Enaminone Substituents Attached to Cyclopentadienes: *3E/3Z* Stereochemistry of 1-Metalla-1,3,5-hexatriene Intermediates (M = Cr, W) as a Functional Criterion for the Formation of Cyclopentadienes and Six-Membered Heterocycles, Respectively**

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Abstract: Reactions of *NH*-enaminones **2** with [2-(1-cycloalkenyl)ethynyl]carbene complexes **7** (M = W, Cr) gave tetrahydropentalenes, tetrahydroindenes, and hexahydroazulenes **8a–i**, in which the *NH*-enaminone moiety is attached to the cyclopentadiene unit. The reaction involved formation of (*3E*)-1-metalla-1,3,5-hexatriene intermediates, which underwent π cyclization faster than *3E/3Z* isomerization. Tungsten complexes **12** and **13** were characterized as reaction intermediates. Compounds **8** are potentially bidentate ligands with respect to coordination both of the cyclopentadienyl and the enaminone moieties.

Keywords: alkynes · C–C coupling · carbene complexes · chromium · cyclopentadienyl ligands · tungsten

Introduction

(1-Alkynyl)carbene complexes $[(CO)_5M{=}C(OEt)C{\equiv}CR]$ **1** (M = W, Cr) have been applied as stochiometric reagents in a number of high-yield transformations of potential usefulness in organic synthesis.[2] It has been shown recently that cyclopentadienes can be generated in [3+2] fashion from the reaction between (1-alkynyl)carbene complexes **1** and cycloalkenylamines $-CH{=}C(NR_2)-$.[3, 4] It was shown in subsequent studies that treatment of *NH*-enaminones **2** with (1-alkynyl)carbene complexes **1** did not afford cyclopentadienes, but gave *O*- and *N*-heterocyclic compounds instead (Scheme 1). We now report that cyclopentadienes were obtained in high yields from the reactions of *NH*-enaminones **2** with [2-(1-cycloalkenyl)ethynyl]carbene complexes **7** (Scheme 2). This new approach to the formation of cyclopentadienes involves the incorporation of a cycloalkenyl unit—instead of an enamino moiety—into the cyclopentadiene ring.

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[+] Crystal structure analysis

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To understand the basics of these transformations, it should be noted that 6-amino-1-metalla-1,3,5-hexatrienes $[(CO)_5M{=}C(OEt)CH{=}C(Ph)C(COR^1){=}C(Me)NHR]$ **3** (M = W, Cr) were found to be key intermediates in these transformations. It was possible to generate compounds (*3Z*)-**3** from reaction of *NH*-enaminones **2** with (2-phenyl-1-ethynyl)carbene complexes **1**, and they were shown by crystal structure analyses to exhibit a trough-shaped geometry, perfectly meeting the steric requirements for a π cyclization to give cyclopentadiene complexes.[5] This type of π cyclization has been observed for 6-amino-1-metalla-1,3,5-hexatrienes, such as $[(CO)_5M{=}C(OEt)CH{=}C(Ph){-}C{=}C(NR_2){-}]$ generated from (1-alkynyl)carbene complexes $[(CO)_5M{=}C(OEt)C{\equiv}CPh]$ **1** and cycloalkenyl amines $-HC{=}C(NR_2)-$,[4, 5] but was not observed for the present case of compounds (*3Z*)-**3**, in which it was outrun by an intramolecular attack of the nitrogen and oxygen atom, respectively, on the carbene carbon atom, to give homopyrroles **4**, pyridinium carbonylmetalates **5**, and pyrylium carbonylmetalates **6**, respectively (Scheme 1).[6]

To avoid formation of O- and N-heterocyclic compounds, but instead obtain cyclopentadienes by π cyclization, it was necessary for steric reasons to apply (*3E*)- rather than (*3Z*)-1-metalla-1,3,5-hexatrienes (Scheme 1). As a further prerequisite, the π cyclization must be faster than the *3E/3Z* isomerization. Even though compounds (*3E*)-**3** actually fulfill the steric requirement for a π cyclization to an indene, for example, this approach to the formation of cyclopentadiene rings failed, due to the low *ortho* reactivity of the phenyl

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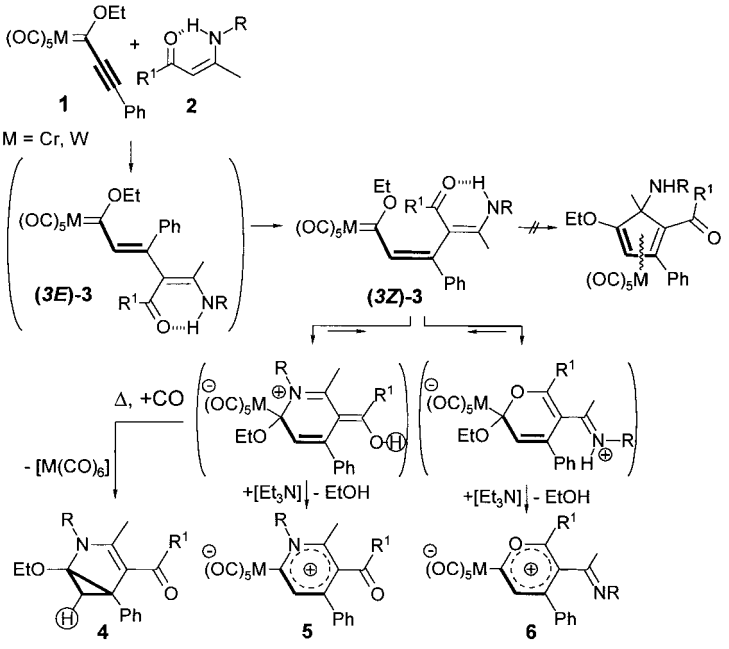
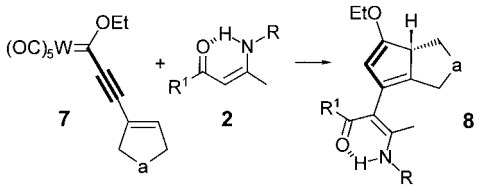


Scheme 1. O- and N-Heterocyclic compounds from addition of *NH*-enaminones to (1-alkynyl)carbene complexes **1**.



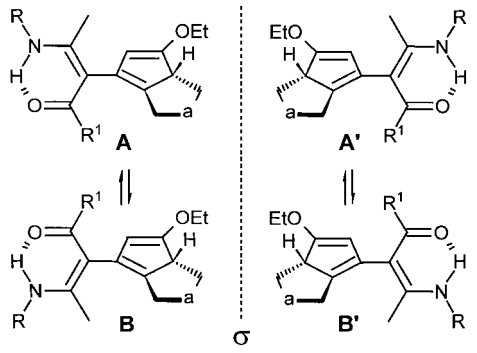
7	M	a	**8**	a	R	R^1	**8** [%][a]
a	W	CH_2	**a**	CH_2	Ph	Me	[b]
b	W	CH_2CH_2	**b**	CH_2CH_2	Ph	Me	76
c	W	$CH_2CH_2CH_2$	**c**	$CH_2CH_2CH_2$	Ph	Me	75
d	Cr	CH_2CH_2	**d**	CH_2	Tol	Me	–
			e	CH_2CH_2	Tol	Me	73 (71)[c]
2		R, R^1	**f**	$CH_2CH_2CH_2$	Tol	Me	75
a		Me, Ph	**g**	CH_2	*t*Bu	Ph	–
b	Me, Tol		**h**	CH_2CH_2	*t*Bu	Ph	78
c	Ph, *t*Bu		**i**	$CH_2CH_2CH_2$	*t*Bu	Ph	74

[a] Yields of isolated product after chromatography. [b] Not isolated due to thermal instability. [c] Yields given in brackets apply for the preparation from chromium carbene complex **7d**.

Scheme 2. Tetrahydropentalenes, tetrahydroindenes, and hexahydroazulenes from addition of *NH*-enaminones **2** to [2-(1-cycloalkenyl)ethynyl]-carbene complexes **7**.

group; in this case *3E/3Z* isomerization was faster than the actually intended π cyclization. We now wish to report, however, that π cyclization products were finally obtained when the phenyl group was replaced by a more reactive alkenyl substituent. Treatment of *NH*-enaminones **2** with 2-(1-cycloalkenyl)ethynyl]carbene complexes **7** under reaction conditions essentially identical to those described above did not yield N- and O-heterocyclic compounds of type **4**–**6**, but instead gave tetrahydropentalene, tetrahydroindene, and hexahydroazulene frameworks in 74–78% yields, thus involving the olefinic functionality of the cycloalkenyl unit in a π cyclization, to form a cyclopentadiene ring (Scheme 2). Notably, the reaction pattern outlined in Scheme 2 involves a reversal of the normal reaction pattern, in which substituents can be introduced into cyclopentadiene rings with electrophilic reagents but not with nucleophilic ones.

The spectroscopic features most characteristic of compounds **8** are provided by the NMR signals of the bridgehead proton 3′a-H (tetrahydroindenes **8b**, **8e**, **8h**: $\delta = 2.68-2.71$, dd, $^3J \approx 5.5$ and 12.2 Hz; hexahydroazulenes **8c**, **8f**, **8i**: $\delta = 2.88-2.98$, dd, $^3J \approx 3.3$ and 10.4 Hz), the bridgehead carbon atom C3′a (tetrahydroindenes **8b**, **8e**, **8h**: $\delta = 50.4-50.6$; hexahydroazulenes **8c**, **8f**, **8i**: $\delta = 53.3-53.7$), and the enol ether moiety (all compounds **8**: 2′-H, $\delta = 4.87-5.04$; C2′, $\delta = 101.4-103.4$). Two sets of ^{13}C and ^1H NMR signals are observed, thanks to formation of atropisomers **A** and **B** (**A′** and **B′**), due to hindered rotation of the enaminone moiety against the cyclopentadiene unit.



Structural details were obtained from a crystal structure analysis of tetrahydroindene **8e** (Figure 1). The enaminone unit is almost planar (dihedral angles C1-C2-C3-C4 170.6(2)°, O2-C2-C3-C4 −8.7(4)°, C2-C3-C4-C5 −175.5(2)° and C2-C3-C4-N6 5.6(3)°) and its plane is strongly inclined against both the tetrahydroindene framework (C4-C3-C11-C12 −88.8(3)° and C4-C3-C11-C17A 96.7(3)°) and the tolyl substituent (C4-N6-C61-C62 50.2(4) and C4-N6-C61-C66 −132.7(3)).

