Organic Syntheses via Transition Metal Complexes. 86. Regioselective [$C_3 + C_2$] Cyclopentadiene Annulation to Enamines with Alkynylcarbene Complexes of Chromium and Tungsten as Novel C_3 Building Blocks

Rudolf Aumann,* Adam G. Meyer, and Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster, Orléans-Ring 23, D-48149 Münster, Germany

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Alkynylcarbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (**10**) (M = Cr, W) react with tertiary 1-aminocycloalkenes $\overline{CH{=}C(NR_2)CH_2}$ **17**−**23** (cyclopentenes, -hexenes, and -heptenes, dihydronaphthalenes and -phenanthrenes; $NR_2 = NMe_2$, pyrrolidino, and morpholino) to afford cyclopentadiene annulation products **24**−**30** in an overall [3 + 2] cycloaddition process. The reaction is highly regioselective and proceeds under very mild conditions in 60−99% yields. 1-Metalla-1,3,6-heptatrienes $(CO)_5M{=}C(OEt)CH{=}C(Ph){-}\overline{CHC(NR_2){=}CH}$ (**G**) and 1-metalla-1,3,5-hexatrienes $(CO)_5M{=}C(OEt)CH{=}C(Ph){-}\overline{C{=}C(NR_2)CH_2}$ (**H**) are formed as key intermediates. Compounds **H** cyclize to give cyclopentadiene complexes as precursors to the cyclopentadienes **24**−**30**. Hydrolysis of 1-metalla-1,3,6-heptatrienes **G** leads to the production of pyran-2-ylidene complexes, e.g., **32a**,**b**.

Due to the importance of five-membered carbocycles as part of biologically relevant compounds, e.g., steroids and prostaglandins, methods for their preparation remain an area of continuous attention in organic chemistry. Typically, five-membered carbocycles are constructed by condensation or rearrangement of an acyclic precursor or by ring contraction.[2] Among organometallic methods, the cocyclization of alkynes with alkenes and carbon monoxide in a [$C_2 + C_2 + C_1$] process by cobalt to form cyclopentenones (known as the Pauson−Khand reaction) has received widespread application.[3] However, there are few examples only of simple [$C_3 + C_2$] cycloadditions for the generation of five-membered carbocycles as a synthetic counterpart to the Diels−Alder [$C_4 + C_2$] cycloaddition reaction. This is mainly due to considerable difficulties in creating the odd-numbered carbon unit.[4,5]

The utility of Fischer carbene complexes to yield a rich source of novel and synthetically valuable reactions has become established.[6] In the past 10 years, α,β-unsaturated carbene complexes (= 1-metalla-1,3-butadienes)[7] of chromium have gained critical acceptance as efficient tools for ring annulation reactions, which have greatly simplified the ability to assemble a variety of cyclic and polycyclic structures from acyclic precursors.[8] A most widely utilized method is the [$C_3 + C_2 + C_1$] benzannulation of α,β-unsaturated carbene complexes of chromium with alkynes by concomitant carbonyl insertion (known as the Dötz reaction).[6,8,9] Although

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(5) For reviews see: (a) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 109−128. (b) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 899−970.

(6) For reviews on the chemistry of Fischer carbene complexes see: (a) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573−594; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587−608. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Chemistry*; Verlag Chemie: Deerfield Beach, FL, 1984. (c) Wulff, W. D. In *Advances in Metal−Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1989; Vol. 1, pp 209−393. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 1065−1113. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II;* Abel, A. W., Stone, F. G. A., Wikinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 469−547. (f) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II* Abel, A. W., Stone, F. G. A., Wikinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, pp 549−576.

(7) The terms 1-metalla-1,3-diene and also 1-metalla-1,3,5-hexatriene, in place of vinylcarbene and butadien-1-ylcarbene complex, respectively, have been suggested (see: Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537−540) to allow for a simple systematic nomenclature of alkenylcarbene complexes with differing substitution patterns and stereochemistry. It is widely accepted in terms of simplicity of use.

(8) For example see: (a) Dötz, K. H. In *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field*; de Meijere, A., tom Dieck, H., Eds; Springer: Berlin, 1988; pp 85−104. (b) Dötz, K. H.; Popall, M. *Chem. Ber.* **1988**, *121*, 665−672. (d) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433−445. (e) Wulff, W. D.; Bauda, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642−3659. (f) Hegedus, L. S. *Pure Appl. Chem.* **1990**, *62*, 691−698. (g) Aumann, R. *Angew. Chem.* **1988**, *100*, 1512−1524; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456−1467.

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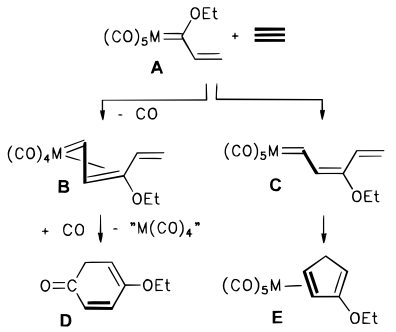
Scheme 1. Insertion of Alkynes into the M=C Bond of a 1-Metalla-1,3-diene A with and without Prior Loss of Carbon Monoxide



this reaction is usually considered to yield six-membered 1,4-dioxyaryl compounds, a number of cases are reported where five-membered-ring carbocycles are produced by insertion of carbon monoxide[10] (e.g., cyclopentenones,[11] cyclopentadienones,[12] and cyclopentendiones[13]) or without insertion of carbon monoxide[14] (e.g., indene derivatives,[7,15,16] cyclopentenes,[17] cyclopentylidenes,[18] cyclopenta[*b*]pyranes,[19] and coordinated fulvenes[20]).

Addition of alkynes to 1-metalla-1,3-dienes **A** may proceed in two different fashions (Scheme 1). It is generally assumed that Dötz-type reactions are initiated by the exchange of a *cis* carbon monoxide ligand of **A** for an alkyne followed by regioselective insertion of the alkyne into the M=C bond to produce a cyclic 3,4-η^2-1-metalla-1,3,5-hexatriene **B**.[8,21] The latter compound may either subsequently undergo an insertion of carbon monoxide into the M=C bond to give products of type **D** or form cyclization products without insertion of carbon monoxide. The ultimate product distribution of the reaction depends upon both the nature of substituents on each of the reaction partners and the conditions under which the reaction is conducted. Although 1-metalla-1,3,5-hexatrienes **B** have long been postulated as intermediates in these processes,[22] to date, few examples have been experimentally observed.[23] A second type of alkyne insertion into the M=C bond of compound **A** is observed with electron-rich alkynes, e.g., 1-aminoalkynes. It seems to occur without prior loss of a *cis* carbon monoxide ligand by a nucleophilic addition of the alkyne to the carbene carbon atom and thus does not afford a chelated 1-metalla-1,3,5-hexatriene of type **B** but leads to formation of an open chain 1-metalla-1,3,5-hexatriene of type **C** (= butadien-1-ylcarbene complex).[24] Moreover, in contrast to tetracarbonyl-metallatriene complexes **B**, pentacarbonyl-1-metalla-1,3,5-trienes of type **C** have been isolated in crystalline form and have been characterized crystallographically. The most prominent feature of compounds **C** is that they do not undergo an insertion of carbon monoxide but readily cyclize to give cyclopentadiene complexes **E** (Scheme 1).[25]

The latter process is illustrated by the regioselective insertion of the alkyne $Et_2NC{\equiv}CMe$ (**2**) into the M=C bond of metalladiene **1** to give 1-tungsta-1,3,5-hexatriene **3**, which has been characterized by X-ray structural analysis.[24] This compound subsequently undergoes a smooth ring closure under very mild conditions ($t_{1/2}$ = 14 h, 20 °C), without loss of carbon monoxide, to give the novel type of zwitterionic η^1-cyclopentadiene complex **4** whose structure has also been elucidated by X-ray analysis.[25] The cyclopentadiene **5** is finally obtained by a thermally induced disengagement of the metal unit from complex **4** (Scheme 2).

Interestingly, a variety of other reactions involving the formation of the cyclopentadiene moiety from pentacarbonyl α,β-unsaturated carbene complexes and alkynes have been reported recently.[26] These processes, the

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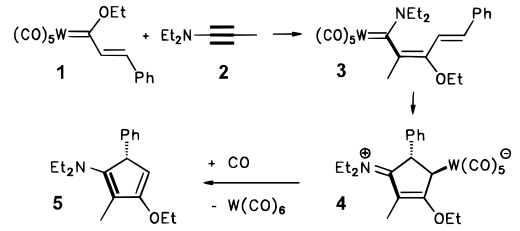
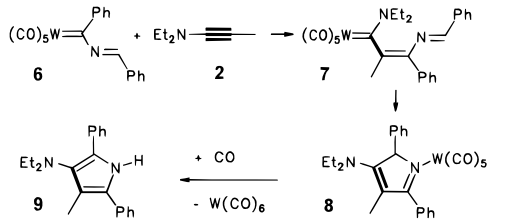
Scheme 2. Cyclopentadiene Formation by Cyclization of a 1-Tungsta-1,3,5-hexatriene 3



Scheme 3. Pyrrole Formation by Cyclization of a 3-Aza-1-metalla-1,3,5-hexatriene 7



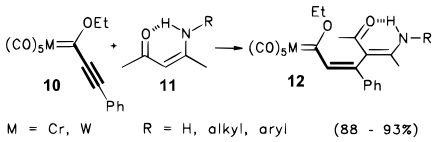
"alkyne routes" to cyclopentadienes, are based upon the annulation of a C_3 unit of a metalladiene complex to a C_2 unit of an alkyne, and 1-metalla-1,3,5-hexatrienes, formed by insertion of the alkyne into the M=C bond, may conceptually be assumed as key intermediates, though experimental evidence has not been presented in these cases.

