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Organic Syntheses via Transition Metal Complexes. Part 103:[1] Pyrylium Carbonylmetalates and Related Compounds Derived from (1-Alkynyl)carbene Complexes (M=Cr, W)

Rudolf Aumann,* Michael Kößmeier, Klaus Roths and Roland Fröhlich†

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

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Abstract—Cyclic tertiary enaminones **2a-e** and (2-phenylalkynyl)carbene tungsten complex $(OC)_5W{=}C(OEt)C{\equiv}CPh$ (**1a**) gave cross-conjugated carbiminium carbonylmetalates **3**, which isomerized to pyrilium carbonylmetalates **4** in 62–90% yields. The isomerization involves a skeletal rearrangement of a cross-conjugated carbiminium carbonyltungstate to a (conjugated) 1-tungsta-1,3,5-hexatriene by formation of (4-aminocyclobutenyl)carbene complexes as intermediates. Dinuclear carbene derivatives of dihydrobarrelene **5** were derived from pyrilium carbonylmetalates **4** by [4+2] cycloaddition to (1-alkynyl)carbene complexes **1** in 63–73% yields. Reactions of cyclic 1,3-diketones **7** with (1-alkynyl)carbene complexes **1** gave pyrilium carbonylmetalates **10** and **11** in 35–91%.

Introduction

Reactions of (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ **1** (M=Cr, W) with carbon nucleophiles were shown to provide a rich source of novel and synthetically useful routes to carbocyclic compounds.[2] The reaction paths unravelled so far include the production of cyclopentadienes in [3+2]-fashion by addition of enamines,[3,4] and the formation of (cyclobutenyl)carbene compounds by [2+2]-addition of enol ethers.[5–7] Interestingly, the enols derived from 1,3-dicarbonyl compounds did not afford carbocyclic compounds, but instead gave pyrylium carbonylmetalates (=pyranylidene complexes),[5c–h,6,8,9] (Scheme 1, Eq. (1)) and 5-oxo-1-metalla-1,3,6-heptatrien-8-ones {=[2-(alken-1-oxy)ethenyl]carbene complexes}[8c] (Scheme 1, Eq. (2)) by *C*- and *O*- alkenylation of the enol unit, respectively. Open-chain secondary *NH*- enaminones derived from 1,3-dicarbonyl compounds were found to yield 6-amino-1-metalla-1,3,5-hexatrienes,[10] which could be isolated and smoothly transformed into pyrylium carbonylmetalates and pyridinium carbonylmetalates (=dihydropyridinylidene complexes)[11], respectively (Scheme 1, Eq. (3)), as well as into homopyrroles[11a] (Scheme 1, Eq. (4)), depending on the reaction conditions. Whilst pursuing studies on enaminones, a further reaction mode significantly different from the aforementioned was found, by which open-chain tertiary NR_2-enaminones gave cross-conjugated carbiminium carbonylmetalates instead of (conjugated) 6-amino-1-metalla-1,3,5-hexatrienes (Scheme 1, Eq. (5)).[12]

Up to date, ample evidence has been accumulated, indicating that the products generated by Eqs. (1)–(5) could be profitably utilized as building blocks in organic synthesis. In order to enable a broad range of applications, our studies were focused also to the influence of conformational effects on the reaction course. We now wish to report on the reactions between (1-alkynyl)carbene complexes **1** and cyclic 1,3-diketones **7** (Scheme 4), and cyclic enaminones **2** (Scheme 2), respectively.

Reactions of Cyclic Tertiary Enaminones 2 with (1-Alkynyl)carbene Complexes 1

Reactions of open-chain tertiary NR_2-enaminones with (1-alkynyl)carbene complexes **1** were found to follow exclusively the reaction paths outlined in (Eq. (5), Scheme 1) to give the cross-conjugated carbiminium carbonylmetalates. The latter compounds proved reasonably stable except for one case, in which a spontaneous transformation into a (3-alkenyl)pyrilium carbonylmetalate by intramolecular condensation took place (Eq. (5), Scheme 1).[12a] Based on this observation, we anticipated that cyclic tertiary enaminones **2** might form cross-conjugated carbiminium carbonyltungstates **3** and/or (5-alkenyl)pyrilium carbonyltungstates **4** with compound **1a** (Scheme 2).

Keywords: 1-alkynyl carbene complexes; enaminones; cyclopentadienes; mesoionic pyrylium compounds; tungsten complexes; chromium complexes.

* Corresponding author. Fax: +49-251-833-6502;
e-mail: aumannr@uni-muenster.de

† Crystal structure analyses.

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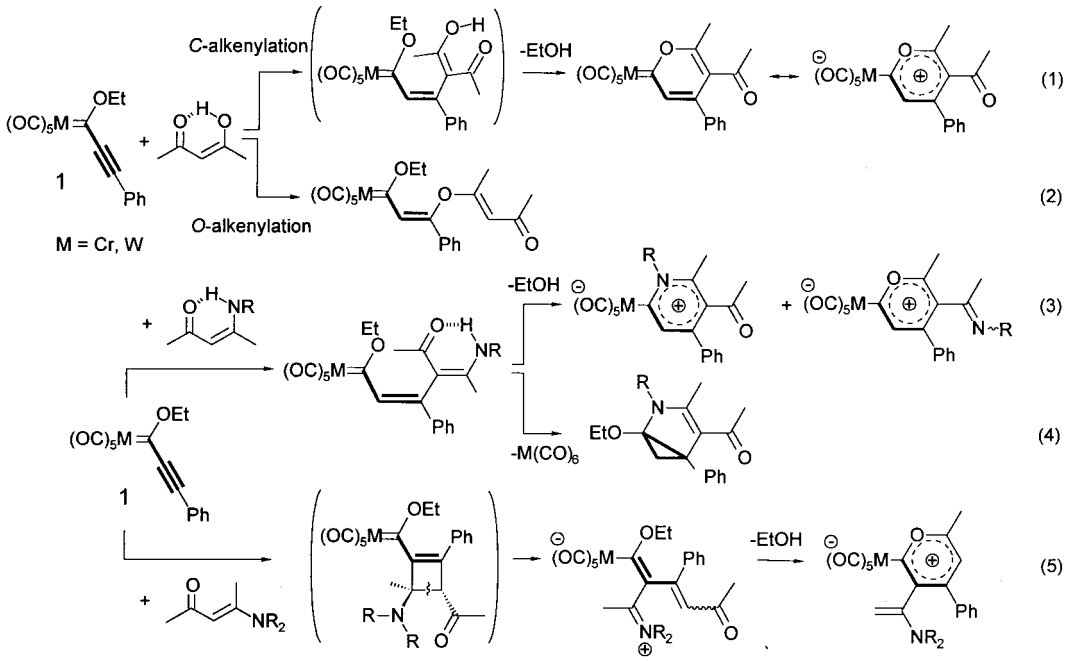
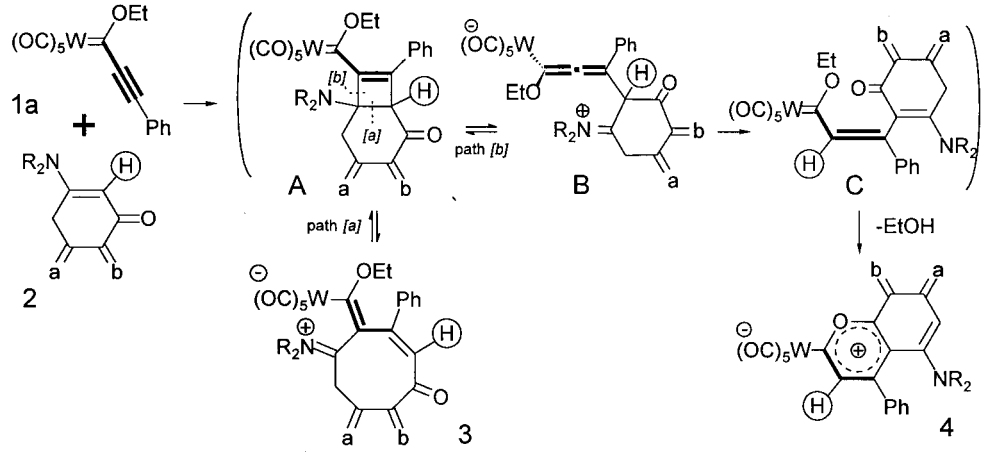


Scheme 1. Some reactions of (1-Alkynyl)carbene complexes **1** with open-chain 1,3-diketones and enaminones.

Transformation of cross-conjugated carbiminium carbonyltungstates 3 into pyrilium carbonyltungstates 4

The reaction between cyclic tertiary enaminones **2a–e** and the (1-alkynyl)carbene tungsten complex **1a** proved to be difficult to control, since seemingly quite different products were generated on even slight changes of conditions. Reproducible results leading to (5-alkenyl)pyrilium carbonyltungstates **4a–e** in good yields were finally achieved in benzene at 40–50°C, 12–14 h with a molar ratio 1:1 of starting components (Scheme 2), but untractable mixtures were inevitably formed on shorter reaction times, except for



2-4	NR_2	=a	=b	3	4[c]
a	NMe_2	Me,Me	H,H	[a]	90
b	pyrrolidino	Me,Me	H,H	[a]	80
c	pyrrolidino	H,H	Me,Me	[a]	62
d	morpholino	H,H	H,H	82[b]	86
e	morpholino	Me,Me	H,H	[a]	92

[a] Compound not isolated. [b] Isolated yield of compound **3** from reaction in diethyl ether. [c] Isolated yields of compounds **4** from reaction in benzene at 40 - 50 °C.

Scheme 2. Generation of cross-conjugated carbiminium carbonylmetalates **3** and their conversion into pyrilium carbonylmetalates **4**.

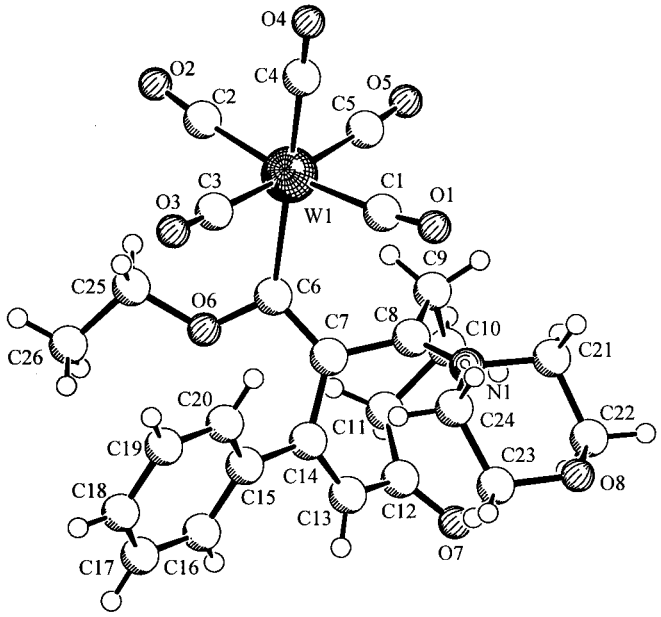


Figure 1. Crystal structure analysis of carbiminium carbonyltungstate **3d** with selected bond lengths (Å), bond angles (°) and dihedral angles (°): W1–C6 2.278(5), N1–C8 1.308(6), C6–C7 1.400(7), C7–C8 1.459(7), C7–C14 1.485(7), C8–C9 1.501(7), C9–C10 1.541(8), C10–C11 1.522(8), C11–C12 1.508(8), C12–C13 1.464(7), C13–C14 1.357(7); C7–C6–W1 125.0(3), C6–C7–C8 119.3(4), C6–C7–C14 123.4(4), C8–C7–C14 117.0(4), N1–C8–C7 123.3(5), N1–C8–C9 119.7(4), C7–C8–C9 116.7(4), C8–C9–C10 109.7(4), C11–C10–C9 112.9(4), C12–C11–C10 112.6(4), C13–C12–C11 120.7(4), C14–C13–C12 126.0(5), C13–C14–C7 120.9(4); W1–C6–C7–C8 −39.0(6), W1–C6–C7–C14 147.6(4), C6–C7–C8–N1 34.1(5), C14–C7–C8–N1 −52.2(7), C6–C7–C8–C9 −53.1(6), C14–C7–C8–C9 120.7(5), N1–C8–C9–C10 86.0(6), C7–C8–C9–C10 −87.2 (5), C8–C9–C10–C11 45.1(6), C9–C10–C11–C12 −82.5(6), C10–C11–C12–C13 112.7(5), C11–C12–C13–C14 −32.8(8), C12–C13–C14–C7 −14.9(8), C6–C7–C14–C13 138.9(5), C8–C7–C14–C13 −34.6(7).

