Organic Syntheses via Transition Metal Complexes. 118.[1] Retro-Fischer Reaction Induced by a β-Imino Functionality of (Alkyl,ethoxy)carbene Complexes (M = W, Cr): Efficient Access to *C*-Enamino and *N*-Enamino Carbene Complexes

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Received January 24, 2002

Condensation of (ethoxy,methyl)carbene complexes $(OC)_5M{=}C(OEt)CH_3$ **1a**,**b** (M = W, Cr) with α,β-unsaturated secondary acid amides PhCH=CHC(=O)NHR **7a**−**c** in the presence of $POCl_3/Et_3N$ affords *C*-enamino carbene complexes (3*Z*)-**3a**−**f** (= 4-*NH*-amino-1-metalla-1,3,5-hexatrienes). A fundamental change of the reaction course was induced by an α-substituent of the carbene complex **1**. Thus, (*n*-butyl,ethoxy)carbene complex **1c** under similar conditions yields *N*-enamino carbene complexes **8h**−**l** instead of *C*-enamino carbene complexes (Scheme 2). Formation of compounds **8** involves an unprecedented retro-Fischer reaction, by which the C,C bond between the α-carbon atom and the carbene carbon atom is broken under the influence of a β-imino functionality.

Fischer carbene complexes have been applied as stoichiometric reagents in a number of high-yielding transformations of potential use in organic synthesis.[2] Prominent examples include formation of cyclopentadienes by π-cyclization of 1-metalla-1,3,5-hexatrienes.[3,4] Up to date, 1-metalla-1,3,5-hexatrienes were generated mainly from (1-alkynyl)carbene complexes.[5] More recently, attempts have been made to obtain these compounds also from (alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R$ **1** (M = W, Cr) through condensation with α,β-unsaturated organic carbonyl compounds (Scheme 1).[6]

On the basis of earlier studies, in which 1-metalla-1,3-butadienes $(CO)_5M{=}C(OEt)CH{=}CHR$ and $(CO)_5M{=}C(OEt)CH{=}C(NR_2)R^1$ were obtained by condensation of (ethoxy,methyl)carbene complexes $(CO)_5M{=}C(OEt)CH_3$ **1a**,**b** (M = W, Cr) with aldehydes and ketones,[7,8] acid chlorides,[9] and acid amides,[10] respectively, we succeeded in obtaining vinylogous systems, like 4-amino-1-metalla-1,3,5-hexatrienes by condensation of compounds **1a**,**b** with α,β-unsaturated *tertiary* acid amides PhCH=CHC(=O)NR_2. In line with expectation, these compounds underwent a π-cyclization to zwitterionic η^1-cyclopentadiene complexes (Scheme 1). Interestingly, a remarkable change of the reaction mode was triggered by the presence of an α-substituent in compounds **1**. Thus, it was found that condensation of (*prim*-alkyl,ethoxy)carbene complexes $(CO)_5M{=}C(OEt)CH_2R^1$ **1** (M = Cr, W; R^1 = *n*-Pr, *c*-C_7H_7) with α,β-unsaturated tertiary amides did not afford 2-alkyl-4-amino-1-metalla-1,3,5-hexatrienes, but quite unexpectedly gave (cyclobutenyl)-

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† X-ray structure analysis of compound **3b**.
‡ X-ray structure analysis of compound **8h**.

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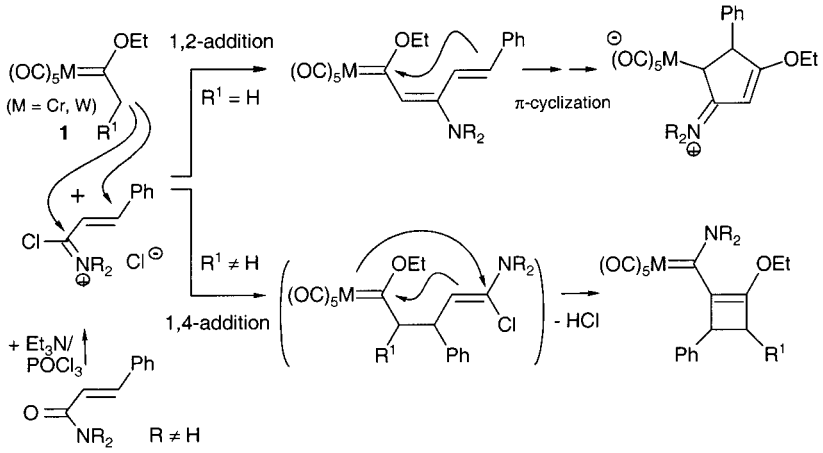
10.1021/om0200499 CCC: $22.00
Publication on Web 05/24/2002

Scheme 1. 1-Metalla-1,3,5-hexatrienes and Carbocyclic Rings by Condensation of (Alkyl,ethoxy)carbene Complexes with α,β-Unsaturated Tertiary Acid Amides; Influence of α-Substituents R[1] on the Reaction Course



carbene complexes instead.[6] Subsequent studies on condensation reactions of compounds **1** with α,β-unsaturated *secondary* amides produced a further example of the strong influence of α-substituents on the reaction course, which is presented in this paper.

Condensation of (ethoxy,methyl)carbene complexes $(OC)_5M{=}C(OEt)CH_3$ **1a**,**b** (M = W, Cr) with α,β-unsaturated *secondary* amides PhCH═CHC(═O)NHR **7a**−**c** in the presence of $POCl_3/Et_3N$ gave 4-*NH*-amino-1-metalla-1,3,5-hexatrienes (3*Z*)-**3a**−**f** in quite smooth reaction (Scheme 2). It should be noted that the central double bond of compounds **3** exhibits a 3*Z* configuration, which was typically observed also with 4-*NH*-amino-1-metalla-1,3-butadienes, but not with 4-*NR*$_2$-amino-1-metalla-1,3,5-hexatrienes (Scheme 1).[11] The reaction appears to be initiated by formation of imidoyl chlorides **4a**−**c** from the corresponding α,β-unsaturated secondary amides PhCH═CHC(═O)NHR **7** and $POCl_3/Et_3N$. Compounds **4** and (ethoxy,methyl)carbene complexes **1a**,**b** are assumed to afford (β-imino)alkylcarbene complexes **2a**−**f** [= (alkylidenamine-2-yl)carbene complexes]. To our knowledge, compounds of the latter type have not previously been investigated. They are expected to be very labile and readily undergo a base-induced 1,3 hydrogen migration to give 1-metalla-1,3,5-hexatrienes (3*Z*)-**3a**−**f**.

While reactions of (*prim*-alkyl,ethoxy)carbene complexes with iminium chlorides were found to be initiated by 1,4 addition of the conjugate base of a carbene complex **1** (Scheme 1), this turned out to not be the case with imidoyl chlorides **4**. The latter compounds seem to react in 1,2 fashion even with (*prim*-alkyl,ethoxy)-carbene complexes, which may be attributed to the different charge delocalization in these systems but also to the fact that an imino group is sterically less demanding than an iminium functionality. The ease by which an α-hydrogen atom of compound **5** is removed, and for example transferred to the nitrogen atom, is influenced by the geometric arrangement of the corresponding α-CH bond toward the neighboring π-system which is responsible for its activation. Quite obviously, this geometry is dependent on steric interactions imposed by an α-substituent R[1].[12] It thus appears that the α-methine proton of a compound **5** is much less acidic than an α-methylene proton in a compound **2**, and for this reason formation of a (3*Z*)-4-*NH*-amino-1-metalla-1,3,5-hexatriene by rearrangement of a compound **5** seems to be outrun by a process yielding a *N*-butadienyl aminocarbene complex **8** instead (Scheme 2). This unanticipated transformation involves breaking of a bond between the α-carbon atom and the carbene carbon atom by a "retro-Fischer reaction". This process might be induced by interaction of the β-imino group with the carbene carbon atom to give a zwitterionic dihydroazetium carbonylmetalate **6**, which is expected to undergo fragmentation to a (*N*-enamino)carbene complex *anti*-**8** (Scheme 2). Up to date we cannot exclude a different pathway involving an ion pair carbyne/enaminide mechanism, especially since it was found that amides **7b**,**d** containing secondary *N*-alkyl substituents (R = *i*-Pr or *c*-C_6H_{11}) react faster than amides **7a**,**c** with primary *N*-alkyl substituents (R = allyl, *n*-Pr, or Me) and also afford higher chemical yields.