A 1-metalla-1,3,5-hexatriene/cyclopentadiene ring closure has been found to occur also with aza heterometallatrienes. It was shown that, e.g., addition of the alkyne **2** to the 3-aza-1-tungsta-1,3-diene **6** leads to production of a (crystalline) 5-aza-1-tungsta-1,3,7-hexatriene **7**,[27] which in solution cyclizes smoothly to a (crystalline) 2*H*-pyrrole complex **8**[28] from which a pyrrole **9** is finally obtained (Scheme 3).[29−31]

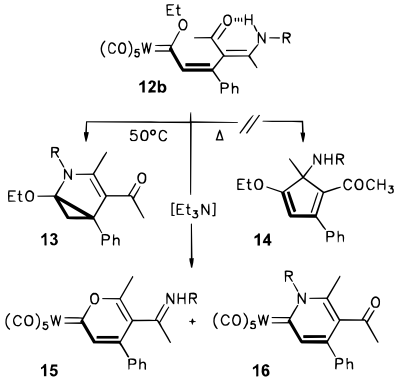
While we were studying the scope of reactions of 1-metalla-1,3,5-hexatrienes, a novel entry into the formation of these compounds was found. Other than by addition of alkynes to alk*enyl*carbene complexes (Scheme 1 and 2), such compounds became available in our hands also by addition of (electron-rich) alkenes to alk*ynyl*carbene complexes, for example, by the Michael-type addition of open chain secondary (*NH*)-enamin-3-ones **11** to alkynylcarbene complexes **10** (M = Cr, W) to generate open-chain-conjugated metallatrienes **12** (Scheme 4).[32] Other than reactions of enamines with alkenylcarbene or phenylcarbene complexes,[33] studies on reactions of enamines with alkynylcarbene complexes had not been previously reported.

1-Metalla-1,3,5-hexatrienes **12** generated from secondary enamines have been utilized in a variety of

Scheme 4. Generation of 1-Metalla-1,3,5-hexatrienes by the Enamine Route



Scheme 5. Cyclization Products from 1-Metalla-1,3,5-hexatrienes 12



reactions. For instance, they can be readily cyclized under the influence of a base as catalyst to give pyran-2-ylidene **15** and 1,2-dihydropyridin-2-ylidene **16** complexes,[32] but when heated in absence of a base they quite unprecedently formed 2,3-homopyrroles **13** in high yields[32b] (Scheme 5). Conceivably, formation of a cyclopentadiene **14** in an analogous manner to that depicted in Scheme 2 may have occurred but ultimately was not observed due to the mobility of the hydrogen atom attached to the nitrogen atom in compound **12** and the probably diminished double bond character in the distal C=C(N) π-bond due to (vinylogous amide) resonance of the enaminone part of this molecule.

However, and contrastingly, when open-chain tertiary enamin-3-ones,[34] or simple open-chain tertiary enamines,[35] were reacted with alkynylcarbene complexes **10**, cross-conjugated metallatrienes (= butadien-2-ylcarbene complexes) resulting from a formal metathesis reaction of the C=C(N) bond at the C≡C bond were isolated instead of (conjugated) 1-metalla-1,3,5-hexatrienes needed as precursor to the formation of a cyclopentadiene ring. This type of reaction is assumed to proceed *via* the formation of a cyclobutene ring by [2 + 2] cycloaddition, as has been previously reported for reactions of open-chain enol ethers with compounds **1**.[36] The relative rates of the competing reactions leading to formation of conjugated and cross-conjugated metallatrienes, respectively, on addition of enamines or enaminones to alkynylcarbene complexes **1**, seem to be strongly influenced by the orientation of the C=N$^+$ iminium bond,

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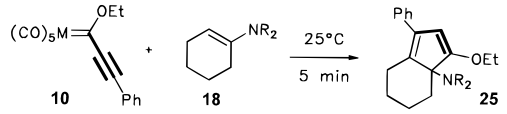
(36) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727−8729.

Scheme 6. Regioselective [$C_3 + C_2$] Cyclopentadiene Annulation to Tertiary 1-Aminocycloalkenes, e.g., 18, with Alkynylcarbene Complexes 10



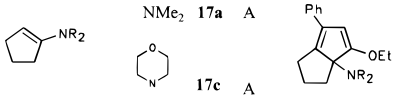
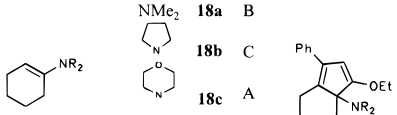
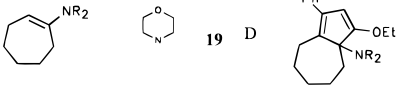
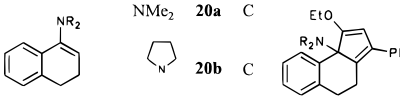
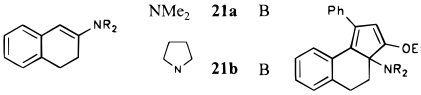
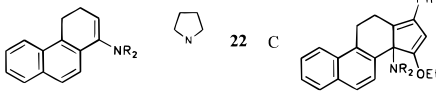
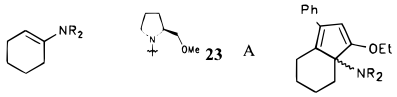
syn or *anti*, relative to the central carbon atom of the allene unit in the zwitterionic allene intermediate (a *syn* type species of which is represented by intermediate **F** in Scheme 8), generated in the initial reaction step (*vide infra*). Since a *syn* arrangement of the C=N$^+$ bond, as it is achieved in an intermediate **F** under the influence of the ring tether, is expected to be less favorable for generation of a transition state geometry leading to a cyclobutene ring (which is considered to be a prerequisite for formation of a cross-conjugated metallatriene) than an *anti* arrangement of the C=N$^+$ bond would be, the *syn* configuration depicted for intermediate **F** should favor a reaction path leading to generation of a conjugated 1-metalla-1,3,5-triene.

Cyclopentadiene Annulation to Cyclic Tertiary 1-Aminocycloalkenes

A logical progression of our studies toward the formation of cyclopentadiene rings involved reacting alkynylcarbene complexes **10** with tertiary 1-aminocycloalkenes. This was expected to produce 1-metalla-1,3,5-hexatrienes (analogous to compounds **12**, Scheme 4) that would conceivably lead to cyclopentadienes in an overall [$C_3 + C_2$] annulation of carbon templates.[37] The annulation was found to proceed readily with a variety of cyclic five-, six-, and seven-membered ring tertiary enamines **17**−**23**.[38] The resultant cyclopentadiene products **24**−**30** were shown to be produced in good yields, most often at ambient temperature, and in an entirely regiospecific manner (Scheme 6). Bicyclic ring systems reported herein are widely found as skeletons in a diverse array of natural products. For example, the type [3.3.0] is present as diquinanes[3a] and the type [5.3.0] as hexahydroazulenes.

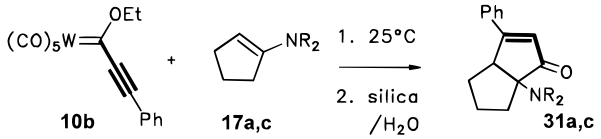
It should be noted that this annulation reaction, the "enamine route" to cyclopentadienes, stands alone as the first to be described where the C_3 unit is derived from an alk*yn*ylcarbene complex and the C_2 unit from an (electron-rich) alk*ene* (*i.e.*, it can be considered to be an annulation such that each carbon template is related in a converse sense to the assembly of templates in the "alkyne route" to cyclopentadienes, shown in Scheme 2, in which case a cyclopentadiene ring is formed from an alk*en*ylcarbene ligand and an alk*yne*). The high regiospecificity of this reaction combined with the ready availability of both the enamines and the alkynylcarbene complexes[39] serves to further enhance the nature and attractiveness of this template-assembling process.

Table 1. Reaction Conditions and Yields of the Cyclopentadiene Annulation[a]

entry	enamine	NR_2		cdt[a]	cyclopentadiene annulation product		yield [%][b] M=W	Cr
1a		NMe_2	**17a**	A		**24a**	73[c]	-
1b			**17c**	A		**24b**	67[c]	-
2a		NMe_2	**18a**	B		**25a**	94	77
2b			**18b**	C		**25b**	72	87
2c			**18c**	A		**25c**	82	-
2d		$N(CH_2Ph)_2$	**18d**	C		**25d**	95	-
3			**19**	D		**26**	76	-
4a		NMe_2	**20a**	C		**27a**	80	-
4b			**20b**	C		**27b**	99	94
5a		NMe_2	**21a**	B		**28a**	76	56
5b			**21b**	B		**28b**	61	75
6			**22**	C		**29**	60	65
7			**23**	A		**30**	85	-

[a] Conditions: (A) To a CH_2Cl_2 solution of complexes **10**, in a screw-top vial, was added 1.0 equiv of the enamine, and the reaction shaken briefly and allowed to stand at 25 °C for 15 h. (B) As for A except at 25 °C for 5 min. (C) As for A except warmed at 50 °C for 1 h. (D) As for A except at 25 °C for 30 min. These reactions were also performed in diethyl ether and found to proceed in the same manner as that reported for CH_2Cl_2, although generally the isolated yields were marginally lower. [b] Isolated after chromatography on silica gel. [c] Isolated as cyclopentenones **31a**,**b** after chromatography on silica gel.

