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Organic Syntheses via Transition Metal Complexes. 116.[1] Carbocyclic Four-, Five-, and Six-Membered Rings by Condensation of (Alkyl,ethoxy)carbene Complexes (M = W, Cr) with α,β-Unsaturated Tertiary Acid Amides

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4-Amino-1-tungsta-1,3,5-hexatrienes $(CO)_5W{=}C(OEt)CH{=}C(NR_2)CH{=}CHPh$ (3*E*)-**2** and (cyclohexan-4-on-1-yl)carbene tungsten complexes **6** were obtained by condensation of (ethoxy,methyl)carbene tungsten complex $(OC)_5W{=}C(OEt)CH_3$ **1a** with α,β-unsaturated tertiary acid amides $PhCH{=}CHC({=}O)NR_2$ **7** in the presence of $POCl_3/Et_3N$ and $(COCl)_2/Et_3N$, respectively. Compounds **2** underwent a π-cyclization to zwitterionic η^1-cyclopentadiene complexes **3**. Condensation of (*prim*-alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R^1$ **1** (M = W, Cr; R^1 = *c*-C_7H_7, *n*-Pr) with compounds **7** afforded (cyclobutenyl)carbene complexes **9**.

Fischer carbene complexes have been applied as stoichiometric reagents in a number of high-yielding transformations of potential use in organic synthesis.[2] Recent examples include the formation of cyclopentadienes by π-cyclization of 1-metalla-1,3,5-hexatrienes,[3,4] which were derived from (1-alkynyl)carbene complexes,[5] e.g., by addition of enamines[6] or by addition of protic nucleophiles NuH [e.g., $R(R'CO)CH_2$,[7] R_2NH,[8,9] R_2PH,[8] $RC({=}O)OH$ and ROH,[10,11] $RC({=}X)SH$ (X = O, NH, NR),[12] and RSH[13]].[8,14] The latter procedure provides access to highly reactive bicyclic cyclopentadienes, such as tetrahydropentalenes[8,9] or tetrahydroindenes,[9,10] and most notable also to the attachment of *nucleophilic* substituents to the cyclopentadiene ring, which is complementary to more conventional routes by which *electrophilic* substituents are introduced to cyclopentadiene rings.

We now wish to report on studies directed toward the formation of cyclopentadienes from readily available Fischer carbene complexes other than (1-alkynyl)carbene complexes, namely, (ethoxy,methyl)carbene complexes and substituted (*prim*-alkyl,ethoxy)carbene complexes. Up to date, only a few examples of this transformation have been reported.

A reaction sequence leading to cyclopentadienes from (ethoxy,methyl)carbene tungsten complex $(CO)_5W{=}C(OEt)CH_3$ (**1a**) has been previously achieved but it required four steps (Scheme 1), involving the condensation of compound **1a** with an aryl carbaldehyde ArCHO in the presence of Me_3SiCl/Et_3N to give a 2-ethoxy-1-

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[§] X-ray structure analysis.

[⊥] X-ray structure analyses of compound **6b**.

(1) For part 115 of this series see: Wu, H.-P.; Aumann, R.; Fröhlich, R.; Wegelius, E. *Eur. J. Org. Chem.* **2002**, 361−368.

(2) For the application of Fischer carbene complexes to organic syntheses see: (a) Dötz, K.-H. *Angew. Chem.* **1984**, *96*, 573−594; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587−608. (b) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5, p 1065−1113. (c) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, pp 469−547. (d) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, pp 387−420. (e) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (f) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271−288. (g) Frühauf, H.-W. *Chem. Rev.* **1997**, 97, 523−596. (h) Schirmer, H.; Duetsch, M.; deMeijere, A. *Angew. Chem.* **2000**, *112*, 4124−4162; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 3964−4002.

(3) For the basics of this π-cyclization reaction see: (a) Aumann, R.; Heinen, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343−2347. (b) Aumann, R.; Heinen, H.; Hinterding, N.; Sträter, B. Krebs *Chem. Ber.* **1991**, *124*, 1229−1236.

(4) For a recent review on 1-metallahexatrienes see: Aumann, R. *Eur. J. Org. Chem.* **2000**, 17−31.

(5) For a recent review on (1-alkynyl)carbene complexes see: Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163−242.

(6) (a) Meyer, A. G.; Aumann, R. *Synlett* **1995**, 1011−1013. (b) Aumann, R.; Meyer, A. G.; Fröhlich, R. *Organometallics* **1996**, *15*, 5018−5827. (c) Aumann, R.; Kössmeier, M.; Zippel, F. *Synlett* **1997**, 621−623. (d) Aumann, R.; Kössmeier, M.; Jäntti, A. *Synlett* **1998**, 1120−1122. (e) Aumann, R.; Kössmeier, M.; Mück-Lichtenfels, Ch.; Zippel, F. *Eur. J. Org. Chem.* **2000**, 37−49.

(7) Aumann, R.; Göttker-Schnetmann, I.; Fröhlich, R.; Saarenketo, P.; Holst, Ch. *Chem. Eur. J.* **2001**, *7*, 711−720.

(8) Aumann, R.; Fröhlich, R.; Prigge, J.; Meyer, O. *Organometallics* **1999**, *18*, 1369−1380.

(9) Wu, H.-P.; Aumann, R.; Fröhlich, R.; Wegelius, E. *Organometallics* **2001**, *20*, 2183−2190.

(10) Wu, H.-P.; Aumann, R.; Wibbeling, B. *Eur. J. Org. Chem.* **2000**, 1183−1192.

(11) Wu, H.-P.; Aumann, R.; Fröhlich, R.; Saarenketo, P. *Chem. Eur. J.* **2001**, *7*, 700−710.

(12) Wu, H.-P.; Aumann, R.; Fröhlich, R.; Wegelius, E.; Saarenketo, P. *Organometallics* **2000**, *19*, 2373−2381.

(13) Wu, H.-P.; Aumann, R.; Venne-Dunker, S.; Saarenketo, P. *Eur. J. Org. Chem.* **2000**, *19*, 3463−3473.

(14) For related studies, in which 1-metalla-1,3,5-trienes were generated by addition of dienes to (1-alkynyl)carbene complexes, see: (a) Barluenga, J.; Aznar, F.; Barluenga, S.; Fernández, M.; Martín, A.; García-Granda, S.; Pinera-Nicolás, A. *Chem. Eur. J.* **1998**, *4*, 2280−2298. (b) Barluenga, J.; Aznar, F.; Palomero, M. A.; Barluenga, S. *Org. Lett.* **1999**, 541−543.

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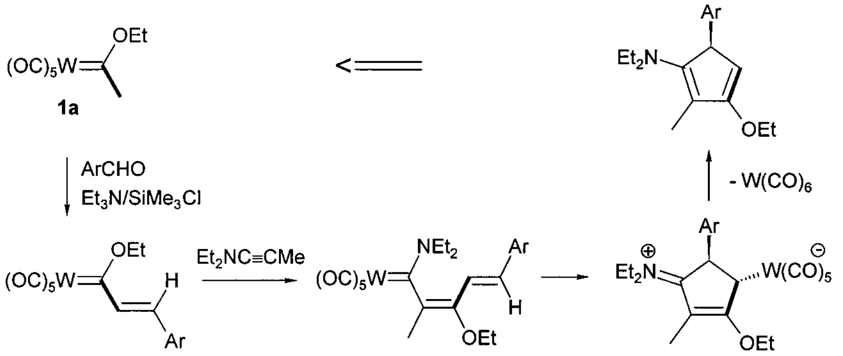
Scheme 1. Amino,ethoxy Cyclopentadienes from (Ethoxy,methyl)carbene Tungsten Complex 1a



tungsta-1,3-butadiene $(CO)_5W{=}C(OEt)CH{=}CHPh$.[15] Addition of 1-diethylaminopropyne to the latter compound afforded a (3*Z*)-2-amino-4-ethoxy-1-tungsta-1,3,5-hexatriene,[3a] which underwent a smooth π-cyclization to a zwitterionic η^1-cyclopentadiene pentacarbonyltungsten complex already at 20 °C, and finally gave an amino, ethoxy cyclopentadiene by disengagement of the pentacarbonyl tungsten unit.[3b]

We aimed for a new and efficient approach to the formation of cyclopentadienes, involving the generation of 1-metalla-1,3,5-hexatrienes by condensation of (ethoxy, methyl)carbene complexes $(CO)_5M{=}C(OEt)CH_3$ **1** (M = W, Cr) with α,β-unsaturated organic carbonyl compounds. Condensation reactions of this type were known of saturated aldehydes and ketones,[16] acid chlorides,[17] and acid amides,[18] but also α,β-unsaturated ketones, aldehydes, esters, and lactones.[19] Both 1,2-addition as well as 1,4-addition reactions were found, but in a few cases only, these reactions have been utilized for the generation of carbocyclic compounds.[20]

We now report for the first time on condensation reactions of (alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R^1$ **1a**−**e** (M = W, Cr; R^1 = H, *c*-C_7H_7, *n*-Pr) with α,β-unsaturated acid amides **7a**−**c** [$PhCH{=}CHC({=}O)NR_2$], leading to formation as well of carbocyclic five-, four-, and six-membered rings.

Condensation of α,β-Unsaturated Tertiary Acid Amides 7a−c with (Alkyl,ethoxy)carbene Complexes 1a−e (M = Cr, W). (Alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R^1$ **1a**−**e** undergo a condensation with unsaturated tertiary acid amides **7a**−**c** in the presence of triethylamine/phosphorus oxychloride and triethylamine/oxalyl dichloride, respectively. The process is initiated by the transformation of acid amides **7a**−**c** into more reactive iminium chlorides **4a**−**c** (Scheme 2). Two major reaction paths, initiated by 1,2- and 1,4-addition to these compounds, respectively, were observed. A marked influence of substituents R^1 at the α-carbon atom of the carbene complexes **1a**−**e** was found. For example, the (ethoxy,methyl)carbene tungsten complex $(CO)_5W{=}C(OEt)CH_3$ (**1a**) (R^1 = H) was shown to mainly afford 1-metalla-1,3,5-hexatrienes (3*E*)-**2a**,**b** by 1,2-addition. In line with expectation, these compounds underwent a π-cyclization to η^1-cyclopentadiene complexes **3a**,**b**.[3,4] While monitoring this reaction more carefully, we found red tungsten compounds **6a**,**b** as byproducts. Quite obviously, compounds **6a**,**b** result from 1,4-addition of (ethoxy,methyl)carbene complex **1a** to *2* equiv of α,β-unsaturated iminium chlorides **4a**,**b**. It is assumed that adducts **5** were formed as intermediates, which underwent a hitherto unknown Dieckmann type cyclization. The overall process involves a high diastereoselectivity, leading to an equatorial arrangement of all substituents of the six-membered ring.