Structure Elucidation of Compounds 3 and 8. *C*-Enamino carbene complexes **3** of tungsten and chromium exhibit NMR chemical shifts of the carbene carbon atoms in a narrow range characteristic of the metal (e.g., δ W═C **3a**, 267.1; **3b**, 265.3; δ Cr═C **3d**, 289.2) and signals of the β-carbon atoms C═*C*N (δ **3a**, 153.9; **3b**, 153.1; **3d**, 150.5) in range clearly different from iminium carbonylmetalates[13] or (amino,alkoxy)-carbene complexes **8**.

The ligand backbone W−C2−C3−C4−N10 of compound (3*Z*)-**3b** adopts an essentially planar sickle shape [W−C2−C3−C4 175.8(3), C2−C3−C4−N10−4.0(7), C2−C3−C4−C5 178.2(4) Å]. Short bond distances between C2−C3 1.393(5) Å and C4−N10 1.329(5) Å indicate a strong charge delocalization within the π-system (Figure 1). The system appears to be stabilized by a hydrogen bond N10−H10···O7 (corresponding distances N10−H10 0.86, H10···O7 1.91 Å, angle N10−H10···O7 138°).

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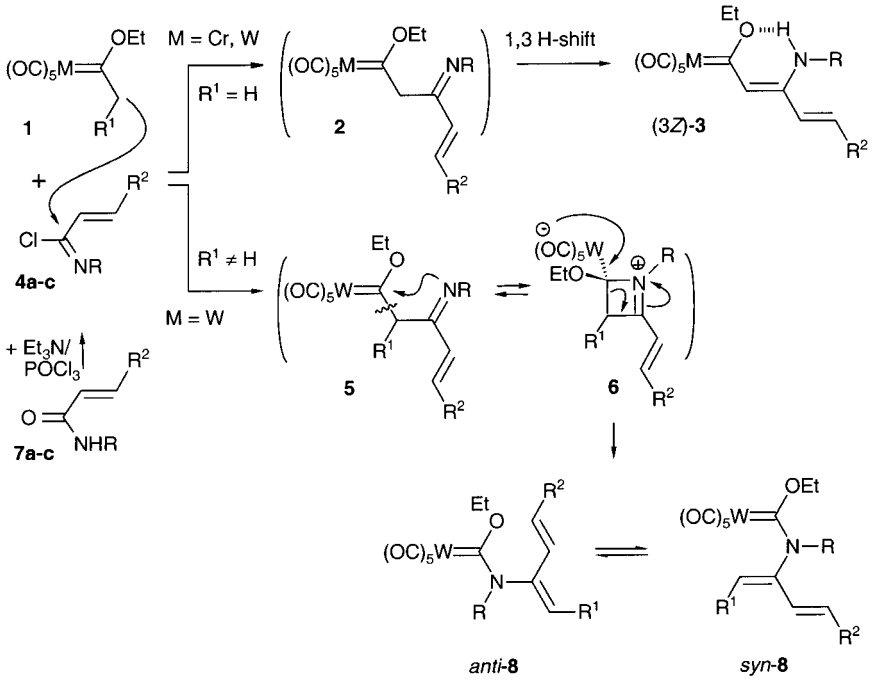
Scheme 2 *C*- and *N*-Enamino Carbene Complexes 3 and 8, Respectively, by Condensation of (Alkyl,ethoxy)carbene Complexes 1 with α,β-Unsaturated Secondary Acid Amides 7; Influence of α-Substituents R¹ on the Reaction Course



4,7	R^2	NR
a	Ph	N(allyl)
b	Ph	N(*i*-Pr)
c	Ph	NMe
d	Ph	N(*c*-C_6H_{11})
e	Ph	N(*n*-Pr)
f	Me	N(*i*-Pr)

1	M	R^1
a	W	H
b	Cr	H
c	W	*n*-Pr

(3*Z*)-**3**,**8**	M	R^1	R^2	NR	**3**[%][a]	**8**[%][a]	*anti*/*syn*-**8**
a	W	H	Ph	N(allyl)	84	-	-
b	W	H	Ph	N(*i*-Pr)	76	-	-
c	W	H	Ph	NMe	72	-	-
d	Cr	H	Ph	N(allyl)	72	-	-
e	Cr	H	Ph	N(*i*-Pr)	79	-	-
f	Cr	H	Ph	NMe	69	-	-
g	W	H	Me	N(*i*-Pr)	72	-	-
h	W	*n*-Pr	Ph	N(*i*-Pr)	-	62	1:1
i	W	*n*-Pr	Ph	N(*c*-C_6H_{11})	-	70	2:1
j	W	*n*-Pr	Ph	N(*n*-Pr)	-	19	9:1
k	W	*n*-Pr	Ph	N(allyl)	-	25	8:1
l	W	*n*-Pr	Ph	NMe	-	12	3:1
m	W	*n*-Pr	Me	N(*i*-Pr)	-	64	3:2

[a] Isolated chemical yields.

The CH=CHPh unit is planar [C4−C5−C6−C61 179.1(4)°, C5−C6−C61−C62−177.6(4)°] and somewhat tilted against the (*C*-enamino)carbene moiety [C3−C4−C5−C6−20.8(6)°].

The ^{13}C NMR signal of the carbene carbon atom in (*N*-enamino)carbene complexes **8** is shifted upfield compared to (*C*-enamino)carbene complexes **3** (e.g., W=C *syn*-**8h**, δ 230.4; (3*Z*)-**3a**, 267.1). The compounds **8** and **3** are readily distinguished by the positions of the A1 bands in the IR spectrum in *n*-hexane (e.g., A1 *syn*-**8h**, 2064.9 cm^{-1}; (3*Z*)-**3a**, 2056.1 cm^{-1}). Two different stereoisomers *syn*-**8** and *anti*-**8** are obtained, due to hindered rotation of the (W=C)−N bond in compounds **8**. These isomers can be separated by flash chromatography on silica gel, but they interconvert in solution at 20 °C within several hours. The compounds are readily distinguished by a strong downfield shift of the proton signal NC*H*Me_2 in compounds *anti*-**8** compared to compounds *syn*-**8**. According to NOE measurements, both compounds *syn*-**8** and *anti*-**8** exhibit an *E* configuration at the (N)C=CHPr bond.

The 2-amino butadienyl moiety of the (*N*-enamino)carbene complex *syn*-**8m** is planar, and the C20−C11−C12−C13 unit is twisted by 89.1° against the plane defined by the atoms C6−N7−C8 (Figure 2). The bonds to the nitrogen atom lie in a plane as indicated by the sum of bond angles 359.9° (C6−N7−C8 122.2(2)° + C6−N7−C11 120.4(2)° + C11−N7−C8 117.3° = 359.9°). All bond distances are within expectation.

