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Rearrangement of carbiminium carbonylmetalates by mutual exchange of alkoxy- and amino functionalities (M = W, Cr)☆ Crystal structure analyses

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Abstract

Reaction of (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (**1a**,**b**) (M = Cr, W) with enamines $R'(R_2N)C{=}CHR''$ (**4a**–**d**) (R_2N = morpholine) yielded carbiminium carbonylmetalates $^{-}(OC)_5M{-}C(OEt){=}C[C(=N^{+}R_2)R']C(Ph){=}CHR''$ (**5**) by metathesis of the (N)C=C at the C≡C bond. Compounds **5** are stable in solid state, but in solution they undergo a mutual exchange of the ethoxy- and the amino functionality to give isomers $^{-}(OC)_5M{-}C(=N^{+}R_2)]C[=C(OEt)R']C(Ph){=}CHR''$ (**6**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; Metallahexatrienes; Carbiminium carbonylmetalates; Chromium and tungsten complexes; Enamines

1. Introduction

(1-Alkynyl)carbene complexes, e.g. $(CO)_5M{=}C(OEt)$-$C{\equiv}CPh$ (**1a**,**b**) (M = Cr, W) are potentially useful reagents for the synthesis of organic compounds [1]. It was shown only recently that secondary enaminones, e.g. compounds **2** [2a,b] as well as tertiary cyclic enamines $\sim CH{=}C(NR_2)\sim$ [2c,d,e] undergo a 4-addition to the C≡C bond of (1-alkynyl)carbene complexes **1a**,**b** under exceedingly mild conditions to afford conjugated 6-amino-1-metalla-1,3,5-hexatrienes $(OC)_5M{=}CC{=}CC{=}C(N)$, e.g. compounds **3** (Scheme 1), which could be further transformed into π- and α-cyclisation products [3]. Whilst pursuing these studies, a second reaction mode significantly different from the forementioned one was found, which yields 'cross conjugated' metallahexatrienes $(OC)_5M{=}CC[{=}C(NR_2)]C{=}C$, e.g. compounds (1*E*)-**5** (Scheme 1) by dichotomy of the (N)C=C bond at the C≡C bond instead of conjugated metallahexatrienes, e.g. compounds **3** by a Michael-type addition [4,5]. Although there is ample precedence for reactions of enamines with alkynes, e.g. propargylic esters, in which cyclobutene derivatives are generated in the first reaction step and subsequently undergo ring opening to butadiene derivatives [6,7], reactions of enamines with (1-alkynyl)carbene complexes **1** leading to formation of stable 'cross-conjugated' metallatrienes of type (1*E*)-**5** instead of conjugated 1-metalla-1,3,5-trienes (**3**) had not been reported [8].

2. Results and discussion

It has been found that carbiminium carbonylmetalates (1*E*)-**5** containing a pyrrolidine unit ($R_2N{=}C_4H_8N$) would undergo a (1*E*/1*Z*) isomerisation, which appears to be reversible and seems to be governed by the dipole moment of the corresponding isomers (Scheme 2) [4b]. We now wish to report that this type of (1*E*/1*Z*) rearrangement strongly depends on the type of amine substituent. Whilst it was found to be the major reaction of pyrrolidine derivatives **5** it became a minor side reaction in case of compounds (1*E*)-**5** containing a (less basic) morpholine unit ($R_2N{=}C_4H_8NO$) instead of a (more basic) pyrrolidine moiety, since it was outrun by a mutual exchange of the ethoxy- and the morpholine group to give compounds **6**.

☆ Part 108 of the series: Organic Syntheses via Transition Metal Complexes. For preceding paper see Ref. [11].

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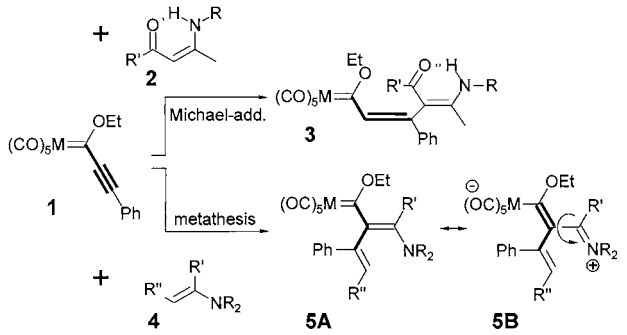
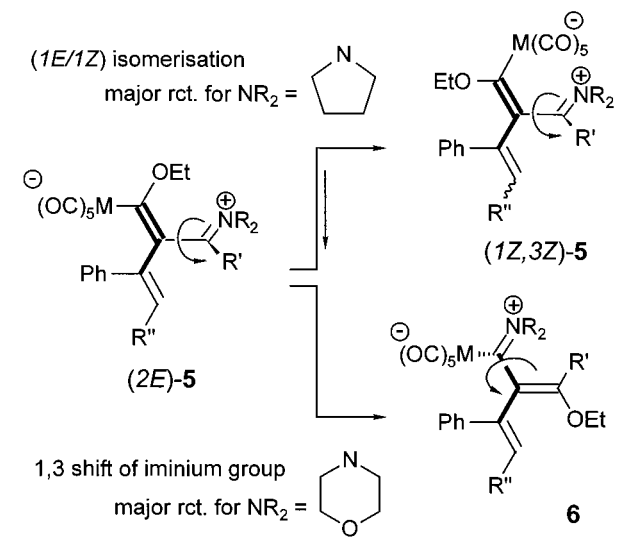
It is suggested that the transformation of carbiminium carbonylmetalates (1*E*)-**5** into (thermodynamically more stable) isomers **6** would involve an equilibrium between zwitterionic intermediates **A** and **C** via formation of vinylidene complexes **B** (Scheme 3).



