Unprecedented Formation of Azulenylidene Ligands by Reaction of the Vinylidene Ligand in Arylvinylidene Pentacarbonyl Complexes of Chromium and Tungsten with Alkoxyacetylenes

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Arylvinylidene(pentacarbonyl)chromium and -tungsten complexes $[(CO)_5M{=}C{=}C(C_6H_4R^1\text{-}p)R^2]$ (M = Cr, W; R^1 = H; R^2 = Me, $C_6H_4R^3$-*p* [R^3 = H, Me, OMe, Cl, ^{t}Bu]; R^1 = Me; R^2 = C_6H_4Cl-*p*) react with alkoxyacetylenes, HC≡COR′ (R′ = Et, ^{t}Bu, adamantyl), by 1,3-addition of the CC triple bond to the vinylidene ligand and ring expansion to give azulenylidene complexes $[(CO)_5M{=}C{-}CH{=}C(OR')\text{-}C(CR){=}CHCH{=}C(R)CH{=}CH]$. When monosubstituted and unsymmetrically bis-substituted bis(aryl)-vinylidene complexes are employed, mixtures of two isomers are obtained. In the two isomers the substituent either is attached to the seven-membered ring or resides in the *para* position of the phenyl group. In general, the selectivity of the reactions is low; the isomeric ratio varies between 0.5 and 2 depending on the metal and the substituent. DFT calculations on the reaction mechanism indicate that the reactions are initiated by a nucleophilic addition of the terminal carbon atom of the alkoxyacetylene to the metal-bound C_α atom of the vinylidene ligand. The low selectivity of the reactions is in accord with the results of the calculations. The structure of several azulenylidene complexes was established by X-ray structure analyses.

Introduction

Vinylidene complexes[1] such as $[(CO)_5M{=}C{=}C(R^1)R^2]$ (M = Cr, W) may be regarded as the first member of a series of unsaturated carbene complexes $[L_nM{=}(C)_x{=}C(R^1)R^2]$. As in Fischer-type carbene complexes (x = 0) the C_α atom in vinylidene complexes is an electrophilic center and the LUMO is predominantly localized on the C_α atom;[2] the HOMO is mainly concentrated on the metal and on the C_β atom. Consequently, strong electrophiles add to the metal or to the C_β atom. Examples include (a) the protonation of *trans*-$[Cl(P^iPr_3)_2Ir{=}C{=}CHR]$ (R = H, Me, Ph) with HBF_4 to afford an equilibrium mixture of $[Cl(P^iPr_3)_2(H)Ir{=}C{=}CHR]^+$ and $[Cl(P^iPr_3)_2Ir{\equiv}C{-}CH_2R]^+$,[3] (b) the formation of the carbyne complexes *trans*-$[I(CO)_4W{\equiv}C{-}C^tBu(H)R]$ in the reaction of $[(CO)_5W{=}C{=}C(R)^tBu]$ (R = Me, Et) with $CF_3SO_3H/[NMe_4]I$,[4] and (c) the formation of $[Tp'(CO)_2W{\equiv}CEt]$ in the reaction of the vinylidene anion $[Tp'(CO)_2W{=}C{=}CH_2]^-$ with MeI.[5] In contrast, nucleophiles add to the C_α atom of vinylidene complexes.

The reactions of $[(CO)_5M{=}C{=}C(R^1)R^2]$ have turned out to be remarkably versatile. They react with imines to give either iminocarbene complexes,[6] zwitterionic adducts from addition of the imine to the C_α atom,[6] or azetidinylidene complexes[7] by subsequent cyclization. The type of product depends on the substitution pattern of the imine. Cycloaddition of the C≡C bond in π-donor-substituted alkynes R−C≡C−XR′ (R = alkyl, aryl; XR′ = OR; SR; NR_2) to the $C_\alpha{=}C_\beta$ bond of the vinylidene ligand affords cyclobutenylidene complexes.[8] The cycloaddition methodology can be extended to the synthesis of di-, tri-, and tetranuclear cyclobutenylidene complexes by using alkynyl complexes as the C≡C component.[9] In contrast, dimethylcyanamide leads to demetalation of the vinylidene ligand and formation of its dimer, butatriene.[8a] The coupling of a carbonyl and the vinylidene ligand and the regio- and stereoselective formation of cyclobutane-1,3-diones is observed on photolysis of vinylidene complexes.[10] Carbonyl-vinylidene complexes of tungsten were for instance also proposed to be involved in the photoassisted polymerization of terminal alkynes,[11] in the

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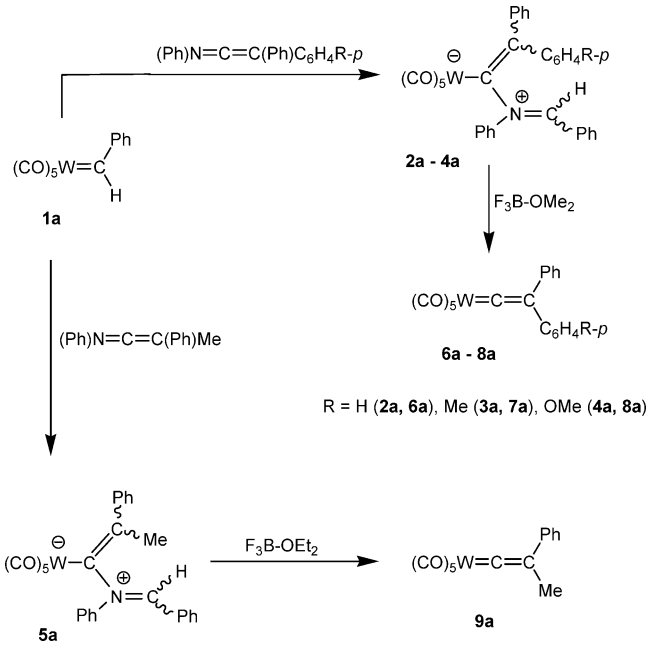
Scheme 1



tungsten-triggered valence isomerization of *cis*-1-acetyl-2-ethynylcyclopropanes,[12] and in the $(CO)_5W$-promoted cyclization of 1-iodo-1-alkynes.[13]

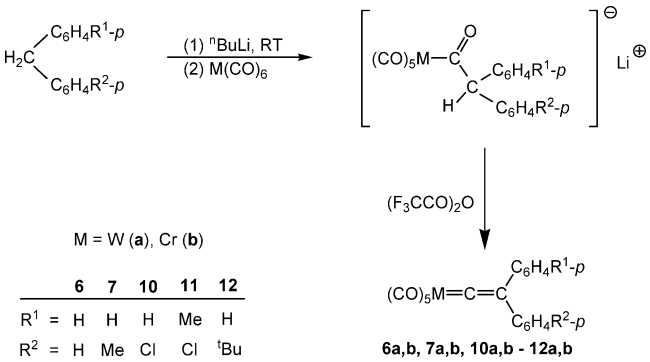
We now report on a new and unprecedented cyclization of $(CO)_5M$-coordinated arylvinylidene ligands (M = Cr, W) with alkoxyalkynes to yield azulenylidene ligands.

2. Results

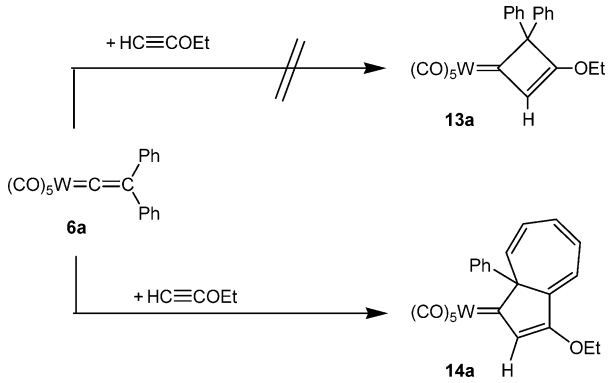
The pentacarbonyl vinylidene complexes were prepared either by M=C/N=C metathesis[14] or by sequential reaction of the corresponding metal hexacarbonyl with lithiated methane derivatives and trifluoroacetic acid anhydride. The addition of triaryl ketenimine to solutions of the benzylidene tungsten complex **1a**[15] initially gave, via insertion of the N=C bond of the ketenimine into the W=C(carbene) bond, the benzylidenimine adducts **2a**−**4a** of the green vinylidene complexes **6a**−**8a** (Scheme 1). Elimination of the benzylidenimine was achieved by addition of boron trifluoride diethyl etherate. The analogous reaction of **1a** with *N*-phenyl phenyl(methyl)ketenimine and subsequently with $BF_3{\cdot}Et_2O$ afforded pentacarbonyl methyl(phenyl)vinylidene tungsten (**9a**) (Scheme 1).

An alternative procedure involved reaction of $[M(CO)_6]$ with diarylmethanides followed by trifluoroacetic acid anhydride-induced elimination of OH^-. Addition at room temperature of $[M(CO)_6]$ to solutions of diarylmethanides, obtained by deprotonation of the sp^3-C atom of suitable diarylmethanes, generated acyl metalates. The reaction was accompanied by a color change of the solution from red to yellow or violet. The formation of the acyl metalate could also be followed easily by IR spectroscopy. Treatment of these acyl metalates with trifluoroacetic acid anhydride at −30 °C (M = W) or −80 °C (M = Cr) yielded the vinylidene complexes **6a**,**b**, **7a**,**b**, and **10a**,**b**−**12a**,**b** (Scheme 2).

Scheme 2



Scheme 3



These vinylidene complexes were thermally labile and readily decomposed at room temperature. Therefore only a few complexes were isolated in a pure form and fully characterized. All others were characterized by their IR and NMR spectra and immediately used for the subsequent reactions with alkoxyacetylenes.

When green solutions of the vinylidene complex **6a** in CH_2Cl_2 were treated with 3 equiv of ethoxyacetylene, the color of the solutions slowly (within about 2 h) turned dark violet and the CO stretching vibrations strongly shifted toward smaller wavenumbers. Column chromatographic separation of the reaction mixture yielded violet crystals in ca. 36% yield. From the NMR spectra it followed that, surprisingly, the 3-ethoxycyclobutenylidene complex **13a** (Scheme 3) had not been formed as expected on the basis of previous results with ynamines and ethoxypropyne.[8a] The ν(CO) absorptions of the new complex (**14a)** are at *lower* wavenumbers than those of the 3-ethoxy-2-methylcyclobutenylidene complex **15a** (Scheme 4) obtained by addition of ethoxypropyne to the $C_\alpha{=}C_\beta$ bond of **6a**. The ν(CO) absorptions of **13a**, formed by addition of ethoxyacetylene to the $C_\alpha{=}C_\beta$ bond of **6a**, are expected at higher wavenumbers. In addition, the ^{13}C NMR spectrum of the new complex showed 11 resonances in the aromatic and olefin region between δ = 115 and 185 ppm instead of 6 as expected. On the basis of the spectroscopic results the new complex was assigned the structure **14a**, containing a bicyclic azulenylidene ligand (Scheme 3) instead of an unsaturated four-membered carbocyclic carbene ligand.