The marked difference in reactivity of (1-alkynyl)carbene complexes **1** and **7** is caused by the configuration of the central C=C bond of the corresponding 1-metalla-1,3,5-hexatriene intermediates, and also by the higher reactivity towards electrophilic attack by the carbene carbon atom of the cycloalkenyl substituents, relative to phenyl groups. On the basis of earlier studies, addition of *NH*-enaminones **2** to

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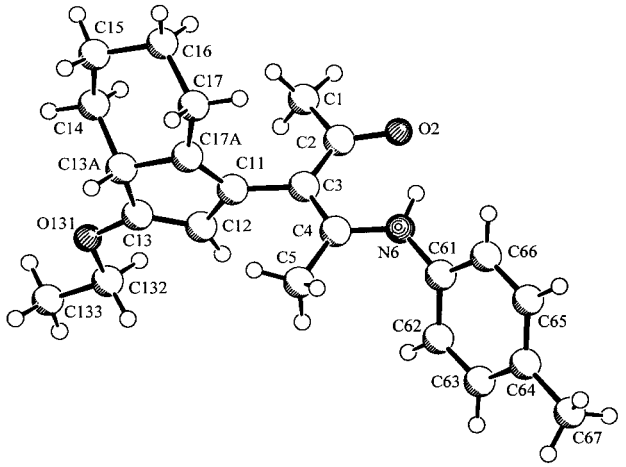
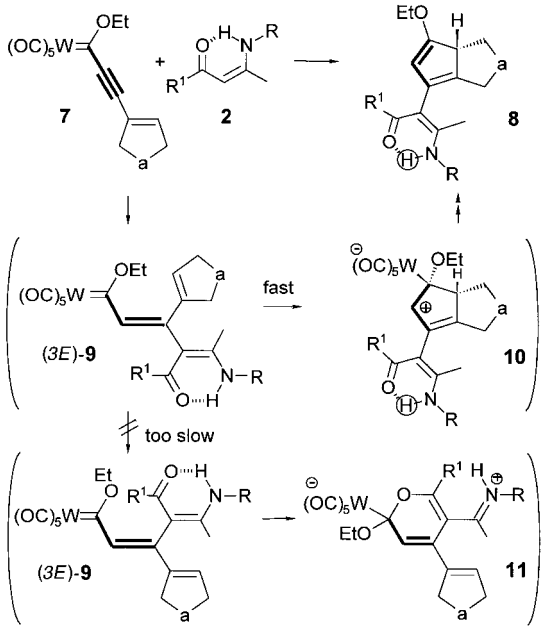


Figure 1. Molecular structure of tetrahydroindene **8e**. Selected bond lengths [Å] and angles [°]: C1–C2 1.508(3), C2–O2 1.251(2), C2–C3 1.431(3), C3–C11 1.491(3), C3–C4 1.387(3), C4–C5 1.496(3), C4–N6 1.354(2), N6–C61 1.420(3), C11–C12 1.474(3), C11–C17A 1.342(3); C1-C2-O2 117.4(2), C1-C2-C3 118.9(2), O2-C2-C3 123.7(2) (sum of bond angles at C2 360.0 ± 0.6°), C2-C3-C4 121.1(2), C2-C3-C11 118.4(2), C4-C3-C11 120.3(2) (sum of bond angles at C3 359.8 ± 0.6°), C3-C4-N6 120.3(2), C3-C4-C5 121.4(2), C5-C4-N6 118.3(2) (sum of bond angles at C4 360.0 ± 0.6°), C4-N6-C61 127.4(2), C3-C11-C12 122.7(2), C3-C11-C17A 127.8 (2); C1-C2-C3-C4 170.6(2), O2-C2-C3-C4 −8.7(4), O2-C2-C3-C11 176.8(2), C2-C3-C4-N6 5.6(3), C2-C3-C4-C5 −175.5(2), C11-C3-C4-N6 180.0(2), C4-N6-C61-C62 50.2(4), C4-N6-C61-C66 −132.7(3), C11-C3-C4-C5 −1.1(3), C4-C3-C11-C12 −88.8(3), C4-C3-C11-C17A 96.7(3).

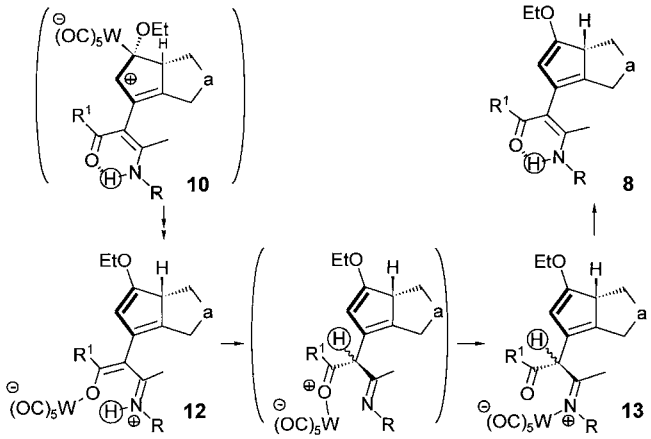
(1-alkynyl)carbene complexes **1** should afford 1-metalla-1,3,5-hexatrienes **3** of *3E* configuration, which do not undergo a π cyclization involving *ortho* attack at the phenyl group, but rather undergo a *3E/3Z* rearrangement to compounds (*3Z*)-**3**, as precursors to *N*- and *O*-heterocyclic compounds of types **4**–**6** (Scheme 1).

Addition of *NH*-enaminones **2** to (1-alkynyl)carbene complexes **7** is assumed to follow a similar reaction path, to give (*3E*)-1-metalla-1,3,5-hexatrienes (*3E*)-**9** (Scheme 3). Because of the higher reactivity of the cycloalkenyl group relative to its phenyl counterpart, the π cyclization of compounds (*3E*)-**9** into cyclopentadienes **8** seems to outrun *3E/3Z* isomerization, which would yield N- and O-heterocyclic compounds of type **4**–**6** (Scheme 1), such as compounds **11** (Scheme 3).

The reaction between compounds **2** and **7** was monitored by NMR spectroscopy. It was shown that intermediates (*3E*)**-9** did not accumulate in the reaction mixture, but that metal compounds **12** and **13** were formed in appreciable amounts (Scheme 4). For example, a tetrahydropentalene complex **13a** was generated on treatment of [2-(1-cyclopentenyl)ethynyl]-carbene complex **7a** with 4-phenylamino-pent-3-en-2-one (**2a**) in [D_8]toluene after 60 h at −20 °C. Because of the inherent ring strain of the tetrahydropentalene system and the resulting high reactivity, compound **13a** could not be isolated. However, we succeeded in isolating the corresponding tetrahydroindene complexes **12h** and **13c** and **13e** in 71–79% yields, by crystallization from the reaction mixtures in *n*-pentane at −20 °C. Even though these compounds proved to be very thermolabile and, in solution at 30 °C, afforded metal-free tetrahydroindenes **8e** and **8h** and hexahydroazulene **8c**, respectively, it was possible to characterize com-



Scheme 3. Consideration of reaction pathways.



8,11–13	a	R	R¹	12 [%][a]	13 [%][a]
a	CH_2	Ph	Me	–	ca. 65[b]
b	CH_2CH_2	Ph	Me	–	84
c	$CH_2CH_2CH_2$	Ph	Me	–	71
e	CH_2CH_2	Tol	Me	–	79[c]
f	$CH_2CH_2CH_2$	Tol	Me	–	73
h	CH_2CH_2	tBu	Ph	73[c]	–
i	$CH_2CH_2CH_2$	*t*Bu	Ph	68	–

[a] Yields of product isolated by crystallization, analyzed by NMR experiments at −20 °C. [b] Not isolated, but characterized by NMR experiments at −20 °C. [c] Compound was characterized by NMR experiments and by a crystal structure analysis.

Scheme 4. Tungsten complexes **12** and **13**, which could be characterized as reaction intermediates.

pounds **12h** and **13e** by crystal structure analyses (vide infra). A course of reaction for the generation of these compounds, based on normal reactivity patterns, is given in Scheme 4.

Compounds **13** were characterized by ^1H and ^{13}C NMR spectroscopy at −20 °C, including NOEMULT, TOCSY, (^1H,^1H), and (^{13}C,^1H) correlation experiments (COSY, GHSQC, GHMBC). They are readily distinguished from

compounds **12**, since the latter exhibit an NH signal at $\delta \approx 9$, whilst the former show hydrogen signals CH(R)C$\sim$N$^+$ (a singlet for each diastereomer) in the range of $\delta = 5.7 - 5.4$ and carbon signals CH(R)C=N$^+$ at $\delta = 69.1 - 67.1$. The carbon signal of the C=N unit is shifted strongly downfield, by about 28 ppm, if the nitrogen atom is coordinated to the tungsten atom (**13b**: $\delta = 186.1$; **8b**: 158.0). Compounds **13** were obtained as approximate 1:3 mixtures of (configurationally stable) diastereomers. The rotation barrier of the 4-imino-2-pentenone moiety against the cyclopentadiene unit seems to be very low, since no further isomers could be frozen out in the NMR spectra at lower temperatures. NOEMULT experiments with diastereomeric mixtures of compounds **13a** and **13e** indicated a positive enhancement between the cyclopentadiene signals *H*C=C(OEt) and both the C*H*$_3$CO and the C*H*$_3$C=N$^+$ group, as well as the *H*CC=N unit of each diastereomer, but neither "cross-over" NOEs nor chemical exchange phenomena were observed for the α-protons CHC=N$^+$ of diastereomers, thus ruling out epimerization by slow chemical exchange reactions. Whilst the diastereomeric ratio of compounds **13a** and **13e** was monitored by ^{1}H NMR spectra in [D$_8$]toluene at $-20\,^\circ$C over a period of 40 h, it seemed to invert. It was found later, however, that this inversion resulted from spontaneous crystallization of the major product from the reaction mixture. After the sample had been redissolved, the initially observed ratio of diastereomers was obtained once more. Since epimerization of the C3 center was ruled out under our reaction conditions, it is assumed that the stereochemistry at C3 is determined by kinetic control over the reaction path between compounds **12** and **13**.

Further structural details were provided by a crystal structure analysis of the major isomer of compound **13e** (Figure 2). The structure shows an almost planar subunit

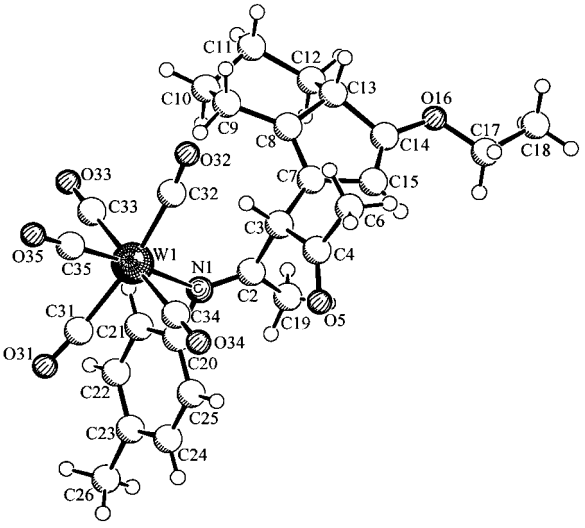


Figure 2. Molecular structure of *N*-imino tungstate complex **13e**. Selected bond lengths [Å] and angles [°] : W1–N1 2.310(3), N1–C2 1.283(5), N1–C20 1.450(5), C2–C3 1.503(6), C2–C19 1.510(6), C3–C4 1.522(6), C3–C7 1.511(5), C4–O5 1.206(5); W1-N1-C20 110.4(2), W1-N1-C2 133.7(3), C20-N1-C2 115.9(3), N1-C2-C3 119.3(4), N1-C2-C19 124.4(4), C3-C2-C19 116.3(3), C2-C3-C4 110.0(3), C2-C3-C7 114.1(4), C3-C4-O5 120.5(4), C3-C4-C6 116.7 (4), C4-C3-C7 113.4(3); W1-N1-C2-C3 1.1(6), W1-N1-C2-C19 179.5(3), N1-C2-C3-C4 93.0(4), N1-C2-C3-C7 $-138.3(4)$, C2-C3-C4-O5 $-2.1(5)$, C20-N1-C2-C19 0.8(6), C20-N1-C2-C3 $-177.6(3)$. defined by the atoms W1, C20, N1, C2, C3, and C19 (dihedral angles W1-N1-C2-C3 1.1(6)°, W1-N1-C2-C19 179.5(3)°, C20-N1-C2-C3 $-177.6(3)$°, and C20-N1-C2-C19 0.8(6)°), with the expected pattern of alternating bond lengths W1–N1 2.310(3), N1–C2 1.283(5), N1–C20 1.450(5), C2–C3 1.503(6), and C2–C19 1.510(6) Å. The bonds to atoms N1 and C2 are in a plane, as is indicated by the sum of bond angles at N1 being 360.0 ± 0.8° (W1-N1-C20 110.4(2)°, W1-N1–C2 133.7(3)°, C2-N1-C20 115.9(3)°) and 360.0 ± 1.1° at C2 (N1-C2-C19 124.4(4)°, N1-C2-C3 119.3(4)°, C3-C2-C19 116.3(3)°). The calculated hydrogen at C3 is in good agreement with the bond lengths C3–C2 1.503(6), C3–C4 1.522(6), and C3–C7 1.511(5) Å and bond angles C2-C3-C4 110.0(3)°, C2-C3-C7 114.1(4)°, and C4-C3-C7 113.4(3)°, and a zwitterionic carbiminium pentacarbonyltungstate structure attached to C3. The acetyl group O5-C4-C6 at C3 is almost orthogonally twisted against the W1-N1-C2-C3 subunit (dihedral angle N1-C2-C3-C4 93.0(4)°). Notably, predominantly one pair of enantiomers ($Z = 2$) was found in the crystal under investigation, whilst the second pair of enantiomers was identified by means of the cyclohexyl group C8–C13, which was refined with split positions in the ratio 0.66(1):0.34(1).