the reaction of 3-(morpholin-4-yl)cyclohex-2-enone (**2d**) in diethyl ether at 20°C, which gave an orange precipitate of the cross-conjugated carbiminium carbonylmetalate **3d** in 82% yield. Interestingly, the zwitterionic eight-membered ring compound **3d** proved to be reasonably stable in solid state, but in solution it was transformed into the pyrilium carbonylmetalate **4d** in smooth reaction. This transformation, which could be nicely followed by NMR spectra in C_6D_6 at 50°C, involves an unusual skeletal rearrangement of a cross-conjugated carbiminium carbonyltungstate **3** into

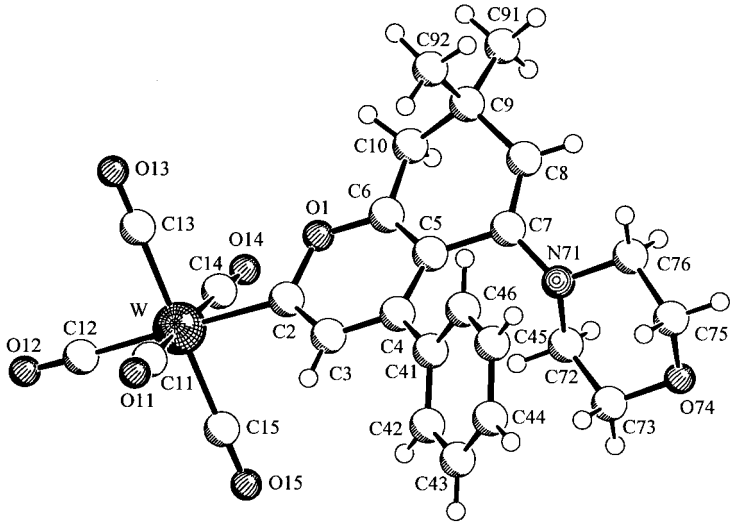
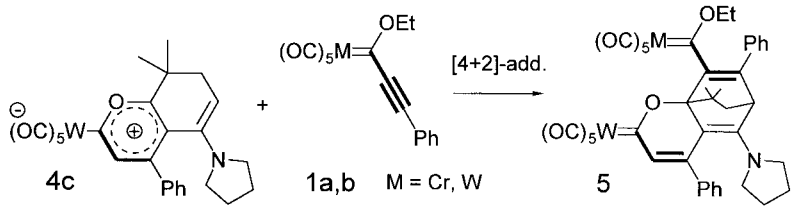


Figure 2. Crystal structure analysis of (5-alkenyl)pyrilium carbonyltungstate **4e** with selected bond lengths (Å), bond angles (°) and dihedral angles (°): W–C2 2.186(4), C2–O1 1.377(4), O1–C6 1.340(4), C2–C3 1.395(5), C3–C4 1.392(5), C4–C5 1.425(5), C5–C6 1.366(5), C5–C7 1.495(5), C6–C10 1.482(5), C10–C9 1.545(5), C9–C8 1.517(6), C8–C7 1.334(5), C7–N71 1.401(5); C2–O1–C6 123.5(3), W–C2–O1 117.0(2), W–C2–C3 129.0(3), O1–C2–C3 114.0(3), C2–C3–C4 124.3(3), C3–C4–C5 117.5(3), C4–C5–C6 116.8(3), C4–C5–C7 127.2(3), C7–C5–C6 115.9(3), C5–C6–O1 122.8(3), C5–C6–C10 123.0(3), O1–C6–C10 114.2(3), C6–C10–C9 111.6 (3), C10–C9–C8 107.2(3), C9–C8–C7 123.0(3), C8–C7–C5 118.9(3), C8–C7–C5 118.9(3), C5–C7–N71 115.5(3), C8–C7–N71 125.6(3); W–C2–O1–C6 −172.7(3), W–C2–C3–C4 177.7(3), C6–O1–C2–C3 8.2(5), O1–C2–C3–C4 −3.3(5), C2–C3–C4–C5 −5.9(5), C3–C4–C5–C6 10.4(5), C4–C5–C6–O1 −6.2(5), C5–C6–O1–C2−3.6(5), C3–C4–C5–C7 −167.9(3), C4–C5–C7–C8 −157.6(4), C4–C5–C7–N71 −155.5(3), C5–C7–C8–C9 0.1(6), N71–C7–C8–C9 179.6(4), C7–C8–C9–C10−35.9(5), C8–C9–C10–C47.6(4), C9–C10–C6–O1 150.7(3), C9–C10–C6–C5 −29.0(5), C10–C6–O1–C2 176.7(3), C10–C6–C5–C4 173.5(3).



5c: M = W, 73%, **5d**: M = Cr, 63%

Scheme 3. Dinuclear complexes **5** by [4+2]-addition of pyrilium carbonylmetalate **4c** to (1-alkynyl)carbene complexes **1a**,**b**.

a (conjugated) 1-tungsta-1,3,5-hexatriene **C**. On first sight, this type of rearrangement is quite astounding, but it has found precedence already in reactions between 1-aminocycloheptenes and compound **1a**.[3d,3e] Its crucial step involves formation of a (4-aminocyclobutenyl)carbene complex **A** as precursor to both compounds **3** and **4**, which are derived thereof by different type reversible ring-opening reactions, *path [a]* and *path [b]* (Scheme 2).[3d,3e]

Carbiminium carbonylmetalates **3** were generated in a kinetically controlled reaction, and could be isolated by crystallization from hydrocarbon solvents, in which they were only sparingly soluble. On the other hand, carbiminium carbonyltungstates of type **B**, once formed, appear to readily undergo a 1,3-proton transfer to 1-tungsta-1,3,5-hexatrienes **C**. Whilst it is well known that pyrilium carbonylmetalates are formed via 1-metalla-1,3,5-hexatrienes, which are generated from reaction of secondary *NH*-enaminones with (1-alkynyl)carbene complexes (Scheme 1, Eq. (3)),[11a] it has not yet been reported that reaction of tertiary NR_2-enaminones would afford (5-alkenyl)pyrilium carbonylmetalates by elimination of an α-hydrogen atom from 1-tungsta-1,3,5-hexatrienes of type **C** (Scheme 2).

Compounds **3** were characterized by NMR ^{1}J(C,H)- and $^{2,3}J$(C,H)-correlation experiments. In line with the assignment of a zwitterionic carbiminium carbonylmetalate structure $^{-}(OC)_5W{-}C(OEt){=}C(\sim){-}C(\sim){=}N^{+}$ is the high-field ^{13}C NMR shift of W,*C* (**3d**: δ 265.1), the pattern of alternating bond distances [W1–C6 2.278(5) Å, C6–C7

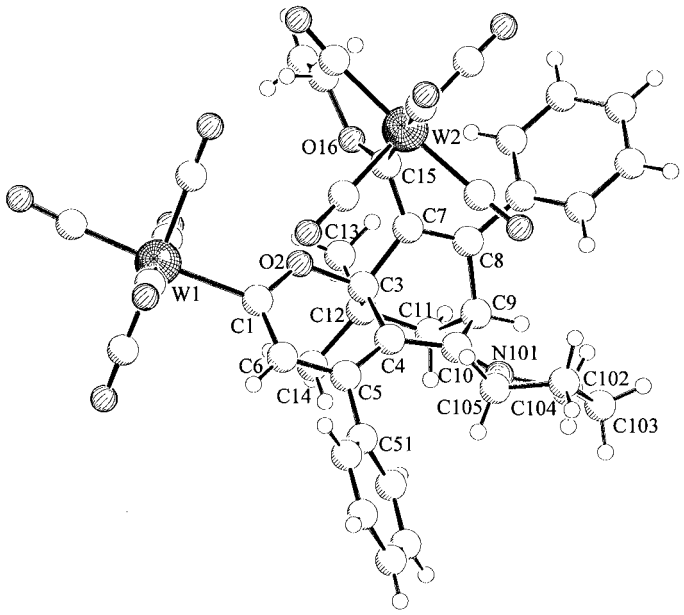
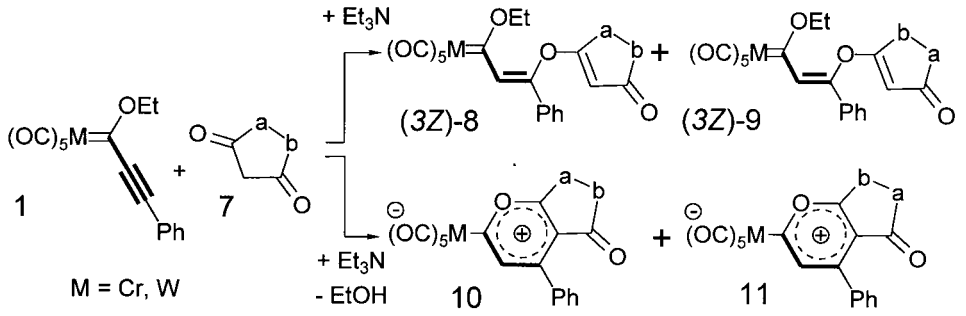


Figure 3. Crystal structure analysis of the dinuclear [4+2] adduct **5c** with selected bond lengths (Å), bond angles (°) and dihedral angles (°): W1–C1 2.211(9), W2–C15 2.177(8), C1–O2 1.361(9), C1–C6 1.388(10), O2–C3 1.443(9), C3–C7 1.519(10), C3–C4 1.540(10), C3–C12 1.564(10), C4–C5 1.399(11), C4–C10 1.419(12), C5–C6 1.398(11), C7–C8 1.337(11), C7–C15 1.503(10), C8–C9 1.535(10), C9–C10 1.524(11), C9–C11 1.537(12), C10–N101 1.302(10), C11–C12 1.542(13); O2–C1–C6 116.3(8), O2–C1–W1 114.9(5), C6–C1–W1 128.8(7), C1–O2–C3 124.4(6), O2–C3–C7 108.7(6), O2–C3–C4 113.7(6), C7–C3–C4 108.9(7), O2–C3–C12 109.5 (7), C7–C3–C12 108.4(6), C4–C3–C12 107.5(6), C5–C4–C10 132.0(7), C5–C4–C3 117.0 (7), C10–C4–C3 110.5(7), C4–C5–C6 119.7(7), C1–C6–C5 125.0(8), C8–C7–C15 125.1 (8), C8–C7–C3 113.7(7), C15–C7–C3 121.2(8), C7–C8–C9 111.8(8), C10–C9–C8 104.5(6), C10–C9–C11 109.9(7), C8–C9–C11 108.8(7), N101–C10–C4 129.1(8), N101–C10–C9 120.3(9), C4–C10–C9 110.4(8), C9–C11–C12 111.4(6), C11–C12–C3 105.1(7), C7–C15–W2 119.3(6); C6–C1–O2–C3 11.9(10), W1–C1–O2–C3 −167.4(5), C1–O2–C3–C7 −144.6(7), C1–O2–C3–C4 −23.1(9), C1–O2–C3–C12 97.1(7), O2–C3–C4–C5 20.4(9), C7–C3–C4–C5 141.8(7), C12–C3–C4–C5 −101.0(8), O2–C3–C4–C10 −166.7(6), C7–C3–C4–C10 −45.3(8), C12–C3–C4–C10 71.9(8), C10–C4–C5–C6 −179.3(8), C3–C4–C5–C6 −8.2(10), O2–C1–C6–C5 3.1(11), W1–C1–C6–C5 −177.6(5), C4–C5–C6–C1 −4.2(11), O2–C3–C7–C8 −177.9(7), C4–C3–C7–C8 57.8(10), C12–C3–C7–C8 −59.0(10), O2–C3–C7–C15 0.2(10), C4–C3–C7–C15 −124.1(8), C12–C3–C7–C15 119.2(8), C15–C7–C8–C9 177.9(7), C3–C7–C8–C9 −4.1(10), C7–C8–C9–C10 −56.9(10), C7–C8–C9–C11 60.4(10), C5–C4–C10–N101 −27.4(13), C3–C4–C10–N101 161.1(7), C5–C4–C10–C9 156.3(8), C3–C4–C10–C9 −15.2(8), C8–C9–C10–N101 −109.1(8), C11–C9–C10–N101 134.3(8), C5–C4–C10–N101 −27.4 (13), C8–C9–C10–C4 67.6(8), C11–C9–C10–C4 −49.1(8), C10–C9–C11–C12 62.1(9), C8–C9–C11–C12 −51.7(9), C9–C11–C12–C3 −7.2(9), O2–C3–C12–C11 −179.5(6), C7–C3–C12–C11 62.1 (8), C4–C3–C12–C11 −55.5(9), C8–C7–C15–W2 −80.3(10), C3–C7–C15–W2 101.9(8).