(1*E*)-**5**	M	NR_2	R'	R''	**5**[%]	δ(M=*C*)	δ(*C*=N^+)	δ(4-H)	Lit.
a	W	morpholino	Me	CO_2Me	93	254.4	180.5	5.90	*[b]*
b	Cr	morpholino	Me	CO_2Me	91	*[a]*	174.7	5.74	*[b]*
c	W	morpholino	Me	CO_2CH_2Ph	87	*[a]*	180.2	5.98	*[b]*
d	W	morpholino	Me	CO_2tBu	89	252.2	180.1	5.97	*[b]*
e	W	morpholino	Me	Ph	90	*[a]*	*[a]*	6.80	*[b]*
f	W	morpholino	H	Me	93	277.8	167.1	5.51	5
g	W	morpholino	H	*i*Pr	95	278.1	166.8	5.16	5

[a] Not observed due to dynamic broadening at 242 K. *[b]* This paper.

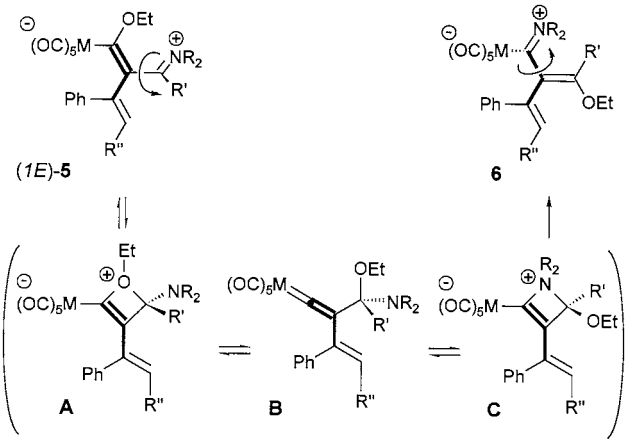
Scheme 1. Different reaction modes of secondary enaminones and tertiary enamines, respectively, with (1-alkynyl)carbene complexes **1** (M = W, Cr); chemical yields and characteristic NMR shifts of carbiminium carbonylmetalates (1*E*)-**5** (in $CDCl_3$ at 242 K).



(1*E*)-**5,6**	M	NR_2	R'	R'	(1*Z*)-**5**/**6**[a]	**6**: δ(M=*C*)	Lit.
a	W	morpholino	Me	CO_2Me	1 / 6	254.7	*[b]*
b	Cr	morpholino	Me	CO_2Me	0 / 1	273.7	*[b]*
c	W	morpholino	Me	CO_2CH_2Ph	1 / 2	253.8	*[b]*
d	W	morpholino	Me	CO_2tBu	1 / 6	254.2	*[b]*
e	W	morpholino	Me	Ph	0 / 1	254.7	*[b]*
f	W	morpholino	H	Me	0 / 1	252.9	5
g	W	morpholino	H	*i*Pr	0 / 1	255.0	5

[a] Product ratio according to NMR spectra of the mixture. *[b]* This paper.

Scheme 2. Thermal (1*E*/1*Z*) isomerisation of 4-iminium carbonylmetalates **5** and formation of 2-iminium carbonylmetalates **6** by a 1,3 shift of the imino unit.



Scheme 3. Reaction path suggested for a 1,3 shift of the iminium functionality of carbiminium carbonylmetalates (1*E*)-**5**.

The transformation of the 4- into 2-carbiminium complexes, (1*E*)-**5** and **6**, respectively, was followed by ^{1}H-NMR spectra. Characteristic spectral changes include a significant high-field shift of the signals OCH_2 [e.g. (1*E*)-**5a**: δ 4.21; **6a**: AB-system δ 3.73 and 3.27], a strong diastereotopic splitting of the methylene protons [e.g. NCH_2 and OCH_2 of **6a**: δ 5.70–3.30] as well as of the corresponding carbon signals [e.g. (1*E*)-**5a**: δ (OCH_2CH_3) 73.9; (OCH_2 morpholine) 66.1; (NCH_2 morpholine) 51.8. **6a**: 67.6, 67.0, 64.2, 63.0 and 53.3]. The chemical shifts of the carbene carbon atoms of compounds (1*E*)-**5a**–**d** and **6a**–**d** are in a range typically observed for carbiminium carbonylmetalates [e.g. (1*E*)-**5a**: δ (W–C) 254.4, **6a**: 254.7], at somewhat higher field than observed for 4-amino-tungsta-1,3-butadienes [e.g. $(OC)_5W{=}C(OEt)CH{=}C(NMe_2)Ph$ δ 269.7). Furthermore, a relative high field shift of 4-H is observed for compounds **6** compared to iminium complex (1*E*)-**5** [e.g. (1*E*)-**5a**: δ 5.90; **6a**: 5.41]. The transformation of compounds (1*E*)-**5a** into **6a** involves a configurational change of C3=C4 leading to a NOE enhancement of OCH_2 (morpholine) as well as of *ortho*-phenyl on irradiation of 4-H.