N-Coordination in compounds **13** becomes quite unfavorable if a *tert*-butyl substituent is attached to the nitrogen atom. Accordingly, treatment of compounds **7a** and **7b** with 3-(*tert*-butylamino)-1-phenyl-but-2-en-1-one (**2c**) in *n*-pentane at $-20\,^\circ$C (60 h) did not afford *N*-coordination products **13**, but O-coordination compounds **12** instead.

The ^{1}H NMR spectra of compounds **12** exhibit =N$^+$H(*t*Bu) signals in the range of $\delta = 11.83 - 11.97$ and a strong highfield shift of the axial protons in the major isomers (**12h**: 4′-H$_{ax}$ of major isomer $\delta = 0.57$ (minor isomer 0.22); 6′-H$_{ax}$ -0.03 (-0.40); **12i**: 4′-H$_{ax}$: 0.36 (-0.16), 6′-H$_{ax}$: 1.02 (0.51)). Assignment of the ring protons of the six- and seven-membered rings of compounds **12h** and **12i** for both atropisomers was achieved by means of TOCSY experiments. GHSQC experiments on **12h** and **12i** revealed remarkable shift differences between axial and equatorial protons, probably because of the anisotropic effect of the phenyl group, which is even enhanced by its orientation, from steric interaction with the pentacarbonyltungstate unit. The ^{13}C NMR signals at $\delta = 191.0 - 191.4$ could be unambiguously assigned by GHMBC experiments to the alkenoxy tungstate unit (OC)$_5$W–O*C*(Ph)=C for compounds **12h** and **12i** (both atropisomers) on the basis of a $^3J(^1\text{H},^{13}\text{C})$ correlation observed with *m*-H of the phenyl group. The signals of (OC)$_5$W–O–C(Ph)=*C* were found in the expected range of $\delta = 105.3 - 106.0$, N=*C*(CH$_3$) at $\delta = 170.0 - 170.6$. Two sets of NMR signals were observed for compounds **12h** and **12i** at $-20\,^\circ$C; these were assigned to different atropisomers (vide supra).

Structural details for the tungsten enolate **12h** were obtained by a crystal structure analysis (Figure 3). The compound contains an essentially sickle-shaped W1-O1-C2-C3-C4-N6-C7 backbone, of which only W1 is slightly distorted out of plane (dihedral angles W1-O1-C2-C3 158.6(2)°, O1-C2-C3-C4 $-0.1(4)$°, C2-C3-C4-N6 $-1.9(4)$°, C3-C4-N6-C7 177.0(2)°). The W1-O1-C2 bond angle of 135.3(2)° is much larger than, for example, C18-O20-C21 (114.8(2)°) of an enol

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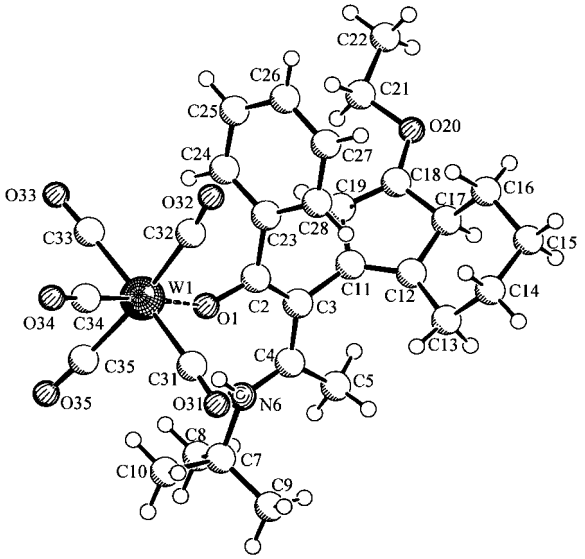


Figure 3. Molecular structure of *O*-alkenoxy tungstate complex **12h**. Selected bond lengths [Å], angles [°], and dihedral angles [°]: W1–O1 2.226(2), O1–C2 1.296(3), C2–C3 1.394(3), C3–C4 1.426(3), C4–N6 1.320(3); W1-O1-C2 135.3(2), O1-C2-C3 123.2(2), O1-C2-C23 117.1(2), C2-C3-C4 122.3(2), C3-C4-N6 119.9(2), C4-N6-C7 132.0(2); W1-O1-C2-C3 158.6(2), W1-O1-C2-C23 −22.8(4), O1-C2-C3-C4 −0.1(4), C2-C3-C4-N6 −1.9(4), C2-C3-C4-C5 177.5(3), C3-C4-N6-C7 177.0(2), C2-C3-C11-C12 117.1(3).

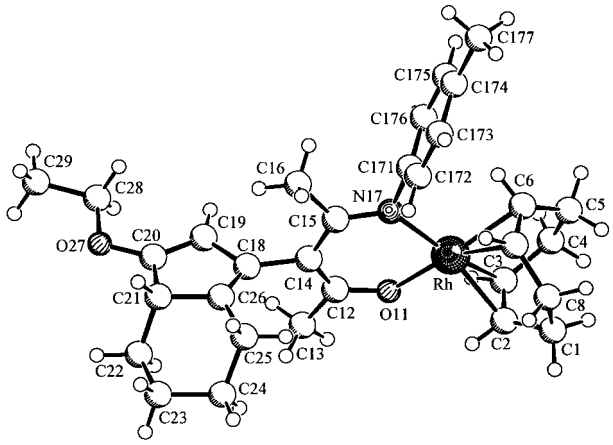
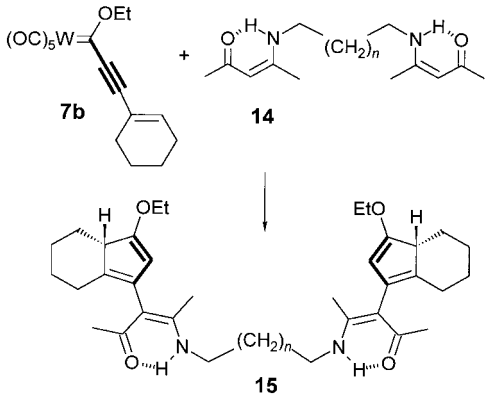


Figure 4. Molecular structure of *O,N*-enaminonorhodium complex **16e**. Selected bond lengths [Å], angles [°], and dihedral angles [°]: Rh–C2 2.134(4), Rh–C3 2.117(3), Rh–C6 2.137(3), Rh–C7 2.108(3), Rh–O11 2.012(2), Rh–N17 2.072(3), O11–C12 1.296(4), C12–C13 1.510(5), C12–C14 1.376(5), C14–C15 1.427(5), C14–C18 1.497(5), C15–C16 1.514(5), C15–N17 1.324(4); C2-Rh-O11 87.9(1), C3-Rh-O11 85.5(1), C6-Rh-O11 160.4(1), C7-Rh-O11 159.6(1), O11-Rh-N17 88.7(1) Rh-O11-C12 128.1(2), O11-C12-C13 112.5(3), O11-C12-C14 126.2(3), C12-C14-C18 117.3(3), C12-C14-C15 125.2(3), C14-C15-C16 117.0(3), C14-C15-N17 124.3(3), C15-N17-C171 116.8(3), C15-N17-Rh 126.1(2); Rh-O11-C12-C13 −175.5(2), Rh-O11-C12-C14 5.0(5), O11-C12-C14-C18 −175.2(3), O11-C12-C14-C15 6.4(6), C12-C14-C15-C16 171.8(4), C12-C14-C15-N17 −7.7(6), C12-C14-C18-C19 −84.8(5), C14-C15-N17-C171 176.6(3), C14-C15-N17-Rh −2.2(5), C15-N17-Rh-O11 8.7(3), N17-Rh-O11-C12 −10.2(3), C171-N17-Rh-O11 −170.1(3).

ether unit. Furthermore, the bond length O1–C2 (1.296(3) Å) is much shorter than C18–O20 (1.357(3) Å). On the basis of the pattern of bond lengths (O1–C2 1.296(3), C2–C3 1.394(3), C3–C4 1.426(3), and C4–N6 1.320(3) Å) and bond angles (O1-C2-C3 123.2(2)°, O1-C2-C23 117.1(2)°, C2-C3-C4 122.3(2)°, C3-C4-N6 119.9(2)° and C4-N6-C7 132.0(2)°), the W1-O1-C2-C3-C4-N6 unit is best considered a zwitterionic carbiminium alkenoxy tungstate. The experimentally located hydrogen at N6 is in good agreement with the C4-N6-C7 bond angle of 132.0(2)°. The plane of the phenyl group C23–C28 is rotated by 70.7° relative to the plane defined by O1, C2, and C3. The W1–O1 bond length (2.226(2) Å) in the "vinylogous imidate" compound **12h** is similar to the W–O distance (ca. 2.22 Å) found in corresponding carboxylato derivatives,[7] but much longer than the W–O distance (ca. 2.16 Å) in corresponding phenoxy compounds.[8]

Complexation onto the enamine unit of compounds **8** was extended to the formation of a chelate complex **16e** to a rhodium atom. This compound was obtained by treatment of ligand **8e** with $[\{(cod)RhCl\}_2]$ (cod = 1,5-cyclooctadiene) in the presence of a base. It was characterized by NMR spectroscopy as well as by a crystal structure analysis (Figure 4). Notably, compounds **8** contain a cyclopentadiene unit and an enaminone unit, both of which are common ligand systems as such. To date, a combination of both systems in one ligand has not to our knowledge been reported. Binuclear metal compounds in which the two coordination sites are occupied by different metal units might offer fresh challenges from the point of view of potential application in catalysis. The broad scope of our synthetic route was also demonstrated by the generation of polydentate systems **14** (Scheme 5).



7	M	14,15	*n*	15 [%][a]
b	**W**	**a**	0	79 (80)[b]
d	**Cr**	**b**	1	76 (74)[b]

[a] Yield of isolated product. [b] Yields given in brackets apply for the preparation from chromium carbene complex **7d**.

Scheme 5. Application of the reaction sequence outlined in Scheme 2 for the generation of potentially polydentate ligand systems.

Conclusion

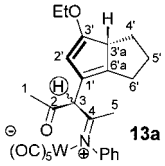
Tetrahydroindenes and hexahydroazulenes **8**, in which an *NH*-enaminone unit is attached to a cyclopentadiene group were obtained by addition of *NH*-enaminones **2** to [2-(1-cycloalkenyl)ethynyl]carbene complexes **7** (M = Cr, W). Tungsten complexes **12** and **13**, with an oxygen–tungsten

and a nitrogen – tungsten bond, respectively, were shown to be reaction intermediates. Compounds **8** are of interest both as organic building blocks and as a novel type of polydentate ligands to organometallic catalysts.

