Organic Syntheses via Transition Metal Complexes. 83.[1] *cis*-1-Metalla-1,3,5-hexatrienes (Butadienylcarbene Complexes) of Tungsten *via* Ring Opening of Pyranylidene Complexes[†]

Rudolf Aumann,* Klaus Roths, Beate Jasper, and Roland Fröhlich

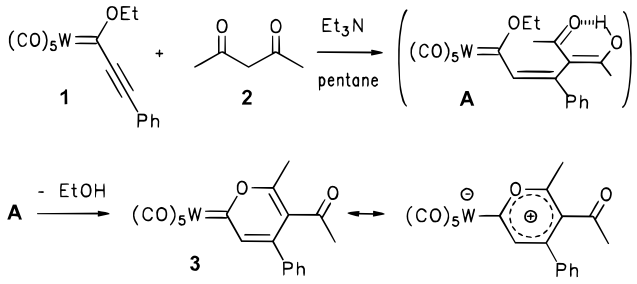
Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

Received September 18, 1995[⊗]

Aminolysis of the 2*H*-pyran-2-ylidenetungsten complex **3** affords amino-1-tungsta-1,3,5-hexatrienes with different structures, depending on the reaction temperature and the type of amine involved. Addition of primary amines RNH_2 (**4a**−**d**) (R = allyl, *n*-Bu, CH_2Ph, *i*-Pr) to **3** at −15 °C yields salt-type (3*Z*)-6-amino-1-tungsta-1,3,5-hexatrienes **5a**−**d** by reversible ring opening of the pyranylidene ring. Addition of **4a**−**c** at 20 °C affords (3*Z*)-2-amino-1-tungsta-1,3,5-hexatrienes **6a**−**c** by an irreversible ring opening of the pyranylidene ring. Secondary amines RR^1NH **8a**−**c** [RR^1N = Me_2N, 2-(hydroxymethyl)pyrrolidine, pyrrolidine] undergo an irreversible ring opening to 2-amino-1-tungsta-1,3,5-hexatrienes **9a**−**c**. Aminolysis of **3** in the presence of Me_3SiCl/Et_3N affords acetimino pyranylidene complexes **10**, from which (*3Z*)-2,6-diamino-1-tungsta-1,3,5-hexatrienes **11** are derived upon aminolysis. Thermolysis of **6a** in THF/pyridine affords the captodative 1-amino-1,3-hexadien-5-one **12**. 2*H*-Pyran-2-ylidene complex **3**, $C_{19}H_{12}O_7W$, was characterized by X-ray diffraction.

2*H*-Pyran-2-ylidene Complexes. Ring-opening reactions of six-membered rings provide a convenient means for the generation of open-chain products with *cis* stereochemistry. While we were pursuing ring precursors of (conjugated) *cis*-1-tungsta-1,3,5-hexatrienes $(CO)_5W{=}CXCR{=}CRCR{=}CRY$ (X, Y = OR′, NR′$_2$; R = hydrogen, alkyl, aryl),[2] our attention was drawn to 2*H*-pyran-2-ylidene complexes, e.g., compound **3**, as potential starting materials. Among several routes available for the generation of pyranylidene complexes[2−11] the condensation of enolizable carbonyl compounds, e.g., 2,4-pentanedione (**2**), with a 1-alkynylcarbene complex, e.g., $(CO)_5W{=}C(OEt)C{\equiv}CPh$ (**1**), appeared to be the best suited in view of its high versatility.[6]

Scheme 1. Pyranylidene Complex 3 by Condensation of the 1,3-Diketone 2 with the Alkynylcarbene Complex 1



Condensation of **2** with **1** is induced by catalytic amounts of triethylamine in pentane and affords a 90% yield of crystalline complex **3** directly from the reaction mixture. This reaction most probably proceeds *via* the 2-ethoxy-1-metalla triene **A**, which due to the presence of base rapidly undergoes ring closure[2a,b] to the pyranylidene complex **3** by elimination of EtOH. Therefore, the reverse reaction, *i.e.*, an attempt to generate 2-ethoxy-1-metalla trienes by ring opening of compound **3** with EtOH, does not appear to be promising.

We have previously demonstrated that a Michael-type addition of enamines to the alkynylcarbene complex **1** affords 6-amino-2-ethoxy-1-tungsta-1,3,5-hexatrienes.[2b,c] These compounds are quite stable and can be isolated in crystalline form in high yields. Since Fischer carbene complexes are known to become more stable if oxy substituents are replaced by amino substituents, we anticipated that aminolysis of pyranylidene complex **3** would provide an entry to stable 2-amino-1-tungsta-1,3,5-hexatrienes.

Complex **3** can be considered to be a resonance hybrid between a pyranylidene and a zwitterionic pyrylium

[†] Dedicated to Prof. Max Herberhold on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) Part 82: Meyer, A.; Aumann, R. *Synlett* **1995**, 1011.

(2) For earlier preparation of such compounds, see: (a) Aumann, R.; Roths, K.; Grehl, M. *Synlett* **1993**, 669. (b) Aumann, R.; Kössmeier, M.; Roths, K.; Fröhlich, R. *Synlett* **1994**, 1041. (c) Aumann, R.; Kössmeier, M.; Roths, K. Unpublished. (d) Aumann, R.; Roths, K.; Laege, M.; Krebs, B. *Synlett* **1993**, 667.

(3) (a) Rees, Ch. W.; von Angerer, E. *J. Chem. Soc., Chem. Commun.* **1972**, 420. (b) Gilchrist, T. L.; Livingstone, R.; Rees, Ch. W.; von Angerer, E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2535.

(4) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *36b*, 929.

(5) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

(6) (a) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4551. (b) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419.

(7) (a) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (b) Camps, F.; Jordi, L.; Moretó, J. M.; Ricart, S.; Castaño, Echavarren, A. M. *J. Organomet. Chem.* **1992**, *436*, 189. (c) Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Organomet. Chem.* **1993**, *444*, C28. (d) Jordi, L.; Camps, F.; Ricart, S.; Viñas, J. M.; Moretó, J. M.; Mejias, M.; Molins, E. *J. Organomet. Chem.* **1995**, *494*, 53.

(8) Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762.

(9) Licandro, E.; Maiorana,S.; Papagni, A.; Zanotti Gerosa, A.; Cariati, F.; Bruni, S.; Moret, M.; Chiesi Villa, A. *Inorg. Chim. Acta* **1994**, *220*, 233.

(10) (a) Adams, R. D.; Chen, L. *J. Am. Chem. Soc.* **1994**, *116*, 4467. (b) Adams, R. D.; Chen, L.; Huang, M. *Organometallics* **1994**, *13*, 2696.

(11) Garlaschelli, L.; Malatesta, M. C.; Panzeri, S.; Albinati, A.; Ganazzoli, F. *Organometallics* **1987**, *6*, 63.

0276-7333/96/2315-1257$12.00/0

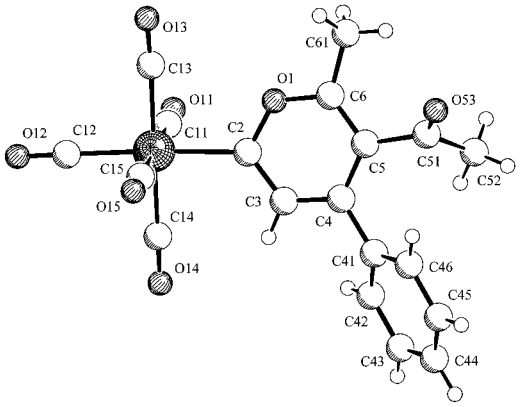
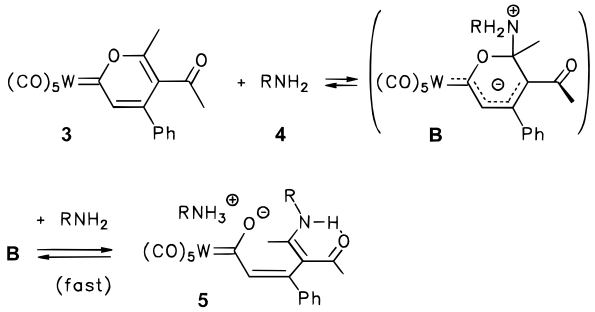


Figure 1. Molecular structure of pyranylidene complex **3**.

Scheme 2. 6-Amino-1-metalla Trienes 5 by Reversible Aminolysis of 3 with Primary Amines 4



ylide (Scheme 1). The pyrylium character is indicated by the pattern of nonalternating bond distances between the ring atoms [C2−O1 136.8(6), O1−C6 135.3(7), C2−C3 140.1(7), C3−C4 138.1(7), C6−C5 137.4(8), and C4−C5 142.0(7) pm, found by X-ray structural analysis (Figure 1, Tables 5−8)]. Furthermore, the distance W−C2 = 219.3(5) pm is significantly longer than the distance W=C = 205 pm in $(CO)_5W$=C(OMe)Ph.[12] Little, if any, π-conjugation of the acetyl group with the π-electron system of the pyranylidene ring is expected since ν(C=O) is 1702.4 cm^{-1} in the IR spectrum, and C4−C5−C51−C52 = 60.4° was found by X-ray analysis.

Further indication of the pyrylium character of **3** is based upon the strong deshielding of NMR signals of C6 (δ 173.9) and 3-H (δ 8.05) and a significant upfield shift of C2 (δ 258.4) compared to the carbene carbon atom of $(CO)_5W$=*C*(OEt)Ph (δ 319.6).[13] In line with the pyrylium character of **3**, *both* ring carbon atoms attached to the oxygen atom (i.e., C2 and C6) are expected to be the most susceptible to nucleophilic attack by, for example, an amine.

