Organic syntheses via transition metal complexes, LXXXVIII [1] 1-Metalla-1,3,5,7-octatetraenes from (1-alkynyl)carbene complexes of chromium and tungsten via [6-(1-alkenyl)]pyranylidene complexes [2]

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Abstract

[6-(1-Ethenyl)]pyran-2-ylidene complexes **4a,b** and [6-(1-butadienyl)]pyran-2-ylidene complexes **6a,b** are obtained as major products together with the corresponding regioisomeric pyranylidene complexes **5a,b** and **7a,b** respectively as minor products by base-induced condensation of (1-alkynyl)carbene complexes $(CO)_5M=C(OEt)-C\equiv CPh$ **1a,b** (M = Cr, W) with *trans*-6-phenyl-5-hexene-2,4-dione (**2b**) and *trans,trans*-8-phenyl-octa-5,7-diene-2,4-dione (**2c**) in moderate yields. X-ray data of the isomeric tungsten complexes **4b** and **5b** [$C_{26}H_{16}O_7W$, blue (red), triclinic (monoclinic), space group $P\bar{1}$ ($P2_1/c$), $Z = 2$ (4)] and the pyranylidene compound **6b** [$C_{28}H_{18}O_7W$, triclinic, space group $P\bar{1}$, $Z = 2$] are reported. Amination of compound **4b** with dimethylamine affords 1-metalla-1,3,5,7-octatetraenes (Z,Z,E)-**9A** and (Z,Z,E)-**9B** (2:1) in 89% total yield. © 1997 Elsevier Science S.A.

Keywords: 1-Metalla-1,3,5,7-octatetraenes; Carbene complexes; Chromium and tungsten complexes; Pyranylidene complexes; Aminocarbene complexes; Conjugated π systems

1. Introduction

The usefulness of Fischer carbene complexes [2,3] (first example in Ref. [2]) to organic synthesis has been amply demonstrated over the last decades. Several reviews have been published covering both thermal [4,5] and photochemical [6] reactions of such compounds with a broad array of various organic functional groups. Reactions of (1-alkynyl)carbene complexes $(CO)_5M=C(OEt)-C\equiv CPh$ **1a,b** (M = Cr, W) with carbon nucleophiles, e.g. enol ethers [5,7–9] or enamines [10–14], offer useful routes to the generation of carbocyclic ring compounds. For example, it has been found recently that an overall [3 + 2] cycloaddition of compounds **1** to tertiary 1-amino cycloalkenes yields cy-

clopentadiene annulation products [13,15], and the annulation process was shown to proceed via the initial formation of 1-metalla-1,3,5-hexatrienes $(CO)_5M=C(OEt)-CH=C(Ph)-CR=CRX$ (X = OR', NR'_2; R = H, alkyl, aryl) [10–12]. It has also been demonstrated that six-membered *2H*-pyran-ylidene complexes, e.g. compounds **3**, are very suitable starting materials for the generation of 1-metalla-1,3,5-trienes by ring-opening reactions [16]. This route to the formation of 1-metalla-1,3,5-trienes proves to be very convenient, especially since pyranylidene complexes **3** can easily be obtained by condensation of enolizable carbonyl compounds, e.g. 2,4-pentanedione (**2a**), with (1-alkynyl)carbene complexes **1a,b** (Scheme 1) [1,16,17].

With respect to the high versatility of compounds **3a,b** in regioselective cycloaddition reactions [1] as well as precursors to 1-metalla-1,3,5-hexatrienes [16], we intend to extend our studies to the formation of the vinylogous compounds, 1-metalla-1,3,5,7-tetraenes $M=C-C=C-C=C-C=C$ and 1-metalla-1,3,5,7,9-pentaenes $M=C-C=C-C=C-C=C-C=C$, from alkenyl (butadienyl) *2H*-pyran-ylidene precursors. In this paper, we report on the synthesis and the crystal structures of several new precursors of 1-metalla-1,3,5,7-tetraene and
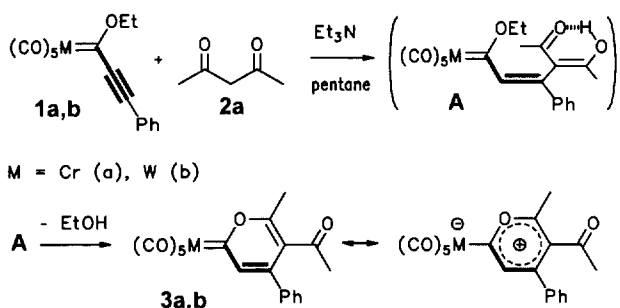

Scheme 1. Pyranylidene complexes **3a,b** via condensation of 2,4-di-ketone **2a** with (1-alkynyl)carbene complexes **1a,b**.

1-metalla-1,3,5,7,9-pentaene complexes, which were obtained via condensation of compounds **1a,b** with α,β-unsaturated 2,4-diones **2b** and **2c** respectively (Scheme 2). We also report on the generation of 1-tungsta-1,3,5,7-octatetraenes by aminolysis of the alkenyl 2*H*-pyran-ylidene tungsten complex **4b**.

2. Results and discussion

Compound **2b**, needed as substrate for the generation of alkenyl pyranylidene complexes, can be prepared by condensation of methyl cinnamate with acetone in the presence of sodium wires [18], but a small scale preparation, which affords a very clean product in our hands, is based on the dehydration of δ-hydroxy-β-diketone, obtained from the reaction of the 2,4-pentanedione dianions and benzaldehyde [19] (Scheme 2). Compound **2c** was prepared in an analogous manner, by condensation of the dianion with cinnamaldehyde instead of benzaldehyde. The IR and NMR spectra of the diketones **2b** and **2c** indicate that enol tautomers **2′b** and **2′c** respectively are present almost exclusively in solution, due to stabilization by π conjugation of the CH=CHPh with the β-C=O group (Scheme 2).
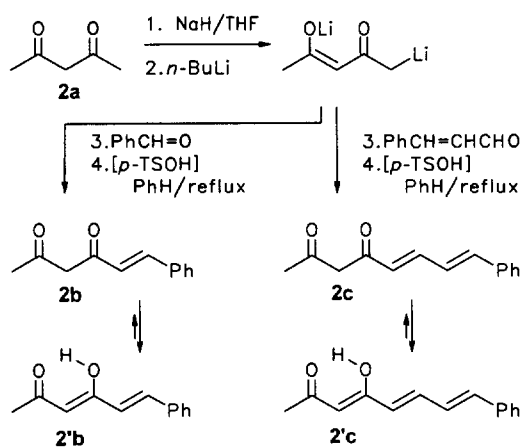
Scheme 2. Preparation of enolizable 2,4-diketones **2b,c** via 2,4-penta-nedione dianions.
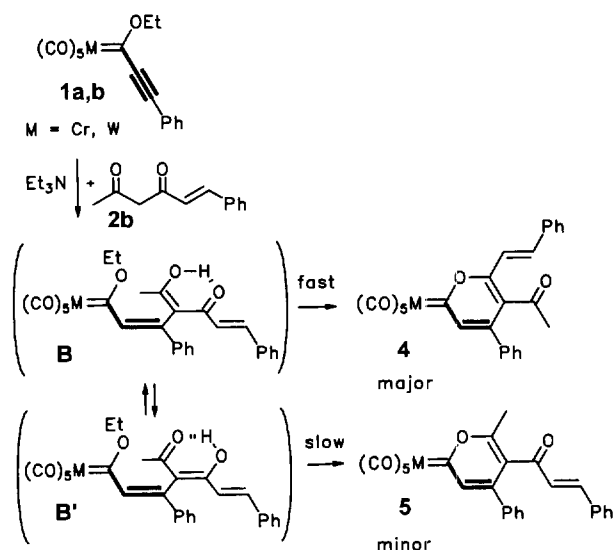
Scheme 3. Synthesis of the pyranylidene complexes **4** and **5**.

Since the enolizable 2,4-diketone **2a** forms a pyranylidene complex (Scheme 1), it can reasonably be expected that the introduction of one or two conjugated C=C bonds into the carbon skeleton of **2** may result in some additional stabilization of such compounds as well as of the pyranylidene complexes prepared thereof. Condensation of 2,4-diketones **2b** and **2c** respectively with (1-alkynyl)carbene complexes **1a,b** was carried out in the presence of catalytic amounts of triethylamine in pentane at 20 °C [1,16]. It seems that the reactions proceed via initial formation of 2-ethoxy-1-metalla-1,3,5,7-tetraenes **B** and **B′** (and 2-ethoxy-1-metalla-1,3,5,7,9-pentaenes **C** and **C′** respectively), which rapidly undergo ring-closure at ambient conditions to the pyranylidene complexes **4** and **5** (**6** and **7** respectively) by elimination of EtOH (Schemes 3 and 4). Complexes **4** and **6** are formed as major products, in
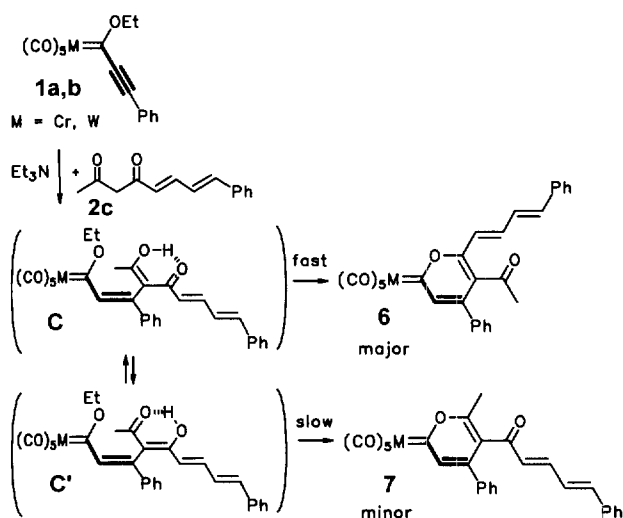
Scheme 4. Synthesis of the pyranylidene complexes **6** and **7**.

line with expectations based on the relative nucle-ophilicity of the C=O groups of compounds **B** and **B′** (**C** and **C′** respectively).