Experimental Section

All operations were carried out under an atmosphere of argon. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 360, Bruker AMX 400, and Varian U 600 instruments. All tetrahydroindenes and hexahydroazulenes were analyzed by ^{1}H NMR, ^{13}C NMR, {^{1}H,^{1}H}COSY, GHSQC, GHMBC, and NOE-DIFF experiments on the Bruker AMX 400 instrument. IR: FT-IR Bio-rad Digilab Division FTS-45. MS and HRMS: Finnigan MAT8200. ESI: Micromass Quattro LCZ. Elemental analyses: HERAEUS CHN-O Rapid. Column chromatography: Merck silica gel 60. Flash chromatography was performed for each organic compound under an argon pressure of 1.1 bar within about 20 min. TLC: Merck silica gel 60F$_{254}$. R_f values refer to TLC tests. All reaction were performed under argon. Diethyl ether, *n*-pentane, C_6D_6, $CDCl_3$, and [D_8]toluene were used as purchased and were not dried further. The pentacarbonyl[3-(cycloalkenyl)-1-ethoxy-2-propyn-1-ylidene]tungsten and chromium compounds were prepared according to ref.[9].

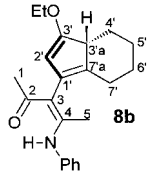
(3a*R)-Pentacarbonyl[3-(3-ethoxy-4,5,6-tetrahydro-3a*H*-pentalen-1-yl)-4-(4-phenylimino)pentan-2-one, *N*]tungsten (13a)**: To pentacarbonyl-[3-cyclopent-1-enyl-1-ethoxy-2-propyn-1-ylidene]tungsten(0) (**7a**) (236 mg, 0.50 mmol) in a precooled NMR tube (−78 °C) was slowly added, by syringe, a solution of 4-(phenylamino)-pent-3-en-2-one (**2a**) (87 mg, 0.50 mmol) in 0.8 mL of [D_8]toluene. The sample was allowed to warm to −20 °C and kept at this temperature for 60 h to allow reaction to reach completion. According to an NMR spectrum of the solution at −20 °C, compound **13a** was formed with approximately 65 % conversion of starting compound **2a**, whilst compound **7a** was consumed completely. The structural assignment of compound **13a** is based on ^{1}H and ^{13}C NMR spectra, including ^{1}H, ^{1}H COSY, GHSQC, GHMBC, NOE-DIFF, and TOCSY experiments at −20 °C. Dynamic line-broadening of signals was studied in the range between −80 °C and −20 °C. Paramagnetic line-broadening due to decomposition was observed after a few min at +20 °C.



13a

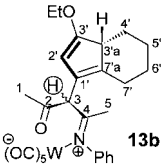
Compound 13a: ^{1}H NMR (600 MHz, [D_8]toluene, 253 K, 4:3 mixture of diastereomers, chemical shifts of the second diastereomer in brackets): δ = 6.99, 6.81, 6.69, and 6.67 {6.98, 6.80, 6.60, and 6.67} (each m, 2:1:1:1 H; Ph), 5.55 {5.45} (s, 1 H; 3-H), 5.01 {4.94} (s, 1 H; 2′-H), 3.39 {3.39} (m, 2 H; OCH_2), 3.18 {3.18} (m, 1 H; 3′a-H), 2.32 and 1.96 {2.32 and 1.96} (each m, 1:1 H; 5′-H_2), 2.19 {2.18} (s, 3 H; 1-H_3), 1.96 and 1.85 {1.96 and 1.85} (each m, 1:1 H; 6′-H_2), 1.85 and 0.87 {1.85 and 0.87} (each m, 1:1 H; 4′-H_2), 1.63 {1.62} (s each, 3 H; 5-H_3), 1.09 {1.08} (each t, ^3J = 7.0 Hz each, 3 H; OCH_2CH_3); ^{13}C NMR (150 MHz, [D_8]toluene , 253 K): δ = 204.6 {204.0} (C_q, C2), 203.4 {203.3}, and 198.8 {198.8} [each C_q, *trans*- and *cis*-CO W(CO)$_5$], 186.1 {185.7} (C_q, C4), 168.8 {168.5} (C_q, C3′), 155.7 {155.4} (C_q, *i*-C Ph), 145.9 {145.1} (C_q, C1′); 129.7, 126.4, 124.2, 121.1, and 119.8 {129.6, 126.3, 124.1, 120.9, and 119.8} (each CH, *o*-, *m*-, and *p*-C Ph), 127.6 {126.5} (C_q, C6′a, 101.9 {100.6} (CH, C2′), 69.1 {69.0} (CH, C3), 65.6 {65.6} (OCH_2), 57.6 {57.5} (CH, C3′a), 31.3 {31.3} (CH_2, C6′), 28.9 {28.7} (CH_3, C1), 27.4 {27.0} (CH_2, C4′), 23.2 {22.8} (CH_2, C5′), 21.0 {20.8} (CH_3, C5), 14.6 {14.6} (OCH_2CH_3).

(3a*R)-*3*-(3-Ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-4-(phenylamino)-pent-3-en-2-one (8b) and (3a*R**,3R*{S*})-pentacarbonyl[3-(3-ethoxy-4,5,6-tetrahydro-3a*H*-pentalen-1-yl)-4-(4-phenylimino)pentan-2-one, *N*]tungsten (13b)**: To pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (486 mg, 1.00 mmol) in a 5 mL screw-top vessel was added 4-(phenylamino)-pent-3-en-2-one (**2a**) (175 mg, 1.00 mmol) in diethyl ether (4 mL). The mixture was stirred for 18 h at 20 °C and separated by flash column chromatography on silica gel to give compound **8b** (257 mg, 76 %, R_f = 0.3 in *n*-pentane/diethyl ether 9:1, pale yellowish oil). If the reaction was performed *n*-pentane/diethyl ether (4:1; 4 mL) at −20 °C for 60 h, yellow-brown crystals could be collected by centrifugation; these were washed with precooled *n*-pentane (2 × 2 mL) and dried under reduced pressure (20 °C, 10^{-3} mbar) to give a 3:1 mixture of diastereomers of thermolabile compound **13b** (560 mg, 84 %, R_f = 0.7 in *n*-pentane/diethyl ether 9:1), which was analyzed by ^{1}H and ^{13}C NMR experiments at −20 °C.



8b

Compound 8b: ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 14.1 (m, br., 1 H; NH), 7.03 and 6.91 (each m, 2:3 H; *o*-, *m*-, and *p*-H Ph), 4.92 (s, 1 H; 2′-H), 3.61 (m, 2 H; OCH_2CH_3), 2.70 (dd, ^3J = 5.8 Hz and 12.4 Hz, 1 H; 3′a-H), 2.44 (m, br., 2 H; 4′-H and 7′-H), 2.29 (s, 3 H; 1-H_3), 1.88 (s, 3 H; 5-H_3), 1.83 (m, br., 1 H; 7′-H), 1.64 (m, br., 2 H; 5′-H and 6′-H), 1.16 (t, ^3J = 7.1 Hz and m, br., 6 H; OCH_2CH_3, 4′-H, 5′-H, and 6′-H); ^{13}C NMR (100 MHz, C_6D_6, 300 K): δ = 196.6 (C_q, C2), 168.3 (C_q, C3′), 158.0 (C_q, C4), 140.0 (C_q, *i*-C Ph), 134.2 (C_q, C1′), 132.3 (C_q, br., C7′a); 129.2, 124.9, and 124.8 (each CH, *o*-, *m*-, and *p*-C Ph), 105.2 (C_q, C3), 102.0 (CH, C2′), 65.0 (OCH_2CH_3), 50.4 (CH, C3′a), 31.3 (CH_2, br., C7′), 28.9 (CH_3, br., C1); 28.6, 26.3 (br) and 25.6 (each CH_2, C4′, C5′, and C6′), 17.5 (CH_3, br., C5), 14.6 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu}$ = 2931 (100), 2854 (87), 1728 (54), 1567 (94), 1419 (87), 1254 (99), 1043 (81); MS (70 eV): *m/z* (%): 337 (67) [*M*]$^+$, 308 (100), 266 (61), 244 (11), 215 (13), 173 (10), 118 (50); elemental analysis calcd (%) for $C_{22}H_{27}NO_2$ (337.5): C 78.30, H 8.06, N 4.15; found: C 78.35, H 8.15, N 3.93.



13b

Compound 13b: ^{1}H NMR (360 MHz, [D_8]toluene, 253 K, second diastereomer in brackets): δ = 6.91, 6.72, 6.58, and 6.52 {6.91, 6.72, 6.68, and 6.38} (each m, 2:1:1:1 H; *o*-, *m*-, and *p*-H Ph), 5.65 {5.60} (s, 1 H; 3-H), 4.70 {4.82} (s, 1 H; 2′-H), 3.24 {3.24} (m, 2 H; diastereotopic OCH_2), 2.68 and 1.92 {2.68 and 1.84} (each m, 1:1 H; 7′-H_2), 2.41 {2.46} (dd, ^3J = 7.0 Hz and 14.0 Hz, 1 H; 3′a-H), 2.23 and 0.69 {2.26 and 0.78} (each m, 1:1 H; 4′-H_2), 2.20 {2.19} (s, 3 H; 1-H_3), 1.69 and 0.98 {1.69 and 0.77} (each m, 1:1 H; 6′-H_2), 1.60 {1.60} (s, 3 H; 5-H_3), 1.41 and 0.99 {1.47 and 0.99} (each m, 1:1 H; 5′-H_2), 1.02 {1.02} (t, ^3J = 6.9 Hz, 3 H; OCH_2CH_3); ^{13}C NMR (90 MHz, [D_8]toluene, 253 K): d = 205.2 {205.2} (C_q, C2), 203.3 and 199.0 {203.3 and 199.0} [each C_q, *trans*- and *cis*-CO W(CO)$_5$], 186.1 {186.1} (C_q, C4), 170.2 {170.0} (C_q, C3′), 155.7 {156.0} (C_q, *i*-C Ph), 138.0 {138.0} (C_q, C1′); 130.0, 129.7, 126.3, 121.3, and 119.3 {129.9, 129.6, 126.3, 121.1, and 119.7} (each CH, *o*-, *m*-, and *p*-C Ph), C7′a not detected, 97.6 {97.4} (CH, C2′), 67.8 {67.7} (CH, C3), 66.1 {65.4} (OCH_2), 51.0 {50.7} (CH, C3′a); 31.3, 28.9, 26.6, and 24.9 {31.5, 28.7, 26.4, and 24.9} (each CH_2, C4′ – C7′), 29.0 {29.0} (CH_3, C1), 20.8 {20.8} (CH_3, C5), 14.6 {14.6} (OCH_2CH_3).

(3a*R)-3-(3-Ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-4-(4-tolylamino)-pent-3-en-2-one (8e) and (3a*R**,3R*{S*})-pentacarbonyl[3-(3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-3-(4-tolylimino)-pentan-2-one, *N*]tungsten (13e)**: To pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (486 mg, 1.00 mmol) in a 5 mL screw-top vessel was added a solution of 4-(4-tolylamino)-pent-3-en-2-one (**2b**) (189 mg, 1.00 mmol) in diethyl ether (4 mL). The mixture was stirred at 20 °C for 18 h and separated by flash column chromatography on silica gel to give compound **8e** (257 mg, 73 %, R_f = 0.3 in *n*-pentane/diethyl ether 9:1, pale yellowish oil). Compound **8e** was also obtained from pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)chromium(0) (**7d**) (354 mg,

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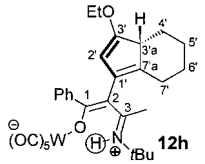
1.00 mmol) and 4-(4-tolylamino)-pent-3-en-2-one (**2b**) (189 mg, 1.00 mmol) by the procedure described above (251 mg, 71%). If the reaction of **7b** and **2b** was performed in *n*-pentane/diethyl ether (4:1; 4 mL) at −20 °C for 60 h, yellow-brown crystals could be collected by centrifugation; these were washed with precooled *n*-pentane (2 × 2 mL) and dried under reduced pressure (20 °C, 10^{-3} mbar) to give a 3:2 mixture of diastereomers of thermolabile compound **13e** (531 mg, 79%, $R_f = 0.7$ in *n*-pentane/diethyl ether 9:1), which was analyzed by ^{1}H and ^{13}C NMR experiments at −20 °C, as well as by a crystal structure analysis. Generation of compound **8e** from **13e** was monitored by ^{1}H NMR experiments in C_6D_6 at +30 °C.