6-Amino-1-metalla Trienes 5 from 3 *via* Reversible Ring Opening with Primary Amines 4. It is plausible to suggest that the addition of an amine **4** to the pyrylium ligand of **3** should initially occur at C6 and give a zwitterion **B** (Scheme 2),[2a] which provides a better delocalization of negative charge than zwitterion **C** (Scheme 3), resulting from the addition of **4** to the carbene carbon atom C2. Direct experimental proof is provided by NMR studies with primary alkylamines **4a**−**d**. Hence, the addition of excess *i*-$PrNH_2$ (**4d**) to a

Scheme 3. 2-Amino-1-metalla Trienes 6 and Dihydropyridinylidene Complexes 7 by Irreversible Aminolysis of 3

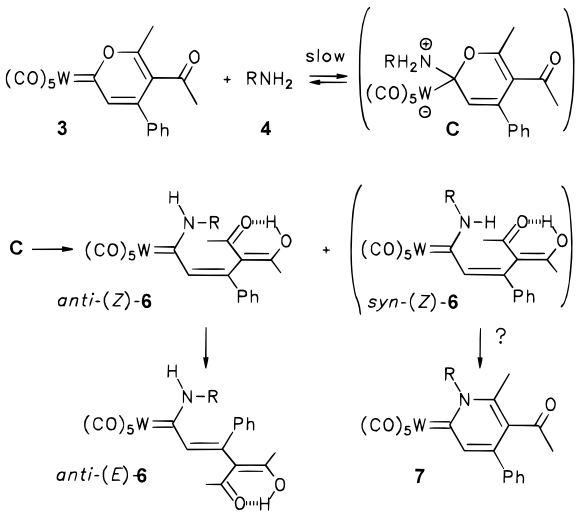


Table 1. Influence of Temperature and Concentration of a Primary Amine 4 on the Equilibrium Ratio of 3:5

4 and **5**	R	+20 °C[a]	−30 °C[a]	−30 °C[b]
a	allyl	>20:1	2:1	<1:20
b	*n*-Bu	>20:1	1:10	<1:20
c	CH_2Ph	>20:1	2:1	<1:20
d	*i*-Pr	>20:1	[c]	<1:20

[a] Molar ratio of compounds **3**:**5** according to ^{1}H NMR measurements in $CDCl_3$ at the temperature indicated in the presence of 2 equiv of **4**. [b] Molar ratio of compounds **3**:**5** if an excess of 4 equiv of **4** is applied. [c] Not determined.

(dark red) solution of **3** in diethyl ether did not produce an obvious change in color within 20 min at 20 °C; however, at −15 °C the solution immediately turned yellow, and yellow crystals of compound **5d** began to precipitate within minutes. These crystals were isolated by decantation and dried at −15 °C, but were found to be unstable at 20 °C and formed a dark-red solution in $CDCl_3$, which (at 20 °C) exhibited ^{1}H NMR signals of an apparent 4:2:3 mixture of **4d**, **3**, and Et_2O. At −30 °C this solution turned yellow, and (at this temperature) ^{1}H NMR signals of the 1-metalla triene **5d** were observed (Table 1). The structure assigned to compounds **5a**−**d** is based on the stoichiometry in the solid state as well as on NMR measurements in solution. The signal of the carbene carbon atom lies within the range expected for related carbenetungsten complexes [**5d**, δ 290.2; e.g. $(CO)_5W$=*C*($ONMe_4$)Tol, δ 278.1[14]] and is shifted by 32 ppm to lower field than C2 of the ylide-type pyranylidene precursor **3** (δ 258.4).[13] Nuclear Overhauser effects were observed between the *o*-hydrogen atoms of the phenyl group and *both* methyl groups of **5d**, in line with the open-chain structure suggested for **5d**. The presence of an (*NH*) amino enone unit [**5d**: δ(C=O) 195.1, δ [=*C*(NHR)CH_3] 162.8] and a hydrogen bridge between the NH and C=O groups [**5d**, δ(NH) 11.73] is also clearly indicated by the NMR spectra.

Formation of a hydrogen bridge in **5a**−**d** seems to provide the driving force for the reversible ring opening of the pyranylidene ring of **3**, since aminolysis of this type is not observed with secondary amines **8** (*vide infra*).

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

(13) For similar effects, see: Aumann, R.; Hinterding, P. *Chem. Ber.* **1992**, *125*, 2765−2772.

(14) Fischer, E. O.; Weiss, K. *Chem. Ber.* **1976**, *109*, 1128−1139.

Table 2. 2-Amino-1-metalla Trienes 6 and Dihydropyridinylidene Complexes 7 by Aminolysis of 3 with Amines 4a−d at 20 °C

4, 6	R	6 + 7 (%)[a]	(*Z*)-6:(*E*)-6[b]:7[c]
a	allyl	84	10:1:1
b	*n*-Bu	52	10:1:2
c	CH_2Ph	50	10:1:2
d	*i*-Pr	*d*	

[a] Isolated total yield of compounds **6** and **7** (*vide infra*) in percent. [b] Compounds (*E*)-**6** are formed by thermal isomerization of (*Z*)-**6**. [c] A dihydropyridinylidene complex **7** (*vide infra*) is the purported product of cyclization of *syn*-(*Z*)-**6**. [d] Formation of **6d** is not observed at 20 °C within 24 h.

2-Aminometalla Trienes 6 by Irreversible Aminolysis of 3 with Primary Amines 4. Concomitant with the (fast reversible) formation of salt-type 6-aminometalla trienes **5** by the addition of primary alkylamines **4a−d** to C6 of the pyranylidene ring of **3** (Scheme 2), 2-aminometalla trienes **6a−c** are generated by a slow but irreversible aminolysis of compound **3** *via* an intermediate **C** resulting from amine addition to C2 (Scheme 3). This reaction is influenced by the bulkiness of the amine **4** and is strongly retarded by α-branched alkyl substituents (e.g., R = *i*-Pr).

2-Amino-1-tungsta-1,3,5-hexatrienes (*Z*)-**6a−c** are generated from the cyclic precursor **3** at 20 °C, with the retention of configuration at the central C=C bond. These compounds are expected to form *syn* and *anti* stereoisomers (with respect to the configuration of the amino function). The isomers *anti*-(*Z*)-**6a−c** are isolated as major products (Scheme 3, Table 2). The *anti* configuration seems to be a consequence of the, presumably, *anti* periplanar arrangement of the N^+-R *versus* the C2−W bond in the zwitterionic intermediate **C**. Stereoisomers *syn*-(*Z*)-**6** are not detected, but in addition pyranylidene complexes **7** are obtained, which could possibly result from a (base-induced) cyclization of *syn*-(*Z*)-**6**. Due to the slow *E*/*Z* isomerization of *anti*-(*Z*)-**6a−c** at the central C=C bond, the isomers *anti*-(*E*)-**6a−c** are obtained as byproducts in amounts increasing with reaction time and temperature.

The structure assignment of compounds **6a−c** is based on the chemical shift of the carbene carbon atom in the ^{13}C NMR spectrum, which unambiguously lies within the range expected for aminocarbenetungsten complexes [e.g., *anti*-(*Z*)-**6b**, δ 251.6; *anti*-(*E*)-**6b**, δ 252.8]. In line with the pyridinium ylide character of compounds **7a−c**, the signal of the carbon atom attached to the tungsten atom is shifted upfield appreciably[2a,c,13] (e.g., **7b**, δ 211.1). The (*E*) and (*Z*) configurations of **6** are distinguished by ^1H NMR spectra, since the vinyl proton 3-H is strongly deshielded by the anisotropic influence of the neighboring phenyl ring [e.g., *anti*-(*Z*)-**6a**, δ 6.66; *anti*-(*E*)-**6a**, δ 5.96]. A positive NOE enhancement is observed between 3-H and the $COCH_3$ group in *anti*-(*E*)-**6a**. An *anti* configuration is assigned to the amino function due to the upfield shift observed for the NCH_2 signal [e.g., *anti*-(*Z*)-**6a**, δ 2.98; expected for *syn*-(*Z*)-**6a**, δ 4.00] and the overall downfield shift of the NH signal by the anisotropic influence of the $(CO)_5W$ moiety.[15] For vinyl proton 3-H, only minor changes are induced by *E*/*Z* configurational changes of the central C=C bond [e.g., *anti*-(*Z*)-**6a**, δ 8.03; *anti*-(*E*)-**6a**, δ 8.17].

(15) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275−282; **1968**, *13*, 387−398.

Scheme 4. 2-Amino-1-metalla Trienes 9 by Irreversible Aminolysis of 3 with Secondary Amines 8

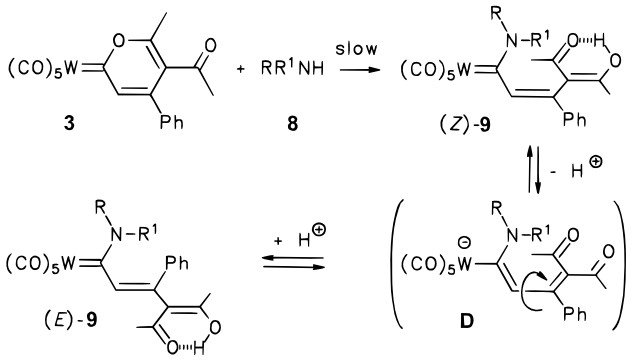


Table 3. Configuration and Chemical Yield of 2-Amino-1-tungsta Trienes 9

8, 9	NRR[1]	9 (%)	(*Z*)/(*E*)-9
a	NMe_2	81	(*Z*) only
b	2-(hydroxymethyl)pyrrolidino	89	(*Z*) only
c	pyrrolidino	83	(*E*) only

2-Aminometalla Trienes 9 by Irreversible Aminolysis of 3 with Secondary Amines 8. The observed reversible generation of 6-aminotungsta-1,3,5-hexatrienes **5** from **1** upon the addition of primary amines **4a−d** to pyranylidene complex **3** (Scheme 2) could not be established with secondary amines **8**. The overall reaction of secondary amines **8a−c** with compound **3** is faster than the irreversible aminolysis of these compounds with primary amines [e.g., the addition of $HNMe_2$ (**8a**) to **3** was complete within 20 min at 20 °C] and afforded 2-amino-1-tungsta trienes **9** (Scheme 4, Table 3).

