Photochemical route to unusual tri-tungsten ferrocenylacetylene cluster [W₃{μ-η²,η²- (H)C≡CFc}₂(CO)₁₂] and a dimetallacyclodecatetraene[W₂{μ-η²,η²,η²,η²-(Fc)C=C(H)C(H)=C(Fc)C(Fc)=C(H)C(H)=C(Fc)}(CO)₆]

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Abstract

Low temperature photoreaction between tungsten hexacarbonyl and ferrocenylacetylene yielded two unusual metal containing stable compounds, the tritungsten cluster, [W₃(μ-η²,η²- (H)C≡CFc)₂(CO)₁₂] (**1**), and ditungsten-1,4,5,8-ferrocenylcyclodecatetraene, [W₂{μ-η²,η²,η²,η²-(Fc)C=C(H)C(H)=C(Fc)C(Fc)=C(H)C(H)=C(Fc)}(CO)₆] (**2**). Both compounds were characterised by IR and ¹H and ¹³C NMR spectroscopy and their molecular structures established by single crystal X-ray diffraction methods.
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Keywords: Tungsten carbonyl cluster; Dimetallacyclodecatetraene; Ferrocenylacetylene; Crystal structures

1. Introduction

Metal-assisted alkyne oligomerisation reactions have been continued to be of considerable interest [1–6]. Formation of cyclobutendiones occurs from reactions of a number of alkynes with iron pentacarbonyl in presence of trimethylamine-*N*-oxide and subsequent oxidation by CuCl₂ · 2H₂O [7]. Recently, oligomerisations, including co-cyclooligomerisations of ferrocenylacetylenes using metal carbonyls, have yielded some interesting products. For instance, thermal reaction of ferrocenylacetylene with mononuclear Fe(CO)₅ gave three coupling products [Fe(CO)₂{η⁵-2,5-Fc₂C₅H₂CO}C(Fc)=CH], [Fe(CO)₂{η²:η²-2,5-Fc₂C₄H₂Fe(CO)₃}μ-CO] and [Fe(CO)₃{η²:η²-2,5-Fc₂C₄H₂CO}] [8]. Low temperature photolysis of solutions containing ferrocenylacetylene and iron pentacar-

bonyl in presence of carbon monoxide forms 2,5- and 2,6-diferrocenylquinones [9]. These have been shown to form via an intermediacy of a ferrole type compound, tetracarbonyl(2-ferrocenylmaleoyl)iron. In this paper, we report on the formation of two unusual products, a tritungsten cluster bearing two uncoupled ferrocenylacetylene ligands and the other, a spirocyclic dimetallacyclodecatetraene, formed by coupling of four molecules of ferrocenylacetylene and two tungsten carbonyl units.

2. Results and discussion

When a hexane solution containing ferrocenylacetylene and an excess of tungsten hexacarbonyl was photolysed at −10 °C, two new compounds formed in approximately equal amounts, and these were identified as [W₃(μ-η²,η²-(H)C≡CFc)₂(CO)₁₂] (**1**) and ditungsten-1,4,5,8-ferrocenyl-cyclodecatetraene [W₂{μ-η²,η²,η²,η²- (Fc)C=C(H)C(H)=C(Fc)C(Fc)=C(H)C(H)=C(Fc)}(CO)₆] (**2**) (Scheme 1). The relative yields of the two products depend on the