Compound 8e: ^{1}H NMR (400 MHz, C_6D_6, 300 K):[10] $\delta = 14.15$ (m, br., 1H; NH), 6.84 (s, 4H; *o*- and *m*-H Tol), 4.94 (s, 1H; 2′-H), 3.62 (m, 2H; OCH_2CH_3), 2.71 (dd, $^3J = 5.3$ Hz and 12.2 Hz, 1H; 3′a-H), 2.46 (m, 2H; 4′-H and 7′-H), 2.32 (s, 3H; 1-H_3), 2.06 (s, 3H; Tol-CH_3), 1.92 (s, br., 3H; 5-H_3), 1.83 (m, 1H; 4′-H), 1.63 (m, 2H; 5′-H and 6′-H), 1.15 (t, $^3J = 7.0$ Hz and m, br., 6H; OCH_2CH_3, 4′-H, 5′-H, and 6′-H); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 196.3$ (C_q, C2), 168.3 (C_q, C3′), 158.5 (C_q, C4), 137.4 (C_q, *i*-C Tol), 134.6 (C_q, *p*-C Tol), 134.2 (C_q, br., C1′), 132.5 (C_q, br., C7′a), 129.8 and 125.1 (CH, *o*- and *m*-H Tol), 104.9 (C_q, C3), 102.1 (CH, C2′), 65.0 (OCH_2CH_3), 50.5 (CH, C3′a), 31.2 (CH_2, br., C7′), 28.5 (CH_3, br., C1), 28.6, 26.4 (each br), and 25.7 (each CH_2, C4′, C5′, and C6′), 20.7 (CH_3, Tol), 17.4 (CH_3, br., C5), 14.6 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu}$ = 2932 (94), 1572 (100), 1435 (74), 1256 (94), 1046 (69); MS (70 eV): *m/z* (%): 351 (65) $[M]^+$, 322 (100), 280 (51), 245 (12), 215 (10), 132 (40); elemental analysis calcd (%) for $C_{23}H_{29}NO_2$ (351.5): C 78.59, H 8.32, N 3.98; found: C 78.41, H 8.49, N 3.67. X-ray crystal structure analysis of compound **8e** (code aum.1267), formula $C_{23}H_{29}NO_2$, $M_r = 351.47$, light yellow crystal 0.25 × 0.15 × 0.10 mm, $a = 22.054(3)$, $b = 6.459(1)$, $c = 28.789(1)$ Å, $\beta = 91.35(1)°$, $V = 4099.8(9)$ Å^3, $\rho_{calcd} = 1.139$ g cm^{-3}, $\mu = 5.60$ cm^{-1}, empirical absorption correction by ψ scan data ($0.873 \le T \le 0.946$), $Z = 8$, monoclinic, space group *C*2/c (no. 15), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4280 reflections collected ($+h$, $-k$, $\pm l$), $[(\sin\phi)/\lambda] = 0.62$ Å^{-1}, 4170 independent (R_{int} = 0.047) and 2267 observed reflections [$I \ge 2\sigma(I)$], 243 refined parameters, $R = 0.050$, $wR^2 = 0.129$, max. residual electron density 0.21 (−0.19) e Å^{-3}, hydrogens calculated and refined as riding atoms.[11]

Compound 13e: ^{1}H NMR (600 MHz, [D_8]toluene, 253 K, second diastereomer in brackets):[10] $\delta = 6.76$, 6.57, and 6.49 {6.76, 6.66, and 6.38} (each m, 2:1:1H; Tol), 5.67 {5.63} (s, 1H; 3-H), 4.94 {4.85} (s, 1H; 2′-H), 3.38 {3.38} (m, 2H; diastereotopic OCH_2), 2.71 and 1.93 {2.71 and 1.85} (each m, 1:1H; 7′-H_2), 2.47 {2.44} (dd, $^3J = 12.2$ and 5.6 Hz, 1H; 3′a-H), 2.27 and 0.84 {2.22 and 0.70} (each m, 1:1H; 4′-H_2), 2.21 {2.19} (s, 3H; 1-H_3), 1.96 {1.96} (s, 3H; Tol-CH_3), 1.71 and 1.02 {1.71 and 0.81} (each m, 1:1H; 6′-H_2), 1.69 {1.70} (s, 3H; 5-H_3) 1.48 and 0.97 {1.42 and 0.97} (each m, 1:1H; 5′-H_2), 1.05 {1.05} (t, $^3J = 6.9$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (150 MHz, [D_8]toluene, 253 K): δ = 205.1 {204.0} (C_q, C2), 203.2 and 199.1 {203.2 and 199.0} [each C_q, *trans*- and *cis*-CO W(CO)$_5$], 186.1 {186.0} (C_q, C4), 170.2 {170.0} (C_q, C3′), 153.9 {153.6} (C_q, *i*-C Tol), 137.9 {137.3} (C_q, C1′) 135.9 {135.8} (C_q, *p*-C Tol); 130.5, 130.1, 121.1, and 119.5 {130.4, 130.0, 121.0, and 119.2} (each CH, Tol), 126.0 {125.4} (C_q, C7′a), 97.6 {97.5} (CH, C2′), 67.9 {67.8} (CH, C3), 65.4 {65.4}(OCH_2), 51.0 {50.8} (CH, C3′a), 31.4 {31.4} (CH_2, dynamically br., C4′), 29.0 {29.0} (CH_3, C1), 28.7 {28.7} (CH_2, C6′), 26.7 {26.4} (CH_2, C7′), 25.0 {24.9} (CH_2, C5′), 20.8 and 20.7 {20.7 and 20.7} (each CH_3, C5 and CH_3 Tol), 14.5 {14.5} (OCH_2CH_3). X-ray crystal structure analysis of compound **13e** (code aum.1149): formula $C_{28}H_{29}NO_7W$, $M_r = 675.37$, red crystal 0.30 × 0.25 × 0.10 mm, $a = 11.034(1)$, $b = 12.534(1)$, $c = 12.785(1)$ Å, $\alpha = 111.50(1)$, $\beta = 98.63(1)$, $\gamma = 90.59(1)°$, $V = 1622.4(2)$ Å^3, $\rho_{calcd} = 1.382$ g cm^{-3}, μ = 35.98 cm^{-1}, absorption correction by SORTAV ($0.412 \le T \le 0.715$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 12095 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 7411 independent ($R_{int} = 0.021$) and 6964 observed reflections [$I \ge 2\sigma(I)$], 384 refined parameters, $R = 0.028$, $wR^2 = 0.094$, max. residual electron density 1.15 (−1.22) e Å^{-3}, the cyclohexyl group (C8–C13) was refined with split positions in the ratio 0.66(1):0.34(1); petroleum ether solvent molecules were located around *x*, 0.5, 0.0, not identified, and used in refinement; hydrogens calculated and refined as riding atoms.[11]

(3a*R)-3-(*tert*-Butylamino)-2-(3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-1-phenylbut-2-en-1-one (8h) and (3a*R**)-pentacarbonyl[3-(*tert*-butylamino)-2-(3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-1-phenylbut-2-en-1-one, *O*]tungsten (12h)**: To pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (486 mg, 1.00 mmol) in a 5 mL screw-top vessel was added a solution of 3-(*tert*-butylamino)-1-phenyl-but-2-en-1-one (**2c**) (217 mg, 1.00 mmol) in diethyl ether (4 mL). The reaction mixture was stirred for 30 h at 20 °C. After separation by flash column chromatography on silica gel, compound **8h** was obtained in 78% yield (297 mg, 0.78 mmol, $R_f = 0.2$ *n*-pentane/diethyl ether 9: 1) as a pale yellowish oil. If the reaction was performed in *n*-pentane/diethyl ether (4:1; 4 mL) at −20 °C for 60 h, yellow-brown crystals could be collected by centrifugation; these were washed with precooled *n*-pentane (2 × 2 mL) and dried under reduced pressure (20 °C, 10^{-3} mbar) to give an 8:1 mixture of isomers of thermolabile compound **12h** (513 mg, 73%), which was analyzed by ^{1}H and ^{13}C NMR experiments at −20 °C, as well as by crystal structure analysis. Generation of compound **8h** from compound **12h** was monitored by ^{1}H NMR experiments in C_6D_6 at +30 °C.

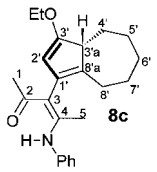
Compound 8h: ^{1}H NMR (400 MHz, C_6D_6, 300 K):[10] $\delta = 13.72$ (m, br., 1H; NH), 7.82 (m, 2H; *o*-H Ph), 7.09 (m, 2H; *m*-H Ph), 7.03 (m, 1H; *p*-H Ph), 5.04 (s, 1H; 2′-H), 3.61 (m, 2H; OCH_2CH_3), 2.68 (m, br., 1H; 3′a-H), 2.46 and 2.26 (each m, each br., 1:1H; 4′-H and 7′-H), 2.09 (s, 3H; 4-H_3), 1.72 (m, br., 1H; 4′-H); 1.52, 1.40, 1.16, 1.11, and 1.02 (mmmst, $^3J = 6.9$ Hz, 1:2:9:3:2H; 7′-H, 5′-H_2, 6′-H_2, $NC(CH_3)_3$, and OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 191.2$ (C_q, C1), 167.5 (C_q, C3′), 164.7 (C_q, C4), 144.4 (C_q, br., *i*-C Ph), 133.1, and 132.6 (each C_q, each br., C1′ and C7′a); 128.7, 128.6, and 127.1 (each CH, *o*-, *m*-, and *p*-C Ph), 104.0 (C_q, C2), 102.5 (CH, C2′), 65.0 (OCH_2CH_3), 52.2 (C_q, $NC(CH_3)_3$]), 50.6 (CH, br., C3′a), 30.8 ($C(CH_3)_3$), 29.4 (CH_2, br., C7′); 26.9, 26.4, and 25.5 (each CH_2, each br., C4′, C5′, and C6′), 18.3 (CH_3, C4), 14.6 (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu}$ = 2934 (95), 2870 (85), 1719 (30), 1580 (100), 1554 (100), 1288 (85), 1174 (90); MS (70 eV): *m/z* (%): 379 (35) $[M]^+$, 350 (25), 322 (55), 294 (25), 277 (5), 236 (3), 105 (100); elemental analysis calcd (%) for $C_{25}H_{33}NO_2$ (379.5): C 79.11, H 8.76, N 3.69; found: C 78.72, H 8.82, N 3.64.