The formation of azulenylidene complexes is not confined to the reaction of **6a** with ethoxyacetylene. The corresponding products were obtained when instead of ethoxyacetylene the bulkier alkyne *tert*-butyloxyacetylene was employed in the

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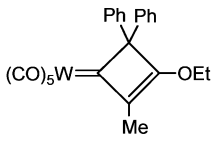
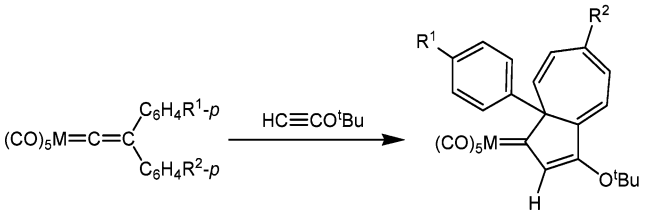
Scheme 4



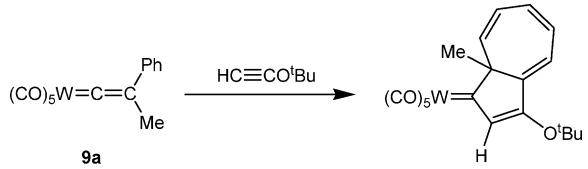
15a



16a - 19a; 16b; 17'a; 18'a

	16	**17**	**17'**	**18**	**18'**	**19**
M = W (**a**) Cr (**b**)						
R^1 =	H	Me	H	Cl	H	OMe
R^2 =	H	H	Me	H	Cl	H
ratio (M = W):		5 : 4		3 : 4		

Scheme 5



9a **20a**

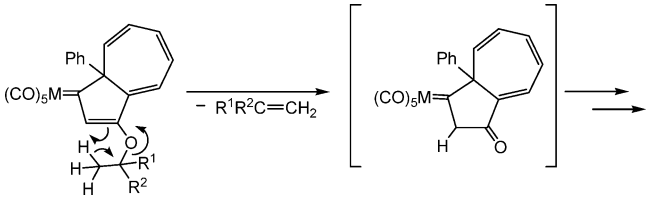
reactions with the vinylidene tungsten complexes **6a**−**8a** and **10a** and the vinylidene chromium complex **6b**. The new azulenylidene complexes (Scheme 4) were isolated in moderate yields. These complexes were formed independently of whether pure vinylidene complexes or those solutions were employed that were obtained by the acyl route (Scheme 2). However, when these solutions were used, they first had to be filtered over silica or aluminum oxide. After addition of *tert*-butyloxyacetylene, the volume of the solutions was reduced at low temperatures to a few milliliters, thus reducing the amount of decomposition of the starting complex and increasing the yields. Again, complexes containing the four-membered cyclobutenylidene ligand were not detected.

The reaction of the monosubstituted diarylvinylidene tungsten complexes **7a** and **10a** with *tert*-butyloxyacetylene yielded mixtures of two isomeric azulenylidene complexes. It was not possible to separate these isomers by column chromatography. However, on the basis of 2D NMR spectroscopy (HMBC and HSQC spectra) it was possible to assign the resonances of both isomers and to determine the isomeric ratio after chromatographic purification of the complexes. The isomeric ratio was close to 1:1 in both cases (5:4 for **17a**/**17a′** and 3:4 **18a**/**18a′**). There obviously is no pronounced preference for the formation of either one of the isomers. In contrast, only one isomer (**19a**) was detected in the product mixture of the reaction of **8a** with *tert*-butyloxyacetylene.

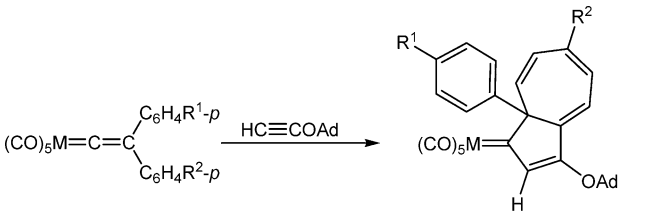
In the reaction of the methyl(phenyl)vinylidene complex **9a** with *tert*-butyloxyacetylene the 8a-methyl azulenylidene complex **20a** was formed in 39% isolated yield (Scheme 5).

Most of the new complexes turned out to be quite labile and readily decomposed at room temperature. A potential decomposition pathway involving β-elimination is shown in Scheme 6. Similar thermal olefin elimination reactions proceeding via six-membered intermediates have been proposed by Ficini[16] and Arens[17] to account for the facile decomposition of alkoxyalkynes.

Scheme 6



Scheme 7



21a,b - 25a,b; 22′a,b -24'a,b

	21	**22**	**22'**	**23**	**23'**	**24**	**24'**	**25**
R^1 =	H	Me	H	Cl	H	Me	Cl	^{t}Bu
R^2 =	H	H	Me	H	Cl	Cl	Me	H
M = W (**a**)		3 : 2		5 : 4		1 : 2		
M = Cr (**b**)		2 : 1		3 : 4		2 : 1		

To prevent the decomposition of the azulenylidene complexes by such a β-elimination pathway, *tert*-butyloxyacetylene was replaced by adamantyloxyacetylene. The reaction rates were similar and the adamantyloxy-substituted azulenylidene tungsten complexes **21a**−**25a** (Scheme 7) were obtained in modest yields.

In accord with expectation, the adamantyloxy-substituted complexes **21**−**25** proved to be somewhat more stable than the corresponding *tert*-butyloxy derivatives. But despite their enhanced stability, they were unstable at room temperature. Due to the increased stability, the chromium complexes **21b**−**25b** could likewise be isolated. However, the reactions of the chromium vinylidene complexes proceeded much slower than those of the tungsten complexes and the temperature had to be raised from −30 °C to 0 °C.

The azulenylidene complexes, derived from monosubstituted diarylvinylidene complexes, were again obtained as mixtures of isomers nonseparable by column chromatography. The determination of exact isomeric ratios was hampered by insufficient separation of the relevant resonances. Nevertheless, the isomeric ratios were found to be again close to 1:1 and were similar to those listed in Scheme 5. In general replacing the *p*-methyl substituent by the electron-withdrawing *p*-chloro group in monosubstituted vinylidene complexes shifted the ratio toward those azulenylidene complexes (**22′a**,**b** and **23′a**,**b**) having the substituent attached to the seven-membered ring. A pronounced change in the isomeric ratio was not observed when the influences of both substituents were combined (see **24′a**,**b**).

Surprisingly, only one isomer was obtained from the reaction of the phenyl(4-*tert*-butylphenyl)vinylidene complex **12** with

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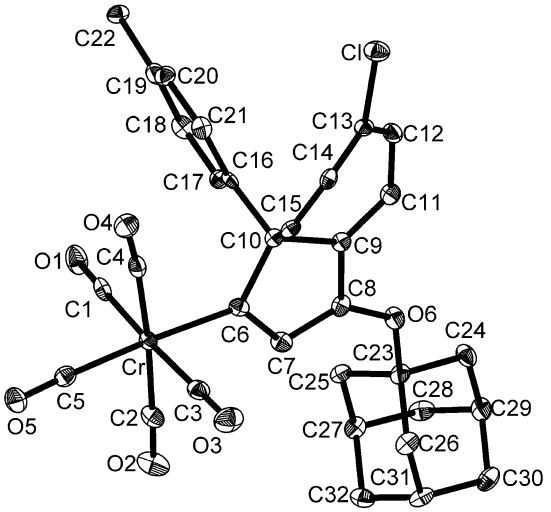


Figure 1. Structure of complex **24b** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important angles (deg): C1−Cr1−C6 87.97(12), C2−Cr1−C6 88.98(12), C3−Cr1−C6 88.59(12), C4−Cr1−C6 95.50(12), C5−Cr1−C6 176.84(12), C6−C10−C9 104.1(2), C6−C10−C16 109.1(2), C6−C7−C8 112.2(2), C8−C9−C10 106.9(2), C7−C8−O6 133.2(3), C9−C11−C12 125.6(3), C12−C13−C14 128.2(3), C14−C15−C10 125.0(3); for distances see Table 1.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 24b and 25a

	24b	**25a**
M−C5[a]	1.893(3)	2.022(5)
M−CO_{cis} (av)[a]	1.908	2.039
M−C6[a]	2.048(3)	2.169(5)
C6−C7	1.402(4)	1.409(6)
C6−C10	1.555(4)	1.558(6)
C7−C8	1.393(4)	1.386(7)
C8−C9	1.444(4)	1.453(6)
C9−C10	1.517(4)	1.513(6)
C9−C11	1.346(4)	1.337(7)
C11−C12	1.434(4)	1.433(7)
C12−C13	1.355(4)	1.361(7)
C13−C14	1.445(4)	1.444(8)
C14−C15	1.332(4)	1.336(7)
C10−C15	1.511(4)	1.511(7)

[a] M = Cr (**24b**), W (**25a**).

adamantyloxyacetylene. On the basis of the NMR spectroscopic results the product complex was assigned the structure containing the *tert*-butyl substituent in position 4 of the phenyl ring (Scheme 7, **25a**,**b,** R^1 = *tert*-butyl, R^2 = H).

All new azulenylidene complexes were characterized by their IR, NMR, and mass spectra and, whenever possible, also by elemental analyses. The structures of **24b** and **25a** (Table 1, Figure 1 and 2) were additionally established by X-ray structure analyses. In both cases, a few crystals suitable for diffraction studies were obtained at −30 °C by slow diffusion of petroleum ether into solution of **24b**/**24′b** and **25a** in CH_2Cl_2, respectively.

The five-membered ring in both complexes only slightly deviates from planarity (torsion angle C6−C10−C9−C8: −2.5(5)° in **25a** and 4.1(3)° in **24b**) and is almost staggered with respect to the *cis*-CO ligands (torsion angle C2−Cr1−C6−C7: −7.0(3)° in **24b**, C3−W1−C6−C7: 13.6(4)° in **25a**). In contrast, the seven-membered ring is strongly puckered and adopts a boat conformation, C9, C11, C14, and C15 forming the bottom part of the "boat". The angle between the planes formed by C9/C10/C15 and C9/C11/C14/C15 is 45.3° in **24b** and 47.5° in **25a**. The olefin planes C6/C7/C8 and C8/C9/C11 are coplanar, thus allowing for optimal conjugation. Consequently, the C8−C9 bond is short and corresponds to a conjugated C(sp^2)−C(sp^2) single bond.[18] The C−C distances within the five-membered ring and the C9−C11 distance compare well with those found in the only cyclopentenylidene complex (**26**) characterized until now by an X-ray structure analysis.[19] The distances within the bicyclic ring system are also similar to those in 3-hydroxy-9-phenyl-1,9-dihydroazulen-1-one (**27**).[20] However, due to the strong acceptor properties of the pentacarbonylmetal fragment, the C−C single bonds C6−C7 and C8−C9 are somewhat shorter and the C7═C8 double bond is longer than in **27**. The remaining ring distances agree well.

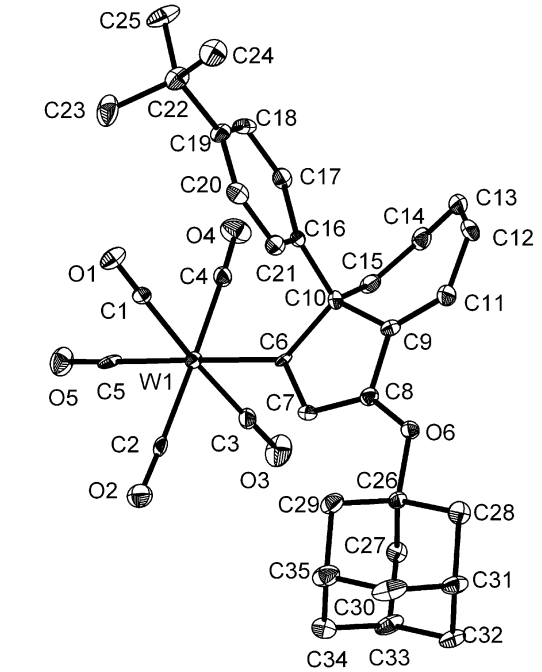
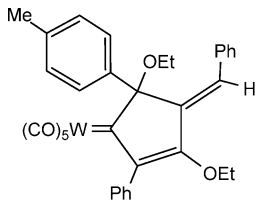


Figure 2. Structure of complex **25a** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Important angles (deg): W1−C6−C7 128.1(3); W1−C6−C10 126.1(3), C6−C10−C9 104.6(4), C6−C10−C16 108.1(4), C6−C7−C8 112.8(4), C8−C9−C10 106.7(4), C7−C8−O6 133.7(4), C9−C11−C12 125.0(4), C12−C13−C14 125.8(5), C14−C15−C10 123.3(5); for distances see Table 1.