It should be noted that the reaction of diketone **2c** with the chromium complex **1a** affords low yields of complexes **6a** and **7a** only, but mainly as yet unidenti-fied organic products as well as metal complexes. Inter-estingly, condensation of compounds **2** with the tung-sten complex **1b** is much faster than with the chromium complex **1a**. Petroleum ether, dichloromethane, and
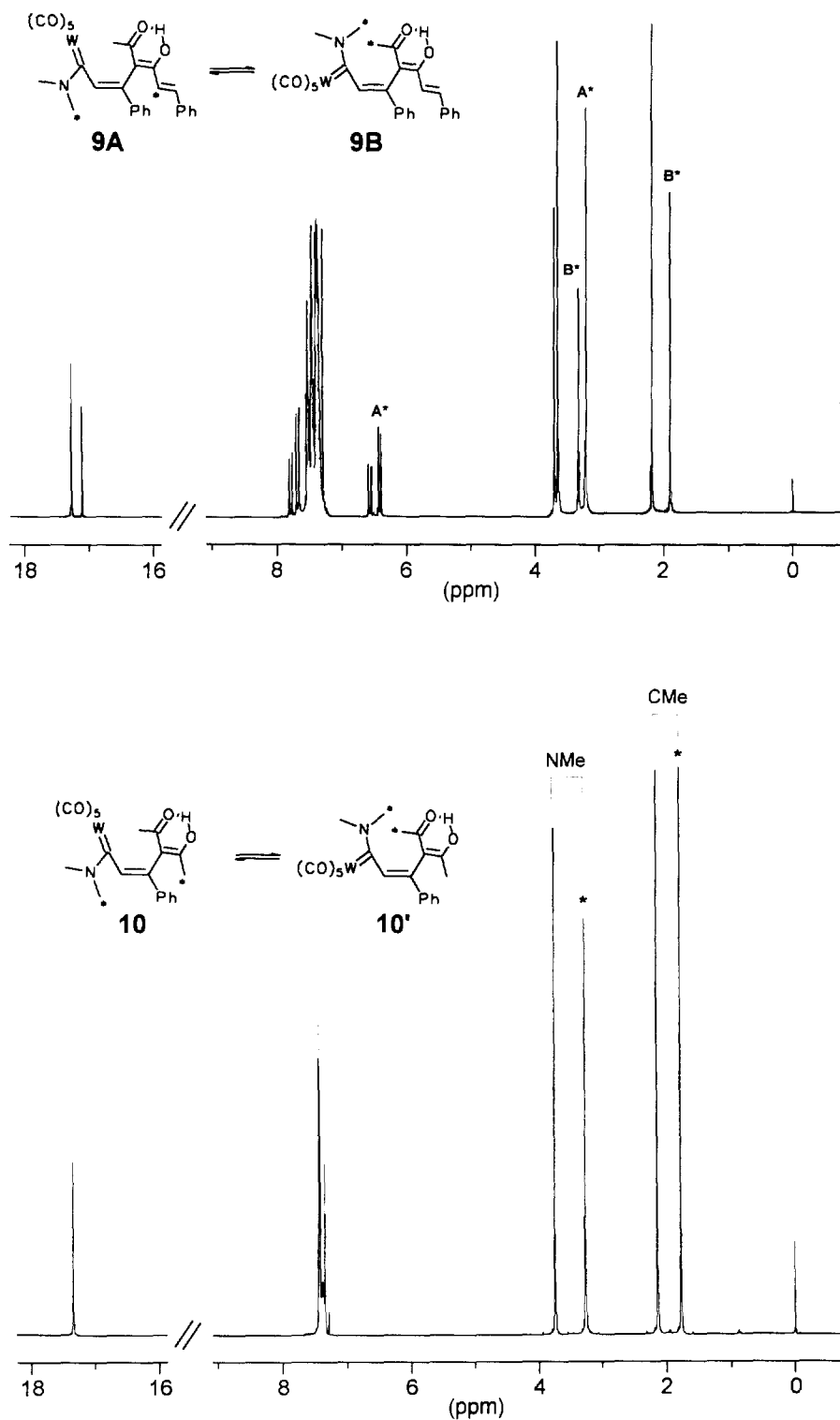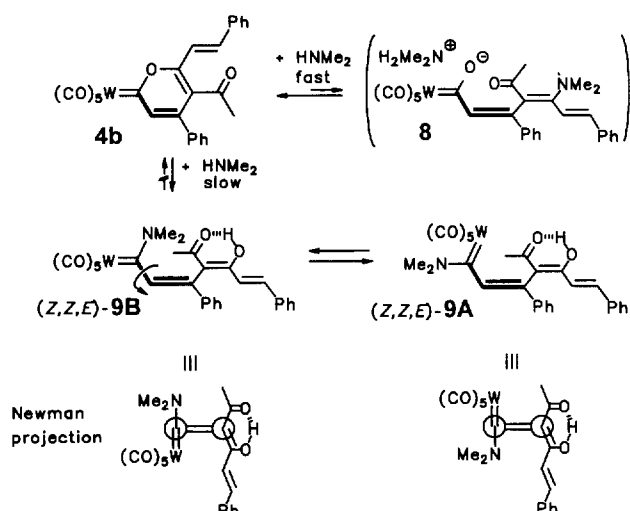

Fig. 1. ¹H NMR spectra of the 1-tungsta-1,3,5,6-octatetraenes **9A / 9B** and the 1-tungsta-1,3,5-hexatriene **10**.

Scheme 5. 1-Tungsta-1,3,5,7-octatetraenes **9** by ring-opening aminolysis of pyranylidene complex **4b**.

pentane are suitable reaction media. Preparation of the pyranylidene complex **4b** has also been achieved by condensation of pyranylidene complex **3b** with benzaldehyde in the presence of triethylamine/trimethylchlorosilane [1], though in small yield only. It is quite obvious that condensation of (1-alkynyl)carbene complexes **1a,b** with **2b,c** is a more efficient route to the preparation of alkenyl pyranylidene complexes than condensation of compound **3** with an aldehyde.

3. Spectroscopy of alkenyl pyranylidene complexes

The strong bands in the region 2060–1897 cm^{-1} of the IR spectra of these complexes exhibit typical patterns expected for an M(CO)$_5$ unit. The moderately strong stretching vibrations of the C=C bonds of the *trans*-CH=CHPh groups are present in the region 1702–1621 cm^{-1}. The strong bands of C=O groups observed in the spectra of the free diketones **2b,c** disappear on complexation and are red-shifted in those of the pyranylidene complexes to [ν(C–O)] 1100–1200 cm^{-1}. The proton signals of the AB-systems of *trans*-CH=CHPh in ^{1}H NMR spectra of the free diketones are shifted downfield in the corresponding pyranylidene complexes, probably due to anisotropic deshielding by the pyrylium π system. A singlet assigned to the CH group of the enol moiety HOC=CH of the free diketones **2b,c** is not present in the spectra of the pyranylidene complexes. The proton shifts of the methyl groups in the major complexes (**4** and **6**) are at lower field than in the minor complexes (**5** and **7**), which indicates that the methyl groups are present in the acetyl (O=C–CH$_3$) in case of the major complexes and

attached to the ring-carbon atoms C6 (6-CH$_3$) in the minor complexes. The resonance of 3-H is shown at low field (7.89–8.11 ppm) due to the anisotropic influence of the neighboring phenyl group. The ^{13}C resonance signals of C6 at 168–176 ppm and M=C (282–283 ppm, M = Cr; 256–257 ppm, M = W) are very similar to those of compounds **3** (**3a** in C$_6$D$_6$ [1]: C6 175.9 ppm, Cr=C 283.4; **3b** in CDCl$_3$ [16]: C6 173.9; W=C 258.4). The signal of C2 is significantly shifted upfield compared to the carbene carbon atoms of (CO)$_5$Cr=C(OEt)–C≡CPh (δ 314.1 ppm) [20] and (CO)$_5$W=C(OEt)–Ph (δ 319.6 ppm) [21], indicating a strong contribution of a pyrylium ylide resonance struc-