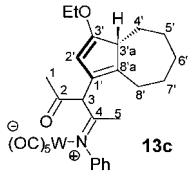
Compound 12h: ^{1}H NMR (360 MHz, $CDCl_3$, 253 K, 8:1 mixture of atropisomers, second atropisomer in brackets): $\delta = 11.97$ {11.87} (s, br., 1H; NH), 7.29 and 7.18 {7.29 and 7.18} (each m, 3:2H; *o*-, *m*-, and *p*-H Ph), 5.04 {4.96}, (s, 1H; 2′-H), 3.77 {3.77} (m, 2H; OCH_2), 2.50 {2.40} (dd, $^3J = 12.3$ and 5.6 Hz, 1H; 3′a-H), 2.20 {2.19} (s, 3H; 4-H_3), 2.13 and 1.75 {2.13 and 1.75} (each m, 1:1H; 7′-H_2), 1.95 and 0.57 {1.95 and 0.22} (each m, 1:1H; 4′-H_2), 1.68 and −0.03 {1.65 and −0.40} (each m, 1:1H; 6′-H_2), 1.53 {1.53} [s, 9H; $C(CH_3)_3$], 1.43 and 1.08 {1.43 and 1.06} (each m, 1:1H; 5′-H_2), 1.34 {1.34} (t, $^3J = 7.0$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (90 MHz, $CDCl_3$, 253 K): $\delta = 203.9$, and 198.6 {203.9 and 198.5} (each C_q, *trans*- and *cis*-CO W(CO)$_5$), 191.4 {191.0} (C_q, C1), 170.6 {170.3} (C_q, C3), 166.9 {166.6} (C_q, C3′), 140.5 {140.0} (C_q, C1′), 135.5 and 129.4 {134.4 and 129.3} (each C_q, C7′a and *ipso*-C Ph); 129.2, 127.7, and 126.3 {128.6, 127.4, and 126.3} (each CH, *o*-, *m*-, and *p*-C Ph), 105.4 {105.3} (C_q, C2), 102.6 {101.8} (CH, C2′), 64.9 {64.9} (OCH_2), 54.2 {54.2} [C_q, $C(CH_3)_3$], 49.5 {49.0} (CH, C3′a), 30.5 {30.5} [$C(CH_3)_3$]; 30.2, 28.0, 25.7, and 24.7 {29.2, 26.4, 25.3, and 24.4} (each CH_2, C4′–C7′), 19.1 {19.0} (CH_3, C4), 14.4 {14.2} (OCH_2CH_3). X-ray crystal structure analysis of compound **12h** (code aum.1180), formula $C_{30}H_{33}NO_7W$, M_r = 703.42, yellow crystal 0.25 × 0.20 × 0.15 mm, $a = 11.112(1)$, $b = 11.459(1)$, $c = 13.141(1)$ Å, $\alpha = 113.89(1)$, $\beta = 98.75(1)$, $\gamma = 91.63(1)°$, V = 1504.6(2) Å^3, $\rho_{calcd} = 1.553$ g cm^{-3}, $\mu = 38.83$ cm^{-1}, absorption correction by SORTAV ($0.444 \le T \le 0.594$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 10108 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\phi)/\lambda] = 0.65$ Å^{-1}, 6901 independent ($R_{int} = 0.022$) and 6379 observed reflections [$I \ge 2\sigma(I)$], 368 refined parameters, $R = 0.024$, wR^2 = 0.052, max. residual electron density 1.12 (−1.01) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.[11]

(3a*R)-3-(3-Ethoxy-3a,4,5,6,7,8-hexahydroazulen-1-yl)-4-(phenylamino)-pent-3-en-2-one (8c) and (3a*R**,3*R**[*S**])-pentacarbonyl[3-(3-ethoxy-3′a,4,5,6,7,8-hexahydroazulen-1-yl)-4-(phenylimino)pentan-2-one, *N*]tungsten (13c)**: To pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (498 mg, 1.00 mmol) in a 5 mL screw-top vessel was added a solution of 4-(phenylamino)-pent-3-en-2-one (**2a**) (175 mg, 1.00 mmol) in diethyl ether (4 mL). After the mixture had been stirred

for 18 h at 20 °C, it was separated by flash column chromatography on silica to afford the atropisomeric compound **8c** (265 mg, 75 %, $R_f = 0.4$, *n*-pentane/diethyl ether 9:1, pale yellowish oil). If the reaction was performed in *n*-pentane/diethyl ether (4:1; 4 mL) at −20 °C for 80 h, yellow-brown crystals of a 1:1 atropisomeric mixture of thermolabile compound **13c** (480 mg, 71 %) could be collected by centrifugation; these were washed with precooled *n*-pentane (2 × 2 mL) and dried under reduced pressure (20 °C, 10^{-3} mbar) and analyzed by ^{1}H and ^{13}C NMR experiments at −20 °C. A spontaneous transformation of compound **13c** into compound **8c** was monitored by ^{1}H NMR spectroscopy in C_6D_6 at +30 °C.



Compound 8c: ^{1}H NMR (400 MHz, C_6D_6, 300 K, second atropisomer in brackets): $\delta = 14.09$ {14.09} (s, br., 1H; NH), 7.03 and 6.91 {7.03 and 6.91} (m, 2:3H; *o*-, *m*-, and *p*-H Ph), 4.87 {4.87} (s, 1H; 2′-H), 3.62 {3.62} (m, 2H; OCH_2CH_3), 2.97 {2.97} (dd, $^3J = 3.3$ Hz and 10.4, 1H; 3' a-H), 2.34 {2.34} (m, 3H; 8′-H_2 and 4′-H}, 2.31 {2.26} (s, 3H; 1-H_3), 1.91 {1.86} (s, 3H; 5-H_3), 1.73 {1.73} (m, 2H; 5′-H_2), 1.61 {1.61} (m, 1H; 6′-H), 1.41 {1.41} (m, 2H; 7′-H and 6′-H), 1.22 {1.22} (m, 2H; 7′-H and 4′-H), 1.16 {1.16} (t, $^3J = 7.1$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 196.3$ {196.3} (C_q, C2), 166.9 {166.9} (C_q, C3′), 157.6 {157.6} (C_q, C4), 140.0 {140.0} (C_q, *i*-C Ph), 137.4 {137.3} (C_q, C1′), 135.7 {135.6} (C_q, C8′a); 129.9, 124.9, and 124.9 {129.9, 124.9, and 124.9} (each CH, *o*-, *m*-, and *p*-C Ph), 105.9 {105.9} (C_q, C3), 101.4 {101.4} (CH, C2′), 65.0 {65.0} (OCH_2CH_3), 53.7 {53.6} (CH, C3′a); 31.7, 30.6, 30.4, and 29.4 {31.2, 30.6, 30.1, and 29.4} (each CH_2, C4′, C5′, C7′, and C8′), 28.5 {28.5} (CH_3, C1), 27.6 {27.7} (CH_2, C6′), 17.1 {17.1} (CH_3, C5), 14.6 {14.6} (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu} =$ 2922 (98), 2849 (84), 1560 (100), 1420 (88), 1250 (98), 1038 (78); MS (70 eV): *m/z* (%): 351 (51) $[M]^+$, 322 (100), 280 (49), 258 (40), 229 (17), 215 (23), 187 (13), 118 (54); HRMS calcd for $C_{23}H_{29}NO_2$: 351.21982; found 351.21959 (+0.6 ppm, +0.2 mmu); elemental analysis calcd (%) for $C_{23}H_{29}NO_2$ (351.5): C 78.59, H 8.32, N 3.98; found: C 78.49, H 8.52, N 3.90.



Compound 13c: ^{1}H NMR (360 MHz, [D_8]toluene, 253 K, 1:1 mixture of atropisomers, second atropisomer in brackets): $\delta = 6.93$, 6.75, and 6.58 {6.93, 6.75, and 6.36} (each m, 2:2:1H; *o*-, *m*-, and *p*-H Ph), 5.60 {5.59} (s, 1H; 3-H), 4.70 {4.70} (s, 1H; 2′-H), 3.19 {3.19} (m, 2H; diastereotopic OCH_2), 2.84 {2.84} (m, 1H; 3′a-H), 2.8 – 2.5 {2.8 – 2.5} (m, 2H; cycloheptane), 2.26 {2.24} (s, 3H; 1-H_3), 2.2 – 1.75 {2.2 – 1.75} (m, 2H; cycloheptane), 1.72 {1.66} (s, 3H; 5-H_3), 1.6 – 1.4 {1.6 – 1.4} (m, 3H; cycloheptane), 1.4 – 1.15 {1.4 – 1.15} (m, 3H; cycloheptane), 1.06 {1.06} (t, $^3J = 7.0$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (90 MHz, [D_8]toluene, 253 K): $\delta = 205.3$ {205.1} (C_q, C2), 203.3 and 199.1 {203.3 and 199.1} [C_q, *trans*-, and *cis*-CO $W(CO)_5$], 185.7 {185.4} (C_q, C4), 168.1 {168.1} (C_q, C3′), 156.3 {156.3} (C_q, *i*-C Ph), 141.1 {141.1} (C_q, C1′); 130.0, 129.7, 126.2, 121.3, and 119.6 {130.0, 129.6, 126.2, 121.2, and 119.3} (each CH, *o*-, *m*-, and *p*-C Ph), 128.5 {128.5} (C_q, C8′a), 97.1 {97.0} (CH, C2′), 67.1 {67.0} (CH, C3), 65.3 {65.3} (OCH_2), 53.8 {53.6} (CH, C3′a); 34.6 {34.6}, 31.4 {31.4}, 29.8, 29.1, and 28.6 {29.8, 29.1, and 28.3} (each CH_2, C4′ – C8′), 29.3 {29.3} (CH_3, C1), 21.0 {20.8} (CH_3, C5), 14.6 {14.5} (OCH_2CH_3).

(3a*R)-3-(3-Ethoxy-3a,4,5,6,7,8-hexahydroazulen-1-yl)-4-(4-tolylamino)-pent-3-en-2-one (8f) and (3a*R**,3*R**{*S**})-pentacarbonyl[3-(3-ethoxy-3′a,4,5,6,7,8-tetrahydroazulen-1-yl)-4-(4-tolylimino)pentan-2-one, *N*]tungsten (13f)**: To pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (498 mg, 1.00 mmol) in a 5 mL screw-top vessel was added a solution of 4-(4-tolylamino)-pent-3-en-2-one (**2b**) (189 mg, 1.00 mmol) in diethyl ether (4 mL). The reaction mixture was stirred for 18 h at 20 °C and separated by flash column chromatography on silica gel to give atropisomeric compound **8f** (275 mg, 75 %, $R_f = 0.4$, *n*-pentane/diethyl ether 9:1, pale yellowish oil). If the reaction was performed in *n*-pentane/diethyl ether (4:1; 4 mL) at −20 °C for 80 h, yellow-brown crystals of a 5:4 mixture of atropisomers of the thermolabile compound **13f** (504 mg, 73 %) could be collected by centrifugation; these were washed with precooled *n*-pentane (2 × 2 mL), dried under reduced pressure (20 °C, 10^{-3} mbar), and were analyzed by ^{1}H and ^{13}C NMR experiments at −20 °C.

Compound 8f: ^{1}H NMR (400 MHz, C_6D_6, 300 K, second atropisomer in brackets):[12] $\delta = 14.10$ {14.08} (m, br., 1H; NH), 6.86 {6.85} (m, 4H; *o*- and *m*-H Tol), 4.89 {4.89} (s, 1H; 2′-H), 3.61 {3.61} (m, 2H; OCH_2CH_3), 2.98 {2.98} (dd, $^3J = 10.4$ and 3.2, 1H; 3′a-H), 2.36 {2.36} (m, 3H; 4′-H and 8′-H_2), 2.32 {2.27} (s, 3H; 1-H_3), 2.07 {2.07} (s, 3H; Tol-CH_3), 1.94 {1.88} (s, 3H; 5-H_3), 1.73 {1.73} (m, 2H; 5′-H_2), 1.61 {1.61} (m, 1H; 6′-H), 1.41 {1.41} (m, 2H; 7′-H and 6′-H), 1.22 {1.22} (m, 2H; 4′-H and 7′-H), 1.16 {1.16} (t, $^3J = 7.0$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 195.9$ {195.9} (C_q, C2), 166.9 {166.9} (C_q, C3′), 158.1 {158.0}, (C_q, C4), 137.4 {137.4} (C_q, *i*-C Tol), 137.4 {137.3} (C_q, C8′a), 135.8 {135.7} (C_q, *p*-C Tol), 134.6 {134.6} (C_q, C1′), 129.8 and 125.0 {129.8 and 125.0} (each CH, *o*- and *m*-C Tol), 105.5 {105.5} (C_q, C3), 101.5 {101.5} (CH, C2′), 65.0 {65.0} (OCH_2CH_3), 53.7 {53.6} (CH, C3′a); 31.4, 30.7, 30.4, and 29.5 {31.2, 30.6, 30.1, and 29.4} (each CH_2, C4′, C5′, C7′, and C8′), 28.5 {28.4} (CH_3, C1), 27.6 {27.6} (CH_2, C6′), 20.8 {20.8} (CH_3 Tol), 17.1 {17.1} (CH_3, C5), 14.6 {14.6} (OCH_2CH_3); IR (diffuse reflection): cm^{-1} (%): $\tilde{\nu} = 2920$ (100), 2849 (75), 1572 (100), 1516 (90), 1432 (70), 1250 (90), 1041 (60); MS (70 eV): *m/z* (%): 365 (50) $[M]^+$, 336 (100), 294 (50), 258 (40), 229 (20), 215 (20), 187 (10), 132 (60); elemental analysis calcd (%) for $C_{24}H_{31}NO_2$ (365.5): C 78.86, H 8.55, N 3.83; found: C 78.69, H 8.91, N 3.84.