7-11	M	a–b	(3Z)-8[a]	(3Z)-9[a]	10[a]	11[a]	lit.
a	W	$CH_2CH_2CH_2$	35	-	46	-	[b]
b	W	$CH_2CH_2CMe_2$	18	8	52	17	[b]
c	W	$CH_2CMe_2CH_2$	38	-	52	-	8c
d	W	CH_2CH_2	56	-	38	-	8c
e	Cr	CH_2CH_2	54	-	35	-	8c
f	W	Me,Me	[c]	-	90	-	8a
g	Cr	Me,Me	[c]	-	91	-	8b
h	W	Me,OMe	[c]	-	85	-	8b

[a] Isolated yields in %. [b] This paper. [c] Not detected.

Scheme 4. (Non-conjugated) 5-oxo-1-tungsta-1,3,6-heptatrienes **8** and **9** as well as pyrilium carbonylmetalates **10** and **11** from enolizable cyclic 1,3-dicarbonyl compounds **7** and (1-alkynyl)carbene complexes **1**.

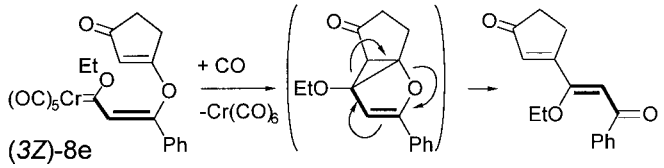
1.400(7) Å, C7–C8 1.459(7) Å, C8–N1 1.308(6) Å] and—above all—the strong distortion of the W–C6=C7–C8=N1 bond unit [W1–C6–C7–C8 −39°, C6–C7–C8–N1 134.1(5)°] found in the crystal structure analysis of compound **3d** (Fig. 1).[3d]

Characteristic of (5-alkenyl)pyrilium carbonyltungstates **4** are the low-field shifts of NMR signals 3-H, C3 and C8a (e.g. **4c**: δ 7.91, 142.0 and 184.6) and the high-field shift of 6-H, C6 and W=*C* (**4c**: 5.00, 106.6 and 246.9). A crystal structure analysis[13] of compound **4e** reveals a bond pattern typical of pyrilium carbonylmetalates,[8a] including a long distance W–C2 2.186 (4) Å, and short distances within the ring, C2–O1 1.377(4) Å, O1–C6 1.340(4), C5–C6 1.366(5), C4–C5 1.425(5), C3–C4 1.392(5) and C2–C3 1.395(5) (Fig. 2).

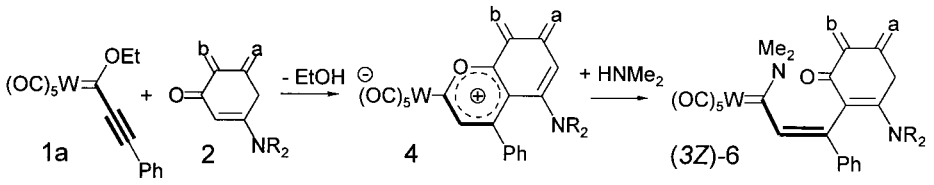
Dihydrobarrelene derivatives by cycloaddition of pyrilium carbonylmetalates 4

The amino-1,3-diene portion of the pyrilium carbonylmetalates **4** was found to undergo a [4+2] cycloaddition with electron-poor dienophiles. This type of reaction was exemplified by addition of (1-alkynyl)carbene complexes **1a**,**b** (M=Cr, W) to compound **4c** to give dinuclear dihydrobarrelenes **5c**,**d** (Scheme 3).

Compounds **5c**,**d** were characterized by ^{1}H- and ^{13}C NMR spectra and ^1J(C,H)-, $^{2,3}J$(C,H)- and J(H,H) correlation experiments. The ^{1}H NMR spectra exhibit singlets each for the signal of the olefinic proton (**5c**: δ 6.55, s) and the bridge-head proton (**5c**: 4.18, s). The ^{13}C NMR signals M=*C* of the 1-metalla-1,3-butadiene unit (**5c**: W=C δ 327.5; **5d**: Cr=C 358.4) are observed in a range typical of non-conjugated carbene complexes, thus indicating only little if any π-conjugation. On the other hand, strong π-conjugation within the 6-amino-1-tungsta-1-3,5-hexatriene moiety is implied by the up-field shift of W=C (**5c**: W=*C* δ 263.3, **5d**: W=*C* 263.6) and the down-field shift of the C=*C*(N) group (**5c**: *C*=N$^+$, δ 164), which is typical of a zwitterionic carbiminium carbonyltungstate. The latter structural feature is confirmed by the crystal structure analysis of compound **5c**, which exhibits a pattern of almost equidistant C,C bond lengths [W1–C1 2.211(9) Å, C1–C6 1.388(10), C6–C5 1.398(11), C5–C4 1.399(11), C4–C10 1.419(12), C10–N101 1.302(10)] and an almost planar $^-$(OC)$_5$W1–C1=C6–C5=C4–C10=$^+$N101 backbone [W1–C1–C6–C5 −177.6(5)°, C1–C6–C5–C4 −4.2(12), C6–C5–C4–C10 −8.3 (10), C5–C4–C10–N101 −27.4(13)] (Fig. 3). The bond distance W1–C1 2.211 (9) Å of the conjugated π-system is slightly longer than W2=C15 2.177(8) of the non-conjugated one, which is characteristically twisted by W2–C15–C7–C8 −80.3(10)°.



Scheme 5. 2,4-Hexadien-1,6-diones by fragmentation of 5-oxo-1-chroma-1,3,6-heptatrien-8-ones.



2,4,(3Z)-6	NR_2	=a	=b	(3Z)-6[a]
a	NMe_2	Me,Me	H,H	69
c	pyrrolidino	H,H	Me,Me	55
e	morpholino	Me,Me	H,H	65

[a] Isolated yields in %.

Scheme 6. (Conjugated) 2,6-diamino-1-tungsta-1,3,5-hexatrienes **6** by ring-opening of pyrilium carbonyltungstates **4**.

Reactions of Enolizable Cyclic 1,3-Diketones with (1-Alkynyl)carbene Complexes 1

A structural feature characteristic of cyclic 1,3-dicarbonyl compounds is the W-shape arrangement of its *O*,*C*,*C*,*C*,*O* backbone (in contrast to the U-shape arrangement in open-chain compounds), by which an electrophilic addition to the oxygen atom becomes favored over an addition to the α-carbon atom.

C- versus *O*-Alkenylation of cyclic 1,3-dicarbonyl compounds

Addition of enolizable cyclic 1,3-dicarbonyl compounds **7** to (1-alkynyl)carbene complexes **1a**,**b** requires catalysis by a base, e.g. Et_3N (Scheme 4). In order to gain optimal yields, this reaction must be carefully controlled with respect to temperature, time and solvent. The *C*-alkenylation is assumed to follow the pattern outlined in Scheme 1, Eq. (1). Based on earlier investigation, it is suggested that the *O*-alkenylation would involve formation of (3*E*)-1-metalla-1,3,5-hexatrienes initially, which subsequently would isomerize to the corresponding (3*Z*)-derivative.[8c] With respect to chemical yields, it should be noted that altogether four different isomeric adducts are derived from unsymmetrically substituted 1,3-dicarbonyl compounds, like 4,4-dimethylcyclohexan-1,3-dione (**7b**) (Scheme 4).[8c]

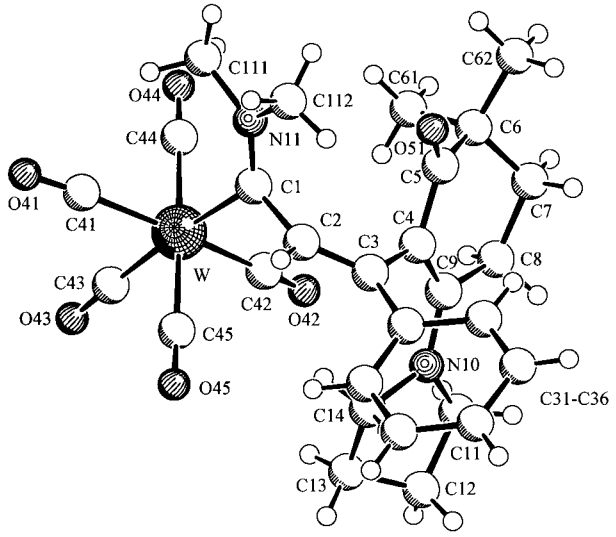


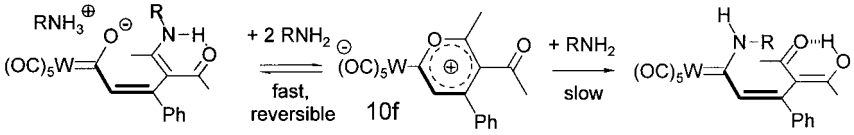
Figure 4. Crystal structure analysis of (conjugated) 2,6-diamino-1-tungsta-1,3,5-hexatriene (3*Z*)-**6c** with selected bond lengths (Å), bond angles (°) and dihedral angles (°): W–C1 2.267 (5), C1–N11 1.306(7), C1–C2 1.488(7), C2–C3 1.347(7), C3–C4 1.518(7), C4–C9 1.371(8), C4–C5 1.449(8), C5–O51 1.228(8), C9–N10 1.352(8); N11–C1–C2 112.7(5), N11–C1–W 129.0 (4), C2–C1–W 116.8(4), C3–C2–C1 130.8(5), C2–C3–C4 122.2(5), C9–C4–C5 120.7(5), C9–C4–C3 124.6(5), C5–C4–C3 114.4(5), O51–C5–C4 121.3(5), N10–C9–C4 126.6(5); N11–C1–C2–C3 −110.1(7), W–C1–C2–C3 82.7(7), C1–C2–C3–C4 7.2(9), C2–C3–C4–C9 −124.1(6), C2–C3–C4–C5 62.1(7), C9–C4–C5–O51 −163.1(0.7), C3–C4–C5–O51 11.0(10), C5–C4–C9–N10 −179.9(6), C3–C4–C9–N10 6.7(9).

Characteristic of 5-oxo-1-tungsta-1,3,6-heptatrien-8-ones **8** and **9** (Scheme 4) is the range of chemical shifts of 3-H and 2′-H [(3*Z*)-**8a**: δ 7.58 and 5.26] as well as of M=C, C1′ and C2′ [(3*Z*)-**8a**: δ 304.7, 174.6 and 107.8]. The assignment of a (3*Z*)-configuration to compounds **8** and **9** is based on the comparison of ^1H and ^{13}C NMR shifts with structurally related compounds, which have been characterized by NOE measurements and also by crystal structure analyses.[8] The structural isomers (3*Z*)-**8** and (3*Z*)-**9** were distinguished on the basis of ^1J(C,H)- and $^{2,3}J$(C,H)-correlation experiments. Characteristic of the pyrilium carbonylmetalates **10** and **11** are the (relative) low-field shift of 3-H (**10a**: δ 7.91), C3 (**10a**: δ 144.8) and C8a (**10a**: δ 182.6) as well as the high-field shift of W=C (**10a**: δ 262.7).[8b]

It should be noted that 5-oxo-1-chroma-1,3,6-heptatrienes of type **8** (and **9**) are thermolabile and readily undergo fragmentation to a dienedione by elimination of $Cr(CO)_6$, which is exemplified for the chromium complex (3*Z*)-**8e** in Scheme 5.[8c]

6-Diamino-1-tungsta-1,3,5-hexatrienes from pyrilium carbonyltungstates 4

Whilst 6-amino-2-ethoxy-1-tungsta-1,3,5-hexatrienes **C** (Scheme 2) are not stable under conditions by which they are generated from (1-alkynyl)carbene complex **1a**, but undergo a spontaneous cyclo-condensation to pyrilium carbonylmetalates **4** (Scheme 2), it is possible to obtain (reasonably) stable 2,6-diamino-1-tungsta-1,3,5-hexatrienes (3*Z*)-**6** by aminolysis of pyrilium carbonylmetalates (3*Z*)-**4** (Scheme 6).[8a]



Scheme 7. Reversible and irreversible aminolysis of pyrilium carbonyltungstate **10f** (R=H_2C=$CHCH_2$, $PhCH_2$, *n*-Bu, *i*-Pr).