Compounds **9a,b** are isolated isomerically pure in the (*Z*) configuration, while the pyrrolidine derivative **9c** acquired the (*E*) configuration. An apparently rapid configuration change of (*Z*)-**9c** to (*E*)-**9c** may be initiated by deprotonation to give an anionic intermediate **D**, in which rotation at the crucial C−C bond is expected to be a facile process (Scheme 4). Stereocontrol seems to be governed not only by the bulkiness of the amine but also by hydrogen bridge interactions. The latter may play an important role in retaining the (*Z*) configuration of the *anion* derived from **9b**.

It is interesting to note that only one single isomer, (*Z*)-**9b**, is obtained from the addition of the unsymmetrical 2-(hydroxymethyl)pyrrolidine (**8b**) to complex **3**. According to NMR measurements of (*Z*)-**9b**, the $NCH(CH_2OH)$ group is arranged *syn* to the metal unit [δ[$NCH(CH_2OH)$] 3.65, δ[$NCH(CH_2OH)$] 63.2; (*E*)-**9c**, δ (*syn*-NCH_2) 3.72 and 3.35; δ(*syn*-NCH_2) 62.3]. This configuration seems to result from the orientation of amine **8b** in the precursor (of type **C**) under the directing influence of a N···H···O hydrogen bridge. The structures suggested for the 6-amino-1-tungsta-1,3,5-hexatrienes **9a−c** are in line with spectroscopic evidence that is similar to that outlined earlier for compounds **6a−c**.

Acetimino Pyranylidene Complexes 10. The acetyl group of pyranylidene complex **3** is not subjected to direct attack by an amine for kinetic reasons, since the addition to C6 and/or C2 (resulting in the formation of 1-tungsta trienes **5**, **6**, and **9**, respectively) is a much faster process. Nevertheless, iminoacetyl compounds **10a−d** are derived from **3** in smooth reaction with

Scheme 5. Generation of Acetimino Complex 10 from Acetylpyranylidene Complex 3

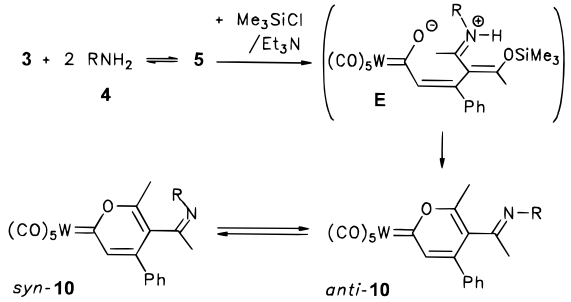


Table 4. Acetimino Pyranylidene Complexes by Aminolysis of 3 with Primary Amines 4a−d in Presence of Me_3SiCl/Et_3N

4, **10**	R	**10** (%)	*anti*/*syn*-**10**
a	allyl	91	1:1[a]
b	*n*-Bu	90	1:1[a]
c	CH_2Ph	70	1:1[a]
d	*i*-Pr	90	>10:1

[a] *anti*/*syn* equilibrium of compound **10** after contact with silica gel.

Table 5. Crystal Data and Structure Refinement for 3

formula	$C_{19}H_{12}O_7W$
mol wt	536.14
cryst color	red-purple
cryst system	triclinic
space group (no.)	$P\bar{1}(2)$
a (Å)	6.667(1)
b (Å)	10.282(1)
c (Å)	14.279(2)
α (deg)	97.45(1)
β (deg)	100.45(1)
γ (deg)	103.23(1)
V (Å^3)	921.9(2)
Z	2
D_{calc} (g cm^{-3})	1.931
μ (cm^{-1})	0.63
wavelength (Å)	0.71073
F(000) (e)	512
diffractometer	Enraf-Nonius MACH3
scan mode	$\omega-2\theta$
$[(\sin\theta)/\lambda]_{max}$ (Å^{-1})	0.62
T (°*C*)	−50
abs corr	ψ-scan (empirical)
transm	60.9 ⇔ 99.9%
no. of measd reflcns	3896 ($\pm h$, $\pm k$, $+l$)
no. of indep reflcns	3738
no. of obsd reflcns [$>2\sigma(I)$]	3510
R_{av}	0.018
no. of refined params	246
R(all data/obsd data)	0.036/0.033
wR^2 (all data/obsd data)	0.095/0.094
resid elec dens (e Å^{-3})	1.78 (−2.92)
H-atoms	calculated, riding
programs used	EXPRESS, SHELX-86, SHELXL-93, SCHAKAL-92

primary amines **4a**−**d** in the presence of Me_3SiCl/Et_3N (Scheme 5, Table 4). The condensation reaction is presumed to proceed *via* an intermediate **E**, involving initial *O*-silylation of a 1-tungsta triene **5** (Scheme 2) and subsequent ring closure[2] by elimination of a trimethylsiloxy unit.

According to NMR measurements, the acetimino derivatives **10a**−**d** are generated in an *anti* configuration with respect to the C═N bond initially, but they form an *anti*/*syn* mixture in solution. The *anti*/*syn* equilibration is slow in neutral solution at 20 °C, but it

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 3

W−C(2)	2.193(5)	C(5)−C(6)	1.374(8)
C(2)−O(1)	1.368(6)	C(5)−C(51)	1.503(7)
C(2)−C(3)	1.401(7)	C(6)−O(1)	1.353(7)
C(3)−C(4)	1.381(7)	C(6)−C(61)	1.481(8)
C(4)−C(5)	1.420(7)	C(51)−O(53)	1.207(7)
C(4)−C(41)	1.474(7)	C(51)−C(52)	1.503(9)
O(1)−C(2)−C(3)	114.2(4)	C(4)−C(5)−C(51)	124.6(5)
O(1)−C(2)−W	118.0(3)	O(1)−C(6)−C(5)	120.9(5)
C(3)−C(2)−W	127.6(4)	O(1)−C(6)−C(61)	111.0(5)
C(4)−C(3)−C(2)	123.8(4)	C(5)−C(6)−C(61)	128.0(5)
C(3)−C(4)−C(5)	118.6(5)	C(6)−O(1)−C(2)	124.8(4)
C(3)−C(4)−C(41)	119.0(4)	O(53)−C(51)−C(52)	123.0(6)
C(5)−C(4)−C(41)	122.5(4)	O(53)−C(51)−C(5)	120.2(6)
C(6)−C(5)−C(4)	117.7(5)	C(52)−C(51)−C(5)	116.7(5)
C(6)−C(5)−C(51)	117.7(5)		

Table 7. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 3[a]

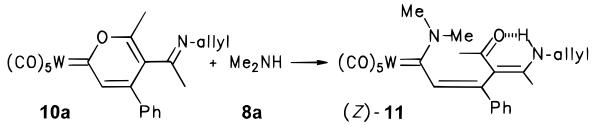
	x	*y*	*z*	*U*(eq)
W	7325(1)	2201(1)	3783(1)	23(1)
C(2)	7363(8)	194(5)	3057(4)	24(1)
C(3)	8558(8)	−99(5)	2383(3)	26(1)
C(4)	8293(7)	1382(5)	1868(3)	24(1)
C(41)	9567(8)	1557(5)	1141(4)	26(1)
C(42)	11699(8)	−899(5)	1351(4)	32(1)
C(43)	12932(10)	1020(6)	682(5)	42(1)
C(44)	12018(11)	−1824(7)	−221(5)	46(1)
C(45)	9888(12)	−2491(8)	−453(5)	47(2)
C(46)	8666(9)	−2371(6)	229(4)	36(1)
C(5)	6773(8)	−2481(5)	2049(4)	28(1)
C(6)	5658(9)	−2203(5)	2737(4)	30(1)
O(1)	5969(6)	−919(4)	3208(3)	30(1)
C(61)	4098(11)	−3173(7)	3097(5)	45(2)
C(51)	6338(10)	−3933(6)	1559(4)	39(1)
C(52)	8151(13)	4579(7)	1699(7)	58(2)
O(53)	4576(7)	4544(5)	1122(4)	55(1)
C(11)	9150(10)	2006(7)	5065(5)	37(1)
O(11)	10132(9)	1938(7)	5783(4)	60(2)
C(12)	7241(10)	4101(6)	4355(5)	37(1)
O(12)	7163(8)	5161(5)	4656(4)	61(1)
C(13)	4648(10)	1322(7)	4229(5)	37(1)
O(13)	3123(9)	881(7)	4444(5)	60(2)
C(14)	9992(10)	3059(6)	3336(5)	34(1)
O(14)	11494(8)	3533(6)	3106(4)	51(1)
C(15)	5517(9)	2388(6)	2521(4)	32(1)
O(15)	4510(9)	2491(6)	1820(4)	51(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

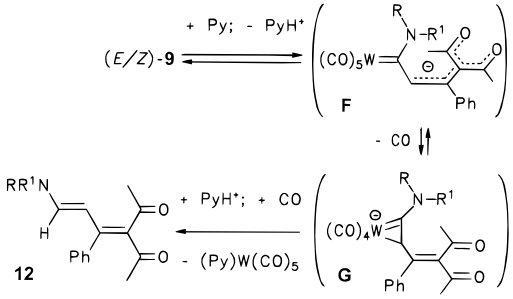
is accelerated appreciably upon contact with silica gel (Table 4). The isomers can be easily distinguished by their ^{1}H NMR spectra. In compounds *syn*-**10**, the ═NC*H* signal is shifted upfield compared to the corresponding signal of the *anti* isomer due to the anisotropic influence of the pyranylidene ring, whereas the NCC*H*$_3$ group in *syn*-**10** appears to be less shielded than in the *anti* product [e.g., *anti*-**10a**, δ(═NC*H*) 3.58, δ(NCC*H*$_3$) 0.86; *syn*-**10a**, δ(═NC*H*) 3.36, δ (NCC*H*$_3$) 1.42]. Dynamic line-broadening is observed for the signals of the diastereotopic methyl group of the isopropyl unit in *anti*-**10d** (but not in *syn*-**10d**), which is due to racemization by (an apparently fast) rotation of the acetimino group against the pyranylidene ring.