Compound 13f: ^{1}H NMR (360 MHz, [D_8]toluene, 253 K, 5:4 mixture of diastereomers, second diastereomer in brackets):[12] $\delta = 6.75$ {6.75} and 6.57 {6.48} (each m, 3:1H; Tol), 5.61 {5.60} (s, 1H; 3-H), 4.74 {4.73} (s, 1H; 2′-H), 3.20 {3.20} (m, 2H; diastereotopic OCH_2), 2.82 {2.82} (m, 1H; 3a′-H), 2.7 – 2.5 {2.7 – 2.5} (m, 2H; cycloheptane), 2.28 {2.26} (s, 3H; 1-H_3), 2.15 and 1.7 – 1.4 {2.15 and 1.7 – 1.4} (each m, 4H; cycloheptane), 1.99 {1.99} (s, 3H; Tol-CH_3), 1.79 {1.74} (s, 3H; 5-H_3), 1.4 – 1.2 {1.4 – 1.2} (m, 4H; cycloheptane), 1.07 {1.07} (t, $^3J = 7.1$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (90 MHz, [D_8]toluene, 253 K, 5:4 mixture of diastereomers): $\delta = 205.3$ {205.1} (C_q, C2), 203.3 and 199.1 {203.3 and 199.1} [each C_q, *trans*- and *cis*-CO $W(CO)_5$], 185.8 {185.5} (C_q, C4), 168.1 {168.1} (C_q, C3′), 154.2 {154.1} (C_q, *i*-C Tol), 141.1 {141.0} (C_q, C1′), 135.8 {135.8} (C_q, *p*-C Tol); 130.5, 130.2, 121.1, and 119.4 {130.4, 130.1, 121.0, and 119.2} (each CH, Tol), 129.2 {129.2} (C_q, C8′a), 97.2 {97.0} (CH, C2′), 67.2 {67.2} (CH, C3), 65.3 {65.3} (OCH_2), 53.8 {53.7} (CH, C3′a); 34.6, 31.4, 29.8, 29.1, and 28.1 {34.6, 31.4, 29.8, 28.9, and 28.1} (each CH_2, C4′ – C8′), 30.1 {30.1} (CH_3, C1); 21.0 {21.0} and 20.7 {20.7} (each CH_3, C5 and CH_3 Tol), 14.6 {14.5} (OCH_2CH_3).

(3a*R)-3-(*tert*-Butylamino)-2-(3-ethoxy-3a,4,5,6,7,8-hexahydroazulen-1-yl)-1-phenylbut-2-en-1-one (8i) and (3a*R**)-pentacarbonyl[3-(*tert*-butylamino)-2-(3-ethoxy-3a,4,5,6,7-hexahydroazulen-1-yl)-1-phenylbut-2-en-1-one, *O*]tungsten (12i)**: To pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (500 mg, 1.00 mmol) in a 5 mL screw-top vessel was added a solution of 3-(*tert*-butylamino)-1-phenyl-but-2-en-1-one (**2c**) (217 mg, 1.00 mmol) in diethyl ether (4 mL). After the reaction mixture had been stirred for 30 h at 20 °C, it was separated by flash column chromatography on silica gel to give atropisomeric compound **8i** (292 mg, 74 %, $R_f = 0.4$ *n*-pentane/diethyl ether 9:1, pale yellowish oil). If the reaction was performed in *n*-pentane/diethyl ether (4:1; 4 mL) at −20 °C for 60 h, yellow-brown crystals of a 5:4 mixture of diastereomers of thermolabile compound **12i** (489 mg, 68 %) could be collected by centrifugation, washed with precooled *n*-pentane (2 × 2 mL) and dried under reduced pressure (20 °C, 10^{-3} mbar). Compound **12c** was analyzed by ^{1}H and ^{13}C NMR experiments at −20 °C.

Compound 8i: ^{1}H NMR (360 MHz, C_6D_6, 303 K, mixture of atropisomers, second atropisomer in brackets):[12] $\delta = 13.59$ {13.59} (m, br., 1H; NH), 7.80 {7.80} (m, 2H; *o*-H Ph), 7.07 {7.07} (m, 3H; *m*- and *p*-H Ph), 5.02 {5.01} (s, 1H; 2′-H), 3.63 {3.63} (m, 2H; OCH_2CH_3), 2.88 {2.88} (m, 1H; 3a′-H), 2.21 {2.21} (m, 1H; 4′-H), 2.08 {2.08} (m, 2H; 8′-H_2), 2.04 {2.04} (s, 3H; 4-H_3); 1.64, 1.45, and 1.24 {1.64, 1.45, 1.24} (each m, 2:1:4H; 4′-H, 5′-H_2, 6′-H_2, and 7′-H_2), 1.19 {1.19} [s, 9H; $NC(CH_3)_3$], 1.14 {1.14} (t, $^3J = 6.9$ Hz, 3H; OCH_2CH_3); ^{13}C NMR (90 MHz, C_6D_6, 303 K): $\delta = 190.8$ {190.6} (C_q, C1), 166.4 {166.2} (C_q, C3′), 164.3 {164.3} (C_q, C3), 144.3 {144.3} (C_q, *i*-C Ph),

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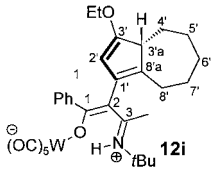
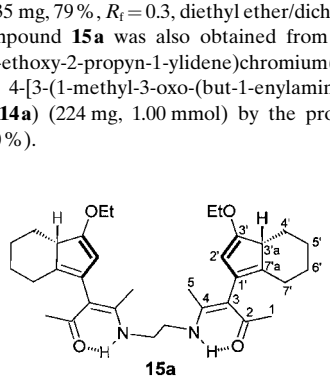
137.5 {136.9} (C_q, C8′a), 135.6 {135.6} (C_q, C1′); 128.5, 128.3, and 126.9 {128.5, 128.3, and 126.9} (each CH, *o*-, *m*-, and *p*-C Ph), 103.4 {103.4} (CH, C2′), 103.1 {103.1} (C_q, C2), 65.0 {65.0} (OCH_2CH_3), 53.6 {53.3} (CH, C3′a), 52.2 {52.2} [C_q, $NC(CH_3)_3$], 32.4, 30.1, 29.7, 29.3, and 27.7 {31.3, 29.7, 29.7, 29.1, and 27.0} (each CH_2, C4′–C8′) 30.8 {30.8} [$NC(CH_3)_3$] 18.1 {18.1} (CH_3, C4), 14.6 {14.6} (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): 2978 (95), 2854 (71), 1554 (100), 1442 (69), 1289 (89), 1197 (95); MS (70 eV): *m/z* (%): 393 (35) $[M]^+$, 364 (22), 336 (76), 308 (21), 291 (6), 105 (100); HRMS: calcd for $C_{26}H_{35}NO_2$: 393.26491); found 393.26678 (+4.8 ppm, +1.9 mmu); elemental analysis calcd (%) for $C_{26}H_{35}NO_2$ (393.6): C 79.35, H 8.96, N 3.56; found: C 79.11, H 9.11, N 3.40.



12i

Compound 12i: ^1H NMR (600 MHz, $CDCl_3$, 253 K, 3:1 mixtures of atropisomers, second atropisomer in brackets): $\delta = 11.87$ {11.83} (s, br., 1H; NH), 7.46–7.12 {7.46–7.12} (m, 5H; Ph), 4.97 {4.93} (s, 1H; 2′-H), 3.81 {3.81} (m, 2H; OCH_2), 2.72 {2.62} ("d", br., 1H; 3′a-H), 2.24 and 1.96 {2.24 and 1.89} (each m, 1:1H; 8′-H_2), 2.16 {2.12} (s, 3H; 4-H_3), 1.80 and 0.36 {1.80 and −0.16} (each m, 1:1H; 4′-H_2), 1.69 and 1.02 {1.69 and 0.51} (each m, 1:1H; 6′-H_2), 1.66 and 1.22 {1.66 and 1.20} (each m, 1:1H; 5′-H_2), 1.62 {1.61} (s, 9H; $C(CH_3)_3$), 1.49 and 1.24 {1.49 and 1.24} (each m, 1:1H; 7′-H_2), 1.35 {1.35} (q, 3H; OCH_2CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 253 K) : $\delta = 203.9$ and 198.6 {203.9 and 198.6} (each C_q, *trans*- and *cis*-CO W(CO)$_5$), 191.3 {191.1} (C_q, C1), 170.0 {170.0} (C_q, C3), 165.7 {165.4} (C_q, C3′), 140.1 {140.1} (C_q, C1′), 138.4 {138.3} (C_q, C8′a), 132.7 {132.5} (C_q, *i*-C Ph); 129.1, 127.2, and 126.7 {129.0, 127.0, and 126.6} (each CH, *o*-, *m*-, and *p*-H Ph), 106.0 {105.9} (C_q, C2), 102.8 {101.8} (CH, C2′), 64.9 {64.8} (OCH_2), 54.2 {54.2}, [C_q, $NC(CH_3)_3$], 52.4 {52.3} (CH, C3′a); 31.2, 30.2, 29.8, 29.0, and 26.1 {31.1, 30.2, 29.7, 28.9, and 26.1} (each CH_2, C4′–C8′), 30.7 {30.7} ($NC(CH_3)$), 18.8 {18.7} (CH_3, C4), 14.5 {14.4} (OCH_2CH_3).

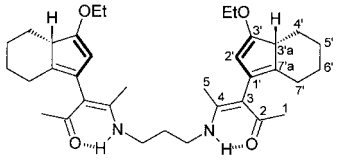
(3′a*R,3″a*S**{*R**})-3-(3-Ethoxy-4,5,6,7-tetrahydro-3′a*H*-inden-1-yl)-4-{2-[2-(3-ethoxy-4,5,6,7-tetrahydro-3″a*H*-inden-1-yl)-1-methyl-3-oxo-but-1-enylamino](ethylamino)}-pent-3-en-2-one (15a)**: To pentacarbonyl-(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (996 mg, 2.00 mmol) and 4-[3-(1-methyl-3-oxo-(but-1-enylamino)]ethylamino)}-pent-3-en-2-one (**14a** (224 mg, 1.00 mmol) in a 5 mL screw-top vessel was added diethyl ether (4.5 mL). After the mixture had been stirred for 30 h at 20 °C, it was separated by flash column chromatography on silica gel to give compound **15a** (435 mg, 79 %, $R_f = 0.3$, diethyl ether/dichloromethane 10:1, white solid). Compound **15a** was also obtained from pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)chromium(0) (**7d**) (708 mg, 2.00 mmol) and 4-[3-(1-methyl-3-oxo-(but-1-enylamino)]-(ethylamino)-pent-3-en-2-one (**14a**) (224 mg, 1.00 mmol) by the procedure described above (441 mg, 80 %).