Other than (ethoxy,methyl)carbene complexes **1a**,**b**, (*prim*-alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)$-CH_2R^1 **1c**−**e** (M = Cr, W; R^1 = *c*-C_7H_7, *n*-Pr) did not yield 1-metalla-1,3,5-hexatrienes (3*E*)-**2c**−**k**, but instead formed (cyclobutenyl)carbene complexes **9c**−**k** by 1,4-addition (Scheme 3).

The marked influence of substituents R^1 at the α-carbon atom of (alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R^1$ **1c**−**e** on the condensation of this compounds with α,β-unsaturated iminium chlorides **4a**−**c** is explained on the assumption that the conjugate base of (alkyl,ethoxy)carbene complexes **1c**−**e** having a secondary α-carbon atom would be a "softer" nucleophile than the conjugate base of (ethoxy,methyl)carbene complexes **1a**,**b** and therefore should preferentially add to the "soft" β-carbon atom of α,β-unsaturated iminium chlorides **4a**−**c**. A 1,4-addition provides indeed a good explanation for the experimental finding that the thermodynamically less favorable "*cis*" diastereomers *rel*-(3*S*,4*S*)-**9c**−**k** are obtained as major isomers, with diastereoselectivities ranging from 2:1 to 20:1 (see legend to Scheme 3). It appears that the "*cis*" configuration of these compounds is determined by the stereochemistry of the 1,4-adducts *erythro*-**8** (Scheme 4). Compounds *erythro*-**8** are expected to be generated preferentially over compounds *threo*-**8**, and they are expected to be transformed through intermediates "*cis*"-**10** and "*cis*"-**11** into the "*cis*" isomer of the corresponding (cyclobutenyl)carbene complexes **9**.

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(15) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537−540.

(16) (a) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503−505. (b) Wulff, W. D.; Anderson, B. A.; Toole, A. *J. Am. Chem. Soc.* **1989**, *111*, 5485−5487. (c) Wulff, W. D.; Anderson, B. A.; Toole, A.; Xu, Y.-C. *Inorg. Chim. Acta* **1994**, *220*, 215−231, and references therein. (d) Powers, T. S.; Shi, Y.; Wilson, K. J.; Wulff, W.-D. *J. Org. Chem.* **1994**, *59*, 6882−6884. (e) Wang, H.; Hsung, R. P.; Wulff, W.-D. *Tetrahedron Lett.* **1998**, *39*, 1849−1852.

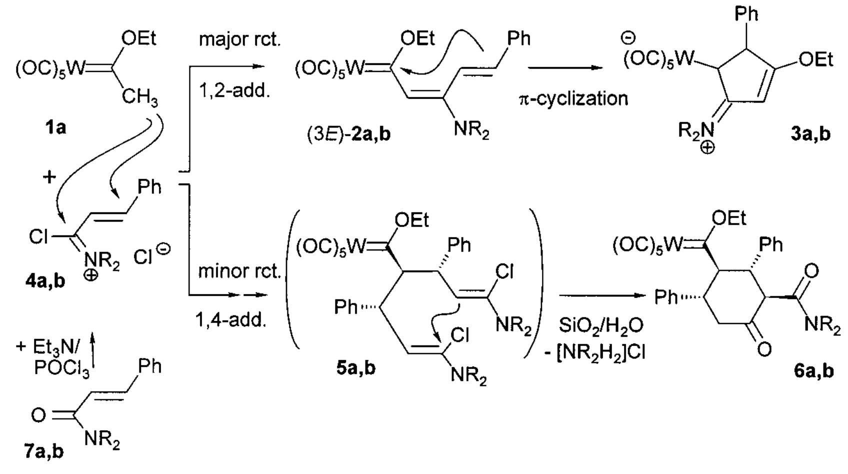
(17) (a) Casey, C. P.; Boggs, R. A.; Anderson, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 8947−8949. (b) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3510−3516.

(18) (a) Lattuado, L.; Licandro, E.; Maiorana, S.; Papagni, A.; Chiesi Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1988**, 1092−1093. (b) Aumann, R.; Hinterding, P. *Chem. Ber.* **1990**, *123*, 2047−2051. (c) Aumann, R.; Hinterding, P. *Chem. Ber.* **1990**, *123*, 611−620. (d) Aumann, R.; Hinterding, P. *Chem. Ber.* **1989**, *122*, 365−370.

(19) (a) Casey, C. P.; Brunsvold, W. R.; Scheck, M. D. *Inorg. Chem.* **1977**, *16*, 3059−3063. (b) Wulff, W. D.; Anderson, B. A.; Rahm, A. *J. Am. Chem. Soc.* **1993**, *115*, 4602−4611. (c) Iyoda, M.; Zhao, L.; Matsuyama, H. *Tetrahedron Lett.* **1995**, *36*, 3699−3702.

(20) Mongin, C.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 3873−3875.

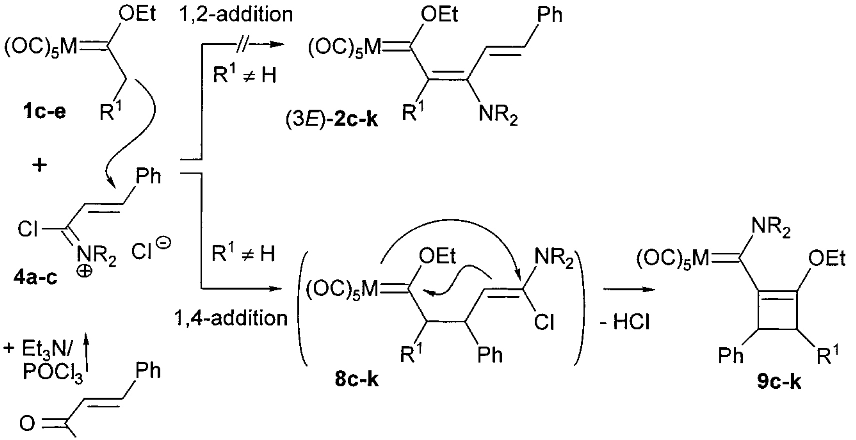
Scheme 2. Condensation of (Methyl,ethoxy)carbene Tungsten Complex 1a with α,β-Unsaturated Tertiary Acid Amides 7a,b Involving a 1,2- and a 1,4-Addition, Respectively



2–7	NR₂	$\mathbf{2}^{[a]}$	$\mathbf{3}^{[a]}$	$\mathbf{6}^{[a]}$
a	NMe_2	8 (64)	36 (3)	(16)
b	pyrrolidino	12 (73)	42 (8)	(15)

[a] Isolated yields in %, of reactions achieved by condensation with $POCl_3/Et_3N$; yields given in parentheses were obtained if $(COCl)_2/Et_3N$ was used instead of $POCl_3/Et_3N$.

Scheme 3. Condensation of (Alkyl,ethoxy)carbene Complexes 1c–e (M = Cr, W) with α,β-Unsaturated Tertiary Acid Amides 7a–c Involving a 1,4-Addition as the Only Reaction Path



1	M	R^1
c	W	c-C_7H_7
d	Cr	c-C_7H_7
e	W	n-Pr

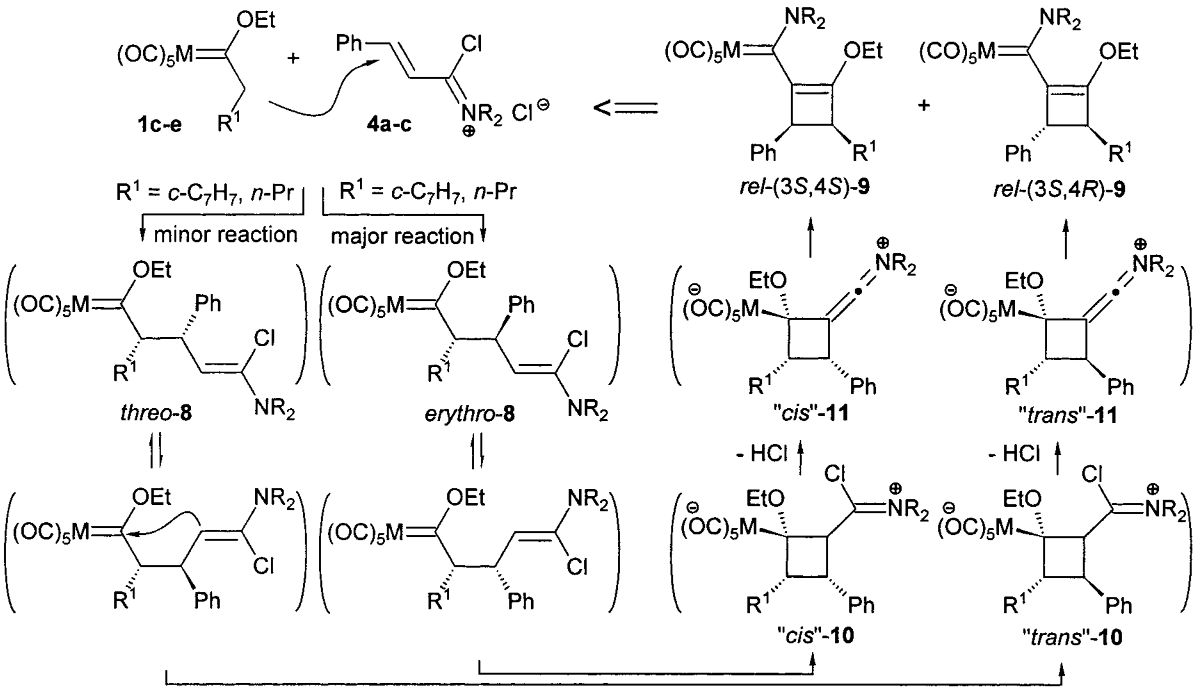
4,7	NR₂
a	NMe_2
b	pyrrolidino
c	morpholino

(3*E*)-2,8,9	M	R^1	NR₂	$\mathbf{2}^{[a]}$	$\mathbf{9}^{[a]}$	„*cis/trans*“-$\mathbf{9}^{[b]}$
c	W	c-C_7H_7	NMe_2	-	86	8 : 1
d	W	c-C_7H_7	pyrrolidino	-	66	3 : 1
e	W	c-C_7H_7	morpholino	-	62	20 : 1
f	Cr	c-C_7H_7	NMe_2	-	72	5 : 2
g	Cr	c-C_7H_7	pyrrolidino	-	68	2 : 1
h	Cr	c-C_7H_7	morpholino	-	52	9 : 1
i	W	n-Pr	NMe_2	-	53	7 : 1
j	W	n-Pr	pyrrolidino	-	43	5 : 1
k	W	n-Pr	morpholino	-	48	20 : 1

[a] Isolated yields in %, of reactions achieved by condensation with $POCl_3/Et_3N$. [b] Product ratio of diastereomers "*cis*"-**9**:"*trans*"-**9** according to the integration of ^1H NMR signals.