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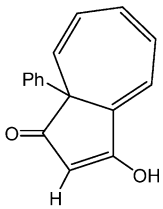

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3. Calculations and Discussion

The reactions of arylvinylidene(pentacarbonyl)chromium and -tungsten with π-donor-substituted alkynes are highly chemoselective. The product formation strongly depends on the substituent at the C_β atom of the alkyne. Ynamines and ethoxypropyne add to the C_α−C_β bond of the diphenylvinylidene ligand to form cyclobutenylidene ligands; the formation of an azulenylidene ligand is not observed.[8a] Conversely, the reactions of

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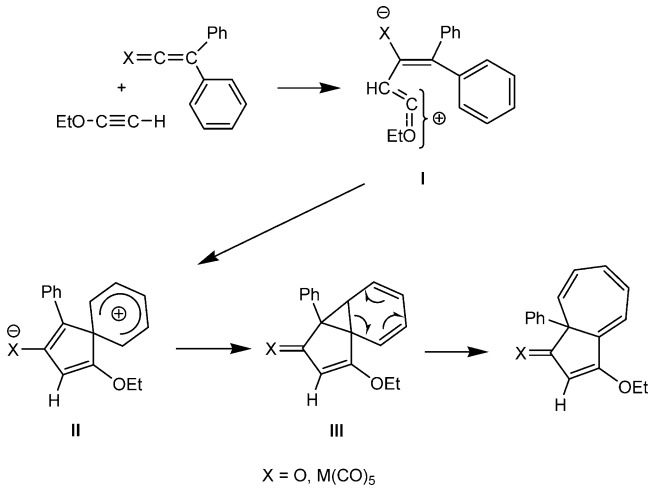
(19) Fischer, H.; Meisner, T.; Hofmann, J. *Chem. Ber.* **1990**, *123*, 1799.
(20) van de Grample, J. C.; Cuperus, A. J.; Vos, A. *Rec. Trav. Chim. Pays-Bas* **1971**, *90*, 587.

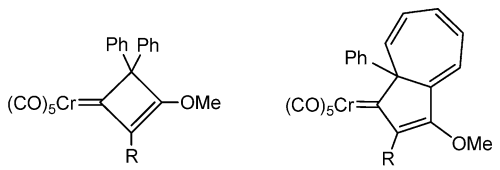
Scheme 8



alkoxyacetylene with arylvinylidene complexes afford azulenylidene complexes, and the formation of cyclobutenylidene complexes is not observed.

The reactions leading to azulenylidene complexes are reminiscent of those of arylketenes with ethoxyacetylene.[21] Already earlier it was reported that diphenylketenes react with ethoxyacetylene to give two cyclic ketones, 3-ethoxy-4,4-diphenylcyclobut-2-enone *and* 3-ethoxy-8a-phenyl-8a*H*-azulen-1-one.[21] Both ketones, the cyclobutenones and the azulenones, are formed in nearly equal amounts.[21c] Both types of reactions, those of vinylidene complexes and of ketenes, are obviously closely related, and pentacarbonyl(vinylidene) complexes may be regarded as organometallic analogues of ketenes. However, the reactions of vinylidene complexes with alkoxyalkynes proceed considerably more chemoselectively, yielding *exclusively* either cyclobutenylidene *or* azulenylidene complexes.

DFT calculations indicate that the cyclobutenylidene complex **28** is more stable than the azulenylidene complex **29** by 54 kJ/mol.



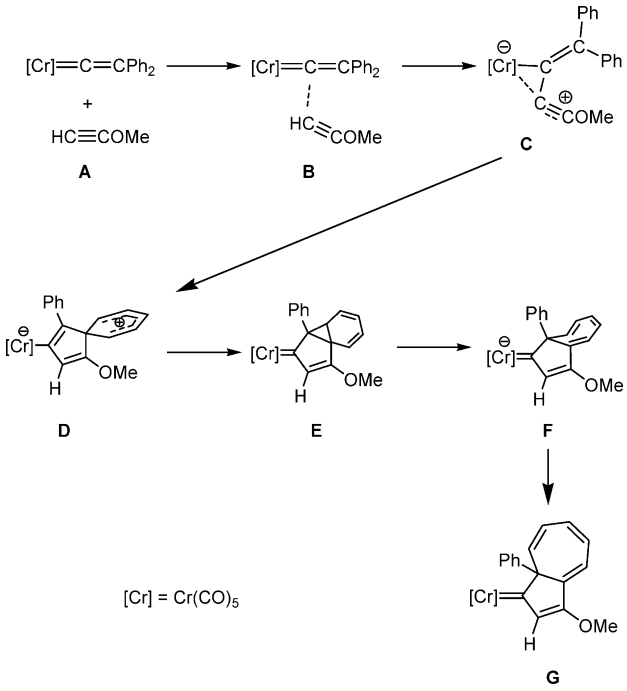
R = Me: **28** **29**
R = H: **30** **31**

This is in accord with the exclusive formation of a cyclobutenylidene complex in the reaction of pentacarbonyl(diphenylvinylidene)tungsten with ethoxypropyne.[8a] The calculated energy difference in favor of the cyclobutenylidene complex decreases by about 47 kJ/mol when R = Me is replaced by R = H.

For the formation of 3-ethoxy-8a-phenyl-8a*H*-azulen-1-one a mechanism involving initial addition (**I**) of ethoxyacetylene to the carbonyl group of diphenylketene was proposed followed by a ring closure to give the spirocarbonium ion **II** (Scheme 8). Subsequent formation of the norcaradiene derivative **III** and ring enlargement afford the azulen-1-one.[21c]

(21) (a) Jenny, E. F.; Schenker, K.; Woodward, R. B. *Angew. Chem.* **1961**, *73*, 756. (b) Barton, D. H. R.; Gardner, J. N.; Petterson, R. C.; Stamm O. A. *J. Chem. Soc.* **1962**, 2708. (c) Druey, J.; Jenny, E. F.; Schenker, K.; Woodward, R. B. *Helv. Chim. Acta* **1962**, *71*, 600. (d) Teufel, H.; Jenny, E. F. *Tetrahedron Lett.* **1971**, *21*, 1769.

Scheme 9



A similar mechanism seems plausible to account for the formation of the azulenylidene complexes and is supported by the results of DFT calculations.

Based on these calculations the energetically most feasible sequence for the reaction of pentacarbonyl(diphenylvinylidene)chromium (**6b**) with methoxyacetylene is shown in Scheme 9. The LUMO in vinylidene complexes is an in-plane orbital predominantly localized on the metal-bound C_α atom. In alkoxyacetylenes the nucleophilic center is the C_β atom. Thus, the reaction is initiated by an in-plane nucleophilic approach of the C_β atom of the alkyne to the C_α atom of the vinylidene complex (**A** → **B**). Interaction of the C_β atom with the C_α atom leads to lengthening of the Cr=C_α bond, the C=C bond of the vinylidene complex, and the C≡C bond of the alkyne as well as to a bending of the Cr−C−C angle away from the approaching alkyne. In the transition state (**B**) the C_α(vinylidene)−C_β(alkyne) distance has been reduced to 2.37 Å and the axis of the alkyne is almost perpendicularly oriented with respect to the vinylidene plane. The overall Gibbs free energy for the process **A** → **B** is 41 kJ/mol. Further lengthening of the Cr−C and the C−C bonds, reduction of the Cr−C_α−C_β angle, and interaction of the C_β atom of the alkyne with the metal give **C**. Formation of this complex (**A** → **C**) stabilizes the system (**6b** + methoxyacetylene) by 78 kJ/mol. The barrier for the rearrangement of the ligand in **C** into the norcaradienylidene ligand in **E** ($\Delta G = -91$ kJ/mol) via **D** is slightly lower ($\Delta G^{\ddagger} = 39$ kJ/mol) than that for the addition step **A** → **C**. In contrast, the barrier for alkyne dissociation from **C** to re-form the starting compounds (**C** → **B** → **A**) is much higher (119 kJ/mol). The final transformation of the norcaradienylidene ligand in **E** into the azulenylidene ligand in the product complex **G** ($\Delta G = -15$ kJ/mol) via **F** proceeds almost barrierless ($\Delta G^{\ddagger} = 6$ kJ/mol) (Scheme 9 and Figure 3).

The overall reaction is characterized by an early transition state, and the reaction rate is determined by the approach of the alkyne and formation of the adduct **C**.

Since the initial reaction step is an in-plane attack of the alkyne at the C_α atom of the vinylidene ligand, two different directions for an alkyne approach are possible when monoaryl-

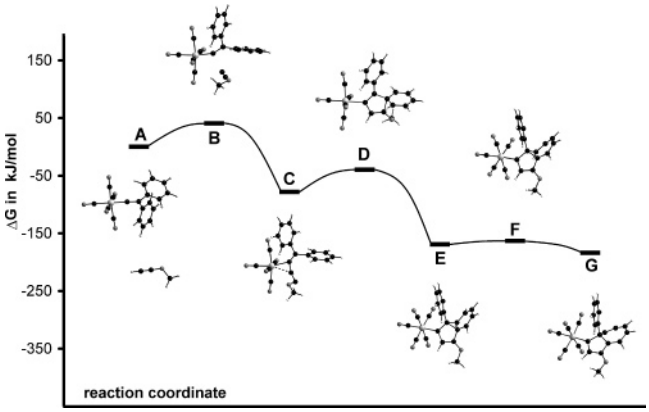


Figure 3. Gibbs free energy profile for the reaction of $[(CO)_5Cr{=}C{=}CPh_2]$ with HC≡COMe at 298 K (see also Scheme 9).

Table 2. Gibbs Free Energies (in kJ/mol) for the Steps "A" → "B" and "B" → "C" (see also Figure 4) of the Reactions of Methoxyacetylene with $[(CO)_5Cr{=}C{=}C(C_6H_4R\text{-}p)Ph]$ (R = H, Cl, Me, ^{t}Bu) at 298 K as Calculated at the LACPV*/BP86 Level of Theory

	R			
	H	Cl	Me	^{t}Bu
Δ*G*("**A**"→"**B**"), *syn* approach	40.5	43.0	43.7	39.7
Δ*G*("**A**"→"**B**"), *anti* approach	40.6	45.7	39.0	40.4
Δ*G*("**B**"→"**C**"), *syn* approach	−78.2	−72.3	−75.0	−78.1
Δ*G*("**B**" →"**C**"), *anti* approach	−78.2	−72.8	−73.5	−79.1

substituted diarylvinylidene complexes are used. The alkyne can add to C_α of the vinylidene ligand either adjacent to the substituted phenyl group (*syn* approach) or from the opposite side (*anti* approach). The *syn* approach then leads via interaction of the alkyne-C_β atom with the *ipso* carbon atom of the substituted phenyl group to azulenylidene complexes carrying the substituent X at the seven-membered ring (**X′a**,**b**). Conversely, an *anti* approach gives azulenylidene complexes having the group X in the phenyl substituent (**Xa**,**b**). Thus, the isomer preferentially formed is determined by the direction of the approaching alkyne, and the energy differences of the initial intermediates **B**/**B′** and **C**/**C′** will determine the isomeric ratio. On the basis of the experimentally found isomeric ratios (see Schemes 4 and 7) the energies of **B** and **B′** (and **C** and **C′**) are expected to be similar. The calculated energies for the transition states **B** for *syn* and *anti* approach of methoxyacetylene to the methyl-substituted vinylidene chromium complex **7b**, the chloro-substituted vinylidene complex **10b**, and the *tert*-butyl-substituted complex **12b** are very similar. The same applies to the various *syn* and *anti* intermediates **C** and **C′** (Table 2). For instance, the transition state "**B**" for the *syn* addition of methoxyacetylene to the chloro-substituted vinylidene chromium complex **10b** is only 2.7 kJ/mol lower in energy than that for the *anti* addition. Conversely, for the reaction of methoxyacetylene with **7b** ΔG_{anti} is 4.7 kJ/mol less than ΔG_{syn}. Therefore, in the reactions of methoxyacetylene (a) with the chloro-substituted complex **10b** formation of the *syn* isomer and (b) with the methyl-substituted complex **7b** formation of the *anti* isomer should be slightly favored. Note that the experimentally determined *syn*/*anti* ratios of the azulenylidene complexes formed in the reactions of adamantyloxyacetylene with **10b** (4:3) and with **7b** (1:2) are in accord with these expectations. However, the agreement should be regarded with care considering error limits and the difficulties in measuring exact isomeric ratios. The corresponding energy difference $\Delta G_{syn} - \Delta G_{anti}$ for the reaction of **12b** with methoxyacetylene is −0.7 kJ/mol.

The reactions of alkoxyacetylenes with vinylidene complexes and with ketenes differ not only in their chemoselectivity but also in the *syn*/*anti* selectivity of the alkyne approach. In general, those reactions of alkoxyacetylenes that tend to be *syn* selective with vinylidene complexes are *anti* selective with ketenes and vice versa. The extreme case is observed in the reactions with the methoxyphenyl-substituted compounds. Whereas the reaction of ethoxyacetylene with $O{=}C{=}C(Ph)C_6H_4OMe\text{-}p$ is highly *syn* selective [*syn*/*anti* ratio = 50 (±30) in nitromethane and 16 (± 5) in pentane], in the corresponding reaction of *tert*-butyloxyacetylene with $[(CO)_5W{=}C{=}C(Ph)C_6H_4OMe\text{-}p]$ the formation of only the *anti* isomer **19** (Scheme 4) was detected.