15a

Compound 15a: ^1H NMR (400 MHz, C_6D_6, 300 K, ca. 1:1 mixture of diastereomers): $\delta = 12.24$ {12.24} ("q", br., 2H; 2 × NH), 4.96–4.92 {4.96–4.92} (5 × s, 2H; 5 × 2′-H), 3.62 {3.62} (m, 4H; 2 × OCH_2), 2.89 {2.89} (m, br., 4H; 2 × NCH_2), 2.66 {2.64} (m, 2H; 2 × 3′a-H), 2.43 and 1.81 {2.43 and 1.81} (each m, 2:2H; 2 × 6′-H_2), 2.38 and 1.06 {2.38 and 1.06} (each m, 2:2H; 4′-H_2), 2.16 {2.15} (s, 6H; 2 × 1-H_3), 1.74 {1.71} (s, 6H; 2 × 5-H_3), 1.63 and 1.02 {1.63 and 1.02} (each m, 2:2H; 2 × 7′-H_2), 1.61 and 1.14 {1.61 and 1.14} (each m, 2:2H; 2 × 5′-H_2), 1.13–1.09 {1.13–1.09} (m, 6H; 2 × OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 195.1$ {195.1} (C_q, 2 × C2), 168.0 {168.0} (C_q, 2 × C3′), 161.4 {161.4} (C_q, br., 2 × C4), 133.9 {133.8} (C_q, br., 2 × C7′a), 133.0 {132.9} (C_q, br., 2 × C1′), 103.0 {103.0} (C_q, br., 2 × C3), 102.6 {102.6} (CH, 2 × C2′), 65.0 {65.0} (2 × OCH_2), 50.4 {50.4} (CH, 2 × C3′a), 43.8 {43.8} (CH_2, br., 2 × NCH_2), 31.4 {31.1} (CH_2, br., 2 × C4′), 28.7 {28.6} (CH_3, br., 2 × C1), 28.5 {28.5} (CH_2, br., 2 × C7′), 26.3 {26.2} (CH_2, br., 2 × C6′), 25.7 {25.7} (CH_2, br., 2 × C5′), 16.0 {15.7} (CH_3, br., 2 × C5), 14.6 {14.6} (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu} = 2927$ (38), 1602 (25), 1571 (100), 1445 (33), 1338 (31), 1261 (32); MS (70 eV): *m/z* (%): 548 (94) $[M]^+$, 519 (100), 505 (74), 473 (16), 385 (31), 274 (46), 258 (31), 216 (41), 186 (23), 163 (83); HRMS calcd for $C_{34}H_{48}N_2O_4$: 548.36139; found 548.36212 (−1.3 ppm, −0.7 mmu); elemental analysis calcd (%) for $C_{34}H_{48}N_2O_4$ (548.8): C 74.42, H 8.82, N 5.10; found C 74.07, H 8.88, N 5.15.

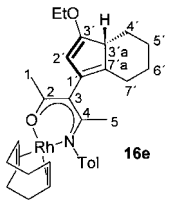
(3′a*R,3″a*S**{*R**})-3-(3-Ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-4-{3-[2-(3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-1-methyl-3-oxo-but-1-enylamino]propylaminopent-3-en-2-one} (15b)**: To pentacarbonyl(3-cyclohept-1-enyl-1-ethoxy-2-propyn-1-ylidene)tungsten(0) (**7b**) (996 mg, 2.00 mmol) and 4-[3-(1-methyl-3-oxo-but-1-enylamino)(propylamino)]-pent-3-en-2-one (**14b**) (238 mg 1.00 mmol) in a 5 mL screw-top vessel was added diethyl ether (4.5 mL). The mixture was stirred for 30 h at 20 °C. Flash column chromatography on silica gel afforded compound **15b** (430 mg, 76 %, $R_f = 0.4$, diethyl ether/dichloromethane 10:1, pale yellowish oil. Compound **15a** was also obtained from pentacarbonyl(3-cyclohex-1-enyl-1-ethoxy-2-propyn-1-ylidene)chromium(0) (**7d**) (708 mg, 2.00 mmol) and 4-[3-(1-methyl-3-oxo-but-1-enylamino)propylamino]pent-3-en-2-one (**14b**) (238 mg, 1.00 mmol) by the procedure described above (418 mg, 74 %).



15b

Compound 15b: ^1H NMR (400 MHz, C_6D_6, 300 K, ca. 1:1 mixture of diastereomers): $\delta = 12.39$ {12.39} ("q", 2H; 2 × NH), 4.95–4.91 {4.95–4.91} (5 × s, 2H; 5 × 2′-H), 3.56 {3.56} (m, 4H; OCH_2), 2.92 {2.92} (m, 4H; 2 × NCH_2), 2.72 {2.72} ("q", 2H; 2 × 3′a-H), 2.46 and 1.82 {2.46 and 1.82} (each m, 2:2H; 2 × 6′-H_2), 2.43 and 1.08 {2.43 and 1.08} (each m, 2:2H; 2 × 4′-H_2), 2.30–2.28 {2.30–2.28} (4 × s, 6H; 4 × 1-H_3), 1.79–1.75 {1.79–1.75} (4 × s, 6H; 4 × 5-H_3), 1.63 and 1.06 {1.63 and 1.06} (each m, 2:2H; 2 × 7′-H_2), 1.61 and 1.20 {1.61 and 1.20} (each m, 2:2H; 5′-H_2), 1.37 {1.37} ("q", 2H; $(NCH_2)_2CH_2$), 1.16–1.11 {1.16–1.11} (m, 6H; 2 OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 195.0$ {195.0} (C_q, 2 × C2), 168.1 {168.1} (C_q, 2 × C3′), 161.6 {161.6} (C_q, 2 × C4), 133.9 {133.8} (C_q, br., 2 × C7′a), 133.0 {132.8} (C_q, br., 2 × C1′), 102.7 {102.7} (C_q, br., 2 × C3), 102.6 {102.6} (CH, 2 × C2′), 65.0 {64.9} (2 × OCH_2), 50.4 {50.4} (CH, 2 × C3′a), 40.2 {40.1} (CH_2, br., 2 × NCH_2), 31.4 {31.2} (CH_2, br., 2 × 4′), 30.4 {30.4} (CH_2, br., $(NCH_2)_2CH_2$), 28.7 {28.6} (CH_3, br., 2 × C1), 28.6 {28.5} (CH_2, br., 2 × C5′), 26.3 {26.2} (CH_2, br., 2 × C6′), 25.7 {25.7} (CH_2, br., 2 × C7′), 15.9 {15.7} (CH_3, br., 2 × C5), 14.6 {14.6} (2 × OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu} = 2927$ (25), 1600 (37), 1572 (100), 1445 (15), 1339 (14), 1264 (36); MS (70 eV), *m/z* (%): 562 (80) $[M]^+$, 533 (100), 519 (81), 487 (14), 399 (41), 272 (26), 245 (16), 202 (30), 163 (65); elemental analysis calcd (%) for $C_{35}H_{50}N_2O_4$ (562.8): C 74.70, H 8.96, N 4.98; found: C 74.75, H 9.33, N 4.82.

Cyclooctadiene rhodium-(3a*R)-{3-(3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-4-(4-tolylamino)-pent-3-en-2-onate} (16e)**: To bis(cyclooctadiene rhodium chloride) (51 mg, 0.10 mmol) was added a solution of 3-(3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl)-4-(4-tolylamino)-pent-3-en-2-one (**8e**) (74 mg, 0.21 mmol) and triethylamine (101 mg, 1.0 mmol) in diethyl ether (4 mL). The mixture was stirred for 80 h at 20 °C and the precipitate was isolated by centrifugation, and washed with diethyl ether (2 × 4 mL). The combined organic layers were reduced to approximately 4 mL and, after 12 h at −20 °C and subsequently 1 h at −40 °C, gave fine yellow needles of compound **16e**, which were collected and dried in vacuo (10^{-3} mbar) (81 mg, 0.12 mmol, 62 %). Formation of compound **16e** from $[(COD)RhCl]_2$ and compound **8e** in the presence of triethylamine in a molar ratio of 1:2:2 was monitored by ^1H NMR spectroscopy in C_6D_6 at 30 °C.



16e

Compound 16e: ^{1}H NMR (400 MHz, C_6D_6, 300 K, 2:1 mixture of atropisomers, second atropisomer in brackets): $\delta = 6.95$, 6.80, and 6.71 {6.95, 6.80, and 6.71} (each m, 2:1:1 H; *o*- and *m*-H Tol), 4.93 {4.92} (s, 1 H; 2′-H), 4.78 and 3.33 {4.78 and 3.33} (each m, 2:2 H; COD), 3.57 {3.57} (m, 2 H; OCH_2), 2.70 {2.66} (m, 1 H; 3′a-H), 2.46 and 1.77 {2.46 and 1.77} (each m, 1:1 H; 6′H_2), 2.38 and 0.98 {2.38 and 0.98} (each m, 1:1 H; 4′-H_2), 2.33, 1.65, and 1.57 {2.33, 1.65, and 1.57} (each m, 4:2:2 H; COD), 2.28 {2.28} (s, 3 H; 1-H_3), 2.07 {2.07} (s, 3 H; Tol-CH_3), 1.91 {1.86} (s, 3 H; 5-H_3}, 1.55 and 0.98 {1.55 and 0.98} (each m, 1:1 H; 5-H_2), 1.52 and 1.09 {1.52 and 1.09} (each m, 1:1 H; 7-H_2), 1.10 {1.10} ("t", 3 H; OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6, 300 K): $\delta = 177.4$ {177.2} (C_q, C2), 168.3 {168.2} (C_q, C3′), 165.3 {165.3} (C_q, C4), 149.5 {149.5} (C_q, *p*-C Tol), 135.4, 133.5, and 132.9 {135.3, 133.5, and 132.9} (each C_q, C1′, C7′a, and *i*-C Tol), 129.2, 125.0, and 124.9 {129.1, 124.9, and 124.8} (each CH, *o*- and *m*-C Tol), 104.0 {103.9} (C_q, C3), 102.5 {102.5} (CH, C2′); 81.6, 81.3, 75.4, and 75.1 {81.5, 81.2, 75.2, and 74.9} (each CH, $^2J(^{103}Rh,^{13}C)$ not resolved, COD), 64.9 {64.9} (OCH_2), 50.3 {50.3} (CH, C3′a); 32.1, 31.9, 29.6, and 29.5 {32.0, 31.8, 29.5, and 29.2} (each CH_2, COD), 31.0 {30.9} (CH_2, C4′), 27.3 {27.1} (CH_3, C1), 26.2 {26.0} (CH_2, C6′), 25.7 {25.7} (CH_2, C7′), 23.5 {23.4} (CH_3, C5), 20.8 {20.8} (CH_3, CH_3 Tol), 14.6 {14.6} (OCH_2CH_3); IR (diffuse reflection), cm^{-1} (%): $\tilde{\nu} = 2927$ (100), 1566 (36), 1545 (30), 1416 (20), 1382 (20), 1254 (24); MS (ESI, 50 *V* cone potential): *m*/*z*(%): 910 (18), 790 (28), 580 (42), 564 (18) $[M+2H]^+$, 548 (100); elemental analysis calcd (%) for $C_{31}H_{40}NO_2Rh$ ($M_r = 561.6$): C 66.30, H 7.18, N 2.56; found: C 63.69, H 7.52, N 2.56. X-ray crystal structure analysis of compound **16e** (code aum.1400), formula $C_{31}H_{40}NO_2Rh$, $M_r = 561.55$, yellow crystal $0.15 \times 0.10 \times 0.05$ mm, $a = 22.483(1)$, $b = 9.686(1)$, $c = 12.648(1)$ Å, $\beta = 94.67(1)^\circ$, $V = 2745.2(4)$ Å^3, $\rho_{calcd} = 1.359$ g cm^{-3}, $\mu = 6.49$ cm^{-1}, absorption correction by SORTAV ($0.909 \le T \le 0.968$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 20479 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 6232 independent ($R_{int} = 0.059$) and 4210 observed reflections [$I \ge 2\sigma(I)$], 375 refined parameters, $R = 0.047$, $wR^2 = 0.088$, max. residual electron density 0.54 (-0.53) e Å^{-3}, positional disorder in the cyclohexyl group C21 to C26, refined with geometrical split positions (0.77(1):0.23(1)), hydrogens calculated and refined as riding atoms.

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[12] For the numbering of atoms see corresponding formula **c** above.

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