112.3 (C, *p*-$OCH_3(C_6H_4)$), 115.3 (CH, system AA′, *p*-$OCH_3(C_6H_4)$), 134.0 (≡C-*p*-$OCH_3(C_6H_4)$), 135.8 (C, system BB′, *p*-$OCH_3(C_6H_4)$), 163.7 (C, *p*-$OCH_3(C_6H_4)$), 216.8 (CO *cis*), 225.6 (CO *trans*), 311.2 (Cr=C); FABMS (3 eV; *m*/*z* (%)) 380 (M$^+$, 40), 324 (100), 296 (70), 268 (42), 240, (33), 189 (13), 159 (45), 154 (30), 129 (15), 52 (9); HRMS (EI) calcd for $C_{17}H_{12}O_7{}^{52}Cr$ 379.9988, found 379.9983. Anal. Calcd for $C_{17}H_{12}O_7{}^{52}Cr$ (380.26): C, 53.69; H, 3.18. Found: C, 53.46; H, 3.05.

Pentacarbonyl[1-ethoxy-3-(*p*-methylphenyl)-2-propyn-1-ylidene]chromium(0) (1c). Following the general procedure, complex **1c** was prepared and isolated as a dark purple solid in 63% yield: mp 66−67 °C; FT-IR ν_{max} 2147, 2051, 1913 cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 1.58 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.43 (s, 3H, CH_3), 4.92 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 7.41 (d, *J* = 9 Hz, 2H, system AA′, *p*-$CH_3(C_6H_4)$), 7.61 (d, *J* = 9 Hz, 2H, system BB′, *p*-$CH_3(C_6H_4)$); ^{13}C NMR (75.4 MHz, $(CD_3)_2CO$) δ 14.5 (OCH_2CH_3), 21.2 (CH_3), 77.2 (OCH_2CH_3), 92.5 (C≡), 117.7 (≡C-*p*-$CH_3(C_6H_4)$), 130.2 (CH, system AA′, *p*-$CH_3(C_6H_4)$), 133.3 (CH, system BB′, *p*-$CH_3(C_6H_4)$), 143.9 (C, *p*-$CH_3(C_6H_4)$), 216.7 (CO *cis*), 225.7 (CO *trans*), 313.1 (Cr=C); FABMS (3 eV; *m*/*z* (%)) 364 (M$^+$, 32), 308 (100), 280 (55), 252 (30), 224 (25), 143 (19); HRMS (EI) calcd for $C_{17}H_{12}O_6{}^{52}Cr$ 364.0039, found 364.0033. Anal. Calcd for $C_{17}H_{12}O_6{}^{52}Cr$ (364.27): C, 56.05; H 3.32. Found: C, 56.14; H, 3.26.

Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten(0) (2). Following the general procedure, complex **2** was prepared and isolated as a brown solid in 75% yield: mp 76−77 °C; FT-IR ν_{max} 2134, 2053, 1916 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 4.71 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 7.40−7.63 (m, 5H, Ph); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.8 (OCH_2CH_3), 76.0 (OCH_2CH_3), 88.4 (C≡), 121.1 (C, Ph), 129.1 (CH, Ph), 131.6 (CH, Ph), 132.8 (CH, Ph), 135.7 (≡CPh), 197.5 (CO *cis*), 205.8 (CO *trans*), 288.0 (W=C); EIMS (70 eV; *m*/*z* (%)) 482 (M$^+$, 32), 426 (100), 398 (35), 370 (33), 342 (25); HRMS (EI) calcd for $C_{16}H_{10}O_6{}^{184}W$ 481.9986, found 481.9979.

Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)molybdenum(0) (3). Following the general procedure, complex **3** was prepared and isolated as a black solid in 45% yield: mp 45−46 °C; FT-IR ν_{max} 2136, 2056, 1926 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 4.80 (br m, 2H, OCH_2CH_3), 7.30−7.63 (m, 5H, Ph); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.9 (OCH_2CH_3), 76.2 (OCH_2CH_3), 121.0 (C, Ph), 131.6 (CH, Ph), 132.0 (CH, Ph), 132.7 (CH, Ph), 205.7 (CO *cis*), 208.3 (CO *trans*) (none of the signals corresponding to the triple bond carbon atoms or the carbene carbon were observed in the spectrum); EIMS (70 eV; *m*/*z* (%)) 394 (M$^+$, 27), 338 (100), 310 (22), 382 (26), 342 (13); HRMS (EI) calcd for $C_{16}H_{10}O_6Mo$ 395.9531, found 395.9550.