The 2,6-diamino-1-tungsta-1,3,5-hexatrienes (3*Z*)-**6** were characterized spectroscopically. Structural details of these compounds could be derived from a crystal structure analysis of compound (3*Z*)-**6c** (Fig. 4). The latter reveals a typical trough-shape of the ligand backbone, in which both the W=C bond as well as the the C=C(N) bond are strongly twisted against the central C=C bond, W–C1–C2–C3 82.7(6)°, C1–C2–C3–C4 7.2(9) and C2–C3–C4–C9 −124.1(6). Similar structural features have been detected in the crystal structure analysis of compound (3*Z*)-**6e**.[14]

Eventhough complexes **4** seem to behave towards secondary amines as dictated by the general reactivity rules of Fischer (alkoxy)carbene complexes (Scheme 6), this is probably not the full truth, since it has been previously demonstrated that salt-like 6-amino-1-metalla-1,3,5-hexatrienes are generated from pyrilium carbonylmetalates **10f**,**g** by addition of two equivalents of a primary amine in a fast and reversible reaction, whilst 2-amino-1-metalla-1,3,5-hexatrienes are generated much slower by an irreversible aminolysis (Scheme 7).[8c]

2-Amino-6-hydroxy-1-tungsta-1,3,5-hexatrienes from pyrilium carbonylmetalates 10

Whilst 2-ethoxy-6-hydroxy-1-tungsta-1,3,5-hexatrienes (Scheme 1) are kinetically quite unstable and could not be isolated, since they readily undergo cyclization to pyrilium carbonylmetalates **10** or **11** in the presence of a base (Scheme 4), it was possible to generate and characterize the structurally related 2-amino-6-hydroxy-1-tungsta-1,3,5-hexatrienes (3*Z*)-**13a**,**b** by aminolysis of pyrilium carbonyltungstate **10c** (Scheme 8).

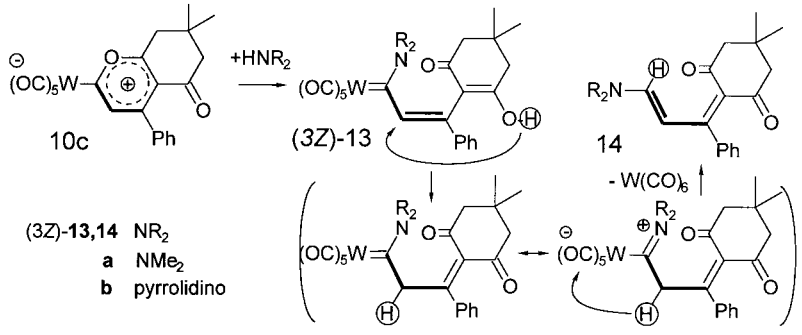
Compounds **13** were characterized spectroscopically, the 2-dimethylamino-6-hydroxy-1-tungsta-1,3,5-hexatriene (3*Z*)-**13a** also by a crystal structure analysis (Fig. 5). The latter compound forms a crystalline adduct with two molecules of dimethylamine, which are attached to the oxygen atoms by unsymmetrical hydrogen bridges (N51–H51a 0.90 Å, H51a–O10* 1.783(8), N51–H51a–O10* 168.4(2)°; N51–H51b 0.90, H51b–O6 1.832(7), N51–H51b–O6 161.9(2), symmetry code for O10*: $-x+0.5$, $y-0.5,z$). The 1-tungsta-1,3,5-hexatriene unit adopts a typical trough-shape geometry and exhibits a pattern of alternating bond distances, W–C2 2.282(7) Å, C2–N1 1.289(9), C2–C3 1.470(10), C3–C4 1.342(9), C4–C5 1.485(9), C5–C6 1.408(9). Based on the short distance C2–N1 1.289(9) Å and the long distance W–C2 2.282(7) observed for 2-dimethylamino-6-hydroxy-1-tungsta-1,3,5-hexatriene (3*Z*)-**13a**, these compounds are best considered carbiminium carbonylmetalates (Scheme 8). In line with expectation,[15] they were found to readily undergo protolysis of the W–C2 bond to give enamine dienones **14**.

4-Aminocyclohexadienes by 'vinylogous aminolysis' of pyrilium carbonylmetalates

The addition of enamines to pyrylium carbonylmetalates follows a reaction pattern similar to that outlined for amines in Scheme 7. This reaction, which has been first described by Wulff et al.[5] affords 5-amino-cyclohexa-1,3-dienes by fragmentation of the initially formed [4+2] cycloadduct. A variety of polycyclic ring-systems has been obtained by this route (Scheme 9).[8b] A reaction similar to that of enamines was found to provide the key-step of a high-yield self-condensation of pyrilium carbonylmetalates **10f**,**g** in presence of a base catalyst (Scheme 9).[8b]

α-Addition of (1-alkynyl)carbene complexes 1 to pyrilium carbonylmetalates

The type product resulting from addition of (1-alkynyl)carbene complexes to pyrilium carbonylmetalates depends very much on structural details. Whilst [4+2] adducts are obtained from addition of (1-alkynyl)carbene complexes **1a**,**b** to pyrilium carbonylmetalate **4c** (Scheme 3), an α-condensation was observed in the reaction of (1-alkynyl)-carbene complexes **1a**,**b** with pyrilium carbonylmetalates **10a**,**b** (Scheme 10). An adduct **D** could not be detected,



Scheme 8. 2-Amino-6-hydroxy-1-tungsta-1,3,5-hexatrienes by aminolysis of pyrilium carbonylmetalates **10**.

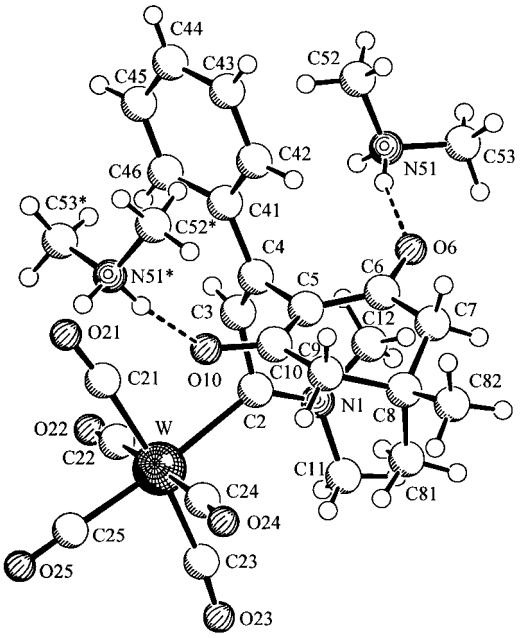


Figure 5. Crystal structure analysis of (conjugated) 2-dimethylamino-1-tungsta-1,3,5-hexatriene (3*Z*) -**13a** (=AUM_018) with selected bond lenghts (Å), bond angles (°) and dihedral angles (°): W–C2 2.282(7), C2–N1 1.289(9), C2–C3 1.470(10), C3–C4 1.342(9), C4–C5 1.485 (9), C5–C6 1.408(9), C5–C10 1.410(9), C10–O10 1.251(8), C6–O6 1.265(7), C6–C7 1.501(9), C7–C8 1.515(9), C8–C9 1.509(9), C9–C10 1.510(9); W–C2–N1 130.1(5), W–C2–C3 113.3(5), N1–C2–C3 116.2(6), C2–C3–C4 127.0(7), C3–C4–C5 122.0(6), C4–C5–C6 119.7(6), C4–C5–C10 118.5(6), C5–C10–O10 122.0(6), C5–C10–C9 118.4(6), O10–C10–C9 119.5(6), C5–C6–O6 123.7(6), C5–C6–C7 119.7(6), O6–C6–C7 116.5(6), C6–C7–C8 116.4(6), C7–C8–C9 107.6(6), C8–C9–C10 116.5(5); W–C2–C3–C4 98.4(8), W–C2–N1–C11 −9.9 (12), W–C2–N1–C12 167.9 (6), N1–C2–C3–C4 −89.0(9), C2–C3–C4–C5 8.8(11), C3–C4–C5–C6 94.1(8), C3–C4–C5–C10 −97.2(8), C4–C5–C10–O10 −0.4(11), C5–C10–C9–C8 −23.8(9), O10–C10–C9–C8 159.9(7), C4–C5–C6–O6 1.9(11), C4–C5–C6–C7 178.8(6), C5–C6–C7–C8 19.0(10), O6–C6–C7–C8 −163.8(6), C6–C7–C8–C9 −46.5(8), C7–C8–C9–C10 49.0(8).

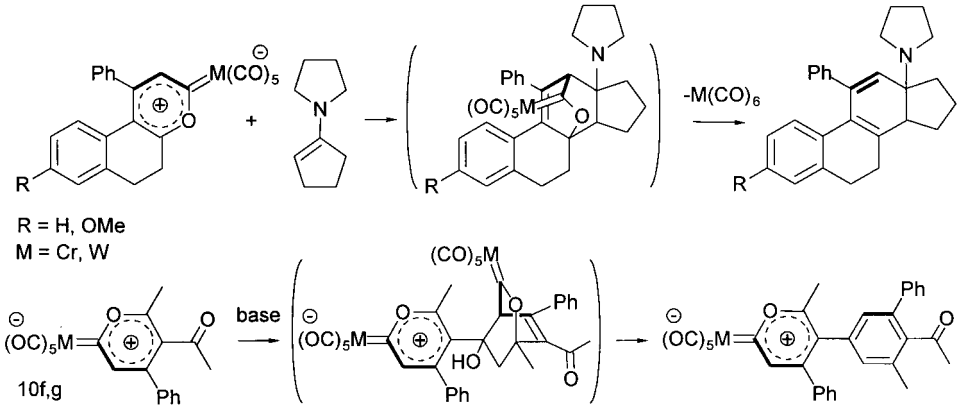
but the products *syn*- and *anti*-**12a**,**b** supposedly derived thereof by a 1,5-hydrogen transfer to the tungsten atom and subsequent reductive elimination, have been isolated. Compounds **12** can be generated without isolation of pyrilium carbonylmetalates **10** from the reaction of 1,3-diketones **7** with two equivalents of (1-alkynyl)carbene complex **1** in presence of a base catalyst.[11b]

Characteristic of compounds **12** are the chemical shifts of the NMR signals of the pyrylium unit [W–C (*syn*-**12a**: δ 257.7, *anti*-**12a**: 260.1), C3 (*syn*-**12a**: δ 151.5, *anti*-**12a**: 150.8), 3-H (*syn*-**12a**: δ 7.83, *anti*-**12a**: 7.70), C8a (*syn*-**12a**: δ 176.3, *anti*-**12a**: 177.2)] and the olefinic side chain [1′-H (*syn*-**12a**: δ 7.27, *anti*-**12a**: 6.41, d ^3J=12 Hz each), 2′-H (*syn*-**12a**: δ 6.30, *anti*-**12a**: 6.20, d ^3J=12 Hz each), C1′ (*syn*-**12a**: δ 162.0, *anti*-**12a**: 160.1), C2′ (*syn*-**12a**: δ 110.0, *anti*-**12a**: 108.3), C8 (*syn*-**12a**: δ 117.7, *anti*-**12a**: 118.7)]. The configurational assignment is based on the NOE enhancement observed between 1′-H and 7-H_2 for compound *anti*-**12a**.

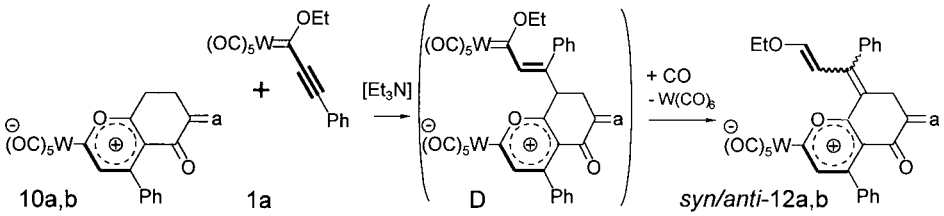
Experimental

All operations were performed under argon in dried solvents. Melting points are not corrected. ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker ARX 300, Bruker AM 360 and Varian U 600 spectrometers. ^{13}C NMR shifts were assigned by ^1J(C,H)- and $^{2,3}J$(C,H) correlation experiments. Diffractometer: Enraf–Nonius MachIII and Enraf–Nonius CAD4 with sealed tube. Other instrumentation: IR Digilab FTS 45; MS Finnigan MAT 312; Perkin–Elmer 240 elemental analyzer. TLC with Merck DC–Alufolien Kieselgel 60 F254. R_f values refer to TLC tests. Column chromatography on Merck Kieselgel 100. 3-Amino-cyclohexenones **2a**–**e** were prepared according to literature.[16]

Pentacarbonyl(7,7-dimethyl-5-dimethylamino-4-phenyl-7,8-dihydro-2H-chromen-2-ylidene)tungsten (4a). To pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) in 3 mL of pentane in a 5-mL screw-top vessel is added 5,5-dimethyl-3-dimethylamino-cyclohex-2-enone (**2a**) (168 mg, 1.00 mmol) in 1 mL of pentane. After stirring for 14 h, 20°C the mixture is separated by fast chromatography on silica gel with pentane/dichloromethane 1:1 to yield a red–violet main fraction containing compound **4a** (543 mg, 90%, R_f=0.5 in pentane/diethyl ether 1:1 on silica gel, red needles from pentane/dichloromethane 4:1 at −15°C, dec. 93°C). ^{1}H NMR ($CDCl_3$): δ 7.89 (1H, s, 3-H), 7.38 and 7.31 (1:2:2H, Ph), 4.85 (1H, s, NC=CH), 2.85 (2H, s, 8-H_2), 1.97 [6H, s, $N(CH_3)_2$], 1.17 [6H, s, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 247.8 (W=C), 203.9 and 198.5 [1:4, *trans*-



Scheme 9. Condensation of electron-rich alkenes with pyrilium carbonylmetalates.