Spectroscopy and Crystal Structure Analyses of Compounds 2, 6, and 9. The structures of the (cyclobutenyl)aminocarbene complexes **9** are based on ^1H and ^{13}C NMR spectra and on a crystal structure analysis of compound "*cis*"-**9c** (Figure 1). ^3J = ca. 5 Hz was typically observed for the "*cis*" isomers and ^3J = ca. 1 Hz for the "*trans*" products. The cyclobutene ring exhibits a trapezoid shape with C3–C4 1.342(6) Å, C4–C5 1.503(6) Å,

Scheme 4. Reaction Path to Diastereomeric (Cyclobutenyl)carbene Complexes 9



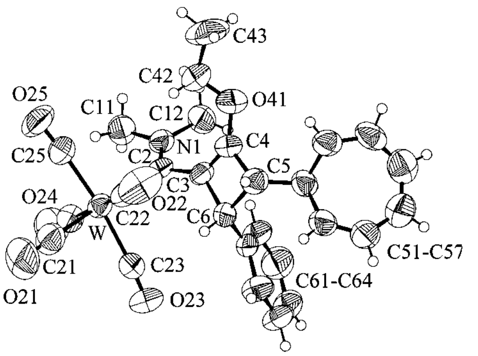


Figure 1. Molecular structure of (cyclobutenyl)carbene complex **9c** with selected bond lengths (Å), bond angles (deg), and dihedral angle (deg): W−C2 2.283(5), C2−N1 1.302(5), C2−C3 1.460(6), C3−C4 1.342(6), C3−C6 1.535(6), C4−O41 1.344(5), C4−C5 1.503(6), C5−C6 1.586(6); C3−C2−W 115.6(3), C4−C3−C2 135.2(4), C4−C3−C6 91.6(4), C2−C3−C6 131.6(4), C3−C4−O41 135.0(5), C3−C4−C5 97.7(4), C4−C5−C6 83.9(3), C3−C6−C5 86.8(3); W−C2−C3−C4 −115.3(6).

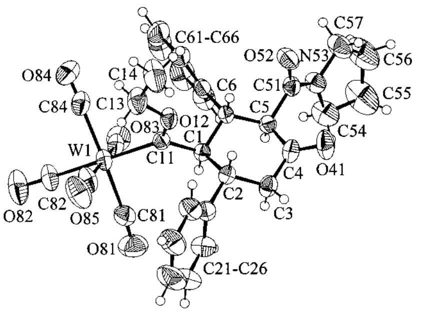


Figure 2. Molecular structure of (cyclohexanonyl)carbene complex **6b** with selected bond lengths (Å) and bond angles (deg) (averaged values from two independent molecules): W−C11 2.183(6), C11−C1 1.535(8), C1−C2 1.553(8), C1−C6 1.565(8), C2−C3 1.540(8), C3−C4 1.494(9), C4−O41 1.205(8), C4−C5 1.519(8), C5−C6 1.531(8), C5−C51 1.527(8), C51−O52 1.236(8), C51−N53 1.330(7); W−C11−C1 126.7(4), C11−C1−C2 110.5(4), C11−C1−C6 109.6(5), C1−C2−C3 110.1(5), C2−C3−C4 112.5(5), C3−C4−C5 115.0(5), C3−C4−O41 122.8(6), C5−C4−O41 122.3(6), C4−C5−C6 112.3(5), C5−C6−C1 112.4(5), C4−C5−C51 108.9(5), C6−C5−C51 110.5(5), C5−C51−O52 120.3(6), C5−C51−N53 118.5(5), O52−C51−N53 121.3(6).

C5−C6 1.586(6) Å, and C3−C6 1.535(6) Å. The plane defined by the atoms W,C2,C3 is strongly tilted against the cyclobutene ring C3,C4,C5 by 55.5°, thus implying little if any π-conjugation.

The structures of compounds **6a**,**b** were elucidated by ^{1}H and ^{13}C NMR measurements and also by a crystal structure analysis of compound **6b** (Figure 2).

The structures of the 4-amino-1-metallahexatrienes (3*E*)-**2** and (3*Z*)-**2** are based on ^{1}H and ^{13}C NMR spectra, including ^1J(C,H) and $^{2,3}J$(C,H) correlation experiments and NOE studies. Compound (3*E*)-**2b** was analyzed also by a crystal structure analysis (Figure 3). The ^{13}C signals of the M=C unit are typically observed in a narrow range of δ 265−268 for the tungsten compounds and 286−289 for the chromium compounds.

The ligand backbone W−C4−C5−C6−N of compound (3*E*)-**2b** is nearly planar and exhibits a *W* shape, C2−O3−C4−W −4.1(12)°, C2−O3−C4−C5 177.9(8)°, O3−C4−C5−C6−3.8(12)°, W−C4−C5−C6 178.1(6)°, and C4−C5−C6−N61 158.7(8)°. The bond distances C4−C5 1.389(10) Å, C5−C6 1.426(10) Å, and C6−N61 1.324(9) Å indicate a charge delocalization by π-conjugation within this unit.

Conclusion. Condensation of α,β-unsaturated acid amides **7** with (alkyl,ethoxy)carbene complexes **1** (M = W, Cr) in the presence of $POCl_3/Et_3N$ and $(COCl)_2/Et_3N$, respectively, has been found to provide a new and efficient entry into the formation of carbocyclic four-, five-, and six-membered rings. The reaction is strongly influenced by substituents on the α-carbon atom of the carbene complex. Thus, condensation of (ethoxy,methyl)-carbene tungsten complexes $(OC)_5W{=}C(OEt)CH_3$ **1a**,**b**

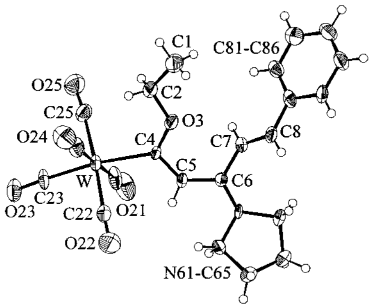


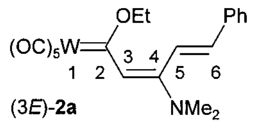
Figure 3. Molecular structure of 4-pyrrolidino-1-tungsta-1,3,5-hexatriene (3*E*)-**2b** with selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): W−C4 2.250(7), C4−C5 1.389(10), C5−C6 1.426(10), C6−C7 1.468(10), C7−C8 1.325(11), C8−C81 1.461(11), C6−N61 1.324(9), C4−O3 1.362(10); C5−C4−W 120.2(5), O3−C4−W 127.8(5), C4−C5−C6 129.8(7), C5−C6−C7 120.2(7), C8−C7−C6 128.3(7), C7−C8−C81 125.6(8); C2−O3−C4−W −4.1(12), C2−O3−C4−C5 177.9(8), C24−W−C4−O3 −49.9(7), O3−C4−C5−C6 −3.8(12), W−C4−C5−C6 178.1(6), C4−C5−C6−N61 158.7(8), C5−C6−N61−C62 −2.5(11), C4−C5−C6−C7 −24.6(12), C6−C7−C8−C81 −178.9(7).

(M = W, Cr) with *1* equiv of α,β-unsaturated tertiary acid amides $PhCH{=}CHC({=}O)NR_2$ **7a**,**b** provides a new access to 4-amino-1-tungsta-1,3,5-hexatrienes $(CO)_5W{=}C(OEt)CH{=}C(NR_2)CH{=}CHPh$ (3*E*)-**2a**,**b** with 3*E* configuration. Compounds **2a**,**b** undergo a π-cyclization to zwitterionic η^1-cyclopentadiene complexes **3a**,**b**. Condensation of compounds **1a**,**b** with *2* equiv of **7a**,**b** leads to generation of (cyclohexan-4-on-1-yl)carbene tungsten complexes **6a**,**b** with high diastereoselectivity. Condensation of (alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R$ **1c**−**e** (M = W, Cr; R = *c*-C_7H_7, *n*-Pr) with compounds **7a**−**c** affords (cyclobutenyl)carbene complexes **9c**−**k**.

Experimental Section

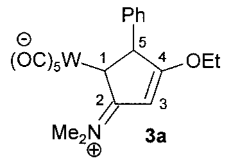
All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. All ^1H and ^{13}C NMR spectra were routinely recorded on Bruker ARX 300 and AM 360 instruments. COSY, HMQC, HMBC, and NOE experiments were performed on a Bruker AMX 400 and a Varian 600 U instrument. IR spectra were recorded on a BIORAD Digilab Division FTS-45 FT-IR spectrophotometer. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien silica gel 60_{F240}, were viewed by UV light (254 nm) and stained by iodine. R_f values refer to TLC tests. Compounds **1a**,**b** were prepared according to ref 21; compound **1c**, according to ref 22.

(3*E*,5*E*)-1,1,1,1-Pentacarbonyl-2-ethoxy-4-*N*,*N*-(dimethylamino)-6-phenyl-1-tungsta-1,3,5-hexatriene [(3*E*)-2a], Pentacarbonyl[4-ethoxy-2-(dimethylazonia)-5-phenyl-3-cyclopentenyl]tungstate (3a), and Pentacarbonyl{1-ethoxy-1-[2,6-bisphenyl-3-(dimethylamine-1-carbonyl)-cyclohexan-4-on-1-yl]methylene}tungsten [(1′*R,2′*R**,3′*R**,6′*R**)-6a].** To (2*E*)-*N*,*N*-dimethyl-3-phenylacrylamide (**7a**) (175 mg, 1.00 mmol) and phosphorus oxychloride (153 mg, 1.00 mmol) in 2 mL of dry dichloromethane in a 5 mL screw-top vessel was added after 15 min at 0 °C with stirring a solution of (ethoxy,methyl)carbene complex **1a** (198 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) in 1 mL of dichloromethane. Flash chromatography after 4 h at 25 °C on silica gel (20 × 2 cm, 3:1 *n*-pentane/dichloromethane) afforded a red fraction with compound **2a** (22 mg, 8%, $R_f = 0.6$ in 2:1 *n*-pentane/dichloromethane, orange crystals at −20 °C, dec 62 °C) and a yellow-orange fraction with compound **3a** (99 mg, 36%, $R_f = 0.5$ in 2:1 *n*-pentane/dichloromethane). Condensation of compounds **7a** with **1a** with oxalyl chloride (140 mg, 1.10 mmol) (instead of phosphorus oxychloride) was complete after 30 min at 0 °C and gave a higher yield of compound (3*E*)-**2a** (177 mg, 64%), a lower yield of compound **3a** (9 mg, 3%), and additionally also compound **6a** (57 mg, 16%, $R_f = 0.3$ in 10:1 dichloromethane/diethyl ether, orange crystals from 1:10 dichloromethane/*n*-pentane at −20 °C, dec 163 °C).