2,6-Diamino-1-metalla Trienes *via* Acetimino Complexes 10. 2,6-Diamino-1-metalla trienes have been previously obtained by aminolysis of 2-ethoxy-6-amino-1-metalla trienes.[2b,c] An alternate route for the generation of such compounds is based on the aminolysis of acetimino pyranylidene complexes **10**. For example, the addition of Me_2NH (**8a**) to compound **10a**

Scheme 6. 2,6-Diamino-1-metalla Triene 11 by Aminolysis of 10



Scheme 7. Enamine 12 from Metalla Triene 9



leads to ring opening and formation of the 2,6-diamino-1-metalla triene (*Z*)-**11** in 78% yield (Scheme 6).

This aminolytic ring opening of compound **10a** is highly regioselective and provides a means for the introduction of two different amino functions into a 1-metalla-1,3,5-hexatriene skeleton.

Enamine 12 *via* 2-Amino-1-metalla Trienes. Since 2-amino-1-metalla trienes are easily accessible compounds, we initiated studies on their applicability to organic synthesis.[1, 2] Here we wish to illustrate an example for the formation of a captodative 1-amino-1,3-hexadienone **12** by base-induced ligand disengagement. Thermolysis of (*E*/*Z*)-**9a** in THF in the presence of pyridine (Py) at 90 °C for 1.5 h afforded the enamine **12** together with (pyridine)$W(CO)_5$. The reaction most probably involves the formation of an anionic intermediate[16] such as **F**, which after loss of CO may give an anionic tungstacyclopropene[17] **G**, from which the enamine **12** is eliminated after protonation[16c] (Scheme 7).

Experimental Section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone. Melting points are uncorrected. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker WM 300 and WP 360 spectrometers. (Multiplicities were determined by DEPT. Chemical shifts refer to $\delta_{TMS} = 0.00$ ppm.) Other analyses: IR Digilab FTS 45; MS Finnigan MAT 312; elemental analysis, Perkin-Elmer 240 elemental analyzer; column chromatography, Merck-Kieselgel 100; TLC, Merck DC-Alufolien Kieselgel 60 F 254. R_f values refer to TLC tests. Complex **3** has been prepared by a modified procedure given in the literature.[6]

Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (3). To pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (482 mg, 1.00 mmol) in a 5-mL screw-top vessel was added a solution of pentane-2,4-dione (**2**) (100 mg, 1.00 mmol) and triethylamine (50 mg, 0.50 mmol) in 4 mL of pentane with vigorous stirring at 20 °C until a dark solution was obtained (after 3−5 min), from which rust-brown crystals of **3** began to precipitate within 10 min at 20 °C. After 2 h at 20 °C, crystallization was continued at −15 °C for 12 h to give (additional) compound **3** (482 mg, 90%, R_f = 0.5, 1:1 diethyl ether/pentane, rust-brown powder from pentane, violet needles from diethyl ether, mp 106 °C): ^{1}H NMR ($CDCl_3$) δ 8.05 (1 H, s, 3-H), 7.54 (3 H, m, *o*- and *m*-H, Ph), 7.40 (2 H, m, *o*-H, Ph), 2.67 (3 H, s, 6-CH_3), 1.92 (3 H, s, $OCCH_3$); ^{13}C NMR ($CDCl_3$) δ 258.4 (W=C), 204.5 and 198.6 [*trans*- and *cis*-CO, $W(CO)_5$], 204.5 (Cq, C=O), 173.9 (Cq, C6), 143.1 (Cq, C4), 141.5 (CH, C3), 135.4 (Cq, *i*-C, Ph), 131.5, 129.9, and 128.2 (CH each, Ph), 127.9 (Cq, C5), 31.7 (6-CH_3), 19.8 ($OCCH_3$); IR (diffuse reflection, cm^{-1}) 2060.3, 1975.4, 1900.0, 1702.4, 1589.8; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 536 (20) [M^+], 395 (40) [$M^+ - 5CO$], 212 (20) [ligand$^+$], 179 (100). Anal. Calcd for $C_{19}H_{12}O_7W$ (536.2): C, 42.56; H, 2.26. Found: C, 42.81; H, 2.46.

Allylammonium (3*Z*)-5-Acetyl-6-(allylamino)-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-trien-2-ate (5a). To a freshly prepared solution of pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (134 mg, 0.25 mmol) in 1 mL of CD_2Cl_2 was added allylamine (**4a**) (57 mg, 1.00 mmol) at −30 °C (with a microsyringe). A yellow solution formed; NMR spectra were taken at −30 °C. TLC indicated the presence of a very polar yellow compound, from which the (violet) pyranylidene complex **3** was eluted due to the redissociation of **5** on silica gel into **3** and **4**: ^{1}H NMR (CD_2Cl_2, 243 K, signals of the allylammonium species render prominent intensity) δ 11.63 (1 H, t, ^3J = 5 Hz, O···H−N), 7.52 (2 H, d, *o*-H, Ph), 7.52 (1 H, s, 3-H), 7.37 and 7.29 (2:1 H, m each, *m*- and *p*-H, Ph), 5.95 (m, N^+H_3 and N^+CH_2CH=CH_2), 5.20 (m, N^+CH_2CH=CH_2), 5.77 (1 H, m, CH=CH_2, 6-allyl), 5.13 (2 H, m, CH=CH_2, 6-allyl), 3.80 (2 H, m, NCH_2, 6-allyl), 3.47 (m, N^+CH_2), 1.98 (3 H, s, $OCCH_3$), 1.77 (3 H, s, $NCCH_3$); ^{13}C NMR (CD_2Cl_2, 243 K) δ 292.5 (W=C), 207.3 and 202.4 [*trans*- and *cis*-CO, $W(CO)_5$], 195.8 (Cq, C=O), 164.6 (Cq, =CN), 149.2 (CH, C3), 141.8 (Cq, C4), 134.8 (N^+CH_2CH=CH_2), 133.9 (CH=CH_2, 6-allyl), 128.5, 127.4, and 126.7 (CH each, Ph), 123.2 (Cq, *i*-C, Ph), 116.9 (N^+CH_2CH=CH_2), 116.0 (CH=CH_2, 6-allyl), 104.3 (Cq, C5), 45.5 (NCH_2, 6-allyl), 42.9 (N^+CH_2), 28.2 ($OCCH_3$), 16.4 ($NCCH_3$).

***n*-Butylammonium (3*Z*)-5-Acetyl-6-(*n*-butylamino)-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-trien-2-ate (5b).** Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) was reacted as described earlier with 4 equiv of *n*-butylamine (**4b**) to give a solution of **5b**: ^{1}H NMR (CD_2Cl_2, 243 K, 600 MHz, signals of the *n*-butylammonium species render prominent intensity) δ 11.71 (1 H, t, ^3J = 5 Hz, O···H−N), 7.52 (2 H, d, *o*-H, Ph), 7.37 (1 H, s, 3-H), 7.29 and 7.22 (2:1 H, m each, *m*- and *p*-H, Ph), 4.37 (m, NH_3^+), 3.47 and 3.15 (m each, 6-NCH_2 and N^+CH_2), 1.91 (3 H, s, $OCCH_3$), 1.77 (3 H, s, $NCCH_3$), 1.51 and 1.45 (m each, 6-NCH_2CH_2 and $N^+CH_2CH_2$), 1.33 and 1.30 [m each, $N^+(CH_2)_2CH_2$ and 6-$N(CH_2)_2CH_2$], 0.91 and 0.89 [t each, $N^+(CH_2)_3CH_3$ and 5-$N(CH_2)_3CH_3$]; ^{13}C NMR (CD_2Cl_2, 243 K) δ 289.9 (W=C), 207.7 and 202.6 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 195.0 (Cq, C=O), 163.7 (Cq, =CN), 149.4 (CH, C3), 142.4 (Cq, C4), 128.5, 127.3, and 126.8 (2:1:2, CH each, Ph), 123.1 (Cq, *i*-C, Ph), 103.5 (Cq, C4), 43.5 and 40.3 (5-NCH_2 and N^+CH_2), 34.2 and 31.9 ($N^+CH_2CH_2$ and 5-NCH_2CH_2), 28.3 ($OCCH_3$), 20.9 and 20.2 [$N^+(CH_2)_2CH_2$ and 6-$N(CH_2)_2CH_2$], 15.5 ($NCCH_3$), 13.7 and 13.5 [6-$N(CH_2)_3CH_3$ and $N^+(CH_2)_3CH_3$].

Benzylammonium (3*Z*)-5-Acetyl-6-(*n*-benzylamino)-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-trien-2-ate (5c). Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene-)tungsten (**3**) is reacted as described earlier with 4 equiv of benzylamine (**4c**) to give **5c**: ^{1}H NMR (CD_2Cl_2, 243 K, 600 MHz, signals of benzylammonium the species render prominent intensity) δ 11.94 (1 H, t, ^3J = 5 Hz, O···H−N), 7.67 (2 H, d, *o*-H, 4-Ph), 7.62 (1 H, s, 3-H), 7.45−7.18 (m, *m*- and *p*-H, 4-Ph, 6-NCH_2Ph and N^+CH_2Ph), 6.62 (H_3N^+), 4.29 and 3.69 (m each, 6-NCH_2 and $H_3N^+CH_2$), 2.05 (3 H, s, $OCCH_3$), 1.88 (3 H, s, $NCCH_3$); ^{13}C NMR (CD_2Cl_2, 243 K), δ 291.4 (W=C), 207.6 and 202.7 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 196.3 (Cq,

(16) See also: (a) Kreiter, C. G. *Angew. Chem.* **1967**, *79*, 900; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 879. (b) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (c) Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875.

