Articles

Organic Syntheses via Transition-Metal Complexes. 99.[1] Cyclopentadiene Annelation to Enolizable Cyclic Ketones via (1-Alkynyl)carbene Complexes (M = Cr, W)†

Rudolf Aumann,* Roland Fröhlich,‡ Jörg Prigge,‡ and Oliver Meyer‡

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

Received December 22, 1998

The procedure for a metal-mediated cyclopentadiene annelation to enolizable cycloalkanones is described. Its key step is based on the cyclization of a 1-metalla-1,3,5-hexatriene intermediate, which is generated from the 1-metalla-1,5-hexadien-3-yne $(CO)_5M{=}C(OEt)C{\equiv}CC(\sim){=}CH(\sim)$ (**3**; M = Cr, W) precursor. Addition of secondary amines **4a**,**b** to [2-(1-cyclopentenyl)ethynyl]carbene complexes **3a**,**b** (M = W, Cr) affords the 4-amino-1-metalla-1,3,5-hexatrienes (3*E*)-**5a**−**d**, which cyclize spontaneously to the η^1(*C*,*M*)-cyclopentadiene complexes **6a**−**d**. The ring closure is highly stereoselective and involves an *anti* addition (!) of the M=C bond to the terminal C=C bond of the 1-metalla-1,3,5-hexatriene unit. Ligand displacement from compound **6a** is achieved by protonation to give an iminium salt **7a**. Addition of aniline to compounds **3a**,**b** yields 4-(*NH*-amino)-1-metalla-1,3,5-hexatrienes (*3Z*)-**10a**,**b**, which subsequently cyclize to cyclopentenimine(*N*,*M*) complexes *syn*-**11a**,**b** and *anti*-**11a**,**b** and finally afford the cyclopentenimine **12** by oxidative ligand disengagement. Addition of secondary phosphanes **13a**,**b** to compound **3a** produces a mixture of the isomeric cyclopentadiene(*P*,*W*)−tungsten complexes *anti*-**14a**,**b**, *anti*-**15a**,**b,** and *anti*-**16b**. X-ray structure analyses are reported of compounds (3*E*)-**5a**, **6c**, *anti*-**11a**, *anti*-**16b**, and *anti*-**17a**.

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = W, Cr) have been applied as stoichiometric reagents in a number of high-yield transformations of potential usefulness to organic synthesis.[2] It has been shown recently that cyclopentadienes can be generated in a [3 + 2] fashion from reaction of (1-alkynyl)carbene complexes with cycloalkenylamines $(\sim)CH{=}C(\sim)NR_2$ in solvents such as dichloromethane. 6-Amino-1-metalla-1,3,5-hexatrienes $(CO)_5M{=}C(OEt)CH{=}C(Ph)C(\sim){=}C(\sim)(NR_2)$ (M = W, Cr) were found to be key intermediates in these transformations (="alkene route to cyclopentadienes").[3] An alternate route to the formation of cyclopentadienes by [3 + 2] cycloaddition is based upon the reaction of the (2-amino-1-alkenyl)carbene−chromium complexes (=4-amino-1-chroma-1,3-butadienes) $(CO)_5Cr{=}C(OEt)CH{=}C(R')NR_2$ with alkynes $RC{\equiv}CH$, and the 6-amino-1-chroma-1,3,5-hexatrienes $(CO)_5Cr{=}C(R)CH{=}C(OEt)CH{=}C(R')NR_2$ (generated by insertion of the C≡C into the Cr=C bond) are thought to be key intermediates (="alkyne route to cyclopentadienes").[2a] A strong driving force for the cyclization of 1-metalla-1,3,5-hexatrienes to cyclopentadienes is provided by amino substituents and not only 6-amino- (vide supra) but also 2-amino- and 4-amino substituents were found to enhance this reaction. Examples of the latter type comprise cyclization both of the 2-amino-1-tungsta-1,3,5-hexatriene $(CO)_5W{=}C(NEt_2)C(Me){=}C(OEt)CH{=}CHPh$ (generated by insertion of the 1-aminoalkyne $Et_2NC{\equiv}CMe$ into the W=C bond of the 1-tungsta-1,3-butadiene $(CO)_5W{=}C(OEt)CH{=}CHPh$)[4a] as well as the 4-amino-1-tungsta-1,3,5-hexatriene $(CO)_5W{=}C(OEt)CH{=}C(NEt_2)C(Me){=}CHPh$ (generated by insertion of the 1-aminoalkyne $Et_2NC{\equiv}CMe$ into the C=C bond of the 1-tungsta-1,3-butadiene $(CO)_5W{=}C(OEt)CH{=}CHPh$)[4b] to η^1-cyclopentadiene complexes under very mild conditions at 20 °C.[4b] It should be noted that, to date, experimental proof of cyclopentadiene formation by cyclization of 1-metalla-1,3,5-hexatrienes is limited to the forementioned 2-amino, 4-amino, and 6-amino derivatives.

We now wish to report on a newly developed metal-mediated cyclopentadiene annelation to enolizable cy-

† Dedicated to Prof. H. Werner on the occasion of his 65th birthday.
‡ X-ray structure analyses.

(1) For part 98 of this series see: Aumann, R.; Kössmeier, M.; Jäntti, A. *Synlett* **1998**, 1120.

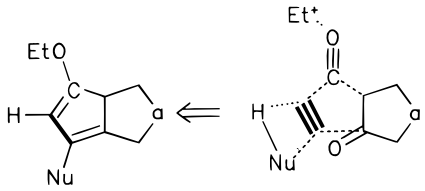
(2) For recent reviews see: (a) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61. (b) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 161.

(3) (a) Aumann, R.; Roths, K.; Grehl, M. *Synlett* **1993**, 669. (b) Aumann, R.; Kössmeier, M.; Roths, K.; Fröhlich, R. *Synlett* **1994**, 1041. (c) Meyer, A. G.; Aumann, R. *Synlett* **1995**, 1011. (d) Aumann, R.; Roths, K.; Jasper, B.; Fröhlich, R. *Organometallics* **1996**, *15*, 1257. (e) Aumann, R.; Kössmeier, M.; Zippel, F. *Synlett* **1997**, 621. (f) Aumann, R.; Meyer, A. G.; Fröhlich, R. *Organometallics* **1996**, *15*, 5018.

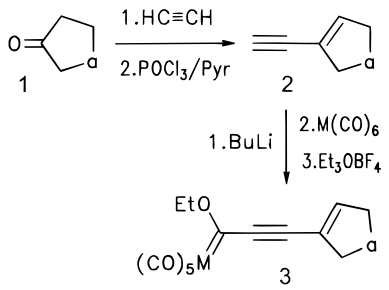
(4) (a) Aumann, R.; Heinen, H., Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 1229. (b) Aumann, R.; Heinen, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343.

10.1021/om9810394 CCC: $18.00
Publication on Web 03/13/1999

Scheme 1. Principle of the Metal-Mediated Cyclopentadiene Annelation to Enolizable Cycloalkanones in Overall [2 + 2 + 1] Fashion



Scheme 2. 1-Metalla-1,5-hexadien-3-ynes 3 from Cycloalkanones



1,2	a	3	a	M	[%][a]
a	CH_2	**a**	CH_2	W	84
b	CH_2CH_2	**b**	CH_2	Cr	89
c	$CH_2CH_2CH_2$	**c**	CH_2CH_2	W	78
		d	$CH_2CH_2CH_2$	W	72

[a] Isolated chemical yields.

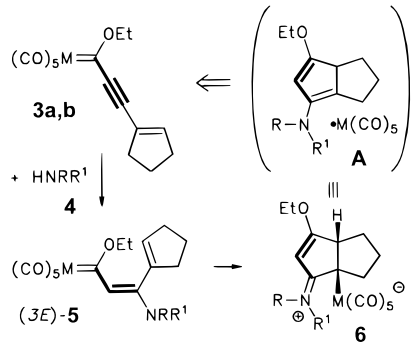
cloalkanones involving the successive addition of acetylene, carbon monoxide, an alkyl group, and a protic nucleophile NuH (Scheme 1). The key step of this reaction sequence is based on the cyclization of a 1-metalla-1,3,5-hexatriene intermediate, which is generated by addition of a protic nucleophile NuH to the C≡C bond of a 1-metalla-1,5-hexadien-3-yne precursor $(CO)_5M{=}C(OEt)C{\equiv}CC(\sim){=}CH(\sim)$ (M = Cr, W). It will be demonstrated that amino as well as phosphanyl substituents at the 4-position of the 1-metalla-1,3,5-hexatriene are well-suited to trigger the π-cyclization of such compounds under mild conditions.

[2-(1-Alkenyl)ethynyl]carbene Complexes (=1-Metalla-1,5-hexadien-3-ynes)

The first part of our investigation took aim at the preparation of 1-metalla-1,5-hexadien-3-ynes $(CO)_5M{=}C(OEt)C{\equiv}CC(\sim){=}CH(\sim)$ (**3a**−**d**; M = Cr, W) from cycloalkenones **1a**−**c**. Our procedure is straightforward and involves formation of 1-ethynylcycloalkenes **2a**−**c** from ketones **1a**−**c** and acetylene via carbinoles.[5] Compounds **2** are finally transformed into the (1-alkynyl)-carbene complexes **3** by the Fischer route (Scheme 2).[6]

Reaction of (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = Cr, W; R = aryl, alkyl) with secondary and primary amines, respectively, was previously shown to yield 4-amino-1-metalla-1,3-dienes of opposite configurations, 3*E* and 3*Z*, respectively, with high stereoselectivity.[2b,7] On the basis of these results, it could be predicted that (3*E*)-4-amino-1-metallatrienes **5** would be generated by addition of secondary amines to [2-(1-cyclopentenyl)ethynyl]carbene complexes of chromium and tungsten (**3a,b**; Scheme 3), and (*3Z*)-4-amino-1-metallatrienes **10** of opposite stereochemistry by addition of primary arylamines (Scheme 7). We subsequently present details of the formation of compounds **3** and **10**, as well as its cyclization reactions to cyclopentadiene complexes and cyclopentenimine complexes, respectively.

Scheme 3. Generation of (3*E*)-4-Amino-1-metalla-1,3,5-trienes 5 and η^1-Cyclopentadiene Complexes 6 by Addition of Secondary Amines to (1-Alkynyl)carbene Complexes 3a,b[a]



1,2	a	3	a	M	[%][a]
a	CH_2	**a**	CH_2	W	84
b	CH_2CH_2	**b**	CH_2	Cr	89
c	$CH_2CH_2CH_2$	**c**	CH_2CH_2	W	78
		d	$CH_2CH_2CH_2$	W	72

[a] Isolated chemical yields.

(3*E*)-4-Amino-1-metalla-1,3,5-hexatrienes 5 and η^1-Aminocyclopentadiene Complexes 6

(3*E*)-4-Amino-1-metalla-1,3,5-hexatrienes (3*E*)-**5a**−**d** are obtained as yellow crystals, if secondary amines **4a**,**b** [$HNMe_2$ and (2*S*)-(methoxymethyl)pyrrolidine] are added to [2-(1-cyclopentenyl)ethinyl]carbene complexes **3a**,**b** (M = W, Cr) in diethyl ether at 0 °C (Scheme 3). The reaction is fast, and the point of equivalency is visually recognized by a color change from dark brown to bright yellow. If isolation of compounds (3*E*)-**5** is intended, solvent must be removed immediately, since compounds (3*E*)-**5a**−**d** are stable in the solid state but undergo ring closure in solution at ambient temperature to give the zwitterionic η^1-cyclopentadiene complexes **6a**−**d** (vide infra). Recrystallization of compounds **5** from diethyl ether may be achieved with minor loss, if carried out quickly at low temperature.

The ^{13}C NMR chemical shifts of the M=C group (e.g. tungsten complex (3*E*)-**5a**, δ 268.5; chromium complex (3*E*)-**5b**, δ 287.1) as well as of the C6−N unit (e.g. (3*E*)-**5a**, δ 157.2; (3*E*)-**5b**, 154.2) of compounds (3*E*)-**5** are typically observed with planar and highly polarized enamino carbene complexes $(OC)_5M{=}C(OEt)CH{=}C$-

(5) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1998; p 204.

(6) (a) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47. (b) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57. (c) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164.

(7) (a) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. (b) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421.

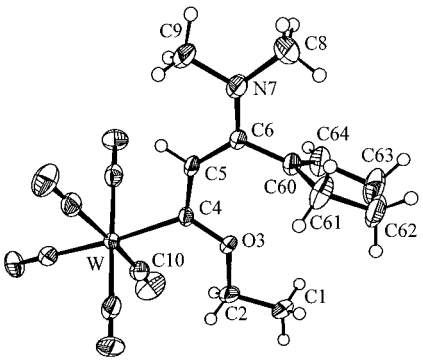


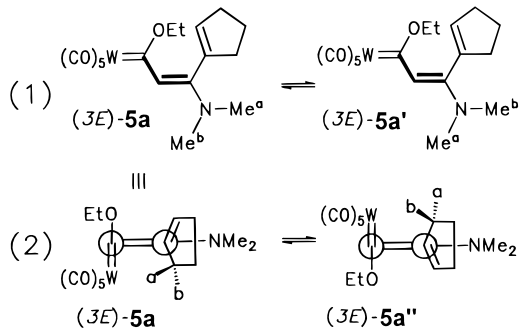
Figure 1. Molecular structure of 4-amino-tungsta-1,3,5-hexatriene species (3*E*)-**5a**. Selected bond lengths (Å) and angles (deg): W−C4 = 2.281(6), C4−O3 = 1.336(8), C4−C5 = 1.391(9), C5−C6 = 1.392(9), C6−N7 = 1.346(9), C6−C60 = 1.490(9), C60−C61 = 1.443(11), C60−C64 = 1.373(12); W−C4−O3 = 127.7(5), W−C4−C5 = 119.2(4), O3−C4−C5 = 113.1(6), C4−C5−C6 = 129.1(6), C5−C6−N7 = 120.9(6), C5−C6−C60 = 123.4(6), C60−C6−N7 = 115.7(6), C6−C60−C61 = 123.2(7), C6−C60−C64 = 124.0(7), C61−C60−C64 = 112.7(7), C60−C61−C62 = 106.1(7), C60−C64−C63 = 108.6(8), C10−W−C4−C5 = 136.7(6).