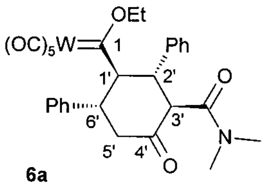
(3*E*)-**2a**

(3*E*)-2a: ^1H NMR ($CDCl_3$, 25 °C) δ 7.46 (2 H, "d", Ph), 7.38 (3 H, m, Ph), 6.80 (1 H, d, ^3J = 16.5 Hz, 5-H), 6.73 (1 H, d, ^3J = 16.5 Hz, 6-H), 6.46 (1 H, s, 3-H), 4.48 (2 H, q, OCH_2), 3.17 (6 H, s, 2 NCH_3), 1.20 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) δ 268.2 (C_q, W=C), 204.2 and 199.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 157.2 (C_q, C4), 137.8 (CH, C6), 135.3 (*i*-C Ph), 129.3, 128.9 and 126.8 (1:2:2, CH each, Ph), 124.2 (CH, C5), 121.0 (CH, C3), 76.1 (OCH_2), 40.0 (2 NCH_3), 15.5 (OCH_2CH_3); IR (*n*-hexane), cm^{-1} (%) 2055.5 (15), 1925.8 (100) [ν(C≡O)]; MS (70 eV), ^{184}W, *m/e* (%) 553 (2) [M^+], 525 (0) [$M^+ - CO$], 497 (3) [$M^+ - 2\ CO$], 469 (1) [$M^+ - 3\ CO$], 441 (4) [$M^+ - 4\ CO$], 413 (3) [$M^+ - 5\ CO$], 229 (79) [$M^+ - W(CO)_5$], 200 (100). Anal. Calcd for $C_{20}H_{19}NO_6W$ (553.2): C, 43.42; H, 3.46; N, 2.53. Found: C, 43.38; H, 3.59; N, 2.41.



3a

3a: ^1H NMR ($CDCl_3$, 25 °C) δ 7.27 (3 H, m, Ph), 7.07 (2 H, "d", Ph), 5.58 (1 H, s, EtOC=C*H*), 4.51 (1 H, s, C*H*Ph), 4.08 (2 H, m, diastereotopic OCH_2), 3.30 and 3.04 (3 H each, s each, NCH_3 each), 2.72 [1 H, C*H*W(CO)$_5$], 1.36 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) δ 202.8 and 201.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 192.3 (C_q, $C{=}N^+$), 183.3 (C_q, EtO-*C*), 141.1 (C_q, *i*-C Ph), 128.9, 127.0 and 126.4 (2:1:2, CH each, Ph), 94.5 (CH, C2), 68.0 (OCH_2), 65.7 (CH, CHPh), 40.9 and 40.7 (NCH_3 each), 38.0 [CH, $CHW(CO)_5^-$], 14.0 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%) 2052.6 (10), 1974.9 (70), 1891.1 (100) [ν(C≡O)], 1589.9 (25) [ν($C{=}N^+$)]; MS (70 eV), ^{184}W, *m/e* (%) 553 (1) [M^+], 525 (0) [$M^+ - CO$], 497 (0) [$M^+ - 2\ CO$], 469 (3) [$M^+ - 3\ CO$], 441 (5) [$M^+ - 4\ CO$], 413 (3) [$M^+ - 5\ CO$], 229 (81) [$M^+ - W(CO)_5$], 200 (100).



6a

6a: ^1H NMR (600 MHz, $CDCl_3$) δ 7.33 and 7.27 (2 H each, "t" each, *m*-CH Ph each), 7.23 and 7.18 (3 H each, m each, *o*- and *p*-CH Ph each), 4.92 (1 H, dd, ^3J = 11 and 11 Hz, 1′-H), 4.78 (2 H, m, diastereotopic OCH_2), 4.19 (1 H, d, ^3J = 11 Hz, 3′-H), 4.03 (1 H, dd, ^3J = 11 and 11 Hz, 2′-H), 3.45 (1 H, ddd; ^3J = 13, 11 and 4 Hz, 6′-H), 2.98 (1 H, dd, ^2J = −14 and ^3J = 13 Hz, 5′-H_{ax}), 2.86 and 2.77 [3 H each, s broad each, $N(CH_3)_2$],

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(21) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954−962.
(22) Aumann, R.; Runge, M. *Chem. Ber.* **1992**, *125*, 259−264.

2.74 (1 H, dd, $^2J = -14$ and $^3J = 4$ Hz, 5′-H$_{eq}$), 1.82 (3 H, t, $^3J = 7$ Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 340.8 (W═C), 203.8 (C$_q$, C4′), 202.4 and 196.4 [C$_q$ each, 1:4, *trans*- and *cis*-CO, W(CO)$_5$], 167.5 (NCO), 140.1 and 139.2 (C$_q$ each, *i*-C Ph each); 129.1, 129.0, 127.9, 127.7, 127.6, and 127.5 (2:2:1:2:2:1, CH each, Ph each), 80.1 (OCH$_2$), 77.9 (CH, C1′), 58.9 (CH, C3′), 50.6 (CH, C2′), 48.0 (CH$_2$, C5′), 47.2 (CH, C6′), 37.3 and 35.7 [CH$_3$ each, broad each, N(CH$_3$)$_2$], 14.9 (OCH$_2$*C*H$_3$); IR (*n*-hexane), cm^{-1} (%) 2063.8 (30), 1982.5 (5), 1959.0 (100) [ν(C≡O)], 1734 (50) [ν(C═O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 701 (2) [M$^+$], 673 (5) [M$^+$ − CO], 617 (30) [M$^+$ − 3 CO], 589 (50) [M$^+$ − 4 CO], 561 (20) [M$^+$ − 5 CO]. Anal. Calcd for $C_{29}H_{27}NO_8W$ (701.4): C, 49.66; H, 3.88; N, 2.00. Found: C, 49.99; H, 4.01; N, 1.75.

(3*E*,5*E*)-1,1,1,1,1-Pentacarbonyl-2-ethoxy-6-phenyl-4-pyrrolidino-1-tungsta-1,3,5-hexatriene [(3*E*)-2b], Pentacarbonyl[4-ethoxy-5-phenyl-2-pyrrolidinium-3-cyclopentenyl]tungstate (3b), and Pentacarbonyl{1-ethoxy-1-[2,6-bisphenyl-3-(pyrrolidine-1-carbonyl)cyclohexan-4-on-1-yl]methylene}tungsten [(1′*R,2′*R**,3′*R**,6′*R**)-6b].** 3-Phenyl-1-pyrrolidinoprop-2-en-1-one (**7b**) (201 mg, 1.00 mmol), phosphorus oxychloride (153 mg, 1.00 mmol), (ethoxy,methyl)carbene tungsten complex **1a** (198 mg, 0.50 mmol), and triethylamine (202 mg, 2.00 mmol) were reacted as described above to give compound (3*E*)-**2b** (35 mg, 12%, $R_f = 0.6$ in 2:1 *n*-pentane/dichloromethane, orange crystals, dec 65 °C) and compound **3b** (122 mg, 42%, $R_f = 0.5$ in 2:1 *n*-pentane/dichloromethane, yellow crystals, mp 95 °C). If the condensation was performed with oxalyl chloride as described above, it afforded compound (3*E*)-**2b** (211 mg, 73%), compound **3b** (23 mg, 8%), and also compound **6b** (56 mg, 15%, $R_f = 0.3$ in 10:1 dichloromethane/diethyl ether, orange crystals from 1:10 dichloromethane/*n*-pentane at −20 °C, mp 166 °C).

(3*E*)-2b: ^{1}H NMR (CDCl$_3$, 25 °C) δ 7.48 (2 H, "d", Ph), 7.39 (3 H, m, Ph), 6.89 (1 H, d, $^3J = 16.6$ Hz, 5-H), 6.69 (1 H, d, $^3J = 16.6$ Hz, 6-H), 6.38 (1 H, s, 3-H), 4.46 (2 H, q, OCH$_2$), 3.57 (4 H, m broad, 2 NCH$_2$), 2.01 (4 H, m broad, 2 NCH$_2$C*H*$_2$), 1.20 (3 H, t, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 25 °C) δ 267.6 (C$_q$, W═C), 204.3 and 200.0 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 153.4 (C$_q$, C4), 135.7 (CH, C6), 135.0 (*i*-C Ph), 128.7, 128.5, and 126.4 (1:2:2, CH each, Ph), 124.5 (CH, C5), 120.5 (CH, C3), 75.5 (OCH$_2$), 50.5 (2 NCH$_2$, broad), 24.8 (2 NCH$_2$*C*H$_2$, broad), 15.1 (OCH$_2$*C*H$_3$); IR (*n*-hexane), cm^{-1} (%) 2055.4 (15), 1924.9 (100) [ν(C≡O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 579 (1) [M$^+$], 551 (0) [M$^+$ − CO], 523 (4) [M$^+$ − 2 CO], 495 (1) [M$^+$ − 3 CO], 467 (3) [M$^+$ − 4 CO], 439 (3) [M$^+$ − 5 CO], 255 (82) [M$^+$ − W(CO)$_5$], 226 (100). Anal. Calcd for $C_{22}H_{21}NO_6W$ (579.3): C, 45.62; H, 3.65; N, 2.42. Found: C, 45.59; H, 3.72; N, 2.02. X-ray crystal structure analysis (code AUM_1078): formula $C_{22}H_{21}NO_6W$, $M = 579.25$, orange crystal, 0.50 × 0.20 × 0.10 mm, $a = 6.465(1)$ Å, $b = 11.510(1)$ Å, $c = 15.575(1)$ Å, $\alpha = 73.21(1)°$, $\beta = 84.07(1)°$, $\gamma = 84.08(1)°$, $V = 1100.4(3)$ Å^3, $\rho_{calc} = 1.748$ g cm^{-3}, $F(000) = 564$ e, $\mu = 52.86$ cm^{-1}, empirical absorption correction via φ scan data ($0.178 \le T \le 0.620$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4859 reflections collected ($-h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 4446 ($R_{int} = 0.025$) independent and 4035 observed reflections [$I \ge 2\sigma(I)$], 272 refined parameters, $R = 0.050$, $wR_2 = 0.131$, max. residual electron density 3.36 (−3.94) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.[23]