10,12	a=	12[a]	anti-12 : syn-12
a	H,H	78	1 : 4
b	Me,Me	52	1 : 2

[a] Isolated yields in %.

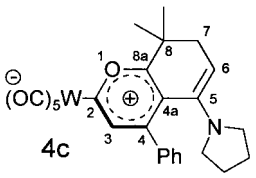
Scheme 10. α-Condensation of pyrilium carbonyltungstates **10**.

and *cis*-CO, $W(CO)_5$], 178.5 (C_q, C8a), 143.9 (C_q, C4), 142.2 (CH, C3), 141.9 (C_q, =C–N), 135.8 (C_q, *i*-C Ph); 129.3, 128.2 and 126.5 (CH each, Ph), 117.1 (C_q, C4a), 115.1 (NC=CH), 42.9 (CH_2, C8), 40.6 [$N(CH_3)_2$] 31.4 [$C(CH_3)_2$], 28.6 [$C(CH_3)_2$]. IR (diffuse reflection), cm^{-1}: 2058.1, 1936.7 and 1907.9 [ν(C≡O)], 1621.1 [ν(C=O)]. MS (70 eV), *m/e* (%): 603 (30) [M^+], 463 (30) [M^+-5 CO], 279 (30) [ligand$^+$], 55 (100). $C_{24}H_{21}NO_6W$ (603.3): calcd C 47.78, H 3.51, N 2.32; found C 47.91, H 3.74, N 2.52.

Pentacarbonyl(7,7-dimethyl-4-phenyl-5-pyrrolidino-7,8-dihydro-2*H*-chromen-2-ylidene)tungsten (4b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) in 3 mL of pentane is reacted with 5,5-dimethyl-3-pyrrolidino-cyclohex-2-enone (**2b**) (193 mg, 1.00 mmol) as described above to give **4b** (429 mg, 68%, R_f=0.5 in pentane/diethyl ether 1:1 on silica gel, red crystals from pentane/dichloromethane 4:1 at −15°C). ^{1}H NMR ($CDCl_3$): δ 7.89 (1H, s, 3-H), 7.40 and 7.31 (3:2H, m each, Ph), 4.83 (1H, s, NC=CH), 2.88 (2H, s, 8-H_2), 2.40 (4H, m, NCH_2), 1.19 [10H, s and m, $C(CH_3)_2$ and CH_2]. ^{13}C NMR ($CDCl_3$): δ 247.7 (W=C), 204.5 and 199.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 179.1 (C_q, C8a), 144.2 (C_q, C4), 142.5 (CH, C3), 139.2 (C_q, =C−N), 136.2 (C_q, *i*-C Ph); 130.9, 128.9 and 127.0 (CH each, Ph), 116.0 (C_q, C4a), 114.1 (NC=CH), 50.6 (2 NCH_2) 43.7 (CH_2, C8), 32.2 [C_q, $C(CH_3)_2$], 25.6 [$C(CH_3)$], 23.3 (CH_2CH_2). IR (hexane), cm^{-1} (%): 2059.3 (25), 1932.4 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 629 (15) [M^+], 545 (10) [M^+-3 CO], 517 (10) [M^+-4 CO], 489 (60) [M^+-5 CO], 305 (5) [$M^+-W(CO)_5$], 55 (100).

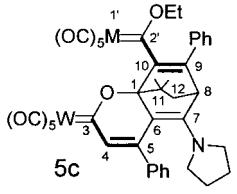
Pentacarbonyl(8,8-dimethyl-4-phenyl-5-pyrrolidino-7,8-dihydro-2*H*-chromen-2-ylidene)tungsten (4c), pentacarbonyl{11,11-dimethyl-5,9-diphenyl-7-pyrrolidino-2-oxa-tricyclo[6.2.2.0^{1,6}]dodeca-4,6,9-trien-10-yl[1,1,1,1,1-pentacarbonyl-(2-ethoxycarbene)-tungsten]-2-ylidene}tungsten (5c) and pentacarbonyl{11,11-dimethyl-5,9-diphenyl-7-pyrrolidino-2-oxa-tricyclo[6.2.2.0^{1,6}]dodeca-4,6,9-trien-10-yl[1,1,1,1,1-pentacarbonyl-(2-ethoxycarbene)chromium]-2-ylidene}tungsten (5d). Pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 6,6-dimethyl-3-pyrrolidino-cyclohex-2-enone (**2c**) (193 mg, 1.00 mmol) is reacted as described above to afford compound **4c** (390 mg, 62%, R_f=0.5 in pentane/diethyl ether 1:1 on silica gel, red crystals from pentane/dichloromethane 4:1 at −15°C, dec. 99°C). Reaction of compound **1a** (482 mg, 1.00 mmol) in 3 mL of dichloromethane with one half equivalent of compound **2c** (97 mg, 0.50 mmol) in 1 mL of dichloromethane affords a red–brown solution (containing compound **4c** and compound **1a**) initially, from which a dark blue suspension of compound **5c** is generated after stirring at 20°C for 14 h, which is separated by chromatography on silica gel (406 mg, 73%, R_f=0.5 in diethyl ether on silica gel, blue crystals from pentane/dichloromethane 4:1 at −15°C, dec. 92°C). Reaction of pentacarbonyl(8,8-dimethyl-4-phenyl-5-pyrrolidino-7,8-dihydro-2*H*-chromen-2-ylidene)tungsten (**4c**) (126 mg, 0.20 mmol) with pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)chromium (**1b**) (88 mg, 0.20 mmol) affords compound **5d** (123 mg, 63%, R_f=0.5 in diethyl ether on silica gel, blue crystals, dec. 87°C).

4c. ^{1}H NMR ($CDCl_3$, 303 K, 300 MHz): δ 7.91 (1H, s, 3-H), 7.42–7.32 (5H, m, Ph), 5.00 (1H, t, ^3J=5.1 Hz, 6-H), 2.45 (4H, m, 2 NCH_2), 2.37 (2H, d, ^3J=5.1 Hz, 7-H_2), 1.46 (6H, s, 2 CH_3), 1.18 (4H, m, 2 NCH_2CH_2). ^{13}C NMR ($CDCl_3$, 303 K, 75 MHz): δ 246.9 (W=C), 204.6 and 198.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 184.6 (C_q, C8a), 144.8 and 140.0 (C_q each, C4 and C5), 142.0 (CH, C3), 136.4 (C_q, *i*-C Ph); 129.7, 128.8 and 126.9 (1:2:2, CH each, Ph), 117.7 (C_q, C4a), 106.6 (CH, C6), 48.4 (2 NCH_2), 37.0 (C_q, C8), 36.3 (CH_2, C7), 24.1 (2 NCH_2CH_2), 22.9 (2 CH_3). IR (hexane), cm^{-1} (%): 2058.6 (24), 1932.2 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 629 (10) [M^+], 545 (6) [M^+-3 CO], 517 (8) [M^+-4 CO], 489 (48) [M^+-5 CO], 305 (6) [$M^+-W(CO)_5$], 55 (100).



5c. ^{1}H NMR ($CDCl_3$, 298 K, 600 MHz): δ 7.41–7.11 (10H, m, 2 Ph), 6.55 (1H, s, 4-H), 5.10 and 4.91 (1:1H, m each, diastereotopic OCH_2), 4.18 (1H, t, ^3J=3.0 Hz, 8-H), 2.99 and 2.80 (2:2H, m broad each, 2 NCH_2), 1.84 (3H, t, OCH_2CH_3), 1.72 and 1.60 (2:2H, m broad each, 2 NCH_2CH_2), 1.50 (2H, ^2J=12.0 Hz, ^3J=3.0 Hz, 12-H_2),

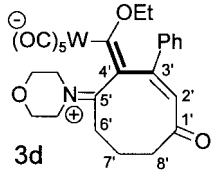
1.31 and 1.19 (3:3H, s each, 2 11-CH_3). ^{13}C NMR ($CDCl_3$, 298 K, 150 MHz): δ 327.5 (W=C2′), 263.3 (W=C3); 205.6, 203.1, 199.7 and 196.3 [1:1:4:4, *trans*- and *cis*-CO, 2 $W(CO)_5$], 164.4 and 164.1 (C_q each, C7 and C9), 142.5 (C_q, C10), 141.0 (C_q, C5), 135.3 (C_q, *i*-C 5-Ph); 129.7, 129.6, 128.5, 128.2, 127.7, 127.3 and 126.8 (2:2:1:2:1:1:1, CH, 2 Ph), 129.3 (CH, C4), 124.5 (C_q, *i*-C 9-Ph), 103.3 (C_q, C6), 92.5 (C_q, C1), 80.7 (OCH_2), 53.7 (2 NCH_2), 45.1 (CH, C8), 44.1 (C_q, C11), 36.3 (CH_2, C12), 27.0 and 26.1 (11-CH_3 each), 25.2 (2 NCH_2CH_2), 14.6 (OCH_2CH_3). IR (hexane), cm^{-1} (%): 2069.3 (20), 2053.6 (30), 1929.4 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 1111 (0) [M^+], 731 (2) [$M^+-W(CO)_5-2$ CO], 56 (100). $C_{42}H_{33}NO_{12}W_2$ (1111.4): calcd C 45.39, H 2.99, N 1.26; found C 44.99, H 3.06, N 1.36. Crystal structure analysis of compound **5c** (code **AUM_692**),[17] formula $C_{42}H_{33}NO_{12}W_2$, M=1111.39, red crystal, 0.10×0.10×0.10 mm^3, a=12.767(3), b=15.260(4), c=21.904(4) Å, β=103.88(2)°, V=4143(2) $Å^3$, ρ_{calc}=1.782 g cm^{-3}, $F(000)$=2144e, μ=56.11 cm^{-1}, empirical absorption correction via ϑ scan data ($0.653 \le C \le 0.999$), Z=4, monoclinic, space group $P2_1/c$ (No. 14), λ=0.71073 Å, T=293 K, $\omega/2\theta$ scans, 7645 reflections collected ($-h$, $-k$, $\pm l$), $[(\sin\theta)/\lambda]$=0.59 $Å^{-1}$, 7297 independent and 4075 observed reflections [$I \ge 2\sigma(I)$], 475 refined parameters, R=0.042, wR^2=0.078, max. residual electron density 1.00 (−0.80) $eÅ^{-3}$, hydrogens calculated and refined as riding atoms.



5d. ^{1}H NMR ($CDCl_3$, 298 K, 600 MHz): δ 7.44–7.09 (10H, m, 2 Ph), 6.55 (1H, s, 4-H), 5.31 and 5.11 (1:1H, m each, diastereotopic OCH_2), 4.16 (1H, t broad, 8-H), 3.07 and 2.78 (2:2H, m broad each, 2 NCH_2), 1.87 (3H, t, OCH_2CH_3), 1.76 and 1.58 (2:4H, m broad each, 2 NCH_2CH_2 and 12-H_2), 1.31 and 1.23 (3:3H, s each, 2 11-CH_3). ^{13}C NMR ($CDCl_3$, 298 K, 150 MHz): δ 358.4 (Cr=C), 263.6 (W=C), 223.4 and 215.0 [1:4, *trans*- and *cis*-CO, $Cr(CO)_5$], 205.6 and 199.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 164.7 and 163.0 (C_q each, C7 and C9), 142.9 (C_q, C10), 141.0 (C_q, C5), 135.5 (C_q, *i*-C 5-Ph), 129.8 (CH, C4); 129.6, 129.4, 129.2, 128.5, 128.2, 127.3 and 126.8 (2:2:1:2:1:1:1, CH, 2 Ph), 123.7 (C_q, *i*-C 9-Ph), 103.0 (C_q, C6), 93.0 (C_q, C1), 78.5 (OCH_2), 53.7 (2 NCH_2), 45.5 (CH, C8), 44.6 (C_q, C11), 36.0 (CH_2, C12), 26.9 and 26.2 (11-CH_3 each), 25.2 (2 NCH_2CH_2), 14.8 (OCH_2CH_3).