Experimental Section

All operations were performed in an inert gas atmosphere (argon or nitrogen) using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (petroleum ether), and sodium/benzophenone ketyl (THF, Et_2O). The silica gel used for chromatography (Baker, silica gel for flash chromatography) was nitrogen-saturated. The yields refer to analytically pure compounds and are not optimized. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer or on a Varian Inova 400 spectrometer at −50 °C. Chemical shifts are reported relative to the residual solvent peaks. IR spectra were recorded on a Biorad FTS 60. MS measurements were carried out on a Finnigan MAT 312 instrument. The UV/vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. The photochemical reactions were performed in a Duran glass apparatus using a Hg high-pressure lamp (Heraeus TQ 250). The following compounds were prepared according to literature procedures: the complexes **1a**,[15] **6a**,[14] and **6b**,[8c] adamantyloxyacetylene,[22] *tert*-butyloxyacetylene,[22] and ethoxyacetylene.[23] The ketenimines were synthesized from the corresponding amides.[24] Phenyl(4-tolyl)methane, phenyl(4-chlorophenyl)methane, phenyl(4-*tert*-butylphenyl)methane, and 4-chlorophenyl(4′-methylphenyl)methane were prepared from the corresponding alcohols according to published methods.[25] The ylide complexes **2a**−**5a** were likewise synthesized following a published procedure.[14] The alcohols of phenyl(4-*tert*-butylphenyl)methane and 4-chlorophenyl(4′-methylphenyl)methane were obtained by the method of Blackwell et al.[26] All other chemicals were used as obtained from commercial suppliers.

General Procedure for the Preparation of Vinylidene Complexes. Method A. An equimolar amount of the corresponding ketenimine was added at −70 °C to a solution of **1a** in dichloromethane. The dark red solution turned light red. On addition of pentane, a red precipitate was formed. Filtration over sodium sulfate at −70 °C and washing with cold (−70 °C) pentane afforded the red ylide complexes **2a**−**5a** in ca. 80% yield. These were immediately dissolved at −70 °C in a large volume of dichloromethane. An equimolar amount of $BF_3{\cdot}Et_2O$ in 5 mL of CH_2Cl_2 was added. When the red reaction mixture was slowly warmed to room temperature, the red color turned to a dirty brownish-green. The solvent was removed in vacuo at −30 °C. The residue was dissolved in 30 mL of pentane, and the solution was chromatographed at −30 °C on silica gel with pentane/CH_2Cl_2. The green band was collected. Removal of the solvent in vacuo at −30 °C gave the vinylidene complexes **6a**−**9a** in 11−90% yield (based on the ylide complex **2a**−**5a**).

Method B. At room temperature, a solution of 3.1 mL of BuLi (5 mmol, 1.6 M in hexane) was added dropwise to a solution of 5

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(23) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988; p 171.
(24) Stevens, C. L.; Singhal, G. H. *J. Org. Chem.* **1964**, *29*, 34.
(25) Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1674.
(26) Blackwell, J.; Hickinbottom, W. J. *J. Chem. Soc.* **1961**, 1405−1407.

mmol of the appropriate diarylmethane in 50 mL of THF. The orange solution was stirred for 1 h at room temperature. Then 5 mmol of $M(CO)_6$ (M = W: 1.76 g; M = Cr: 1.10 g) was added. The solution turned yellow (violet for **10a**,**b** and **11a**,**b**). After 30 min, the solvent was removed in vacuo. The remaining oily residue was dissolved in 50 mL of CH_2Cl_2 and treated at −30 °C (M = W) or −80 °C (M = Cr) with 0.7 mL (5 mmol) of $(F_3CCO)_2O$. The solution was stirred for 5 min and subsequently filtered over neutral Al_2O_3 (M = W) or silica gel (M = Cr). Rapid elution with 50 mL of cold petroleum ether gave green solutions of **6a**,**b**−**12a**,**b**. These solutions were immediately used for the subsequent reactions.

Pentacarbonyl[phenyl(*p*-tolyl)vinylidene]tungsten (7a). Method A. The reaction of 600 mg (0.86 mmol) of complex **3a** in 250 mL of CH_2Cl_2 with $BF_3{\cdot}Et_2O$ (reaction time: about 3 h) and chromatography with pentane/CH_2Cl_2 (20:3) gives green **7a** in yields varying between 22 and 33% (based on **3a**).

Method B. Acyl tungstate: IR (THF): ν(CO) 2047 m, 1907 vs, 1890 sh cm^{-1}.

Complex 7a. Mp: 53 °C (dec). IR (petroleum ether): ν(CO) 2093 m, 2003 sh, 1982 s, 1974 sh cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.20 (s, 3H, CH_3), 7.03−7.24 (m, 9H, C_6H_5, C_6H_4); (250 MHz, d_6-acetone): δ 2.33 (s, 3H, CH_3), 7.1−7.5 (m, 9H, C_6H_5, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.1 (CH_3), 125.2, 127.7, 127.86, 127.9, 128.3, 134.7, 137.5, 140.9 (C_6H_5, C_6H_4), 192.2 (*cis*-CO, J_{WC} = 127.5 Hz), 208.6 (*trans*-CO), 376.1 (W═C); (62.5 MHz, d_6-acetone): δ 21.0 (CH_3), 125.6, 127.9, 128.7, 129.0, 129.4, 129.8, 130.5, 132.3, 137.7 (C_6H_5, C_6H_4), 193.8 (*cis*-CO, J_{WC} = 124.7 Hz), 209.0 (*trans*-CO), 373.7 (W═C). EI-MS (70 eV): *m*/*z* (%) 516 (8) [M$^+$], 488 (36) [(M$^+$ − CO)$^+$], 460 (21) [(M − 2CO)$^+$], 432 (54) [(M − 3CO)$^+$], 404 (33) [(M − 4CO)$^+$], 376 (100) [(M − 5CO)$^+$], 192 (54) [(C═C(C_6H_5)$C_6H_4CH_3$)$^+$]. Anal. Calcd for $C_{20}H_{12}O_5W$ (516.16): C, 46.54; H, 2.34. Found: C, 46.57; H, 4.41.

Pentacarbonyl[phenyl(*p*-tolyl)vinylidene]chromium (7b). Method B. Acyl chromate: IR (THF): ν(CO) 2036 s, 1908 vs, 1890 sh cm^{-1}. **7b**: IR (petroleum ether): ν(CO) 2087 m, 2026 vw, 2005 s, 1987 s, 1982 sh cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.0 (s, 3H, CH_3), 7.03−7.38 (m, 9H, C_6H_5, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 21.1 (CH_3), 123.4, 124.7, 125.4, 125.9, 126.1, 127.3, 127.4, 127.7, 128.2, 128.8 (C_6H_5, C_6H_4, C_β), 212.4 (*cis*-CO), 224.2 (*trans*-CO), 413.3 (Cr═C).

Pentacarbonyl[*p*-methoxyphenyl(phenyl)vinylidene]tungsten (8a). Method A. The reaction of 500 mg (0.75 mmol) of complex **4a** in 250 mL of CH_2Cl_2 with $BF_3{\cdot}Et_2O$ (reaction time: about 3 h) and the chromatography with pentane/CH_2Cl_2 (10:4) afforded green crystals in yields varying from 26 to 31% (based on **4a**). Mp: 52 °C. IR (pentane): ν(CO) 2094 m, 2004 s, 1988 vs, 1975 s cm^{-1}. ^{1}H NMR (250 MHz, d_6-acetone): δ 3.79 (s, 3H, CH_3), 7.0−7.5 (m, 9H, C_6H_5, C_6H_4). ^{13}C NMR (62.5 MHz, d_6-acetone): δ 55.2 (CH_3), 115.2, 119.6, 127.8, 128.5, 129.7, 129.8, 130.5, 132.0, 159.6 (C_6H_5, C_6H_4, C_β), 193.8 (*cis*-CO), 209.3 (*trans*-CO), 375.1 (W═C). EI-MS (70 eV): *m*/*z* (%) 532 (3) [M$^+$], 504 (8) [(M − CO)$^+$], 476 (6) [(M − 2CO) $^+$], 448 (4) [(M − 3CO)$^+$], 420 (7) [(M − 4CO)$^+$], 392 (15) [(M − 5CO)$^+$]. $C_{20}H_{12}O_6W$ (532.16).

Pentacarbonyl[methyl(phenyl)vinylidene]tungsten (9a). Method A. The reaction of 1.2 g (1.93 mmol) of **5a** in 450 mL of CH_2Cl_2 at −80 °C with $BF_3{\cdot}Et_2O$ (reaction time: about 3.5 h) and the chromatography with pentane/CH_2Cl_2 (10:1) gave green **9a** in yields between 12 and 28% (based on **5a**). Mp: 35 °C (dec). IR (pentane): ν(CO) 2095 m, 1997 sh, 1989 vs, 1979 sh cm^{-1}. ^{1}H NMR (250 MHz, d_6-acetone): δ 2.11 (s, 3H, CH_3), 7.1−7.4 (m, 5H, C_6H_5). ^{13}C NMR (62.5 MHz, d_6-acetone): δ 25.7 (CH_3), 122.7, 125.9, 127.1, 129.5, 130.3 (C_6H_5, C_β), 193.8 (*cis*-CO, J_{WC} = 124.37 Hz), 210.1 (*trans*-CO), 380.4 (W═C). FAB-MS (NBOH/CH_2Cl_2): *m*/*z* (%) 440 (37) [M$^+$], 412 (100) [(M − CO) $^+$], 384 (22) [(M − 2CO)$^+$], 356 (11) [(M − 3CO)$^+$], 300 (40) [(M − 5CO)$^+$]. Anal. Calcd for $C_{14}H_8O_5W$ (440.1): C, 38.21; H, 1.83. Found: C, 38.51; H, 2.00.

Pentacarbonyl[*p*-chlorophenyl(phenyl)vinylidene]tungsten (10a). Method B. Acyl tungstate: IR (THF): ν(CO) 2048 m, 1908 s, 1893 s, 1862 w cm^{-1}. **10a**: IR (petroleum ether): ν(CO) 2094 m, 2004 sh, 1983 s, 1976 sh cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.24−7.45 (m, 9H, C_6H_5, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 126.2, 128.5, 128.6, 128.8, 130.3, 131.5, 140.0, 140.8 (C_6H_5, C_6H_4, C_β), 192.8 (*cis*-CO, J_{WC} = 126.1 Hz), 208.6 (*trans*-CO), 373.4 (W═C).

Pentacarbonyl(*p*-chlorophenyl(phenyl)vinylidene]chromium (10b). Method B. Acyl chromate: IR (THF): ν(CO) 2036 m, 1908 s, 1892 s, 1864 w cm^{-1}. **10b**: IR (petroleum ether): ν(CO) 2089 m, 2007 sh, 1983 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.26−7.49 (m, 9H, C_6H_5, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 126.3, 128.5, 128.6, 128.8, 130.3, 131.5, 140.0, 140.9 (C_6H_5, C_6H_4, C_β), 212.2 (*cis*-CO), 222.6 (*trans*-CO), 404.6 (Cr═C).

Pentacarbonyl[*p*-chlorophenyl(*p*-tolyl)vinylidene]tungsten (11a). Method B. Acyl tungstate: IR (THF): ν(CO) 2049 m, 1911 s, 1894 sh, 1866 w cm^{-1}. **11a**: IR (petroleum ether): ν(CO) 2095 m, 2003 sh, 1979 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.41 (CH_3), 7.16−7.63 (m, 8H, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.9 (CH_3), 128.4, 128.6, 129.1, 129.2, 129.5, 130.2, 135.8, 136.9, 137.7, 140.3 (C_6H_4, C_β), 192.8 (*cis*-CO, J_{WC} = 126.1 Hz), 209.0 (*trans*-CO), 375.1 (W═C).