Scheme 7. Reaction of 1-Aminocyclopentenes 17a,c with Alkynylcarbene Complex 10b



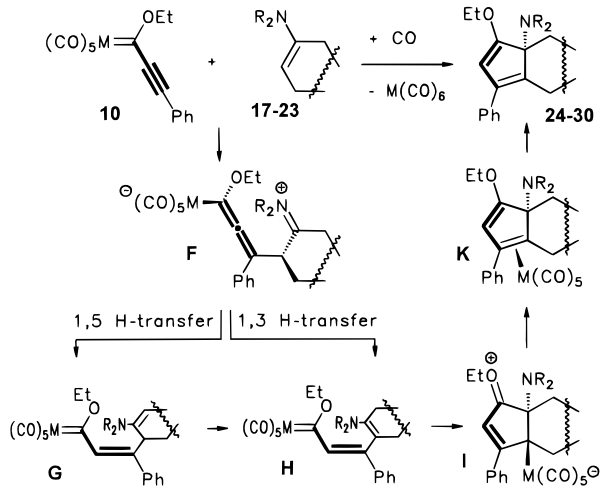
The cyclopentadienes derived from the annulation reaction to five-membered ring tertiary enamines **17a,c** (entries 1a,b, Table 1), although readily observable by ^{1}H NMR spectra in the original reaction mixture, could not be isolated by chromatography on silica gel. Due to the lability of the enol ether unit on silica in the presence of water, cyclopentenones **31a** and **31c** were obtained instead (Scheme 7). Furthermore, and suprisingly, reaction of the analogous five-membered pyrrolidine enamine **17b** in our hands resulted only in an intractable mixture of products. Only *ca*. 5% of 4-pyr-

(37) It should be pointed out that this type of reaction is in marked contrast to the reaction of simple propargylic esters (instead of alkynylcarbene complexes) with similar cyclic enamines where seven-membered ring products, resulting from [2 + 2] cycloaddition followed by ring opening, are isolated: (a) Berchtold, G. A.; Uhlig, G. F. *J. Org. Chem.* **1963**, *28*, 1459−1462. (b) Huebner, C. F.; Dorfman, L.; Robison, M. M.; Donoghue, E.; Pierson, W. G.; Strachan, P. *Ibid.* **1963**, *28*, 3134−3140. (c) Brannock, K. C.; Burpitt, R. D.; Goodlett, V. W.; Thweatt, J. G. *Ibid.* **1964**, *29*, 818−823. A further example, which ultimately gives pyridones, is: Pettit, G. R.; Fleming, W. C.; Paull, K. D. *J. Org. Chem.* **1968**, *33*, 1089−1092.

(38) Meyer, A. G.; Aumann, R. *Synlett* **1995**, 1011−1013.

(39) (a) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47-C51. (b) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421−427.

Scheme 8. Intermediates in the Cyclopentadiene Annulation



rolidino-1-pentacarbonyltungsta-1,3-diene was isolated that presumably resulted from the partial decomposition of the enamine substrate to the parent amine and its subsequent Michael addition to the alkynylcarbene complex.[40] This was despite the reaction visually proceeding in a similar manner to that which occurred for the other two cases (i.e., immediate color change from brown to red/maroon upon reaction of enamine **17b** with the alkynylcarbene complex **10b** followed by precipitation of $W(CO)_6$ within 30 min).

Mechanistic Considerations

A logical reaction pathway is shown in Scheme 8. The reaction is initiated by a Michael-type addition of the nucleophilic tertiary cycloalkenylamine to the electrophilic alkynylcarbene complex **10** resulting in the formation of a zwitterionic allene-type intermediate **F**.[41] This would subsequently undergo a base-catalyzed intramolecular hydrogen transfer to give a 1-metalla-1,3,6-hexatriene **G** (kinetically favored path) or yield a 1-metalla-1,3,5-hexatriene **H** (thermodynamically favored path). The (*Z*)-configuration of species **H** is a geometric prerequisite for its cyclization to a cyclopentadiene. Considering the mild reaction conditions, it is assumed that the cyclization of a 1-metalla-1,3,5-hexatriene does not involve an intermediate loss of carbon monoxide. Thus, perhaps an intermediate such as **I** (structurally analogous to the structurally fully characterized compound **4**, Scheme 2) could be formed and undergo a rapid decomplexation *via* an intermediate **K** to give the cyclopentadiene product. Importantly, all of the steps depicted in Scheme 8 are based upon structures of species analogous to previously isolated and fully characterized compounds (**F**,[41] **H**,[24,32b] **I**[25]) or they were observed directly. Experimental proof for the intermediacy of a metallatriene **H** in this process was obtained from low-temperature (238 K) ^{1}H NMR measurements. For example, when enamine **21b** was reacted with alkynylcarbene complex **10b** in $CDCl_3$, a singlet at δ 8.19 (3-H) in the ^{1}H and a signal at δ 290.1 (W=*C*) in the ^{13}C NMR spectrum were observed, which we assign to a metallatriene of type **H**, on the basis of similar shifts observed for previously isolated and fully characterized species such as (3*Z*)-5-acetyl-2-ethoxy-4-phenyl-6-(*p*-tolylamino)-1-pentacarbonyltungsta-1,3,5-heptatriene (**12**) (3-H δ 8.02, W=*C* 306.2).[32b] When the sample was allowed to warm to 20 °C, while undergoing measurement, a smooth conversion of the intermediate **H** to the cyclopentadiene **28b** was noted.

We were intrigued to find that during the course of several of the annulation reactions, particularly of six-membered-ring enamines (entries 2a,c,d, Table 1), formation of a transient organometallic species was observed in the ^{1}H and ^{13}C NMR spectra. These species could be induced to disappear with extended reaction times at 20 °C or with mild heating for short periods (*ca.* 1 h at 50 °C). For example, when enamine **18d** was reacted with alkynylcarbene complex **10a** at 0 °C and the reaction followed by ^{1}H NMR spectra, a complex that can reasonably be ascribed the structure of a nonconjugated 1-metalla-1,3,6-heptatriene **G** was observed. Such a complex was readily characterized by a clearly resolved triplet of the *H*C=C(N) proton 7-H (δ 4.95, ^3J = 3.8 Hz) in the ^{1}H NMR spectrum. Evidence for this structure was also gained from the ^{13}C NMR spectrum (W=*C*: δ 313.3, C3: 147.9, C7: 103.7, C5: 44.2).[42] Presumably, complex **G** arises *via* a 1,5 H-transfer from the secondary carbon of the allene intermediate **F**,[43] a process that should be kinetically favored over a 1,3 H-transfer from the tertiary carbon to give 1,3,5-metallatriene **H**. It should be noted that similar types of nonconjugated 1-metalla-1,3,6-trienes have been previously reported to be formed in the reaction of alkynylcarbene complexes **10** with enol ethers. However, in such cases the isomers reported were assigned the (*E*) configuration.[44] From our results that under mild conditions all of 1-metalla-1,3,6-hexatriene **G** is converted to a cyclopentadiene, we conclude that this complex must exist in the (*Z*) configuration (as has been demonstrated by X-ray structure analyses to be the case with conjugated metallatrienes, e.g., compound **12**). Two different reaction paths could be operating in tandem with both a conjugated (**H**) and a nonconjugated (**G**) metallatriene species being formed from intermediate **F**. It seems that, once formed, conjugated 1,3,5-metallatriene **H** reacts rapidly to produce a cyclopentadiene, whereas the nonconjugated 1,3,6-heptatriene species **G** must first be converted by a (catalyzed) 1,3 hydrogen transfer to the more stable conjugated metallatriene isomer.

As an alternative to the reaction course depicted above, it might be postulated that the reaction may involve 1-metalla-1,3,5-hexatriene **H** undergoing loss of

(40) (a) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57−64. (b) Deutsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051−2065. (c) Stein, F.; Deutsch, M.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556−2564. See also ref 39b.

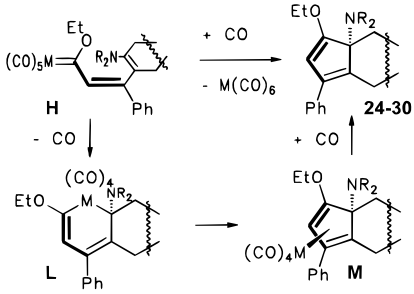
(41) Structural evidence for the intermediacy of allene-type complexes arises from the isolation of zwitterionic phosphonium allenide complexes from the Michael-type addition of tertiary phosphanes to alkynylcarbene complexes **10**, which were characterized crystallographically: Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 2475−2482.

(42) Cf. ^{13}C NMR: δ 306.9 (W=C), 144.7 (CH, C3), 140.2 (Cq, C5), 17.8 (NCH_3) for pentacarbonyl[(3*Z*)-5-acetyl-2-ethoxy-4-phenyl-6-(*p*-tolylamino)-3,5-hexadienylidene]tungsten in ref 32b.

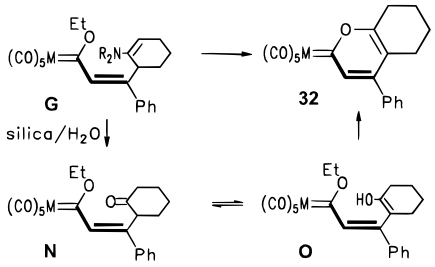
(43) In general, these types of processes have been termed ene reactions; however, the belief that these metallatrienes are generated *via* allenylidene complexes renders this terminology somewhat misleading.