Pentacarbonyl[ethoxy-(5-morpholinium-3-phenyl-cyclo-2-octen-4-yliden-1-one)methylen-1-yl]tungstate (3d) and pentacarbonyl(4-phenyl-5-morpholino-7,8-dihydro-2*H*-chromen-2-ylidene)tungsten (4d). To pentacarbonyl-(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) in 3 mL of diethyl ether in a 5-mL screw-top vessel is added with stirring at 20°C 3-morpholino-4-yl-cyclohex-2-enone (**2d**) (181 mg, 1.00 mmol) in 1 mL of diethyl ether. The mixture is stirred 14 h at 20°C and affords an orange colored residue of compound **3d**, which is separated by centrifugation, washed with pentane (3×1 mL each) (544 mg, 82%, R_f=0.8 in pentane/diethyl ether 1:1, orange crystals from pentane/diethyl ether 4:1 at −15°C, dec. 102°C). Compound **3d** (132 mg, 0.20 mmol) in 1 mL of C_6D_6 is heated in an NMR tube for 14 h, 50°C, during which time it is smoothly transformed into compound **4d**. The latter was isolated by chromatography on silica gel (106 mg, 86%, R_f=0.5 in pentane/diethyl ether 1:1, red crystals from pentane/diethyl ether 4:1 bei −15°C, dec. 85°C).

3d. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.45–7.39 and 7.36–7.33 (2:3H, m, Ph), 5.94 (1H, s, 2-H), 4.05 (2H, m broad, OCH_2CH_3), 3.76 and 3.55 (4:4H, m each, 2 OCH_2CH_2 and 2 NCH_2), 3.15 and 2.40 (2:4H, m broad each, 6-H_2-8-H_2), 0.71 (3H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 265.1 (W=C), 202.5 and 199.6 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 191.0 (C_q, C1), 154.8 (C_q, C5), 139.2 (C_q, C4), 132.8 (C_q, *i*-C Ph); 129.0, 128.6 and 127.7 (1:2:2, CH each, Ph), 124.4 (CH, C2), 75.1 (OCH_2CH_3), 64.8 and 51.0 (2 OCH_2CH_2 and 2 NCH_2); 43.0, 40.0 and 31.5 (CH_2 each, C6, C7 and C8), 14.0 (OCH_2CH_3). IR (hexane), cm^{-1} (%): 2055.4 (34), 1928.1 (100) [ν(C≡O)], 1634.0 [ν(C=O)]. MS (70 eV), ^{184}W, *m/e* (%): 663 (1) [M^+], 523 (1) [M^+-5 CO], 339 (52) [$M^+-W(CO)_5$], 310 (100). $C_{26}H_{25}NO_8W$ (663.3): calcd C 47.08, H 3.80, N 2.11; found C 46.89, H 4.27, N 2.29. Crystal structure analysis von compound **3d** (code **AUM_722**),[17] formula $C_{27}H_{26}NO_8Cl_3W$, M=782.69, red crystal, 0.20×0.20×0.10 mm^3, a=7.829(2), b=29.959(2), c=12.368(2) Å, β=92.73(2)°, V=2897.6(9) $Å^3$, ρ_{calc}=1.794 g cm^{-3}, $F(000)$=1536*e*, μ=43.13 cm^{-1}, empirical absorption correction via ϑ scan data ($0.943 \le C \le 0.999$), Z=4, monoclinic, space group $P2_1/c$ (No. 14), λ=0.71073 Å, T=223 K, $\omega/2\theta$ scans, 6312 reflections collected ($+h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda]$=0.62 $Å^{-1}$, 5878 independent and 4452 observed reflections [$I \ge 2\sigma(I)$], 360 refined parameters, R=0.035, wR^2=0.080, max. residual electron density 1.42 (−1.45)*e* $Å^{-3}$, hydrogens calculated and refined as riding atoms.

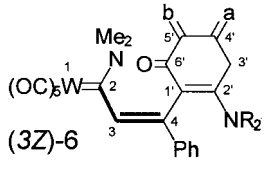


4d. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.92 (1H, s, 3-H), 7.53–7.38 (5H, m, Ph), 5.24 (1H, t, ^3J=5.1 Hz, 6-H), 3.02 (2H, m, 8-H_2), 2.90 (4H, m broad, 2 OCH_2), 2.47 (2H, m, 7H_2), 2.40 (4H, m, 2 NCH_2). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 248.7 (W=C), 204.3 and 198.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 180.1 (C_q, C8a), 144.3 and 143.8 (C_q each, C4 and C5), 142.8 (CH, C3), 136.2 (C_q, *i*-C Ph); 130.1, 129.1 and 127.5 (1:2:2 CH, Ph), 117.6 (C_q, C4a), 105.1 (CH, C6), 65.5 (2 OCH_2), 49.3 (2 NCH_2), 28.9 and 20.2 (CH_2 each, C7 and C8). IR (hexane), cm^{-1} (%): 2060.0 (38), 1932.4 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 617 (15) [M^+], 477 (18) [M^+-5 CO], 293 (10) [$M^+-W(CO)_5$], 99 (100). $C_{24}H_{19}NO_7W$ (617.3): calcd C 46.70, H 3.10, N 2.27; found C 46.77, H 3.85, N 2.31.

Pentacarbonyl(7,7-dimethyl-5-morpholino-4-phenyl-7,8-dihydro-2*H*-chromen-2-ylidene)tungsten (4e). Pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**)

(482 mg, 1.00 mmol) and 5,5-dimethyl-3-pyrrolidino-cyclohex-2-enone (**2e**) (168 mg, 1.00 mmol) is reacted as described above to yield compound **4e** (593 mg, 92%, R_f=0.5 in pentane/diethyl ether 1:1 on silica gel, red crystals from pentane/dichloromethane 4:1 at −15°C, dec. 83°C). ^{1}H NMR ($CDCl_3$): δ 7.88 (1H, s, 3-H), 7.46 and 7.35 (3:2H, m, Ph), 4.96 (1H, s, NC═CH), 2.90 (2H, s, 8-H_2), 2.38 (4H, m, 2 NCH_2), 1.19 [6H, s, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 249.5 (W═C), 204.3 and 198.8 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 179.0 (C_q, C8a), 143.7 (C_q, C4), 142.8 (CH, C3), 142.4 (C_q, ═C–N), 136.2 (C_q, *i*-C Ph); 130.1, 129.0 and 127.5 (CH each, Ph), 117.4 (NC═CH), 116.8 (C_q, C4a), 65.5 (OCH_2), 49.5 (NCH_2), 43.1 (CH_2, C8), 31.6 [$C(CH_3)_2$], 28.1 [$C(CH_3)_2$]. IR (diffuse reflection), cm^{-1}: 2062.9 and 1920.6 [ν(C≡O)], 1620.7 [ν(C═O)]. MS (70 eV), *m/e* (%): 645 (20) [M^+], 505 (20) [M^+−5 CO], 321 (10) [ligand$^+$], 285 (100). $[C_{26}H_{23}NO_7]_2$×$CDCl_3$ (1411.0): calcd C 46.23, H3.37, N 2.03; found C 46.05, H 3.25, N 1.95. X-Ray crystal structure analysis of compound **4e** (code **AUM _018**),[17] formula $C_{26}H_{23}NO_7W$=645.30, red crystal 0.6×0.4×0.3 mm^3, *a*=8.511(1), *b*=13.657(1), *c*=21.909(2) Å, β=91.00(1)°, *V*=2546.2(4) $Å^3$, ρ_{calc}=1.683 g cm^{-3}, *F*(000)=1264*e*, μ=45.81 cm^{-1}, empirical absorption correction via ψ scan data (0.925≤*C*≤0.999), *Z*=4, monoclinic, space group $P2_1/n$ (No. 14), λ=0.71073 Å, *T*=223 K, ω/2θ scans, 5510 reflections collected (−*h*, −*k*, ±*l*), [(sin θ)/λ]=0.62 $Å^{-1}$, 5156 independent and 3983 observed reflections [*I*≥2σ(*I*)], 318 refined parameters, *R*=0.025, wR^2=0.057, max. residual electron density 0.52 (−1.26)*e* $Å^{-3}$, hydrogens calculated and riding.

(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-dimethylamino-4-(2-dimethylamino-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-4-phenyl-1-tungsta-buta-1,3-diene (6a). Pentacarbonyl-[(7,7-dimethyl-5-dimethylamino-4-phenyl-7,8-dihydro-2H-chromen-2-ylidene)tungsten (**4a**) (603 mg, 1.00 mmol) and dimethylamine (ca. 90 mg, 2.00 mmol) were reacted in diethyl ether at 20°C, 5 days to give compound (3*Z*)-**6a** (447 mg, 69%, R_f=0.6 in pentane/diethyl ether 1:1, dec. 131°C, yellow crystals). ^{1}H NMR ($CDCl_3$): δ 7.44–7.16 (5H, m, Ph), 6.37 (1H, s broad, 3-H), 3.78 (3H, s, *syn*-NCH_3), 3.51 83H, s, *anti*-NCH_3), 2.85 [6H, s, 6-$N(CH_3)_2$], 2.45 (2H, m, 5′-H_2), 2.28 (2H, m, 3′-H_2), 2.85 (6H, s, 2 4′-CH_3). ^{13}C NMR $CDCl_3$): δ 246.6 (W═C), 202.2 and 198.6 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 194.6 (C_q, C6′), 163.8 (C_q, C2′), 143.3 (C_q, C4), 140.3 (CH, C3), 132.2 (C_q, *i*-C Ph); 129.0, 126.6 and 126.3 (2:1:2, CH each, Ph), 107.1 (C_q, C1′), 53.2 (*syn* 2-NCH_3), 50.9 (CH_2, C5′), 45.7 (*anti* 2-NCH_3), 44.8 (CH_2, C3′), 42.5 [$N(CH_3)_2$], 32.3 (C_q, C4′), 28.6 and 27.3 (4′-CH_3, each). IR (diffuse reflection), cm^{-1}: 2953.0, 2055.5, 1914.8. IR (hexane), cm^{-1} (%): 2056.4 (8), 1921.3 (100). MS (70 eV), ^{184}W, *m/e* (%): 648 (1) [M^+], 564 (3) [M^+−3 CO], 508 (3) [M^+−5 CO], 324 (98) [M^+−$W(CO)_5$], 281 (100). $C_{26}H_{28}N_2O_6W$ (648.4): calcd C 48.16, H 4.35, N 4.32; found C 47.58, H 4.43, N 4.07.



(3*Z*)-6

(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-dimethylamino-4-(5,5-dimethyl-6-oxo-2-pyrrolidin-1-yl-cyclohex-1-enyl)-4-phenyl-1-tungsta-buta-1,3-diene (6c) and 6,6-dimethyl-2-(1-phenyl-vinyl)-3-pyrrolidin-1-yl-cyclohex-2-enone. Pentacarbonyl(8,8-dimethyl-4-phenyl-7,8-dihydro-2*H*-chromen-5-yl-2-ylidene)pyrrolidin]tungsten (**4c**) (629 mg, 1.00 mmol) and dimethylamine (ca. 90 mg, 2.00 mmol) were reacted as described above to give compound (3*Z*)-**6c** (371 mg, 55%, R_f=0.7 in pentane/diethyl ether 1:1, dec. 131°C, yellow crystals) and 6,6-dimethyl-2-(1-phenyl-vinyl)-3-pyrrolidin-1-yl-cyclohex-2-enone (ca. 35%, resulting from oxidative decomposition of compound **6c**. Typical NMR signals in $CDCl_3$: ═CH_2: δ 5.88 and 4.93, AB-system, ^2J=1.7 Hz; ═CH_2: δ 115.7).