Pentacarbonyl[*p*-chlorophenyl(*p*-tolyl)vinylidene]chromium (11b). Method B. Acyl chromate: IR (THF): ν(CO) 2037 w, 1907 s, 1891 sh, 1866 w cm^{-1}. **11b**: IR (petroleum ether): ν(CO) 2089 s, 2001 sh, 1979 vs cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.49 (CH_3), 7.26−7.71 (m, 8H, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 21.0 (CH_3), 126.7, 128.5, 128.7, 129.3, 129.6, 130.3, 131.5, 135.9, 136.9, 137.8, 140.4 (C_6H_4, C_β), 212.3 (*cis*-CO), 223.0 (*trans*-CO), 406.0 (Cr═C).

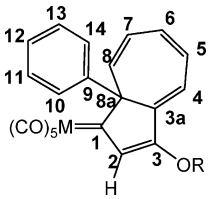
Pentacarbonyl[*p*-*tert*-butylphenyl(phenyl)vinylidene]tungsten (12a). Method B. Acyl tungstate: IR (THF): ν(CO) 2047 m, 1909 vs, 1888 sh cm^{-1}. **12a**: IR (petroleum ether): ν(CO) 2092 m, 2002 m, 1983 s, 1973 m cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.15 (s, 9H, CH_3), 7.00 − 7.19 (m, 9H, C_6H_5, C_6H_4). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 31.3 (CH_3), 34.4 ($C(CH_3)_3$), 125.5, 126.1, 128.4, 128.6, 128.8, 138.6, 141.8, 148.7 (C_6H_5, C_6H_4, C_β), 193.1 (*cis*-CO, J_{WC} = 126.1 Hz), 209.6 (*trans*-CO), 377.2 (W═C)

Pentacarbonyl[*p*-*tert*-butylphenyl(phenyl)vinylidene]chromium (12b). Method B. Acyl chromate: IR (THF): ν(CO) 2036 m, 1908 vs, 1891 sh cm^{-1}. **12b**: IR (petroleum ether): ν(CO) 2086 m, 2004 s, 1986 s, 1981 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.15 (s, 9H, CH_3), 7.35 − 7.67 (m, 9H, C_6H_5, C_6H_4, C_β). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 30.1 (CH_3), 34.6 ($C(CH_3)_3$), 126.2−150.8 (C_6H_5, C_6H_4, C_β), 213.1 (*cis*-CO), 224.5 (*trans*-CO), 409.3 (Cr═C)

General Procedure for the Reaction of Vinylidene Complexes with Alkoxyacetylenes. Method C. Solutions of vinylidene complexes (1 mmol dissolved in 5 mL of CH_2Cl_2) were treated at temperatures between −10 and −30 °C with 3 equiv of alkoxyacetylene dissolved in 5 mL of CH_2Cl_2. The progress of the reaction was controlled by IR spectroscopy. The reactions of the tungsten complexes required between 3 and 6 h, and those of the chromium complexes up to 5 days. In the course of the reactions the green color turned dark violet. The solvent was removed in vacuo at −30 °C. The residue was dissolved at −30 °C in pentane/CH_2Cl_2 and chromatographed on silica gel at −50 °C. With pentane/CH_2Cl_2 a violet to blue band (color depending on the type of complex) was eluted. Evaporation of the solvent in vacuo at −50 °C gave the azulenylidene complexes in yields ranging from 20 to 40% (based on vinylidene complex).

Method D. Alkoxyacetylene (2 mmol; 0.23 mL of *tert*-butyloxyacetylene or 0.36 g of adamantyloxyacetylene) was added at −30 °C to a freshly prepared solution of the vinylidene complexes obtained by method B. The volume of the solution was reduced at −30 °C to 10 mL. The progress of the reactions was controlled by IR spectroscopy. The color of the solution changed from green to dark violet (M = W) or blue (M = Cr). The conversion of the vinylidene complex was complete after 24 h (M = W, −30 °C) or 6 h (M = Cr: adamantyloxyacetylene, 0 °C). The solvent was removed in vacuo at −30 °C, and the residue was twice chromatographed on silica at −50 °C first with petrolether/CH_2Cl_2 (5:1) and then with petroleum ether/Et_2O (5:1) to give pure azulenylidene complexes.

The following numbering scheme has been applied for assigning the NMR resonances of the azulenylidene complexes:



Pentacarbonyl(3-ethoxy-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (14a). Method C. The reaction was complete after about 2 h. The reaction mixture was chromatographed at −40 °C on silica with pentane/CH_2Cl_2 (20:3). Violet crystal. Yield: 36% (based on **6a**). Mp: 118 °C (dec). IR (pentane): ν(CO) 2058 m, 1986 vw, 1958 vs, 1941 m, 1924 s cm^{-1}. ^{1}H NMR (250 MHz, d_6-acetone): δ 1.53 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_2CH_3), 4.80 (m, 2H, OCH_2CH_3), 6.3−6.9 (m, 5H, 4-H, 5-H, 6-H, 7-H, 8-H), 7.0−7.2 (m, 5H, C_6H_5), 7.79 (s, 1H, 2-H). ^{13}C NMR (62.5 MHz, d_6-acetone): δ 14.4 (OCH_2CH_3), 71.4 (C-8a), 73.15 (OCH_2), 119.8, 127.3, 128.2, 128.4, 129.7, 137.9, 138.4, 139.1, 140.8, 140.9 (C-2, C-3a, C-4, C-5, C-6, C-7, C-8, C_6H_5), 180.5 (C-3), 198.5 (*cis*-CO, J_{WC} = 126.7 Hz), 207.3 (*trans*-CO), 309.2 (W=C). FAB-MS (NBOH): *m*/*z* (%) 572 (8) [M$^+$], 544 (3) [(M − CO)$^+$], 516 (18) [(M − 2CO)$^+$], 488 (19) [(M − 3CO)$^+$], 460 (30) [(M − 4CO)$^+$], 432 (11) [(M$^+$ − 5CO)$^+$], 249 (46) [(M$^+$ − W(CO)$_5$)$^+$]. UV/vis: λ_{max} (log ϵ) 234 (4.8), 336 (4.04), 574 (4.3) [pentane]. Anal. Calcd for $C_{23}H_{16}O_6W$ (572.2): C, 48.27; H, 2.81. Found: C, 48.00; H, 2.81.

Pentacarbonyl(3-*tert*-butoxy-8a-phenylbicyclo[5.3.0]deca-2,-3a,5,7-tetraenylidene)tungsten (16a). Method C. The reaction was complete after about 2 h. The reaction mixture was chromatographed at −40 °C on silica with pentane/CH_2Cl_2 (20:3). Violet crystal. Yield: 36% (based on **6a**). **Method D.** Yield: 0.22 g (19% based on *tert*-butyloxyacetylene).

Mp: 64−66 °C. IR (petroleum ether): ν(CO) 2055 m, 1954 s, 1938 m, 1920 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.67 (s, 9H, CH_3), 6.25 (dd, ^3J = 6.7 Hz and ^3J = 10.4 Hz, 1H, 5-H), 6.58 (dd, ^3J = 6.7 and 10.5 Hz, 1H, 7-H), 6.61 (d, ^3J = 6.5 Hz, 1H, 4-H), 6.67 (d, ^3J = 10.0 Hz, 1H, 8-H), 6.74 (dd, ^3J = 6.8 and 10.2 Hz, 1H, 6-H), 7.12 (m, 5H, C_6H_5), 7.62 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 27.8 ($C(CH_3)_3$), 70.9 (C-8a), 87.1 ($OC(CH_3)_3$), 118.2 (C-4), 126.4 (C-12), 127.0 (C-7), 127.3 (C-10, -11, -13, -14), 128.2 (C-5), 136.9 (C-6), 137.3 (C-8), 139.6 (C-3a), 140.5 (C-9), 141.0 (C-2), 176.2 (C-3), 198.1 (*cis*-CO, J_{WC} = 127.2 Hz), 208.0 (*trans*-CO, J_{WC} = 122.9 Hz), 309.0 (W=C). FAB-MS (NBOH): *m*/*z* (%) 600 (8) [M$^+$], 544 (13) [(M − 2CO)$^+$], 516 (47) [(M − 3CO)$^+$], 488 (92) [(M − 4CO)$^+$], 460 (30) [(M − 5CO)$^+$], 432 (76) [(M − 4CO − C_4H_8)$^+$], 404 (100) [(M − 5CO − C_4H_8)$^+$]. Anal. Calcd for $C_{25}H_{20}O_6W$ (600.28): C, 50.02; H, 3.36. Found: C, 49.79; H, 3.31.

Pentacarbonyl(3-*tert*-butoxy-8a-phenylbicyclo[5.3.0]deca-2,-3a,5,7-tetraenylidene)chromium (16b). Method C. Yield: 21% (based on **6b**). **Method D.** Yield: 0.13 g (14% based on *tert*-butyloxyacetylene). Mp: 115 °C (dec). IR (petroleum ether): ν-(CO) 2045 m, 1956 s, 1946 m, 1925 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.67 (s, 9H, CH_3), 6.28 (dd, $^3J_{HH}$ = 6.7 and 10.9 Hz, 1H, 5-H), 6.40 (d, $^3J_{HH}$ = 6.4 Hz, 1H, 4-H), 6.60 ($dd_{overlapped}$ and $d_{overlapped}$, 2H, 7-H, 8-H), 6.67 (dd, $^3J_{HH}$ = 6.8 and 10.9 Hz, 1H, 6-H), 7.11 (m, 5H, C_6H_5), 7.72 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 27.8 ($C(CH_3)_3$), 70.6 (C-8a), 86.7 ($OC(CH_3)_3$), 116.8 (C-4), 126.4 (C-12), 127.0 (C-7), 127.2 (C-10, -11, -13, -14), 127.8 (C-5), 136.3 (C-8), 137.0 (C-6), 137.8 (C-9), 138.9 (C-2), 139.9 (C-3a), 172.7 (C-3), 217.3 (*cis*-CO), 228.8 (*trans*-CO), 338.2 (Cr=C). FAB-MS (NBOH): *m*/*z* (%) 468 (7) [(M$^+$)], 440 (4) [(M − CO)$^+$], 412 (11) [(M − 2CO)$^+$], 384 (46) [(M − 3CO)$^+$], 356 (66) [(M − 4CO)$^+$], 328 (100) [(M − 5CO)$^+$], 300 (8) [(M − 4CO − C_4H_8)$^+$], 272 (57) [(M − 5CO − C_4H_8)$^+$]. UV/vis: λ_{max} (log ϵ) 606 (4.160), 338 (3.910) [pentane]. Anal. Calcd for $C_{25}H_{20}O_6Cr$ (468.43): C, 64.09; H, 4.31. Found: C, 64.16; H, 4.47.

Pentacarbonyl(3-*tert*-butoxy-8a-*p*-tolylbicyclo[5.3.0]deca-2,-3a,5,7-tetraenylidene)tungsten (17a) and Pentacarbonyl(3-*tert*-butoxy-6-methyl-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (17′a). Method C. The reaction employing 8 equiv of *tert*-butyloxyacetylene was complete after about 5.5 h. The reaction mixture was chromatographed at −50 °C on silica with pentane/CH_2Cl_2 (5:1). Violet powder. Yield: 33% (based on **7a**). **Method D.** Yield: 0.29 g (24% based on *tert*-butyloxyacetylene).