(44) (a) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419−6420. (b) Camps, F.; Jordi, L.; Moreto, J. M.; Ricart, S.; Castano, A. M.; Echavarren, A. M. *J. Organomet. Chem.* **1992**, *436*, 189−198.

Scheme 9. Consideration of a Different Reaction Course



Scheme 10. Pyran-2-ylidene Complexes 32a,b from Hydrolysis of 1-Metalla-1,3,6-heptatriene G



carbon monoxide to give a 16-electron metallacyclohexadiene **L** (Scheme 9).[26d] This intermediate may then isomerize to give the 18-electron η^4-bound cyclopentadiene complex **M**. However, this pathway rests uneasily with the fact that the cyclopentadiene annulations reported herein generally take place under very mild conditions (20 °C) and Dötz-type processes normally proceed at elevated temperatures (*ca.* 80 °C) in order to promote the rate-limiting loss of the *cis* carbon monoxide ligand.[22a]

Pyran-2-ylidene Complexes 32 from 1-Metalla-1,3,6-heptatrienes

As indicated in Scheme 5, pyran-2-ylidene complexes **15** are formed from the reaction of (*NH*)-enamin-3-ones with alkynylcarbene complexes **10** *via* 1-metalla-1,3,5-trienes.[32,45] This methodology has been applied to our present studies to give experimental proof of the intermediacy of 1-metalla-1,3,6-heptatrienes **G** in the cyclopentadiene annulation reaction. Due to the slightly enhanced stability of **G** generated from a reaction of 1-cyclohex-1-enylmorpholine enamine **18c** (entry 2c, Table 1) with the alkynylcarbenetungsten complex **10b**, intermediate **G**, as evidenced by the characteristic *H*C═C(N) vinyl triplet signal in the ^{1}H NMR spectrum (*vide supra*), could be hydrolyzed if the reaction mixture after 5 min at 25 °C was subjected to rapid flash chromatography on silica gel. In addition to the expected cyclopentadiene derivative **25c**, a nonpolar red oil was then collected from the eluting column, which was subsequently identified as pyranylidene complex **32b**. This complex could also be obtained (albeit only in *ca.* 40% yield) by addition of water to the reaction mixture of **10b** and **18c** after 5 min at 25 °C. Complex **32b** quite obviously arises from hydrolysis of the enamine functionality of the 1-metalla-1,3,6-heptatriene **G**

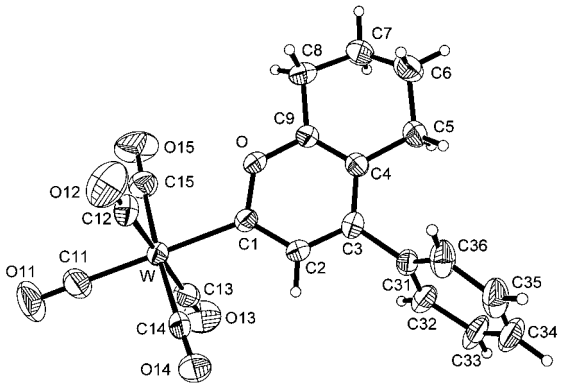


Figure 1. Molecular structure of **32b**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 32b

W−C(1)	2.190(6)	C(4)−C(5)	1.515(9)
C(1)−O	1.364(7)	C(5)−C(6)	1.520(10)
C(1)−C(2)	1.407(9)	C(6)−C(7)	1.502(12)
C(2)−C(3)	1.373(9)	C(7)−C(8)	1.519(11)
C(3)−C(4)	1.416(8)	C(8)−C(9)	1.509(9)
C(3)−C(31)	1.499(8)	C(9)−O	1.360(7)
C(4)−C(9)	1.343(9)		
O−C(1)−C(2)	112.8(5)	C(3)−C(4)−C(5)	122.3(6)
O−C(1)−W	118.1(4)	C(4)−C(5)−C(6)	111.9(6)
C(2)−C(1)−W	129.1(5)	C(7)−C(6)−C(5)	110.5(7)
C(3)−C(2)−C(1)	124.3(6)	C(6)−C(7)−C(8)	110.4(7)
C(2)−C(3)−C(4)	118.8(6)	C(9)−C(8)−C(7)	109.5(6)
C(2)−C(3)−C(31)	119.8(6)	C(4)−C(9)−O	121.9(6)
C(4)−C(3)−C(31)	121.3(5)	C(4)−C(9)−C(8)	125.6(6)
C(9)−C(4)−C(3)	117.3(6)	O−C(9)−C(8)	112.5(6)
C(9)−C(4)−C(5)	120.4(6)	C(9)−O−C(1)	124.9(5)

to give ketone **N**. Subsequent cyclization of **N** *via* the enol **O** by elimination of ethanol then yields complex **32b**. Furthermore, the reaction of 1-cyclohex-1-enyldimethylamine (**18a**) with alkynylcarbenechromium complex **10a** and similar subsequent rapid chromatography affords pyran-2-ylidene complex **32a** (Scheme 10). The structure of both pyran-2-ylidene complexes was confirmed by spectral and X-ray crystallographic data. What can be inferred from this observation is that since the intermediate metallatrienes can be trapped as pyran-2-ylidene complexes **32**, the argument that the process of cyclopentadiene formation proceeds through metallatriene species is strengthened.[46]

Complex **32b** (Figure 1) is considered to be a resonance hybrid between a pyranylidene and a pyrylium ylide. The pyrylium character is indicated by the pattern of (essentially) nonalternating bond distances between the ring atoms [C(1)−O 1.364(7) Å, C(1)−C(2) 1.407(9) Å, C(2)−C(3), 1.373(9) Å, C(3)−C(4) 1.416(8) Å, C(4)−C(9) 1.343(9) Å, C(9)−O 1.360(7) Å] found by X-ray structural analysis (Figure 1, Tables 2 and 3), which is closely related to that found for pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten.[45b] Furthermore, the distance W−C1 2.190(6) Å is significantly longer than the distance W═C 205 pm in, e.g., $(CO)_5$W═C(OMe)Ph.[47]

(45) (a) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550−4552. (b) Aumann, R.; Roths, K.; Jasper, B., Fröhlich, R. *Organometallics* **1996**, *15*, 1257−1264 and literature cited therein.

(46) Pyran-2-ylidene complexes **32** cannot be derived from decomposition of the enamine substrate because the parent amine would react much faster with the alkynylcarbene complex than the enamine: see ref 40. Furthermore, the base-catalyzed Michael-type addition of cyclohexanone to the alkynylcarbene complex has been found not to occur under these conditions.

(47) Mills, O. S.; Redhouse, A. D. *Angew. Chem.* **1965**, *77*,1142; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*,1082.

Table 3. Crystal Data and Structure Refinement Details for 32b

emp. formula	$C_{20}H_{14}O_6W$
formula w	534.16
T (K)	223(2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space grp	$C2/c$ (No. 15)
a (Å)	25.671(3)
b (Å)	9.322(1)
c (Å)	17.129(2)
β (deg)	113.17(3)
vol (Å^3)	3768.4(7)
Z	8
absorptn coeff (mm^{-1})	6.164
absorptn corr.	empirical ($0.551 < T < 0.999$)
cryst size (mm)	$0.4 \times 0.3 \times 0.1$
diffractometer	Enraf-Nonius MACH 3
θ-range (deg)	2.35−26.30
collected reflns	3965
unique reflns	3828
reflns with $I \geq 2\sigma(I)$	3060
refined param	244
R1 (all/obsd)	0.064/0.042
wR2 (all/obsd)	0.144/0.111
GoF	1.035
programs used	MolEN, SHELXS-86, SHELXL-93, XP

Further indication of the pyrylium character of **32b** is based upon the strong deshielding of NMR signals of C9 (δ 176.1) and 2-H (δ 7.89) and a significant upfield shift of C1 (δ 251.4) compared to the carbene carbon atom of $(CO)_5W{=}C(OEt)Ph$ (δ 319.6).[48]

Experimental Section

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. In particular, dichloromethane was dried and distilled from P_2O_5 and stored over 4 Å molecular sieves. Hexane (bp 70 °C) was distilled and stored over sodium wire prior to use. Pentane refers to that fraction boiling between 40 and 60 °C. All ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker ARX 300 instrument in $CDCl_3$, unless otherwise indicated, and all chemical shift values refer to $\delta_{TMS} = 0.00$. ^{13}C NMR multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements. NOE, DR spin decoupling, and low-temperature ^{1}H NMR measurements were carried out on a Bruker AM 360 instrument. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. GC/IR spectra were recorded on a Shimadzu gas chromatograph GC-14A coupled to a Biorad digilab division GC/C32. GC analyses were conducted on a Shimadzu GC-14A. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kieselgel 60$_{F240}$, were viewed by UV light (254 nm) and stained by a 5% aqueous acidic ammonium molybdate solution. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100. Parent ketones of all enamines synthesized and enamines **17b**, **18b**,**c**, **19**, and **21b** were obtained commercially and used without purification. Enamines **17a** and **18a**,[49] **18d**,[50] **20b**, **22,** and **23**[51] were synthesized according to literature procedures. The parent ketone of enamine **22** was generated using a modified Haworth synthesis.[52]

Preparation of Enamines 20a and 21a. To a dry 250 ml two-necked flask, fitted with a reflux condenser and magnetic stirrer and containing hexane (100 ml), was added dimethylammonium dimethylcarbamate (68.4 mmol) and cooled to 0 °C with an ice bath. Titanium tetrachloride (1.0 M solution in dichloromethane) (17.8 mmol) was then added dropwise over 10 min. Once the addition was complete, α- or β-tetralone (13.7 mmol) was added in one portion to the dark red solution, and the reaction was heated to reflux for 10 h. After being cooled to 20 °C, the reaction was filtered through a sintered glass filter of porosity 3 and then a filter of porosity 4. The solvent was removed under reduced pressure and the crude material purified by short-path distillation.