Table 1
Selected bond lengths (Å) and angles (°) of complexes **4b** and **5b**

Complex 4b			
W–C(2)	2.180(5)	C(6)–O(1)–C(2)	124.9(4)
O(1)–C(6)	1.354(5)	O(1)–C(2)–C(3)	113.8(4)
O(1)–C(2)	1.380(6)	O(1)–C(2)–W	115.8(3)
C(2)–C(3)	1.396(7)	C(3)–C(2)–W	130.1(4)
C(3)–C(4)	1.383(7)	C(4)–C(3)–C(2)	124.1(4)
C(4)–C(5)	1.426(6)	C(3)–C(4)–C(5)	118.2(4)
C(4)–C(41)	1.480(6)	C(3)–C(4)–C(41)	119.4(4)
C(5)–C(6)	1.367(7)	C(5)–C(4)–C(41)	122.2(4)
C(5)–C(51)	1.518(6)	C(6)–C(5)–C(4)	118.2(4)
C(51)–O(51)	1.196(7)	C(6)–C(5)–C(51)	119.6(4)
C(51)–C(52)	1.494(8)	C(4)–C(5)–C(51)	122.2(4)
C(6)–C(7)	1.454(6)	O(51)–C(51)–C(52)	122.9(5)
C(7)–C(8)	1.329(7)	O(51)–C(51)–C(5)	119.3(5)
C(8)–C(81)	1.458(7)	C(52)–C(51)–C(5)	117.8(5)
		O(1)–C(6)–C(5)	120.6(4)
		O(1)–C(6)–C(7)	112.7(4)
		C(5)–C(6)–C(7)	126.6(4)
		C(8)–C(7)–C(6)	122.6(4)
		C(7)–C(8)–C(81)	127.6(5)
Complex 5b			
W–C(2)	2.186(7)	C(6)–O(1)–C(2)	125.1(5)
O(1)–C(6)	1.351(8)	O(1)–C(2)–C(3)	114.0(6)
O(1)–C(2)	1.363(8)	O(1)–C(2)–W	117.3(4)
C(2)–C(3)	1.404(9)	C(3)–C(2)–W	128.6(5)
C(3)–C(4)	1.377(8)	C(4)–C(3)–C(2)	123.6(6)
C(4)–C(5)	1.414(8)	C(3)–C(4)–C(5)	118.8(5)
C(4)–C(41)	1.478(8)	C(3)–C(4)–C(41)	120.5(5)
C(5)–C(6)	1.374(9)	C(5)–C(4)–C(41)	120.6(5)
C(5)–C(7)	1.507(9)	C(6)–C(5)–C(4)	117.8(5)
C(6)–C(61)	1.489(9)	C(6)–C(5)–C(7)	118.7(5)
C(7)–O(7)	1.228(9)	C(4)–C(5)–C(7)	123.5(5)
C(7)–C(8)	1.456(9)	O(1)–C(6)–C(5)	120.6(6)
C(8)–C(9)	1.321(10)	O(1)–C(6)–C(61)	111.9(6)
C(9)–C(10)	1.474(9)	C(5)–C(6)–C(61)	127.5(6)
		O(7)–C(7)–C(8)	122.0(6)
		O(7)–C(7)–C(5)	119.5(6)
		C(8)–C(7)–C(5)	118.5(6)
		C(9)–C(8)–C(7)	124.0(5)
		C(8)–C(9)–C(10)	126.6(6)
		C(11)–C(10)–C(9)	123.2(6)
		C(15)–C(10)–C(9)	118.5(5)

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the complexes **4b** and **5b**

Atom	x	y	z	U_{eq} [a]
Complex 4b				
W	1374(1)	644(1)	6881(1)	31(1)
C(11)	3531(6)	617(5)	6553(5)	40(1)
O(11)	4751(5)	572(5)	6387(6)	66(1)
C(12)	1688(6)	−766(5)	5964(5)	41(1)
O(12)	1894(6)	−1518(4)	5405(5)	63(1)
C(13)	−795(7)	685(6)	7235(6)	46(1)
O(13)	−2021(5)	751(6)	7427(6)	76(2)
C(14)	1192(6)	−498(6)	8519(5)	44(1)
O(14)	1063(6)	−1170(5)	9451(5)	68(1)
C(15)	1072(6)	2158(5)	7638(5)	42(1)
O(15)	889(7)	3032(4)	8023(5)	71(2)
O(1)	402(3)	2746(3)	5126(3)	30(1)
C(2)	1456(5)	1825(4)	5098(4)	29(1)
C(3)	2335(5)	1739(4)	3901(4)	31(1)
C(4)	2147(5)	2461(4)	2825(4)	30(1)
C(41)	3075(5)	2225(4)	1601(4)	32(1)
C(42)	4539(6)	2083(5)	1365(5)	40(1)
C(43)	5427(6)	1777(6)	244(6)	53(2)
C(44)	4808(7)	1586(6)	−620(5)	54(2)
C(45)	3347(8)	1691(6)	−374(5)	54(2)
C(46)	2473(6)	2024(6)	719(5)	41(1)
C(5)	991(5)	3357(4)	2940(4)	29(1)
C(51)	666(5)	4165(5)	1813(4)	35(1)
O(51)	−470(4)	4117(4)	1646(4)	52(1)
C(52)	1769(7)	5030(6)	990(6)	52(2)
C(6)	140(5)	3466(4)	4109(4)	29(1)
C(7)	−1109(5)	4293(4)	4421(4)	30(1)
C(8)	−2021(5)	4200(5)	5562(4)	33(1)
C(81)	−3359(5)	4912(5)	5966(5)	34(1)
C(82)	−3772(6)	5940(5)	5218(5)	38(1)
C(83)	−5089(6)	6544(5)	5635(6)	47(1)
C(84)	−6017(6)	6139(6)	6793(6)	52(2)
C(85)	−5624(7)	5150(7)	7537(6)	64(2)
C(86)	−4296(7)	4532(7)	7132(5)	54(2)
Complex 5b				
W	4080(1)	3153(1)	3253(1)	53(1)
O(1)	5986(4)	3557(3)	2024(4)	49(1)
C(2)	5738(6)	3011(4)	2763(5)	46(1)
C(3)	6590(5)	2405(4)	3082(4)	45(1)
C(4)	7590(4)	2356(3)	2687(4)	38(1)
C(41)	8469(6)	1720(4)	3089(5)	38(1)
C(42)	9605(6)	1944(4)	3375(6)	49(2)
C(43)	10410(6)	1333(5)	3760(5)	57(2)
C(44)	10099(7)	525(5)	3840(6)	64(2)
C(45)	8965(7)	286(5)	3568(6)	62(2)
C(46)	8150(6)	884(4)	3200(5)	49(1)
C(5)	7767(5)	2932(4)	1899(4)	40(1)
C(6)	6938(6)	3529(4)	1590(5)	48(1)
C(61)	6934(8)	4195(5)	781(6)	68(2)
C(7)	8794(6)	2907(5)	1366(5)	50(1)
O(7)	9471(5)	3499(3)	1478(5)	68(1)
C(8)	8934(5)	2184(4)	708(4)	45(1)
C(9)	8142(5)	1602(4)	432(5)	44(1)
C(10)	8209(5)	879(4)	−267(4)	42(1)
C(11)	9122(6)	742(4)	−770(5)	51(2)
C(12)	9151(7)	51(5)	−1417(6)	61(2)
C(13)	8252(8)	−518(5)	−1559(6)	65(2)
C(14)	7343(8)	−382(6)	−1075(6)	70(2)
C(15)	7312(6)	312(5)	−431(5)	59(2)
C(21)	3997(8)	1886(6)	3385(8)	72(3)

Table 2 (continued)

Atom	x	y	z	U_{eq} [a]
Complex 5b				
O(21)	4031(7)	1158(5)	3484(7)	104(3)
C(22)	2535(7)	3289(6)	3658(8)	72(3)
O(22)	1644(5)	3377(6)	3885(8)	115(3)
C(23)	4811(6)	3138(4)	4770(7)	50(2)
O(23)	5203(7)	3098(3)	5640(6)	71(2)
C(24)	3331(10)	3149(6)	1700(10)	87(3)
O(24)	2933(11)	3156(7)	869(8)	149(5)
C(25)	4304(7)	4423(6)	3204(7)	68(2)
O(25)	4449(7)	5130(5)	3188(7)	105(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ture. The signals at ca. 19 ppm and 31–32 ppm are assigned to the methyl groups $C=C–CH_3$ and $CO–CH_3$ respectively.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **6b**