Mp: 80−83 °C. IR (petroleum ether): ν(CO) 2055 m, 1953 s, 1936 m, 1920 s cm^{-1}. Isomer **17a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.66 (s, 9H, $C(CH_3)_3$), 2.19 (s, 3H, CH_3), 6.24 (dd, $^3J_{HH}$ = 6.6 and 11.0 Hz, 1H, 5-H), 6.57 (dd br, 1H, 7-H), 6.59 (d, $^3J_{HH}$ = 6.6 Hz, 1H, 4-H), 6.65 (d, $^3J_{HH}$ = 10.1 Hz, 1H, 8-H), 6.73 (dd, $^3J_{HH}$ = 6.3 and 11.0 Hz, 1H, 6-H) , 6.94−7.18 (m br, 9H, C_6H_4, C_6H_5, both isomers), 7.60 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.6 (CH_3), 27.8 ($C(CH_3)_3$), 70.7 (C-8a), 87.0 ($OC(CH_3)_3$), 118.1 (C-4), 126.3, 127.4, 127.9, 136.0, 134.4, 140.6 (aryl of **17a** and **17′**a), 126.9 (C7), 128.1 (C-5), 136.9 (C-6), 137.3 (C-8), 139.8 (C-3a), 140.9 (C-2), 176.2 (C-3), 198.2 (*cis*-CO, J_{WC} = 127.3 Hz), 208.0 (*trans*-CO), 309.3 (W=C). Isomer **17′a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.66 (s, 9H, $(C(CH_3)_3)$, 1.95 (s, 3H, CH_3), 6.03 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 5-H), 6.43 (d , $^3J_{HH}$ = 10.3 Hz, 1H, 7-H), 6.52 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 4-H), 6.54 (d, $^3J_{HH}$ = 4.5 Hz, 1H, 8-H), 6.94−7.18 (m br, 9H, C_6H_4, C_6H_5, both isomers), 7.60 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 25.3 (CH_3), 27.8 ($C(CH_3)_3$), 70.5 (C-8a), 86.9 ($OC(CH_3)_3$), 118.9 (C-4), 125.5 (C-5), 126.3, 127.4, 127.9, 136.0, 134.4, 140.6 (aryl of **17a** and **17′a**), 130.2 (C-7), 136.1 (C-8), 139.6 (C-3a), 140.8 (C-2), 148.8 (C-6), 176.9 (C-3), 198.3 (*cis*-CO, J_{WC} = 126.8 Hz), 207.8 (*trans*-CO), 306.1 (W=C). FAB-MS (NBOH): *m*/*z* (%): 558 (15) [(M − 2CO)$^+$], 530 (38) [(M − 3CO)$^+$], 502 (90) [(M − 4CO)$^+$], 474 (27) [(M − 5CO)$^+$], 446 (89) [(M − 4CO − C_4H_8)$^+$], 418 (100) [(M − 5CO − C_4H_8)$^+$]. Anal. Calcd for $C_{26}H_{22}O_6W$ (614.31): C, 50.83; H, 3.61. Found: C, 46.82; H, 4.39.

Pentacarbonyl(3-*tert*-butoxy-8a-*p*-chlorophenylbicyclo[5.3.0]-deca-2,3a,5,7-tetraenylidene)tungsten (18a) and Pentacarbonyl-(3-*tert*-butoxy-6-chloro-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (18′a). Method D. Yield: 0.10 g (8% based on *tert*-butyloxyacetylene). IR (petroleum ether): ν(CO) 2055 m, 1957 m, 1941 m, 1922 s cm^{-1}. Isomer **18a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.66 (s, 9H, CH_3), 6.26 (dd, $^3J_{HH}$ = 6.7 and 11.2 Hz, 1H, 5-H), 6.58 ($dd_{overlapped}$, 1H, 7-H), 6.63 ($d_{overlapped}$, 1H, 4-H), 6.67 ($d_{overlapped}$, $^3J_{HH}$ = 10.6 Hz, 1H, 8-H), 6.75 (dd, $^3J_{HH}$ = 6.0 and 11.0 Hz, 1H, 6-H), 7.12−7.17 (m, 9H, C_6H_4, C_6H_5, both isomers), 7.63 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 27.8 (CH_3), 70.3 (C-8a), 87.3 ($OC(CH_3)_3$), 118.3 (C-4), 126.8 (C-7), 127.3, 127.4, 127.6, 131.5, 138.4, 140.3 (aryl of **18a** and **18′a**), 128.5 (C-5), 136.9 (C-6), 137.1 (C-8), 139.1 (C-3a), 141.2 (C-2), 176.1 (C-3), 198.1 (*cis*-CO), 207.8 (*trans*-CO), 308.2 (W=C). Isomer **18′a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.66 (s, 9H, CH_3),

6.39 (d, $^3J_{HH}$ = 7.2 Hz, 1H, 5-H), 6.54 (d, $^3J_{HH}$ = 7.3 Hz, 1H, 4-H), 6.59 ($d_{overlapped}$, 1H, 7-H), 6.66 ($d_{overlapped}$, $^3J_{HH}$ = 10.5 Hz, 1H, 8-H), 7.12 − 7.17 (m, 9H, C_6H_4,C_6H_5, both isomers), 7.61 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 27.8 (CH_3), 70.6 (C-8a), 87.3 (O*C*(CH_3)$_3$), 116.4 (C-4), 127.2 (C-5), 127.3, 127.4, 127.6, 131.5, 138.4, 140.3 (aryl of **18a** and **18′a**), 128.5 (C-7), 136.7 (C-8), 140.5 (C-3a), 141.1 (C-2), 141.4 (C-6), 175.4 (C-3), 197.9 (*cis*-CO), 208.0 (*trans*-CO), 309.3 (W═C). FAB-MS: *m*/*z* (%) 578 (19) [(M − 2CO)$^+$], 550 (34) [(M − 3 CO)$^+$], 522 (100) [(M − 4CO)$^+$], 494 (40) [(M − 5CO)$^+$], 466 (97) [(M − 4CO − C_4H_8)$^+$], 438 (78) [(M − 5CO − C_4H_8)$^+$]. $C_{25}H_{19}ClO_6W$ (634.73).

Pentacarbonyl(3-*tert*-butoxy-3a-*p*-methoxyphenylbicyclo[5.3.0]-deca-2,3a,5,7-tetraenylidene)tungsten(0) (19a). Method C. The reaction employing 10 equiv of *tert*-butyloxyacetylene was complete after about 6 h. The reaction mixture was chromatographed at −50 °C on silica with pentane/CH_2Cl_2 (5:2). Violet powder. Yield: 27% (based on **8a**). Yield: 27% (based on **8a**). Mp: 43−48 °C (dec). IR (pentane): ν(CO) 2057 m, 1984 w, 1955 vs, 1937 s, 1920 s cm^{-1}. ^{1}H NMR (250 MHz, d_6-acetone): δ 1.75 (s, 9H, C(CH_3)$_3$), 3.66 (s, 3H, OCH_3), 6.3−7.1 (m, 9H, 4-H−8-H, C_6H_4), 7.86 (s, 1H, 2-H). ^{13}C NMR (62.5 MHz, d_6-acetone): δ 27.8 (C(*C*H_3)$_3$), 55.0 (OCH_3), 70.9 (C-8a), 88.8 (O*C*(CH_3)$_3$), 119.9−141.5 (C-2, C-4−C-11, C-13, C-14), 158.7 (C-12), 178.2 (C-3), 198.8 (*cis*-CO, J_{WC} = 125.13), 208.1 (*trans*-CO), 308.6 (W═C). UV/vis: λ_{max} (log ϵ) 230 (4.8), 244 (4.8), 336 (4.31), 578 (4.38) [pentane]. FAB-MS (NBOH/CH_2Cl_2): *m*/*z* (%) 630 (5) [M$^+$], 574 (15) [(M − 2CO)$^+$], 546 (35) [(M − 3CO)$^+$], 518 (77) [(M − 4CO)$^+$], 490 (21) [(M − 5CO)$^+$], 462 (58) [(M − 4CO − C_4H_8)$^+$], 434 (49) [(M − 5CO − C_4H_8)$^+$], 251 (100) [(M − C_4H_8 − W(CO)$_5$)$^+$]. Anal. Calcd for $C_{26}H_{22}O_7W$ (630.30): C, 49.54; H, 3.52. Found: C, 49.80; H, 3.26.

Pentacarbonyl(3-*tert*-butoxy-8a-methylbicyclo[5.3.0]deca-2,-3a,5,7-tetraenylidene)tungsten(0) (20a). Method C. The reaction employing 5 equiv of *tert*-butyloxyacetylene was complete after about 5 h. The reaction mixture was chromatographed at −50 °C on silica with pentane/CH_2Cl_2 (20:3). Violet powder. Yield: 39% (based on **9a**). Mp: 64−66 °C (dec). IR (pentane): ν(CO) 2057 m, 1977 vw, 1954 vs, 1940 m, 1923 s cm^{-1}. ^{1}H NMR (250 MHz, d_6-acetone): δ 1.15 (s, 3H, CH_3), 1.68 (s, 9H, C(CH_3)$_3$), 6.3−7.1 (m, 5H, 4-H, 5-H, 6-H, 7-H, 8-H), 7.79 (s, 1H, 2-H). ^{13}C NMR (62.5 MHz, d_6-acetone): δ 23.0 (CH_3), 27.8 (C(*C*H_3)$_3$), 65.5 (C-8a), 88.4 (O*C*(CH_3)$_3$), 120.5, 126.0, 129.3, 138.2 (C-4−C-8), 141.5 (C-3a), 141.9 (C-2), 175.7 (C-3), 199.5 (*cis*-CO), 206.6 (*trans*-CO), 310.4 (W═C). UV/vis: λ_{max} (log ϵ) 244 nm (4.73), 336 (3.92), 568 (4.22) [pentane]. FAB-MS (NBOH): *m*/*z* (%) 538 (5) [M$^+$], 482 (15) [(M − 2CO)$^+$], 454 (12) [(M − 3CO)$^+$], 426 (25) [(M − 4CO)$^+$], 398 (7) [(M − 5CO)$^+$], 370 (27) [(M − 4CO − C_4H_8)$^+$], 342 (10) [(M − 5CO − C_4H_8)$^+$], 159 (35) [(M − C_4H_8 − W(CO)$_5$)$^+$]. $C_{20}H_{18}O_6W$ (538.21). The crystals contain 1 equiv of pentane. Anal. Calcd for $C_{20}H_{18}O_6W{\cdot}C_5H_{12}$ (610.36): C, 49.20; H, 4.95. Found: C, 49.19; H, 4.99.

Pentacarbonyl(3-adamantyloxy-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (21a). Method D. Yield: 0.27 g (20% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2055 m, 1953 s, 1942 sh, 1953 s, 1919 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.24 (dd, $^3J_{HH}$ = 6.6 and 10.8 Hz, 1H, 5-H), 6.57 (dd, $^3J_{HH}$ = 6.3 and 10.0 Hz, 1H, 7-H), 6.63 (d, $^3J_{HH}$ = 6.4 Hz, 1H, 4-H), 6.67 (d, $^3J_{HH}$ = 10.1 Hz, 1H, 8-H), 6.74 (dd, $^3J_{HH}$ = 6.3 and 11.0 Hz, 1H, 6-H), 7.12 (m, 5H, C_6H_5), 7.70 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 30.8 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 41.0 (2-, 6-, and 7-CH_2), 70.7 (C-8a), 86.8 (OAd), 118.2 (C-4), 126.4 (C-12), 127.0 (C-7), 127.3 (C-10, -11, -13, -14), 128.3 (C-5), 136.9 (C-6), 137.3 (C-8), 139.6 (C-3a), 140.7 (C-9), 141.7 (C-2), 176.1 (C-3), 198.2 (*cis*-CO, $^1J_{WC}$ = 127.0 Hz), 208.0 (*trans*-CO), 308.1 (W═C). FAB-MS: *m*/*z* (%) 678 (5) [(M)$^+$], 622 (34) [(M − 2CO)$^+$], 584 (48) [(M − 3CO)$^+$], 584 (100) [(M − 4CO)$^+$], 538 (33) [(M − 5CO)$^+$]. $C_{31}H_{26}O_6W$ (678.39).

Pentacarbonyl(3-adamantyloxy-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)chromium (21b). Method D. Yield: 0.26 g (24% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2045 s, 1956 m, 1944 m, 1923 m cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.28 (dd br, 1H, 5-H), 6.42 (d, $^3J_{HH}$ = 5.7 Hz, 1H, 4-H), 6.60 ($dd_{overlapped}$, 2H, 7-H and 8-H), 6.67 (dd br, 1H, 6-H), 7.11−7.54 (m, 5H, C_6H_5), 7.80 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 30.8 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 41.0 (2-, 6-, and 7-CH_2), 70.4 (C-8a), 86.5 (OAd), 116.8 (C-4), 126.4 (C-12), 127.0 (C-7), 127.2 (C-10, -11, -13, -14), 127.8 (C-5), 136.3 (C-8), 137.0 (C-6), 138.4 (C-9), 138.9 (C-2), 140.1 (C-3a), 172.6 (C-3), 217.3 (*cis*-CO), 228.8 (*trans*-CO), 337.0 (Cr═C). FAB-MS: *m*/*z* (%) 546 (3) [(M)$^+$], 518 (1) [(M − CO)$^+$], 490 (3) [(M − 2CO)$^+$], 462 (40) [(M − 3CO)$^+$], 434 (38) [(M − 4CO)$^+$], 406 (100) [(M − 5CO)$^+$]. $C_{31}H_{26}O_6Cr$ (546.54).