$(NR_2)\sim$ of 3*E* configuration[7] in a range clearly distinct from (nonplanar) *torquo*-carbiminium carbonylmetalates $^{-}(OC)_5M-C(OEt)=CHC(=N^{+}R_2)\sim$.[8] The (planar) enamine structure of compounds (*E*)-**5** is confirmed in the X-ray structure analysis of compound (3*E*)-**5a** by the dihedral angles C4−C5−C6−N7 = −173.8(8)°, C5−C6−N7−C8 = −174.6(9)°, and W−C4−C5−C6 = −176.7(6)° as well as by the pattern of nonalternating bond distances C4−C5 = 1.391(9) Å, C5−C6 = 1.392(9) Å, and C6−N7 = 1.346(9) Å within the ligand backbone, which indicates strong π-delocalization (Figure 1).

The methylene protons of (3*E*)-**5a** are diastereotopic due to chirality induced by distortion of the 1-cyclopentenyl group from planarity by C5−C6−C60−C64 = 86.3(10)° (Figure 1). A sharp set of clearly separated signals is observed in the ^{1}H NMR spectra of compound (3*E*)-**5a** below −40 °C ($CDCl_3$, 600 MHz), but line broadening caused by rapid exchange processes is found above this temperature. Two degenerate reactions (Scheme 4; (1) and (2), respectively) can be distinguished from different activation enthalpies at the coalescence temperatures. $\Delta G^{\ddagger}$ = ca. 60 kJ/mol was found for the interconversion (1) of structures (3*E*)-**5a** and (3*E*)-**5a′** (leading to an exchange of the magnetic environments of the $N-CH_3$ groups); $\Delta G^{\ddagger}$ = ca. 51 kJ/mol was determined for the interconversion (2) of structures (3*E*)-**5a** and (3*E*)-**5a″** (involving an exchange of the magnetic environments of the diastereotopic methylene protons OCH_2 as well as 3′-H_2, 4′-H_2, and 5′-H_2 of the cyclopentene ring) (Scheme 4).

Introduction of a chiral amine substituent into the 1-metalla-1,3,5-hexatriene (3*E*)-**5** leads to generation of diastereomers. Four diastereomers were found to be present in the solution of (3*E*)-**5c**, in which (2*S*)-(methoxymethyl)pyrrolidine (**4b**) is attached to the metallatriene unit. These are rapidly interconverting on the NMR time scale, but two sets of signals in a ratio of ca. 1:2 can be distinguished in the ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) at −10 °C for the stereoisomers (3*E*)-**5c** and (3*E*)-**5c′** resulting from different configurations of the C3−N bond. Two more sets of signals, which appear at −40 °C, are attributed to right- and left-handed spiral structures, respectively, of the 1-metallahexatriene (3*E*)-**5c** (analogous to the structures (3*E*)-**5a** and (3*E*)-**5a″** in Scheme 4). 4-Amino-1-metallahexatrienes (3*E*)-**5** are stable in the solid state but undergo smooth rearrangement in solution within a few hours at ambient temperature to zwitterionic η^1-cyclopentadiene complexes **6**. The reaction can be monitored by NMR spectra.

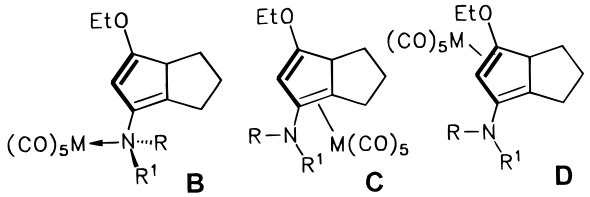
Scheme 4. Degenerate Rearrangements, (1) and (2), Respectively, of Metallatriene (3*E*)-5a[a]



Interconversion	H atoms observed	Δν [Hz] in $CDCl_3$ 600 Mz, 213 K	T_c [K]	$\Delta G^{\ddagger}$ [KJ/mol]
(3*E*)-**5a** and (3*E*)-**5a'**	$N(CH_3)_2$	22	283	ca. 60
(3*E*)-**5a** and (3*E*)-**5a''**	OCH_2	28	240	ca. 52
(3*E*)-**5a** and (3*E*)-**5a''**	3'-H_2	36	243	ca. 50
(3*E*)-**5a** and (3*E*)-**5a''**	4'-H_2	56	253	ca. 51
(3*E*)-**5a** and (3*E*)-**5a''**	5'-H_2	178	270	ca. 52

[a] $\Delta G^{\ddagger}$ values are estimated from NMR measurements at different temperatures.

Chart 1. Alternate (Experimentally Unobserved) Coordination Modes of Cyclopentadiene Complexes 6



It should be noted that a zwitterionic η^1 coordination of the bridgehead α-carbon atom of the aminocyclopentadiene unit to the $W(CO)_5$ group (Scheme 3) is favored over the coordination mode **B** of the nitrogen atom of the NR_2 group or a η^2 coordination modes **C** and **D**, respectively, of a C=C bond (Chart 1).

The η^1 coordination[4b] in cyclopentadiene complexes **6** is indicated in the ^{13}C NMR spectrum by a high-field shift of the M−C unit (**6c**, W−C δ 50.6; **6d**, Cr−C δ 54.3) and a low-field shift of the C=N unit (**6c**, δ 190.3; **6d**, δ 187.8). The carbiminium carbonylmetalate structure is further documented in the X-ray structure analysis of compound **6c** by the long distance of the W−C single bond, W1−C1 = 2.43(2) Å, and the short distance C8−N9 = 1.37(3) Å of the C−N double bond (Figure 2).[9]

The ring closure of the 4-amino-1-metalla-1,3,5-hexatriene (3*E*)-**5c** to the η^1-cyclopentadiene complex

(8) Aumann, R.; Roths, K.; Fröhlich, R. *Organometallics* **1997**, *16*, 5893.

(9) Structural data for a vinylogous carbiminium carbonyltungstate are reported in ref 4b.

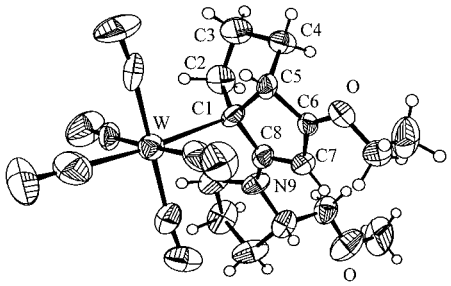
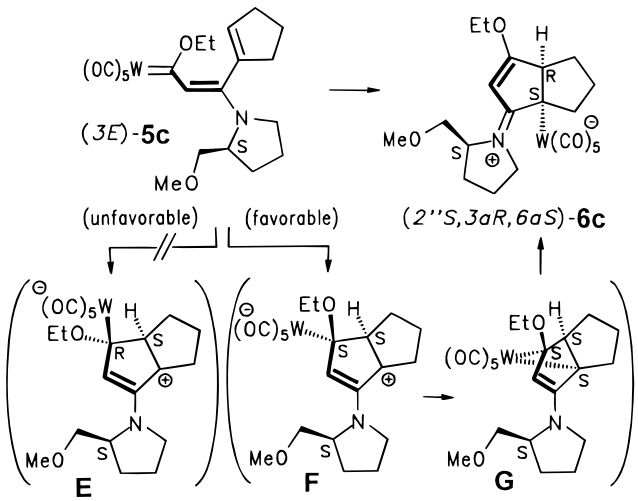


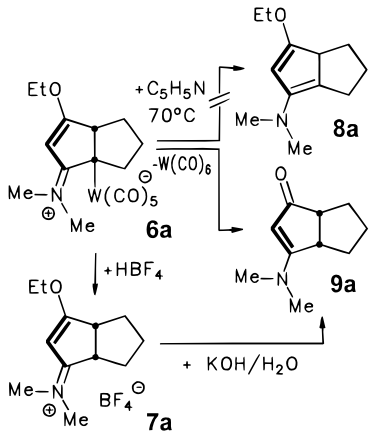
Figure 2. Molecular structure of the dihydropentalene carbiminium carbonylmetalate **6c**. Selected bond lengths (Å) and angles (deg): W1−C1 = 2.43(2), C1−C2 = 1.59(2), C1−C5 = 1.55(3), C1−C8 = 1.37(3), C2−C3 = 1.51(4), C3−C4 = 1.37(4), C4−C5 = 1.58(3), C5−C6 = 1.54(3), C6−O = 1.32(3), C6−C7 = 1.33(3), C7−C8 = 1.50(2), C8−N9 = 1.37(3), N9−C10 = 1.48(2); W−C1−C2 = 116(2), W−C1−C8 = 106.4(12), W−C5−C1 = 108.7(13), C2−C1−C5 = 102-(2), C2−C1−C8 = 117(2), C5−C1−C8 = 105(2), C1−C8−N9 = 128(2).

Scheme 5. Cyclization of 1-Metallatrienes by *anti* Addition of the M=C Bond to the 5,6-C=C Bond



(2″*S*,3a*R*,6a*S*′)-**6c** involves an *anti* addition of the M=C bond to the terminal C=C bond (Scheme 5). This stereochemical course is not restricted to the specific geometrical requirements of the bicyclo[3.3.0]octene ring skeleton; it was previously observed also with monocyclic systems.[4b] An *anti*-addition mode for this ring closure is quite unexpected, considering the fact that metallacyclohexenes or $(CO)_4M$ chelate complexes would normally be anticipated as intermediates. On the basis of the reasonable assumption that the overall reaction is intramolecular, it can be stated that neither a 1-metallacyclohexa-2,4-diene nor a cyclic $(CO)_4W$ complex (=(5,6-η)-1-metalla-1,3,5-hexatriene) would be an intermediate en route to the cyclopentadiene complex, since either of these structures should necessarily result in *syn* addition of the M=C bond to the terminal C=C bond. To meet the stereochemical requirements for the ring closure, it is suggested that the zwitterionic species **F** is formed initially, from which the cyclopentadiene complex (2″*S*,3a*R*,6a*S*′)-**6c** is generated by migration of the $W(CO)_5$ unit, possibly through the intermediate **G**. The stereocontrol of the reaction is based on the assumption that formation of an *exo*-$W(CO)_5$ group in the zwitterion **F** should be kinetically strongly favored over formation of the *endo* derivative **E**. Moreover, the reaction path outlined in Scheme 6 does not imply an intermediate disengagement of a carbonyl ligand from the $W(CO)_5$ group, in line with the exceedingly mild reaction conditions of 20 °C required for the π-cyclization to proceed. Chelation of a pentacarbonyl-1-tungsta-1,3,5-hexatriene by elimination of carbon monoxide to a (5,6-η)-tetracarbonyl-1-tungsta-1,3,5-hexatriene (characterized by an X-ray structure analysis)[3e] was indeed observed at temperatures above 90 °C.

Scheme 6. Ligand Displacement from η^1-Cyclopentadiene Complexes 6 by Protonation



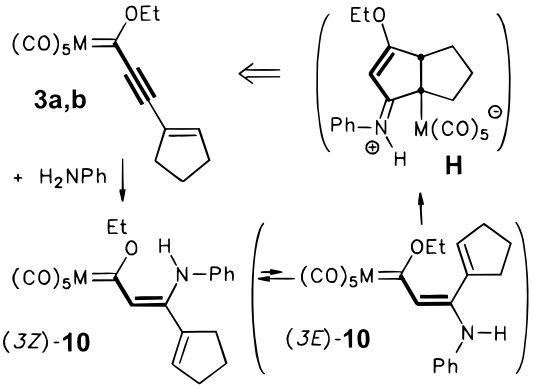
Even though facile ligand elimination is indicated in the mass spectrum of compound **6a** by the base peak *m*/*e* 193 (100%) and the strong fragment peak *m*/*e* 165 (90%) resulting from elimination of ethylene, generation of cyclopentadiene **8a** from complex **6a** could not, to date, be achieved on a preparative scale, supposedly due to the low stability of compound **8a** on one side and the high stability of complex **6a** on the other side. Compounds **6a**−**d** do not exhibit the reactivity expected of an olefin π-complex but rather that of a σ-complex. Thus, ligand displacement from compound **6a** is not achieved, e.g., with pyridine at 70 °C. Extension of the reaction time to 5 h at 70 °C results in partial decomposition of compound **6a** and production of cyclopentenone **9a** (possibly by elimination of ethylene?) and $W(CO)_6$. On the other hand, addition of HBF_4 in diethyl ether to compound **6a** yields the iminium salt **7a** in a smooth reaction together with $W(CO)_6$. Addition of 10% KOH/90% H_2O to compound **7a** does not produce the cyclopentadiene **8a** but the cyclopentenone **9a** instead (Scheme 6).