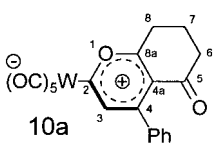
(3*Z*)-6c. ^{1}H NMR ($CDCl_3$): δ 7.41–7.06 (5H, m, Ph), 6.55 (1H, s broad, 3-H), 3.81 [3H, s broad, W(*Z*) NCH_3], 3.60 [3H, s broad, W(*E*) NCH_3], 2.91 (4H, m, 2 NCH_2), 1.88 (4H, m, 3′-H_2 and 4′-H_2), 1.22 and 1.19 (3:3H, s each, 2 5′-CH_3), 1.20 (4H, m, 2 NCH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 248.3 (W═C), 202.7 (C_q, C6′), 202.5 and 199.3 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 161.2 (C_q, C2′), 145.9 (C_q, C4), 141.5 (CH, C3), 133.0 (C_q, *i*-C Ph); 128.5, 127.1 and 126.2 (2:1:2, CH each, Ph), 115.8 (C_q, C1′), 53.9 (*syn* 2-NCH_3), 50.7 (2 NCH_2), 46.6 (*anti* 2-NCH_3), 39.9 (C_q, C5′), 26.3 and 25.5 (CH_2 each, C3′ and C4′), 27.6 and 25.2 (5′-CH_3, each), 22.3 (2 NCH_2CH_2). IR (diffuse reflection), cm^{-1}: 2953.0, 2055.5, 1914.8. IR (hexane), cm^{-1} (%): 2053.2 (16), 1924.7 (100). MS (70 eV), ^{184}W, *m/e* (%): 674 (1) [M^+], 350 (98) [M^+−$W(CO)_5$], 71 (100). X-Ray crystal structure analysis of compound (3*Z*)-**6c** (code **AUM_542**),[17] formula $C_{28}H_{30}N_2O_6W$*$CHCl_3$, *M*=793.76, orange crystal, 0.50×0.30×0.10 mm^3, *a*=11.571(2), *b*=12.513(2), *c*=13.208(1) Å, α=63.19(1), β=71.24(1), γ=78.94(1)°, *V*=1613.6(4) $Å^3$, ρ_{calc}=1.634 g cm^{-3}, *F*(000)=784*e*, μ=38.70 cm^{-1}, empirical absorption correction via ϑ scan data (0.717≤*C*≤0.999), *Z*=2, triclinic, space group $P1_bar$ (No. 2), λ=0.71073 Å, *T*=293 K, ω/2θ scans, 6881 reflections collected (−*h*, ±*k*, ±*l*), [(sin θ)/λ]=0.62 $Å^{-1}$, 6544 independent and 5395 observed reflections [*I*≥2σ(*I*)], 373 refined parameters, *R*=0.038, wR^2=0.102, max. residual electron density 1.36 (−1.14)*e* $Å^{-3}$, trichlormethane disordered, hydrogens calculated and refined as riding atoms.

(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-dimethylamino-4-(4,4-dimethyl-2-morpholino-4-yl-6-oxo-cyclohex-1-enyl)-4-phenyl-1-tungsta-buta-1,3-diene (6e). Pentacarbonyl[(7,7-dimethyl-4-phenyl-7,8-dihydro-2*H*-chromen-5-yl-2-ylidene)-morpholin]tungsten (**4e**) (645 mg, 1.00 mmol) and dimethylamine (ca. 90 mg, 2.00 mmol) were reacted as described above to give compound (3*Z*)-**6e** (407 mg, 65%, R_f=0.6 in pentane/diethyl ether 1:1, dec. 125°C, yellow crystals). ^{1}H NMR ($CDCl_3$): δ 7.33–7.18 (5H, m, Ph), 6.38 (1H, s, 3-H), 3.78 [3H, d, ^5J=1 Hz, *syn* NCH_3], 3.53 [3H, s, *anti* NCH_3]; 3.45, 3.28 and 3.09 (1:2:1H, m each, 2 NCH_2CH_2O); 2.59, 2.42 and 2.18 (1:1:2H, m each, 3′-H_2 and 5′-H_2), 1.16 and 1.14 (3:3H, s each, 4′-CH_3 each). ^{13}C NMR ($CDCl_3$): δ 246.8 (W═C), 202.1 and 199.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 196.2 (C_q, C6′), 162.6 (C_q, C2′), 141.9 (C_q, C4), 141.7 (CH, C3), 131.5 (C_q, *i*-C Ph); 129.0, 128.4 and 126.9 (2:1:2, CH each, Ph), 109.1 (C_q, C1′), 66.5 (2 OCH_2), 53.4 (*syn* 2-NCH_3), 50.9 (CH_2, C5′), 49.7 (2 NCH_2), 46.0 (*anti* 2-NCH_3), 43.4 (CH_2, C3′), 30.7 and 27.5 (4′-CH_3, each), 28.6 (C_q, C4′). IR

(diffuse reflection), cm^{-1}: 2958.4, 2055.8, 1922.2, 1635.8, 1509.9. IR (hexane), cm^{-1}: 2056.7 (20), 1920.2 (100). MS (70 eV), ^{184}W, *m/e* (%): 690 (0) [M^+], 366 (80) [$M^+-W(CO)_5$], 322 (100). $C_{28}H_{30}N_2O_7W$ (690.4): calcd C 48.71, H 4.38, N 4.06; found C 49.14, H 4.41, N 3.94.

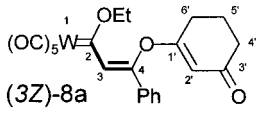
(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-(3-oxo-cyclohex-1-enyloxy)-4-phenyl-1-tungsta-1,3-butadien (8a), pentacarbonyl(5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (10a) and pentacarbonyl[8-(3-ethoxy-1-phenyl-allylidene)-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene]tungsten (12a). To pentacarbonyl-(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and cyclohexan-1,3-dione (**7a**) (112 mg, 1.00 mmol) in a 5-mL screw-top vessel is added triethylamine (50 mg, 0.50 mmol) in 2 mL of diethyl ether dropwise and with vigorous stirring at 20°C. After 5 min at 20°C 2 mL of pentane is added and the mixture is homogenized by stirring or treatment with ultrasonic radiation. Recrystallisation of the residue from pentane/dichloromethane 1:1 at −15°C affords compound **10a** (252 mg, 46%, R_f=0.5 in pentane/dichloromethane 2:1 on silica gel, red crystals, dec. 121°C). Chromatography of the mother liquor on silica gel with pentane/dichloromethane (5:1) yields a violet fraction containing a second crop of compound **10a**. Compound (3*Z*)-**8a** is eluted with dichloromethane in a brown fraction (208 mg, 35%, R_f=0.2 in pentane/dichloromethane 2:1 on silica gel, brown crystals from pentane/dichloromethane 4:1 at −15°C, dec. 101°C). Reaction of pentacarbonyl(5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (**10a**) (121 mg, 0.22 mmol) with compound **1a** (107 mg, 0.22 mmol) and triethylamine (22 mg, 0.22 mmol) in 4 mL diethyl ether yields the α-condensation product **12a** (4:1 mixture of *syn*-**12a** and *anti*-**12a**) after 7 days at 20°C, which was isolated by chromatography on silca gel with dichloromethane (112 mg, 78%, R_f=0.6 in dichloromethane on silica gel, dark-red oil). Compound **12a** was also obtained from reaction of **1a** with **7a** in a molar ratio 2:1.

10a. ^1H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.91 (1H, s, 3-H), 7.56–7.25 (5H, m, Ph), 3.26 (2H, dd, 8-H_2), 2.62 (2H, dd, 6-H_2), 2.26 (2H, m, 7-H_2). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 262.7 (W=C), 204.4 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 193.4 (C_q, C5), 182.6 (C_q, C8a), 144.8 (CH, C3), 143.6 (C_q, C4), 136.2 (C_q, *i*-C Ph); 129.8, 128.2 and 127.7 (1:2:2, CH each, Ph), 119.4 (C_q, C4a), 38.4 (CH_2, C8), 29.7 (CH_2, C6), 19.5 (CH_2, C7). IR (hexane), cm^{-1} (%): 2063.3 (40), 1943.0 (100) [ν(C≡O)], 1700.4 (15) [ν(C=O)]. MS (70 eV), ^{184}W, *m/e* (%): 548 (38) [M^+], 520 (12) [M^+−CO], 492 (2) [M^+−2 CO], 464 (65) [M^+−3 CO], 436 (8) [M^+−4 CO], 408 (58) [M^+−5 CO], 224 (6) [$M^+-W(CO)_5$], 99 (100). $C_{20}H_{12}O_7W$ (548.2): calcd C 43.82, H 2.21; found C 43.64, H 3.07.



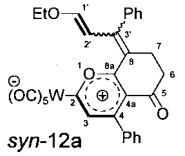
10a

(3*Z*)-8a. ^1H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.58 (1H, s, 3-H), 7.54–7.36 (5H, m, Ph), 5.26 (1H, s, 2′-H), 4.86 (2H, q, OCH_2), 2.57 (2H, t, 4′-H_2), 2.28 (2H, dd, 6′-H_2), 2.01 (2H, m, 5′-H_2), 1.58 (3H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 304.7 (W=C), 203.6 and 197.1 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 198.6 (C_q, C3′), 174.6 (C_q, C1′), 143.3 (C_q, C4), 132.8 (C_q, *i*-C Ph); 132.3, 131.3, 129.3 and 126.8 (1:1:2:2, CH each, Ph and C3), 107.8 (CH, C2′), 79.7 (OCH_2), 36.3 (CH_2, C4′), 27.9 and 21.0 (CH_2 each, C5′ and C6′), 15.0 (OCH_2CH_3). IR (hexane), cm^{-1} (%): 2067.4 (40), 1945.3 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 594 (1) [M^+], 482 (2) [M^+−4 CO −1], 270 (0) [$M^+-W(CO)_5$], 105 (100). $C_{22}H_{18}O_8W$ (594.2): calcd C 44.47, H 3.05; found C 44.67, H 3.24.



(3*Z*)-8a

***syn*-12a [*anti*-12a].** ^1H NMR ($CDCl_3$, 298 K, 600 MHz): δ 7.83 [7.70] (1H, s, 3-H), 7.47–7.23 [7.47–7.23] (10H, m, 2 Ph), 7.27 [6.41] (1H, d, ^3J=12 Hz, 2′-H), 6.30 [6.20] (1H, d, ^3J=12 Hz, 2′-H), 3.92 [3.68] (2H, q, OCH_2), 2.50 and 2.45 [3.04 and 2.74] (2:2H, m each, 6-H_2 and 7-H_2), 1.28 [1.31] (3H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 298 K, 150 MHz): δ 257.7 [260.1] (W=C), 204.2 and 198.0 [204.0 and 197.9] [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 193.9 [194.1] (C_q, C5), 176.3 [177.2] (C_q, C8a), 162.0 [160.1] (CH, C1′), 151.5 [150.8] (C_q, C3′), 144.8 [142.9] (C_q, C4), 143.4 [144.1] (CH, C3), 139.0 [137.8] (C_q, *i*-C 3′-Ph), 137.1 [136.6] (C_q, *i*-C 4-Ph); 130.7–127.6 [130.7–127.6](10 CH each, 2 Ph), 118.4 [120.1] (C_q, C4a), 117.7 [118.7] (C_q, C8), 110.0 [108.3] (CH, C2′), 68.5 [67.7] (OCH_2), 39.0 [39.2] (CH_2, C6), 28.1 [28.9] (CH_2, C7), 14.8 [14.9] (OCH_2CH_3). IR (hexane), cm^{-1} (%): 2060.6 (40), 1937.2 (100) [ν(C≡O)], 1700.4 (10) [ν(C=O)]. MS (70 eV), ^{184}W, *m/e* (%): 706 (0) [M^+], 566 (0) [M^+−5 CO], 382 (100) [$M^+-W(CO)_5$].



syn-12a

(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-(4,4-dimethyl-3-oxo-cyclohex-1-enyloxy)-4-phenyl-1-tungsta-1,3-butadiene (8b), (3*Z*)-1,1,1,1,1-pentacarbonyl-2-ethoxy-4-(6,6-dimethyl-3-oxo-cyclohex-1-enyloxy)-4-phenyl-1-tungsta-1,3-butadiene (9b), pentacarbonyl(6,6-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (10b), pentacarbonyl(8,8-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (11b) and pentacarbonyl[8-(3-ethoxy-1-phenyl-allylidene)-6,6-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene]tungsten (12b). Pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**) (482 mg, 1.00 mmol) and 4,4-dimethyl-cyclohexan-1,3-dione (140 mg, 1.00 mmol) (**7b**) was reacted as described above and gave compound **10b** (104 mg, 18%, R_f=0.6 in pentane/dichloromethane 2:1 on silica gel, red crystals, dec. 100°C), compound **11b** (47 mg, 8%, R_f=0.3 in pentane/dichloromethane 2:1 on silica gel, red crystals, dec. 98°C), compound (3*Z*)-**8b** (224 mg, 36%, R_f=0.2 in pentane/dichloromethane 2:1 on

silica gel, brown crystals, dec. 88°C) and compound (3*Z*)-**9b** (106 mg, 17%, R_f=0.1 in pentane/dichloromethane 2:1 on silica gel, brown oil). Reaction of pentacarbonyl(6,6-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (**10b**) (144 mg, 0.25 mmol) with compound **1a** (121 mg, 0.25 mmol) as described above affords compound **12b** (95 mg, 52%, R_f=0.6 in dichloromethane on silica gel, 2:1-mixture of *syn*-**12b** and *anti*-**12b**, dark-red oil).