Pentacarbonyl(3-adamantyloxy-8a-*p*-tolylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (22a) and Pentacarbonyl(3-adamantyloxy-6-methyl-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (22′a). Method D. Yield: 0.35 g (25% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2054 s, 1952 s, 1935 m, 1917 s cm^{-1}. Isomer **22a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.20 (s, 3H, CH_3), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.24 (dd, $^3J_{HH}$ = 7.0 and 10.2 Hz, 1H, 5-H), 6.56 (dd br, 1H, 7-H), 6.62 (d, $^3J_{HH}$ = 6.4 Hz, 1H, 4-H), 6.67 (d, $^3J_{HH}$ = 10.1 Hz, 1H, 8-H), 6.74 (dd, $^3J_{HH}$ = 6.5 Hz and $^3J_{HH}$ = 10.7 Hz, 1H, 6-H) , 6.96−7.16 (m br, 9H, C_6H_4 and C_6H_5, both isomers), 7.71 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.7 (CH_3), 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.5 (C-8a), 86.72 (OAd), 118.1 (C-4), 126.4, 127.4, 128.0, 136.2, 136.5, 140.8 (aryl of **22a** and **22′a**), 127.0 (C-7), 128.2 (C-5), 136.9 (C-6), 137.4 (C-8), 139.9 (C-3a), 141.5 (C-2), 176.0 (C-3), 198.3 (*cis*-CO, $^1J_{WC}$ = 127.1 Hz), 207.8 (*trans*-CO, $^1J_{WC}$ = 118.7 Hz), 308.6 (W═C). Isomer **22′a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 1.97 (s, 3H, CH_3), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.04 (d, $^3J_{HH}$ = 6.1 Hz, 1H, 5-H), 6.44 (d , $^3J_{HH}$ = 10.3 Hz, 1H, 7-H), 6.54 (d br, 1H, 4-H), 6.58 (d, br, 1H, 8-H), 6.96−7.16 (m br, 9H, C_6H_4 and C_6H_5, both isomers), 7.71 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 25.4 (CH_3), 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.3 (C-8a), 86.67 (OAd), 118.9 (C-4), 125.6 (C-5), 126.4, 127.4, 128.0, 136.2, 136.5, 140.8 (aryl of **22a** and **22′a**), 130.3 (C-7), 136.2 (C-8), 139.8 (C-3a), 141.5 (C-2), 148.8 (C-6), 176.7 (C-3), 198.3 (*cis*-CO, J_{WC} = 127.0 Hz), 208.0 (*trans*-CO, J_{WC} = 118.8 Hz), 305.4 (W═C). FAB-MS: *m*/*z* (%) 692 (3) [(M)$^+$], 636 (61) [(M − 2CO)$^+$], 608 (35) [(M − 3CO)$^+$], 580 (100) [(M − 4CO)$^+$], 552 (28) [(M − 5CO)$^+$]. $C_{32}H_{28}O_6W$ (692.42).

Pentacarbonyl(3-adamantyloxy-8a-*p*-tolylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)chromium (22b) and Pentacarbonyl(3-adamantyloxy-6-methyl-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)chromium (22′b). Method D. Yield: 0.23 g (21% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2045 s, 1955 s, 1942 m, 1922 s cm^{-1}. Isomer **22b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.20 (s, 3H, CH_3), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.28 (dd, $^3J_{HH}$ = 6.6 and 10.8 Hz, 1H, 5-H), 6.40 (d, $^3J_{HH}$ = 6.2 Hz, 1H, 4-H), 6.60 ($dd_{overlapped}$, 2H, 7-H and 8-H), 6.67 (dd, $^3J_{HH}$ = 5.2 and 10.9 Hz, 1H, 6-H), 6.94−7.31 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.79 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.7 (CH_3), 31.0 (3-, 5-, 8-CH), 35.2 (4-, 9-, 10-CH_2), 40.8 (2-, 6-, 7-CH_2), 70.1 (C-8a), 86.42 (OAd), 116.7 (C-4), 126.3−128.9 and 136.1 (C_6H_5, C_6H_4, both isomers), 126.9 (C-7), 127.7 (C-5), 136.4

(C-8), 137.0 (C-6), 138.5 (C-2), 140.2 (C-3a), 172.6 (C-3), 217.4 (*cis*-CO), 228.2 (*trans*-CO), 337.2 (Cr═C). Isomer **22′b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.00 (s, 3H, CH_3), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.06 (d, $^3J_{HH}$ = 6.4 Hz, 1H, 5-H), 6.43 (d, $^3J_{HH}$ = 10.3 Hz, 1H, 4-H), 6.51 (d, $^3J_{HH}$ = 10.2 Hz, 1H, 7-H), 6.54 ($d_{overlapped}$, 1H, 8-H), 6.94−7.31 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.79 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 25.1 (CH_3), 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.0 (C-8a), 86.37 (OAd), 117.4 (C-4), 125.1 (C-5), 126.3−128.9 (C_6H_5, C_6H_4, both isomers), 130.2 (C-7), 135.3 (C-8), 138.5 (C-2), 139.3 (C-3a), 148.9 (C-6), 173.2 (C-3), 217.5 (*cis*-CO), 228.6 (*trans*-CO), 333.6 (Cr═C). FAB-MS: *m*/*z* (%) 560 (4) [(M)$^+$], 476 (14) [(M − 3CO)$^+$], 448 (27) [(M − 4CO)$^+$], 420 (100) [(M − 5CO)$^+$]. $C_{32}H_{28}O_6Cr$ (560.57).

Pentacarbonyl(3-adamantyloxy-8a-*p*-chlorophenylbicyclo-[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (23a) and Pentacarbonyl(3-adamantyloxy-6-chloro-8a-phenylbicyclo[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (23′a). Method D. Yield: 0.10 g (7% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2054 m, 1956 m, 1940 m, 1920 m cm^{-1}. Isomer **23a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.26 (dd, $^3J_{HH}$ = 6.7 and 10.8 Hz, 1H, 5-H), 6.57 (dd br, 1H, 7-H), 6.62 (d, $^3J_{HH}$ = 5.1 Hz, 1H, 4-H), 6.66 ($d_{overlapped}$, $^3J_{HH}$ = 10.6 Hz, 1H, 8-H), 6.75 (dd, $^3J_{HH}$ = 6.0 and 11.0 Hz, 1H, 6-H) , 6.96−7.31 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.71 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.4 (C-8a), 87.1 (OAd), 118.4 (C-4), 127.2 (C-7), 128.2 (C-5), 126.8 − 131.5 and 140.5 (C_6H_5, C_6H_5, both isomers), 136.9 (C-6), 137.1 (C-8), 139.1 (C-3a), 141.1 (C-2), 175.9 (C-3), 198.9 (*cis*-CO, J_{WC} = 127.4 Hz), 208.0 (*trans*-CO, J_{WC} = 118.7 Hz), 308.2 (W═C). Isomer **23′a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.39 (d, $^3J_{HH}$ = 7.2 Hz, 1H, 5-H), 6.54 (dbr , 1H, 4-H), 6.57 ($d_{overlapped}$, 1H, 7-H), 6.66 ($d_{overlapped}$, $^3J_{HH}$ = 10.6 Hz, 1H, 8-H), 6.96−7.31 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.69 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.0 (C-8a), 87.0 (OAd), 116.4 (C-4), 127.3 (C-5), 126.8 − 130.5 and 138.4 (C_6H_5,C_6H_5, both isomers), 128.5 (C-7), 136.7 (C-8), 140.4 (C-3a), 141.2 (C-6), 141.4 (C-2), 175.3 (C-3), 198.1 (*cis*-CO, J_{WC} = 127.6 Hz), 207.8 (*trans*-CO, J_{WC} = 118.8 Hz), 307.1 (W═C). FAB-MS: *m*/*z* (%) 713 (2) [(M)$^+$], 657 (12) [(M − 2CO)$^+$], 629 (32) [(M − 3CO)$^+$], 601 (100) [(M − 4CO)$^+$], 573 (27) [(M − 5CO)$^+$], $C_{31}H_{25}O_6ClW$ (712.84).

Pentacarbonyl{3-adamantyloxy-8a-*p*-chlorphenylbicyclo[5.3.0]-deca-2,3a,5,7-tetraenylidene}chromium (23b) and Pentacarbonyl{3-adamantyloxy-6-chloro-8a-phenylbicyclo[5.3.0]deca-2,-3a,5,7-tetraenylidene}chromium (23′b). Method D. Yield: 0.19 g (17% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2045 s, 1958 m, 1947 m, 1925 m cm^{-1}. Isomer **23b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.29 (dd, $^3J_{HH}$ = 6.8 and 10.8 Hz, 1H, 5-H), 6.42 ($d_{overlapped}$, 1H, 4-H), 6.58 ($dd_{overlapped}$ and $d_{overlapped}$, 2H, 7-H, 8-H), 6.70 (dd, $^3J_{HH}$ = 6.1 and 10.4 Hz, 1H, 6-H) , 6.99−7.32 (m, 4H, C_6H_5,C_6H_5, both isomers), 7.81 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 69.7 (C-8a), 86.74 (OAd), 117.0 (C-4), 126.9 (C-7), 126.8 − 132.2 and 131.5 (C_6H_5,C_6H_5, both isomers), 128.0 (C-5), 135.8 (C-8), 137.0 (C-6), 138.6 (C-2), 139.8 (C-3a), 172.4 (C-3), 217.1 (*cis*-CO), 228.9 (*trans*-CO), 336.4 (Cr═C). Isomer **23′b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.33 (d, $^1J_{HH}$ = 7.3 Hz, 1H, 4-H), 6.42 ($d_{overlapped}$, 1H, 5-H), 6.59 ($d_{overlapped}$, 1H, 7-H), 6.59 (dbr, 1H, 8-H), 6.99−7.32 (m, 5H, C_6H_5,C_6H_5, both isomers), 7.83 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.0 (C-8a), 86.70 (OAd), 115.1 (C-4), 126.8 (C-5), 126.8−132.2 (C_6H_5,C_6H_5, both isomers), 128.5 (C-7), 136.2 (C-8), 138.6 (C-2), 140.5 (C-3a), 140.7 (C-6), 171.8 (C-3), 217.3 (*cis*-CO), 228.7 (*trans*-CO), 337.7 (Cr═C). FAB-MS: *m*/*z* (%) 581 (4) [(M)$^+$], 525 (4) [(M − 2CO)$^+$], 497 (4) [(M − 3CO)$^+$], 469 (41) [(M − 4CO)$^+$], 441 (100) [(M − 5CO)$^+$]. $C_{31}H_{25}O_6ClCr$ (580.98).

Pentacarbonyl(3-adamantyloxy-6-chloro-8a-*p*-tolylbicyclo-[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (24a) and Pentacarbonyl(3-adamantyloxy-6-methyl-8a-*p*-chlorphenylbicyclo[5.3.0]-deca-2,3a,5,7-tetraenylidene)tungsten (24′a). Method D. Yield: 0.07 g (5% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2054 m, 1954 s, 1938 m, 1919 s cm^{-1}. Isomer **24a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 ($s_{overlapped}$, 3H, CH_3), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.39 (d, $^3J_{HH}$ = 7.2 Hz, 1H, 5-H), 6.53 ($d_{overlapped}$, 1H, 4-H), 6.56 (d, $^3J_{HH}$ = 8.9 Hz, 1H, 7-H), 6.65 (d, $^3J_{HH}$ = 10.5 Hz, 1H, 8-H), 6.99 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.69 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.7 (CH_3), 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.1 (C-8a), 87.0 (OAd), 116.0 (C-4), 127.2 (C-5), 127.4, 128.2, 128.5, 131.4, 136.0, 136.6 (C_6H_5,C_6H_5, both isomers), 128.4 (C-7), 137.3 (C-8), 140.5 (C-3a), 141.2 (C-6), 141.7 (C-2), 176.3 (C-3), 198.0 (*cis*-CO, J_{WC} = 127.0 Hz), 207.8 (*trans*-CO, J_{WC} = 118.7 Hz), 308.5 (W═C). Isomer **24′a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 1.95 (s, 3H, CH_3), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.04 (d, $^3J_{HH}$ = 6.8 Hz, 1H, 5-H), 6.42 (d , $^3J_{HH}$ = 10.3 Hz, 1H, 7-H), 6.54 ($d_{overlapped}$, 1H, 4-H), 6.51 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 8-H), 7.04−7.20 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.68 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 25.3 (CH_3), 31.0 (3-, 5-, and 8-CH), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, 7-CH_2), 69.6 (C-8a), 86.9 (OAd), 119.0 (C-4), 125.8 (C-5), 127.4, 128.2, 128.5, 131.4, 136.0, 136.6 (C_6H_5,C_6H_5, both isomers), 130.4 (C-7), 135.7 (C-8), 139.5 (C-3a), 141.9 (C-2), 148.8 (C-6), 176.9 (C-3), 198.3 (*cis*-CO, J_{WC} = 127.3 Hz), 208.0 (*trans*-CO, J_{WC} = 118.8 Hz), 304.2 (W═C). FAB-MS: *m*/*z* (%) 727 (10) [(M)$^+$], 671 (30) [(M − 2CO)$^+$], 615 (100) [(M − 4CO)$^+$]. $C_{32}H_{27}O_6ClW$ (726.87).