Atom	x	y	z	U_{eq} [a]
W	3912(1)	3582(1)	9379(1)	25(1)
C(21)	1649(6)	4025(4)	9047(5)	64(2)
O(21)	384(5)	4313(5)	8874(6)	136(3)
C(22)	3838(5)	5226(4)	8341(3)	38(1)
O(22)	3745(5)	6129(3)	7705(3)	64(1)
C(23)	3233(4)	4168(3)	10802(3)	34(1)
O(23)	2872(4)	4474(3)	11615(2)	48(1)
C(24)	6143(4)	3138(3)	9789(3)	29(1)
O(24)	7392(3)	2842(3)	10051(3)	50(1)
C(25)	3932(4)	1890(3)	10220(3)	34(1)
O(25)	3984(4)	917(3)	10638(3)	55(1)
O(1)	4111(3)	3470(2)	6907(2)	32(1)
C(2)	4770(4)	2844(3)	7928(3)	28(1)
C(3)	5939(4)	1753(3)	7916(3)	29(1)
C(4)	6391(4)	1308(3)	6982(3)	26(1)
C(41)	7487(4)	64(3)	7096(3)	25(1)
C(42)	7113(4)	−734(3)	6673(3)	31(1)
C(43)	8027(5)	−1950(3)	6909(3)	40(1)
C(44)	9309(5)	−2342(3)	7544(3)	43(1)
C(45)	9710(4)	−1548(4)	7947(3)	40(1)
C(46)	8805(4)	−345(3)	7729(3)	32(1)
C(5)	5673(4)	2025(3)	5948(3)	27(1)
C(6)	4533(4)	3104(3)	5944(3)	30(1)
C(7)	3697(5)	3963(3)	4984(3)	37(1)
C(8)	2489(5)	4941(3)	5040(3)	37(1)
C(9)	1666(5)	5806(3)	4076(3)	39(1)
C(10)	437(5)	6750(4)	4149(3)	39(1)
C(101)	−442(4)	7684(3)	3220(3)	32(1)
C(102)	−13(5)	7696(3)	2101(3)	39(1)
C(103)	−847(5)	8608(4)	1241(3)	46(1)
C(104)	−2152(5)	9503(4)	1486(4)	50(1)
C(105)	−2595(5)	9507(4)	2570(4)	51(1)
C(106)	−1748(5)	8599(4)	3446(4)	44(1)
C(11)	6169(5)	1659(3)	4862(3)	32(1)
O(11)	5236(4)	1579(3)	4317(2)	47(1)
C(12)	7834(5)	1454(4)	4480(3)	46(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4. Tungsta-1,3,5,7-octatetraenes

It has been demonstrated for compound **3b** that both ring-carbon atoms attached to the ring-oxygen atom (i.e. C2 and C6) are susceptible to nucleophilic attack by, for example, an amine. Accordingly, addition of an amine to compound **4b** is assumed to set up a non-productive equilibrium initially by addition of the amine to C6 of the pyrylium ring [16] with formation of compound **8** (Scheme 5). Addition of the amine to C2 is slower than to C6, but leads to production of stable 2-amino-1-tungsta-1,3,5,7-tetraenes **9** in an isomer ratio (Z,Z,E)-**9A**/(Z,Z,E)-**9B** = 2:1, according to NMR measurements. It is quite obvious that the NMR spectra of (Z,Z,E)-**9B** are very similar to those of compound **2′b** with respect to the enol portion of the molecules as well as the NMe_2 unit (Fig. 1). Pure crystals of the minor product (Z,Z,E)-**9B** were obtained by recrystallization of (Z,Z,E)-**9A**/(Z,Z,E)-**9B** mixtures from petroleum ether/diethyl ether at $-15\,^{\circ}C$, and its structure was confirmed by a preliminary X-ray analysis (vide infra).

Isomers **9A** and **9B** (ratio 2:1) result from steric congestion leading to formation of an *ansa*-type arrangement of the planes defined by the atoms W=C–N versus the plane of the 1,3-diketone unit (see Newman projection in Scheme 5). The configurational assignment is based on NOE measurements at 233 K, 600 MHz, which indicate strong signal enhancements between the atoms marked by an asterisk (Fig. 1). The chemical shifts of the methyl groups of compounds **9A** and **9B** correlate with those of compound **10** (Fig. 1) [16]. It has been demonstrated by spin-saturation transfer ^1H NMR experiments that an interconversion of isomers (Z,Z,E)-**9A** and (Z,Z,E)-**9B** is rapid on the

NMR timescale at 273 K. Other than the interconversion of compounds **9A** and **9B**, the rearrangement between the isomers **10** and **10′** is degenerate. It is fast on the NMR timescale, which is unambiguously proven by the strong line-broadening observed for both CCH_3 hydrogen signals of compound **10** (360 MHz, $CDCl_3$) at $50\,^{\circ}C$, whilst the signals of the $N(CH_3)_2$ group remain unchanged under these conditions, and also by spin-saturation transfer experiments at $50\,^{\circ}C$.

5. Crystal structure analyses of compounds 4b, 5b, 6b, and 9B

Diffraction measurements were made on an Enraf–Nonius MACH III diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) at 223 K. The crystal structures were solved by means of the program SHELXS-86 and refined by a full-matrix least-squares procedure on F^2 with the program SHELXL-93. Table 1 lists selected bond lengths and angles of **4b** and **5b**. Atomic coordinates of **4b**, **5b** and **6b** are given in Tables 2 and 3. Table 4 gives selected bond lengths and angles for compound **6b**. Crystal data and refinement

Table 4
Selected bond lengths [Å] and angles [°] for **6b**

W–C(2)	2.177(3)	C(6)–O(1)–C(2)	124.7(3)
O(1)–C(6)	1.356(4)	O(1)–C(2)–C(3)	114.3(3)
O(1)–C(2)	1.373(4)	O(1)–C(2)–W	119.0(2)
C(2)–C(3)	1.397(5)	C(3)–C(2)–W	126.7(2)
C(3)–C(4)	1.375(5)	C(4)–C(3)–C(2)	124.1(3)
C(4)–C(5)	1.424(4)	C(3)–C(4)–C(5)	118.1(3)
C(4)–C(41)	1.486(4)	C(3)–C(4)–C(41)	119.8(3)
C(5)–C(6)	1.371(5)	C(5)–C(4)–C(41)	121.9(3)
C(5)–C(11)	1.504(5)	C(6)–C(5)–C(4)	118.4(3)
C(6)–C(7)	1.442(5)	C(6)–C(5)–C(11)	119.5(3)
C(7)–C(8)	1.334(5)	C(4)–C(5)–C(11)	122.1(3)
C(8)–C(9)	1.443(5)	O(1)–C(6)–C(5)	120.3(3)
C(9)–C(10)	1.323(5)	O(1)–C(6)–C(7)	113.0(3)
C(10)–C(101)	1.462(5)	C(5)–C(6)–C(7)	126.6(3)
C(11)–O(11)	1.209(5)	C(8)–C(7)–C(6)	124.5(4)
C(11)–C(12)	1.497(5)	C(7)–C(8)–C(9)	124.3(4)
		C(10)–C(9)–C(8)	123.6(4)
		C(9)–C(10)–C(101)	127.3(4)
		O(11)–C(11)–C(12)	122.5(3)
		O(11)–C(11)–C(5)	120.4(4)
		C(12)–C(11)–C(5)	117.0(3)

Table 5
Crystal data and refinement details for the pyranylidene complexes **4b** and **5b**

Complex	**4b** (blue)	**5b** (red)
Empirical formula	$C_{26}H_{16}O_7W$	$C_{26}H_{16}O_7W$
Formula weight	624.24	624.24
Temperature	$< 223(2)$ K	$< 223(2)$ K
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.805(2)	11.873(1)
b (Å)	11.309(2)	15.872(2)
c (Å)	11.511(2)	12.978(1)
α (°)	77.69(1)	90.00
β (°)	71.85(1)	100.33(1)
γ (°)	83.50(2)	90.00
V (Å^3)	1183.5(4)	2406.0(4)
Z	2	4
D_c (g cm^{-3})	1.752	1.723
μ (cm^{-1})	49.2	48.4
$F(000)$	604	1208
Crystal size (mm^3)	$0.50 \times 0.30 \times 0.10$	$1.20 \times 0.60 \times 0.60$
θ limits (°)	2.19–26.32	2.16–26.28
Empirical abs. corr.	71.5–99.8%	72.4–99.9%
No. of data collected	5087	5104
No. of unique data	4797	4869
R_{av}	0.013	0.047
No. of data observed with $I > 2\sigma(I)$	4458	4000
No. of refined parameters	308	309
Goodness of fit	1.071	1.043
R (all data/obsd. data)	0.037/0.032	0.078/0.062
wR^2 (all data/obsd. data)	0.092/0.089	0.168/0.155
Residual ρ_{max} (e Å^{-3})	2.00 (-2.79)	2.05 (-3.23)

Table 6
Crystal data and structure refinement for **6b**

Identification code	AUM_520
Empirical formula	$C_{28}H_{18}O_7W$
Formula weight	650.27
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	$a = 9.213(1)$ Å $\quad \alpha = 73.17(1)°$
	$b = 12.251(1)$ Å $\quad \beta = 82.17(1)°$
	$c = 12.401(1)$ Å $\quad \gamma = 69.66(1)°$
Volume	1255.2(2) Å^3
Z	2
Density (calc.)	1.721 Mg m^{-3}
Absorption coefficient	46.5 cm^{-1}
F(000)	632
Crystal size	$0.4 \times 0.2 \times 0.2$ mm^3
Theta range for data collection	2.16 to 26.31°
Index ranges	$-10 \leq h \leq 11, 0 \leq k \leq 15,$ $14 \leq l \leq 15$
Reflections collected	5351
Independent reflections	5105 [R(int) = 0.0186]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/ parameters	5104/0/326
Goodness-of-fit on F^2	1.052
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0225, wR^2 = 0.0558$
R indices (all data)	$R_1 = 0.0312, wR^2 = 0.0589$
Largest diff. peak and hole	1.028 and -1.170 e Å^{-3}