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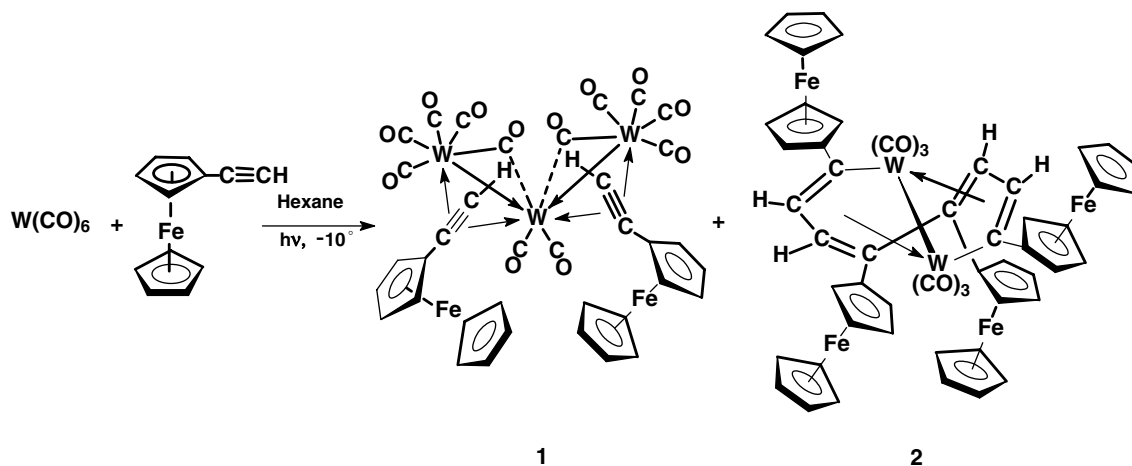
Scheme 1.

Table 1
Amounts of reactants used and yields of products obtained

[W(CO)$_6$] [mg (mmol)]	[FcC≡CH] [mg (mmol) (used)], [mg (mmol) (recovered)]	Products obtained	Yield[a]: mg (%)
[165 (0.45)]	[46 (0.22)], [5 (0.02)]	1	48 (37%)
		2	16 (24%)
[165 (0.45)]	[32 (0.15)], [5 (0.02)]	1	37 (44%)
		2	6 (13%)
[88 (0.25)]	[105 (0.5)], [12 (0.06)]	1	40 (14%)
		2	47 (29%)
		3a + 3b	24 (26%)

[a] Based on amount of FcC≡CH consumed.

reactant stoichiometry; using a three-fold excess of tungsten hexacarbonyl forms compound **1** as the major product and **2** in minor amounts, whereas, using a two-fold excess of ferrocenylacetylene yields compound **2** as the major product along with a reduced amount of **1** and trace amounts of previously reported cyclotrimerised products, 1,3,5- and 1,2,4-triferrocenylbenzene (**3a** and **3b**) (Table 1) [8].

The two new compounds, **1** and **2**, were characterised by IR and ^{1}H and ^{13}C NMR spectroscopy. Infrared spectra of **1** and **2** confirm the presence of terminal carbonyls. Additionally, the spectrum of **1** displays a peak at 1956 cm^{-1}, compatible with the presence of semibridging carbonyl. ^{1}H NMR spectra of both show signals in the range δ 4.0–4.8 ppm for the Cp protons (substituted and unsubstituted). The two equivalent acetylenic protons for compound **1** show a peak at δ 6.96, whereas for compound **2** peaks at δ 5.69 (doublet) and δ 7.33 (doublet) corresponding to olefinic protons have been observed. ^{13}C NMR spectra show the presence of terminal carbonyl carbons and acetylenic carbons along with cyclopentadienyl carbons in their respective regions. Unambiguous determination of molecular structures of **1** and **2** was made on the basis of single crystal X-ray diffraction analysis.

Molecular structure of **1** (Fig. 1) consists of a bent tritungsten chain bearing a total of 12 terminally bonded car-
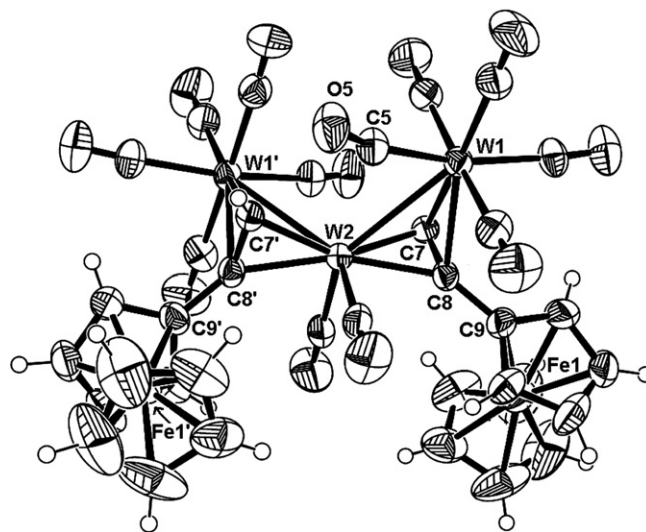