(*Z*)-4-(*NH*-Amino)-1-metalla-1,3,5-hexatrienes 10, Cyclopentenimine Complexes 11, and Cyclopentenimine 12

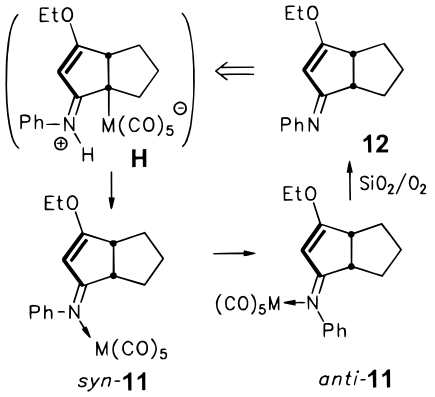
Addition of primary arylamines $ArNH_2$ to a (1-alkynyl)carbene complex, e.g. $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (M = W, Cr), was shown to afford 4-(arylamino)-1-metalla-1,3-butadienes $(CO)_5M{=}C(OEt)CH{=}C(NHAr)$-Ph.[7] The reaction is highly regioselective and also stereoselective with respect to the formation of 3*Z* stereoisomers, which seem to be stabilized by an O···H−N hydrogen bridge.[10] In line with expectation, (3*Z*)-4-*NH*-amino-1-metalla-1,3,5-trienes (3*Z*)-**10a**,**b** could be

(10) Aumann, R.; Roths, K.; Kössmeier, M.; Fröhlich, R. *J. Organomet. Chem.* **1998**, *556*, 119.

Scheme 7. Generation of 4-(*NH*-Amino)-1-metalla-1,3,5-hexatrienes (3*Z*)-10 and Its Supposed Course of Cyclization



Scheme 8. Cyclopentenimine Complexes: Generation, *syn/anti* Isomerization, and Metal Disengagement



generated with high stereoselectivity by addition of aniline to [2-(1-cyclopentenyl)ethynyl]carbene complexes **3a**,**b** (M = W, Cr) in diethyl ether at 0 °C (Scheme 7). Though 3*Z* stereoisomers are isolated as the only products, it could be demonstrated by spin saturation transfer NMR techniques that 3*E* stereoisomers will be present in solution, although only in small equilibrium concentrations.[10]

4-(*NH*-Amino)-1-metallahexatrienes (3*Z*)-**10** undergo clean cyclization in solution at 50 °C within 4 h to give a mixture of the cyclopentenimine complexes *syn*-**11** and *anti*-**11** (Scheme 8). The products could be separated by column chromatography on silica gel, and it was demonstrated by NMR spectra that the compounds *anti*-**11a**,**b** are generated from the compounds *syn*-**11a**,**b** at 50 °C. Cyclization of 4-(*NH*-amino)-1-metalla-1,3,5-hexatrienes (3*Z*)-**10a**,**b** to compounds **11a**,**b** is assumed to follow the route outlined in Scheme 7. The reaction path suggested is similar to that depicted for the generation of compounds (3*E*)-**5c** in Scheme 5, except that zwitterionic carbiminium metalates **H** are assumed to be unstable and undergo proton transfer from the $=NH^+$ nitrogen atom to the α-carbon atom. Coordination of the imino function to the $M(CO)_5$ group appears to stereoselectively produce initially the *syn*-compounds **11** (Scheme 8).

Cyclopentenimine complexes **11** prove quite stable toward attempted ligand displacement with triphenylphosphine or pyridine, but the (metal-free) imine **12** is readily generated from both the chromium complexes

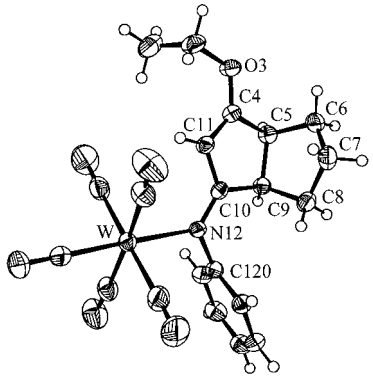


Figure 3. Molecular structure of the imine complex *anti*-**11a**. Selected bond lengths (Å) and angles (deg): W−N12 = 2.276(3), N12−C10 = 1.296(5), N12−C120 = 1.452(5), C10−C9 = 1.528(5), C9−C8 = 1.547(6), C9−C5 = 1.559(5), C8−C7 = 1.526(6), C7−C6 = 1.528(6), C6−C5 = 1.520(6), C5−C4 = 1.503(5), C4−C11 = 1.348(5), C4−O3 = 1.327(5), C11−C10 = 1.434(5); W−N12−C10 = 128.3(2), W−N12−C120 = 114.4(2), C120−N12−C10 = 117.1(3), N12−C10−C9 = 126.0(3), N12−C10−C11 = 125.0(3), C11−C10−C9 = 109.1(3), C10−C9−C8 = 113.2(3), C10−C9−C5 = 104.3(3), C5−C9−C8 = 104.2(3), C9−C8−C7 = 105.4(3), C8−C7−C6 = 102.4(4), C7−C6−C5 = 103.6(3), C6−C5−C4 = 112.8(3), C6−C5−C9 = 106.7(3), C9−C5−C4 = 102.7(3), C5−C4−O3 = 115.7(3), C5−C4−C11 = 114.1(3), O3−C4−C11 = 130.2(4), C4−C11−C10 = 109.4(3).

syn-**11b** and *anti*-**11b** (but not from the corresponding tungsten complexes) by chromatography on silica gel in the presence of air.

The structures of compounds **11** and **12** are based on spectroscopic evidence, as well as on an X-ray structure analysis of *anti*-**11a** (Figure 3).

(3*E*)-4-Phosphanyl-1-metalla-1,3,5-hexatrienes and Phosphanylcyclopentadiene Complexes

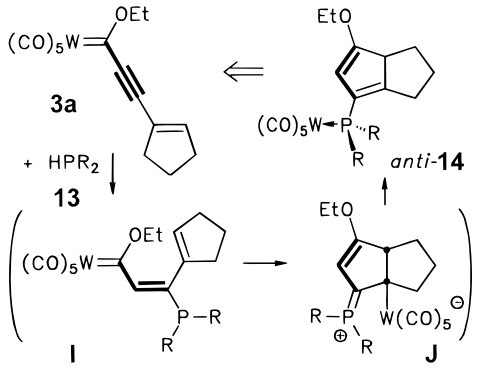
Addition of secondary phosphanes to the (1-alkynyl)-carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (M = W, Cr) was previously shown to afford the (3*E*)-4-phosphanyl-1-metalla-1,3-butadienes $(CO)_5M{=}C(OEt)CH{=}C(PR_2)$-Ph, which were isolated and characterized by X-ray structure analyses.[11] Reaction of the tungsten compound **3a** with secondary phosphanes **13a**,**b** was found to be fast even at 0 °C and yielded mixtures of phosphanylcyclopentadiene complexes *anti*-**14**−**16** (Schemes 9 and 10), which are coordinated through the phosphorus atom. Reaction intermediates, e.g. compounds **I** and **J** (Scheme 9) could not be detected in this case.[11]

The overall yield of phosphanylcyclopentadiene complexes is high, but the relative amount of isomers *anti*-**14**−**16** was found to depend on the details of the preparation, since these compounds are interconverted by 1,5-hydrogen shifts as outlined in Scheme 10.

The tungsten compounds *anti*-**14a**,**b**, *anti*-**15a**,**b**, and *anti*-**16b** were separated by chromatography on silica gel, under which conditions compounds *anti*-**17a**,**b** are generated in small amounts by hydrolysis of the enol ether unit. The structures of the phosphanyl compounds could be easily derived from the NMR spectra. The *anti* configuration is assigned on the basis of a low-field shift

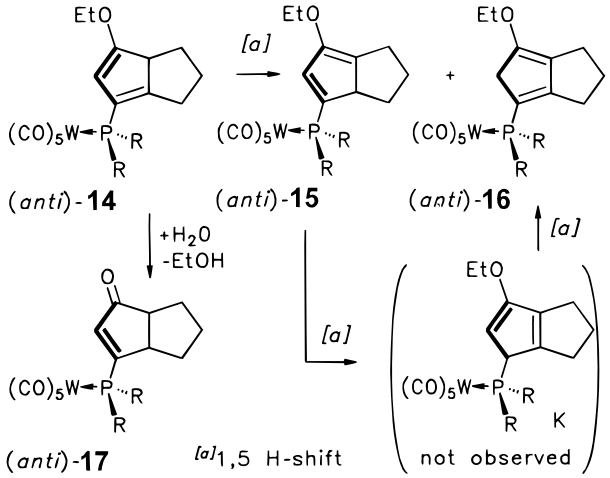
(11) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 2475.

Scheme 9. Phosphanylcyclopentadiene Complexes



13, *anti*-14	R
a	*t*-Bu
b	*c*-C_6H_{11}

Scheme 10. Phosphanylcyclopentadiene Complexes: Isomerization by 1,5-H Shifts and Hydrolysis



anti-14 - *anti*-17	R
a	*t*-Bu
b	*c*-C_6H_{11}

observed for the =CH signal due to the anisotropic influence of the $W(CO)_5$ group and could also be confirmed by X-ray structure analyses of *anti*-**16b** and *anti*-**17a** (Figures 4 and 5). Compounds with a *syn* configuration were not detected in the case of phosphanylcyclopentadiene complexes, nor was any indication found for a possible coordination mode of one (or two) carbon atoms.

Experimental Section

All operations were carried out under an atmosphere of dry argon. All solvents were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were routinely recorded on Bruker ARX 300 and AM 360 instruments. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. ^1J(H,C)−^2J(H,C)−^3J(H,C) decoupling experiments were performed on a Varian 600 instrument. 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.

Pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (3a). $W(CO)_6$ (3.52 g, 10.00 mmol) is

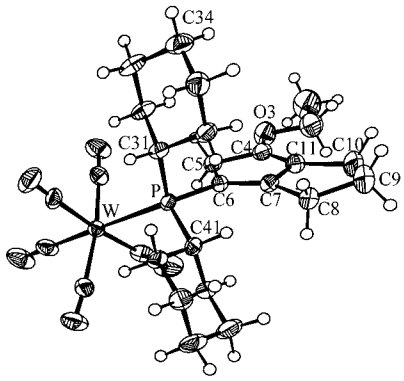


Figure 4. Molecular structure of the dihydropentalene phosphine complex *anti*-**16b**. Selected bond lengths (Å) and angles (deg): W−P = 2.5604(10), P−C31 = 1.858(4), P−C41 = 1.846(4), P−C6 = 1.812(4), C6−C7 = 1.348(5), C7−C8 = 1.491(6), C7−C11 = 1.458(6), C8−C9 = 1.533(6), C9−C10 = 1.517(7), C10−C11 = 1.514(6), C11−C4 = 1.324(6), C4−O3 = 1.354(5), C4−C5 = 1.504(5), C5−C6 = 1.516(5); W−P−C31 = 114.51(13), W−P−C41 = 114.80(12), W−P−C6 = 115.22(13), C31−P−C41 = 103.26(17), C31−W−C6 = 103.47(17), C41−P−C6 = 104.08(18), P−C6−C5 = 122.3(3), P−C6−C7 = 130.8(3), C5−C6−C7 = 106.9(3), C6−C7−C8 = 139.3(4), C6−C7−C11 = 111.2(4), C11−C7−C8 = 109.5(4), C7−C8−C9 = 105.5(4), C8−C9−C10 = 108.5(4), C9−C10−C11 = 104.6(4), C10−C11−C7 = 110.0(4), C10−C11−C4 = 141.3(4), C7−C11−C4 = 108.7(4), C11−C4−O3 = 134.0(4), C11−C4−C5 = 109.8(4), O3−C4−C5 = 116.2(4), C4−C5−C6 = 103.4(3).