Conclusion

Up to date (β-iminoalkyl)carbene complexes have scarcely been investigated. On the basis of the chemistry of these compounds, which in our hand became readily available by condensation of α,β-unsaturated secondary acid amides PhCH=CHC(=O)NHR **7** with (*prim*-alkyl,-ethoxy)carbene complexes $(OC)_5M{=}C(OEt)CH_2R$ **1** (M = W, Cr; R = H, *n*-Pr) in the presence of $POCl_3/Et_3N$, we could establish two different reaction paths leading either to *C*-enamino carbene complexes (3*Z*)-**3** or to *N*-enamino carbene complexes **8**. It is attributed to

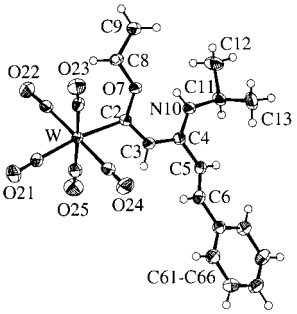


Figure 1. Molecular structure of the (*C*-enamino)carbene complex (3*Z*)-**3b** with selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): W−C2 2.256(4), C2−C3 1.393(5), C3−C4 1.414(5), C4−C5 1.466(5), C5−C6 1.320(5), C4−N10 1.329(5), C2−O7 1.361(4); C3−C2−W 120.4(3), O7−C2−W 128.4(2), C2−C3−C4 130.4(4), C3−C4−C5 119.8(3), C6−C5−C4 124.7(3), C5−C6−C61 127.3-(4), N10−C4−C3 121.7(3); W−C2−O7−C8 6.5(5), C3−C2−O7−C8−176.4(3), C22−W−C2−O7 42.9(3), O7−C2−C3−C4−1.6(6), W−C2−C3−C4 175.8(3), C2−C3−C4−N10−4.0(7), C2−C3−C4−C5 178.2(4), C4−C5−C6−C61 179.1(4), C5−C6−C61−C62−177.6(4), C3−C4−C5−C6−20.8(6), C3−C4−N10−C11−177.6(4).

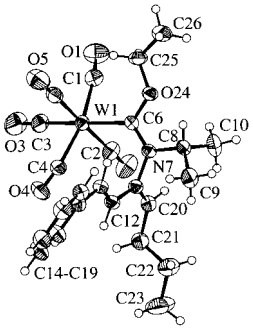


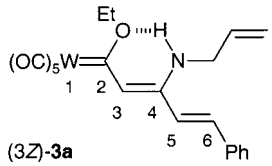
Figure 2. Molecular structure of the (*N*-enamino)carbene complex *syn*-**8m** with selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): W−C6 2.297(3), C6−N7 1.337(3), C6−O24 1.342(3), C11−C20 1.336(4), C11−C12 1.455(4), C12−C13 1.337(4), C20−C21 1.504(4), N7−C6−O24 107.4(2), N7−C6−W1 127.2(2), C6−N7−C8 122.2(2), C6−N7−C11 120.4(2), C11−N7−C8 117.3, O24−C6−W1 125.3(2), C11−N7−C8 117.3(2), C20−C11−N7 118.2(3), C20−C11−C12 124.5(3), N7−C11−C12 117.1(2), W−C6−N7−C11−2.1(3), C6−N7−C11−C12−93.1(3), N7−C11−C12−C13 0.8(4), C20−C11−C12−C13 175.6(3).

conformational effects induced by α-substituents of compounds **1**, whether the corresponding reaction is driven in one or the other direction. Formation of compounds **8** was shown to involve a retro-Fischer reaction, by which the C,C bond between the α-carbon atom and the carbene carbon atom is broken under the influence of a *β*-imino functionality.

Experimental Section

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. All ^{1}H 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 14, and compound **1c** according to ref 15.

(3*Z*,5*E*)-4-Allylamino-2-ethoxy-6-phenyl-1-pentacarbonyltungsta-1,3,5-hexatriene [(3*Z*)-3a]. To (2*E*)-*N*-allyl-3-phenylacrylamide (**7a**) (374 mg, 2.00 mmol) in 2 mL of dry dichloromethane in a 5 mL screw-top vessel was added phosphorus oxychloride (306 mg, 2.00 mmol) with stirring at 0 °C. (1-Ethoxyethylidene)tungsten complex **1a** (396 mg, 1.00 mmol) and triethylamine (404 mg, 4.00 mmol) in 1 mL of dichloromethane were added after 15 min at 0 °C. Chromatography after 14 h at 25 °C on silica gel (column 20 × 2 cm, *n*-pentane/dichloromethane, 3:1) afforded compound (3*Z*)-**3a** (475 mg, 84%, R_f = 0.6 in *n*-pentane/dichloromethane, 2:1, orange crystals, mp 108 °C).



(3*Z*)-**3a**

(3*Z*)-3a: ^{1}H NMR ($CDCl_3$): *δ* 9.08 (1 H, br, NH), 7.50 (2 H, m, Ph), 7.39 (3 H, m, Ph), 7.37 (1 H, d, ^3J = 16 Hz, 6-H), 6.69 (1 H, d, ^3J = 16 Hz, 5-H), 6.66 (1 H, s, 3-H), 5.93 (1 H, m, NCH_2CH), 5.38 (2 H, "t", $CH{=}CH_2$), 4.69 (2 H, q, OCH_2), 3.98 (2 H, "t", NCH_2), 1.53 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): *δ* 267.1 (C_q, W=C), 203.9 and 199.5 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 153.9 (C_q, C4), 141.0 (CH, C6), 134.9 (C_q, *i*-C Ph), 132.2 (CH, allyl); 130.2, 129.0, and 127.8 (each CH, 1:2:2, Ph), 119.7 (CH, C5), 118.5 (CH_2, allyl), 118.0 (CH, C3), 76.4 (OCH_2), 46.8 (NCH_2), 15.6 (CH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2056.1 (12), 1925.4 (100) [*ν*(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 565 (40) [M^+], 537 (20) [M^+ − CO], 509 (20) [M^+ − 2 CO], 481 (40) [M^+ − 3 CO], 453 (60) [M^+ − 4 CO], 425 (80) [M^+ − 5 CO], 55 (100). Anal. Calcd for $C_{21}H_{19}NO_6W$ (565.2): C, 44.62; H, 3.39; N, 2.48. Found: C, 44.32; H, 3.42; N, 2.52.

(3*Z*,5*E*)-2-Ethoxy-6-phenyl-4-isopropylamino-1-pentacarbonyltungsta-1,3,5-hexatriene [(3*Z*)-3b]. (2*E*)-*N*-Isopropyl-3-phenylacrylamide (**7b**) (378 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), (1-ethoxyethylidene)tungsten **1a** (396 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give compound (3*Z*)-**3b** (430 mg, 76%, R_f = 0.6 in *n*-pentane/dichloromethane, 2:1, orange crystals, mp 102 °C).