Structural details of compounds (1*Z*)-**5a** were provided by a crystal structure analysis (Fig. 1). The compound shows a carbiminium carbonylmetalate unit, which is characterized by a pattern of alternating bond distances of the W–C=C–C=N^+ backbone [W–C2 2.292(5) Å, C2=C3 1.418(7), C3–C6 1.463(7), C6=N1 1.312(7)], a slightly distorted *cisoid* arrangement of the W–C2=C3–C6 moiety [dihedral angle −34.4(7)°] and a stronger distortion of the *transoid* C2=C3–C6=N1 unit [dihedral angle 143.3(6)°]. Especially the latter feature excludes the presence of an enamino unit, since this would imply a planar C3=C6 double bond. The

C2=C3–C4=C5 portion of the molecule adopts a *transoid* conformation [dihedral angle 140.1(6)°], and shows an essential planar *cis* arrangement of the C3–C4–C5–C51 −9.2(10) group as well as a slightly distorted ester functionality [dihedral angle C4–C5–C51–O51 −20.7(10)].

Carbiminium carbonylmetalates **6** were characterized by NMR spectra and a crystal structure analysis of compound **6a** (Fig. 2). The latter compound exhibits a long distance between C2–C3 1.514(15) and a short distance C2=N2 1.318(13) as well as a strong distortion of W–C2–C3=C6 96.3(9)° [N2–C2–C3=C6 −80.5(12)]. The C6=C3–C4=C5–C51 diene portion of the molecule shows alternating bond distances [C3=C6 1.331(14), C3–C4 1.464(14), C4–C5 1.38(2) and C5–C51 1.44(2)] and adopts a *transoid* conformation, C6=C3–C4=C5 148.7(11)°, C3–C4–C5–C51 175.6(11) and C4–C5–C51–O51 −21.3(23).

3. Experimental

All operations were performed under argon. Dried solvents were used in all experiments. Melting points are not corrected. Instrumentation: ^{1}H- and ^{13}C-NMR spectra were obtainend with Bruker ARX 300, Bruker AM 360 und Varian U 600 spectrometers. Chemical shifts refer to $\delta_{TMS} = 0.00$ ppm. Other analyses: IR Digilab FTS 45; MS Finnigan MAT 312; elemental analysis with Perkin–Elmer 240 elemental analyzer; TLC with Merck DC-Alufolien Kieselgel 60 F_{254}. R_f values refer to TLC tests. Column chromatographic purifications were achieved with Merck Kieselgel 100. Pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)-tungsten (**1a**) and -chromium (**1b**) were prepared according to the procedure given in Ref. [1].

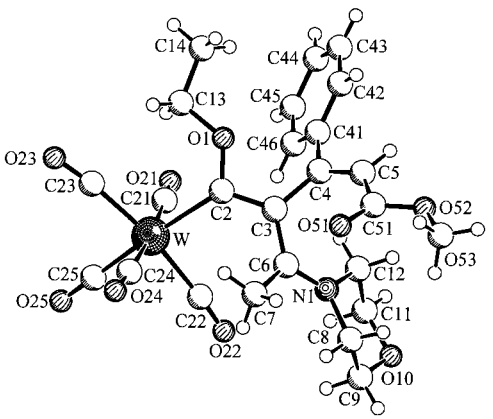


Fig. 1. Molecular structure of carbiminium carbonyltungstate (1*Z*)-**5a**. Selected bond distances (Å) and angles (°): W–C2 2.292(5), C2–O1 1.355(6), C2–C3 1.418(7), O1–C13 1.441(7), C13–C14 1.490(9), C3–C6 1.463(7), C3–C4 1.499(8), C4–C5 1.328(8), C5–C51 1.466(8), C51–O51 1.212(7), C51–O52 1.324(7), O52–C53 1.436(7), C6–N1 1.312(7), C6–C7 1.491(8), N1–C8 1.483(7), N1–C12 1.482(8), C8–C9 1.472(11), C9–O10 1.413(12), O10–C11 1.420(9), C11–C12 1.494(9); O1–C2–C3 106.1(5), O1–C2–W 124.5(4), C3–C2–W 127.7(4), C2–O1–C13 123.8(4), O1–C13–C14 108.7(5), C2–C3–C4 120.4(5), C2–C3–C6 120.8(5), C4–C3–C6 118.8(5), C5–C4–C41 117.9(5), C3–C4–C5 123.8(5), C3–C4–C41 118.1(5), C4–C41–C42 121.0(6), C4–C41–C46 121.4(5), C4–C5–C51 128.9(6), C5–C51–O51 126.4(6), C5–C51–O52 111.6(6), O51–C51–O52 122.0(6), C51–O52–C53 117.5(5), C3–C6–N1 121.0(5), C3–C6–C7 120.2(5), N1–C6–C7 118.5(5), C6–N1–C8 124.6(6), C6–N1–C12 125.3(5), C8–N1–C12 110.1(5), N1–C8–C9 111.1(6), C8–C9–O10 114.2(9), C9–O10–C11 109.1(7), O10–C11–C12 110.4(7), C11–C12–N1 111.1(6).

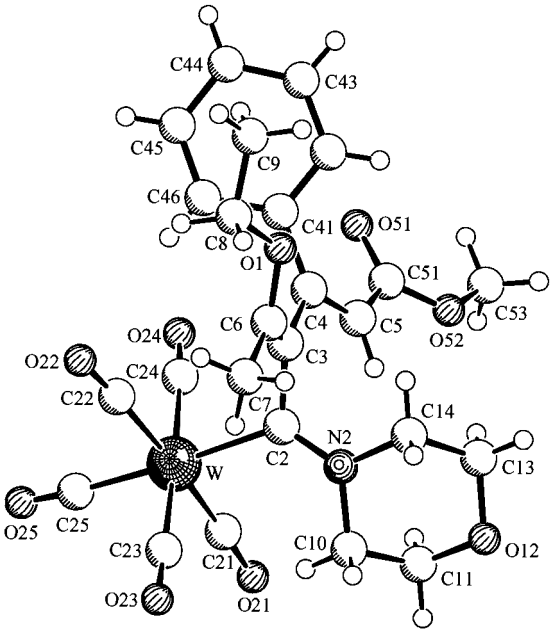
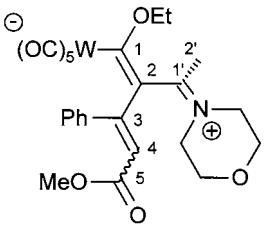