Fig. 1. Molecular structure (ORTEP plot at 50% probability) of [W$_3$(μ-C$_2$HFc)$_2$(CO)$_{12}$] (**1**) (Fc = (η^5-C$_5$H$_5$)$_2$Fe). Selected bond lengths (Å) and bond angles (°): W(1)–W(2) = 3.1017(3), W(2)–C(7) = 2.117(6), W(2)–C(8) = 2.173(6), W(1)–C(7) = 2.372(6), W(1)–C(8) = 2.474(6), C(7)–C(8) = 1.326(8), C(8)–C(9) = 1.463(8), W(1)–W(2)-W(1′) = 110.012(14), W(1)–C(7)–W(2) = 87.2(2), W(1)–C(8)–W(2) = 83.5(2), C(7)–C(8)–C(9) = 135.7(6), C(8)–W(2)–C(8′) = 162.3(3), W(1)–C(5)–O(5) = 165.3(6).

bonyls, five each on the end tungsten atoms and two on the middle tungsten atom. One carbonyl on each of the end tungsten pentacarbonyl units shows semi-bridging character (W(1)–C(5)–O(5) = 165.3(6)°), consistent with the presence of donor–acceptor metal–metal bonds (vide infra). Two ferrocenylacetylene molecules straddle the W–W bonds by means of η^2,η^2 bonding in a similar fashion to that observed in $[Pt_3(\mu_2-\eta^2-PhC_2Ph)_2(Et_3P)_4]$ [10]. The average W–W bond distance (3.1 Å) is longer than that of W–W bond in $[W_2(OPr^i)_6(py)(\mu-C_2H_2)]$ (2.567(1) Å) [11], $[W_2(\eta-C_5H_4Pr^i)_2Cl_2(\mu-NPh)(\mu-C_2Et_2)]$ (2.5923(5) Å) [12], $[W_2(\eta-C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu-Cl)(\mu-C_2Et_2)]$ (2.814 (2) Å) [12], $[W_2(\mu-PhC_2AuPPh_3)(CO)_4(\eta-C_5H_5)_2]$ (2.958 (1) Å) [13] and $[Cp*W_2Fe_2(CO)_6(O)_2(\mu-O)(\mu_3-S)_2(\eta^2-CC(Me)C{=}CH_2)]$ (2.8535(7) Å) [14], but comparable to that in complex $[Cp_2W_2Os(CO)_7(C_2Tol_2)]$ (3.087 Å (av)) [15]. The acetylenic C–C distances of the coordinated ferrocenylacetylene (1.33 Å) are consistent with the type of bonding present and observed in related molecules: $[Pt_3\{\mu_2(\eta^2-PhC_2Ph)_2(Et_3P)_4]$ (1.34(3) Å) [11], $[Mo_2(\mu-\eta^2-HC_2Ph)(CO)_4(\eta-C_5H_5)_2]$ (1.354(5) Å) [16], $[Co_2(CO)_4(\mu-\eta^2-PPh_2C{\equiv}CSiMe_3)(dppm)]$ (1.344(9) Å) [17], $[W_2(\eta-C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu-Cl)(\mu-C_2Et_2)]$ (2.814(2) Å) [12], $[W_2(\eta-C_5H_4Pr^i)_2Cl_2(\mu-NPh)(\mu-C_2Et_2)]$ (1.36(1) Å) [12] and $[W_2(OPr^i)_6(py)(\mu-C_2H_2)]$ (1.39(2) Å) [11]. Electron counting rules are satisfied if one assumes that the two W–W bonds are of donor–acceptor type.

The core structure of **2** consists of an unusual cyclic tetraferrocenyldimetallacyclodecatetraene unit (Fig. 2). Each tungsten atom in the twisted W_2C_8 ring bears three terminal carbonyls and is also attached to the rest of the ring by means of two η^2-interactions with the olefinic components of the ring, thereby satisfying the 18-electron rule (Fig. 3). The W–C, C–C single and double bond distances are within the expected ranges for such bonds and require no further comment.