General Procedure for the Synthesis of Cyclopentadienes from Tertiary 1-Aminocycloalkenes and Alkynylcarbene Complexes 10. To a (carefully) dried dichloromethane solution (0.5 mL) of pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten or -chromium (**10**) (241 and 192 mg, respectively, 0.50 mmol) in a 1-mL screwtop vessel was added a solution of cyclic tertiary enamine (0.50 mmol) in 0.5 mL of dichloromethane with efficient stirring at 20 °C. The brown solution was stirred (or indeed shaken) until a dark (homogeneous) solution (often red/magenta in color for five- and black for six-membered ring enamine substrates) was obtained (after 3−5 min). After the solution was allowed to stand for varying periods of time (5 min to 15 h) at 25 °C (or gentle warming for short periods, *ca*. 1 h at 50 °C), subsequent TLC analysis revealed the total consumption of **10**. A precipitation of $W(CO)_6$ and $Cr(CO)_6$, respectively, which indicated that the reaction was complete, was removed by centrifugation. After a small sample was taken for NMR analysis, solvent was removed (10^{-3} kPa, 20 °C), and the residue was separated by column chromatography on silica gel (column 15 × 2 cm) by elution, first with pentane, then with pentane/dichloromethane (3:1 to 1:1), and finally with dichloromethane to first afford colorless $W(CO)_6$ and then $Cr(CO)_6$, respectively, and minor amounts of colored products, which were discarded. The cyclopentadiene products were then eluted with pentane/diethyl ether (9:1) and generally obtained as pale yellow oils. Higher purity products were obtained by further chromatography of these oils with pentane/ethyl acetate (9:1). For the cyclopentadiene products **28a** and **28b**, further purification was achieved by recrystallization.

(4-Ethoxy-6-phenyl-2,3-dihydro-1*H*-pentalen-3a-yl) dimethylamine (24a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclopent-1-enyl)dimethylamine (**17a**) (51 mg, 0.50 mmol) for 15 h at 25 °C. Solvent was removed, and the crude reaction mixture was characterized spectroscopically. ^{1}H NMR (C_6D_6): δ 7.26, 7.09, and 7.00 (2:1:2 H, m each, Ph), 5.11 (1 H, s, 5-H), 3.45 (1 H each, m each, diastereotopic 4-OCH_2); 2.48, 2.12, 1.99, 1.78, and 1.03 (2:1:1:1:1 H, m each, 1-H_2−3-H_2), 2.40 [6 H, s, $N(CH_3)_2$], 0.98 (3 H, t, $^3J = 7.2$ Hz, CH_3). ^{13}C NMR (C_6D_6): δ 169.0 (Cq, C4); 143.5, 136.8, and 134.7 (Cq each, C6, C6a, and *i*-C, Ph); 128.5, 127.4, and 126.9 (2:2:1, CH each, Ph), 98.2 (CH, C5), 80.8 (Cq, C3a), 64.9 (CH_2, OCH_2), 39.4 [$N(CH_3)_2$]; 30.5, 29.7, and 23.2 (CH_2 each, C1−C3), 14.9 (CH_3).

4-(4-Ethoxy-6-phenyl-2,3-dihydro-1*H*-pentalen-3a-yl)-morpholine (24b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclopent-1-enyl)morpholine (**17b**) (77 mg, 0.50 mmol) for 15 h at 25 °C. Solvent was removed, and the crude reaction mixture was characterized spectroscopically. ^{1}H NMR (C_6D_6): δ 7.42, 7.27, and 7.12 (2:1:2 H, m each, Ph); 5.24 (1 H, s, 5-H), 3.66 (1 H each, m each, diastereotopic 4-OCH_2), 3.62 (4 H, m, morpholine), 3.02 and 2.69 (2 H each, m each, morpholine); 2.61, 2.49, 2.28, 2.06,

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1.91, and 1.69 (1 H each, m each, 1-H_2−3-H_2), 1.14 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR (C_6D_6): δ 168.9 (Cq, C4); 142.2, 136.6, and 135.4 (Cq each, C6, C6a, and *i*-C, Ph), 127.5, 127.4, and 127.1 (2:2:1, CH each, Ph), 98.3 (CH, C5), 80.7 (Cq, C3a), 65.0 (OCH_2), 39.4 and 47.6 (2 CH_2 each, morpholine); 30.3, 28.3, and 23.2 (CH_2 each, C1−C3), 14.8 (CH_3).

(3-Ethoxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)dimethylamine (25a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclohex-1-enyl)dimethylamine (**18a**) (63 mg, 0.50 mmol) for 1 h at 50 °C. Chromatography yielded compound **25a** as a pale yellow oil (133 mg, 94%, R_f = 0.6 pentane/diethyl ether 1:1). The analogous reaction was conducted with pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (175 mg, 0.50 mmol) to give compound **25a** (109 mg, 77%). ^{1}H NMR ($CDCl_3$): δ 7.34 and 7.22 (4:1 H, m each, Ph), 5.26 (1 H, s, 2-H), 3.88 (1 H each, m each, diastereotopic 3-OCH_2); 2.76, 2.50, 2.14, 1.87, 1.73, 1.48, 1.17, and 1.07 (1 H each, m each, 4-H_2−7-H_2), 2.33 [6 H, s, $N(CH_3)_2$], 1.37 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.7 (Cq, C3); 137.4, 135.1, and 131.8 (Cq each, C1, C7a, and *i*-C, Ph); 128.2, 127.9, and 126.3 (2:2:1, CH each, Ph), 98.8 (CH, C2), 71.7 (Cq, C3a), 64.7 (CH_2, OCH_2), 38.4 [$N(CH_3)_2$]; 34.1, 29.5, 23.6, and 20.3 (CH_2 each, C4−C7), 14.8 (CH_3). IR (diffuse reflection), cm^{-1}: 1630.1 (10), 1586.7 (30), 1204.9 (25), 1064.8 (20), 763.4 (100), 747.8 (90), 700.7 (30). GC/MS (70 eV), *m/e*: 283 (20) [M^+], 255 (20) [$M^+ - C_2H_4$], 254 (100) [M^+ − Et], 239 (50) [$M^+ - N(CH_3)_2$], 238 (25) [M^+ − OEt]. HRMS (ref = 280.982 46) for $C_{19}H_{25}NO$: *m/e* 283.192 94 (calcd 283.193 61).

1-(3-Ethoxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)-pyrrolidine (25b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclohex-1-enyl)pyrrolidine (**18b**) (76 mg, 0.50 mmol) for 5 min at 25 °C. Chromatography yielded compound **25b** as a pale yellow (111 mg, 72%, R_f = 0.6 pentane/diethyl ether 1:1). The analogous reaction was conducted with pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (175 mg, 0.50 mmol) to give compound **25b** (135 mg, 87%). ^{1}H NMR ($CDCl_3$): δ 7.33 and 7.19 (4:1 H, m each, Ph), 5.28 (1 H, s, 2-H), 3.84 (1 H each, m each, diastereotopic 3-OCH_2), 2.89 and 2.57 (2 H each, m each, pyrrolidine); 2.74, 2.43, 2.13, 1.81, 1.46, and 1.15 (1:1:1:2:1:2 H, m each, 4-H_2−7-H_2), 1.68 (4 H, m, pyrrolidine), 1.33 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.4 (Cq, C3); 137.5, 136.1, and 130.6 (Cq each, C1, C7a, and *i*-C, Ph); 128.1, 127.8, and 126.2 (2:2:1, CH each, Ph), 98.8 (CH, C2), 70.2 (Cq, C3a), 64.6 (OCH_2), 43.5 and 24.4 (2 CH_2 each, pyrrolidine); 35.3, 29.3, 23.9, and 20.7 (CH_2 each, C4−C7), 14.7 (CH_3). GC/IR, cm^{-1}: 1637.3 (20), 1584.7 (100), 1199.0 (75), 1061.3 (50), 789.2 (100), 760.8 (95), 698.9 (25). GC/MS (70 eV), *m/e*: 309 (60) [M^+], 281 (55) [$M^+ - C_2H_4$], 280 (100) [M^+ − Et], 264 (95) [M^+ − OEt], 239 (60) [$M^+ - NC_4H_8$]. HRMS (ref = 304.982 46) for $C_{21}H_{27}NO$: *m/e* 309.208 55 (calcd 309.209 26).