General Procedure for the Diels−Alder Reactions of Complexes 1a−c with Pentamethylcyclopentadiene (4). Method A. A solution of the corresponding pentacarbonyl (arylethynyl)ethoxycarbene complexes **1** and **3** (0.33 mmol) and 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene **4** (0.66 mmol) in 10 mL of dry THF was stirred at room temperature. After 1−12 h, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using *n*-hexane/EtOAc (7/3) as eluent, to afford the corresponding cycloadducts **5**−**7**.

Method B. Complex **2** (0.33 mmol) and **4** (0.66 mmol) were allowed to react in THF (10 mL) at 50 °C for 4 h. Complex **6** was isolated by column chromatography on silica gel using *n*-hexane/EtOAc (7/3) as eluent, as red crystals in 68% yield.

(1*S,4*R**,7*R**)-[(3-Phenyl-1,4,5,6,7-pentamethylnorbornadien-2-yl)ethoxymethylene]pentacarbonylchromium(0) (5a):** yield 72% (red solid, mp 82−83 °C); FT-IR ν_{max} 2056, 1987, 1921 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (br d, *J* = 5.0 Hz, 3H, H-7a), 1.08 (br s, 3H, H-4a), 1.20 (s, 3H, H-1a), 1.67 (t, *J* = 6.9 Hz, 3H, OCH_2CH_3), 1.78−1.84 (br m, 6H, H-5a and H-6a), 2.40 (br s, 1H, H-7), 4.62−4.80 (br m, 2H, OCH_2CH_3), 6.83 (m, 2H, H-11), 7.27 (m, 3H, H-9 and H-10); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.5 (C-7a), 11.6 (C-4a), 12.1 (C-1a), 12.4 (C-6a), 14.3 (C-5a), 15.5 (OCH_2CH_3), 64.6 (C-4), 68.0 (C-1), 76.3 (OCH_2CH_3), 79.5 (C-7), 127.5 (C-11), 128.3 (C-9 and C-10), 135.7 (C-8), 140.9 (C-6), 143.3 (C-5), 216.0 (CO *cis*), 224.7 (CO *trans*) (none of the signals corresponding to the double bond carbon atoms C-3 and C-2 or the carbene carbon were observed in the spectrum); EIMS (70 eV; *m*/*z* (%)) 486 (M$^+$, 0.1), 430 (2), 402 (38), 374 (8), 346 (100), 318 (60), 300 (70), 289 (40), 249 (28), 234 (72), 187 (35), 186 (25); HRMS (EI) calcd for $C_{26}H_{26}O_6{}^{52}Cr$ 486.1134, found 486.1139.

(1*S,4*R**,7*R**)-{[3-(*p*-Methoxyphenyl)-1,4,5,6,7-pentamethylnorbornadien-2-yl]ethoxymethylene}pentacarbonylchromium(0) (5b):** yield 60% (red solid, mp 84−85 °C); FT-IR ν_{max} 2054, 1985, 1922 cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 0.72 (br d, *J* = 5.0 Hz, 3H, H-7a), 1.10 (br s, 3H, H-4a), 1.26 (s, 3H, H-1a), 1.70 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 1.82 (br s, 3H, H-5a), 1.93 (br s, 3H, H-6a), 2.50 (br s, 1H, H-7), 3.80 (s, 3H, *p*-$OCH_3(C_6H_4)$), 4.80−5.15 (br m, 2H, OCH_2CH_3), 6.90 (s, 4H, system AA′BB′, H-9 and H-10); ^{13}C NMR (75.4 MHz, $(CD_3)_2CO$) δ 9.9 (C-7a), 11.4 (C-5a and C-6a), 11.8 (C-1a and C-4a), 14.8 (OCH_2CH_3), 54.8 (OCH_3), 64.5 (C-4), 67.5 (C-1), 77.6 (OCH_2CH_3), 79.2 (C-7), 113.9 (C-10), 127.7 (C-8), 129.5 (C-9), 141.0 (C-6), 143.3 (C-5), 150.0 (C-3), 159.6 (C-11), 160.0 (C-2), 218.2 (CO *cis*), 224.8 (CO *trans*), 357.1 (Cr=C); FABMS (3 eV; *m*/*z* (%)) 516 (M$^+$, 0.4), 460 (2), 432 (99), 404 (1), 376 (100), 348 (6), 325 (5); HRMS (EI) calcd for $C_{27}H_{28}O_7{}^{52}Cr$ 516.1240, found 516.1233.