3b: ^{1}H NMR (CDCl$_3$, 25 °C) δ 7.28 (3 H, m, Ph), 7.09 (2 H, "d", Ph), 5.47 (1 H, s, EtOC═C*H*), 4.51 (1 H, s, C*H*Ph), 4.09 (2 H, m, diastereotopic OCH$_2$), 3.79, 3.66, 3.58 and 3.16 (1 H each, m each, 2 diastereotopic NCH$_2$), 2.60 [1 H, C*H*W(CO)$_5$], 2.14 and 2.08 (1:3 H, m each, 2 NCH$_2$C*H*$_2$), 1.36 (3 H, t, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 25 °C) δ 202.9 and 201.3 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 188.8 (C$_q$, C═N$^+$), 182.9 (C$_q$, EtO-*C*), 141.3 (C$_q$, *i*-C Ph), 128.9, 126.9, and 126.4 (2:1:2, CH each, Ph), 95.1 (CH, C2), 68.0 (OCH$_2$), 65.7 (CH, CHPh), 50.0 and 49.0 (NCH$_2$ each), 37.5 [CH, CHW(CO)$_5$$^-$], 25.2 (2 NCH$_2$*C*H$_2$), 14.0 (OCH$_2$*C*H$_3$); IR (diffuse reflection), cm^{-1} (%) 2052.6 (10), 1974.9 (70), 1891.1 (100) [ν(C≡O)], 1591.8 (30) [ν(C═N$^+$)]; MS (70 eV), ^{184}W, *m*/*e* (%) 579 (1) [M$^+$], 551 (0) [M$^+$ − CO], 523 (1) [M$^+$ − 2 CO], 495 (3) [M$^+$ − 3 CO], 467 (5) [M$^+$ − 4 CO], 439 (3) [M$^+$ − 5 CO], 255 (82) [M$^+$ − W(CO)$_5$], 226 (100). Anal. Calcd for $C_{22}H_{21}NO_6W$ (579.3): C, 45.62; H, 3.65; N, 2.42. Found: C, 45.59; H, 3.72; N, 2.02.

6b: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.32 and 7.26 (2 H each, "t" each, *m*-CH Ph each), 7.23 and 7.19 (3 H each, m each, *o*- and *p*-CH Ph each), 4.93 (1 H, dd, $^3J = 11$ Hz and 11, 1′-H), 4.77 (2 H, m, diastereotopic OCH$_2$), 4.01 (1 H, dd, $^3J = 11$ and 12 Hz, 2′-H), 3.95 (1 H, d, $^3J = 12$ Hz, 3′-H), 3.46 (1 H, ddd; $^3J = 12$, 11 and 4 Hz, 6′-H); 3.45, 3.34, 3.16, and 3.07 (1 H each, m each, 2 NCH$_2$), 2.95 (1 H, dd, $^2J = -15$ and $^3J = 12$ Hz, 5′-H$_{ax}$), 2.74 (1 H, dd, $^2J = -15$ and $^3J = 4$ Hz, 5′-H$_{eq}$); 1.86, 1.78, and 1.75 (2:4:2 H, m each, 2 NCH$_2$C*H*$_2$), 1.80 (3 H, t, $^3J = 7$ Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 340.8 (W═C), 203.8 (C$_q$, C4′), 202.4 and 196.4 [1:4, *trans*- and *cis*-CO, W(CO)$_5$], 165.8 (C4′),140.2 and 139.1 (C$_q$ each, *i*-C Ph each); 129.2, 129.0, 128.0, 127.7, 127.6, and 127.5 (2:2:1:2:2:1, CH each, Ph each), 80.1 (OCH$_2$), 77.7 (CH, C1′), 61.3 (CH; C3′), 50.4 (CH, C2′), 48.0 (CH$_2$, C5′), 47.1 (CH, C6′), 46.7 and 45.6 (broad each, NCH$_2$ each), 25.8 and 24.22 (broad each, NCH$_2$*C*H$_2$ each), 14.9 (OCH$_2$*C*H$_3$); IR (*n*-hexane), cm^{-1} (%) 2063.4 (30), 1980.9 (5), 1918.0 (100), [ν(C≡O)], 1716.9 (50), [ν(C═O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 643 (20) [M$^+$ − 3 CO], 615 (35) [M$^+$ − 4 CO], 587 (20) [M$^+$ − 5 CO], 403 (45) [M$^+$ − W(CO)$_5$]. X-ray crystal structure analysis of compound **6b** (code AUM_1830): formula $C_{31}H_{29}NO_8W \times (0.25\ C_4H_{10}O)$, $M = 745.93$, orange crystal 0.30 × 0.25 × 0.10 mm, $a = 60.883(1)$ Å, $b = 11.033(1)$ Å, $c = 20.858(1)$ Å, $\beta = 101.54(1)°$, $V = 13727.6(14)$ Å^3, $\rho_{calc} = 1.444$ g cm^{-3}, $F(000) = 5928$ e, $\mu = 34.12$ cm^{-1}, absorption correction via SORTAV ($0.428 \le T \le 0.727$), $Z = 16$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 38 610 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å 16183 ($R_{int} = 0.041$) independent and 11 924 observed reflections [$I \ge 2\sigma(I)$], 752 refined parameters, $R = 0.049$, $wR_2 = 0.138$, max. residual electron density 1.66 (−0.71) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms, solvent molecule refined with isotropic thermal displacement parameters.[23]

Pentacarbonyl{[3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-phenyl-1-cyclobutenyl](dimethylamino)methylene}-tungsten [(3*S,4*S**)-9c and (3*S**,4*R**)-9c].** To *N*,*N*-Dimethyl-3-phenylacrylamide (**7a**) (263 mg, 1.50 mmol) in 2 mL of dry dichloromethane in a 5 mL screw-top vessel was added phosphorus oxychloride (229 mg, 1.50 mmol) with stirring at 0 °C. To the pale yellow precipitate, which was formed within ca. 30 min at 0 °C was added a mixture of pentacarbonyl[2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidene]tungsten (**1c**) (486 mg, 1.00 mmol) and triethylamine (303 mg, 3.00 mmol) in 1 mL of dichloromethane. The mixture was brought to dryness (20 °C, 2 kPa) after 16 h at 20 °C, and the residue was dissolved in dichloromethane/diethyl ether (1:1) and separated by chromatography on silica gel (column 25 × 2 cm). Elution with *n*-pentane afforded colorless hexacarbonyltungsten, which was discarded. Subsequent elution with *n*-pentane/dichloromethane (2:1) gave a yellow fraction containing compounds (3*S**,4*S**)-**9c** and (3*S**,4*R**)-**9c** in a molar ratio 8:1 [553 mg, 86%, $R_f = 0.6$ in 1:2 *n*-pentane/dichloromethane on silica gel,

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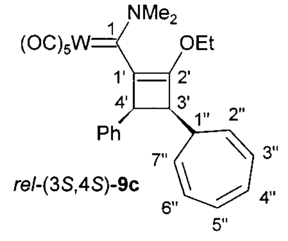
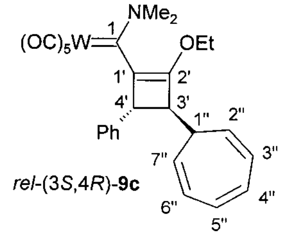
[23] (23) Data sets were collected with Nonius MACH3 and KappaCCD diffractometers, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (Fair, K. Enraf-Nonius B.V., 1990) and Denzo-SMN (Otwinowski, Z., Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction for CCD data SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-86 and SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-93 and SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997).

yellow crystals from 1:1 diethyl ether/*n*-pentane at − 20 °C, mp 66 °C).



rel-(3*S*,4*S*)-**9c**

(3*S,4*S**)-9c**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.17 (3 H, m, Ph), 7.04 (2 H, “d”, Ph), 6.42 (2 H, m, 4″-H and 5″-H C_7H_7), 6.04 and 5.80 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.23 and 4.72 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.70 (1 H, d, ^3J = 4.8 Hz, 4′-H), 3.94 (2 H, m, diastereotopic OCH_2), 3.78 (3 H, s, NCH_3), 3.73 (1 H, dd, ^3J = 9.5 and 4.8 Hz, 3′-H), 3.60 (3 H, s, NCH_3), 1.53 (1 H, m, 1″-H C_7H_7), 1.31 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 243.7 (W═C), 203.1 and 198.5 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 143.5 (C_q, C2′), 139.3 (C_q, *i*-C Ph), 130.8 and 130.3 (1:1, CH each, C4″ and C5″ C_7H_7), 129.0, 127.9 (2:2, CH each, Ph), 127.2 (C_q, C1′), 126.8 (*p*-CH Ph), 124.7 and 124.2 (1:1, CH each, C3″ and C6″ C_7H_7), 122.7 and 122.5 (1:1, CH each, C2″ and C7″ C_7H_7), 66.1 (OCH_2), 53.7 (NCH_3 broad), 48.7 (CH, C3′), 48.2 (CH, C4′), 45.5 (NCH_3 broad), 39.2 (CH, C1″ C_7H_7), 15.7 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%) 2066.3 (43), 1942.0 (88), 1901.6 (100) [ν(C≡O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 643 (5) [M^+], 615 (12) [$M^+ - CO$], 587 (1) [$M^+ - 2\ CO$], 559 (28) [$M^+ - 3\ CO$], 531 (8) [$M^+ - 4\ CO$], 503 (100) [$M^+ - 5\ CO$], 319 (16) [$M^+ - W(CO)_5$]. Anal. Calcd for $C_{27}H_{25}NO_6W\cdot(1/2Et_2O)$ (680.4): C, 51.19; H, 4.44; N, 2.06. Found: C, 52.10; H, 4.84; N, 2.36. X-ray crystal structure analysis (code AUM_849): formula $C_{27}H_{25}NO_6W \times (^1/_2C_4H_{10}O)$, $M = 680.39$, yellow crystal, 0.40 × 0.30 × 0.20 mm, $a = 10.782(1)$ Å, $b = 21.102(2)$ Å, $c = 12.936(1)$ Å, $\beta = 92.35(1)°$, $V = 2940.7(5)$ Å^3, $\rho_{calc} = 1.537$ g cm^{-3}, $F(000) = 1348$ e, $\mu = 39.69$ cm^{-1}, empirical absorption correction via φ scan data ($0.300 \leq T \leq 0.504$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 293$ K, $\omega/2\theta$ scans, 6302 reflections collected ($-h, -k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 5982 independent ($R_{int} = 0.030$) and 3810 observed reflections [$I \geq 2\,\sigma(I)$], 340 refined parameters, $R = 0.032$, $wR_2 = 0.065$, max. residual electron density 0.77 (−0.40) e Å^{-3}, disorder in the OEt group (67:33), half disordered ether molecule in the asymmetric unit, hydrogens calculated and refined as riding atoms.[23]