4-(3-Ethoxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)-morpholine (25c). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclohex-1-enyl)morpholine (**18c**) (84 mg, 0.50 mmol) for 15 h at 25 °C. Chromatography yielded compound **25c** as a pale yellow oil (111 mg, 82%, R_f = 0.6 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$): δ 7.34 and 7.24 (4:1 H, m each, Ph), 5.29 (1 H, s, 2-H), 3.88 (1 H each, m each, diastereotopic 3-OCH_2), 3.68 (4 H, m, morpholine), 2.69 (4 H, m, morpholine); 2.69, 2.48, 2.16, 1.86, 1.72, 1.45, and 1.19 (1:1:1:1:1:1:2 H, m each, 4-H_2−7-H_2), 1.38 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.7 (Cq, C3); 143.0, 141.0, and 132.5 (Cq each, C1, C7a, and *i*-C, Ph); 128.2, 127.8, and 126.4 (2:2:1, CH each, Ph), 98.6 (CH, C2), 70.1 (Cq, C3a), 68.2 and 46.2 (2 CH_2 each, morpholine), 65.4 (OCH_2); 32.8, 30.8, 29.6, and 23.6 (CH_2 each, C4−C7), 14.8 (CH_3). IR (diffuse reflection), cm^{-1}: 1632.7 (5), 1588.4 (15), 1262.9 (25), 1114.9 (20), 763.2 (40), 744.3 (100), 701.7 (25). GC/MS (70 eV), *m/e*: 326 (10) [M^+ + 1], 325 (35) [M^+], 297 (25) [M^+ -C_2H_4], 296 (100) [M^+ − Et], 280 (20) [M^+ − OEt], 239 (40) [$M^+ - N(CH_2)_4O$]. HRMS (ref = 318.979 27) for $C_{21}H_{27}NO_2$: *m/e* 325.203 18 (calcd 325.204 18).

Dibenzyl(3-ethoxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)amine (25d). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with dibenzyl(cyclohex-1-enyl)amine (**22d**) (126 mg, 0.50 mmol) for 1 h at 50 °C. Chromatography yielded compound **25d** as a pale yellow oil (179 mg, 82%, R_f = 0.6 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$): δ 7.37−7.07 (15 H, m, 3 Ph), 5.32 (1 H, s, 2-H), (2 H, br s, CH_2Ph), 3.68 (2 H, d, ^2J = 14.3 Hz, diastereotopic 3-CH_2Ph), 3.91 (2 H, q, ^3J = 7.2 Hz, OCH_2); 2.62, 2.07, 1.75, 1.27, and 1.12 (2:1:2:1:2 H, m each, 4-H_2−7-H_2), 1.41 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.4 (Cq, C3); 141.6, 141.2, 135.4, 137.3, and 132.8 (Cq each, C1, C7a, and 3 *i*-C, Ph); 128.4, 127.6, and 126.1 (4:4:2, CH each, 2 CH_2*Ph*); 128.1, 128.0, and 126.3 (2:2:1, CH each, Ph), 98.9 (CH, C2), 73.5 (Cq, C3a), 64.9 (CH_2, OCH_2), 54.2 (2 *C*H_2Ph); 35.5, 30.0, 24.4, and 20.5 (CH_2 each, C4−C7), 14.9 (CH_3). IR (diffuse reflection), cm^{-1}: 1624.9 (15), 1599.3 (45), 1585.5 (55), 1205.6 (45), 1062.1 (35), 764.5 (60), 742.6 (100), 699.1 (75). MS (70 eV), *m/e*: 436 (40) [M^+ + 1], 407 (50) [$M^+ - C_2H_4$], 390 (40) [M^+ − OEt], 239 (60) [M+ − $N(CH_2Ph)_2$], 91 (100) [$C_7H_7^+$]. HRMS (ref = 430.972 89) for $C_{31}H_{34}NO$ [M^+ + 1]: *m/e* 436.262 64 (calcd 436.264 04).

4-(3-Ethoxy-1-phenyl-5,6,7,8-tetrahydro-4*H*-azulen-3a-yl)morpholine (26). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclohept-1-enyl)morpholine (**19**) (82 mg, 0.50 mmol) for 30 min at 25 °C. Chromatography yielded compound **26** as a pale yellow oil (129 mg, 76%, R_f = 0.5 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$): δ 7.35 and 7.23 (4:1 H, m each, Ph), 5.18 (1 H, s, 2-H), 4.88 (1 H each, m each, diastereotopic 3-OCH_2), 3.66 (4 H, m, morpholine), 2.77 and 2.65 (2 H each, m each, morpholine); 2.34, 2.13, 1.89, 1.65, and 1.50 (1:1:1:3:4 H, m each, 4-H_2−8-H_2), 1.37 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 168.2 (Cq, C3); 137.4, 136.7, and 135.6 (Cq each, C1, C8a, and *i*-C, Ph); 128.1, 127.6, and 126.4 (2:2:1 H, CH each, Ph), 98.5 (CH, C2), 76.0 (Cq, C3a), 68.2 and 47.2 (2 CH_2 each, morpholine), 64.8 (OCH_2); 33.0, 29.4, 26.9, 25.4, and 23.8 (CH_2 each, C4−C8), 14.8 (CH_3). IR (diffuse reflection), cm^{-1}: 1624.9 (50), 1600.1 (55), 1585.6 (60), 1202.5 (85), 1063.6 (75), 788.7 (35), 767.5 (80), 699.7 (100). MS (70 eV), *m/e*: 339 (75) [M^+], 311 (100) [$M^+ - C_2H_4$], 294 (65) [M^+ − OEt], 253 (85) [$M^+ - N(CH_2)_4O$]. HRMS (ref = 330.979 27) for $C_{22}H_{29}NO_2$: *m/e* 339.218 99 (calcd 339.219 83).

(1-Ethoxy-3-phenyl-4,5-dihydrocyclopenta[*a*]naphthalen-9b-yl)dimethylamine (27a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (3,4-dihydronaphthalen-1-yl)dimethylamine (**26a**) (87 mg, 0.50 mmol) for 15 h at 25 °C. Chromatography yielded compound **27a** as a pale yellow oil (139 mg, 84%, R_f = 0.5 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$): δ 7.73 (1 H, m, *o*-Ph), 7.33 (4 H, m, 6-H−8-H), 7.16 (4 H, m, Ph), 5.44 (1 H, s, 2-H), 4.07 (1 H each, m each, diastereotopic 1-OCH_2); 3.53, 2.95, 2.83, and 2.73 (1 H each, m each, 4-H_2 and 6-H_2), 2.29 [6 H, s, $N(CH_3)_2$], 1.51 (3 H, t, ^3J = 5.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 167.2 (Cq, C3); 140.3, 137.5, 136.8, 134.7, and 133.0 (Cq each, C1, C3a, C5a, C9a, and *i*-C, Ph); 128.1, 127.9, and 126.5 (2:2:1, CH each, Ph); 127.9, 127.6, 127.2, and 125.3 (1:1:1:1, CH each, C6−C9), 100.2 (CH, C2), 76.1 (Cq, C9b), 65.1 (OCH_2), 39.4 [$N(CH_3)_2$], 29.5 and 22.8 (CH_2 each, C4 and C5), 15.0 (CH_3). IR (diffuse reflection), cm^{-1}: 1625.3 (30), 1580.0 (60), 762.7 (95), 735.9 (100), 698.7 (70). MS (70 eV), *m/e*: 332 (15) [M^+ + 1], 331 (55) [M^+], 302 (70) [M^+ − Et], 287 (50) [$M^+ - N(CH_3)_2$], 286 (75) [M^+ − OEt], 91 (100). HRMS (ref = 318.979 26) for $C_{23}H_{25}NO$: *m/e* 331.194 57 (calcd 331.193 61).

1-(1-Ethoxy-3-phenyl-4,5-dihydrocyclopenta[*a*]naphthalen-9b-yl)pyrrolidine (27b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with 1-(3,4-dihydronaphthalen-

1-yl)pyrrolidine (**20b**) (99 mg, 0.50 mmol) for 5 min at 25 °C. Chromatography yielded compound **27b** as a pale yellow oil (177 mg, 99%, R_f = 0.6 pentane/diethyl ether 1:1). The analogous reaction was conducted with pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (175 mg, 0.50 mmol) to give compound **27b** (168 mg, 94%). ^{1}H NMR ($CDCl_3$): δ 7.80 (1 H, m, *o*-Ph), 7.33 (4 H, m, 6-H−8-H), 7.16 (4 H, m, Ph), 5.46 (1 H, s, 2-H), 4.00 (1 H each, m each, diastereotopic 1-OCH_2); 3.52, 2.92, 2.83, and 2.74 (1 H each, m each, 4-H_2 and 6-H_2), 2.96 and 2.41 (2 H each, m, 2 NCH_2, pyrrolidine), 1.67 (4 H, m, 2 NCH_2CH_2, pyrrolidine), 1.48 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 167.0 (Cq, C3); 144.4, 140.0, 138.2, 136.9, and 133.8 (Cq each, C1, C3a, C5a, C9a, and *i*-C, Ph); 128.0, 127.6, and 126.4 (2:2:1, CH each, Ph); 127.8, 127.3, 127.0, and 125.3 (1:1:1:1, CH each, C6−C9), 100.2 (CH, C2), 73.5 (Cq, C9b), 65.0 (OCH_2), 46.8 and 24.3 (2 H each, m each, pyrrolidine), 29.9 and 23.3 (CH_2 each, C4 and C5), 15.0 (CH_3). IR (diffuse reflection), cm^{-1}: 1624.6 (45), 1585.9 (95), 1203.9 (100), 1043 (90), 787.4 (45), 763.3 (95), 749.7 (85), 697.4 (95). MS (70 eV), *m/e*: 358 (30) [M^+ + 1], 357 (45) [M^+], 329 (35) [$M^+ - C_2H_4$], 328 (80) [M^+ − Et], 312 (100) [M^+ − OEt], 286 (80) [$M^+ - HNC_4H_8$]. HRMS (ref = 368.976 08) for $C_{25}H_{27}NO$: *m/e* 357.210 28 (calcd 357.209 26).