(17) For a review on metallacyclopropenes, see: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 71. For an X-ray structure of a stable *chroma*cyclopropene of related type, see: Aumann, R.; Heinen, H.; Krüger, C.; Betz, P. *Chem. Ber.* **1990**, *123*, 599.

C═O), 163.4 (Cq, ═CN), 149.4 (CH, C3), 142.0 (Cq, C4), 139.8 and 137.8 (Cq, *i*-C, CH_2Ph and N^+CH_2Ph), 129.3−126.3 (CH each, 2 Ph and N^+CH_2Ph), 123.3 (Cq, *i*-C, 4-Ph), 104.5 (Cq, C5), 44.5 and 43.4 (NCH_2 and N^+CH_2), 28.4 ($OCCH_3$), 16.8 ($NCCH_3$).

Isopropylammonium (2*Z*)-5-Acetyl-6-(isopropylamino)-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-trien-2-ate (5d). Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) was reacted as described earlier with 4 equiv of isopropylamine (**4d**) to give **5d**: ^{1}H NMR (CD_2Cl_2, 243 K, signals of the isopropylammonium species render prominent intensity) δ 11.73 (1 H, t, ^3J = 5 Hz, O···H−N), 7.52 (2 H, d, *o*-H, 4-Ph), 7.41 (1 H, s, 3-H), 7.30 (2 H, m, *m*-H, Ph), 7.23 (1 H, m, *p*-H, Ph), 5.05 (H_3N^+), 3.66 and 3.20 (m each, NCH and H_3N^+), 1.96 (3 H, s, $OCCH_3$), 1.81 (3 H, s, $NCCH_3$), 1.16 and 1.13 [d each, ^3J = 6.6 Hz, $NCH(CH_3)_2$ and $N^+CH(CH_3)_2$]; ^{13}C NMR (CD_2Cl_2, 243 K) δ 290.2 (W═C), 207.5 and 202.7 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 195.1 (Cq, C═O), 162.8 (Cq, ═CN), 149.5 (CH, C3), 142.4 (Cq, C4), 128.5, 127.3, and 126.8 (2:1:2, CH each, Ph), 122.9 (Cq, *i*-C, Ph), 103.6 (Cq, C5), 44.9 and 43.4 (NCH and N^+CH), 28.5 ($OCCH_3$), 23.8 and 23.5 [CH_3 each, $NCH(CH_3)_2$], 24.1 [$N^+CH(CH_3)_2$], 16.3 ($NCCH_3$).

5-Acetyl-2-(allylamino)-6-hydroxy-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene [(*Z*)-6a and (*E*)-6a] and Pentacarbonyl(5-acetyl-1-allyl-6-methyl-4-phenyl-1,2-dihydropyridin-2-ylidene)tungsten (7a). To pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) in 5 mL of dry ethyl ether was added allylamine (**4a**) (74 mg, 1.30 mmol) with stirring. After 4 h at 20 °C, compound **3** was consumed completely and the color of the initially violet solution had become yellow. According to a ^{1}H NMR spectrum in C_6D_6, a mixture of (*Z*)-**6a**:(*E*)-**6a**:**7a** = 10:1:1 was formed. Chromatography on silica gel with pentane/dichloromethane (2:1−1:1) afforded (greenish) yellow **7a** (40 mg, 7%, R_f = 0.8 in 1:1 pentane/dichloromethane, yellow crystals); elution with dichloromethane/diethyl ether (10:1) yielded orange (*Z*)-**6a** (403 mg, 70%, R_f = 0.3 in 1:1 pentane/dichloromethane, R_f = 0.7 in dichloromethane, orange oil) and yellow (*E*)-**6a** (40 mg, 7%, R_f = 0.1 in 1:1 pentane/dichloromethane, yellow oil).

(*Z*)-**6a**: ^{1}H NMR (C_6D_6) δ 17.05 (1 H, s, O···H−O), 8.03 (1 H, s broad, NH), 7.05 and 7.03 (2:3 H, m each, Ph), 6.66 (1 H, s, 3-H), 5.07 (1 H, ddt, ^3J = 17.0, 10.0, and 4.5 Hz, C*H*═CH_2), 4.83 and 4.81 (1 H each, m each, CH═CH_2), 2.98 (2 H, m, NCH_2), 1.90 (6 H, s, 6-CH_3 and $OCCH_3$); ^{13}C NMR (C_6D_6) δ 253.0 (W═C), 201.8 and 198.7 [*trans*- and *cis*-CO, $W(CO)_5$], 192.0 (Cq, C═O and ═COH···O), 141.3 (Cq, C4), 138.0 (CH, C3), 135.5 (Cq, *i*-C, Ph), 130.5 (*C*H═CH_2), 129.5, 128.8, and 126.9 (2:1:1, CH each, Ph), 118.6 (CH═*C*H_2), 111.0 (Cq, C5), 53.4 (NCH_2), 24.6 (2 CH_3); IR (diffuse reflection, cm^{-1}) 3356.3 [ν(N−H) bridge], 3289.6 [ν(N−H) carbene], 2060.1 (25), 1970.1 (10), 1942.6 (60), 1899.5 (100) [ν(C≡O)], 1599.8 (40) [ν(C═O)], 1519.4 (50) [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 593 (30) [M^+], 565 (10), 537 (5), 509 (15), 481 (20), 453 (60), 210 (80), 57 (100). Anal. Calcd for $C_{22}H_{19}NO_7W$ (593.3): C, 44.54; H, 3.23; N, 2.36. Found: C, 44.72; H, 3.40; N, 2.43.

(*E*)-**6a**: ^{1}H NMR (C_6D_6) δ 16.90 (1 H, s, O···H−O), 8.17 (1 H, s broad, NH), 7.05 and 7.02 (2:3 H, m each, Ph), 5.96 (1 H, s, 3-H), 4.95 (1 H, ddt, ^3J = 17.0, 10.0, and 4.5 Hz, C*H*═CH_2), 4.76 and 4.71 (1 H each, m each, CH═CH_2), 3.30 and 2.86 (1 H each, s each, dynamically broadened, NCH_2), 2.01 and 1.70 (3 H each, s each, dynamically broadened, 6-CH_3 and $OCCH_3$); IR (diffuse reflection, cm^{-1}) *m*/*e* (relative intensity) 3351.8 (10, sharp) and 3287.8 (15, broad) [ν(N−H and O−H)], 2060.5 (30), 1971.7 (50), 1945.2 (100) [ν(C≡O)], 1598.6 (30) [ν(C═O)], 1520.0 (30) [ν(C═C)].

7a: ^{1}H NMR (C_6D_6) δ 8.71 (1 H, s, 3-H), 7.22 and 7.00 (2:3 H, m each, Ph), 5.45 (1 H, ddt, ^3J = 17.0, 10.0, and 4.5 Hz, C*H*═CH_2), 5.05 (2 H, s broad, NCH_2), 4.86 and 4.40 (1 H each, dt each, ^3J = 10.0 and 17.0 Hz, ^4J = 2.0 Hz, ═CH_2), 2.32 and 1.48 (3 H each, s each, 6-CH_3 and $OCCH_3$); ^{13}C NMR ($CDCl_3$) δ 212.9 (W═C), 203.1 and 198.8 [*trans*- and *cis*-CO, $W(CO)_5$], 202.8 (Cq, C═O), 147.9 (Cq, C6), 146.8 (CH, C3), 140.2 (Cq, C4), 136.3 (Cq, *i*-C, Ph), 135.2 (Cq, C5), 131.9 (*C*H═CH_2); 128.5, 128.3, and 127.7 (CH each, Ph), 117.8 (CH═*C*H_2), 67.3 (NCH_2), 32.2 ($OCCH_3$), 18.2 (6-CH_3); IR (*n*-hexane, cm^{-1}) 2059.6 (20), 1985.9 (5), 1922.4 (100); IR (diffuse reflection, cm^{-1}): 1705.2 (60) [ν(C═O)] and 1585.4 (50); MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 575 (40) [M^+], 547 (40), 519 (30), 491 (40), 463 (50), 435 (100), 365 (40), 250 (70), 197 (60), 167 (80), 57 (100). Anal. Calcd for $C_{22}H_{17}NO_6W$ (575.2): C, 45.91; H, 2.98; N, 2.44. Found: C, 46.15; H, 3.10; N, 2.54.

5-Acetyl-2-(*n*-butylamino)-6-hydroxy-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene [(*Z*)-6b and (*E*)-6b] and Pentacarbonyl(5-acetyl-1-butyl-6-methyl-4-phenyl-1,2-dihydropyridin-2-ylidene)tungsten (7b). Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) in 5 mL of dry ethyl ether was reacted as described earlier with *n*-butylamine (**4b**) (95 mg, 1.30 mmol) for 24 h at 20 °C to afford a mixture of (*Z*)-**6b**:(*E*)-**6b**:**7b** = 10:1:2. Chromatography on silica gel with pentane/dichloromethane (4:1−1:1) afforded yellow **7b** (81 mg, 14%, R_f = 0.8 in 5:1 pentane/dichloromethane), followed by an orange fraction of (*Z*/*E*)-**6b** (234 mg, 38%, R_f = 0.5 in 5:1 pentane/dichloromethane).