Fig. 2. Molecular structure of carbiminium carbonyltungstate **6a**. Selected bond lengths (Å) and angles (°): W–C2 2.247(9), C2–N2 1.318(13), C2–C3 1.514(15), N2–C10 1.479(14), N2–C14 1.480(14), C11–C10 1.49(2), C3–C6 1.331(14), C3–C4 1.464(14), C6–O1 1.379(12), C6–C7 1.51(2), O1–C8 1.413(14), C8–C9 1.46(2), C4–C5 1.38(2), C4–C41 1.48(2), C5–C51 1.44(2), C51–O51 1.256(14), C51–O52 1.288(14), O52–C53 1.41(2); N2–C2–C3 114.4(9), N2–C2–W 129.8(8), C3–C2–W 115.7(6), C2–N2–C10 124.6(9), C2–N2–C14 125.2(10), C10–N2–C14 110.3(9), N2–C14–C13 109.9(11), N2–C10–C11 109.1(10), C6–C3–C4 123.2(10), C6–C3–C2 119.4(9), C4–C3–C2 117.4(9), C3–C6–O1 118.8(9), C3–C6–C7 124.2(10), O1–C6–C7 116.7(10), C6–O1–C8 118.8(9), C5–C4–C3 115.8(10), C5–C4–C41 123.8(10), C3–C4–C41 120.5(9), C42–C41–C4 120.8(11), C46–C41–C4 120.3(9), C4–C5–C51 128.3(11), O51–C51–O52 121.7(11), O51–C51–C5 125.3(12), O52–C51–C5 113.0(11), C51–O52–C53 122.8(12).

*3.1. Pentacarbonyl[1-ethoxy-5-methoxy-2-(1-morpholinium-1-ethylidene)-5-oxo-3-phenyl-penta-1,3-dien-1-yl]tungstate [(1E)- and (1Z)-**5a**] and pentacarbonyl[2-(1-ethoxy-ethylidene)-5-methoxy-1-morpholinium-5-oxo-3-phenyl-3-penten-1-yl]tungstate (**6a**)*

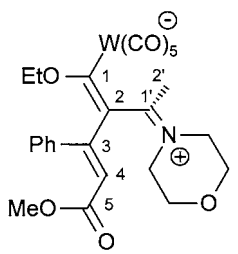
A mixture of pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**, 482 mg, 1.00 mmol) and

3-morpholino-but-2-enoic acid methylester (**4a**, 185 mg, 1.00 mmol) in 20 ml of *n*-pentane is vigorously stirred in a centrifuge tube for 1 h at 20°C to give a yellow precipitate of compound (1*E*)-**5a**, which is isolated by centrifugation and washed twice with 5 ml of *n*-pentane each [606 mg, 98%, m.p. (dec.) 74°C, R_f = 0.1 in diethyl ether–pentane (1:1)]. (1*E*)-**5a** in $CDCl_3$ solution undergoes an isomerisation to a 1:6 mixture of compounds (1*Z*)-**5a** and **6a**, which is completed within 24 h at 20°C.



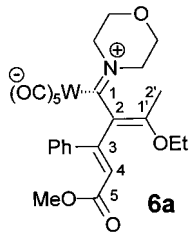
(*1E*)-**5a**

^{1}H-NMR ($CDCl_3$): δ 7.27 (5H, s, C_6H_5), 5.90 (1H, s, 4-H), 4.21 (3H, q, $^3J = 7$ Hz, OCH_2CH_3), 3.72 (4H, m, $2OCH_2$, morpholine), 3.57 (3H, s, OCH_3), 3.53 (4H, m, $2NCH_2$, morpholine), 2.31 (3H, s, N=CCH_3), 1.15 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$, 242 K): δ 254.4 (W–C), 202.8 and 199.4 [1: 4, *trans*- and *cis*-CO W(CO_5], 180.5 (C_q, C=N^+), 166.6 (C_q, $COOCH_3$), 156.5 (C_q, C3), 138.8 and 134.8 (C_q each, C2 and *i*C Ph), 128.7–127.5 (5CH Ph), 118.7 (CH, C4), 73.9 (OCH_2CH_3), 66.1 (broad, 2 diastereotopic OCH_2 of morpholine), 51.8 (broad, $2NCH_2$ morpholine), 51.1 (OCH_3), 26.7 (OCH_2CH_3), 14.9 ($NCCH_3$). IR (diffuse reflection), cm^{-1}: 2051.0 (10), 1921.5 (100) and 1897.4 (80) [ν(C≡O], 1712.6 (20) [ν(C=O].