(3-Ethoxy-1-phenyl-4,5-dihydrocyclopenta[*a*]naphthalen-3a-yl)dimethylamine (28a).[53] Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (3,4-dihydronaphthalen-2-yl)dimethylamine (**21a**) (87 mg, 0.50 mmol) for 1 h at 50 °C. Chromatography yielded compound **28a** as a pale yellow oil (126 mg, 76%, R_f = 0.6 pentane/diethyl ether 1:1, pale yellow cubic crystals from diethyl ether, mp 138−140 °C). The analogous reaction was conducted with pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (175 mg, 0.50 mmol) to give compound **28a** (166 mg, 75%). ^{1}H NMR ($CDCl_3$): δ 7.36 and 7.25 (2:3 H, m each, Ph), 7.14 (1 H, d, ^2J = 7.7 Hz, 6-H), 7.08 (1 H, d, ^2J = 7.9 Hz, 9-H), 7.00 and 6.84 (1 H each, "t" each, 7-H and 8-H), 5.28 (1 H, s, 2-H), 3.92 (1 H each, m each, diastereotopic 3-OCH_2), 3.13 and 2.84 (1 H each, m each, 5-H_2), 2.60 and 1.72 (1 H each, m each, 4-H_2), 2.36 [6 H, s, $N(CH_3)_2$], 1.39 (3 H, t, ^3J = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.1 (Cq, C3); 137.6, 136.8, 134.5, 131.8, and 131.6 (Cq each; C1, C5a, C9a, C9b, and *i*-C, Ph), 128.2 and 125.7 (4:1, CH each, Ph); 128.4, 126.9, 126.5, and 124.9 (1:1:1:1, CH each, C6−C9), 101.9 (CH, C2), 70.9 (Cq, C3a), 65.0 (OCH_2), 38.3 [$N(CH_3)_2$], 29.3 and 26.0 (CH_2 each, C4 and C5), 14.8 (CH_3). IR (diffuse reflection), cm^{-1}: 1620.8 (10), 1599.4 (20), 1574.3 (40), 1283.7 (40), 1203.1 (40), 1071.6 (30), 794.7 (20), 764.4 (100), 745.6 (70), 709.9 (40). MS (70 eV), *m/e*: 331 (40) [M^+], 302 (100) [M^+ − Et], 287 (40) [$M^+ - N(CH_3)_2$], 286 (60) [M^+ − OEt]. HRMS (ref = 318.979 27) for $C_{23}H_{25}NO$: *m/e* 331.192 98 (calcd 331.193 61). Anal. Calcd for $C_{23}H_{25}NO$ (331.5): C, 83.33; H, 7.61; N, 4.23. Found: C, 83.23; H, 7.58; N, 4.24.

1-(3-Ethoxy-1-phenyl-4,5-dihydrocyclopenta[*a*]naphthalen-3a-yl)pyrrolidine (28b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with 1-(3,4-dihydronaphthalen-2-yl)pyrrolidine (**21b**) (100 mg, 0.50 mmol) for 1 h at 50 °C. Chromatography yielded compound **28b** as a pale yellow oil (109 mg, 61%, R_f = 0.6 pentane/diethyl ether 1:1, pale orange crystals from pentane/ethanol, mp 111−113 °C). The analogous reaction was conducted with pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (175 mg, 0.50 mmol) to give compound **28b** (134 mg, 75%). ^{1}H NMR ($CDCl_3$): δ 7.36 and 7.27 (2:3 H, m each, Ph), 7.12 (1 H, d, ^2J = 7.4 Hz, 6-H), 7.08 (1 H, "d", 9-H), 7.00 and 6.83 (1 H each, "t" each, 7-H and 8-H), 5.30 (1 H, s, 2-H), 3.91 (1 H each, m each, diastereotopic 3-OCH_2), 3.15 and 2.82 (1 H each, m each, 5-H_2), 2.55 and 1.75 (1 H each, m each, 4-H_2), 2.92 and 2.65 (2 H each, m each, pyrrolidine), 1.60 (4 H, m, pyrrolidine), 1.37 (3 H, t, ^3J = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 168.9 (Cq, C3); 137.8, 137.5, 133.8, 132.4, and 131.8 (Cq, each, C1, C5a, C9a, C9b, and *i*-C, Ph), 128.2 and 125.4 (4:1, CH each, Ph); 128.3, 126.9, 126.3, and 124.6 (1:1:1:1, CH each, C6−C9), 102.1 (CH, C2), 69.5 (Cq, C3a), 65.0 (OCH_2), 45.5 (2 CH_2, pyrrolidine), 30.5 and 26.5 (CH_2 each, C4 and C5), 24.5 (2 CH_2, pyrrolidine), 14.7 (CH_3). IR (diffuse reflection), cm^{-1}: 1619.3 (15), 1596.8 (35), 1573.6 (100), 1203.3 (60), 1044.6 (30), 792.9 (20), 764.1 (75), 730.3 (45), 699.9 (55). MS (70 eV), *m/e*: 358 (55) [M^+ + 1], 357 (80) [M^+], 329 (80) [$M^+ - C_2H_4$], 328 (100) [M^+ − Et], 312 (47) [M^+ − OEt], 286 (75) [$M^+ - HNC_4H_8$]. HRMS (ref = 368.976 08) for $C_{25}H_{27}NO$: *m/e* 357.208 53 (calcd 357.209 26). Anal. Calcd for $C_{25}H_{27}NO$ (357.5): C, 83.98; H, 7.61; N, 3.92. Found: C, 83.53; H, 7.60; N, 4.05.

1-(15-Ethoxy-17-phenyl-11,12-dihydrocyclopenta[*a*]phenanthren-14-yl)pyrrolidine (29). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with 1-(3,4-dihydrophenanthren-1-yl)pyrrolidine (**22**) (125 mg, 0.50 mmol) for 5 min at 25 °C. Chromatography yielded compound **29** as a pale yellow oil (120 mg, 60%, R_f = 0.5 pentane/diethyl ether 1:1). The analogous reaction was conducted with pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (175 mg, 0.50 mmol) to give compound **29** (132 mg, 65%). ^{1}H NMR ($CDCl_3$): δ 8.18 and 7.69 (1 H each, d each, ^3J = 8.8, 8.8 Hz, 2-H and 3-H), 7.99 and 7.79 (1 H each, "d" each, 5-H and 8-H), 7.38 and 7.19 (6:1 H, m each, 6-H, 7-H and Ph), 5.44 (1 H, s, 16-H), 4.03 (1 H each, m each, 15-OCH_2); 3.64, 3.31, 3.12, and 2.99 (1 H each, m each, 11-H_2 and 12-H_2), 3.95 and 2.55 (2 H each, m each, pyrrolidine), 1.70 (4 H, m, pyrrolidine), 1.50 (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 167.3 (Cq, C15); 136.8, 134.6, 134.0, 133.5, 132.8 131.9, and 128.3 (Cq each, C1, C4, C9, C10, C13, C17, and *i*-C, Ph); 128.3, 128.2, and 126.6 (2:2:1, CH each, Ph); 126.5, 125.6, 125.4, 125.3, 124.0, and 123.4 (CH each, C2, C3, C5, C6, C7, and C8), 100.8 (CH, C16), 72.6 (Cq, C14), 65.3 (CH_2, OCH_2), 46.9 and 24.2 (2 CH_2 each, pyrrolidine), 27.9 and 21.8 (CH_2 each, C11 and C12), 14.9 (CH_3). IR (diffuse reflection), cm^{-1}: 1704.0 (5), 1624.6 (5), 1589.1, 1263.5 (30), 1204.4 (20), 1049.5 (15), 817.5 (15), 764.0 (85), 748.1(100), 700.1 (30). MS (70 eV), *m/e*: 407 (80) [M^+], 378 (80) [M^+ − Et], 362 (85) [M^+ − OEt], 336 (100) [$M^+ - HNC_4H_8$]. HRMS (ref = 416.976 08) for $C_{29}H_{29}NO$: *m/e* 407.225 86 (calcd 407.224 91).