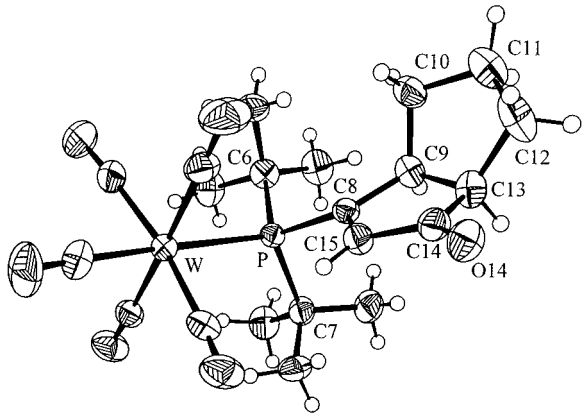


Figure 5. Molecular structure of the dihydropentalene phosphine complex *anti*-**17a**. Selected bond lengths (Å) and angles (deg): W−P = 2.6086(11), P−C6 = 1.887(4), P−C7 = 1.907(4), P−C8 = 1.852(4), C8−C9 = 1.547(5), C9−C10 = 1.519(6), C9−C13 = 1.543(6), C10−C11 = 1.523(7), C11−C12 = 1.511(8), C12−C13 = 1.535(7), C13−C14 = 1.519(6), C14−O14 = 1.215(5), C14−C15 = 1.463(6), C8−C15 = 1.328(6); W−P−C6 = 112.5(2), W−P−C7 = 116.58(14), W−P−C8 = 110.08(13), C6−P−C7 = 110.1(2), C6−P−C8 = 106.8(2), C7−P−C8 = 99.6(2), P−C8−C9 = 130.4(3), P−C8−C15 = 119.7(3), C15−C8−C9 = 109.1(3), C8−C9−C10 = 117.4(4), C8−C9−C13 = 104.6(3), C13−C9−C10 = 103.5(4), C9−C10−C11 = 103.5(4), C10−C11−C12 = 103.3(4), C11−C12−C13 = 103.7(4), C12−C13−C14 = 114.1(4), C12−C13−C9 = 107.6(4), C9−C13−C14 = 104.1(4), C13−C14−C15 = 106.8(4), C13−C14−O14 = 125.4(4), O14−C14−C15 = 127.7(4), C14−C15−C8 = 113.2(4).

placed in a 100 mL two-necked flask fitted with an efficient stirrer bar and a 100 mL dropping funnel. After the apparatus has been flushed with argon, 1-ethynylcyclopentene[12] (0.92 g, 10.00 mmol; **2a**) and dry THF (20 mL) is placed into the dropping funnel, and a solution of *n*-BuLi (10.00 mmol, 6.25 mL of a 1.6 M solution in hexane) is added dropwise at 20 °C, while a slow stream of argon is passed through the solution to achieve efficient mixing. After 15 min at 20 °C the solution of (1-ethynylcyclopentenyl)lithium thus generated is added dropwise within 15 min to the $W(CO)_6$ with rapid stirring. A clear orange solution is obtained, which is very air-sensitive. $W(CO)_6$ dissolves completely after approximately 80% of the reagent has been added. Evaporation to dryness (20 °C, 20 Torr) gives a bright yellow, very air-sensitive solid, from which the remaining THF is removed at 1 Torr and 20 °C. The residue is dissolved in dry dichloromethane (20 mL), and the solution is cooled to −78 °C. Triethyloxonium tetrafluoroborate (2.85 g, 15.00 mmol) in dry dichloromethane (10 mL) is added at −78 °C with rapid stirring. A dark mixture is formed immediately, which is brought to dryness (20 °C, 20 Torr). The residue is extracted efficiently four times with 50 mL portions of Et_2O to leave a grayish residue of $LiBF_4$. Crystallization from pentane at −40 °C affords compound **3a** (3.96 g, 84% brown needles, R_f = 0.5 in pentane, mp 64 °C). ^{1}H NMR (C_6D_6): δ 6.20 (1 H, t, 2′-H), 3.97 (2 H, q, OCH_2), 2.32, 1.98 and 1.52 (2 H each, m each, 3′-H_2 to 5′-H), 0.95 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 284.3 (C_q, W=C), 206.3 and 198.4 [1:4, C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 148.2 (CH, C2′), 135.6 (C_q, broad, C3), 124.9 (C_q, C1′), 99.8 (C_q, broad, C2′), 76.2 (OCH_2), 36.1, 35.0 and 23.7 (CH_2 each, C3′−C5′), 14.6 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2142.3 [ν(C≡C)]; 2068.3 (25), 1983.6 (30), 1958.7 (100) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 472 (40) [M^+], 414 (50) [$M^+ - 2$ CO], 388 (50) [$M^+ - 3$ CO], 330 (90) [$M^+ - 5$ CO], 302 (90), 273 (100). Anal. Calcd for $C_{15}H_{12}NO_6W$ (472.1): C, 38.16; H, 2.56. Found: C, 38.02; H, 2.69.

Pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]chromium (3b). $Cr(CO)_6$ (2.20 g, 10.00 mmol) is reacted as described above with 1-ethynylcyclopentene[12] (0.92 g, 10.00 mmol; **2a**), *n*-BuLi (10.00 mmol), and triethyloxonium tetrafluoroborate (2.85 g, 15.00 mmol) to give compound **3b** (3.05 g, 89% red-brown crystals, R_f = 0.5 in pentane, mp 45 °C). ^{1}H NMR (C_6D_6): δ 6.18 (1 H, t, 2′-H), 4.06 (2 H, q, OCH_2), 2.31, 2.12 and 1.60 (2 H each, m each, 3′-H_2 to 5′-H), 0.99 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 314.4 (C_q, Cr=C), 226.3 and 217.2 [1:4, C_q each, *trans*- and *cis*-CO, $Cr(CO)_5$], 148.0 (CH, C2′), 135.6 (C_q, broad, C3), 124.6 (C_q, C1′), 94.1 (C_q, broad, C2′), 76.1 (OCH_2), 36.1, 35.0, and 23.7 (CH_2 each, C3′−C5′), 14.8 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2139.9 [ν(C≡C)]; 2061.0 (25), 1987.2 (30), 1962.8 (100) [ν(C≡O)]. MS (70 eV; *m/e* (%)): 340 (20) [M^+], 284 (20) [$M^+ - 2$ CO], 256 (20) [$M^+ - 3$ CO], 228 (40) [$M^+ - 4$ CO], 200 (100) [$M^+ - 5$ CO], 156 (50), 143 (60). Anal. Calcd for $C_{15}H_{12}CrNO_6$ (340.1): C, 52.95; H, 3.55. Found: C, 52.76; H, 3.41.

Pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (3c). $W(CO)_6$ (3.52 g, 10.00 mmol) is reacted as described above with 1-ethynylcyclohexene[12] (1.06 g, 10.00 mmol; **2b**), *n*-BuLi (10.00 mmol), and triethyloxonium tetrafluoroborate (2.85 g, 15.00 mmol) to give compound **3c** (3.79 g, 78%, brown crystals, R_f = 0.5 in pentane, mp 67 °C). ^{1}H NMR (C_6D_6): δ 6.28 (1 H, m, 2′-H), 4.01 (2 H, q, OCH_2), 2.03, 1.70, 1.31, and 1.16 (2 H each, m each, 3′-H_2 to 6′-H), 0.98 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 283.3 (C_q, W=C), 206.2 and 198.6 [1:4, C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 145.7 (CH, C2′), 136.5 (C_q, broad, C3), 121.6 (C_q, C1′), 96.9 (C_q, broad, C2′), 76.0 (OCH_2), 28.9, 27.2, 22.3, and 21.3 (CH_2 each, C3′−C6′), 14.7 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2144.7 [ν(C≡C)]; 2067.6 (25), 1983.2 (30), 1955.2 (100) [ν(C≡O)]. Anal. Calcd for $C_{16}H_{14}NO_6W$ (486.1): C, 39.53; H, 2.90. Found: C, 39.84; H, 3.01.

Pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (3d). $W(CO)_6$ (3.52 g, 10.00 mmol) is reacted as described above with 1-ethynylcycloheptene[12] (1.20 g, 10.00 mmol; **2c**), *n*-BuLi (10.00 mmol), and triethyloxonium tetrafluoroborate (2.85 g, 15.00 mmol) to give compound **3d** (3.60 g, 72%, brown crystals, R_f = 0.5 in pentane, mp 32 °C). ^{1}H NMR (C_6D_6): δ 6.62 (1 H, t, ^3J = 7 Hz, 2′-H), 4.01 (2 H, q, OCH_2); 2.28, 1.87, 1.49, 1.38, and 1.26 (2 H each, m each, 3′-H_2 to 7′-H), 1.01 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 286.1 (C_q, W=C), 206.3 and 198.6 [1:4, C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 151.2 (CH, C2′), 136.5 (C_q, broad, C3), 127.6 (C_q, C1′), 97.3 (C_q, broad, C2′), 75.9 (OCH_2), 34.2, 32.0, 30.8, 26.9, and 26.2 (CH_2 each, C3′−C7′), 14.7 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2137.2 [ν(C≡C)]; 2067.3 (25), 1983.9 (30), 1955.0 (100) [ν(C≡O)]. MS (70 eV; *m/e* (%)): 500 (10) [M^+], 444 (20) [$M^+ - 2$ CO], 360 (20) [$M^+ - 5$ CO], 302 (40), 180 (100). Anal. Calcd for $C_{17}H_{16}NO_6W$ (500.2): C, 40.82; H, 3.22. Found: C, 40.98; H, 3.32.

4-(Cyclopent-1-enyl)-4-(dimethylamino)-2-ethoxy-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene ((3*E*)-5a) and Pentacarbonyl[1-(dimethylazonia)-3-ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-yl]tungstate (6a). A solution of 0.5 mmol of dimethylamine (**4a**) in 2 mL of dry diethyl ether is added dropwise with stirring at 0 °C to pentacarbonyl-[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (236 mg, 0.5 mmol; **3a**) in 1 mL of dry diethyl ether in a 5 mL screw-top vessel. After a color change from brown to yellow is observed, indicating the point of equivalency, the solution is cooled to −20 °C to give compound **5a** (217 mg, 84%, yellow crystals). Compound (3*E*)-**5a** (259 mg, 0.5 mmol) in 2 mL of diethyl ether is rearranged completely to compound **6a** at 20 °C and 12 h (pale yellow crystals at −15 °C, 231 mg, 89%, R_f = 0.3 in 1:1 pentane/diethyl ether, mp 111 °C). Addition of 2 mL of pentane to the supernatant affords another crop of ca. 30 mg of compound **6a**. The rearrangement of (3*E*)-**5a** to **6a** is very smooth and can be followed by NMR in $CDCl_3$. Compound **6a** is conveniently prepared also in a one-pot procedure from compound **3a** directly.

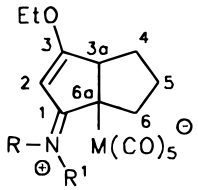
(3*E*)-5a. ^{1}H NMR ($CDCl_3$ at 263 K, freshly prepared sample): δ 6.30 (1 H, s, 3-H), 5.55 (1 H, "s", 2′-H), 4.30 (2 H, m, diastereotopic OCH_2), 3.09 and 3.01 (3 H each, s each, NMe_2), 2.62, 2.51, 2.33, and 2.00 (1:2:1:2 H, m, each 3 CH_2), 1.30 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$ at 263 K): δ 268.5 (C_q, W=C), 204.6 and 199.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 157.2 (C_q, C4), 139.0 (C_q, C1′), 130.5 (CH, C2′), 119.3 (CH, C3), 75.7 (OCH_2), 40.8 and 40.5 [$N(CH_3)_2$], 35.0 (CH_2, C8), 33.2 (CH_2, C6), 22.6 (CH_2, C7), 14.1 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2056.3 (5), 1943.6 (10), 1923.7 (100) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 517 (10) [M^+], 461 (10) [$M^+ - 2$ CO], 433 (30) [$M^+ - 3$ CO], 405 (10) [$M^+ - 4$CO], 377 (20) [$M^+ - 5$ CO], 193 (100). Anal. Calcd for $C_{17}H_{19}NO_6W$ (517.2): C, 39.48; H, 3.70; N, 2.71. Found: C, 39.12; H, 3.57; N, 2.51.

X-ray crystal structure analysis of compound (3*E*)-**5a**: formula $C_{17}H_{19}NO_6W$, M_r = 517.18, 0.30 × 0.25 × 0.10 mm, a = 9.412(1) Å, b = 10.337(1) Å, c = 11.643(4) Å, α = 112.01(1)°, β = 105.69(1)°, γ = 102.42°, V = 945.41(16) Å^3, ρ_{calcd} = 1.817 g cm^{-3}, μ = 61.40 cm^{-1}, empirical absorption correction via ψ scan data (0.85.7 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 4041 reflections collected ($\pm h$, $-k$, $\pm l$), (sin θ)/λ = 0.62 Å^{-1}, 3820 independent and 3368 observed reflections [$I \geq 2\sigma(I)$], 229 refined parameters, R1 = 0.039, wR2 = 0.104, GOF 1.109,

(12) Preparation follows the procedure given in ref 5, but dehydration of the carbinol with phosphoryl chloride/pyridine was carried out at 25 °C, since this reaction was exothermic. Furthermore, the reaction mixture was not hydrolyzed but distilled to give a mixture of 1-ethynylcycloalkene and pyridine as the only volatile products, from which pyridine was extracted by stirring with a small excess of phosphoric acid (ca. 80%) at 20 °C, leaving the 1-ethynylcycloalkene behind in good yields.

maximum (minimum) residual electron density 1.82 (−4.42) e Å^{-3}, hydrogens calculated and riding.[13]

6a. ^{1}H NMR (C_6D_6): δ 4.75 (1 H, s, 2-H), 3.82 (1 H, dd, ^3J = 8 Hz, ^3J = 8, 3a-H), 3.47 (2 H, m, diastereotopic OCH_2), 2.77 and 2.45 (3 H each, s each, NMe_2), 2.25 and 1.70 (1 H each, m each, diastereotopic 6-H_2), 1.90 and 1.51 (1 H each, m each, diastereotopic 5-H_2), 1.81 and 0.85 (1 H each, m each, diastereotopic 4-H_2), 1.00 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.9 [C_q, 5 C, $W(CO)_5$], 193.5 (C_q, C═N), 185.2 (C_q, ═C−O), 93.0 (CH, C2), 67.5 (OCH_2), 67.0 (CH, C3a), 50.1 (C_q, C6a), 43.0 and 41.0 [$N(CH_3)_2$], 38.6 (CH_2, C6), 32.8 (CH_2, C4), 31.9 (CH_2, C5), 14.0 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 2050.5 (5), 1943.6 (10), 1892.4 (100) [ν(C≡O)]; 1584.0 (20) [ν(C═N$^+$)]. MS (70 eV; *m/e* ^{184}W (%)): 517 (10) [M$^+$], 461 (10) [M$^+$ − 2 CO], 433 (30) [M$^+$ − 3 CO], 405 (10) [M$^+$ − 4CO], 377 (20) [M$^+$ − 5 CO], 193 (100), 165 (90). Anal. Calcd for $C_{17}H_{19}NO_6W$ (517.2): C, 39.48; H, 3.70; N, 2.71. Found: C, 39.32; H, 4.05; N, 2.65.