Table 7
Crystal data and structure refinement for compound **9B**

Identification code	AUM_475
Empirical formula	$C_{28}H_{23}NO_7W$
Formula weight	669.32
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	$a = 30.771(4)$ Å
	$b = 12.188(2)$ Å $\quad \beta = 96.64(1)°$
	$c = 14.470(2)$ Å
Volume	5390.4(14) Å^3
Z	8
Density (calc.)	1.650 Mg m^{-3}
Absorption coefficient	4.331 mm^{-1}
F(000)	2624
Crystal size	$0.70 \times 0.60 \times 0.60$ mm^3
Theta range for data collection	2.19 to 25.00°
Index ranges	$-38 \leq h \leq 0, -15 \leq k \leq 0,$ $-17 \leq l \leq 18$
Reflections collected	9713
Independent reflections	9524 [R(int) = 0.0316]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8424/0/677
Goodness-of-fit on F^2	1.243
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1015, wR^2 = 0.2821$
R indices (all data)	$R_1 = 0.1459, wR^2 = 0.5092$
Largest diff. peak and hole	2.973 and -2.694 e Å^{-3}

details are listed in Tables 5–7. The crystal structure of compound **9B** will not be discussed since the data are of bad quality ($R = 0.102$). Due to the presence of a very long unit cell axis ($a = 30.771$ Å) and wide scans in data collection there are many overlaps leading to wrong intensities. Data were also collected with Cu radiation, though an improved data set was not obtained in this case because of the high absorption ($\mu = 83.3$ cm^{-1}; correction via ψ scan data: $0.21 < C < 0.99$).

Further details of the crystal structure of **4b**, **5b**, **6b**, and **9B** may be requested from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-XXXX, the names of the authors and the journal citation.

Fig. 2 is a perspective SCHAKAL-92 drawing of complex **4b** showing the labelling scheme. The molecular structure is in line with the assignment by IR and NMR spectra of the complex. The configuration of the *trans*-styryl group is retained in the complex. The distances W–C2 of 2.180(5) Å and C2–C3 of 1.396(7) Å are shortened compared to those of complex **3b** [W–C2

2.193(5) Å, C2–C3 1.401(7) Å] due to the π conjugation of the *trans*-styryl group with the pyranylidene ring. The bond angles and other bond lengths between the atoms of this six-membered ring are similar to those of **3b** [1,16]. According to the NMR and X-ray crystal data it seems that the introduction of the *trans*-styryl does not obviously influence the structure of the pyranylidene ring. So it can be expected that the oxy-
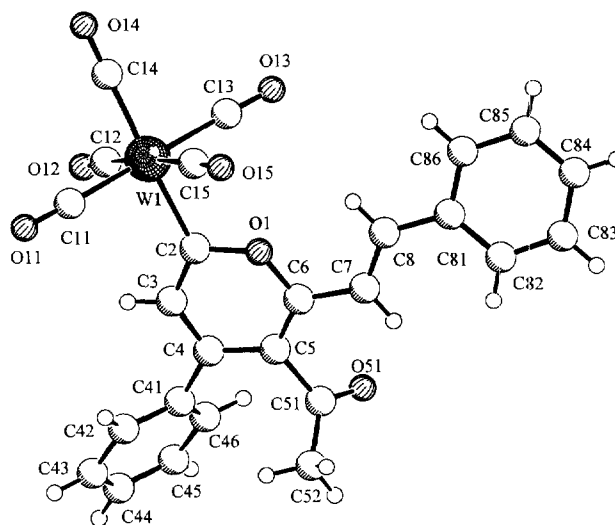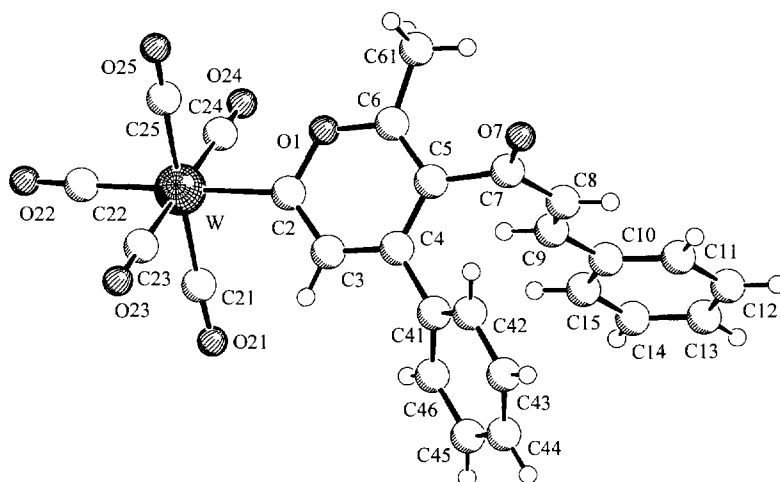

Fig. 2. Molecular structure of the pyranylidene complex **4b**.

Fig. 3. Molecular structure of the pyranylidene complex **5b**.

gen-containing six-membered ring in **4b** is also be-stowed with the pyrylium character (Scheme 1). For complex **5b**, the configuration of the *trans*-styryl group is also retained and the structural data of the six-membered pyranylidene ring are similar to those of its isomer **4b**. The steric hindrance between the 4-phenyl with its neighboring cinnamoyl group may obstruct the formation of **5b** (Fig. 3). According to its structural features, **5b** may very well be considered as a precursor of 1-metalla-hexatrienes or 1-metalla-tetraenes.

There is no obvious difference between the bond distances of the pyranylidene-ring atoms of the 6-

[*trans,trans*-(4-phenyl-1,3-butadienyl)]pyranylidene complex **6b** [W–C(2) 2.177(3) Å, C(2)–C(3) 1.397(5) Å] and those of pyranylidene complexes **4b** and **5b**. The configuration of *trans,trans*-butadienyl is retained in the complex [C(7)–C(8) 1.334(5) Å, C(9)–C(10) 1.323(5) Å] (Fig. 4) and the distances of the C=C bonds of the butadienyl group are similar to that of its analogue, 6-(*trans*-styryl)pyranylidene complex **4b** [C(7)–C(8) 1.329(7) Å]. The structural features indicate that complex **6b** may be a susceptible precursor of 1-tungsta-1,3,5,7,9-pentaenes via a ring-opening reaction (i.e. nucleophilic attack at C2 or C6 by a nucleophile).
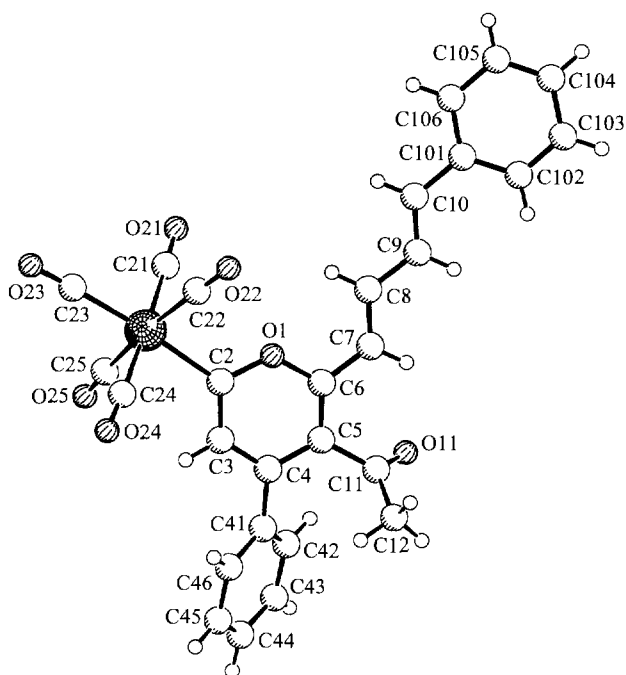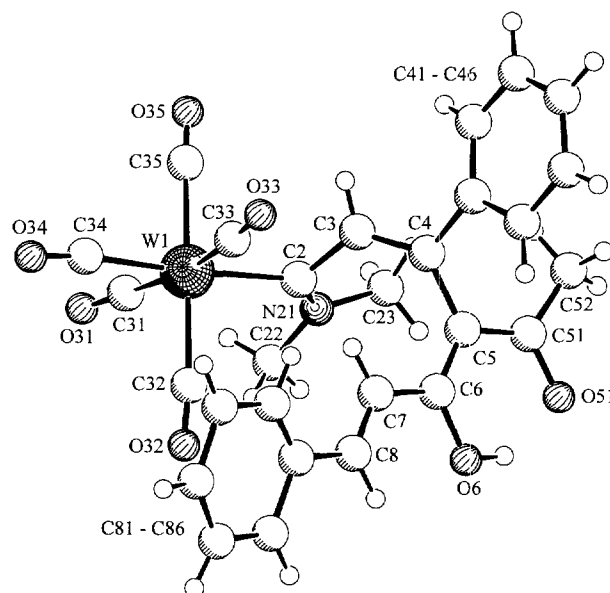
Fig. 5

Fig. 4. Molecular structure of the pyranylidene complex **6b**.

Fig. 5. Molecular structure of the 1-tungsta-1,3,5,7-octatetraene **9B**.