(*1Z*)-**5a**

^{1}H-NMR ($CDCl_3$: δ 7.52 (2H, m, *o*-H Ph), 7.30 (3H, m, *m*- and *p*-H Ph), 6.27 (1H, s, 4-H), 4.39 (2H, q, OCH_2CH_3), 3.84 (4H, m, $2OCH_2$ morpholine), 3.79 (3H, s, OCH_3), 3.60 (4H, m, $2NCH_2$ morpholine), 2.46 (3H, s, N=CCH_3), 1.18 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$) δ (W–C) [9], 203.4 and 200.1 [1:4, *trans*- and *cis*-CO, W(CO_5], δ [9] (C_q, C=N^+), 166.8 (C_q, $COOCH_3$) 157.4 (C_q, C3), 143.7 (C_q, C2), δ [9] (C_q, *i*C Ph); 129.7, 129.0 and 128.6 (CH each, Ph), 117.8 (CH, C4), 75.1 (OCH_2CH_3), 66.6 (broad, $2OCH_2$ morpholine), 52.8 (broad, $2NCH_2$ morpholine), 51.5 (OCH_3) 25.8 (OCH_2CH_3), 15.6 ($NCCH_3$). IR (diffuse reflection, cm^{-1}: 2053.1 (20) and 1897.0 (100) [ν(C≡O], 1710.2 (20) [ν(C=O]. X-ray crystal structure analysis of compound (1*Z*)-**5a**: formula $C_{25}H_{25}NO_9W$, $M = 667.31$, red crystal $0.25 \times 0.20 \times 0.15$ mm, $a = 19.737(1)$, $b = 10.662(1)$, $c = 25.249(1)$ Å, $\beta = 107.56(1)°$, $V = 5065.7(6)$ Å^3, $\rho_{calc} = 1.750$ g cm^{-3}, $\mu = 46.14$ cm^{-1}, empirical absorption correction via ψ-scan data ($0.957 \le C \le 0.999$), $Z = 8$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 0.71073$ Å, $T = 293$ K, ω–2θ scans, 5279 reflections collected ($-h$, $-k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 5129 independent ($R_{int} = 0.023$) and 3548 observed reflections [$I \ge 2\sigma(I)$], 328 refined parameters, $R = 0.033$, $wR^2 = 0.070$, max. residual electron density 1.49 (-1.14) e Å^{-3} close to tungsten, hydrogen calculated and refined as riding atoms [10].



6a

^{1}H-NMR ($CDCl_3$: δ 7.27 (5H, m, Ph), 5.41 (1H, s, 4-H), 5.70–3.30 (8H, m, $2OCH_2$ and $2NCH_2$ morpholine), 3.73 and 3.27 (1H each, diastereotopic OCH_2CH_3), 3.50 (3H, s, OCH_3), 1.79 [3H, s, =C(OEt)CH_3], 0.63 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$) δ 254.7 (W–C=N^+), 202.8 and 198.6 [1:4, *trans*- and *cis*-CO W(CO_5], 166.2 (C_q, $COOCH_3$); 148.6, 146.0 and 140.1 (C_q each; C1′, C2 and C3), 137.5 (C_q, *i*C Ph), 127.9 and 127.7 (CH each, Ph), 120.1 (CH, C4); 67.6, 64.2 and 63.0 (OCH_2 each, Et and morpholine), 53.3 (broad, $2NCH_2$ morpholine), 51.5 (OCH_3), 17.1 (CH_3, C2′), 15.6 (OCH_2CH_3). IR (diffuse reflection), cm^{-1}: 2058.9 (30), 1908.8 (100) [ν(C≡O], 1724.3 (20) [ν(C=O]. MS (70 eV, m/e (%) ^{184}W: 667 (10) [M$^+$], 315 (35) [ligand], 314 (100). Anal. Found: C, 44.78; H, 4.02; N, 2.10. Calc. for $C_{25}H_{25}NO_9W$ (667.3): C, 45.00; H, 3.78; N, 2.10%. X-ray crystal structure analysis of compound **6a**: formula $C_{25}H_{25}NO_9W$, $M = 667.31$, yellow–red crystal $0.40 \times 0.20 \times 0.10$ mm, $a = 8.312(2)$, $b = 11.362(3)$, $c = 15.432(5)$ Å, $\alpha = 108.07(3)$, $\beta = 100.55(2)$, $\gamma = 93.37(2)°$, $V = 1351.7(7)$ Å^3, $\rho_{calc} = 1.640$ g cm^{-3}, $\mu = 83.56$ cm^{-1}, empirical absorption correction via ψ-scan data ($0.583 \le C \le 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 293$ K, ω–2θ scans, 5894 reflections collected ($+h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 5497 independent ($R_{int} = 0.088$) and 4419 observed reflections [$I \ge 2\sigma(I)$], 329 refined parameters, $R = 0.067$, $wR^2 = 0.174$, max. residual

electron density 2.23 (− 2.14) e $Å^{-3}$ close to tungsten, hydrogen calculated and refined as riding atoms [10].

3.2. Pentacarbonyl[1-ethoxy-5-methoxy-2-(1-morpholinium-1-ethylidene)-5-oxo-3-phenyl-penta-1,3-dien-1-yl]chromate [(1E)- and (1Z)-**5b**] and pentacarbonyl[2-(1-ethoxy-ethylidene)-5-methoxy-1-morpholinium-5-oxo-3-phenyl-3-penten-1-yl]chromate (**6b**)

A mixture of pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)chromium (**1b**, 351 mg, 1.00 mmol) and 3-morpholino-but-2-enoic acid methylester (**4a**, 185 mg, 1.00 mmol) in 20 ml of *n*-pentane is reacted as described above to give compound (1*E*)-**5b** [487 mg, 78%, m.p. (dec.) 78°C, $R_f = 0.1$ in diethyl ether–pentane (1:1)]. (1*E*)-**5b** in $CDCl_3$ solution undergoes an isomerisation within 24 h at 20°C to give compound **6b** as the only isolated product.