4-(Cyclopent-1-enyl)-4-(dimethylamino)-2-ethoxy-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene ((3*E*)-5b) and Pentacarbonyl[1-(dimethylazonia)-3-ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-yl]chromate (6b). Dimethylamine (**4a**) is reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]chromium (**3b**) as described above to give a ca. 80% yield of compound (3*E*)-**5b**. Compound (3*E*)-**5b** (222 mg, 0.5 mmol) in 2 mL of diethyl ether (vide supra) is rearranged at 20 °C and 14 h. Compound **6b** is isolated from this solution at −15 °C as a yellow oil, which affords yellow crystals (196 mg, 85%, R_f = 0.3 in pentane/diethyl ether 1:1, mp 92 °C) within 1−2 h.

(3*E*)-5b. ^{1}H NMR (C_6D_6, 278 K, freshly prepared sample): δ 6.34 (1 H, s, 3-H), 5.20 (1 H, "s", 2′-H), 4.54 (2 H, m, diastereotopic OCH_2), 2.20 (6 H, s, NMe_2), 2.15, 1.95, 1.70, 1.62 (1:2:1:2 H, m each 3 CH_2), 1.03 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$ at 263 K): δ 287.1 (C_q, Cr═C), 225.0 and 220.3 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 154.2 (C_q, C4), 139.8 (C_q, C1′), 130.8 (CH, C2′), 118.2 (CH, C3), 73.7 (OCH_2), 39.7 [$N(CH_3)_2$], 35.6 (CH_2, C8), 33.4 (CH_2, C6), 23.2 (CH_2, C7), 15.4 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2044.4 (5), 1959.1 (10), 1915.6 (100) [ν(C≡O)]. Anal. Calcd for $C_{17}H_{19}CrNO_6$ (385.3): C, 52.99; H, 4.97; N, 3.63. Found: C, 52.90; H, 5.12; N, 3.68.

6b. ^{1}H NMR (C_6D_6): δ 4.90 (1 H, s, 2-H), 3.60 (3 H, m, 3a-H and OCH_2), 2.85 and 2.60 (3 H each, s each, NMe_2), 2.50 and 1.80 (1 H each, m each, diastereotopic 6-H_2), 2.15 and 1.62 (1 H each, m each, diastereotopic 5-H_2), 1.81 and 0.90 (1 H each, m each, diastereotopic 4-H_2), 1.10 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 224.6 and 219.5 [C_q each, *trans*- and *cis*-CO, $Cr(CO)_5$], 191.7 (C_q, C═N), 183.6 (C_q, ═C−O), 93.5 (CH, C2), 67.6 (OCH_2), 65.0 (CH, C3a), 51.8 (C_q, C6a), 42.2 and 41.3 [$N(CH_3)_2$], 36.7 (CH_2, C6), 32.3 (CH_2, C4), 31.8 (CH_2, C5), 14.0 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2044.4 (5), 1959.6 (10), 1915.6 (100) [ν(C≡O)], 1591.4 (20) [ν(C═N$^+$)]. MS (70 eV; *m/e* (%)): 385 (10) [M$^+$], 301 (10) [M$^+$ − 3 CO], 273 (10) [M$^+$ − 4 CO], 245 (20) [M$^+$ − 5 CO], 193 (10) [ligand], 165 (40) [ligand − C_2H_4], 124 (100). Anal. Calcd for $C_{17}H_{19}CrNO_6$ (385.3): C, 52.99; H, 4.97; N, 3.63. Found: C, 52.95; H, 5.12; N, 3.68.

4-(Cyclopent-1-enyl)-2-ethoxy-4-[(*S*)-(methoxymethyl)-pyrrolidine]-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene ((3*E*)-5c) and Pentacarbonyl{3-ethoxy-1-[(2*S*)-2-(methoxymethyl)pyrrolidinium]-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-yl}tungstate ((2″*S*,3a*R*,6a*S*)-6c). (*S*)-(−)2-(Methoxymethyl)pyrrolidine (58 mg, 0.5 mmol; **4b**) is reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (236 mg, 0.5 mmol; **3a**) as described above, except that the reaction is performed in 1:1 diethyl ether/pentane, to give compound (3*E*)-**5c** (261 mg, 89%, R_f = 0.6 in 3:1 pentane/diethyl ether, yellow crystals, mp 85 °C). Compound (3*E*)-**5c** (294 mg, 0.5 mmol) in 2 mL of diethyl ether is completely rearranged to compound (2″*S*,3a*R*,6a*S*)-**6c** at 20 °C and 5 h (yellow crystals obtained at −15 °C, 270 mg, 92%, R_f = 0.6 in 3:1 pentane/diethyl ether, mp 85 °C).

(3*E*)-5c. ^{1}H NMR ($CDCl_3$ at 263 K, 600 MHz, freshly prepared sample, shifts of stereoisomer (3*E*)-**5c′** resulting from hindered rotation of the C4−N bond in brackets): δ 6.44 [6.27] (1 H, s, 3-H), 5.61 [5.52] (1 H, "s", 2′-H), 4.40 [4.38] (2 H, m, diastereotopic 2-OCH_2), 4.06 [3.66] (1 H, t, NCH), 3.60−3.02 [3.60−3.02] (4 H, m, diastereotopic 2″-CH_2O), 3.27 [3.24] (3 H, OCH_3), 2.6−2.4 [2.6−2.4] (4 H, 3″-H_2 and 4″-H_2), 2.44 [2.40] and 2.12−1.84 [2.12−1.84] (2:4 H, m each 3′-H_2, 4′-H_2, and 5′-H_2), 1.36 [1.34] (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$ at 263 K): δ 267.8 [265.8] (C_q, W═C), 204.3 [204.2] and 199.7 [199.6] [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 153.4 (C_q dynamically broadened, C4), 140.3 [138.5] (C_q broad, C1′), 129.7 [128.2] (CH broad, C2′), 120.6 [120.6] (CH broad, C3), 76.1 [76.0] (2-OCH_2), 73.0 [70.0] (2″-CH_2O), 59.1 [59.0] (OCH_3), 58.7 [58.7] (NCH), 49.3 [49.0] (NCH_2 broad), 37.0 [35.9] and 22.2 [22.0] (CH_2 each, C3″ and C4″), 34.8 [33.3] (CH_2, C8), 28.5 [27.2] (CH_2, C6), 22.9 [22.8] (CH_2, C7), 15.3 [15.2] (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2056.0 (15), 1943.6 (10), 1923.6 (100) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 587 (10) [M$^+$], 531 (10) [M$^+$ − 2 CO], 503 (30) [M$^+$ − 3 CO], 447 (20) [M$^+$ − 5 CO], 263 (100) [ligand], 248 [100]. Anal. Calcd for $C_{21}H_{25}NO_7W$ (587.3): C, 42.95; H, 4.29; N, 2.39. Found: C, 42.89; H, 5.17; N, 2.55.

(2″*S*,3a*R*,6a*S*)-6c. ^{1}H NMR (C_6D_6): δ 4.95 (1 H, s, 2-H), 3.97 (1 H, m, 2′-H), 3.95 and 3.10 (1 H each, m each, diastereotopic 5′-H_2), 3.90 (1 H, m, 3a-H), 3.55 (2 H, m, diastereotopic 3-OCH_2), 3.10 and 2.95 (1 H each, dd each, diastereotopic 2′-OCH_2), 2.99 (3 H, s, OCH_3), 2.20 and 2.09 (1 H each, m each, diastereotopic 6-H_2), 1.90 and 1.03 (1 H each, m each, diastereotopic 4-H_2), 1.84, 1.72, and 1.50 (2:1:1 H, m each, $NCH_2CH_2CH_2$), 1.63 and 1.58 (1 H each, m each, diastereotopic 5-H_2), 1.05 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.3 [C_q, 5 C, $W(CO)_5$], 190.3 (C_q, C═N$^+$), 184.9 (C_q, ═C−O), 95.0 (CH, C2), 73.8 (2′-CH_2O), 67.6 (3-OCH_2), 66.7 (CH, C3a), 62.2 (NCH), 59.0 (OCH_3), 51.0 (NCH_2), 50.6 (C_q, C6a), 38.3 (CH_2, C6), 32.6 (CH_2, C4), 31.6 (CH_2, C5), 27.4 and 24.2 (CH_2 each, C3′ and C4′), 14.4 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2054.1 (10), 1957.2 (10), 1911.6 (100) [ν(C≡O)], 1587.4 [ν(C═N$^+$)]. MS (70 eV; *m/e* ^{184}W (%)): 587 (5) [M$^+$], 431 (5) [M$^+$ − 2 CO], 503 (5) [M$^+$ − 3 CO], 447 (20) [M$^+$ − 5CO], 263 (65) [ligand], 248 (100). Anal. Calcd for $C_{21}H_{25}NO_7W$ (587.3): C, 42.95; H, 4.29; N, 2.39. Found: C, 42.89; H, 4.27; N, 2.55.

X-ray crystal structure analysis of compound (2″*S*,3a*R*,6a*S*)-**6c**: formula $C_{21}H_{25}NO_7W$, M_r = 587.27, 0.5 × 0.4 × 0.1 mm, a = 10.613(3) Å, b = 18.328(4) Å, c = 12.273(4) Å, β = 105.49-(2)°, V = 2300.6(11) Å^3, ρ_{calcd} = 1.696 g cm^{-3}, μ = 50.60 cm^{-1}, empirical absorption correction via ψ scan data (0.644 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1$ (No. 4), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 4995 reflections collected (±h, +k, +l), (sin θ)/λ = 0.62 Å^{-1}, 4774 independent and 4113 observed reflections [$I \geq 2\sigma(I)$], 528 refined parameters, R1 = 0.066, wR2 = 0.172, GOF 1.029, maximum (minimum) residual electron density 4.45 (−2.07) e Å^{-3}, Flack parameter 0.00(3), group C17−O18−C19 in molecule **I** disordered, refined with isotropic thermal parameters and with restraints, hydrogens calculated and riding.[13]

(13) All data sets were collected with an Enraf-Nonius CAD4/MACH3 diffractometer, equipped with sealed-tube or rotating-anode generators. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93 and SHELXL-97, graphics (with unsystematical numbering schemes) DIAMOND.

4-(Cyclopent-1-enyl)-2-ethoxy-4-[(*S*)-(methoxymethyl)-pyrrolidine-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene ((3*E*)-5d) and Pentacarbonyl{3-ethoxy-1-[2-(methoxymethyl)pyrrolidinium]-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-yl}chromate ((2″*S*,5*S*)-6d). (*S*)-(−)-2-(Methoxymethyl)pyrrolidine (58 mg, 0.5 mmol; **4b**) is reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]-chromium (170 mg, 0.5 mmol; **3b**) as described above to give compound (3*E*)-**5d** (184 mg, 81%, R_f = 0.6 in 2:1 pentane/diethyl ether, yellow crystals, mp 82 °C). Compound (3*E*)-**5d** (227 mg, 0.5 mmol) in 2 mL of diethyl ether is completely rearranged at 20 °C and 4 h to compound (2″*S*,5*S*)-**6d** (yellow crystals obtained at −15 °C, 195 mg, 86%, R_f = 0.6 in 2:1 pentane/diethyl ether, mp 82 °C).

(3*E*)-5d. ^{1}H NMR ($CDCl_3$ at 263 K, 600 MHz, freshly prepared sample, stereoisomer (3*E*)-**5d** in brackets): δ 6.37 [6.21] (1 H, s, 3-H), 5.59 [5.50] (1 H, "s", 2′-H), 4.60 [4.55] (2 H, m, diastereotopic 2-OCH_2), 4.16 [3.80] (1 H, t, NCH), 3.60−3.02 [3.60−3.02] (4 H, m, diastereotopic 2″-CH_2O), 3.35 [3.29] (3 H, OCH_3), 2.6−2.4 [2.6−2.4] (4 H, 3″-H_2 and 4″-H_2), 2.44 [2.44] and 2.12−1.84 [2.12−1.84] (2:4 H, m each 3′-H_2, 4′-H_2, and 5′-H_2), 1.36 [1.30] (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$ at 263 K): δ 279.8 [274.6] (C_q, Cr=C), 224.4 [224.2] and 219.0 [219.0] [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 152.3 [152.3] (C_q dynamically broadened, C4), 142.3 [138.7] (C_q broad, C1′), 129.7 [128.2] (CH broad, C2′), 118.4 [118.4] (CH broad, C3), 73.4 [73.1] (2-OCH_2), 73.0 [70.1] (2″-CH_2O), 59.0 [58.6] (OCH_3), 58.5 (NCH), 49.9 [48.9] (NCH_2 broad), 38.0 [36.0] and 22.6 [22.0] (CH_2 each, C3″ and C4″), 35.0 [33.2] (CH_2, C8), 28.3 [27.2] (CH_2, C6), 22.9 [22.6] (CH_2, C7), 15.4 [15.3] (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2056.0 (15), 1943.6 (10), 1923.6 (100) [ν(C≡O)]. MS (70 eV; *m/e* (%)): 455 (10) [M^+], 399 (10) [M^+ − 2 CO], 343 (30) [M^+ − 4 CO], 315 (20) [M^+ − 5 CO], 263 (100) [ligand], 248 [100]. Anal. Calcd for $C_{21}H_{25}CrNO_7$ (455.3): C, 55.38; H, 5.53; N, 3.08. Found: C, 55.04; H, 5.65; N, 3.16.