(3*Z*)-3b: ^{1}H NMR ($CDCl_3$): *δ* 9.12 (1 H, br, NH), 7.51 (2 H, m, Ph), 7.39 (3 H, m, Ph), 7.37 (1 H, d, ^3J = 14.5 Hz, 6-H), 6.74 (1 H, d, ^3J = 14.5 Hz, 5-H), 6.55 (1 H, s, 3-H), 4.65 (2 H, q, OCH_2), 3.91 (1 H, m, $HCMe_2$), 1.58 (3 H, t, OCH_2CH_3), 1.32 [6 H, d, ^3J = 6.3 Hz, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): *δ* 265.3 (C_q, W=C), 203.9 and 199.6 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 153.1 (C_q, C4), 140.8 (CH, C6), 135.0 (C_q, *i*-C Ph); 130.2, 129.1 and 127.8 (each CH, 1:2:2, Ph), 119.7 (CH, C5), 117.4 (CH, C3), 76.3 (OCH_2), 46.4 (NCH), 23.6 (2 CH_3, *i*-Pr), 15.6 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2055.8 (24), 1973.3 (41), 1912.8 (100) [*ν*(C≡O)], 1870.5 (84). IR (*n*-hexane), cm^{-1} (%): 2056.4 (9), 1928.4 (100) [*ν*(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 567 (2) [M^+], 539 (1) [M^+ − CO], 511 (1) [M^+ − 2 CO], 483 (20) [M^+ − 3 CO], 455 (1) [M^+ − 4 CO], 427 (15) [M^+ − 5 CO], 228 (100). Anal. Calcd for $C_{21}H_{21}NO_6W$ (567.3): C, 44.47; H, 3.73; N, 2.47. Found: C, 44.83; H, 3.58; N, 2.71.

X-ray crystal structure analysis of (3*Z*)-**3b** (code AUM_384): formula $C_{21}H_{21}NO_6W$, M = 567.24, red crystal 0.30 × 0.25 × 0.10 mm, a = 7.904(1) Å, b = 11.489(1) Å, c = 12.423-(1) Å, α = 97.68(1)°, β = 99.13(1)°, γ = 105.65(1)°, V = 1053.9-(2) Å^3, ρ_{calc} = 1.787 g cm^{-3}, F(000) = 552 e, μ = 55.^{16} cm^{-1}, empirical absorption correction via φ scan data (0.786 ≤ C ≤

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

0.999), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4471 reflections collected ($\pm h, +k, \pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 4247 ($R_{int} = 0.016$) independent and 3825 observed reflections [$I \geq 2\sigma(I)$], 268 refined parameters, $R = 0.023$, $wR_2 = 0.060$, max. residual electron density 1.21 (−1.55) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.[16]

(3*Z*,5*E*)-2-Ethoxy-4-methylamino-6-phenyl-1-pentacarbonyltungsta-1,3,5-hexatriene [(3*Z*)-3c]. (2*E*)-*N*-Methyl-3-phenylacrylamide (**7c**) (322 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), (1-ethoxyethylidene)tungsten **1a** (396 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give compound (3*Z*)-**3c** (388 mg, 72%, $R_f = 0.6$ in *n*-pentane/dichloromethane, 2:1, orange crystals, mp 122 °C).

(3*Z*)-3c: ^{1}H NMR ($CDCl_3$): δ 9.08 (1 H, br, NH), 7.52 (2 H, m, Ph), 7.41 (3 H, m, Ph), 7.39 (1 H, d, $^3J = 16$ Hz, 6-H), 6.71 (1 H, d, $^3J = 16$ Hz, 5-H), 6.50 (1 H, s, 3-H), 4.65 (2 H, q, OCH_2), 3.08 (3 H, d, $^3J = 5.5$ Hz, NCH_3), 1.54 (3 H, t, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 265.0 (C_q, W=C), 203.8 and 199.4 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 155.0 (C_q, C4), 140.9 (CH, C6), 134.7 (C_q, *i*-C, Ph); 130.1, 128.9, and 127.7 (each CH, 1:2:2, Ph), 119.3 (CH, C5), 117.4 (CH, C3), 76.0 (OCH_2), 31.0 (NCH_3), 15.6 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2053.0 (40), 1947.2 (70), 1921.0 (65) [ν(C≡O)], 1878.4 (100). IR (*n*-hexane), cm^{-1} (%): 2056.3 (9), 1927.1 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m*/*e* (%): 539 (10) [M$^+$], 511 (5) [M$^+$ − CO], 483 (20) [M$^+$ − 2 CO], 455 (65) [M$^+$ − 3 CO], 427 (20) [M$^+$ − 4 CO], 399 (65) [M$^+$ − 5 CO], 82 (100). Anal. Calcd for $C_{19}H_{17}NO_6W$ (539.2): C, 42.32; H, 3.18; N, 2.60. Found: C, 42.33; H, 3.25; N, 2.69.

(3*Z*,5*E*)-4-Allylamino-2-ethoxy-6-phenyl-1-pentacarbonylchroma-1,3,5-hexatriene [(3*Z*)-3d]. (2*E*)-*N*-Allyl-3-phenylacrylamide (**7a**) (374 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), (1-ethoxyethylidene)chromium **1b** (264 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give compound (3*Z*)-**3d** (312 mg, 72%, $R_f = 0.6$ in *n*-pentane/dichloromethane, 2:1, red crystals, mp 98 °C).

(3*Z*)-3d: ^{1}H NMR ($CDCl_3$): δ 8.92 (1 H, br, NH), 7.51 (2 H, m, Ph), 7.39 (3 H, m, Ph), 7.32 (1 H, d, $^3J = 16$ Hz, 6-H), 6.70 (1 H, d, $^3J = 16$ Hz, 5-H), 6.56 (1 H, s, 3-H), 5.91 (1 H, m, NCH_2CH), 5.35 (2 H, "t", $CHCH_2$), 4.79 (2 H, q, OCH_2), 3.99 (2 H, "t", NCH_2), 1.53 (3 H, t, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 289.2 (C_q, Cr=C), 224.2 and 218.9 [C_q, 1:4, *trans*- and *cis*-CO $Cr(CO)_5$], 150.5 (C_q, C4), 140.8 (CH, C6), 134.9 (C_q, *i*-C, Ph), 132.4 (CH, allyl); 130.1, 129.0 and 127.7 (each CH, 1:2:2, Ph), 120.0 (CH, C5), 118.5 (CH_2, allyl), 115.2 (CH, C3), 73.7 (OCH_2), 46.7 (NCH_2), 15.8 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2048.0 (12), 1929.5 (100) [ν(C≡O)]. MS (70 eV), *m*/*e* (%): 433 (25) [M$^+$], 405 (3) [M$^+$ − CO], 377 (16) [M$^+$ − 2 CO], 349 (5) [M$^+$ − 3 CO], 321 (40) [M$^+$ − 4 CO], 293 (85) [M$^+$ − 5 CO], 194 (100). Anal. Calcd for $C_{21}H_{19}NO_6Cr$ (433.4): C, 58.20; H, 4.42; N, 3.23. Found: C, 56.81; H, 4.53; N, 3.23.

(3*Z*,5*E*)-2-Ethoxy-6-phenyl-4-isopropylamino-1-pentacarbonylchroma-1,3,5-hexatriene [(3*Z*)-3e]. (2*E*)-*N*-Isopropyl-3-phenylacrylamide (**7b**) (378 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), (1-ethoxyethylidene)-chromium **1b** (264 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give compound (3*Z*)-**3e** (343 mg, 79%, $R_f = 0.6$ in *n*-pentane/dichloromethane, 2:1, dark red crystals, mp 119 °C).

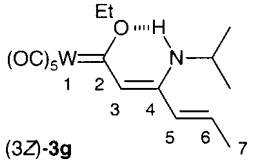
(16) Data sets were collected with Nonius CAD4 and KappaCCD diffractometers, the latter one equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B.V., 1990) and Denzo-SMN (Z. Otwinowski, W. Minor, *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).