1-(3-Ethoxy-1-phenyl-4,5,6,7-tetrahydroinden-3a-yl)-2(*S*)-(methoxymethyl)pyrrolidine (30). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with *N*-(2*S*)-cyclohex-1-enyl-2-(methoxymethyl)pyrrolidine (**23**) (89 mg, 0.50 mmol) for 5 min at 25 °C. Chromatography yielded a 2:1 diastereomeric mixture of compound **30** as a pale yellow oil (150 mg, 85%, R_f = 0.6 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$), isomer A:[B]; 2:[1]: δ 7.32 and 7.20 [7.32 and 7.20] (4:1 H, m each, Ph), 5.28 [5.24] (1 H, s, 3-H); 4.02 and 3.36 [3.84 and 3.06] (1 H each, m each, diastereotopic CH_2OMe), 3.84 [3.84] (1 H each, m each, diastereotopic 3-OCH_2), 3.35 [3.21] (3 H, s, OCH_3); 3.05 [3.13] (1 H, m, NC*H*); 2.61, 2.35, 2.04, 1.85, 1.44, and 1.14 [2.75, 2.46, 2.26, 1.85, 1.44, and 1.14] (1:1:1:2:1:2 H, m each, 4-H_2−7-H_2), 2.75 [2.75] (2 H, m, NCH_2), 1.67 [1.67] (4 H, m, (*S*)-(methylmethoxy)pyrrolidine), 1.32 [1.32] (3 H, t, ^3J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$), isomer A:[B]; 2:[1]: δ 170.1 [172.1] (Cq, C3); 137.4, 136.0, and 131.3 [137.3, 136.0, and 131.8] (Cq each, C1, C7a, and *i*-C, Ph); 128.1, 127.9, and 126.3 [128.1, 127.9, and 126.3] (2:2.1, CH each, Ph); 99.2 [98.8] (CH, C2), 71.2 [71.2] (Cq, C3a), 71.2 [71.2] (OCH_2), 64.9 [64.7] (OCH_2), 58.8 [58.7] (OCH_3), 57.5 [56.0] (NCH), 47.8 [48.0] (NCH_2); 35.8, 36.8, 28.8, and 21.2 [36.2, 29.9, 29.1, and 21.2] (CH_2 each, C4−C7), 24.3 and 24.2 [24.7 and 23.7] (CH2 each, (*S*)-(methylmethoxy)pyrrolidine), 14.7 [14.7] (CH_3). IR (diffuse reflection), cm^{-1}: 1630.4 (20), 1588.9 (60), 1444.1 (40), 1203.6 (55), 1110.3 (55) 1044.4 (45), 764.8 (70), 742.6 (100),

(53) The yield has been improved significantly compared to that reported in ref 33. Assignments of 4-H, 5-H, 6-H, and 9-H are based upon NOE enhancements of 5% between 5-H and 6-H and 3% between 6-H and 5-H.

700.4 (55). MS (70 eV), *m/e*: 354 (30) [$M^+ + 1$], 353 (45) [M^+], 325 (30) [$M^+ - C_2H_4$], 324 (60) [$M^+ - Et$], 308 (100) [$M^+ - C_2H_5O$]. HRMS (ref = 342.979 26) for $C_{23}H_{31}NO_2$: *m/e* 353.2364 (calcd 353.235 48).

6a-(Dimethylamino)-3-phenyl-3a,5,6,6a-tetrahydro-4*H*-pentalen-1-one (31a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclopent-1-enyl)dimethylamine (**17a**) (51 mg, 0.50 mmol) for 15 h at 25 °C. Chromatography of the reaction mixture with dichloromethane and then diethyl ether afforded only $W(CO)_6$ and colored impurities, which were discarded. Elution with acetone/water (10:1) yielded compound **31a** as a pale yellow oil (80 mg, 73%, R_f = 0.3 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$): δ 7.67 and 7.48 (2:3 H, m each, Ph), 6.51 (1 H, s, 2-H), 3.69 (1 H, m, 3a-H), 2.48 [6 H, s, $N(CH_3)_2$]; 2.11, 1.86, 1.74, and 1.30 (2:1:2:1 H, m each, 4-H_2−6-H_2). ^{13}C NMR ($CDCl_3$): δ 210.7 (C=O), 174.8 and 132.6 (Cq each, C3 and *i*-C, Ph), 131.5 (CH, C2); 129.0, 127.9, and 127.4 (2:2:1 H, CH each, Ph), 78.0 (Cq, C6a), 49.4 (CH, C3a), 40.3 [$N(CH_3)_2$]; 34.4, 29.8, and 23.7 (CH_2 each, C4−C6). IR (diffuse reflection), cm^{-1}: 1692.0 [ν(C≡O)] (100), 1594.3 (60), 1570.4 (55), 774.2 (55), 745.1 (30), 690.9 (55). MS (70 eV), *m/e*: 241 (90) [M^+], 213 (60) [$M^+ - C_2H_4$], 212 (60) [$M^+ - Et$], 197 (100) [$M^+ - N(CH_3)_2$]. HRMS (ref = 254.985 65) for $C_{16}H_{19}NO$: *m/e* 241.147 17 (calcd 241.146 66).

6a-Morpholin-4-yl-3-phenyl-3a,5,6,6a-tetrahydro-4*H*-pentalen-1-one (31c). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclopent-1-enyl)morpholine (**17c**) (51 mg, 0.50 mmol) for 15 h at 25 °C. Purification was as described for **31a** to yield compound **31c** as a pale yellow oil (90 mg, 67%, R_f = 0.3 pentane/diethyl ether 1:1). ^{1}H NMR ($CDCl_3$): δ 7.66 and 7.48 (2:3 H, m each, Ph), 6.51 (1 H, s, 2-H), 3.69 (4 H, m, morpholine), 3.62 (1 H, m, 3a-H), 2.86 and 2.63 (2 H each, m each, morpholine); 2.09, 1.76, and 1.33 (2:3:1 H, m each, 4-H_2−6-H_2). ^{13}C NMR ($CDCl_3$): δ 211.4 (C=O), 174.4 and 132.7 (Cq each, C3 and *i*-C, Ph), 131.4 (CH, C2); 129.0, 127.8, and 127.2 (2:2:1 H, CH each, Ph), 78.5 (Cq, C6a), 67.3 and 48.6 (2 CH_2 each, morpholine), 48.8 (CH, C3a); 33.6, 29.8, and 23.4 (CH_2 each, C4−C6). IR (diffuse reflection), cm^{-1}: 1691.6 [ν(C≡O)] (100), 1594.4 (70), 1570.2 (60), 775.0 (60), 748.0 (60), 691.8 (60). MS (70 eV), *m/e*: 283 (45) [M^+], 255 (50) [$M^+ - C_2H_4$], 197 (100) [$M^+ - N(CH_2)_4O$]. HRMS (ref = 280.982 46) for $C_{18}H_{21}NO_2$: *m/e* 283.156 41 (calcd 283.157 23).

Pentacarbonyl(4-phenyl-5,6-cyclohexeno-2*H*-pyran-2-ylidene)chromium (32a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**10a**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclohex-1-enyl)dimethylamine (**18a**) (63 mg, 0.50 mmol) for 5 min at 25 °C. Immediate chromatography with pentane/dichloromethane (4:1) afforded a violet fraction of **32a** (83 mg, 30%, R_f = 0.7 pentane/diethyl ether 1:1, violet crystals from pentane/diethyl ether 4:1 at −78 °C, mp 118−119 °C). ^{1}H NMR ($CDCl_3$): δ 7.88 (1 H, s, 3-H), 7.48 and 7.35 (3:2 H, m each, Ph), 3.07 and 2.48 (2 H each, "t" each, 5a-H_2 and 5d-H_2), 1.95 and 1.72 (2 H each, m each, 5b-H_2 and 5c-H_2). ^{13}C NMR ($CDCl_3$): δ 276.6 (Cr=C), 224.2 and 218.0 [1:4, *trans*- and *cis*-CO], 177.2 (Cq, C6), 145.9 (Cq, C4), 139.1 (CH, C3), 135.5 (Cq, *i*-C, Ph); 129.8, 128.3, and 128.3 (2:2:1, CH each, Ph), 121.2 (Cq, C5); 29.0, 25.3, 22.0, and 21.5 (CH_2 each, C5a−C5d). IR (hexane), cm^{-1}: 2052.2 (30), 1975.5 (5), 1941.6 (100) [ν(C≡O)]. MS (70 eV), *m/e*: 402 (30) [M^+], 374 (10), 346 (30), 318 (20), 290 (40), 262 (80) [$M^+ - 5$ CO], 52 (100). Anal. Calcd for $C_{20}H_{14}CrO_6$ (402.3): C, 59.71; H, 3.51. Found: C, 59.82; H, 3.63.

Pentacarbonyl(4-phenyl-5,6-cyclohexeno-2*H*-pyran-2-ylidene)tungsten (32b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**10b**) (241 mg, 0.50 mmol) was reacted as described above with (1-cyclohex-1-enyl)morpholine (**18c**) (84 mg, 0.50 mmol) for 5 min at 25 °C. Immediate chromatography with pentane/ dichloromethane (4:1) afforded a red fraction of compound **32b** (88 mg, 33%, R_f = 0.7 pentane/diethyl ether 1:1, red crystals from pentane/dichloromethane 4:1 at −78 °C, mp 132−133 °C). ^{1}H NMR ($CDCl_3$): δ 7.89 (1 H, s, 3-H), 7.49 and 7.35 (3:2 H, m each, Ph), 3.03 and 2.50 (2 H each, t each, ^3J = 6.7 and 6.0 Hz, 5a-H_2 and 5d-H_2), 1.96 and 1.74 (2 H each, m each, 5b-H_2 and 5c-H_2). ^{13}C NMR ($CDCl_3$): δ 251.4 (W=C), 204.6 and 198.9 [1:4, *trans*- and *cis*-CO], 176.1 (Cq, C6), 149.0 (Cq, C4), 141.2 (CH, C3), 135.5 (Cq, *i*-C, Ph); 129.9, 128.8, and 128.0 (2:2:1, CH each, Ph), 122.1 (Cq, C5); 29.1, 25.4, 22.0, and 21.4 (CH_2 each, C5a−C5d). IR (hexane), cm^{-1}: 2059.9 (15), 1982.8 (10), 1936.6 (100) [ν(C≡O)]. Anal. Calcd for $C_{20}H_{14}WO_6$ (534.2): C, 44.97; H, 2.64. Found: C, 45.02; H, 2.64.

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Supporting Information Available: Tables of positional and displacement parameters, bond distances, and angles (7 pages). Ordering information is given on any current masthead page.

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