(2″*S*,5*S*)-6d. ^{1}H NMR (C_6D_6): δ 4.95 (1 H, s, 2-H), 3.82 (1 H, m, 2′-H), 3.78 and 3.00 (1 H each, m each, diastereotopic 5′-H_2), 3.70 (1 H, m, 3a-H), 3.65 (2 H, m, diastereotopic 3-OCH_2), 2.92 and 2.81 (1 H each, diastereotopic 2′-CH_2O), 2.85 (3 H, s, OCH_3), 2.10−1.60 (10 H, m, 5 CH_2), 0.90 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 224.6 and 219.8 [C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 187.8 (C_q, C=N^+), 182.8 (C_q, =C−O), 95.0 (CH, C2), 73.7 (2′-CH_2O), 64.6 (CH, C3a), 62.2 (NCH), 59.0 (OCH_3), 54.3 (C_q, C6a), 51.6 (NCH_2), 36.0 (CH_2, C6), 32.0 (CH_2, C5), 31.0 (CH_2, C5), 27.1 and 24.0 (CH_2 each, C3′ and C′4), 14.1 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2047.2 (10), 1986.2 (10), 1926.4 (100) [ν(C≡O)]; 1558.4 [ν(C=N^+)]. MS (70 eV; *m/e* ^{184}W (%)): 587 (5) [M^+], 431 (5) [M^+ − 2 CO], 503 (5) [M^+ − 3 CO], 447 (20) [M^+ − 5CO], 263 (65) [ligand], 248 (100). Anal. Calcd for $C_{21}H_{25}CrNO_7$ (455.3): C, 55.38; H, 5.53; N, 3.08. Found: C, 55.21; H, 5.27; N, 2.95.

1-(Dimethylazonia)-3-ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalene Tetrafluoroborate (7a) and 3-(Dimethylamino)-3a,5,6,6a-tetrahydro-4*H*-pentalen-1-one (9a). Pentacarbonyl-[1-(dimethylazonia)-3-ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-yl]tungstate (259 mg, 0.5 mmol; **6a**) in 5 mL of diethyl ether, water (9 mg, 0.5 mmol), and Et_3OBF_4 (95 mg, 0.5 mmol) was stirred until the mixture turned colorless (at 20 °C, 14 h). The crystalline residue of compound **7a** was washed with diethyl ether in order to remove $W(CO)_6$ and dried in vacuo (125 mg, 89%). Reaction of **7a** with 10% KOH in water affords the colorless ketone **9a**. A 1:1 mixture of compound **6a** and pyridine in C_6D_6 was heated for 5 h at 70 °C to give a 1:1 mixture of compounds **6a** and **9a**.

7a. ^{1}H NMR ($CDCl_3$): δ 5.91 (1 H, s, 2-H), 4.32 (2 H, m, diastereotopic OCH_2), 3.59 and 3.41 (1 H each, m each, 3a-H and 6a-H), 3.40 and 3.39 (3 H each, s each, NMe_2), 2.21 and 1.76 (1 H each, m each, diastereotopic 6-H_2), 1.86 and 1.72 (1 H each, m each, diastereotopic 5-H_2), 1.74 and 1.49 (1 H each, m each, diastereotopic 4-H_2), 1.42 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 193.7 (C_q, =COEt), 187.6 (C_q, C=N), 98.9 (CH, C2), 70.6 (OCH_2), 49.4 and 42.5 (CH each, C3a and C6a), 45.3 and 43.1 [$N(CH_3)_2$], 28.9 and 28.4 (CH_2 each, C6 and C4), 24.6 (CH_2, C5), 13.9 (OCH_2CH_3). IR (diffuse reflection; cm^{-1}): 1652.0 and 1584.3 [ν(C=CC=N^+)]. MS (70 eV; *m/e* ^{184}W (%)): 517 (10) [M^+], 461 (10) [M^+ − 2 CO], 433 (30) [M^+ − 3 CO], 405 (10) [M^+ − 4CO], 377 (20) [M^+ − 5 CO], 193 (100) [ligand], 165 (90) [193 − C_2H_4]. Anal. Calcd for $C_{17}H_{20}BF_4NO$ (341.2): C, 59.85; H, 5.91; N, 4.12. Found: C, 59.12; H, 6.10; N, 3.90.

9a. ^{1}H NMR ($CDCl_3$): δ 4.86 (1 H, s, 2-H), 3.18 and 2.80 (1 H each, m each, 3a-H and 6a-H), 3.05 and 2.85 (3 H each, s each, NMe_2), 1.94 and 1.60 (1 H each, m each, diastereotopic 6-H_2), 1.76 and 1.57 (1 H each, m each, diastereotopic 5-H_2), 1.54 and 1.40 (1 H each, m each, diastereotopic 4-H_2). ^{13}C NMR ($CDCl_3$): δ 205.5 (C_q, C=O), 179.6 (C_q, =CN), 100.2 (CH, C2), 51.4 and 44.1 (CH each, C3a and C6a), 39.5 and 38.5 [$N(CH_3)_2$], 30.3 and 29.3 (CH_2 each, C4 and C6), 24.2 (CH_2, C5). IR (diffuse reflection; cm^{-1}): 1576 [ν(C=O)]. MS (70 eV; *m/e* (%)): 165 (40) [M^+], 137 (20), 124 (100). Anal. Calcd for $C_{10}H_{15}NO$ (165.2): C, 72.69; H, 9.15; N, 8.48. Found: C, 72.24; H, 9.80; N, 8.82.

4-(Cyclopent-1-enyl)-2-ethoxy-1,1,1,1,1-pentacarbonyl-4-(phenylamino)-1-tungsta-1,3-butadiene ((3*Z*)-10a), Pentacarbonyl[(3-ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-ylidene)phenylamine-*N*]tungsten (*syn*-11a and *anti*-11a), and (3-Ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-ylidene)phenylamine (12). A solution of aniline (47 mg, 0.5 mmol) in 1 mL of dry diethyl ether is a added dropwise and slowly at 0 °C with stirring to pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (236 mg, 0.50 mmol; **3a**) in 1 mL of dry diethyl ether. A color change from brown to red is observed at the point of equivalency after ca. 5 min. The solvent is removed immediately by evaporation to leave a red, thermolabile oil of compound (3*Z*)-**10a** (R_f = 0.7 in 10:1 pentane/diethyl ether). Compound (3*Z*)-**10a** generated by reaction of aniline (47 mg, 0.5 mmol) with **3a** (236 mg, 0.5 mmol) is rearranged at 50 °C and 4 h in 1 mL of toluene to give a 2:1 mixture of compounds *syn*-**11a** and *anti*-**11a** (255 mg, 89%, orange oil), which is separated by chromatography on silica gel to give *anti*-**11a** (R_f = 0.8 10:1 pentane/diethyl ether, yellow crystals, mp 136 °C) and *syn*-**11a** (R_f = 0.7 10:1 pentane/diethyl ether, orange crystals, mp 108 °C) and a small fraction of the colorless, very polar compound **12**. Compound *syn*-**11a** rearranges to *anti*-**11a** in C_6D_6 at 50 °C. Compound **12** is generated under the influence of air in solutions both of *syn*-**11a** and *anti*-**11a**.

(3*Z*)-10a. ^{1}H NMR (C_6D_6 at 283 K, freshly prepared sample): δ 10.12 (1 H, s broad, NH), 7.01, 6.92, and 6.75 (2:1:2 H; "t", "t", "d"; C_6H_5), 6.88 (1 H, s, 3-H), 6.08 (1 H, "s" broad, 2′-H), 4.45 (2 H, q, OCH_2), 1.96 and 1.46 (4:2 H, CH_2 each), 0.96 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6 at 283 K): δ 275.0 (C_q, W=C), 204.7 and 199.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 149.7 (C_q, *i*-C NPh), 139.0 and 138.8 (C_q each, C4 and C1′), 139.7 (CH, C2′), 129.7, 129.6, 126.3, 124.8, and 123.5 (CH each, 1:1:1:1:1; 2 *m*-C, *p*-C, and 2 *o*-C; Ph), 122.5 (CH, C2′), 94.0 (CH, C3), 77.0 (OCH_2), 33.8 and 33.4 (CH_2 each, C8 and C6), 24.0 (CH_2, C7), 14.9 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2058.8 (5), 1968.8 (10), 1931.0 (100) [ν(C≡O)]. Anal. Calcd for $C_{21}H_{19}NO_6W$ (565.2): C, 44.62; H, 3.39; N, 2.48. Found: C, 45.01; H, 3.57; N, 2.57.

***anti*-11a.** ^{1}H NMR (C_6D_6): δ 7.16 and 7.12 (1 H each, m each, *m*-H Ph), 6.90 (CH, m, *p*-H Ph), 6.87 and 6.72 (1 H each, *o*-H Ph), 4.48 (1 H, s, 2-H), 3.28 (1 H, m, 6a−H), 2.85 and 2.75 (1 H each, m each, diastereotopic OCH_2), 2.70 (1 H, m, 3a−H), 2.15 and 1.65 (1 H each, m each, diastereotopic 4-H_2), 2.00 and 1.41 (1 H each, m each, diastereotopic 5-H_2), 1.20 (2 H, m each, diastereotopic 6-H_2), 0.70 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 204.4 and 199.7 [C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 190.7 (C_q, C=N), 184.0 (C_q, =C−O), 158.5 (C_q, *i*-C NPh), 129.7 and 129.5 (CH each, *m*-C NPh), 125.7 and 121.4 (CH each, *o*-C NPh), 121.9 (CH, *p*-C NPh), 99.9 (CH, C2), 67.2 (OCH_2), 50.0 and 48.6 (CH each, C6a and C3a), 32.6 (CH_2, C4), 28.5

(CH_2, C6), 24.0 (CH_2, C5), 13.7 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2067.4 (5), 1970.5 (10), 1927.9 (100), 1907.6 (30) [ν(C≡O)]; 1576.4 (20) [ν(C═N)]. MS (70 eV; *m/e* ^{184}W (%)): 565 (10) [M^+], 537 (10), 509 (80) [$M^+ - 2$ CO], 481 (10) [$M^+ - 3$ CO], 453 (40) [$M^+ - 4$CO], 425 (60) [$M^+ - 5$ CO], 241 (100) [ligand]. Anal. Calcd for $C_{21}H_{19}NO_6W$ (565.2): C, 44.62; H, 3.39; N, 2.48. Found: C, 44.79; H, 3.82; N, 2.70.

***syn*-11a.** ^{1}H NMR (C_6D_6): δ 7.07 (2 H, m, *m*-H Ph), 6.84 (CH, m, *p*-H Ph), 6.82 and 6.52 (1 H each, *o*-H Ph), 5.92 (1 H, s, 2-H), 3.62 (2 H, m, diastereotopic OCH_2), 2.62 and 2.51 (1 H each, m each, 6a-H and 3a-H), 1.4−0.8 (6 H, m, 3 CH_2), 0.92 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 203.3 and 199.9 [C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 189.8 (C_q, C═N), 184.6 (C_q, ═C−O), 155.3 (C_q, *i*-C NPh), 129.8 and 129.4 (CH each, *m*-C NPh), 125.6 (CH, *p*-C NPh), 123.9 and 121.3 (CH each, *o*-C NPh), 105.7 (CH, C2), 68.0 (OCH_2), 50.0 and 45.7 (CH each, C6a and C3a), 32.6 (CH_2, C4), 28.7 (CH_2, C6), 26.0 (CH_2, C5), 13.8 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2067.4 (5), 1970.1 (10), 1928.9 (100), 1907.1 (30) [ν(C≡O)]; 1575.4 (20) [ν(C═N)]. MS (70 eV; *m/e* ^{184}W (%)): 565 (20) [M^+], 537 (10), 509 (95) [$M^+ - 2$ CO], 481 (10) [$M^+ - 3$ CO], 453 (40) [$M^+ - 4$CO], 425 (60) [$M^+ - 5$ CO], 241 (100) [ligand]. Anal. Calcd for $C_{21}H_{19}NO_6W$ (565.2): C, 44.62; H, 3.39; N, 2.48. Found: C, 44.63; H, 3.64; N, 2.64.