(3*Z*)-3e: ^{1}H NMR ($CDCl_3$): δ 8.99 (1 H, br, NH), 7.51 (2 H, m, Ph), 7.40 (3 H, m, Ph), 7.34 (1 H, d, $^3J = 15.0$ Hz, 6-H), 6.76 (1 H, d, $^3J = 15.0$ Hz, 5-H), 6.49 (1 H, s, 3-H), 4.78 (2 H, q, OCH_2), 3.88 (1 H, m, $HCMe_2$), 1.59 (3 H, t, OCH_2CH_3), 1.32 [6 H, d, $^3J = 6.5$ Hz, $HC(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 286.0 (C_q, Cr=C), 224.2 and 219.1 [C_q, 1:4, *trans*- and *cis*-CO $Cr(CO)_5$], 149.8 (C_q, C4), 140.6 (CH, C6), 135.0 (C_q, *i*-C, Ph); 130.1, 129.0 and 127.7 (each CH, 1:2:2, Ph), 120.0 (CH, C5), 114.8 (CH, C3), 73.4 (OCH_2), 46.2 (NCH), 23.6 (2 CH_3, *i*-Pr), 15.8 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} (%): 2045.6 (50), 1973.5 (70), 1905.9 (100) [ν(C≡O)], 1876.6 (92). IR (*n*-hexane), cm^{-1} (%): 2056.4 (10), 1928.8 (100) [ν(C≡O)]. MS (70 eV), *m*/*e* (%): 435 (5) [M$^+$], 407 (2) [M$^+$ − CO], 379 (12) [M$^+$ − 2 CO], 351 (10) [M$^+$ − 3 CO], 323 (15) [M$^+$ − 4 CO], 295 (55) [M$^+$ − 5 CO], 52 (100). Anal. Calcd for $C_{21}H_{21}NO_6Cr$ (435.4): C, 57.93; H, 4.86; N, 3.22. Found: C, 57.80; H, 4.93; N, 3.40.

(3*Z*,5*E*)-2-Ethoxy-4-methylamino-6-phenyl-1-pentacarbonylchroma-1,3,5-hexatriene [(3*Z*)-3f]. (2*E*)-*N*-Methyl-3-phenylacrylamide (**7c**) (322 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), (1-ethoxyethylidene)chromium **1b** (264 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above to give compound (3*Z*)-**3f** (280 mg, 69%, $R_f = 0.6$ in *n*-pentane/dichloromethane, 2:1, orange crystals, mp 114 °C).

(3*Z*)-3f: ^{1}H NMR ($CDCl_3$): δ 8.95 (1 H, br, NH), 7.51 (2 H, m, Ph), 7.40 (3 H, m, Ph), 7.34 (1 H, d, $^3J = 16$ Hz, 6-H), 6.72 (1 H, d, $^3J = 16$ Hz, 5-H), 6.55 (1 H, s, 3-H), 4.81 (2 H, q, OCH_2), 3.09 (3 H, d, $^3J = 5.5$ Hz, NCH_3), 1.58 (3 H, t, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 286.9 (C_q, Cr=C), 224.0 and 218.8 [C_q, 1:4, *trans*- and *cis*-CO $Cr(CO)_5$], 151.5 (C_q, C4), 140.6 (CH, C6), 134.7 (C_q, *i*-C, Ph); 129.8, 128.8, and 127.5 (each CH, 1:2:2, Ph), 119.5 (CH, C5), 114.7 (CH, C3), 73.2 (OCH_2), 30.7 (NCH_3), 15.7 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2058.5 (10), 1928.8 (100) [ν(C≡O)]. MS (70 eV), *m*/*e* (%): 407 (15) [M$^+$], 351 (11) [M$^+$ − 2 CO], 323 (10) [M$^+$ − 3 CO], 295 (60) [M$^+$ − 4 CO], 267 (70) [M$^+$ − 5 CO], 82 (100). Anal. Calcd for $C_{19}H_{17}NO_6Cr$ (407.3): C, 56.02; H, 4.21; N, 3.44. Found: C, 55.09; H, 4.35; N, 3.63.

(3*Z*,5*E*)-2-Ethoxy-4-isopropylamino-1-pentacarbonyltungsta-1,3,5-heptatriene [(3*Z*)-3g]. (2*E*)-*N*-Isopropylcrotylamide (**7f**) (127 mg, 1.00 mmol), phosphorus oxychloride (153 mg, 1.00 mmol), (1-ethoxyethylidene)tungsten **1a** (198 mg, 0.50 mmol), and triethylamine (202 mg, 2.00 mmol) were reacted as described above to give compound (3*Z*)-**3g** (182 mg, 72%, $R_f = 0.6$ in *n*-pentane/dichloromethane, 2:1, red crystals, mp 97−98 °C).

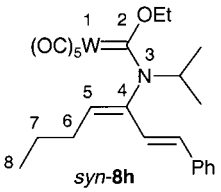


(3*Z*)-**3g**

(3*Z*)-3g: ^{1}H NMR ($CDCl_3$): δ 9.12 (1 H, br, NH), 6.64 (1 H, dq, $^3J = 15$ and 6 Hz, 6-H), 6.36 (1 H, s, 3-H), 6.11 (1 H, d, $^3J = 15$ Hz, 5-H), 4.60 (2 H, q, OCH_2CH_3), 3.81 (1 H, sept, $NCHMe_2$), 1.93 (3 H, d, $^3J = 6$ Hz, 7-H_3), 1.52 (3 H, t, OCH_2CH_3), 1.26 [6 H, d, $^3J = 6$ Hz, $NCH(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 262.6 (C_q, W=C), 203.8 and 199.7 [C_q, 1:4, *trans*- and cis-CO $W(CO)_5$], 153.6 (C_q, C4), 140.1 (CH, C6), 123.4 (CH, C5), 117.3 (CH, C3), 75.8 (OCH_2), 46.1 (NCH), 23.4 [$NCH(CH_3)_2$], 19.2 (CH_3, C7), 15.6 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2058.1 (20), 1983.8 (5), 1931.6 (5), 1924.7 (80) [ν(C≡O)]. MS (70 eV), ^{184}W, *m*/*e* (%): 505 (70) [M$^+$], 477 (20) [M$^+$ − CO], 449 (30) [M$^+$ − 2 CO], 421 (95) [M$^+$ − 3 CO], 419 (100), 393 (50) [M$^+$ − 4 CO]. Anal. Calcd for $C_{16}H_{19}NO_6W$ (505.2): C, 38.04; H, 3.79; N, 2.77. Found: C, 38.06; H, 4.02; N, 2.67.

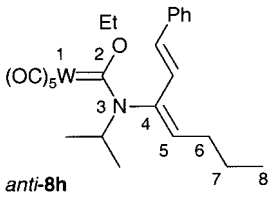
(4*E*)-[2-Ethoxy-3-isopropylamino-4-(*trans*-*β*-styryl)]-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*syn*-8h and *anti*-8h). To (2*E*)-*N*-isopropyl-3-phenylacrylamide (**7b**) (378

mg, 2.00 mmol) and phosphorus oxychloride (306 mg, 2.00 mmol) in dry dichloromethane (2 mL) in a 5 mL screw-top vessel were added after 30 min at 0 °C pentacarbonyl(1-ethoxypentenylidene)tungsten (**1c**) (438 mg, 1.00 mmol) and triethylamine (404 mg, 4.00 mmol) in dry dichloromethane (1 mL). After 2 days at 25 °C the mixture was separated by flash column chromatography on silica gel with *n*-pentane/dichloromethane (20:1) to give compound *anti*-**8h** (185 mg, 30%, R_f = 0.4 in *n*-pentane/dichloromethane, 5:1) and compound *syn*-**8h** (194 mg, 32%, R_f = 0.3 in *n*-pentane/dichloromethane, 5:1, yellow crystals from *n*-pentane at −20 °C, mp 63 °C). According to the NMR spectra, a very slow interconversion of compounds *syn*-**8h** and *anti*-**8h** is observed in solution already at 25 °C.