10b. ^{1}H NMR ($CDCl_3$, 303 K, 300 MHz): δ 7.89 (1H, s, 3-H), 7.45 and 7.25 (3:2H, m each, Ph), 3.26 (2H, dd, 8-H_2), 2.07 (2H, dd, 7-H_2), 1.22 (6H, s, 2 5-CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 75 MHz): δ 262.5 (W=C), 204.3 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 198.4 (C_q, C5), 180.8 (C_q, C8a), 144.8 (CH, C3), 144.4 (C_q, C4), 136.4 (C_q, *i*-C Ph); 129.7, 128.3 and 127.3 (1:2:2, CH each, Ph), 118.2 (C_q, C4a), 42.1 (C_q, C6), 33.0 (CH_2, C8), 26.3 (CH_2, C7), 23.8 (2 CH_3). IR (hexane), cm^{-1} (%): 2062.8 (40), 1945.2 (100) [ν(C≡O)]. IR (diffuse reflection), cm^{-1}: 1690.7 [ν(C=O)]. MS (70 eV), ^{184}W, *m/e* (%): 576 (15) [M^+], 548 (5) [M^+-CO], 492 (30) [M^+-3 CO], 464 (10) [M^+-4 CO], 436 (20) [M^+-5 CO], 57 (100). $C_{22}H_{16}O_7W$ (576.2): calcd C 45.86, H 2.80; found C 45.69, H 2.87.

11b. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.88 (1H, s, 3-H), 7.44 and 7.26 (3:2H, m each, Ph), 2.65 (2H, dd, 8-H_2), 2.10 (2H, dd, 7-H_2), 1.64 (6H, s, 2 CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 262.5 (W=C), 204.4 and 198.0 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 193.6 (C_q, C5), 187.5 (C_q, C8a), 144.5 (CH, C3), 144.1 (C_q, C4), 136.5 (C_q, *i*-C Ph); 129.7, 128.2, 127.7 and 124.9 (1:2:1:1, CH each, Ph), 117.8 (C_q, C4a), 37.6 (C_q, C8), 35.4 and 34.2 (CH_2 each, C6 and C7), 26.7 (2 8-CH_3). IR (hexane), cm^{-1} (%): 2062.7 (35), 1938.9 (100) [ν(C≡O)]. IR (diffuse reflection), cm^{-1}: 1699.9 [ν(C=O)]. MS (70 eV), ^{184}W, *m/e* (%): 576 (48) [M^+], 548 (12) [M^+-CO], 492 (80) [M^+-3 CO], 464 (20) [M^+-4 CO], 436 (42) [M^+-5 CO], 57 (100). $C_{22}H_{16}O_7W$ (576.2): calcd C 45.86, H 2.80; found C 45.58, H 2.95.

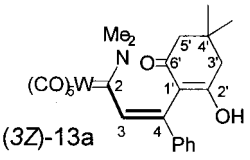
(3*Z*)-8b. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.58 (1H, s, 3-H), 7.56–7.39 (5H, m, Ph), 5.17 (1H, s, 2′-H), 4.87 (2H, q, OCH_2), 2.60 (2H, t, 6′-H_2), 1.84 (2H, t, 5′-H_2), 1.59 (3H, t, OCH_2CH_3), 1.06 (6H, s, 2 CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 304.8 (W=C), 203.6 and 197.2 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 203.4 (C_q, C3′), 172.5 (C_q, C1′), 143.8 (C_q, C4), 133.0 (C_q, *i*-C Ph); 132.4, 131.4, 129.4 and 126.9 (1:1:2:2, CH each, Ph and C3), 106.4 (CH, C2′), 79.8 (OCH_2), 40.1 (C_q, C4′), 34.8 (CH_2, C6′), 25.6 (CH_2, C5′), 24.2 (2 CH_3), 15.1 (OCH_2CH_3). IR (diffuse reflection), cm^{-1}: 1662.8 [ν(C=O)]. IR (hexane), cm^{-1} (%): 2067.1 (30), 1943.9 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 622 (10) [M^+], 482 (30) [M^+-5 CO], 105 (100). $C_{24}H_{22}O_8W$ (622.3): calcd C 46.32, H 3.56; found C 45.96, H 4.08.

(3*Z*)-9b. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.33 (1H, s, 3-H), 7.56–7.35 (5H, m, Ph), 5.10 (1H, s, 2′-H), 4.93 (2H, q, OCH_2), 2.36 (2H, dd, 4′-H_2), 1.88 (2H, dd, 5′-H_2), 1.57 (3H, t, OCH_2CH_3), 1.40 (6H, s, 2 CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 90 MHz): δ 307.7 (W=C), 203.6 and 196.9 [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 198.5 (C_q, C3′), 179.6 (C_q, C1′), 142.5 (C_q, C4), 133.1 (C_q, *i*-C Ph), 133.4 (CH, C3); 130.1, 129.2 and 126.8 (1:2:2, CH each, Ph), 106.6 (CH, C2′), 80.0 (OCH_2), 35.6 (C_q, C6′), 36.5 (CH_2, C5′), 33.8 (CH_2, C4′), 25.9 (2 CH_3), 15.3 (OCH_2CH_3). IR (diffuse reflection), cm^{-1} 1664.2 [ν(C=O)]. IR (hexane), cm^{-1} (%): 2066.9 (30), 1942.6 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e* (%): 622 (1) [M^+], 482 (8) [M^+-5 CO], 99 (100).

***syn*-12b [*anti*-12b].** ^{1}H NMR ($CDCl_3$, 303 K, 300 MHz): δ 7.84 [7.72] (1H, s, 3-H), 7.49–7.19 [7.49–7.19] (10H, m, 2 Ph), 7.23 [6.38] (1H, d, ^3J=12 Hz, 2′-H), 6.29 [6.21] (1H, d, ^3J=12 Hz, 2′-H), 3.91 [3.87] (2H, q, OCH_2), 2.32 [2.86] (2H, m broad, 7-H_2), 1.27 [1.30] (3H, t, OCH_2CH_3), 1.01 [1.27] (6H, s, 2 6-CH_3). ^{13}C NMR ($CDCl_3$, 303 K, 75 MHz): δ 257.6 [259.8] (W=C), 204.2 and 198.1 [204.0 and 198.0] [1:4, *trans*- and *cis*-CO, $W(CO)_5$], 204.2 [204.0] (C_q, C5), 175.4 [176.3] (C_q, C8a), 161.9 [160.1] (CH, C1′), 152.2 [149.9] (C_q, C3′), 144.1 [143.7] (C_q, C4), 143.6 [145.7] (CH, C3), 139.2 [138.1] (C_q, *i*-C 3′-Ph), 137.5 [137.1] (C_q, *i*-C 4-Ph); 130.5–127.3 [130.5–127.3] (10 CH each, 2 Ph), 117.0 and 116.4 [118.7 and 117.7] (C_q each, C4a and C8), 110.2 [108.7] (CH, C2′), 68.6 [67.8] (OCH_2), 43.9 [45.4] (C_q, C6), 42.3 [41.9] (CH_2, C7), 24.1 [24.7] (2 CH_3), 14.9 [14.8] (OCH_2CH_3). IR (diffuse reflection), cm^{-1}: 1696.6 [ν(C=O)]. IR (hexane), cm^{-1} (%): 2060.6 (30), 1936.6 (100) [ν(C≡O)], 1700.4 (10) [ν(C=O)]. MS (70 eV), ^{184}W, *m/e* (%): 734 (10) [M^+], 650 (5) [M^+-3 CO], 594 (5) [M^+-5 CO], 99 (100).

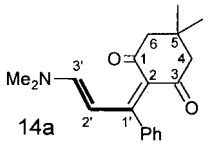
(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-dimethylamino-4-(2-hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-4-phenyl-1-tungsta-1,3-butadiene (13a) and 2-(3-dimethylamino-1-phenyl-2-propenylidene)-5,5-dimethyl-cyclohexan-1,3-dione (14a). To pentacarbonyl(7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (**10c**) (576 mg, 1.00 mmol) in 4 mL of dichloromethane in a 5-mL screw-top vessel was added ca. two equivalents of dimethylamine at 25°C. After color change to yellow (ca. 15 min) solvent is removed to leave an oily residue, which was recrystallized from $CDCl_3/C_6D_6$ to afford pale yellow crystals of compound **13a**×1/2$HNMe_2$. Compound **13a** is unstable in solution and undergoes fragmentation within ca. 15 min at 25°C to enamine **14a** and $(CO)_5W(HNMe_2)$ as the only detected products.

13a. ^{1}H NMR ($CDCl_3$): δ 7.38, 7.28 and 7.19 (2:2:1H, m each, 4-Ph); 6.78 (1H, s, 3-H), 3.62 and 3.42 (6H, s, NMe_2), 2.22 (4H, dd, ^2J=16 Hz, 2 CH_2CO), 1.09 (6H, s, CMe_2). IR (diffuse reflection) cm^{-1}: 2058.3, 1966.4 and 1884.8 [ν(C≡O)], 1593.9 [ν(C=O)]. X-Ray crystal structure analysis of compound **13a** (=code **AUM_018**): formula $C_{26}H_{39}N_2O_7W$, M=666.37, red crystal 0.5×0.4×0.3 mm^3, a=16.094(2), b=14.476(1), c=24.014(2) Å, V=5594.7(9) $Å^3$, ρ_{calc}=1.582 g cm^{-3}, $F(000)$=2640e, μ=41.73 cm^{-1}, empirical absorption correction via ψ scan data (0.85.1≤C≤0.998), Z=8, orthorhombic, space group *Pbcn* (No. 60), λ=0.71073 Å, T=293 K, $\omega/2\theta$ scans, 5654 reflections collected ($+h$, $+k$, $+l$), [(sin θ)/λ]=0.62 $Å^{-1}$, 5654 independent and 3004 observed reflections [$I\geq 2\sigma(I)$], 331 refined parameters, R=0.039, wR^2=0.100, max. residual electron density 1.58 (−0.97)e $Å^{-3}$, hydrogens calculated and refined as riding atoms.



(3Z)-13a

14a. ^{1}H NMR ($CDCl_3$): δ 7.79 (1H, d, ^3J=13 Hz, 3′-H), 7.31 and 7.03 (3:2H, m each, 1′-Ph), 6.77 (1H, d, ^3J=13 Hz, 2′-H), 3.09 and 3.01 (6H, s, NMe_2), 2.35 (4H, s, 2 CH_2CO), 1.04 (6H, s, CMe_2). ^{13}C NMR ($CDCl_3$): δ 197.6 (C_q, C1 and C3), 168.1 (C_q, C1′), 161.5 (CH, C3′), 141.5 (C_q, *i*-C Ph); 128.4, 127.6 and 127.3 (CH each, Ph), 118.3 (C_q, C2), 105.9 (CH, C2′), 54.1 ($OCCH_2$), 51.4 (NMe), 29.9 (CMe_2), 28.5 [$C(CH_3)_2$].



14a

(3*Z*)-1,1,1,1,1-Pentacarbonyl-2-pyrrolidino-4-(2-hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-4-phenyl-1-tungstena-1,3-butadiene (13b) and 2-(3-Pyrrolidino-1-phenyl-2-propenylidene)-5,5-dimethyl-cyclohexan-1,3-dione (14b). Pentacarbonyl(7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-2*H*-chromen-2-ylidene)tungsten (**10c**) (576 mg, 1.00 mmol) is reacted as described above with ca. two equivalents of pyrrolidine at 25°C to give compounds **13b** and **14b**.

13b. ^{1}H NMR ($CDCl_3$): δ 7.39, 7.20 and 7.11 (2:2:1H, Ph); 6.60 (1H, s, 3-H); 4.43, 4.04, 3.83 and 3.50 (1H each, m broad each, 2 NCH_2), 2.19 (4H, s, CH_2CO), 2.01 (4H, m, CH_2CH_2), 1.10 [6H, s, $C(CH_3)_2$]. IR (diffuse reflection) cm^{-1}: 2054.1, 1963.7 and 1878.2 [ν(C≡O)].

14b. ^{1}H NMR ($CDCl_3$): δ 7.73 (1H, d, ^3J=12 Hz, 3′-H), 7.32 and 7.09 (3:2H, m each, 1′-Ph), 7.01 (1H, d, ^3J=12 Hz, 2′-H), 3.54 and 3.41 (4H, m each, 2 NCH_2), 2.36 (4H, s, 2 CH_2CO), 2.05 and 1.91 (4H, m each, 2 CH_2), 1.08 [6H, s, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 198.3 and 197.5 (C_q each, C=O and =COH), 167.0 (C_q, C1′), 157.4 (CH, C3′), 142.5 (C_q, *i*-C Ph), 128.7 and 127.3 (each CH, Ph), 107.5 (CH, C2′), 54.1 (CH_2CO), 53.5 and 45.1 (2 NCH_2), 29.9 [$C(CH_3)_2$], 28.6 [$C(CH_3)_2$], 26.5 and 24.9 (CH_2CH_2).

Acknowledgements

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