X-ray crystal structure analysis of compound *anti*-**11a**: formula $C_{21}H_{19}NO_6W$, $M_r = 565.22$, 0.3 × 0.2 × 0.2 mm, $a = 9.801(4)$ Å, $b = 10.423(3)$ Å, $c = 11.903(3)$ Å, $\alpha = 97.39(2)°$, $\beta = 112.70(2)°$, $\gamma = 104.98(2)°$, $V = 1047.5(6)$ Å^3, $\rho_{calcd} = 1.792$ g cm^{-3}, $\mu = 55.50$ cm^{-1}, empirical absorption correction via ψ scan data ($0.799 \le C \le 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\ 73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4424 reflections collected ($\pm h$, $\pm k$, $+l$), (sin θ)/$\lambda = 0.62$ Å^{-1}, 4215 independent and 3881 observed reflections [$I \ge 2\sigma(I)$], 263 refined parameters, R1 = 0.021, wR2 = 0.056, GOF 1.167, maximum (minimum) residual electron density 0.84 (−1.17) e Å^{-3}, hydrogens calculated and riding.[13]

12. ^{1}H NMR (C_6D_6): δ 7.29 (2 H, m, *m*-H Ph), 7.12 (2 H, m, *o*-H Ph), 6.99 (CH, m, *p*-H Ph), 5.18 (1 H, s, 3-H), 3.18 (1 H, m, 5-H), 3.05 and 2.85 (1 H each, m each, diastereotopic OCH_2), 2.30 (1 H, m, 1-H), 1.7−1.2 (6 H, m, 3 CH_2), 0.82 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 181.5 (C_q, C═N), 177.6 (C_q, ═C−O), 154.5 (C_q, *i*-C NPh), 129.2 (CH, *m*-C NPh), 122.1 (CH, *p*-C NPh), 121.3 (CH, *o*-C NPh), 97.4 (CH, C3), 66.3 (OCH_2), 48.7 and 46.6 (CH each, C5 and C1), 32.3 (CH_2, C8), 29.4 (CH_2, C6), 24.2 (CH_2, C7), 14.0 (OCH_2CH_3). IR (diffuse reflection; cm^{-1} (%)): 1645.4 [ν(C═N)]. MS (70 eV; *m/e* (%)): 241 (100) [M^+], 213 (40), 185 (30), 144 (30). Anal. Calcd for $C_{21}H_{19}NO_6W$ (565.2): C, 44.62; H, 3.39; N, 2.48. Found: C, 44.79; H, 3.82; N, 2.70.

4-(Cyclopent-1-enyl)-2-ethoxy-1,1,1,1,1-pentacarbonyl-4-(phenylamino)-1-chroma-1,3-butadiene ((3*Z*)-10b) and Pentacarbonyl[(3-ethoxy-3a,5,6,6a-tetrahydro-4*H*-pentalen-6a-ylidene)phenylamine-*N*]chromium (*syn*-11b and *anti*-11b). A solution of aniline (47 mg, 0.5 mmol) is reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]chromium (170 mg, 0.5 mmol; **3b**) as described above to give compound (3*Z*)-**10a** ($R_f = 0.7$ in 10:1 pentane/diethyl ether; red, thermolabile oil). Compound (3*Z*)-**10b** generated by reaction of aniline (47 mg, 0.5 mmol) with **3b** (170 mg, 0.5 mmol) as described above is rearranged at 50 °C and 4 h in 1 mL of toluene to give a 1:1 mixture of compounds *syn*-**11b** and *anti*-**11b** (255 mg, 89%, orange oil), which are separated by chromatography on silica gel to give *anti*-**11b** ($R_f = 0.8$ 10:1 pentane/diethyl ether, yellow crystals, mp 99 °C) and *syn*-**11b** ($R_f = 0.7$ 10:1 pentane/diethyl ether) and a fraction of the colorless, very polar compound **12** (vide supra). Compound *syn*-**11b** rearranges to *anti*-**11b** in C_6D_6 at 50 °C. Compound **12** is generated under the influence of air from solutions both of *syn*-**11b** and *anti*-**11b**.

(3*Z*)-10b. ^{1}H NMR (C_6D_6 at 303 K, freshly prepared sample): δ 10.00 (1 H, s broad, NH), 6.90, 6.82, and 6.71 (2:1:2 H, C_6H_5), 6.68 (1 H, s, 3-H), 6.08 (1 H, "s" broad, 2′-H), 4.62 (2 H, q, OCH_2), 1.96 and 1.42 (4:2 H, CH_2 each), 0.90 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6 at 303 K): δ 298.8 (C_q, Cr═C), 224.4 and 219.2 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 145.7 (C_q, *i*-C NPh), 140.0 and 138.8 (C_q each, C4 and C1′), 139.5 (CH, C2′), 129.7, 129.4, 126.9, 125.0, and 122.5 (CH each, 1:1:1:1:1; 2 *m*-C, *p*-C and 2 *o*-C; NPh), 122.5 (CH, C2′), 94.2 (CH, broad, C3), 74.4 (OCH_2), 33.8 and 33.3 (CH_2 each, C8 and C6), 24.0 (CH_2, C7), 15.0 (OCH_2CH_3).

***anti*-11b.** ^{1}H NMR (C_6D_6): δ 7.15 and 7.10 (1 H each, m each, *m*-H Ph), 6.90 (CH, m, *p*-H Ph), 6.85 and 6.73 (1 H each, *o*-H Ph), 4.47 (1 H, s, 2-H), 3.30 (1 H, m, 6a-H), 2.83 and 2.70 (1 H each, m each, diastereotopic OCH_2), 2.74 (1 H, m, 3a-H), 2.10 and 1.62 (1 H each, m each, diastereotopic 4-H_2), 2.03 and 1.41 (1 H each, m each, diastereotopic 5-H_2), 1.23 (2 H, m each, diastereotopic 6-H_2), 0.68 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 222.6 and 215.5 [C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 190.6 (C_q, C═N), 182.6 (C_q, ═C−O), 159.0 (C_q, *i*-C NPh), 129.9 and 129.6 (CH each, *m*-C NPh), 125.1 and 121.5 (CH each, *o*-C NPh), 125.0 (CH, *p*-C NPh), 100.1 (CH, C2), 67.0 (OCH_2), 48.9 and 48.4 (CH each, C6a and C3a), 33.0 (CH_2, C4), 28.5 (CH_2, C6), 24.0 (CH_2, C5), 13.7 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2063.0 (5), 1975.1 (10), 1933.1 (100), 1908.9 (30) [ν(C≡O)]; 1574.1 (20) [ν(C═N)]. MS (70 eV; *m/e* (%)): 433 (5) [M^+], 377 (5) [$M^+ - 2$ CO], 321 (5) [$M^+ - 4$CO], 293 (80) [$M^+ - 5$ CO], 241 (100) [ligand], 99 (80). Anal. Calcd for $C_{21}H_{19}CrNO_6$ (433.4): C, 58.20; H, 4.42; N, 3.23. Found: C, 58.64; H, 4.90; N, 3.52.

***syn*-11b.** ^{1}H NMR (C_6D_6): δ 7.09 (2 H, m, *m*-H Ph), 6.86 (CH, m, *p*-H Ph), 6.79 and 6.51 (1 H each, *o*-H Ph), 5.89 (1 H, s, 2-H), 3.69 (2 H, m, diastereotopic OCH_2), 2.63 and 2.50 (1 H each, m each, 3a-H and 6a-H), 1.4−0.8 (6 H, m, 3 CH_2), 1.00 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 222.1 and 215.5 [C_q each, *trans*- and *cis*-CO, $W(CO)_5$], 189.6 (C_q, C═N), 184.2 (C_q, ═C−O), 155.7 (C_q, *i*-C NPh), 129.2 and 128.8 (CH each, *m*-C NPh), 125.1 (CH, *p*-C NPh), 123.8 and 121.6 (CH each, *o*-C NPh), 103.2 (CH, C2), 67.8 (OCH_2), 48.9 and 46.7 (CH each, C6a and C3a), 31.5 (CH_2, C4), 28.8 (CH_2, C6), 26.0 (CH_2, C5), 13.9 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2063.4 (5), 1975.1 (10), 1932.9 (100), 1908.3 (30) [ν(C≡O)]; 1579.0 (20) [ν(C═N)]. MS (70 eV; *m/e* (%)): 433 (10) [M^+], 377 (5) [$M^+ - 2$ CO], 321 (5 [$M^+ - 4$CO], 293 (60) [$M^+ - 5$ CO], 241 (80) [ligand], 99 (100). Anal. Calcd for $C_{21}H_{19}CrNO_6$ (433.4): C, 58.20; H, 4.42; N, 3.23. Found: C, 58.30; H, 5.07; N, 3.41.

Pentacarbonyl[4-ethoxy-6-(di-*tert*-butylphosphanyl)-1,2,3,3a-tetrahydropentalene-*P*]tungsten (*anti*-14a), Pentacarbonyl[4-ethoxy-6-(di-*tert*-butylphosphanyl)-1,2,3,6a-tetrahydropentalene-*P*]tungsten(*anti*-15a),and Pentacarbonyl[3-(di-*tert*-butylphosphanyl)-3a,5,6,6a-tetrahydro-4*H*-pentalen-1-one-*P*]tungsten (*anti*-17a). To pentacarbonyl-[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (236 mg, 0.5 mmol; **3a**) in 1 mL of pentane is added di-*tert*-butylphosphine (73 mg, 0.5 mmol; **13a**) in 2 mL of pentane dropwise at 0 °C with stirring in a 5 mL screw-top vessel. After the color change to yellow is observed, indicating that the point of equivalency is achieved, the solution separated by fast (!) chromatography on silica gel to give compound *anti*-**14a** ($R_f =$ 0.6 in 50:1 pentane/diethyl ether, yellow crystals, mp 90 °C), compound *anti*-**15a** ($R_f = 0.5$ in 50:1 pentane/diethyl ether, yellow crystals, mp 76 °C), and compound *anti*-**17a** ($R_f = 0.5$ in diethyl ether, yellow crystals, mp 127 °C). The overall yield of compounds *anti*-**14a** + *anti*-**15a** + *anti*-**17a** corresponds to ca. 80%. Since *anti*-**14a** readily undergoes thermal rearrangement to *anti*-**15a** and also is hydrolyzed on silica gel to give *anti*-**17a**, the relative yields depend very much on the details of the preparation.

***anti*-14a.** ^{1}H NMR (C_6D_6): δ 5.68 [1 H, d, ^3J(P,H) = 8 Hz, 5-H], 3.65 (2 H, m, diastereotopic OCH_2), 3.36 (1 H, m, 3a-H), 2.38 (2 H, m, diastereotopic 1-H_2), 1.90 and 1.60 (2 H each, m each, 2-H_2 and 3-H_2), 1.31 and 1.25 [3 H each, d each, ^3J(P,H) = 13 Hz each, diastereotopic P*t*-Bu_2], 1.10 (3 H, t, OCH_2CH_3).

^{13}C NMR (C_6D_6): δ 200.2 [C_q, 4 C, ^2J(P,C) = 7 Hz, *cis*-CO, $(CO)_5W$], 199.2 [C_q, ^2J(P,C) = 24 Hz, *trans*-CO, $(CO)_5W$], 164.5 [C_q, ^3J(P,C) = 9 Hz, C4], 153.5 [C_q, ^2J(P,C) = 0 Hz, C6a], 149.9 [C_q, ^1J(P,C) = 17 Hz, C6], 109.2 [CH, ^2J(P,C) = 17 Hz, C5], 65.4 (OCH_2), 60.4 [CH, ^3J(P,C) = 6 Hz, C3a], 37.9 and 37.4 [C_q each, ^1J(P,C) = 13 Hz each, diastereotopic P*C*Me$_3$], 30.6 (CH_2, C1), 29.2 and 26.3 (CH_2 each, C2 and C3), 31.3 and 31.0 [CH_3 each, ^2J(P,C) = 7 Hz each, diastereotopic C*Me*$_3$], 14.5 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2066.1 (20), 1970.0 (5), 1938.5 (90), 1928.0 (100) [ν(C≡O)]. MS (70 eV; ^{184}W, *m/e* (%)): 618 (20) [M$^+$], 590 (5), 562 (40), 534 (20), 506 (60), 478 (10) [M$^+$ − 5 CO], 417 (70), 294 (20) [ligand], 237 (60), 57 (100). Anal. Calcd for $C_{23}H_{31}O_6PW$ (618.3): C, 44.68; H, 5.05. Found: C, 44.61; H, 4.97.

***anti*-15a.** ^{1}H NMR (C_6D_6): δ 7.40 [1 H, d, ^3J(P,H) = 8 Hz, 5-H], 3.85 (2 H, m, diastereotopic OCH_2), 3.38 (1 H, m, 6a-H), 2.20 (2 H, m, diastereotopic 3-H_2), 2.00 and 1.85 (2 H each, m each, 2-H_2 and 1-H_2), 1.28 and 1.05 [3 H each, d each, ^3J(P,H) = 14 Hz each, diastereotopic P-*t*-Bu$_2$], 1.07 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 199.8 [C_q, 4 C, ^2J(P,C) = 7 Hz, *cis*-CO, $(CO)_5W$], 198.9 [C_q, ^2J(P,C) = 22 Hz, *trans*-CO, $(CO)_5W$], 150.8 [C_q, ^3J(P,C) = 15 Hz, C4], 150.0 [CH, ^2J(P,C) = 19 Hz, C5], 138.9 [C_q, ^1J(P,C) = 20 Hz, C6], 132.0 [C_q, ^3J(P,C) = 0 Hz, C3a], 65.0 (OCH_2), 61.9 (CH, C6a), 38.9 and 36.5 [C_q each, ^1J(P,C) = 13 and 15 Hz, respectively, diastereotopic P*C*Me$_3$], 32.7 (CH_2, C3), 31.0 and 22.5 (CH_2 each, C2 and C1), 30.8 and 30.4 [CH_3 each, ^2J(P,C) = 6 Hz each, diastereotopic C*Me*$_3$], 15.3 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2067.1 (20), 1970.3 (5), 1935.5 (100) [ν(C≡O)]. MS (70 eV; ^{184}W, *m/e* (%)): 618 (10) [M$^+$], 590 (5), 534 (30), 506 (20), 478 (30) [M$^+$ − 5 CO], 154 (60), 57 (100). Anal. Calcd for $C_{23}H_{31}O_6PW$ (618.3): C, 44.68; H, 5.05. Found: C, 44.31; H, 5.07.