rel-(3*S*,4*R*)-**9c**

(3*S,4*R**)-9c**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.78 (3 H, m, Ph), 7.18 (2 H, m, Ph), 6.64 (2 H, m, 4″-H and 5″-H C_7H_7), 6.26 and 6.19 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.41 and 5.35 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.07 (1 H, d, ^3J = ca. 2.3 Hz, 4′-H), 3.89 (2 H, m, diastereotopic OCH_2), 3.75 and 3.41 (3 H each, s each, NCH_3 each), 3.28 (1 H, dd, ^3J = 8.0 and 2.3 Hz, 3′-H), 2.17 (1 H, m, 1″-H C_7H_7), 1.29 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) (partial assignment only, due to overlapping signals)[26] δ[24]? (Cr═C) and [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 146.8 (C_q, C2′), 142.0 (C_q, *i*-C Ph), 131.1 and 131.0 (1:1, CH each, C4″ and C5″ C_7H_7); 128.7, 127.2, and 126.8 (2:2:1, CH each, Ph), 125.7 (CH C_7H_7), 125.5 (C_q, C1′), 125.3 (CH, C_7H_7), 66.1 (OCH_2), 53.9 (NCH_3 broad), 53.1 (CH, C3′), 48.6 (CH, C4′), 45.9 (NCH_3 broad), 40.8 (CH, C1″ C_7H_7), 15.5 (OCH_2CH_3).

Pentacarbonyl{[3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-phenyl-1-cyclobutenyl]pyrrolidinomethylene}tungsten [(3*S,4*S**)-9d and (3*S**,4*R**)-9d].** 3-Phenyl-1-pyrrolidinoprop-2-en-1-one (**7b**) (302 mg, 1.50 mmol) and phosphorus oxychloride (230 mg, 1.50 mmol) were reacted with pentacarbonyl[2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidene]tungsten (**1c**) (486 mg, 1.00 mmol) and triethylamine (303 mg, 3.00 mmol) as described above to give a 3:1 mixture of compounds (3*S**,4*S**)-**9d** and (3*S**,4*R**)-**9d** [440 mg, 66%, $R_f = 0.6$ in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow oil].

(3*S,4*S**)-9d**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.19 (3 H, m, Ph), 7.07 (2 H, “d”, Ph), 6.46 (2 H, m, 4″-H and 5″-H C_7H_7), 6.03 and 5.82 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.24 and 4.72 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.63 (1 H, d, ^3J = 4.9 Hz, 4′-H), 4.06 and 4.00 (2:4, m each, 2 NCH_2 and diastereotopic OCH_2), 3.72 (1 H, dd, ^3J = 9.2 and 4.9 Hz, 3′-H), 2.15 (4 H, m, 2 NCH_2CH_2), 1.62 (1 H, m, 1″-H C_7H_7), 1.35 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 237.4 (W═C), 203.1 and 199.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 142.1 (C_q, C2′), 139.3 (C_q, *i*-C Ph), 130.7 and 130.2 (1:1, CH each, C4″ and C5″ C_7H_7), 128.9 (2 CH, Ph), 128.8 (C_q, C1′), 127.8 and 126.7 (2:1, CH each, Ph), 124.7 and 124.2 (1:1, CH each, C3″ and C6″ C_7H_7); 122.5 and 122.1 (1:1, CH each, C2″ and C7″ C_7H_7), 66.3 (OCH_2), 61.9 and 55.5 (NCH_2 each), 48.6 (CH, C3′), 48.0 (CH, C4′), 39.1 (CH, C1″ C_7H_7), 25.7 and 24.9 (NCH_2CH_2 each), 15.6 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%) 2065.8 (33), 1942.2 (88), 1900.6 (100) [ν(C≡O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 669 (6) [M^+], 641 (11) [$M^+ - CO$], 613 (0) [$M^+ - 2\ CO$], 585 (32) [$M^+ - 3\ CO$], 557 (7) [$M^+ - 4\ CO$], 529 (100) [$M^+ - 5\ CO$], 345 (12) [$M^+ - W(CO)_5$]. Anal. Calcd for $C_{29}H_{27}NO_6W$ (669.4): C, 52.04; H, 4.07; N, 2.09. Found: C, 52.45; H, 4.27; N, 1.98.

(3*S,4*R**)-9d**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.31 (3 H, m, Ph), 7.21 (2 H, m, Ph), 6.69 (2 H, m, 4″-H and 5″-H C_7H_7), 6.29 and 6.22 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.45 and 5.32 (1 H each, m each, 2″-H and 7″-H C_7H_7), 3.99 and 3.79 (3:3, m each, diastereotopic OCH_2 and 2 NCH_2), 3.29 (1 H, dd, ^3J = 7.2 and 0.9 Hz, 3′-H), 2.12 and 1.93 (3:2, m each, 1″-H C_7H_7 and 2 NCH_2CH_2), 1.32 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) (partial assignment only, due to overlapping signals)[26] δ 236.1 (W═C), 203.1 and 199.7 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 147.7 (C_q, C2′), 144.6 (C_q, *i*-C Ph), 131.1 (2 CH, C4″ and C5″ C_7H_7), 128.7, 127.1, and 126.8 (2:2:1, CH each, Ph), 125.9 (C_q, C1′); 125.8, 125.5, and 122.2 (2:2:2, CH each, C_7H_7),[25] 66.1 (OCH_2), 62.3 and 55.8 (NCH_2 each), 53.5 (CH, C3′), 48.6 (CH, C4′,), 40.2 (CH, C1″ C_7H_7), 25.9 and 24.9 (NCH_2NCH_2 each), 15.3 (OCH_2CH_3).

Pentacarbonyl{[3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-phenyl-1-cyclobutenyl]morpholinomethylene}tungsten [(3*S,4*S**)-9e and (3*S**,4*R**)-9e].** 1-Morpholino-3-phenylprop-2-en-1-one (**7c**) (326 mg, 1.50 mmol) and phosphorus oxychloride (230 mg, 1.50 mmol) were reacted with pentacarbonyl[2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidene]tungsten (**1c**) (486 mg, 1.00 mmol) and triethylamine (303 mg, 3.00 mmol) as described above to give a 20:1 mixture of compounds (3*S**,4*S**)-**9e** and (3*S**,4*R**)-**9e** (424 mg, 62%, $R_f = 0.4$ in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow crystals from *n*-pentane, mp 46 °C).

(3*S,4*S**)-9e**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.19 (3 H, m, Ph), 7.05 (2 H, “d”, Ph), 6.45 (2 H, m, 4″-H and 5″-H C_7H_7), 6.06 and 5.80 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.22 and

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(24) Signal not observed due to dynamic line-broadening.

(25) One signal missing probably due to overlap with signals of the major isomer.

(26) The NMR data were derived from spectra of the mixture of compounds (3*S**,4*S**)-**9** and (3*S**,4*S**)-**9**, but they are listed separately for each compound. The assignment of signals C3′ and C4′, and 3′-H and 4′-H, respectively, is based on the pattern, which has been derived from compound **9a** by ^1J(C,H) and $^{2,3}J$(C,H) correlation experiments.

4.68 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.75 (1 H, d, ^3J = 4.9 Hz, 4′-H); 4.43, 4.32, 4.26, and 4.18 (1 H each, m each, 2 OCH_2CH_2N), 3.95 (6 H, m, diastereotopic OCH_2CH_3 and 2 NCH_2), 3.79 (1 H, dd, ^3J = 9.3 and 4.9 Hz, 3′-H), 1.60 (1 H, m, 1″-H C_7H_7), 1.30 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 241.5 (W═C), 202.8 and 198.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 142.7 (C_q, C2′), 139.0 (C_q, *i*-C Ph), 130.9 and 130.1 (1:1, CH each, C4″ and C5″ C_7H_7), 128.9, 127.8 (2:2, CH each, Ph), 127.1 (C_q, C1′), 126.9 (*p*-CH), 125.0 and 124.3 (1:1, CH each, C3″ and C6″ C_7H_7), 122.1 and 121.8 (1:1, CH each, C2″ and C7″ C_7H_7), 67.8 and 67.6 (OCH_2CH_2N each), 66.3 (OCH_2), 62.9 and 55.0 (NCH_2 each), 48.5 (CH, C3′), 48.4 (CH, C4′), 39.0 (CH, C1″ C_7H_7), 15.6 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%) 2066.8 (33), 1940.1 (88), 1900.1 (100) [ν(C≡O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 685 (2) [M^+], 657 (8) [$M^+ - CO$], 629 (0) [$M^+ - 2\ CO$], 601 (34) [$M^+ - 3\ CO$], 573 (9) [$M^+ - 4\ CO$], 545 (100) [$M^+ - 5\ CO$], 361 (15) [$M^+ - W(CO)_5$]. Anal. Calcd for $C_{29}H_{27}NO_7W$ (685.4): C, 50.82; H, 3.97; N, 2.04. Found: C, 50.76; H, 3.93; N, 1.80.

(3*S,4*R**)-9e**: spectroscopic data were not collected.

Pentacarbonyl{[3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-phenyl-1-cyclobutenyl](dimethylamino)methylene}-chromium [(3*S,4*S**)-9f and (3*S**,4*R**)-9f].** *N*,*N*-Dimethyl-3-phenylacrylamide (**7a**) (175 mg, 1.00 mmol) and oxalyldichloride (140 mg, 1.10 mmol) were reacted with pentacarbonyl-[2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidene]chromium (**1d**) (177 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) to give a 5:2 mixture of compounds (3*S**,4*S**)-**9f** and (3*S**,4*R**)-**9f** (184 mg, 72%, R_f = 0.6 in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow oil).