(1*S,4*R**,7*R**)-{[3-(*p*-Methylphenyl)-1,4,5,6,7-pentamethylnorbornadien-2-yl]ethoxymethylene}pentacarbonylchromium(0) (5c):** yield 77% (red solid, mp 96−97 °C); FT-IR ν_{max} 2058, 1977, 1921 cm^{-1}; ^{1}H NMR (300 MHz, $(\mathrm{CD_3})_2\mathrm{CO}$) δ 0.70 (br d, J = 5.7 Hz, 3H, H-7a), 1.06 (br s, 3H, H-4a), 1.26 (s, 3H, H-1a), 1.71 (t, J = 7.2 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.83 (br s, 3H, H-5a), 1.90 (br s, 3H, H-6a), 2.28 (s, 3H, *p*-$\mathrm{CH_3(C_6H_4)}$), 2.48 (br s, 1H, H-7), 4.78−515 (br m, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.87 (d, J = 7.8 Hz, 2H, H-9), 7.15 (d, J = 7.8 Hz, 2H, H-10); ^{13}C NMR (75.4 MHz, $(\mathrm{CD_3})_2\mathrm{CO}$) δ 10.5 (C-7a), 12.1 (C-6a and C-5a), 12.4 (C-4a and C-1a), 15.5 ($\mathrm{OCH_2}C\mathrm{H_3}$), 21.4 ($\mathrm{CH_3}$, *p*-$\mathrm{CH_3(C_6H_4)}$), 64.5 (C-4), 67.8 (C-1), 76.2 ($\mathrm{O}C\mathrm{H_2CH_3}$), 79.4 (C-7), 128.2 (C-10), 129.0 (C-9), 132.7 (C-8), 137.4 (C-11), 140.0 (C-6), 143.4 (C-5), 216.1 (CO *cis*), 224.8 (CO *trans*), 326.1 (Cr=C) (none of the signals corresponding to the double bond C-2 and C-3 atoms were observed in the spectrum); FABMS (70 eV; *m*/*z* (%)) 500 (M$^+$, 4), 472 (1), 444 (4), 416 (100), 388 (2), 360 (80), 332 (22), 309 (20); HRMS (EI) calcd for $\mathrm{C_{27}H_{28}O_6{}^{52}Cr}$ 500.1291, found 500.1289.

(1*S,4*R**,7*R**)-[(3-Phenyl-1,4,5,6,7-pentamethylnorbornadien-2-yl)ethoxymethylene]pentacarbonyltungsten(0) (6):** yield 68% (red solid, mp 106−107 °C); FT-IR ν_{max} 2056, 1985, 1925 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.69 (d, J = 6.0 Hz, 3H, H-7a), 1.06 (s, 3H, H-4a), 1.15 (s, 3H, H-1a), 1.69 (t, J = 7.2 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.78 (br s, 6H, H-6a and H-5a), 2.43 (br s, 1H, H-7), 4.77 (q, J = 7.2 Hz, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.89−7.30 (m, 5H, Ph); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 10.2 (C-7a), 11.8 (C-6a and C-5a), 12.3 (C-4a and C-1a), 15.1 ($\mathrm{OCH_2}C\mathrm{H_3}$), 64.0 (C-4), 66.0 (C-1), 78.2 ($\mathrm{O}C\mathrm{H_2CH_3}$), 127.2 (C-11), 128.0 (C-9), 128.9 (C-10), 135.0 (C-8), 140.4 (C-6), 142.8 (C-5), 177.0 (C-2), 196.8 (CO *cis*), 204.1 (CO *trans*) (none of the signals corresponding to the carbene carbon or C-7 and C-3 were observed in the spectrum); EIMS (70 eV; *m*/*z* (%)) 618 (M$^+$, 0.2), 590 (0.1), 562 (0.7), 534 (100), 506 (7), 478 (72), 420 (68); HRMS (EI) calcd for $\mathrm{C_{26}H_{26}O_6{}^{184}W}$ 618.1238, found 632.1231.