3.2.1. (1E)-**5b**

^{1}H-NMR ($CDCl_3$): δ 7.29 (5H, s, Ph), 5.74 (1H, s, 4-H), 4.35 (2H, diastereotopic OCH_2CH_3), 3.61 (4H, m, $2OCH_2$, morpholine), 3.57 (3H, s, OCH_3), 3.31 (4H, m, $2NCH_2$, morpholine), 2.20 (3H, s, $NCCH_3$), 1.31 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$ 242 K): δ [9] (Cr=C), 224.0 and 218.6 [1: 4, *trans*- and *cis*-CO, $Cr(CO_5]$, 174.7 (C_q, C=N^+), 166.7 (C_q, *C*$OOCH_3$), 155.3 (C_q, C3), 138.3 (C_q, C2), 134.8 (C_q, *i*C Ph); 128.8, 127.6 and 127.3 (CH each, Ph), 118.4 (CH, C4), 72.6 (OCH_2CH_3), 66.4 (broad, $2OCH_2$, morpholine), 51.6 (broad, $2NCH_2$, morpholine), 51.3 (OCH_3), 25.9 (OCH_2CH_3), 15.4 ($NCCH_3$). IR (diffuse reflection, cm^{-1}: 2049.1 (30), 1925.9 (100), 1898.6 (90) [ν(C≡O], 1720.7 (20) [ν(C=O].

3.2.2. Compound **6b**

^{1}H-NMR ($CDCl_3$): δ 7.27 (5H, m, Ph), 5.31 (1H, s, 4-H), 4.70–3.10 (8H, m, OCH_2 and NCH_2, morpholine), 3.65 and 3.21 (1H, diastereotopic OCH_2CH_3), 3.48 (3H, s, OCH_3), 1.73 [3H, s, =C(OEt)CH_3], 0.61 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 273.7 (Cr=C), 222.5 and 217.2 [1:4, *trans*- and *cis*-CO, $Cr(CO_5]$, 165.6 (C_q, *C*$OOCH_3$); 148.1, 146.0 and 139.7 (C_q each; C1′, C2 and C3), 131.1 (C_q, *i*C Ph), 127.5–127.2 (5CH, Ph), 119.3 (CH, C4); 67.2, 63.6 and 60.3 (OCH_2 each, OCH_2CH_3 and morpholine), 54.0 ($2NCH_2$ morpholine), 51.0 (OCH_3), 16.5 [=C(OEt)CH_3], 14.1 (OCH_2CH_3). IR (diffuse reflection), cm^{-1}: 2050.2 (30), 1972.7 (90), 1905.2 (100) [ν(C≡O], 1724.4 (20) [ν(C=O]. MS (70 eV), *m*/*e* (%), ^{184}W: 535 (4) [M^+], 395 (20) [$M^+ - 5CO$], 211 (20) [ligand], 141 (95), 52 (100). Anal. Found: C, 55.94; H, 4.87; N, 2.82. Calc. for $C_{25}H_{25}NO_9Cr$ (535.5): C, 56.08; H, 4.71; N, 2.62%.

3.3. Pentacarbonyl[1-ethoxy-5-benzoxy-2-(1-morpholinium-1-ethylidene)-5-oxo-3-phenyl-penta-1,3-dien-1-yl]tungstate [(1E)- and (1Z)-**5c**] and pentacarbonyl[2-(1-ethoxy-ethylidene)-5-benzoxy-1-morpholinium-5-oxo-3-phenyl-3-penten-1-yl]tungstate (**6c**)

A mixture of pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**, 482 mg, 1.00 mmol) and 3-morpholino-but-2-enoic acid benzylester (**4b**, 227 mg, 1.00 mmol) in 20 ml of *n*-pentane is reacted as described above to give compound (1*E*)-**5c** [660 mg, 87%, m.p. (dec.) 80°C, $R_f = 0.1$ in diethyl ether–pentane (1:1)]. (1*E*)-**5c** in $CDCl_3$ solution undergoes an isomerisation within 24 h at 20°C to give compound (1*Z*)-**5c** and **6c** in a molar ratio 1:2.

3.3.1. (1E)-**5c**

^{1}H-NMR (C_6D_6, 360 MHz, 242 K): δ 7.40–7.00 (10H, m, Ph and CH_2Ph), 5.98 (1H, s, 4-H), 4.96 (2H, s, OCH_2Ph), 4.15 (2H, m, diastereotopic OCH_2CH_3), 3.62 (4H, broad, $2OCH_2$ morpholine), 3.39 (4H, broad, $2NCH_2$ morpholine), 2.19 (3H, s, N=CCH_3), 1.12 (3H, OCH_2CH_3). ^{13}C-NMR (C_6D_6, 360 MHz, 242 K): δ [9] (W–*C*), 202.9 and 199.5 [1: 4, *trans*- and *cis*-CO, $W(CO_5]$, 180.2 (C_q, C=N^+), 166.2 (C_q, *C*$OOCH_2Ph$), 157.1 (C_q, C3), 139.1 (C_q, C2), 135.5 and 135.3 (C_q each, *i*C, Ph), 129–127 (5CH, Ph), 118.9 (CH, C4), 74.4 (OCH_2CH_3), 66.2 ($2OCH_2$ morpholine), 65.7 (OCH_2Ph), 51.9 ($2NCH_2$ morpholine), 27.1 (OCH_2CH_3), 15.1 ($NCCH_3$). IR (diffuse reflection), cm^{-1}: 2051.6 (20), 1919.5 (90) and 1876.2 (100) [ν(C≡O], 1712.6 (20) [ν(C=O].