(*Z*)-**6b**: ^{1}H NMR ($CDCl_3$) δ 17.05 (1 H, s, ═COH···O), 8.52 (1 H, s broad, HN), 7.50−7.10 (5 H, m, Ph), 6.98 (1 H, s, 3-H), 3.25 (2 H, m, NCH_2), 1.91 (6 H, s, $OCCH_3$), 1.63 (2 H, m, NCH_2CH_2), 1.38 [2 H, m, $N(CH_2)_2CH_2$], 0.95 [3 H, t, $N(CH_2)_3CH_3$; ^{13}C NMR ($CDCl_3$) δ 251.6 (W═C), 201.8 and 198.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 191.9 (2 Cq, C═O and ═COH···O), 140.9 (Cq, C5), 138.2 (CH, C4), 134.0 (Cq, *i*-C, Ph), 129.2, 128.8, and 126.9 (CH each, Ph), 110.9 (Cq, C6), 51.9 (NCH_2), 31.1 (NCH_2CH_2), 24.7 ($OCCH_3$), 19.8 [$N(CH_2)_2CH_2$], 13.5 [$N(CH_2)_3CH_3$].

(*E*)-**6b**: ^{1}H NMR ($CDCl_3$) δ 16.78 (1 H, s, ═COH···O), 8.52 (1 H, s broad, HN), 7.50−7.10 (5 H, m, Ph), 6.43 (1 H, s, 3-H), 3.42 and 3.00 (1 H each, m each, diastereotopic NCH_2), 2.07 (6 H, s, $2CCH_3$), 1.50 (2 H, m, NCH_2CH_2), 1.27 (2 H, m, $NCH_2CH_2CH_2$), 0.87 [3 H, t, $N(CH)_3CH_3$]; ^{13}C NMR ($CDCl_3$) δ 252.8 (W═C), 201.6 and 198.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 191.9 (2 Cq, C═O and ═COH···O), 140.9 (Cq, C5), 139.9 (CH, C4), 134.0 (Cq, *i*-C, Ph), 128.9, 128.7, and 128.4 (CH each, Ph), 114.9 (Cq, C6), 51.2 (NCH_2), 30.4 (NCH_2CH_2), 24.2 ($OCCH_3$), 19.9 [$N(CH_2)_2CH_2$], 13.4 [$N(CH_2)_3CH_3$]; IR (diffuse reflection, cm^{-1}) 2060.1, 1970.2, 1915.4 [ν(C≡O)], 1598.7 [ν(C═O)], 1530.2 [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 609 (10) [M^+], 469 (20) [M^+ − 5CO], 285 (30) [ligand$^+$], 57 (100); exact mass calcd for $C_{23}H_{23}NO_7W$ 609.098823, found 609.10021.

7b: ^{1}H NMR ($CDCl_3$) δ 8.46 (1 H, s, 3-H), 7.45 (3 H, m, *m*- and *p*-H, Ph), 7.33 (2 H, m, *o*-H, Ph), 4.87 (2 H, s dynamically broadened, NCH_2), 2.61 (3 H, s, 6-CH_3), 1.93 (3 H, s, $OCCH_3$), 1.79 (2 H, m, NCH_2CH_2), 1.53 [2 H, m, $N(CH_2)_2CH_2$], 1.01 [3 H, t, N(CH2)$_3$CH_3]; ^{13}C NMR ($CDCl_3$) δ 211.1 (W═C), 203.4 and 199.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 202.8 (Cq, C═O), 147.0 (Cq, C6), 146.9 (CH, C_3), 139.9 (Cq, C4), 136.5 (Cq, *i*-C, Ph), 135.4 (Cq, C5), 129.9, 129.3, and 128.5 (CH each, Ph), 64.3 (NCH_2), 32.7 (NCH_2CH_2), 32.2 ($OCCH_3$), 19.8 [$N(CH_2)_2CH_2$], 18.9 (6-CH_3), 13.7 [$N(CH_2)_3CH_3$]; IR (diffuse reflection, cm^{-1}) 2057.0, 1985.1, 1898.2 [ν(C≡O)], 1705.6 [ν(C═O)], 1584.7 [ν-(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 591 (10) [M^+], 451 (10) [M^+ − 5CO], 267 (40) [ligand$^+$], 196 (100); exact mass calcd for $C_{23}H_{21}NO_6W$ 591.087840, found 591.08660.

5-Acetyl-2-(benzylamino)-6-hydroxy-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene [(*Z*)-6c and (*E*)-6c] and Pentacarbonyl(5-acetyl-1-benzyl-6-methyl-4-phenyl-1,2-dihydropyridin-2-ylidene)tungsten (7c). Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) in 5 mL of dry ethyl ether was reacted as described earlier with benzylamine (**4c**) (139 mg, 1.30 mmol) to afford a mixture of (*Z*)-**6c**:(*E*)-**6c**:**7c** = 10:1:2. Chromatography on silica gel with pentane/dichloromethane (1:1−2:1) afforded (greenish) yellow **7c** (81 mg, 13%, R_f = 0.8 in 5:1 pentane/dichloromethane); elution with dichloromethane/di-

ethyl ether (10:1) yielded an orange mixture of **6c** (Z/E = 10:1) (237 mg, 37%, R_f = 0.5 in 5:1 pentane/dichloromethane).

(*Z*)-**6c**: ^{1}H NMR ($CDCl_3$) δ 17.10 (1 H, s, O···H—O), 8.52 (1 H, s broad, HN), 7.40 (10 H, m, 2 Ph), 7.08 (1 H, s, 3-H), 4.46 (2 H, m, NCH_2), 1.95 (6 H, s, $OCCH_3$); ^{13}C NMR ($CDCl_3$) δ 252.6 (W═C), 201.7 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 191.9 (2 Cq, C═O and ═COH···O), 140.9 (Cq, C5), 138.1 (CH, C4), 135.1 and 133.7 (Cq each, *i*-C, 2 Ph), 130—126 (CH each, 2 Ph), 110.9 (Cq, C6), 55.9 (NCH_2), 24.2 ($OCCH_3$); IR (diffuse reflection, cm^{-1}) 2060.2, 1970.9, 1909.3 [ν(C≡O)], 1597.2 [ν(C═O)], 1522.5 [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 643 (10) [M^+], 503 (10) [$M^+ - 5CO$], 319 (10) [ligand$^+$], 91 (100); exact mass calcd for $C_{26}H_{21}NO_7W$ 643.082755, found 643.08086.

(*E*)-**6c**: ^{1}H NMR ($CDCl_3$) δ 16.75 (1 H, s, O···H-O), 8.82 (1 H, s broad, HN), 7.50—7.00 (10 H, m, 2 Ph), 6.49 (1 H, s, 3-H), 5.57 and 3.95 (1 H each, m each, NCH_2), 2.01 (6 H, s, $OCCH_3$); ^{13}C NMR ($CDCl_3$) δ 253.6 (W═C), 202.0 and 198.1 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 191.9 (2 Cq, C═O and ═COH···O), 140.9 (Cq, C5), 139.9 (CH, C4), 138.2 and 133.5 (Cq each, *i*-C each, 2 Ph), 130—126 (CH each, 2 Ph), 114.9 (Cq, C6), 55.3 (NCH_2), 24.7 ($OCCH_3$).

7c: ^{1}H NMR ($CDCl_3$) δ 8.60 (1 H, s, 3-H), 7.50—7.24 (8 H, m, Ph, *m*- and *p*-H, benzyl), 6.97 (2 H, m, *o*-H, benzyl), 6.29 (2 H, s dynamically broadened, NCH_2), 2.40 (3 H, s, 6-CH_3), 1.91 (3 H, s, $OCCH_3$); ^{13}C NMR ($CDCl_3$) δ 214.5 (W═C), 203.0 and 198.7 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 202.6 (Cq, C═O), 148.3 (Cq, C6), 146.5 (CH, C3), 140.5 (Cq, C4), 136.3 and 134.6 (Cq each, *i*-C each, 2 Ph), 135.5 (Cq, C5), 129.9, 129.4, 128.6, 128.2, and 125.6 (CH each, 2 Ph), 63.4 (NCH_2), 32.2 ($OCCH_3$), 19.3 (6-CH_3); IR (diffuse reflection, cm^{-1}) 2058.7, 1966.6, 1899.8 [ν-(C≡O)], 1704.3 [ν(C═O)], 1585.5 [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 625 (10) [M^+], 485 (30) [$M^+ - 5CO$], 301 (30) [ligand$^+$], 91 (100); exact mass calcd for $C_{26}H_{19}NO_6W$ 625.072191, found 625.06959.

(3*Z*)-5-Acetyl-2-(dimethylamino)-6-hydroxy-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene (9a). To pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)-tungsten (**3**) (536 mg, 1.00 mmol) in 1 mL of dichloromethane was added dimethylammonium dimethylaminocarbamate (**8a**) (134 mg, 1.00 mmol) with stirring. A yellow solution was obtained after 20 min at 20 °C, from which yellow crystals began to precipitate after the addition of 3 mL of pentane (470 mg, 81%, R_f = 0.2 in 1:1 pentane/dichloromethane, yellow crystals, mp 121 °C): ^{1}H NMR (C_6D_6) δ 16.80 (1 H, s broad, O···H—O), 7.19 (1 H, s, 3-H), 7.13 and 7.00 (2:3, m each, Ph), 2.45 and 2.12 (3 H each, s each, NMe_2), 2.00 and 1.30 (3 H each, s dynamically broadened each, CCH_3 each); ^{13}C NMR ($CDCl_3$) δ 250.3 (W═C), 200.6 and 198.7 [*trans*- and *cis*-CO, $W(CO)_5$], 193.6 and 191.2 (Cq each, C═O and ═COH···O), 141.3 (CH, C3), 141.2 (Cq, C4), 129.1 (Cq, *i*-C, Ph), 129.0, 128.4, and 126.0 (2:1:2, CH each, Ph), 110.6 (Cq, C6), 54.0 and 45.9 (NCH_3 each), 24.8 and 24.7 (CCH_3 each); IR (diffuse reflection, cm^{-1}) 2059.2, 1988.2, 1908.7; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 581 (10) [M^+], 441 (20) [$M^+ - 5CO$], 257 (30) [ligand$^+$], 198 (100), 165 (90), 115 (100). Anal. Calcd for $C_{21}H_{19}NO_7W$ (581.2): C, 41.25; H, 2.73; N, 2.53. Found: C, 41.38; H, 2.95; N, 2.72.