(1*S,4*R**,7*R**)-[(3-Phenyl-1,4,5,6,7-pentamethylnorbornadien-2-yl)ethoxymethylene]pentacarbonylmolybdenum(0) (7):** yield 40% (brown solid, mp 45−46 °C); FT-IR ν_{max} 2066, 1957, 1930 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.69 (d, J = 6.3 Hz, 3H, H-7a), 1.09 (s, 3H, H-4a), 1.17 (s, 3H, H-1a), 1.70 (t, J = 6.6 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.80 (br s, 6H, H-6a and H-5a), 2.42 (br s, 1H, H-7), 4.87 (q, J = 7.2 Hz, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.87−7.29 (m, 5H, Ph); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 10.3 (C-7a), 11.8 (C-5a and C-6a), 12.3 (C-4a and C-1a), 15.2 ($\mathrm{OCH_2}C\mathrm{H_3}$), 68.0 (C-4), 72.0 (C-1), 77.8 ($\mathrm{O}C\mathrm{H_2CH_3}$), 127.2 (C-10), 127.9 (C-9), 128.9 (C-11), 135.6 (C8), 140.4 (C-6), 142.8 (C-5), 204.9 (CO *cis*), 214.1 (CO *trans*) (none of the carbene carbon atom signals or C-2, C-3, and C-7 were observed in the spectrum); EIMS (70 eV; *m*/*z* (%)) 532 (M$^+$, 15), 504 (3), 476 (15), 448 (50), 420 (13), 392 (30), 346 (100), 235 (35). HRMS (EI) calcd for $\mathrm{C_{26}H_{26}O_6Mo}$ 532.0783, found 532.0766.

General Procedure for the Preparation of Naphthofurandione Derivatives 9−11 and 13b,c. Method A. A solution of the corresponding carbene chromium complexes **1a**−**c** (0.33 mmol) and 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (**4**) (0.66 mmol) in 10 mL of dry THF was stirred at 50 °C. After 12−14.5 h the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/EtOAc (7:3) as eluent to give the naphthofurandiones derivatives **9**−**11** and **13b**−**13c**.

Method B. Complexes **5a**−**c** (0.33 mmol) and **4** (0.66 mmol) were allowed to react in THF (5 mL) at 50 °C. Adducts **9**−**11** and **13b**,**c** were isolated by column chromatography on silica gel using *n*-hexane/EtOAc (7/3) as eluent.

(1*R,3a*R**,10b*R**)-3a,10b-Dihydro-1,2,3,3a,10b-pentamethylcyclopenta[2,3]naphtho[2,3-*d*]furan-5,10-dione (9a):** yield 26% (yellow solid, mp 141−142 °C); FT-IR ν_{max} 2924, 1678, 1645, 1616, 1451, 1372, 1271 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.05 (d, J = 6.0 Hz, 3H, H-12), 1.31 (s, 3H, H-11), 1.50 (s, 3H, H-15), 1.62 (br s, 3H, H-13), 1.66 (br s, 3H, H-14), 3.20 (q, J = 6.0 Hz, 1H, H-1), 7.60−7.72 (m, 2H, H-7 and H-8), 8.00−8.05 (m, 2H, H-6 and H-9); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 9.3 (C-14), 12.8 (C-12), 15.9 (C-13), 16.0 (C-11), 19.3 (C-15), 49.6 (C-1), 54.2 (C-10b), 107.2 (C-3a), 125.7 (C-6), 125.9 (C-9), 129.8 (C-10a), 131.4 (C-2), 132.4 (C-5a), 132.5 (C-7), 133.4 (C-9a), 133.9 (C-8), 141.3 (C-3), 156.9 (C-4a), 179.2 (C-5), 182.4 (C-10); EIMS (70 eV; *m*/*z* (%)) 308 (M$^+$, 100), 293 (10), 275 (10), 265 (15), 247 (7), 136 (25), 121 (11); HRMS (EI) calcd for $\mathrm{C_{20}H_{20}O_3}$ 308.1412, found 308.1438. Anal. Calcd for $\mathrm{C_{20}H_{20}O_3}$ (308.37): C, 77.90; H, 6.54. Found C, 77.64; H, 6.76.