syn-**8h**

***syn*-8h:** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.43−7.26 (5 H, m, Ph), 7.06 and 6.43 (1 H each, d each, AB system, ^3J = 16 Hz, CH=CHPh), 5.62 (1 H, dd, ^3J = 7 and 8 Hz, 5-H), 4.70 (2 H, m, diastereotopic OCH_2), 4.58 (1 H, sept, $NCHMe_2$), 2.40 and 1.58 (2 H each, m each, $CH_2CH_2CH_3$), 1.52 (3H, t, ^3J = 7 Hz, OCH_2CH_3), 1.31 and 1.25 [3 H each, d each, ^3J = 7 Hz, $NCH(CH_3)_2$], 1.03 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 25 °C): δ 230.5 (C_q, W=C), 201.2 and 199.4 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 140.4 (C_q, C4), 136.6 (C_q, *i*-C Ph), 135.9 (CH, C5), 132.0 and 123.3 (CH each, CH=CHPh); 128.7, 128.2, and 126.8 (2:1:2, CH each, Ph), 73.7 (OCH_2), 53.3 ($NCHMe_2$); 29.6, 22.2, and 14.9 ($CH_2CH_2CH_3$), 22.6 and 20.8 [CH_3 each, $NCH(CH_3)_2$], 15.5 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2062.2 (15), 1961.9 (5), 1929.1 (100), 1919.5 (5) [ν(C≡O)]. MS (70 eV), ^{184}W, *m*/*e* (%): 609 (40) [M^+], 581 (70) [M^+ − CO], 553 (90) [M^+ − 2 CO], 525 (35) [M^+ − 3 CO], 497 (40) [M^+ − 4 CO], 469 (100) [M^+ − 5 CO]. Anal. Calcd for $C_{24}H_{27}NO_6W$ (609.3): C, 47.31; H, 4.47; N, 2.30. Found: C, 47.48; H, 4.45; N, 2.22. X-ray crystal structure analysis of *syn*-**8h** (code AUM_1863): formula $C_{24}H_{27}NO_6W$, M = 609.32, light yellow crystal 0.50 × 0.40 × 0.15 mm, a = 11.299(1) Å, b = 11.941(1) Å, c = 12.229(1) Å, α = 61.45(1)°, β = 70.65(1)°, γ = 63.61(1)°, V = 1283.4(2) Å^3, ρ_{calc} = 1.577 g cm^{-3}, $F(000)$ = 600 e, μ = 45.36 cm^{-1}, empirical absorption correction via SORTAV (0.210 ≤ T ≤ 0.549), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 9482 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.68 Å^{-1}, 6297 (R_{int} = 0.019) independent and 5953 observed reflections [$I \geq 2\sigma(I)$], 293 refined parameters, R = 0.024, wR_2 = 0.062, max. residual electron density 0.89 (−1.21) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.[16]



anti-**8h**

***anti*-8h:** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.37−7.30 (5 H, m, Ph), 6.96 and 6.14 (1 H each, d each, AB system ^3J = 16 Hz, CH=CHPh), 5.44 (1 H, sept, $NCHMe_2$), 5.30 (1 H, dd, ^3J = 8 and 8 Hz, 5-H), 4.51 (2 H, m, diastereotopic OCH_2), 2.36 and 1.54 (2 H each, m each, $CH_2CH_2CH_3$), 1.34 and 1.17 [3 H each, d each, ^3J = 7 Hz, $NCH(CH_3)_2$], 1.18 (3 H, t, OCH_2CH_3), 1.01 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 230.4 (C_q, W=C), 200.8 and 197.9 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 136.6 (C_q, C4), 136.0 (C_q, *i*-C Ph), 132.5 (CH, C5), 130.7 and 120.1 (CH each, CH=CHPh); 128.8, 128.0, and 126.6 (2:1:2, CH each, Ph), 72.8 (OCH_2), 58.5 (CH, $NCHMe_2$); 29.5, 22.7, and 13.8 ($CH_2CH_2CH_3$), 23.3 and 20.4 [CH_3 each, $NCH(CH_3)_2$], 15.3 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2064.9 (10), 1983.7 (3), 1929.1 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m*/*e* (%): 609 (70) [M^+], 581 (80) [M^+ − CO], 553 (80) [M^+ − 2 CO], 525 (35) [M^+ − 3 CO], 497 (65) [M^+ − 4 CO], 469 (100) [M^+ − 5 CO].

(4*E*)-2-Ethoxy-3-cyclohexylamino-4-(*trans*-*β*-styryl)-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*syn*-8i and *anti*-8i). (2*E*)-*N*-Cyclohexyl-3-phenylacrylamide (**7d**) (459 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxypentenylidene)tungsten (**1c**) (438 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above for 2 days at 25 °C to give a 2:1 mixture of pale yellow compounds *anti*-**8i** (305 mg, 47%, R_f = 0.4 in *n*-pentane/dichloromethane, 5:1) and *syn*-**8i** (150 mg, 23%, R_f = 0.3 in *n*-pentane/dichloromethane, 5:1).

***anti*-8i:** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.36−7.23 (5 H, m, Ph), 6.90 and 6.13 (1 H each, d each, AB system ^3J = 16 Hz, CH=CHPh), 5.27 (1 H, dd, ^3J = 8 and 9 Hz, 5-H), 5.04 (1 H, m, NCH), 4.51 (2 H, m, diastereotopic OCH_2), 2.36 and 1.52 (2 H each, m each, $CH_2CH_2CH_3$), 1.86−1.20 (10 H, m, cyclohexyl], 1.18 (3 H, t, ^3J = 7 Hz, OCH_2CH_3), 1.01 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 230.3 (C_q, W=C), 200.8 and 197.7 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 137.2 (C_q, C4), 136.7 (C_q, *i*-C Ph), 132.4 (CH, C5), 130.7 and 120.1 (CH each, CH=CHPh); 128.8, 128.0, and 126.6 (2:1:2, CH each, Ph), 72.7 (OCH_2), 66.7 (NCH); 32.9, 31.5, 25.6, 25.3, and 25.1 (CH_2 each, cyclohexyl); 29.5, 22.8, and 13.9 ($CH_2CH_2CH_3$), 15.2 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2064.6 (15), 1928.3 (100) [ν(C≡O)], 1405.3 (5). MS (70 eV), ^{184}W, *m*/*e* (%): 649 (10) [M^+], 621 (50) [M^+ − CO], 593 (70) [M^+ − 2 CO], 565 (20) [M^+ − 3 CO], 537 (35) [M^+ − 4 CO], 509 (55) [M^+ − 5 CO], 55 (100).

***syn*-8i:** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.43−7.26 (5 H, m, Ph), 7.01 and 6.41 (1 H each, d each, AB system ^3J = 16 Hz, CH=CHPh), 5.61 (1 H, dd, ^3J = 7 and 8 Hz, 5-H), 4.69 (2 H, m, diastereotopic OCH_2), 4.35 (1H, m, NCH), 2.42 and 1.52 (2 H each, m each, $CH_2CH_2CH_3$), 1.91−1.20 (10 H, m, cyclohexyl), 1.52 (3 H, t, ^3J = 7 Hz, OCH_2CH_3), 1.04 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 230.4 (C_q, W=C), 201.3 and 199.4 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 139.9 (C_q, C4), 136.6 (C_q, *i*-C Ph), 136.0 (CH, C5), 132.2 and 123.7 (CH each, CH=CHPh); 128.7, 128.2, and 126.8 (2:1:2, CH each, Ph), 73.6 (OCH_2), 61.1 (NCH); 32.8, 31.3, 26.3, 26.2, and 25.5 (CH_2 each, cyclohexyl); 29.6, 22.2, and 14.2 ($CH_2CH_2CH_3$), 15.5 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2062.1 (15), 1965.4 (5), 1928.6 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m*/*e* (%): 649 (30) [M^+], 621 (50) [M^+ − CO], 593 (80) [M^+ − 2 CO], 565 (35) [M^+ − 3 CO], 537 (40) [M^+ − 4 CO], 509 (60) [M^+ − 5 CO], 55 (100).