(3*S,4*S**)-9f**: ^1H NMR ($CDCl_3$, 25 °C) δ 7.18 (3 H, m, Ph), 7.04 (2 H, "d", Ph), 6.44 (2 H, m, 4″-H/5″-H C_7H_7), 6.06 and 5.80 (1 H each, m each, 3″-H/6″-H C_7H_7), 5.26 and 4.73 (1 H each, m each, 2″-H/7″-H C_7H_7), 4.73 (1 H, d, ^3J = 4.8 Hz, 4′-H), 3.92 (2 H, m, diastereotopic OCH_2), 3.86 (3 H, s, NCH_3), 3.69 (1 H, dd, ^3J = 9.5 and 4.8 Hz, 3′-H), 3.64 (3 H, s, NCH_3), 1.54 (1 H, m, 1″-H C_7H_7), 1.31 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 262.1 (Cr═C), 223.3 and 217.6 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 141.9 (C_q, C2′), 139.2 (C_q, *i*-C Ph), 130.7 and 130.2 (1:1, CH each, C4″ and C5″ C_7H_7); 128.8, 127.7, and 126.6 (2:2:1, CH each, Ph), 126.5 (C_q, C1′), 124.6 and 124.1 (1:1, CH each, C3″ and C6″ C_7H_7), 122.8 and 122.6 (1:1, CH each, C2″ and C7″ C_7H_7), 65.9 (OCH_2), 51.0 (NCH_3 broad), 48.8 (CH, C3′), 47.5 (CH, C4′), 46.7 (NCH_3 broad), 39.0 (CH, C1″ C_7H_7), 15.6 (OCH_2CH_3); IR (hexane), cm^{-1} (%) 2051.0 (10), 1926.0 (99) [ν(C≡O)]; MS (70 eV), *m*/*e* (%) 511 (5) [M^+], 483 (12) [$M^+ - CO$], 455 (1) [$M^+ - 2\ CO$], 427 (28) [$M^+ - 3\ CO$], 399 (8) [$M^+ - 4\ CO$], 371 (100) [$M^+ - 5\ CO$], 319 (20) [$M^+ - Cr(CO)_5$], 275 (21), 236 (41), 115 (48), 91 (100), 52 (90).

(3*S,4*R**)-9f**: ^1H NMR ($CDCl_3$, 25 °C) δ 7.29 (3 H, m, Ph), 7.19 (2 H, m, Ph), 6.66 (2 H, m, 4″-H and 5″-H C_7H_7), 6.28 and 6.21 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.41 and 5.36 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.11 (1 H, d, ^3J = ca. 0.7 Hz, 4′-H), 3.90 (2 H, m, diastereotopic OCH_2), 3.78 and 3.46 (3 H each, s each, NCH_3 each), 3.22 (1 H, dd, ^3J = 8.3 and 0.7 Hz, 3′-H), 2.19 (1 H, m, 1″-H C_7H_7), 1.29 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 263.4 (Cr═C), 223.3 and 217.8 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 144.4 (C_q, C2′), 141.9 (C_q, *i*-C Ph), 131.0 and 130.9 (1:1, CH each, C4″ and C5″ C_7H_7); 128.5, 127.1, and 126.6 (2:2:1, CH each, Ph), 125.6 and 125.1 (1:1, CH each, C_7H_7), 124.3 and 122.8 (CH C_7H_7), 65.9 (OCH_2), 53.1 (CH, C3′), 51.2 (NCH_3 broad), 48.3 (CH, C4′), 47.0 (NCH_3 broad), 40.8 (CH, C1″ C_7H_7), 15.4 (OCH_2CH_3).

Pentacarbonyl{[3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-phenyl-1-cyclobutenyl]pyrrolidinomethylene}chromium [(3*S,4*S**)-9g and (3*S**,4*R**)-9g].** 3-Phenyl-1-pyrrolidinoprop-2-en-1-one (**7b**) (201 mg, 1.00 mmol) and oxalyldichloride (140 mg, 1.10 mmol) were reacted with pentacarbonyl-[2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidene]chromium (**1d**) (177 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) as described above to give a 2:1 mixture of compounds (3*S**,4*S**)-**9g** and (3*S**,4*R**)-**9g** (184 mg, 68%, R_f = 0.6 in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow oil).

(3*S,4*S**)-9g**: ^1H NMR ($CDCl_3$, 25 °C) δ 7.18 (3 H, m, Ph), 7.05 (2 H, "d", Ph), 6.45 (2 H, m, 4″-H and 5″-H C_7H_7), 6.04 and 5.80 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.26 and 4.71 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.68 (1 H, d, ^3J = 4.9 Hz, 4′-H), 4.16 and 4.08 (2:2, m each, 2 NCH_2), 3.93 (2 H, m, diastereotopic OCH_2), 3.69 (1 H, dd, ^3J = 9.3 and 4.9 Hz, 3′-H), 2.12 (4 H, m, 2 NCH_2CH_2), 1.57 (1 H, m, 1″-H C_7H_7), 1.31 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 256.5 (Cr═C), 223.6 and 218.3 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 142.4 (C_q, C2′), 139.7 (C_q, *i*-C Ph), 131.0 and 130.5 (1:1, CH each, C4″ and C5″ C_7H_7), 129.2 (2 CH, Ph), 128.4 (C_q, C1′), 128.1 and 126.9 (2:1, CH each, Ph), 124.9 and 124.4 (1:1, CH each, C3″ and C6″ C_7H_7), 123.1 and 122.9 (1:1, CH each, C2″ and C7″ C_7H_7), 66.5 (OCH_2), 59.7 and 57.0 (NCH_2 each), 49.0 (CH, C3′), 47.7 (CH, C4′), 39.3 (CH, C1″ C_7H_7), 25.8 and 25.5 (NCH_2CH_2 each), 16.0 (OCH_2CH_3); IR (hexane), cm^{-1} (%) 2048.8 (15), 1923.9 (99) [ν(C≡O)]; MS (70 eV), *m*/*e* (%) 537 (3) [M^+], 509 (11) [$M^+ - CO$], 481 (0) [$M^+ - 2\ CO$], 453 (30) [$M^+ - 3\ CO$], 425 (6) [$M^+ - 4\ CO$], 397 (97) [$M^+ - 5\ CO$], 345 (21) [$M^+ - Cr(CO)_5$], 275 (23), 262 (25), 238 (25), 115 (52), 103 (21), 91 (92), 52 (100). Anal. Calcd for $C_{29}H_{27}NO_6Cr$ (537.5): C, 64.80; H, 5.06; N, 2.61. Found: C, 65.02; H, 5.17; N, 2.51.

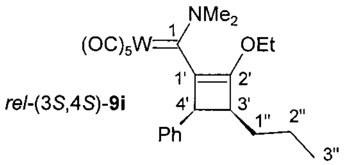
(3*S,4*R**)-9g**: ^1H NMR ($CDCl_3$, 25 °C) δ 7.28 (3 H, m, Ph), 7.19 (2 H, m, Ph), 6.67 (2 H, m, 4″-H/5″-H C_7H_7), 6.28 and 6.20 (1 H each, m each, 3″-H/6″-H C_7H_7), 5.41 and 5.32 (1 H each, m each, 2″-H/7″-H C_7H_7), 4.02 (1 H, d, ^3J = ca. 0.9 Hz, 4′-H), 3.92 (2 H, m, diastereotopic OCH_2), 3.88 and 3.68 (3:1, m each, 2 NCH_2), 3.26 (1 H, dd, ^3J = 7.3 and 0.9 Hz, 3′-H), 2.07 and 1.94 (3:2, m each, 1″-H C_7H_7 and 2 NCH_2CH_2), 1.32 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 258.0 (Cr═C), 223.7 and 218.6 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 147.5 (C_q, C2′), 142.4 (C_q, *i*-C Ph), 131.4 and 131.3 (1:1, CH each, C4″ and C5″ C_7H_7), 128.9, 127.4, and 126.9 (2:2:1, CH each, Ph), 126.2 (C_q, C1′), 126.0, 125.5, 124.6, and 122.8 (1:1:1:1, CH each, C_7H_7), 66.3 (OCH_2), 60.1 and 57.3 (NCH_2 each), 53.8 (CH, C3′), 48.6 (CH, C4′), 40.8 (CH, C1″ C_7H_7), 25.9 and 25.5 (NCH_2NCH_2 each), 14.4 (OCH_2CH_3).

Pentacarbonyl{[3-(2,4,6-cycloheptatrienyl)-2-ethoxy-4-phenyl-1-cyclobutenyl]-morpholinomethylene}chromium [(3*S,4*S**)-9h and (3*S**,4*R**)-9h].** 1-Morpholino-3-phenylprop-2-en-1-one (**7c**) (217 mg, 1.00 mmol) and oxalyldichloride (140 mg, 1.10 mmol) were reacted with pentacarbonyl[2-(2,4,6-cycloheptatrienyl)-1-ethoxyethylidene]chromium (**1d**) (177 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) as described above to give a 9:1 mixture of compounds (3*S**,4*S**)-**9h** and (3*R**,4*S**)-**9h** (144 mg, 52%, R_f = 0.4 in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow crystal from *n*-pentane, mp 72 °C).

(3*S,4*S**)-9h**: ^1H NMR ($CDCl_3$, 25 °C) δ 7.19 (3 H, m, Ph), 7.04 (2 H, "d", Ph), 6.46 (2 H, m, 4″-H and 5″-H C_7H_7), 6.09 and 5.83 (1 H each, m each, 3″-H and 6″-H C_7H_7), 5.22 and 4.68 (1 H each, m each, 2″-H and 7″-H C_7H_7), 4.78 (1 H, d, ^3J = 4.9 Hz, 4′-H); 4.52, 4.41, 4.28, and 4.19 (1 H each, m each, 2 OCH_2CH_2N), 3.93 (6 H, m, diastereotopic OCH_2CH_3 and 2 NCH_2), 3.76 (1 H, dd, ^3J = 9.3 and 4.9 Hz, 3′-H), 1.62 (1 H, m, 1″-H C_7H_7), 1.32 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C)[26] δ 259.9 (Cr═C), 223.0 and 217.4 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 140.9 (C_q, C2′), 139.0 (C_q, *i*-C Ph), 130.8 and 130.0 (1:1, CH each, C4″ and C5″ C_7H_7); 128.8, 127.8, and 126.8 (2:2:1, CH each, Ph), 126.4 (C_q, C1′), 124.9 and 124.2 (1:1, CH each, C3″ and C6″ C_7H_7), 122.2 and 121.9 (1:1, CH each, C2″ and C7″ C_7H_7), 67.8 and 67.6 (OCH_2CH_2N each), 66.1 (OCH_2), 60.5 and 55.9 (NCH_2 each), 48.5 (CH, C3′), 47.7 (CH, C4′), 38.8 (CH, C1″ C_7H_7), 15.6 (OCH_2CH_3); IR (hexane), cm^{-1} (%) 2050.9 (12), 1926.7 (100) [ν(C≡O)]; MS (70 eV), *m*/*e* (%) 553 (2) [M^+], 525 (4) [$M^+ - CO$], 497 (0) [$M^+ - 2\ CO$], 469 (13) [$M^+ - 3\ CO$], 441 (4) [$M^+ - 4\ CO$], 413 (47) [$M^+ - 5\ CO$], 385 (1) [$M^+ - Cr(CO)_5$], 275 (11), 193 (25), 115 (36), 103 (16), 91 (100), 52 (54).