6. Experimental

All operations were performed under argon. Dried solvents were used in all experiments. Melting points are not corrected. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtained with Bruker WM 300 and WP 360 spectrometers (multiplicities were determined by DEPT, chemical shifts refer to $\delta_{TMS} = 0.00$ ppm). Other analyses: IR Diglab FTS 45; MS Finnigan MAT 312; elemental analysis, Perkin–Elmer 240 elemental analyzer; TLC, Merck DC-Alufolien Kieselgel 60 F_{254}. R_f values refer to TLC tests. Column chromatographic purifications were achieved with Merck Kiesegel 100.

6.1. trans-6-Phenyl-5-hexene-2,4-dione (2b)

Compound 2b was prepared according to literature procedure via the dehydration of δ-hydroxy-β-diketone obtained from the reaction of the 2,4-pentanedione dianions and benzaldehyde [19] in moderate yields ($R_f = 0.8$ petroleum ether/ethyl acetate 10:1, recrystallized from diethyl ether at $-15\,^\circ$C, m.p. 85 °C). ^{1}H NMR (CDCl$_3$): δ 7.62 and 6.48 (1 H each, d each, AB-system, $^3J = 15.7$ Hz, trans-CH=CHPh), 7.56–7.53 and 7.41–7.38 (2:3 H, m each, Ph), 5.68 (1 H, s, 3-H), 2.19 (3 H, s, COCH$_3$). ^{13}C NMR (CDCl$_3$): δ 197.8 (Cq, C=O), 176.9 (Cq, =C–OH), 139.7 and 122.8 (CH each, trans-CH=CHPh), 135.1 (Cq, i-C, Ph), 129.8, 128.9 and 127.9 (1:2:2, CH each, Ph), 101.1 (CH, C3), 27.0 (COCH$_3$). IR (diethyl ether): 1635.0 (99), 1585.7 (100), 1449.5 (68), 1434.9 (52), 1361.8 (44), 1304.1 (40), 1277.5 (57), 1230.1 (28), 1162.6 (32), 1142.0 (28), 968.8 (63), 941.1 (56), 786.9 (63), 760.1 (47), 700.0 (69).

6.2. trans,trans-8-Phenyl-octa-5,7-diene-2,4-dione (2c)

2,4-Pentanedione (4.04 g, 40 mmol) in dry tetrahydrofuran (20 ml) was added dropwise to a 0 °C stirred suspension of sodium hydride (1.12 g, 44 mmol) in anhydrous tetrahydrofuran (30 ml). After 40 min, 27 ml of 1.6 M n-BuLi in n-pentane was added dropwise to the white suspension at 0 °C. The resulting yellow–orange solution was then stirred for ca. 15 min before the addition of cinnamaldehyde (5.32 g, 40 mmol) in THF (20 ml). After stirring for 30 min, the reaction was quenched with saturated ammonium chloride solution (50 ml) and the aqueous phase was extracted with THF (4 × 30 ml). The combined organic layer was washed with brine (2 × 40 ml), dried over magnesium sulfate and then concentrated under reduced pressure. Column chromatography on silical gel with n-pentane/ethyl acetate 2.5:1 afforded the yellow oil δ-hydroxy-β-diketone (3.23 g, 34.7%, $R_f = 0.6$ n-pentane/ethyl acetate 1:1). 2.68 g of this yellow oil was dehydrated under reflux for 24 h by using p-toluenesulfonic acid (p-

TsOH · H$_2$O, 5 mg) as the catalyst and dry benzene as the solvent (Scheme 2). Water formed during the reaction was removed azeotropically with a Dean and Stark trap filled with 3Å molecular sieves. The final yellow solution was filtered and concentrated. The separation of the residue on silica gel with petroleum ether/ethyl acetate 5:1 by column chromatography gave the yellow product 2c (0.97 g, 40%, $R_f = 0.72$ petroleum ether/ethyl acetate 5:1, recrystallized from benzene/diethyl ether 5:1 at 20 °C, m.p. 118 °C). ^{1}H NMR (CDCl$_3$): δ 7.47–7.40 and 7.39–7.25 (2:4 H, m each, Ph and 8-H), 6.88 (2 H, t, 7-CH=CH–), 6.02 (1 H, d, 5-H), 5.57 (1 H, s, 3-H), 2.15 (3 H, s, COCH$_3$). ^{13}C NMR (CDCl$_3$): δ 197.9 (Cq, C=O), 176.6 (Cq, =C–OH), 140.0 (CH, C8), 139.5 (CH, C5), 136.3 (Cq, i-C, Ph), 128.8 and 128.7 (1:4, CH each, Ph), 127.0 (CH, C7), 126.2 (CH, C6), 101.0 (CH, C3), 27.1 (COCH$_3$). IR (diethyl ether): 3065.8 (11), 3030.6 (15), 3000.1 (9), 1626.6 (100), 1576.2 (81), 1563.9 (88), 1448.2 (59), 1424.7 (51), 1360.0 (40), 1323.0 (37), 1285.1 (36), 1252.3 (46), 1141.2 (41), 997.6 (89), 938.6 (59), 885.9 (20), 839.9 (22), 779.2 (38), 752.2 (81), 694.4 (45). MS (70 eV), $m/e\%$: 214 (52, [M$^+$]), 196 (24), 171 (100), 153 (70), 128 (78), 115 (38), 91 (54), 85 (40), 57 (37). Anal. Found: C, 78.17; H, 6.58. C$_{14}$H$_{14}$O$_2$ (214.3) Calc.: C, 78.47; H, 6.59%.

6.3. Pentacarbonyl[(5-acetyl-4-phenyl-6-(trans-styryl))-2H-pyran-2-ylidene]chromium (4a) and pentacarbonyl-[(6-methyl-4-phenyl-5-cinnamoyl)-2H-pyran-2-ylidene]chromium (5a)

To pentacarbonyl(1-ethoxyl-3-phenyl-2-propyn-1-ylidene)chromium (1a) (350 mg, 1.0 mmol) and trans-6-phenyl-5-hexene-2,4-dione (2b) (189 mg, 1.0 mmol) in a 5 ml screwtop vessel was added 4 ml of petroleum ether and triethylamine (50 mg, 0.5 mmol) successively with efficient stirring at 20 °C. 24 h later the TLC analysis indicates the complete consumption of the starting complex 1a and a dark blue solution (some dark blue solid precipitated) was obtained. The solvent was removed by passing an argon stream through the mixture and then the residue was dissolved in 3 ml of dichloromethane and separated by column chromatography on silica gel (column 15 × 2 cm^2). Elution with petroleum ether/dichloromethane 3:1 afforded the first fraction, the dark blue compound 4a (310 mg, 62%, $R_f = 0.5$ petroleum ether/dichloromethane 3:1, single crystals were obtained from diethyl ether/petroleum ether 5:1 at $-15\,^\circ$C, m.p. 149 °C). Elution with petroleum ether/dichloromethane 2:1 afforded the second fraction, the purple compound 5a (25 mg, 5%, $R_f = 0.3$ petroleum ether/dichloromethane 2:1, recrystallized from diethyl ether/petroleum ether 5:1 at $-15\,^\circ$C, m.p. 147 °C).

4a: ^{1}H NMR (CDCl$_3$): δ 8.19 and 7.05 (1 H each, d each, AB-system, ^3J = 15.8 Hz, trans-CH=CHPh), 7.99 (1 H, s, 3-H), 7.65–7.58, 7.57–7.50 and 7.48–7.44 (2:3:5 H, m each, 2 Ph), 1.95 (3 H, s, COCH$_3$). ^{13}C NMR (CDCl$_3$): δ 282.8 (Cr=C), 223.3 and 217.0 [1:4, Cq, trans- and cis-CO, Cr(CO)$_5$], 200.0 (Cq, C=O), 168.4 (Cq, C6), 141.0 and 115.2 (CH each, trans-CH=CHPh), 138.7 (Cq, C4), 137.8 (CH, C3), 134.8 and 134.2 (Cq each, i-C each, 2 Ph), 130.5, 130.3, 129.0, 128.5, 128.0 and 127.7 (1:2:2:2:2:1, CH each, 2 Ph), 125.9 (Cq, C5), 31.4 (COCH$_3$). IR (diethyl ether): 2051.3 (65), 1978.5 (21), 1920.4 (100) [ν(C$\equiv$O)], 1699.8 (17), 1621.7 (16), 1558.1 (21), 1460.5 (40), 1433.7 (26), 1305.9 (12), 1152.0 (26), 668.8 (38). MS (70 eV), m/e%: 492 (24, [M$^+$]), 408 (16), 352 (36), 309 (26), 265 (26), 179 (30), 149 (30), 99 (36), 69 (46), 52 (100). Anal. Found: C, 63.55; H, 3.17. C$_{26}$H$_{16}$O$_7$Cr (492.4) Calc.: C, 63.42; H, 3.28%.