(4*E*)-2-Ethoxy-3-propylamino-4-(*trans*-*β*-styryl)-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*syn*-8j and *anti*-8j). (2*E*)-*N*-Propyl-3-phenylacrylamide (**7e**) (378 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxypentenylidene)tungsten (**1c**) (438 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above. The reaction progress was followed by TLC. Workup after 4 days at 25 °C gave unreacted carbene complex **1c** (182 mg, 42%) and a ca. 9:1 mixture of compounds *anti*- and *syn*-**8l** [69 mg, 19%, R_f = 0.5 in *n*-pentane/dichloromethane, 10:1, pale yellow oil].

***anti*-8j:** ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.43−7.26 (5 H, m, Ph), 6.93 and 6.32 (1 H each, d each, AB system ^3J = 16.5 Hz, CH=CHPh), 5.64 (1 H, dd, ^3J = 8 Hz, 5-H), 4.66 (2 H, m, diastereotopic OCH_2), 4.13 and 2.93 (1 H each, ddd each, ^3J = 6 and 10 Hz, ^2J = −15.5 Hz, $NCH_2CH_2CH_3$), 2.40 and 1.52 (2 H each, m each, $CH_2CH_2CH_3$), 1.60 (2H, m, $NCH_2CH_2CH_3$), 1.50 (3H, t, ^3J = 7 Hz, OCH_2CH_3), 1.02 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$), 0.89 (3H, t, ^3J = 7 Hz, $NCH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 230.6 (C_q, W=C), 201.0 and 199.0 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 142.2 (C_q, C4), 136.6 (C_q, *i*-C Ph), 135.5 (CH, C5), 130.7 and 121.5 (CH each, CH=CHPh); 128.7,

128.3, and 126.9 (2:1:2, CH each, Ph), 73.5 (OCH_2); 53.1, 21.9, and 11.6 ($NCH_2CH_2CH_3$); 29.4, 22.1, and 14.0 ($CH_2CH_2CH_3$), 15.4 (OCH_2CH_3). IR, MS, and CHN analysis of 9:1 mixture of compounds *anti*- and *syn*-**8l**: IR (*n*-hexane), cm^{-1} (%): 2063.1 (15), 1930.1 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 609 (5) [M^+], 581 (70) [$M^+ - CO$], 553 (40) [$M^+ - 2\ CO$], 525 (40) [$M^+ - 3\ CO$], 497 (50) [$M^+ - 4\ CO$], 469 (70) [$M^+ - 5\ CO$]. Anal. Calcd for $C_{24}H_{27}NO_6W$ (609.3): C, 47.31; H, 4.47; N, 2.30. Found: C, 47.00; H, 4.77; N, 2.04.

***syn*-8j:** Spectroscopic data were not explicitely collected.

(4*E*)-2-Ethoxy-3-allylamino-4-(*trans*-β-styryl)-aza-1-pentacarbonyltungstaocta-1,4-diene (*syn*-8k and *anti*-8k). (2*E*)-*N*-Allyl-3-phenylacrylamide (**7a**) (375 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl-(1-ethoxypentenylidene) tungsten (**1c**) (438 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above for 5 days at 25 °C to give recovered carbene complex **1c** (122 mg, 28%) and a 8:1 mixture of compounds *anti*- and *syn*-**8k** (111 mg, 25%, R_f = 0.5 in *n*-pentane/dichloromethane, 20:1, crystals from *n*-hexane, mp 74 °C).

***anti*-8k:** ^1H NMR ($CDCl_3$, 25 °C): δ 7.44−7.25 (5 H, m, Ph), 6.94 and 6.34 (1 H each, d each, AB system ^3J = 16 Hz, CH═CHPh), 5.82 (1H, m, $NCH_2CH{=}CH_2$), 5.64 (1 H, dd, ^3J = 7 Hz, 5-H), 5.20 and 5.11 (1H each, dd each, ^3J = 17 and 10 Hz, ^2J = 2 Hz, $NCH_2CH{=}CH_2$), 4.80 and 3.56 (1H each, dd each, ^3J = 7.5 and 14 Hz, NCH_2), 4.67 (2 H, m, diastereotopic OCH_2), 2.37 and 1.57 (2 H each, m each, $CH_2CH_2CH_3$), 1.50 (3H, t, ^3J = 7 Hz, OCH_2CH_3), 1.00 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 232.9 (C_q, W═C), 200.9 and 198.9 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 141.8 (C_q, C4), 136.6 (C_q, *i*-C Ph), 136.2 (CH, C5), 132.2 and 119.0 ($NCH_2CH{=}CH_2$), 130.7 and 121.4 (CH each, CH═CHPh); 128.8, 128.3, and 126.9 (2:1:2, CH each, Ph), 73.7 (OCH_2), 54.6 (NCH_2); 29.4, 22.2, and 13.9 ($CH_2CH_2CH_3$), 15.4 (OCH_2CH_3). IR, MS, and CHN analysis of an 8:1 mixture of compounds *anti*- and *syn*-**8k**: IR (*n*-hexane), cm^{-1} (%): 2063.7 (10), 2029.5 (5), 1946.2 (5), 1931.0 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 607 (20) [M^+], 579 (70) [$M^+ - CO$], 551 (60) [$M^+ - 2\ CO$], 523 (45) [$M^+ - 3\ CO$], 495 (50) [$M^+ - 4\ CO$], 467 (25) [$M^+ - 5\ CO$], 410 (100). Anal. Calcd for $C_{24}H_{25}NO_6W$ (607.3): C, 47.47; H, 4.15; N, 2.31. Found: C, 47.34; H, 3.98; N, 2.22.

***syn*-8k:** spectroscopic data were not explicitely collected.

(4*E*)-2-Ethoxy-3-methylamino-4-(*trans*-β-styryl)-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*syn*-8l and *anti*-8l). To (2*E*)-*N*-methyl-3-phenylacrylamide (**7c**) (322 mg, 2.00 mmol) and phosphorus oxychloride (306 mg, 2.00 mmol) in dry dichloromethane (2 mL) in a 5 mL screw-top vessel were added after 30 min at 0 °C pentacarbonyl(1-ethoxypentenylidene)-tungsten (**1c**) (438 mg, 1.00 mmol) and triethylamine (404 mg, 4.00 mmol) in dry dichloromethane (1 mL). Reaction progress was monitored by TLC. Eventhough after 6 days at 25 °C the reaction had not yet been fully completed, the mixture was separated by flash column chromatography on silica gel with *n*-pentane first in order to recover compound **1c** (152 mg, 35%), then with *n*-pentane/dichloromethane, 20:1, to give a 3:1 mixture of compound **8l** [44 mg, 12% with respect to compound **1c** consumed, R_f = 0.6 in *n*-pentane/dichloromethane, 10:1, pale yellow oil].