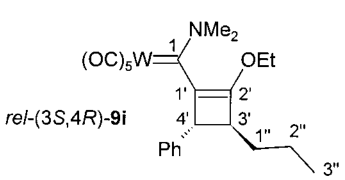
(3*S,4*R**)-9h**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.20 (5 H, m, Ph), 6.65 (2 H, m, 4″-H and 5″-H C_7H_7), 6.23 (2 H, m, 3″-H and 6″-H C_7H_7), 5.39 (2 H, m, 2″-H and 7″-H C_7H_7), 4.19 (4 H, m, 2 OCH_2CH_2N), 3.95 (7 H, m, 4′-H and OCH_2CH_3 and 2 NCH_2), 3.29 (1 H, dd, ^3J = 7.3 and 0.9 Hz, 3′-H), 2.20 (1 H, m, 1″-H C_7H_7), 1.30 (3 H, t, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) (partial assignment only, due to overlapping signals)[26] δ[24] (Cr=C) and [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$],[24] (C_q, C2′), 141.4 (C_q, *i*-C Ph), 131.0 and 130.8 (1:1, CH each, C4″ and C5″ C_7H_7), 128.6 and 127.1 (2:2, CH each, Ph), 125.6 (C_q, C1′), 125.1 and 122.8 (1:1, CH each, C_7H_7), 67.7 and 67.3 (OCH_2CH_2N each), 65.8 (OCH_2), 60.3 and 56.2 (NCH_2 each), 52.2 (CH, C3′), 48.0 (CH, C4′), 40.9 (CH, C1″ C_7H_7), 15.2 (OCH_2CH_3).

Pentacarbonyl[(2-ethoxy-4-phenyl-3-propyl-1-cyclobutenyl)(dimethylamino)methylene]tungsten [(3*S,4*S**)-9i and (3*S**,4*R**)-9i].** *N*,*N*-Dimethyl-3-phenylacrylamide (**7a**) (175 mg, 1.00 mmol) and phosphorus oxychloride (153 mg, 1.00 mmol) were reacted with pentacarbonyl(1-ethoxybutylidene]-tungsten (**1e**) (219 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) to give a 7:1 mixture of compounds (3*S**,4*S**)-**9i** and (3*S**,4*R**)-**9i** (158 mg, 53%, R_f = 0.6 in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow crystals from *n*-pentane, mp 39 °C).



rel-(3*S*,4*S*)-**9i**

(3*S,4*S**)-9i**:[27] ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.25 (3 H, m, Ph), 7.08 (2 H, "d", Ph), 4.59 (1 H, d, ^3J = 4.9 Hz, 4′-H), 4.01 (2 H, m, diastereotopic OCH_2), 3.79 (3 H, s, NCH_3), 3.56 (3 H, s, NCH_3), 3.37 (1 H, m, 3′-H), 1.32 (3 H, t, OCH_2CH_3), 1.00 (4 H, m, 3′-CH_2CH_2), 0.56 (3 H, t, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 241.2 (W=C), 203.0 and 198.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 146.4 (C_q, C2′), 140.0 (C_q, *i*-C Ph); 128.8, 127.9, and 126.6 (2:2:1, CH each, Ph), 125.5 (C_q, C1′), 65.3 (OCH_2), 53.9 (NCH_3 broad), 48.7 (CH, C4′), 46.1 (CH, C3′), 45.3 (NCH_3 broad), 31.2 ($CH_2CH_2CH_3$), 20.2 ($CH_2CH_2CH_3$), 15.6 (OCH_2CH_3), 14.1 ($CH_2CH_2CH_3$); IR (diffuse reflection), cm^{-1} (%) 2065.8 (38), 1941.8 (86), 1901.8 (100) [ν(C≡O)]; MS (70 eV), ^{184}W, *m*/*e* (%) 595 (2) [M^+], 567 (11) [$M^+ - CO$], 539 (0) [$M^+ - 2\ CO$], 511 (32) [$M^+ - 3\ CO$], 483 (7) [$M^+ - 4\ CO$], 455 (100) [$M^+ - 5\ CO$], 271 (22) [$M^+ - W(CO)_5$]. Anal. Calcd for $C_{23}H_{25}NO_6W$ (595.3): C, 46.41; H, 4.23; N, 2.35. Found: C, 46.45; H, 4.33; N, 2.28.



rel-(3*S*,4*R*)-**9i**

(3*S,4*R**)-9i**: ^{13}C NMR ($CDCl_3$, 25 °C) (partial assignment only, due to overlapping signals) δ 128.4, 126.9, 52.1, 50.6, 45.7, 34.5, 21.8, 14.3.

Pentacarbonyl[(2-ethoxy-4-phenyl-3-propyl-1-cyclobutenyl)pyrrolidinomethylene]tungsten [(3*S,4*S**)- and (3*S**,4*R**)-9j].** 3-Phenyl-1-pyrrolidinoprop-2-en-1-one (**7b**) (201 mg, 1.00 mmol) and phosphorus oxychloride (153 mg, 1.50 mmol) were reacted with pentacarbonyl(1-ethoxybutylidene]-tungsten (**1e**) (219 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) as described above to afford a 5:1 mixture of compounds (3*S**,4*S**)-**9j** and (3*S**,4*R**)-**9j** (134 mg, 43%, R_f = 0.6 in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow oil).

(3*S,4*S**)-9j**:[27] ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.26 (3H, m, Ph), 7.09 (2 H, "d", Ph), 4.51 (1 H, d, ^3J = 4.9 Hz, 4′-H), 4.05 (2 H, m, diastereotopic OCH_2), 3.98 (4 H, m, 2 NCH_2), 3.37 (1 H, m, 3′-H), 2.07 (4 H, m, 2 NCH_2CH_2), 1.34 (3 H, t, OCH_2CH_3), 1.00 (4 H, m, $CH_2CH_2CH_3$), 0.60 (3 H, t, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 234.3 (W=C), 203.5 and 199.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 149.3 (C_q, C2′), 140.0 (C_q, *i*-C Ph), 128.8, 127.9, and 126.5 (2:2:1, CH each, Ph), 126.0 (C_q, C1′), 65.4 (OCH_2), 62.1 and 55.3 (NCH_2 each), 48.8 (CH, C4′), 46.2 (CH, C3′), 31.1 ($CH_2CH_2CH_3$), 25.9 and 24.9 (NCH_2CH_2 each), 20.1 ($CH_2CH_2CH_3$), 15.5 (OCH_2CH_3), 14.0 ($CH_2CH_2CH_3$); IR (diffuse reflection), cm^{-1} (%) 2064.8 (35), 1901.6 (100) [ν(C≡O)]; MS (70 eV), 184W, *m*/*e* (%) 621 (4) [M^+], 593 (9) [$M^+ - CO$], 565 (0) [$M^+ - 2\ CO$], 537 (32) [$M^+ - 3\ CO$], 509 (9) [$M^+ - 4\ CO$], 481 (100) [$M^+ - 5\ CO$], 297 (16) [$M^+ - W(CO)_5$]. Anal. Calcd for $C_{25}H_{27}NO_6W$ (621.3): C, 48.33; H, 4.38; N, 2.25. Found: C, 49.18; H, 4.56; N, 2.11.

(3*S,4*R**)-9j**: ^{13}C NMR ($CDCl_3$, 25 °C) (partial assignment only, due to overlapping signals) 149.9, 142.9, 128.4, 126.8, 126.4, 55.6, 52.1, 50.8, 34.6, 29.0, 22.6, 21.4, 14.3, 14.0.

Pentacarbonyl[(2-ethoxy-4-phenyl-3-propyl-1-cyclobutenyl)morpholinomethylene]tungsten [(3*S,4*S**)- and (3*S**,4*R**)-9k].** 1-Morpholino-3-phenylprop-2-en-1-one (**7c**) (217 mg, 1.00 mmol) and phosphorus oxychloride (153 mg, 1.50 mmol) were reacted with pentacarbonyl(1-ethoxybutylidene]-tungsten (**1e**) (219 mg, 0.50 mmol) and triethylamine (202 mg, 2.00 mmol) as described above to give a 20:1 mixture of compounds (3*S**,4*S**)-**9k** and (3*S**,4*R**)-**9k** (153 mg, 48%, R_f = 0.5 in 1:2 *n*-pentane/dichloromethane, on silica gel, yellow crystals from *n*-pentane, mp 51 °C).

(3*S,4*S**)-9k**:[27] ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.29 (3 H, m, Ph), 7.07 (2 H, "d", Ph), 4.68 (1 H, d, ^3J = 4.9 Hz, 4′-H), 4.52 and 4.25 (1:2, m each, OCH_2CH_2N), 4.03 and 3.84 (5:2, m each, diastereotopic OCH_2CH_3 and OCH_2CH_2N), 3.42 (1 H, m, 3′-H), 1.32 (3 H, t, OCH_2CH_3), 1.01 (4 H, m, $CH_2CH_2CH_3$), 0.59 (3 H, t, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 239.6 (W=C), 203.0 and 198.4 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 144.7 (C_q, C2′), 139.7 (C_q, *i*-C Ph), 128.7, 128.0, and 126.7 (2:2:1, CH each, Ph), 124.7 (C_q, C1′), 67.9 and 67.7 (OCH_2CH_2N each), 65.3 (OCH_2), 63.0 and 54.7 (NCH_2 each), 48.9 (CH, C4′), 46.1 (CH, C3′), 31.1 ($CH_2CH_2CH_3$), 20.2 ($CH_2CH_2CH_3$), 15.6 (OCH_2CH3), 14.0 ($CH_2CH_2CH_3$); IR (diffuse reflection), cm^{-1} (%) 2066.8 (33), 1940.1 (88), 1900.1 (100) [ν(C≡O)]; MS (70 eV), 184W, *m*/*e* (%) 637 (2) [M^+], 609 (8) [$M^+ - CO$], 581 (0) [$M^+ - 2\ CO$], 553 (34) [$M^+ - 3\ CO$], 525 (9) [$M^+ - 4\ CO$], 497 (100) [$M^+ - 5\ CO$], 313 (15) [$M^+ - W(CO)_5$]. Anal. Calcd for $C_{25}H_{27}NO_7W$ (637.3): C, 47.11; H, 4.27; N, 2.20. Found: C, 46.92; H, 4.24; N, 2.23.

(3*S,4*R**)-9k**: spectroscopic data were not collected.

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Supporting Information Available: Details of the X-ray crystal structure analyses, including bond distances and angles for compounds **9c**, **6b**, and (3*E*)-**2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0108604

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[27] The configurational assignment is based on the coupling constant ^3J(3′H,4′-H) = 4.9 Hz.