***anti*-17a.** ^{1}H NMR (C_6D_6): δ 6.63 [1 H, d, ^3J(P,H) = 6 Hz, 2-H], 3.30 (1 H, m, 6a−H), 2.60 (1 H, m, 3a-H), 1.95 and 1.70 (1 H each, m each, diastereotopic 4-H_2), 1.30−1.20 (4 H, m, 5-H_2 and 6-H_2), 1.08 and 1.01 [3 H each, d each, ^3J(P,H) = 14 Hz each, diastereotopic P-*t*-Bu$_2$]. ^{13}C NMR (C_6D_6): δ 208.5 (C_q, ^3J(P,C) = 11 Hz, C═O], 199.2 [C_q, 4 C, ^2J(P,C) = 7 Hz, *cis*-CO, $(CO)_5W$], 198.0 [C_q, ^2J(P,C) = 22 Hz, *trans*-CO, $(CO)_5W$], 174.2 (C_q, ^1J = 4 Hz, C3), 143.5 [CH, ^2J(P,C) = 6 Hz, C2], 54.6 (CH, C6a), 53.0 (CH, ^2J = 4 Hz, C3a), 38.3 and 37.9 [C_q each, ^1J(P,C) = 13 and 11 Hz, respectively, diastereotopic P*C*Me$_3$], 34.5 (CH_2, C4), 31.3 and 31.0 [CH_3 each, ^2J(P,C) = 5 Hz each, diastereotopic C*Me*$_3$], 27.2 and 27.1 (CH_2 each, C5 and C6). IR (hexane; cm^{-1} (%)): 2068.4 (20), 1973.2 (5), 1935.9 (100) [ν(C≡O)]; 1710.5 [ν(C═O)]. MS (70 eV; ^{184}W, *m/e* (%)): 590 (10) [M$^+$], 562 (5), 534 (30), 506 (20), 476 (30), 450 (30) [M$^+$ − 5 CO], 421 (30), 391 (20), 266 (10) [ligand], 210 (10), 154 (60), 57 (100). Anal. Calcd for $C_{21}H_{27}O_6PW$ (590.3): C, 42.73; H, 4.61. Found: C, 42.66; H, 4.63.

X-ray crystal structure analysis of compound *anti*-**17a**: formula $C_{21}H_{27}O_6PW$, M_r = 590.25, 0.7 × 0.5 × 0.4 mm, a = 14.810(1) Å, b = 10.653(2) Å, c = 15.583(1) Å, β = 110.19(1)°, V = 2307.5(5) Å^3, ρ_{calcd} = 1.699 g cm^{-3}, μ = 51.07 cm^{-1}, empirical absorption correction via ψ scan data (0.758 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 4854 reflections collected ($\pm h$, $-k$, $-l$), (sin θ)/λ = 0.62 Å^{-1}, 4680 independent and 4173 observed reflections [$I \geq 2\sigma(I)$], 268 refined parameters, R1 = 0.030, wR2 = 0.081, GOF 1.094, maximum (minimum) residual electron density 1.89 (−1.47) e Å^{-3}, refined with isotropic thermal parameters and with restraints, hydrogens calculated and riding.[13]

Pentacarbonyl[4-ethoxy-6-(dicyclohexylphosphanyl)-1,2,3,3a-tetrahydropentalene-*P*]tungsten (*anti*-14b), Pentacarbonyl[4-ethoxy-6-(dicyclohexylphosphanyl)-1,2,3,6a-tetrahydropentalene]tungsten (*anti*-15b), Pentacarbonyl-[4-ethoxy-6-(dicyclohexylphosphanyl)-1,2,3,5-tetrahydropentalene,-*P*]tungsten (*anti*-16b), and Pentacarbonyl[3-(dicyclohexylphosphanyl)-3a,5,6,6a-tetrahydro-4*H*-pentalen-1-one-*P*]tungsten (*anti*-17b). Pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**3a**) (236 mg, 0.5 mmol) is reacted with dicyclohexylphosphine (99 mg, 0.5 mmol; **13b**) as described above to give compound *anti*-**14b** (202 mg, 30%, R_f = 0.5 in 50:1 pentane/diethyl ether), compound *anti*-**15b** (45 mg, 7%, R_f = 0.6 in 50:1 pentane/diethyl ether), compound *anti*-**16b** (240 mg, 36%, R_f = 0.6 in 50:1 pentane/diethyl ether, mp 151 °C), and compound *anti*-**17b** (140 mg, 22%, R_f = 0.3 in 4:1 pentane/dichloromethane, mp 163 °C). Since *anti*-**14b** readily undergoes thermal rearrangement to *anti*-**15b** and *anti*-**16b** and is readily hydrolyzed on silica gel to give *anti*-**17b**, the relative yields depend very much on the details of preparation.

***anti*-14b.** ^{1}H NMR (C_6D_6): δ 5.52 [1 H, d, ^3J(P,H) = 2 Hz, 5-H], 3.65 (2 H, m, diastereotopic OCH_2), 3.42 (1 H, m, 1-H), 2.30 (2 H, m, diastereotopic 1-H_2), 2.10−1.10 (26 H, m; 2-H_2, 3-H_2, and 2 Cy), 1.10 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 199.3 [C_q, 4 C, ^2J(P,C) = 6 Hz, *cis*-CO, $(CO)_5W$], 199.5 [C_q, ^2J(P,C) = 22 Hz, *trans*-CO, $(CO)_5W$], 165.9 [C_q, ^3J(P,C) = 9 Hz, C4), 153.6 [C_q, ^2J(P,C) = 0 Hz, C6a], 149.5 [C_q, ^1J(P,C) = 15 Hz, C6], 106.2 [CH, ^2J(P,C) = 26 Hz, C5], 65.4 (OCH_2), 60.4 [CH, ^3J(P,C) = 7 Hz, C3a], 38.5 and 36.5 [CH each, ^1J(P,C) = 24 Hz each, diastereotopic P*C*H], 30.8 (CH_2, C1), 29.6 and 25.8 (CH_2 each, C2 and C3), 29.3−26.0 (10 CH_2, diastereotopic PCy_2), 14.3 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2066.7 (20), 1969.5 (5), 1937.4 (100), 1928.0 (70) [ν(C≡O)]. MS (70 eV; ^{184}W, *m/e* (%)): 670 (20) [M$^+$], 642 (25), 614 (40), 586 (60), 558 (40), 530 (30) [M$^+$ − 5 CO], 55 (100). Anal. Calcd for $C_{27}H_{35}O_6PW$ (670.4): C, 48.37; H, 5.26. Found: C, 48.60; H, 5.36.

***anti*-15b.** ^{1}H NMR (C_6D_6): δ 7.230 [1 H, d, ^3J(P,H) = 8 Hz, 5-H], 3.90 (2 H, m, diastereotopic OCH_2), 3.30 (1 H, m, 6a-H), 2.25 (2 H, m, diastereotopic 1-H_2), 2.20−1.10 (26 H, m; 2-H_2, 3-H_2 and 2 Cy), 1.07 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 199.6 [C_q, 4 C, *cis*-CO, $(CO)_5W$], 198.0 [C_q, *trans*-CO, $(CO)_5W$], 151.2 (C_q, C4), 150.2 (CH, C5), 137.0 (C_q, C6), 132.2 (C_q, C3a), 65.2 (OCH_2), 61.9 (CH, C6a), 38.5 and 36.5 [CH each, diastereotopic PCH], 32.7 (CH_2, C3); 31.0 and 22.8 (CH_2 each, C2 and C1), 29.4−25.9 (10 CH_2, diastereotopic PCy_2), 15.2 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2067.0 (20), 1972.3 (5), 1935.2 (100) [ν(C≡O)].

***anti*-16b.** ^{1}H NMR (C_6D_6): δ 3.78 [2 H, m, 5-H_2], 3.70 (2 H, m, diastereotopic OCH_2), 2.32 (2 H, m, diastereotopic 3-H_2), 2.19 (2 H, m, 2-H_2), 2.10−1.10 (24 H, m, 1-H_2 and 2 Cy), 1.04 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 199.4 [C_q, 4 C, ^2J(P,C) = 8 Hz, *cis*-CO, $(CO)_5W$], 199.3 [C_q, ^2J(P,C) = 21 Hz, *trans*-CO, $(CO)_5W$], 166.5 [C_q, ^3J(P,C) = 0 Hz, C4), 158.9 [C_q, ^1J(P,C) = 9 Hz, C6], 149.5 [C_q, ^2J(P,C) = 6 Hz, C6a], 106.3 [CH, ^3J(P,C) = 43 Hz, C3a], 65.9 (OCH_2), 53.4 (CH_2, ^2J = 20 Hz, C5), 37.5 [2 PCH, ^1J(P,C) = 26 Hz), 30.6 (CH_2, C1), 29.0 (CH_2, C2), 28.8 and 28.4 (CH_2 each, diastereotopic PCH*C*H$_2$), 27.3 and 27.0 (CH_2 each, ^3J = 13 and 11 Hz, diastereotopic PCHC*H*$_2$C*H*$_2$), 26.3 (2 CH_2, PCHCH$_2$CH$_2$*C*H$_2$), 24.4 (CH_2, C2), 15.2 (OCH_2CH_3). IR (hexane; cm^{-1} (%)): 2065.1 (20), 1967.5 (5), 1932.6 (100) [ν(C≡O)]. Anal. Calcd for $C_{27}H_{35}O_6PW$ (670.4): C, 48.37; H, 5.26. Found: C, 48.52 H, 5.42.

X-ray crystal structure analysis of compound *anti*-**16b**: formula $C_{27}H_{35}O_6PW$, M_r = 670.37, 0.4 × 0.3 × 0.2 mm, a = 14.206(2) Å, b = 11.564(2) Å, c = 18.103(3) Å, β = 112.72(1)°, V = 2743.2(8) Å^3, ρ_{calcd} = 1.623 g cm^{-3}, μ = 43.07 cm^{-1}, empirical absorption correction via ψ scan data (0.933 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 5735 reflections collected ($\pm h$, $-k$, $-l$), (sin θ)/λ = 0.62 Å^{-1}, 5558 independent and 4039 observed reflections [$I \geq 2\sigma(I)$], 317 refined parameters, R1 = 0.027, wR2 = 0.047, GOF 1.008, maximum (minimum) residual electron density 0.69 (−0.49) e Å^{-3}, refined with isotropic thermal parameters and with restraints, hydrogens calculated and riding.[13]

***anti*-17b.** ^{1}H NMR (C_6D_6): δ 6.30 [1 H, d, ^3J(P,H) = 6 Hz, 2-H], 3.25 (1 H, m, 6a−H), 2.55 (1 H, m, 3a-H), 1.95−1.20 (27 H, m, 1-H_2−3-H_2, and 2 × CH_2 cyclohexanyl). ^{13}C NMR (C_6D_6): δ 208.4 [C_q, ^3J(P,C) = 11 Hz, C═O], 198.2 [C_q, 4 C,

^2J(P,C) = 7 Hz, *cis*-CO, $(CO)_5W$], 198.5 [C_q, ^2J(P,C) = 22 Hz, *trans*-CO, $(CO)_5W$], 173.0 [C_q, ^1J(P,C) = 16 Hz, C3], 141.5 [CH, ^2J(P,C) = 5 Hz, C2], 53.2 (CH, C6a), 51.3 [CH, ^2J(P,C) = 8 Hz, C3a], 38.7 and 38.0 [CH each, ^1J(P,C) = 22 and 21 Hz, respectively, diastereotopic PCH], 32.3 (CH_2, C4), 29.5 and 29.0 [CH_2 each, ^2J(P,C) = 11 and 4 Hz, respectively, diastereotopic PCHCH_2], 28.5 (CH_2, C5), 27.2 and 27.0 [CH_2 each, ^3J(P,C) = 9 Hz each, PCHCH$_2$$CH_2$], 26.2 (2 CH_2, PCHCH$_2CH_2$$CH_2$), 26.0 ($CH_2$, C6). IR (hexane; cm^{-1} (%)): 2068.7 (20), 1973.0 (5), 1937.1 (100) [ν(C≡O)], 1709.9 [ν(C═O)]. MS (70 eV; ^{184}W, *m*/*e* (%)): 642 (10) [M^+], 614 (5), 586 (30), 558 (20), 530 (30), 502 (30) [$M^+ - 5$ CO], 283 (10) [ligand], 171 (50), 57 (100). Anal. Calcd for $C_{25}H_{31}O_6PW$ (642.3): C, 46.75; H, 4.86. Found: C, 46.66; H, 4.92.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Barbara Hildmann for experimental assistance.

Supporting Information Available: Tables of positional and displacement parameters, bond distances and angles, and hydrogen coordinates for (3*E*)-**5a**, **6c**, *anti*-**11a**, *anti*-**16b**, and *anti*-**17a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9810394