(6b*S,7*S**,9a*S**)-6b,9a-Dihydro-6b,7,8,9,9a-pentamethylcyclopenta[8,9]naphtho[2,1-*d*]furan-5,6-dione (9b):** yield 22% (red solid, mp 126−127 °C); FT-IR ν_{max} 2971, 1696, 1641, 1613, 1570 1489, 1445, 1385, 1345, 1217 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.04 (d, J = 7.0 Hz, 3H, H-14), 1.30 (s, 3H, H-15), 1.58 (s, 3H, H-11), 1.63 (br s, 3H, H-13), 1.70 (br s, 3H, H-12), 3.00 (q, J = 7.0 Hz, 1H, H-7), 7.50−7.65 (m, 3H, H-1, H-2 and H-3), 8.01 (d, J = 7.6 Hz, 1H, H-4); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 9.6 (C-12), 12.7 (C-13), 16.0 (C-14), 16.2 (C-15), 19.5 (C-11), 49.6 (C-7), 53.2 (C-6b), 109.0 (C-9a), 124.0 (C-1), 126.0 (C-6a), 128.2 (C-9), 129.6 (C-3), 129.8 (C-4a), 131.6 (C-10b), 132.0 (C-4), 134.1 (C-2), 142.2 (C-8), 166.8 (C-10a), 175.0 (C-6), 182.0 (C-5); EIMS (70 eV; *m*/*z* (%)) 308 (M$^+$, 100), 293 (40), 275 (35), 265 (43), 247 (15); HRMS (EI) calcd for $\mathrm{C_{20}H_{20}O_3}$ 308.1412, found 308.1420. Anal. Calcd for $\mathrm{C_{20}H_{20}O_3}$ (308.37): C, 77.90; H, 6.54; Found: C, 77.03; H, 6.55.

(1*R,3a*R**,10b*R**)-3a,10b-Dihydro-7-methoxy-1,2,3,3a,-10b-pentamethylcyclopenta[2,3]naphtho[2,3-*d*]furan-5,-10-dione (10a):** yield 22% (yellow oil); FT-IR ν_{max} 2921, 1679, 1643, 1619, 1455, 1378, 1276 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.04 (d, J = 7.2 Hz, 3H, H-12), 1.31 (s, 3H, H-11), 1.50 (s, 3H, H-15), 1.62 (br s, 3H, H-13), 1.66 (br s, 3H, H-14), 3.08 (q, J = 7.2 Hz, 1H, H-1), 3.95 (s, 3H, $\mathrm{OCH_3}$), 7.13 (dd, J = 8.4, 2.7 Hz, 1H, H-8), 7.48 (d, J = 2.7 Hz, 1H, H-9), 7.95 (d, J = 8.4 Hz, 1H, H-6); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 9.3 (C-14), 12.8 (C-12), 15.9 (C-13), 16.1 (C-11), 19.4 (C-15), 49.6 (C-1), 54.2 (C-10b), 55.8 ($\mathrm{OCH_3}$), 106.9 (C-3a), 109.9 (C-9), 119.6 (C-8), 126.7 (C-10a), 127.9 (C-6), 129.8 (C-2), 132.3 (C-5a), 133.2 (C-9a), 141.3 (C-3), 156.6 (C-4a), 163.2 (C-7), 179.3 (C-5), 181.9 (C-10); EIMS (70 eV; *m*/*z* (%)) 338 (M$^+$, 100), 323 (37), 305 (30), 295 (33), 277 (11); HRMS (EI) calcd for $\mathrm{C_{21}H_{22}O_4}$ 338.1518, found 338.1490.

(6b*S,7*S**,9a*S**)-6b,9a-Dihydro-3-methoxy-6b,7,8,9,9a-pentamethylcyclopenta[8,9]naphtho[2,1-*d*]furan-5,6-dione (10b):** yield 20% (red oil); FT-IR ν_{max} 2971, 1689, 1644, 1618, 1575 1490, 1447, 1383, 1346, 1219 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.02 (d, J = 6.9 Hz, 3H, H-14), 1.29 (s, 3H, H-15), 1.56 (s, 3H, H-11), 1.63 (d, J = 0.9 Hz, 3H, H-13), 1.70 (d, J = 0.9 Hz, 3H, H-12), 2.55 (q, J = 6.9 Hz, 1H, H-7), 3.95 (s, 3H, $\mathrm{OCH_3}$), 7.26 (dd, J = 2.7, 8.4 Hz, 1H, H-2), 7.45 (d, J = 2.7 Hz, 1H, H-4), 7.62 (d, J = 8.4 Hz, 1H, H-1); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 8.6 (C-12), 13.0 (C-13), 16.0 (C-14), 16.2 (C-15), 19.5 (C-11), 56.0 ($\mathrm{OCH_3}$), 56.2 (C-7), 112.0 (C-6a), 112.6 (C-2), 120 (C-10b), 126.9 (C-1), 129.6 (C-8), 127.0 (C-4a), 134.0 (C-9), 142 (C-10a), 166.2 (C-3), 174.5 (C-6), 181.7 (C-5); EIMS (70 eV; *m*/*z* (%)) 338 (M$^+$, 100), 323 (44), 305 (26), 295 (24), 277 (14); HRMS (EI) calcd for $\mathrm{C_{21}H_{22}O_4}$ 338.1518, found 338.1524.