***anti*-8l:** ^1H NMR ($CDCl_3$, 600 MHz, 25 °C): δ 7.35−7.25 (5 H, m, Ph), 6.83 and 6.15 (1 H each, d each, AB system ^3J = 16 Hz, CH═CHPh), 5.40 (1 H, dd, ^3J = 7 and 8 Hz, 5-H), 4.51 (2 H, m, diastereotopic OCH_2), 3.67 (3H, s, NCH_3), 2.29 and 1.41 (2 H each, m each, $CH_2CH_2CH_3$), 1.22 (3 H, t, ^3J = 7 Hz, OCH_2CH_3), 0.99 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 231.0 (C_q, W═C), 200.7 and 198.0 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 142.4 (C_q, C4), 136.3 (C_q, *i*-C Ph), 130.0 (CH, C5), 129.4 and 117.8 (CH each, CH═CHPh); 128.8, 128.2, and 126.8 (2:1:2, CH each, Ph), 73.0 (OCH_2), 46.9 (NCH_3); 29.1, 22.5, and 13.7 ($CH_2CH_2CH_3$), 15.3 (OCH_2CH_3). IR, MS, and CHN analysis of 3:1 mixture of compounds *anti*-**8l** and *syn*-**8l**: IR (*n*-hexane), cm^{-1} (%): 2063.7 (10), 2029.5 (5), 1930.3 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 581 (5) [M^+], 553 (70) [$M^+ - CO$], 525 (40) [$M^+ - 2\ CO$], 497 (40) [$M^+ - 3\ CO$], 469 (100) [$M^+ - 4\ CO$], 441 (70) [$M^+ - 5\ CO$]. Anal. Calcd for $C_{22}H_{23}NO_6W$ (581.3): C, 45.46; H, 3.99; N, 2.41. Found: C, 45.44; H, 3.89; N, 2.20.

***syn*-8l:** ^1H NMR ($CDCl_3$, 600 MHz, 25 °C): δ 7.43−7.27 (5 H, m, Ph), 6.94 and 6.29 (1 H each, d each, AB system ^3J = 16 Hz, CH═CHPh), 5.71 (1 H, dd, ^3J = 7 and 8 Hz, 5-H), 4.66 (2 H, m, diastereotopic OCH_2), 3.22 (3 H, s, NCH_3), 2.39 and 1.55 (2 H each, m each, $CH_2CH_2CH_3$), 1.52 (3H, t, ^3J = 7 Hz, OCH_2CH_3), 1.02 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 232.4 (C_q, W═C), 201.0 and 198.9 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 144.0 (C_q, C4), 136.5 (C_q, *i*-C Ph), 134.8 (CH, C5), 130.7 and 121.2 (CH each, CH═CHPh); 128.7, 128.3, and 126.9 (2:1:2, CH each, Ph), 73.6 (OCH_2), 39.6 (NCH_3); 29.3, 22.0, and 14.0 ($CH_2CH_2CH_3$), 15.5 (OCH_2CH_3).

(4*E*)-2-Ethoxy-3-isopropylamino-4-(*trans*-1-propenyl)-3-aza-1-pentacarbonyltungstaocta-1,4-diene (*syn*-8m and *anti*-8m). (2*E*)-*N*-Isopropylcrotylamide (**7f**) (254 mg, 2.00 mmol), phosphorus oxychloride (306 mg, 2.00 mmol), pentacarbonyl(1-ethoxypentenylidene)tungsten (**1c**) (438 mg, 1.00 mmol), and triethylamine (404 mg, 4.00 mmol) were reacted as described above for 2 days at 25 °C to give a 3:2 mixture of compounds *anti*-**8m** (209 mg, 38%, R_f = 0.4 in *n*-pentane/dichloromethane, 10:1) and *syn*-**8m** (144 mg, 26%, R_f = 0.3 *n*-pentane/dichloromethane, 10:1).

***anti*-8m:** ^1H NMR ($CDCl_3$, 25 °C): δ 6.18 and 5.26 (1 H each, dq each, AB system ^3J = 15 Hz, ^4J = 2 Hz and ^3J = 7 Hz, $CH{=}CHCH_3$), 5.33 (1 H, sept, $NCHMe_2$), 5.06 (1 H, dd, ^3J = 7 and 8 Hz, 5-H), 4.56 (2 H, m, diastereotopic OCH_2), 2.22 and 1.46 (2 H each, m each, $CH_2CH_2CH_3$), 1.78 (3H, dd, ^4J = 2 Hz and ^3J = 7 Hz, $CH{=}CHCH_3$), 1.29 and 1.12 [3 H each, d each, ^3J = 7 Hz, $NCH(CH_3)_2$], 1.22 (3 H, t, ^3J = 7 Hz, OCH_2CH_3), 0.97 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 229.5 (C_q, W═C), 200.9 and 197.5 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 136.2 (C_q, C4), 129.6 (CH, C5), 127.3 and 123.0 (CH each, $CH{=}CHCH_3$), 72.5 (OCH_2), 58.4 ($NCHMe_2$); 29.2, 22.7, and 13.8 ($CH_2CH_2CH_3$), 20.8 and 20.7 [CH_3 each, $NCH(CH_3)_2$], 18.2 ($CH{=}CHCH_3$), 15.2 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2065.0 (10), 1929.1 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 547 (30) [M^+], 519 (40) [$M^+ - CO$], 491 (40) [$M^+ - 2\ CO$], 463 (30) [$M^+ - 3\ CO$], 435 (30) [$M^+ - 4\ CO$], 407 (90) [$M^+ - 5\ CO$].

***syn*-8m:** ^1H NMR ($CDCl_3$, 25 °C): δ 6.31 and 5.61 (1 H each, dq each, AB system ^3J = 15 Hz, ^4J = 2 Hz and ^3J = 7 Hz, $CH{=}CHCH_3$), 5.41 (1 H, dd, ^3J = 7 and 8 Hz, 5-H), 4.64 (2 H, m, diastereotopic OCH_2), 4.47 (1 H, sept, $NCHMe_2$), 2.28 and 1.50 (2 H each, m each, $CH_2CH_2CH_3$), 1.82 (3H, dd, ^3J = 2 and 7 Hz, $CH{=}CHCH_3$), 1.47 (3H, t, ^3J = 7 Hz, OCH_2CH_3), 1.26 and 1.20 [3 H each, d each, ^3J = 7 Hz each, $NCH(CH_3)_2$], 0.99 (3 H, t, ^3J = 7 Hz, $CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 233.7 (C_q, W═C), 201.2 and 197.8 [C_q, 1:4, *trans*- and *cis*-CO $W(CO)_5$], 140.2 (C_q, C4), 132.9 (CH, C5), 129.6 and 126.1 (CH each, CH═CHMe), 73.5 (OCH_2), 53.3 ($NCHMe_2$); 29.2, 20.8, and 14.1 ($CH_2CH_2CH_3$), 22.6 and 22.2 [CH_3 each, $NCH(CH_3)_2$], 18.3 ($CH{=}CHCH_3$), 15.5 (OCH_2CH_3). IR (*n*-hexane), cm^{-1} (%): 2062.3 (10), 1962.3 (5), 1928.7 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 547 (20) [M^+], 519 (40) [$M^+ - CO$], 491 (40) [$M^+ - 2\ CO$], 463 (30) [$M^+ - 3\ CO$], 435 (30) [$M^+ - 4\ CO$], 407 (90) [$M^+ - 5\ CO$]. Anal. Calcd for $C_{19}H_{25}NO_6W$ (547.3): C, 41.70; H, 4.60; N, 2.56. Found: C, 41.89; H, 5.20; N, 2.17.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0200499