5-Acetyl-2-[2-(hydroxymethyl)pyrrolidino]-6-hydroxy-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene [(*Z*)-9b]. Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) in 1 mL of dichloromethane was reacted with 2-(hydroxymethyl)pyrrolidine (**8b**) (100 mg, 1.00 mmol) as described earlier to give yellow (*E*)-**9b** (567 mg, 89%, R_f = 0.5 in 1:1 pentane/diethyl ether): ^{1}H NMR (C_6D_6) δ 17.63 (1 H, s broad, O···H—O), 7.39 (1 H, s, 3-H), 7.26 (2 H, d, *o*-H, Ph), 7.10 (3 H, m, *m*- and *p*-H, Ph), 4.20 (1 H, s, CH_2OH), 3.72 (2 H, m, CH_2OH), 3.65 (1 H, m, *syn*-$NCHCH_2OH$), 2.82 (2 H, m, *anti*-NCH_2), 2.00 and 1.40 (2 H each, s broad each, $NCH_2CH_2CH_2$), 1.23 and 1.00 (3 H each, s broad each, CH_3 each); ^{13}C NMR ($CDCl_3$) δ 247.8 (W═C), 202.9 and 198.9 [*trans*- and *cis*-CO, $W(CO)_5$], 193.7 and 190.9 (Cq each, C═O and ═COH···O), 145.4 (CH, C3), 143.3 (Cq, C4), 129.3 (Cq, *i*-C, Ph), 129.0, 128.3, and 126.5 (2:1:2, CH each, Ph), 111.2 (Cq, C6), 66.2 (CH_2OH), 63.2 ($NCHCH_2OH$), 61.1 (NCH_2), 27.3 and 22.2 (CH_2 each, pyrrolidine), 26.6 and 24.8 (CCH_3 each); IR (*n*-hexane, cm^{-1}) 2060.1 (30), 1988.5 (10), 1924.9 (100) [ν(C≡O)]; IR (diffuse reflection, cm^{-1}) 3500.0 [ν-(O—H)], 2057.1, 1988.4, 1894.7 [ν(C≡O)], 1593.0 [ν(C═O)], 1503.2 [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 637 (10) [M^+], 497 (10) [$M^+ - 5CO$], 252 (30), 303 (5) [ligand$^+$], 298 (80), 296 (60), 182 (100). Anal. Calcd for $C_{24}H_{23}NO_8W$ (637.1): C, 45.21; H, 3.64; N, 2.20. Found: C, 45.44; H, 3.70; N, 2.32.

5-Acetyl-2-pyrrolidino-6-hydroxy-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene [(*E*)-9c]. Pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) in 1 mL of dichloromethane was reacted with pyrrolidine (**8c**) (70 mg, 1.00 mmol) as described earlier to give yellow (*E*)-**9c** (504 mg, 83%, R_f = 0.5 in 2:1 pentane/dichloromethane, yellow crystals from ether at −15 °C): ^{1}H NMR (C_6D_6) δ 17.80 (1 H, s broad, O···H—O), 7.20 (2 H, d, *o*-H, Ph), 7.05 (3 H, m, *m*- and *p*-H, Ph), 6.51 (1 H, s, 3-H), 3.72 and 3.35 (1 H each, s broad each, diastereotopic *syn*-NCH_2), 2.46 (2 H, m, *anti*-NCH_2), 1.87 and 1.54 (2 H each, s broad each, $NCH_2CH_2CH_2$), 1.23 and 1.00 (3 H each, s broad each, CCH_3 each); ^{13}C NMR ($CDCl_3$) δ 243.0 (W═C), 202.3 and 198.9 [*trans*- and *cis*-CO, $W(CO)_5$], 194.4 and 189.3 (Cq each, C═O and ═COH···O), 143.0 (CH, C3), 142.6 (Cq, C4), 132.4 (Cq, *i*-C, Ph), 129.3, 128.4, and 126.9 (2:1:2, CH each, Ph), 111.4 (Cq, C6), 62.3 and 54.7 (NCH_2 each), 25.5 and 24.2 (CH_2 each, pyrrolidine), 25.8 and 23.5 (CCH_3 each); IR (*n*-hexane, cm^{-1}) 2059.6 (30), 1987.7 (10), 1925.3 (100) [ν(C≡O)]; IR (diffuse reflection, cm^{-1}) 3500.0 [ν(O—H)], 2057.1, 1988.5, 1890.0 [ν(C≡O)], 1597.3 [ν(C═O)], 1500.0 [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 607 (10) [M^+], 589 (20), 551 (10), 523 (40), 495 (40), 467 (40) [$M^+ - 5CO$], 283 (30) [ligand$^+$], 268 (80), 266 (60), 224 (100). Anal. Calcd for $C_{23}H_{21}NO_7W$ (607.3): C, 45.49; H, 3.49; N, 2.31. Found: C, 45.64; H, 3.70; N, 2.52.

Pentacarbonyl[1-(*N*-allylacetimino)-6-methyl-4-phenylpyran-2-ylidene]tungsten (10a). To a freshly prepared suspension of pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) and allylamine (**4a**) (57 mg, 1.00 mmol) in 1 mL of dry ethyl ether in a 5-mL screw-top vessel was added a solution of trimethylchlorosilane (308 mg, 3.00 mmol) and triethylamine (409 mg, 4.00 mmol) in 3.5 mL of dry diethyl ether with stirring. Stirring was continued at 20 °C until a (homogeneous) solution was obtained. According to TLC, complex **3** was consumed completely after 24 h at 20 °C, and maroon polar compound **10a** formed. Solvent was removed (20 °C, 1 Torr) and the residue was extracted with small portions of toluene. A ^{1}H NMR spectrum, which was taken immediately after (a fast) workup, indicated the presence of *anti*-**10a** only. *Anti*/*syn* isomerization to give a 1:1 mixture was observed upon standing in solution or upon chromatography (523 mg, 91%, red oil, R_f = 0.2 in 1:1 pentane/diethyl ether, on silica gel). *anti*-**10a** {*syn*-**10a**}: ^{1}H NMR (C_6D_6) δ 8.10 {8.00} (1 H, s, 3-H), 7.05—6.90 {6.95—6.90} (5 H, m, Ph), 5.90 {5.82} (1 H, ddt, ^3J = 17.0, 10.0, and 4.5 Hz, CH═CH_2), 5.18 and 5.04 {5.12 and 5.00} (1 H each, dd each, ^3J = 17.0 and 10.0 Hz, ^2J = 1.5 Hz, ═CH_2), 3.58 {3.36} (2 H each, m each, NCH_2), 1.96 and 0.86 {1.63 and 1.42} (3 H each, s each, 6-CH_3 and $NCCH_3$); ^{13}C NMR (C_6D_6) δ 253.9 {255.7} (Cq, W═C), 204.4 and 199.2 {204.3 and 199.2} [Cq, 1:4, *trans*- and *cis*-CO, $W(CO)_5$], 174.8 {172.3} (Cq, C6), 163.1 {160.7} (Cq, C═N), 145.6 {145.2} (Cq, C4), 141.3 {141.4} (CH, C3), 135.2 {136.1} (CH═CH_2), 135.2 {135.0} (Cq, *i*-C, Ph), 129.4, 128.7, and 127.8 {129.2, 128.6, and 128.1} (2:2:1, CH each, Ph), 130.8 {132.3} (Cq, C6), 115.8 {115.6} (═CH_2), 56.6 {54.6} (NCH_2), 19.0 and 18.8 {27.3 and 19.1} (6-CH_3 and $NCCH_3$); IR (*n*-hexane, cm^{-1}) 2060.6 (40), 1972.2 (5), 1930.3 (100) [ν(C≡O)]; IR (diffuse reflection, cm^{-1}) 1651.4 (15) [ν-(C═N)], 1593.3 (60) [ν(C═C)]; MS (70 eV, ^{184}W) *m*/*e* (relative

intensity) 575 (80) [M^+], 547 (60), 519 (10), 491 (70), 463 (70), 435 (100). Anal. Calcd for $C_{22}H_{17}NO_6W$ (575.2): C, 45.91; H, 2.98; N, 2.44. Found: C, 46.05; H, 3.18; N, 2.62.

Pentacarbonyl[5-(*N*-*n*-butylacetimino)-6-methyl-4-phenylpyran-2-ylidene]tungsten (10b). A freshly prepared suspension of pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) and *n*-butylamine (**4b**) (73 mg, 1.00 mmol) in 1 mL of dry ethyl ether was reacted as described earlier with trimethylchlorosilane/triethylamine to give a 3:1 mixture of *anti*/*syn*-**10b**. After chromatography on silica gel, the *anti:syn* ratio was changed to 1:1 (R_f = 0.5 in 5:1 pentane/dichloromethane, 532 mg, 90%, red oil). *anti*-**10b** {*syn*-**10b**}: ^{1}H NMR ($CDCl_3$) δ 7.96 {8.01} (1 H, s, 3-H), 7.51−7.24 (5 H, m, Ph), 3.36 {3.16} (2 H, m, NCH_2), 2.61 {2.50} (3 H, s, 6-CH_3), 1.80 (2 H, m, NCH_2CH_2), 1.53 {1.96} (3 H, s, $NCCH_3$), 1.36 {1.36} (2 H, m, $NCH_2CH_2CH_2$), 0.95 {0.90} (3 H, t, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 254.6 {256.3} (W=C), 204.4 {204.1} and 198.6 {198.5} [1:4, *trans*- and *cis*-$W(CO)_5$], 173.8 {171.4} (Cq, C6), 163.1 {160.7} (Cq, C=N), 144.9 {144.3} (Cq, C4), 141.2 {141.1} (CH, C3), 135.7 {134.9} (Cq, *i*-C, Ph), 130.3 {130.9}, 129.0 {129.3} and 128.2 {127.6} (CH each, Ph), 129.1 {124.2} (Cq, C5), 52.1 {54.3} (NCH_2), 32.4 {32.6} (NCH_2CH_2), 20.9 {20.9} ($NCH_2CH_2CH_2$), 19.9 and 19.5 {27.8 and 19.4} (6-CH_3 and $NCCH_3$), 13.8 {13.8} ($NCH_2CH_2CH_2CH_3$); IR (diffuse reflection, cm^{-1}) 2058.9, 1973.2, 1938.0, 1898.5 [ν(C≡O)], 1648.9 [ν(C=N)], 1592.8 [ν(C=C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 591 (20) [M^+], 451 (40) [M^+ − 5CO], 67 (40) [ligand$^+$], 57 (100); exact mass calcd for $C_{23}H_{21}NO_6W$ (^{184}W) 591.0882, found 591.0866.