(1*R,3a*R**,10b*R**)-3a,10b-Dihydro-1,2,3,3a,7,10b-hexamethylcyclopenta [2,3]naphtho[2,3-*d*]furan-5,10-dione (11a):** yield 22% (yellow oil); FT-IR ν_{max} 2921, 1696, 1641, 1614, 1570, 1385, 1052 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.05 (d, J = 7.2 Hz, 3H, H-12), 1.32 (s, 3H, H-11), 1.51 (s, 3H, H-15), 1.62 (br s, 3H, H-13), 1.66 (br s, 3H, H-14), 2.44 (s, 3H, $\mathrm{CH_3}$), 3.08 (q, J = 7.2 Hz, 1H, H-1), 7.47 (dd, J = 7.8, 1.6 Hz, 1H, H-8), 7.48 (d, J = 1.6 Hz, 1H, H-9), 7.91 (d, J = 7.8 Hz, 1H, H-6); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 9.3 (C-14), 12.8 (C-12), 15.8 (C-13), 16.0 (C-11), 19.4 (C-15), 21.5 ($\mathrm{CH_3}$), 49.6 (C-1), 54.2 (C-10b), 107.0 (C-3a), 125.9 (C-6), 126.4 (C-9), 129.8 (C-10a), 131.1 (C-2), 131.2 (C-5a),132.3 (C-9a), 134.5 (C-7), 141.3 (C-3), 143.5 (C-8), 156.7 (C-4a), 179.5 (C-5), 182.4 (C-10); EIMS (70 eV; *m/z* (%)) 322 (M^+, 100), 307 (22), 289 (16), 279 (18), 261 (10), 140 (32), 135 (7).

(6b*S,7*S**,9a*S**)-6b,9a-Dihydro-3,6b,7,8,9,9a-hexamethylcyclopenta[8,9]naphtho[2,1-*d*]furan-5,6-dione (11b):** yield 20% (red oil); FT-IR $\nu_{\max}$ 2961, 1692, 1645, 1613, 1573, 1484, 1445, 1386, 1349, 1215 cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.02 (d, $J = 6.9$ Hz, 3H, H-14), 1.27 (s, 3H, H-15), 1.56 (s, 3H, H-11), 1.63 (br s, 3H, H-13), 1.69 (br s, 3H, H-12), 2.41 (s, 3H, $\mathrm{CH_3}$), 3.00 (q, $J = 6.9$ Hz, 1H, H-7), 7.39–7.85 (m, 3H, H-1, H-2, and H-4); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 9.3 (C-12), 12.8 (C-13), 14.1 (C-15), 19.3 (C-11), 20.6 (C-14), 22.6 ($\mathrm{CH_3}$), 49.2 (C-7), 53.0 (C-6b), 108.7 (C-9a), 124.5 (C-2), 124.8 (C-4a), 127.7 (C-1b), 125.5 (C-9), 129.8 (C-4), 130.7 (C-10b), 134.7 (C-1), 141.7 (C-8), 142.2 (C-3), 167.0 (C-10a), 175.2 (C-6), 182.1(C-5); EIMS (70 eV; *m/z* (%)) 322 (M^+, 100), 307 (25), 289 (26), 279 (12), 261 (14), 140 (31), 135 (12); HRMS (EI) calcd for $\mathrm{C_{21}H_{22}O_3}$ 322.1568, found 322.1575.