3.3.2. (1Z)-**5c**

^{1}H-NMR ($CDCl_3$): δ 7.46 (2H, m, *o*-H Ph), 7.30 and 7.00 (6:2H, m, Ph and CH_2Ph), 6.24 (1H, s, 4-H), 5.04 (2H, diastereotopic CH_2Ph), 4.19 (2H, diastereotopic, OCH_2CH_3), 3.64 (4H, m, $2OCH_2$ morpholine), 3.42 (4H, m, $2NCH_2$ morpholine), 2.27 (3H, s, $NCCH_3$), 1.09 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$) δ [9] (W–C), 203.2 and 199.7 [1: 4, *trans*- and *cis*-CO, $W(CO_5]$ [9], (C_q, C=N^+), 165.7 (C_q, *C*$OOCH_2Ph$), 157.6 (C_q, C3), 142.2 (C_q, C2), [9] (C_q, *i*C 3-Ph), 136.4 (C_q, *i*C CH_2Ph), 129–127 (10CH, Ph and CH_2Ph), 117.3 (CH, C4), 73.9 (OCH_2CH_3), 65.9 (OCH_2Ph), 61.9 ($2OCH_2$, morpholine), 52.0 ($2NCH_2$, morpholine), 24.8 ($NCCH_3$) 15.1 (OCH_2CH_3).

3.3.3. Compound **6c**

^{1}H-NMR ($CDCl_3$): δ 7.29–7.15 (10H, m, Ph and CH_2Ph), 5.39 (1H, s, 4-H), 5.14 (2H, diastereotopic CH_2Ph), 4.60–3.10 (10H, m, $2OCH_2$ and $2NCH_2$ morpholine each, and OCH_2CH_3), 1.70 [3H, s,

=C(OEt)CH_3], 0.56 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 253.8 (W–C), 212.3 and 198.7 [1:4, *trans*- and *cis*-CO, $W(CO_5)$], 165.3 (C_q, $COOCH_2Ph$); 147.8, 146.2 and 139.6 (C_q each; C1′, C2 and C3), 135.7 and 131.9 (C_q each, *i*C Ph), 129–127 (CH, Ph and CH_2Ph), 119.9 (CH, C4); 67.2, 66.6, 66.1, 63.8 and 62.6 (OCH_2 each; morpholine, $OCH_2C_6H_5$ and OCH_2CH_3), 52.9 ($2NCH_2$, morpholine), 16.7 [=C(OEt)CH_3], 14.0 (OCH_2CH_3). IR (diffuse reflection), cm^{-1}: 2058.3 (20), 1927.0 (90), 1902.1 (100) [ν(C≡O], 1721.3 (20) [ν(C=O]. MS (70 eV, *m*/*e* (%), ^{184}W: 419 (50) [M^+–$W(CO_5)$], 339 (100), 91 (100) [CH_2Ph^+]. Anal. Found: C, 44.73; H, 4.16; N, 1.61. Calc. for ($C_{31}H_{29}NO_9W \times CHCl_3$) (862.8): C, 44.55; H, 3.50; N, 1.63%.

3.4. Pentacarbonyl[1-ethoxy-5-(t-butoxy)-2-(1-morpholinium-1-ethylidene)-5-oxo-3-phenyl-penta-1,3-dien-1-yl]tungstate [(1E)- and (1Z)-**5d**] and pentacarbonyl[2-(1-ethoxy-ethylidene)-5-(t-butoxy)-1-morpholinium-5-oxo-3-phenyl-3-penten-1-yl]tungstate (**6d**)

A mixture of pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**, 482 mg, 1.00 mmol) and 3-morpholino-but-2-enoic acid *t*-butylester (**4c**, 203 mg, 1.00 mmol) in 20 ml of *n*-pentane is reacted as described above to give compound (1*E*)-**5d** [631 mg, 89%, m.p. (dec.) 99°C, $R_f = 0.1$ in diethyl ether–pentane (1:1)]. (1*E*)-**5d** in $CDCl_3$ solution undergoes an isomerisation within 24 h at 20°C to give compound (1*Z*)-**5c** and **6c** in a molar ratio 1:6.

3.4.1. (1E)-**5d**

^{1}H-NMR (C_6D_6, 360 MHz): δ 7.35 and 7.05 (2:3H, Ph), 5.97 (1H, s, 4-H), 4.19 (2H, diastereotopic OCH_2CH_3), 2.90 (4H, m, $2OCH_2$ morpholine), 2.80 (4H, m, NCH_2 morpholine), 1.70 (3H, s, $NCCH_3$) 1.30 [9H, s, $C(CH_3)_3$], 0.93 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$, 242 K): δ 252.2 (W–C), 203.2 and 199.4 [1: 4, *trans*- and *cis*-CO, $W(CO_5)$], 180.1 (C_q, C=N$^+$), 165.9 (C_q, $COOCMe_3$), 154.3 (C_q, C3), 139.4 and 134.6 (C_q each, C2 and *i*C Ph); 128.9, 128.5 and 127.5 (CH each, Ph), 123.1 (CH, C4), 79.9 (CMe_3), 73.7 (OCH_2CH_3), 66.2 ($2OCH_2$ morpholine), 51.7 ($2NCH_2$ morpholine), 27.4 (CMe_3), 26.2 (OCH_2CH_3), 15.2 ($NCCH_3$). IR (diffuse reflection), cm^{-1}: 2050.6 (20), 1900.2 (100) [ν(C≡O], 1703.6 (20) [ν(C=O].