5a: ^{1}H NMR (C$_6$D$_6$): δ 8.11 (1 H, s, 3-H), 7.20 and 5.99 (1 H each, d each, AB-system, ^3J = 16 Hz, trans-CH=CHPh), 7.08–7.02 and 6.99–6.77 (4:6 H, m each, 2 Ph), 2.08 (3 H, s, 6-CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 283.5 (Cr=C), 224.1 and 218.2 [1:4, Cq, trans- and cis-CO, Cr(CO)$_5$], 190.2 (Cq, C=O), 176.7 (Cq, C6), 144.7 and 126.2 (CH each, trans-CH=CHPh), 141.7 (Cq, C4), 139.0 (CH, C3), 135.4 and 134.0 (Cq each, i-C each, 2 Ph), 131.1, 130.6, 129.3, 129.0, 128.7, 128.5 and 128.3 (1:1:2:1:2:2:1, CH each, 2 Ph), 127.7 (Cq, C5), 19.1 (COCH$_3$). IR (diethyl ether): 2052.6 (56), 1979.4 (23), 1920.5 (100) [ν(C$\equiv$O)], 1596.4 (26), 1474.9 (35), 1109.9 (20), 666.1 (40). MS (70 eV), m/e%: 492 (6, [M$^+$]), 380 (11), 352 (46), 294 (14), 227 (34), 213 (42), 169 (56), 149 (22), 95 (46), 81 (76), 71 (100), 67 (64), 55 (75). Anal. Found: C, 63.40; H, 3.17. C$_{26}$H$_{16}$O$_7$Cr (492.4) Calc.: C, 63.42; H, 3.28%.

6.4. Pentacarbonyl[(5-acetyl-4-phenyl-6-(trans-styryl))-2H-pyran-2-ylidene]tungsten (4b) and pentacarbonyl-[(6-methyl-4-phenyl-5-cinnamoyl)-2H-pyran-2-ylidene]tungsten (5b)

To pentacarbonyl(1-ethoxyl-3-phenyl-2-propyn-1-ylidene)tungsten (**1b**) (482 mg, 1.0 mmol) and trans-6-phenyl-5-hexene-2,4-dione (**2b**) (189 mg, 1.0 mmol) in a 5 ml screwtop vessel was added 4 ml of petroleum ether and triethylamine (50 mg, 0.5 mmol) successively with efficient stirring at 20 °C. 10 h later the TLC analysis indicates the complete consumption of the starting complex **1b** and a blue solution (from which some blue-appearing solid precipitated) was obtained. The reaction mixture was separated by means of the analogous procedure for **4a** and **5a**. Elution with petroleum ether/dichloromethane 3:1 afforded the first fraction, the blue compound **4b** (461 mg, 75%, R_f = 0.5 petroleum ether/dichloromethane 2:1, single crystals were obtained from diethyl ether/petroleum ether 5:1 at

−15 °C, m.p. 142 °C). The second fraction is the red compound **5b** (30 mg, 5%, R_f = 0.3 petroleum ether/dichloromethane 2:1, single crystals were grown in diethyl ether/petroleum ether 5:1 at −15 °C, m.p. 140 °C).

4b: ^{1}H NMR (C$_6$D$_6$): δ 8.20 and 6.94 (1 H each, d each, AB-system, ^3J = 16 Hz, trans-CH=CHPh), 7.89 (1 H, s, 3-H), 7.36–7.33 and 6.85–7.03 (2:8 H, m each, 2 Ph), 1.32 (3 H, s, COCH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 256.4 (W=C), 204.0 and 199.3 [1:4, Cq, trans- and cis-CO, W(CO)$_5$], 199.2 (Cq, C=O), 168.2 (Cq, C6), 143.2 (Cq, C4), 142.1 and 116.1 (CH each, trans-CH=CHPh), 141.0 (CH, C3), 135.7 and 135.2 (Cq each, i-C each, 2 Ph), 130.9, 130.8, 129.5, 129.4, 128.7 and 127.7 (1:1:2:2:2:2, CH each, 2 Ph), 127.1 (Cq, C5), 31.3 (COCH$_3$). IR (diethyl ether): 2057.5 (56), 1977.3 (35), 1919.0 (100) [ν(C$\equiv$O)], 1702.5 (30), 1621.3 (29), 1558.6 (42), 1460.1 (61), 1432.9 (52), 1308.0 (33), 1153.2 (56). MS (70 eV), m/e%: 624 (38, [M$^+$]), 542 (56), 452 (60), 352 (52), 266 (88), 239 (80), 182 (66), 149 (76), 83 (80), 71 (87), 55 (100). Anal. Found: C, 50.10; H, 2.62. C$_{26}$H$_{16}$O$_7$W (624.3) Calc.: C, 50.03; H, 2.58%.

5b: ^{1}H NMR (C$_6$D$_6$): δ 8.06 (1 H, s, 3-H), 7.21 and 5.99 (1 H each, d each, AB-system, ^3J = 16 Hz, trans-CH=CHPh), 7.06–7.03 and 6.77–6.94 (2:8 H, m each, 2 Ph), 2.00 (3 H, s, 6-CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 257.4 (W=C), 204.1 and 199.1 [1:4, Cq, trans- and cis-CO, W(CO)$_5$], 190.2 (Cq, C=O), 175.6 (Cq, C6), 144.8 and 126.2 (CH each, trans-CH=CHPh), 144.4 (Cq, C4), 141.3 (CH, C3), 135.5 and 134.0 (Cq each, i-C each, 2 Ph), 131.2, 130.7, 129.0, 128.5, 128.4 and 128.3 (1:1:2:2:2:2, CH each, 2 Ph), 127.7 (Cq, C5), 19.2 (6-CH$_3$). IR (diethyl ether): 2059.3 (59), 1969.3 (32), 1937.1 (100), 1897.0 (92) [ν(C$\equiv$O)], 1650.8 (41), 1619.5 (22), 1594.2 (44), 1476.5 (52), 1451.1 (39), 1309.2 (18), 1167.1 (34), 1111.9 (30). MS (70 eV), m/e%: 624 (20, [M$^+$]), 540 (30), 456 (16), 352 (18), 265 (40), 213 (34), 183 (43), 169 (42), 149 (58), 95 (62), 81 (71), 71 (100). Anal. Found: C, 50.13; H, 2.65. C$_{26}$H$_{16}$O$_7$W (624.3) Calc.: C, 50.03; H, 2.58%.

6.5. Pentacarbonyl[(5-acetyl-4-phenyl-6-(trans,trans-(4-phenyl-1,3-butadienyl))-2H-pyran-2-ylidene]chromium (6a)

To pentacarbonyl(1-ethoxyl-3-phenyl-2-propyn-1-ylidene) chromium (**1a**) (280 mg, 0.8 mmol) and trans,trans-8-phenyl-octa-5,7-diene-2,4-dione **2c** (171 mg, 0.8 mmol) in a 5 ml screwtop vessel was added 4 ml of dichloromethane and triethylamine (185 mg, 1.7 mmol) successively with effective stirring at 20 °C. 4 days later the TLC analysis indicates the presence of a small amount of the starting complex **1a** and a deep green solution was obtained. The reaction mixture was separated on silica gel by column chromatography. Elu-

tion with petroleum ether/dichloromethane 2:1 afforded the green compound **6a** (88 mg, 21%, $R_f = 0.5$ petroleum ether/dichloromethane 2:1, recrystallized from petroleum ether/diethyl ether 1:3 at $-15\,°C$, m.p. > 150 °C, dec.). ^{1}H NMR (CDCl$_3$): δ 7.94 (1 H, s, 3-H), 8.01–7.92 (1 H, four sets of double peaks, 6-CH=), 7.58–7.50 and 7.46–7.36 (5:5 H, m each, 2 Ph), 7.11–6.99 (2 H, m, =CH–CH=), 6.61 (1 H, d, $^3J = 15\,Hz$, trans-CH=CH–Ph), 1.96 (3 H, s, COCH$_3$). ^{13}C NMR (CDCl$_3$): δ 282.4 (Cr=C), 224.0 and 217.7 [1:4, Cq, trans- and cis-CO, Cr(CO)$_5$], 200.7 (Cq, C=O), 169.1 (Cq, C6), 142.2 (CH, C3), 141.9 (Cq, C4), 139.2, 138.0, 127.3 and 119.0 (CH each, trans,trans-CH=CH–CH=CHPh), 136.0 and 135.4 (Cq each, i-C each, 2 Ph), 131.0, 128.9, 128.2 (1:2:2, CH each, Ph), 129.6 and 129.5 (4:1, CH each, Ph of –CH=CH–Ph), 126.2 (Cq, C5), 32.0 (COCH$_3$). IR (diethyl ether): 2050.9 (34), 1974.0 (14), 1954.3 (45), 1918.7 (100) [ν(C≡O)], 1698.0 (13), 1604.9 (15), 1553.9 (15), 1434.1 (20), 1146.3 (23), 663.6 (32). MS (70 eV), m/e%: 518 (16, [M$^+$]), 406 (36), 378 (100), 165 (18), 149 (29), 95 (26), 69 (47), 57 (52). Anal. Found: C, 64.17; H, 3.72. C$_{28}$H$_{18}$O$_7$Cr (518.0) Calc.: C, 64.86; H, 3.50%.