Spectroscopic Data for (1*R,4*S**,4a*R**,11*R**)-10-Ethoxy-4a-hydroxy-7-methoxy-1,2,3,4,11-pentamethyl-1,4-methano-4,4a-dihydrophenanthren-9(1*H*)-one (13b):** ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.76 (d, $J = 6.3$ Hz, 3H, H-11′), 1.37 (t, $J = 7.2$, 3H, $\mathrm{OCH_2C\mathit{H}_3}$), 1.43 (d, $J = 1.2$, 3H, H-2′), 1.49 (d, $J = 1.5$, 3H, H-3′), 1.53 (s, 3H, H-1′), 1.55 (s, 3H, H-4′), 2.18 (br s, 1H, OH), 2.60 (q, $J = 6.3$ Hz, 1H, H-11), 3.82 (s, 3H, $\mathrm{OCH_3}$), 3.85–4.02 (m, 2H, $\mathrm{OC\mathit{H}_2CH_3}$), 6.99 (dd, $J = 8.4$, 2.7 Hz, 1H, H-6), 7.48 (d, $J = 2.7$ Hz, 1H, H-8), 7.62 (d, $J = 8.4$ Hz, 1H, H-5); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 6.8 (C-11′), 9.9 (C-2′), 10.7 (C-3′), 12.0 (C-4′), 12.5 (C-1′), 15.5 ($\mathrm{OCH_2\mathit{C}H_3}$), 55.4 ($\mathrm{OCH_3}$), 55.6 (C-11′), 57.9 (C-1), 59.5 (C-4), 69.1 ($\mathrm{O\mathit{C}H_2CH_3}$), 78.4 (C-4a), 111.0 (C-8), 118.4 (C-6), 125.8 (C-5), 134.7 (C-8a), 136.2 (C-2), 136.7 (C-10a), 137.1 (C-4b), 143.9 (C-10), 155.3 (C-3), 159.1 (C-7), 184.7 (C-9); EIMS (70 eV; *m/z* (%)) 368 (M^+, 56), 352 (56), 351 (100), 350 (32), 339 (36), 321 (26), 308 (19), 293 (16), 279 (19), 251 (12), 165 (8), 135 (13).

Spectroscopic Data for (1*R,4*S**,4a*R**,11*R**)-10-Ethoxy-4a-hydroxy-1,2,3,4,7,11-hexamethyl-1,4-methano-4,4a-dihydrophenanthren-9(1*H*)-one (13c):** ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.76 (d, $J = 6.6$ Hz, 3H, H-11′), 1.37 (t, $J = 7.2$, 3H, $\mathrm{OCH_2C\mathit{H}_3}$), 1.43 (d, $J = 1.2$, 3H, H-2′), 1.49 (d, $J = 1.2$, 3H, H-3′), 1.53 (s, 3H, H-4′), 1.54 (s, 3H, H-1′), 2.25 (s, 1H, OH), 2.35 (s, 3H, $\mathrm{PhC\mathit{H}_3}$), 2.60 (q, $J = 6.6$ Hz, 1H, H-11), 3.82–4.00 (m, 2H, $\mathrm{OC\mathit{H}_2CH_3}$), 7.26 (dd, $J = 8.1$, 2.1, Hz, 1H, H-6), 7.48 (d, $J = 8.1$, Hz, 1H, H-5), 7.76 (d, $J = 2.1$, Hz, 1H, H-8); ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$) δ 6.8 (C-11′), 9.9 (C-2′), 10.8 (C-3′), 12.0 (C-4′), 12.5 (C-1′), 15.5 ($\mathrm{OCH_2\mathit{C}H_3}$), 21.0 ($\mathrm{PhCH_3}$), 55.8 (C-11), 57.8 (C-1), 59.5 (C-4), 69.0 ($\mathrm{O\mathit{C}H_2CH_3}$), 78.6 (C-4a), 124.2 (C-5), 128.3 (C-8), 132.1 (C-6), 133.1 (C-7), 136.4 (C-8a), 136.9 (C-2), 137.9 (C-10a), 141.2 (C-4b), 143.9 (C-10), 154.8 (C-3), 185.0 (C-9).