Pentacarbonyl(3-adamantyloxy-6-chloro-8a-*p*-tolylbicyclo-[5.3.0]deca-2,3a,5,7-tetraenylidene)chromium (24b) and Pentacarbonyl(3-adamantyloxy-6-methyl-8a-*p*-chlorphenylbicyclo-[5.3.0]deca-2,3a,5,7-tetraenylidene)chromium (24′b). Method D. Yield: 0.10 g (8% based on adamantyloxyacetylene). IR (petroleum ether): ν(CO) 2044 m, 1956 s, 1947 s, 1924 cm^{-1}. Isomer **24b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 6H, 4-, 9-, and 10-CH_2), 2.23 (s, 6H, 2-, 6-, and 7-CH_2), 2.24 (s, 3H, CH_3), 2.31 (s, 3H, 3-, 5-, and 8-CH), 6.30 (d, $^3J_{HH}$ = 8.5 Hz, 1H, 4-H), 6.42 (d, $^3J_{HH}$ = 7.3 Hz, 1H, 5-H), 6.57 (s br, 2H, 7-H, 8-H), 6.88−7.30 (m, 9H, C_6H_5,C_6H_5, both isomers), 7.83 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 20.7 (CH_3), 31.0 (3-, 5-, 8-CH), 35.2 (4-, 9-, 10-CH_2), 40.8 (2-, 6-, 7-CH_2), 69.7 (C-8a), 86.7 (OAd), 114.9 (C-4), 126.8 (C-5), 128.1 (C-11, C-13), 128.9 (C-10, C-14), 128.4 (C-7), 135.9 (C-9), 136.3 (C-8), 136.6 (C-12), 138.6 (C-2), 140.5 (C-3a), 140.7 (C-6), 171.8 (C-3), 217.1 (*cis*-CO), 228.9 (*trans*-CO), 338.1 (Cr═C). Isomer **24′b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.98 (CH_3), 1.71 (s, 6H, 4-, 9-, 10-CH_2), 2.23 (s, 6H, 2-, 6-, 7-CH_2), 2.31 (s, 3H, 3-, 5-, 8-CH), 6.07 (d br, 1H, 5-H), 6.33 ($d_{overlapped}$, 1H, 4-H), 6.42 ($d_{overlapped}$, 1H, 7-H), 6.46 ($d_{overlapped}$, 1H, 8-H), 6.88−7.30 (m, 4H, C_6H_5,C_6H_5, both isomers), 7.81 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 25.0 (CH_3), 31.0 (3-, 5-, 8-CH), 35.2 (4-, 9-, 10-CH_2), 40.8 (2-, 6-, 7-CH_2), 69.4 (C-8a), 86.6 (OAd), 117.7 (C-4), 125.5 (C-5), 128.1−129.1 (C_6H_5,C_6H_5, both isomers), 130.5 (C-7), 131.6 (C-12), 134.8 (C-8), 138.6 (C-2), 139.1 (C-3a), 148.9 (C-6), 173.1 (C-3), 217.5 (*cis*-CO), 228.5 (*trans*-CO), 333.2 (Cr═C). FAB-MS: *m*/*z* (%) 595 (2) [(M)$^+$], 539 (5) [(M − 2CO)$^+$],

Table 3. Crystal Data and Refinement Details for Compounds 24b and 25a

	24b	25a
formula	$C_{32}H_{27}ClCrO_6$	$C_{35}H_{34}O_6W\times CH_2Cl_2$
M_r	1189.97	819.40
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.242(2)	14.096(3)
b (Å)	11.681(2)	18.137(4)
c (Å)	11.758(2)	13.118(3)
α (deg)	88.62(3)	90
β (deg)	86.38(3)	93.17(3)
γ (deg)	81.58(3)	90
V (Å^3)	1388.6(4)	3348.6(12)
Z	2	4
ρ(calcd) (g/cm^3)	1.423	1.625
μ (mm^{-1})	0.553	3.654
F(000)	616	1632
max. 2θ (deg)	51.08	51.42
index range	$-12 \le h \le 12$	$-17 \le h \le 16$
	$-14 \le k \le 14$	$-22 \le k \le 22$
	$-14 \le l \le 14$	$-15 \le l \le 15$
no. of data	16 711	40 986
no. of unique data	5156	6297
no. of params	361	406
$R(F)$ for $I > 2\sigma(I)$	0.0481	0.0394
$wR_2(F^2)$, all data	0.0941	0.0966
goodness-of-fit on F^2	1.038	1.030
max., min. $\Delta\rho$ (e/Å^3)	0.349, −0.370	2.030, −1.749

511 (26) [(M − 3CO)$^+$], 483 (54) [(M − 4CO)$^+$], 455 (100) [(M − 5CO)$^+$]. $C_{32}H_{27}O_6ClCr$ (595.01)

Pentacarbonyl(3-adamantyloxy-8a-*p*-*tert*-butylphenylbicyclo-[5.3.0]deca-2,3a,5,7-tetraenylidene)tungsten (25a). Method D. Yield: 0.41 g (28% based on adamantyloxyacetylene). Only isomer **25a** could be detected. IR (petroleum ether): ν(CO) 2053 m, 1953 s, 1935 m, 1918 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.15 (s, 9H, CH_3), 1.69 (s, 6H, 4-, 9-, and 10-CH_2), 2.21 (s, 6H, 2-, 6-, and 7-CH_2), 2.30 (s, 3H, 3-, 5-, and 8-CH), 6.28 (dd, $^3J_{HH}$ = 6.7 and 11.0 Hz, 1H, 5-H), 6.56 (dd, $^3J_{HH}$ = 6.4 and 10.0 Hz, 1H, 7-H), 6.63 (d, $^3J_{HH}$ = 6.9 Hz, 1H, 4-H), 6.66 (d, $^3J_{HH}$ = 10.4 Hz, 1H, 8-H), 6.75 (dd, $^3J_{HH}$ = 6.3 and 11.0 Hz, 1H, 6-H), 7.14 (d, $^3J_{HH}$ = 8.2 Hz, 4H, 10-, 11-,13-, and 14-H), 7.66 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 30.6 (CH_3), 31.0 (3-, 5-, and 8-CH), 34.0 ($C(CH_3)_3$), 35.2 (4-, 9-, and 10-CH_2), 40.8 (2-, 6-, and 7-CH_2), 70.3 (C-8a), 86.7 (OAd), 118.0 (C-4), 124.2 (C-10, -11, -13, -14), 127.8 (C-7), 128.2 (C-5), 136.75 (C-9), 136.8 (C-6), 137.4 (C-8), 140.5 (C-3a), 141.5 (C-2), 149.1 (C-12), 176.0 (C-3), 198.1 (*cis*-CO, J_{WC} = 127.1 Hz), 208.1 (*trans*-CO, J_{WC} = 117.8 Hz), 308.5 (W═C). FAB-MS: *m*/*z* (%) 734 (3) [(M)$^+$], 678 (26) [(M − 2CO)$^+$], 650 (44) [(M − 3CO)$^+$], 622 (100) [(M − 4CO)$^+$], 594 (59) [(M − 5CO)$^+$]. $C_{35}H_{34}O_6W$ (734.50).

Pentacarbonyl(3-adamantyloxy-8a-*p*-*tert*-butylphenylbicyclo-[5.3.0]deca-2,3a,5,7-tetraenylidene)chromium (25b). Method D. Yield: 0.31 g (26% based on adamantyloxyacetylene). Only isomer **25b** was observed. IR (petroleum ether): ν(CO) 2044 m, 1954 s, 1942 m, 1922 s cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.15 (s, 9H, CH_3), 1.69 (s, 6H, 4-, 9-, 10-CH_2), 2.21 (s, 6H, 2-, 6-, 7-CH_2), 2.30 (s, 3H, 3-, 5-, 8-CH), 6.31 (dd, $^3J_{HH}$ = 6.4 Hz and $^3J_{HH}$ = 10.3 Hz, 1H, 5-H), 6.42 (dd, $^3J_{HH}$ = 6.0 Hz and $^3J_{HH}$ = 10.0 Hz, 1H, 4-H), 6.58 ($dd_{overlapped}$ and $d_{overlapped}$, 2H, 7-H, 8-H), 6.70 (dd, $^3J_{HH}$ = 6.0 Hz and $^3J_{HH}$ = 10.9 Hz, 1H, 6-H), 7.14 (m, 4H, 10-, 11-, 13-H, 14-H), 7.76 (s, 1H, 2-H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 30.7 (CH_3), 31.0 (3-, 5-, 8-CH), 34.0 ($C(CH_3)_3$), 35.2 (4-, 9-, 10-CH_2), 40.8 (2-, 6-, 7-CH_2), 70.1 (C-8a), 86.3 (OAd), 116.6 (C-4), 124.2 (C-10, −11, −13, −14), 126.8 (C-7), 127.8 (C-5), 136.1 (C-9), 136.5 (C-7), 136.8 (C-6), 138.0 (C-2), 139.9 (C-3a), 149.2 (C-12), 172.5 (C-3), 217.3 (*cis*-CO), 229.0 (*trans*-CO), 337.5 (Cr═C). FAB-MS: *m*/*z* (%) 603 (1) [(M)$^+$], 575 (1) [(M − CO)$^+$], 547 (3) [(M − 2CO)$^+$], 619 (15) [(M − 3CO)$^+$], 491 (31) [(M − 4CO)$^+$], 463 (100) [(M − 5CO)$^+$]. $C_{35}H_{34}O_6Cr$ (602.65)

X-ray Structure Analyses of 24b and 25a. Single crystals suitable for X-ray structure analyses were obtained from petroleum ether/CH_2Cl_2 mixtures at −30 °C. The measurements were performed at 100(2) K with a crystal mounted on a glass fiber on a STOE IPDS II diffractometer (graphite monochromator, Mo Kα radiation, λ = 0.71073 Å, scan rate 3−30° min^{-1} in ω). For crystal data and refinement details see Table 3. The structures were solved by direct methods using the SHELX-97 program package.[27] The positions of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as "riding model". All other atoms were refined anisotropically.

DFT-Calculations. All ab initio calculations were performed using Jaguar[28] (version 5.5.016) running on Linux-2.4.20-28.7smp on six Athlon MP 2400+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. Initial structures were obtained by MM+ optimization using Hyperchem.[29] Geometries were optimized using the LACVP* basis set (ECP for Cr and W, N31G6* for all other atoms) and the BP86 density functional. The second derivatives were calculated to ensure that true minima were found, by showing no large negative frequencies. All reported energies are at 298 K. Transition states were approximated by performing a geometry scan along the corresponding atom−atom distances, where new bonds were formed. The maximum energy structures from these geometry scans were used as transition state guesses for standard (simple quasi-Newton) transition state searches implemented in Jaguar. Second derivatives were used for transition state validation.

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Supporting Information Available: CIF files of the complexes **24b** and **25a**, tables giving the bond distances, bond angles, and torsion angles of **24b** and **25a**, and tables giving the Cartesian coordinates and energies (at 298 K) of the calculated structures, optimized minima, and transistion states. This material is available free of charge via the Internet at http://pubs.acs.org.

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