3.4.2. (1Z)-**5d**

^{1}H-NMR ($CDCl_3$): δ 7.52 and 7.25 (2:3 H, m each, Ph), 6.19 (1H, s, 4-H), 4.22 (2H, diastereotopic OCH_2CH_3), 3.87 (4H, m, $2OCH_2$ morpholine), 3.75 (4H, m, $2NCH_2$ morpholine), 2.34 (3H, s, $NCCH_3$), 1.45 [9H, s, $C(CH_3)_3$], 1.14 (3H, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ [9] (W–C), 202.9 and 199.8 [1: 4, *trans*- and *cis*-CO, $W(CO_5)$], 178.0 (C_q, C=N), 165.9 (C_q, $COOCMe_3$), 153.1 (C_q, C3), 139.9 and 135.8 (C_q each, C2 and *i*C Ph); 128.1, 127.6 and 126.9 (CH each, Ph), 123.5 (CH, C4), 79.7 (CMe_3), 74.1 (OCH_2CH_3), 66.2 ($2OCH_2$, morpholine), 52.3 ($2NCH_2$, morpholine), 27.5 [$C(CH_3)_3$], 25.8 ($NCCH_3$), 15.3 (OCH_2CH_3). IR (diffuse reflection), cm^{-1}: 2058.6 (20), 1966.9 (90), 1935.6 (100) [ν(C≡O], 1708.7 (20) [ν(C=O].

3.4.3. Compound **6d**

^{1}H-NMR ($CDCl_3$): δ 7.25 (5H, s, Ph), 5.26 (1H, s, 4-H), 4.60–3.10 (10H, m, OCH_2 and NCH_2 morpholine each, and OCH_2CH_3), 1.78 [3H, s, =C(OEt)CH_3], 1.07 [9H, s, $C(CH_3)_3$], 0.59 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 254.2 (W–C), 202.5 and 199.1 [1:4, *trans*- and *cis*-CO, $W(CO_5)$], 165.6 (C_q, $COOCMe_3$); 145.5, 145.0 and 140.6 (C_q each; C1′, C2 and C3), 131.2 (C_q, *i*C Ph); 128.1, 127.6 and 126.9 (CH each, Ph), 122.7 (CH, C4), 80.2 (CMe_3); 66.7, 66.3, 63.7 and 62.5 ($2OCH_2$ and $1NCH_2$ morpholine each, and OCH_2CH_3), 52.8 (NCH_2 morpholine), 27.8 [$C(CH_3)_3$], 16.6 [=C(OEt)CH_3], 14.1 (OCH_2CH_3). MS (70 eV), *m*/*e* (%), ^{184}W: 709 (10) [M^+], 569 (10) [M^+–5CO], 385 (20) [ligand], 57 (100). Anal. Found: C, 47.78; H, 4.21; N, 2.67. Calc. for $C_{28}H_{31}NO_9W$ (709.4): C, 47.41; H, 4.40; N, 1.97%.

3.5. Pentacarbonyl[1-ethoxy-5-(t-butoxy)-2-(1-morpholinium-1-ethylidene)-5-oxo-3,4-bis(phenyl)-penta-1,3-dien-1-yl]tungstate [(1E)-**5e**] and pentacarbonyl[2-(1-ethoxy-ethylidene)-5-(t-butoxy)-1-morpholinium-5-oxo-3,4-bis(phenyl)-3-penten-1-yl] tungstate (**6e**)

A mixture of pentacarbonyl(1-ethoxy-3-phenyl-2-propin-1-ylidene)tungsten (**1a**, 482 mg, 1.00 mmol) and 2-morpholino-1-phenyl-propene (**4d**, 170 mg, 1.00 mmol) in 20 ml of *n*-pentane is reacted as described above to give compound (1*E*)-**5e** (500 mg, 90%). (1*E*)-**5e** in $CDCl_3$ solution undergoes an isomerisation within 24 h at 20°C to give compound **6e** as the only product.

3.5.1. (1E)-**5e**

^{1}H-NMR ($CDCl_3$): δ 7.40–7.00 (10H, m, Ph), 6.80 (1H, s, 4-H), 4.28 (2H, q, OCH_2CH_3), 3.60 (4H, m, diastereotopic OCH_2 morpholine), 3.49 (4H, m, diastereotopic NCH_2 morpholine), 2.18 (3H, s, $NCCH_3$), 1.22 (3H, t, OCH_2CH_3).

3.5.2. Compound **6e**

^{1}H-NMR ($CDCl_3$): δ 7.30–6.80 (10H, m, Ph), 6.04 (1H, s, 4-H), 4.70–3.00 (10H, m, OCH_2 and NCH_2, morpholine each, and OCH_2CH_3), 1.76 (3H, s, CH_3), 0.54 (3H, t, OCH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 254.7 (W=C), 203.1 and 198.9 [1: 4, *trans*- and *cis*-CO, $W(CO)_5$]; 142.5, 141.0 and 133.7 (C_q each; C1′, C2 and C3), 137.1 and 135.1 (C_q each, *i*C Ph), 131–126 (CH

each, C_6H_5 and C4); 67.7, 64.1, 63.8, 62.6 and 53.2 ($2OCH_2$ and $2NCH_2$, morpholine each, OCH_2CH_3), 16.9 [=C(OEt)CH_3], 14.6 (OCH_2CH_3). IR (diffuse reflection) cm^{-1}: 2058.6, 1979.7 and 1892.2 [ν(C≡O)]. MS (70 eV), m/z (%), ^{184}W: 685 (10) [M^+], 545 (8) [$M^+ - 5CO$], 361 (23) [ligand$^+$], 332 (100).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CSD-147009 (**5a**), and CSD-147010 (**6a**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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