6.6. Pentacarbonyl{[5-acetyl-4-phenyl-6-(trans,trans-(4-phenyl-1,3-butadienyl)]-2H-pyran-2-ylidene}tungsten (6b) and pentacarbonyl{[6-methyl-4-phenyl-5-(trans,trans-5-phenyl-penta-2,4-dienoyl)]-2H-pyran-2-ylidene}tungsten (7b)

To pentacarbonyl(1-ethoxyl-3-phenyl-2-propyn-1-ylidene)tungsten (**1b**) (415 mg, 0.85 mmol) and trans,trans-8-phenyl-octa-5,7-diene-2,4-dione (**2c**) (184 mg, 0.85 mmol) in a 5 ml screwtop vessel was added 4 ml of dichloromethane and triethylamine (44 mg, 0.43 mmol) successively with effective stirring at 20 °C. 24 h later the TLC analysis indicates the complete consumption of the starting complex **1b** and a black solution was obtained. The separation of the reaction mixture on silica gel by column chromatography (petroleum ether/dichloromethane 2:1) afforded the dark compound **6b** (285 mg, 52%, $R_f = 0.7$ petroleum ether/dichloromethane 1:1, recrystallized from dichloromethane/diethyl ether 2:1 at $-15\,°C$, m.p. 151 °C). Subsequent elution with petroleum ether/dichloromethane 1:1 afforded the red compound **7b** (29 mg, 5%, $R_f = 0.6$ petroleum ether/dichloromethane 1:1, recrystallized from diethyl ether/n-pentane 3:1 at $-15\,°C$, m.p. 134 °C).

6b: ^{1}H NMR (CDCl$_3$): δ 7.93 (1 H, s, 3-H), 7.99–7.91 (1 H, four sets of double peaks, 6-CH=), 7.60–7.51 and 7.45–7.31 (5:5 H, m each, 2 Ph), 7.12–6.94 (2 H, m, =CH–CH=), 6.59 (1 H, d, $^3J = 15\,Hz$, trans-CH=CH–Ph), 1.97 (3 H, s, COCH$_3$). ^{13}C NMR (CDCl$_3$): δ 256.0 (W=C), 204.6 and 200.5 [1:4, Cq, trans- and cis-CO, W(CO)$_5$], 198.6 (Cq, C=O), 167.8

(Cq, C6), 142.6 (Cq, C4), 142.4, 142.3, 127.3 and 119.2 (CH each, trans,trans-CH=CH–CH=CHPh), 140.7 (CH, C3), 136.0 and 135.5 (Cq each, i-C each, 2 Ph), 131.0, 128.9, 128.0 and 127.5 (1:1:1:2, CH each, Ph), 129.6 and 129.5 (3:2, CH each, Ph of –CH=CH–Ph), 126.8 (Cq, C5), 32.0 (COCH$_3$). IR (diethyl ether): 2057.6 (39), 1970.0 (19), 1910.8 (100) [ν(C≡O)], 1698.5 (18), 1604.3 (22), 1553.6 (26), 1460.4 (38), 1431.1 (37), 1303.2 (12), 1146.2 (35). MS (70 eV), m/e%: 650 (6, [M$^+$]), 566 (6), 480 (5), 352 (48), 296 (46), 268 (100), 212 (46), 184 (36), 149 (36), 57 (21). Anal. Found: C, 51.23; H, 2.82. C$_{28}$H$_{18}$O$_7$W (650.1) Calc.: C, 51.69; H, 2.79%.

7b: ^{1}H NMR (CDCl$_3$): δ 8.09 (1 H, s, 3-H), 7.50–7.41 and 7.39–7.28 (6:4 H, m each, 2 Ph), 7.13–7.05 and 6.73–6.65 (2 H, CH each, four sets of double peaks each, $^3J = 11\,Hz$, –CH=CH–C=O), 6.97 and 6.07 (1 H each, d each, $^3J = 15.4\,Hz$, AB-system, trans-CH=CHPh), 2.67 (3 H, s, 6-CH$_3$). ^{13}C NMR (CDCl$_3$): δ 257.7 (W=C), 204.2 and 198.5 [1:4, Cq. trans- and cis-CO, W(CO)$_5$], 191.9 (Cq, C=O), 174.4 (Cq, C6), 146.9 (CH, C3), 146.2 (Cq, C4), 143.9 and 127.6 (CH each, trans-CH=CHPh), 141.3 and 125.8 (CH each, trans-CH=CH–), 135.5 and 135.2 (Cq each, i-C each, 2 Ph), 130.9, 129.9, 129.3, 129.2, 128.9 and 128.2 (1:2:1:1:4:1, CH each, 2 Ph), 126.2 (Cq, C5), 19.8 (6-CH$_3$). IR (diethyl ether): 2060.0 (58), 1975.7 (20), 1915.4 (99), 1910.5 (100) [ν(C≡O)], 1650.7 (8), 1612.4 (19), 1589.3 (28), 1474.7 (39), 1449.4 (14), 1110.7 (16). MS (70 eV), m/e%: 650 (26, [M$^+$]), 566 (26), 482 (25), 352 (38), 296 (34), 270 (64), 240 (50), 215 (78), 184 (44), 149 (52), 128 (70), 115 (50), 91 (63), 71 (64), 57 (95), 55 (100). Anal. Found: C, 51.49; H, 2.75. C$_{28}$H$_{18}$O$_7$W (650.1) Calc.: C, 51.69; H, 2.79%.

6.7. 5-Acetyl-2-dimethylamino-6-hydroxy-4,8-diphenyl-1-(pentacarbonyl)tungsta-1,3,5,7-octatetraene (Z,Z,E)-9A and (Z,Z,E)-9B

To a stirred solution of pentacarbonyl{[5-acetyl-4-phenyl-6-(trans-styryl)]-2H-pyran-2-ylidene}tungsten (**4b**) (250 mg, 0.40 mmol) and 1 ml of diethyl ether in a 5 ml screwtop vessel was added the solution of dimethylammonium dimethylcarbamate (54 mg, 0.40 mmol) in 3 ml of diethyl ether. After 2 h at 20 °C a yellow solid began to precipitate on the wall of the vessel and the color of the reaction mixture changed to yellow–brown. TLC after 20 h indicates complete consumption of the starting complex **4b**. The reaction mixture was then decanted and the yellow solid of compounds **9A** and **9B** was collected, washed with diethyl ether and dried [238 mg, 89%, $R_f = 0.8$ dichloromethane, (Z,Z,E)-**9B** was obtained by recrystallization from petroleum ether/diethyl ether 1:3 at $-10\,°C$, m.p. (Z,Z,E)-**9B** 100 °C]. Two sets of resonance signals in the ratio 2:1 are shown in the NMR spectra of the fresh sample of **9**.

^{1}H NMR {CDCl$_3$, 600 MHz, **9A**:[**9B**] = 2:1}: δ 16.98 [16.83] (1 H, s, O $\cdots$ H–O), 7.66 [7.79] (1 H, d, AB-system, ^3J = 15.6 Hz, –CH=CHPh), 7.40 [7.50] (1 H, s, 3-H), 7.52 (2 H, m, 4-o-Ph, **9A** and **9B**), 7.41 (2 H, m, 4-m-Ph, **9A** and **9B**), 7.35–7.25 (6 H, m, styryl-Ph and 4-p-Ph, **9A** and **9B**), 6.38 [6.58] (1 H, d, AB-system, ^3J = 15.6 Hz, –CH=CHPh), 3.63 [3.68] {3 H, s, (W)–Z–NCH$_3$}, 3.19 [3.30] {3 H, s, (W)–E–NCH$_3$}, 2.16 [1.85] (3 H, s, COCH$_3$). ^{13}C NMR (CDCl$_3$, 75.48 Hz): δ 249.5 (W=C, **9A** and **9B**), 202.2 and 198.2 [202.8 and 198.3] [1:4, Cq, $trans$- and cis-CO, W(CO)$_5$, **9A** and **9B**], 197.4 [197.6] (Cq, C=O), 177.8 [177.2] (Cq, =COH), 141.2 [143.1] (CH=CHPh), 151.9 (CH, C3, **9A** and **9B**), 141.0 (Cq, C4, **9A** and **9B**), 134.7 (Cq, 2 i-Ph, **9A** and **9B**), 130.3, 129.2, 128.9, 128.8, 128.6, 128.5, 127.9 and 126.6 (CH each, 2 Ph, **9A** and **9B**), 121.3 [120.5] (CH=CHPh), 110.6 (Cq, C5, **9A** and **9B**), 53.8 [(W)–Z–NCH$_3$, **9A** and **9B**], 46.9 [46.4] [(W)–E–NCH$_3$, **9A** and **9B**], 26.9 [26.2] (COCH$_3$). IR (diethyl ether): 2056.7 (68), 1961.2 (88), 1913.8 (71), 1897.9 (100), 1883.2 (70) [ν(C≡O)], 1623.0 (39), 1579.1 (33), 1541.0 (56), 1445.8 (28), 1374.0 (35), 1280.8 (28), 1167.8 (15), 973.5 (18), 944.1 (20), 767.0 (28). MS (70 eV), $m/e\%$: 669 (0.5, [M$^+$]), 587 (6), 585 (6), 529 (5), 486 (4), 345 (60), 302 (60), 286 (26), 202 (38), 198 (33), 159 (58), 149 (52), 97 (46), 69 (74), 57 (100). Anal. Found: C, 49.81; H, 3.46; N, 2.17. C$_{28}$H$_{23}$NO$_7$W (669.3) Calc.: C, 50.24; H, 3.46; N, 2.09%.

Acknowledgements

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