X-ray Structure Study of 5a, 6, 9a,b, and 13b. Single crystals were obtained by slow evaporation of concentrated solutions of **5a** (*n*-hexane, red solid), **6** (*n*-hexane, red solid), **9a** (chloroform, yellow solid), **9b** (*n*-hexane/EtOAc, red solid), and **13b** (chloroform, yellow solid). These were mounted on glass fibers. Crystallographic measurements were performed on a Siemens P4 diffractometer using Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.710\,73$ Å) at room temperature. Three standard reflections 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 $2 < 2\theta < 20°$. Intensities were corrected for Lorenz 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[30] program on a personal computer. Data for **5a**: formula, $\mathrm{C_{26}H_{26}O_6Cr}$; molecular weight, 487.47; crystal size, 0.42 × 0.54 × 0.94 mm; crystal system, monoclinic; space group, $P2_1/c$; unit cell parameters, $a = 10.3469(9)$ Å, $b = 18.050(2)$ Å, $c = 13.7288(14)$ Å, $\alpha = 90°$, $\beta = 10.687(3)°$, $\gamma = 90°$; $V = 2519.5(4)$ Å^3; temperature, 566(2) K; $Z = 4$; $D_{\mathrm{exptl}} = 1.286$ Mg/m^3; absorption coefficient, 0.491 mm^{-1}: θ scan range, 1.88–25.07°; 15 380 reflections collected; 4468 independent reflections ($R(\mathrm{int}) = 0.1564$); 4468/0/307 observed reflections; $R = 0.0483$; $R_{\mathrm{w}} = 0.0622$; $s = 0.756$. Data for **6**: formula, $\mathrm{C_{26}H_{26}O_6{}^{184}W}$; molecular weight, 618.123; crystal size, 0.28 × 0.48 × 0.80 mm^3; crystal system, orthorhombic; space group, $P2_12_12_1$; unit cell parameters, $a = 9.7402(11)$ Å, $b = 12.8326(10)$ Å, $c = 17.981(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$; $V = 2247.4(4)$ Å^3; temperature, 293(2) K; $Z = 4$; $D_{\mathrm{exptl}} = 1.266$ Mg/m^3; absorption coefficient, 0.540 mm^{-1}: θ scan range, 1.95–24°; 2668 reflections collected; 2485 independent reflections; 2668 observed reflections; $R = 0.442$; $R_{\mathrm{w}} = 0.1043$; $s = 1.065$. Data for **9a**: formula, $\mathrm{C_{20}H_{20}O_3}$; molecular weight, 308.141; crystal size, 0.32 × 0.45 × 0.68 mm; crystal system, orthorhombic; space group, $P2_12_12_1$; unit cell parameters, $a = 8.1827(6)$ Å, $b = 8.7916(6)$ Å, $c = 11.9798(9)$ Å, $\alpha = 93.879(2)°$, $\beta = 97.285(2)°$, $\gamma = 107.102(2)°$; $V = 812.04(10)$ Å^3; temperature, 567(2) K; $Z = 2$; $D_{\mathrm{exptl}} = 1.310$ Mg/m^3; absorption coefficient, 0.087 mm^{-1}; θ scan range, 1.72–24.99°; 4941 reflections collected; 2841 independent reflections; 2841 observed reflections; $R = 0.0697$; $R_{\mathrm{w}} = 0.1905$; $s = 1.059$. Data for **9b**: formula, $\mathrm{C_{20}H_{20}O_3}$; molecular weight, 308.141; crystal size, 0.39 × 0.47 × 0.52 mm; crystal system, orthorhombic; space group, $P2_12_12_1$; unit cell parameters, $a = 8.584(2)$ Å, $b = 9.834(3)$ Å, $c = 10.437(3)$ Å, $\alpha = 76.679(7)°$, $\beta = 74.599(7)°$, $\gamma = 76.230(6)°$; $V = 811.7(4)$ Å^3; temperature, 294(2) K; $Z = 1$; $D_{\mathrm{exptl}} = 0.852$ Mg/m^3; absorption coefficient, 0.061 mm^{-1}: θ scan range, 2.06–25.01°; 4977 reflections collected; 2833 independent reflections; 2833 observed reflections; $R = 0.0502$; $R_{\mathrm{w}} = 0.1382$; $s = 1.057$. Data for **13b**: formula, $\mathrm{C_{23}H_{28}O_4}$; molecular weight, 368.45; crystal size, 0.44 × 0.22 × 0.2 mm^3; crystal system, orthorhombic; space group, *Pbca*; unit cell parameters, $a = 12.396(2)$ Å, $b = 12.021(2)$ Å, $c = 27.324(2)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$; $V = 4071.6(9)$ Å^3; temperature, 293(2) K; $Z = 8$; $D_{\mathrm{exptl}} = 1.202$ Mg/m^3; absorption coefficient, 0.649 mm^{-1}; θ scan range, 3.23–56.95°; 3519 reflections collected; 2737 independent reflections; 2700 observed reflections; $R = 0.0873$; $R_{\mathrm{w}} = 0.2400$; $s = 1.048$.

Acknowledgment. We thank Fernando Labarrios and Luis Velasco for the spectrometry measurements and Dr. José Guadalupe Alvarado for his help in X-ray studies. F.D. acknowledges the CONACyT (Grant 44038) and the CGPI/IPN (Grant 20050297) for financial support. M.A.V. and L.R. are grateful to CONACyT for a graduate scholarship (125226, 162803). F.D., J.T., and H.A.J.-V. are fellows of the EDI/IPN and COFAA/IPN programs.

Supporting Information Available: Figures giving ^{1}H and ^{13}C NMR data for **1**–**6** and **9**–**13** and tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic parameters for **5a**, **6**, **9a**,**b**, and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050159Q