Pentacarbonyl[5-(*N*-benzylacetimino)-6-methyl-4-phenylpyran-2-ylidene]tungsten (10c). A freshly prepared suspension of pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) and benzylamine (**4c**) (107 mg, 1.00 mmol) in 1 mL of dry ethyl ether was reacted as described earlier with trimethylchlorosilane/triethylamine to give a 3:1 mixture of *anti*/*syn*-**10c**. After chromatography on silica gel, the *anti:syn* ratio was changed to 1:1 (R_f = 0.5 in 5:1 pentane/dichloromethane, 438 mg, 70%, red oil). *anti*-**10c** {*syn*-**10c**}: ^{1}H NMR ($CDCl_3$) δ 7.97 {8.05} (1 H, s, 3-H), 7.50−7.24 (10 H, m, 2 Ph), 4.60 {4.44} (2 H, m NCH_2), 2.61 {2.46} (3 H, s, 6-CH_3), 1.73 {2.03} (3 H, s, $NCCH_3$); ^{13}C NMR ($CDCl_3$) δ 254.8 {256.8} (W=C), 204.4 {204.1} and 198.7 {198.6} [1:4, *trans*- and *cis*-$W(CO)_5$], 173.9 {171.5} (Cq, C6), 164.0 {162.3} (Cq, C=N), 144.9 {144.2} (Cq, C4), 141.3 {141.4} (CH, C3), 138.4 {138.2} and 135.7 {134.8} (Cq each, *i*-C each, 2 Ph), 130.3, 129.0, 128.7, 128.2, 128.1, and 127.2 {130.9, 129.3, 128.5, 127.6, 127.5, and 127.2} (CH each, 2 Ph), 128.8 {123.9} (Cq, C5), 56.4 {57.8} (NCH_2), 19.9 and 19.5 {27.9 and 19.4} (6-CH_3 and $NCCH_3$); IR (*n*-hexane, cm^{-1}) 2059.5 (40), 1973.2 (5), 1945.8 (100) [ν(C≡O)]; IR (diffuse reflection, cm^{-1}) 1648.3 (15) [ν(C=N)], 1592.6 (60) [ν(C=C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 625 (10) [M^+], 548 (40) [M^+ − 5CO], 301 (20) [ligand$^+$], 91 (100); exact mass calcd for $C_{26}H_{19}NO_6W$ (^{184}W) 625.07265, found 625.06959.

Pentacarbonyl[5-(*N*-isopropylacetimino)-6-methyl-4-phenylpyran-2-ylidene]tungsten (10d). A freshly prepared suspension of pentacarbonyl(5-acetyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**3**) (536 mg, 1.00 mmol) and isopropylamine (**4d**) (59 mg, 1.00 mmol) in 1 mL of dry ethyl ether was reacted as described earlier with trimethylchlorosilane/triethylamine to give *anti*-**10d** (R_f = 0.5 in 5:1 pentane/dichloromethane, 519 mg, 90%, red crystals, mp 155 °C): ^{1}H NMR ($CDCl_3$) δ 7.74 (1 H, s, 3-H), 7.23 (5 H, m, Ph), 3.57 (1 H, sept, $NCHMe_2$), 2.43 (3 H, s, $NCCH_3$), 1.43 (3 H, s, 6-CH_3); ^{13}C NMR ($CDCl_3$) δ 253.5 (W=C), 204.9 and 198.8 [1:4, *trans*- and *cis*-$W(CO)_5$], 174.5 (Cq, C6), 160.9 (Cq, C=N), 145.9 (Cq, C4), 141.4 (CH, C3), 135.8 (Cq, *i*-C, Ph), 130.8, 129.2, 128.5 (CH each, Ph), 129.6 (Cq, C5), 52.0 ($NCHMe_2$), 22.8 [NCH-$(CH_3)_2$], 19.6 and 19.1 (6-CH_3 and $NCCH_3$); IR (diffuse reflection, cm^{-1}) 2059.0, 1973.6, 1903.9 [ν(C≡O)], 1648.4 [ν(C=N)], 1593.5 [ν(C=C)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 577 (70) [M^+], 437 (60) [M^+ − 5CO], 253 (60) [ligand$^+$], 80 (100). Anal. Calcd for $C_{22}H_{19}NO_6W$ (577.3): C, 45.78; H, 3.32; N, 2.43. Found: C, 45.93; H, 3.04; N, 2.68.

(3*Z*)-5-Acetyl-6-(allylamino)-2-(dimethylamino)-4-phenyl-1-pentacarbonyltungstahepta-1,3,5-triene (11). A mixture of pentacarbonyl[5-(*N*-isopropylacetimino)-6-methyl-4-phenylpyran-2-ylidene]tungsten (**10d**) (577 mg, 1.00 mmol) in 3 mL of diethyl ether and dimethylammonium dimethylaminocarbamate (**8a**) (134 mg, 1.00 mmol) was heated in a 5-mL screw-top vessel for 1 h at 50 °C to give **11** (483 mg, 78%, R_f = 0.5 in 10:1 dichloromethane/diethyl ether, yellow crystals, mp 116 °C): ^{1}H NMR (C_6D_6) δ 12.30 (1 H, s broad, NH bridge), 7.35 (1 H, s, 3-H), 7.40, 7.15, and 7.00 (2:2:1, m each, Ph), 5.42 (1 H, ddt, ^3J = 17.0, 10.0, and 4.5 Hz, CH=CH_2), 4.93 (2 H, m, =CH_2), 3.20 (2 H, m, NCH_2), 3.00 and 2.40 (3 H each, s each, NMe_2), 1.75 and 1.65 (3 H each, s dynamically broadened each, CCH_3 each); ^{13}C NMR ($CDCl_3$) δ 248.8 (W=C), 202.5 and 199.2 [*trans*- and *cis*-CO, $W(CO)_5$], 194.8 (Cq, C=O), 163.1 (Cq, =C−N), 142.6 (Cq, C4), 141.0 (CH, C3), 134.2 (CH=CH_2), 132.6 (Cq, *i*-C, Ph), 129.0, 128.3, and 126.4 (2:1:2, CH each, Ph), 115.7 (CH=CH_2), 104.5 (Cq, C6), 53.4 and 45.3 (NCH_3 each), 28.7 and 17.4 (CCH_3 each); IR (diffuse reflection, cm^{-1}) 2057.6, 1988.7, 1901.2 [ν(C≡O)], 1593 [ν(C=O)]; MS (70 eV, ^{184}W) *m*/*e* (relative intensity) 620 (10) [M^+], 480 (20) [M^+ − 5CO], 196 (100), 165 (90), 57 (100). Anal. Calcd for $C_{24}H_{24}N_2O_6W$ (620.3): C, 46.47; H, 3.90; N, 4.50. Found: C, 46.29; H, 3.85; N, 4.58.

3-Acetyl-6(*E*)-(dimethylamino)-4-phenyl-3,5-hexadien-2-one (12a). Pentacarbonyl[(2*Z*)-4-acetyl-1-(dimethylamino)-5-hydroxy-3-phenyl-2,4-hexadien-1-ylidene]tungsten (**9a**) (290 mg, 0.50 mmol) in 1 mL of dry THF and pyridine (44 mg, 0.55 mmol) were heated in a 2-mL screw-top vessel. According to a TLC test, starting material was consumed after 1.5 h at 90 °C. The solvent was removed and replaced by 2 mL of diethyl ether, from which (pyridine)$W(CO)_5$ (160 mg, 80%) could be removed by crystallization at −45 °C: ^{1}H NMR ($CDCl_3$) δ 7.20−7.00 (5 H, m, Ph), 6.90 (1 H, d, ^3J = 13 Hz, =CHN), 5.98 (1 H, d, ^3J = 13.0 Hz, =CHC), 2.10−1.90 (12 H, dynamically broadened, $OCCH_3$ and NCH_3); ^{13}C NMR ($CDCl_3$) δ 198.8 and 197.7 (Cq each, 2 8C=O), 154.1 (Cq, C3), 152.4 (=CHN), 139.9 (Cq, *i*-C, Ph), 130.3, 128.2, and 126.5 (CH each, Ph), 102.5 (CH, C4), 100.2 (CH, C2), 50.6 (NCH_3), 26.3 ($2OCCH_3$); GC−MS (70 eV) *m*/*e* (relative intensity) 257 (30) [M^+], 256 (30) [M^+ − 1], 242 (50), 213 (100) [M^+ − $COCH_3$], 200 (40), 180 (10), 170 (20) [213 − NMe_2], 158 (10), 141 (15), 128 (20), 115 (25), 43 (100).

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

Supporting Information Available: Tables of positional and displacement parameters and bond distances and angles (13 pages). Ordering information is given on any current masthead page.

OM950741M