In spite of the presence of two {W(CO)$_5$} groups, compound **1** is stable under both photolytic and thermal conditions, eventually decomposing only after prolonged photolysis or after two hours thermolysis under benzene reflux conditions. We were also unsuccessful in carrying out demetallation or substitution of the $W_2(CO)_6$ group of **2** in our attempts to obtain $Fc_4C_8H_4$ or $Fc_5C_{10}H_5$. We are presently looking at ways to produce other
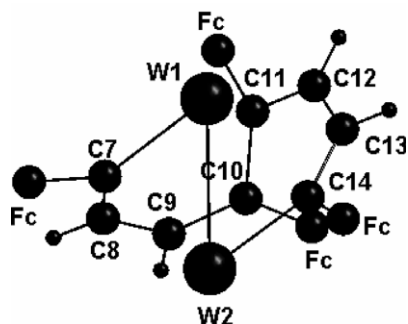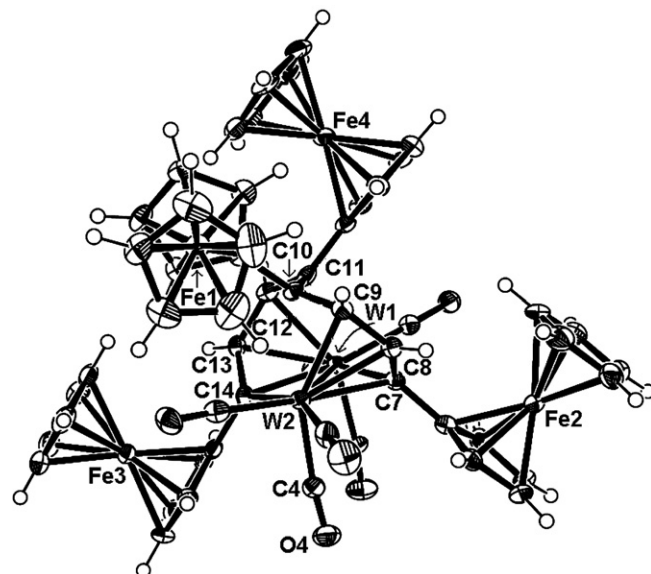

Fig. 3. Molecular structure (ORTEP plot at 50% probability) of $[W_2(\mu-C_8H_4Fc_4)(CO)_6]$ (**2**) (Fc = (η^5-C$_5$H$_5$)$_2$Fe). Solvent molecule (CH$_2$Cl$_2$) is omitted for clarity. Selected bond lengths (Å) and bond angles (°): W(1)–W(2) = 2.911(6), W(1)–C(7) = 2.237(2), W(2)–C(7) = 2.330(4), W(2)–C(8) = 2.327(0), W(2)–C(9) = 2.292(1), W(2)–C(10) = 2.396(6), W(1)–C(11) = 2.396(2), W(1)–C(12) = 2.303(2), W(1)–C(13) = 2.329(1), W(1)–C(14) = 2.364(3), W(2)–C(14) = 2.228(0), C(14)–C(13) = 1.398(4), C(14)–W(2)–W(1) = 52.76(0), C(7)–W(1)–W(2) = 51.83(0).

ferrocenyl-containing spirocyclic compounds like **2** as possible precursors to novel poly-ferrocenyl-substituted compounds.

3. Experimental

3.1. General procedures

All reactions and manipulations were carried out under an inert atmosphere of dry, pre-purified argon or nitrogen using standard Schlenk line techniques. Solvents were purified, dried and distilled under an argon atmosphere prior to use. Photolysis reactions were carried out in a double-walled quartz vessel having a 125 W immersion type mercury lamp operating at 366 nm. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path lengths NaCl cell and NMR spectra on a 400 MHz Varian Mercury spectrometer in CDCl$_3$. Elemental analyses were performed on a Carlo-Erba automatic analyser. TLC plates were purchased from Merck (20 × 20 cm, Silica gel 60 F$_{254}$). FcC≡CH was prepared using a reported method [18]. W(CO)$_6$, purchased from Strem, was used without further purification.

3.2. Photolytic reaction of tungsten hexacarbonyl with ferrocenylacetylene

In a typical reaction, a hexane solution of ferrocenylacetylene and W(CO)$_6$ was subjected to UV irradiation

Fig. 2. Core structure of compound **2**.

for 25 min at $-10\,^{\circ}\mathrm{C}$ in presence of argon. Removal of the solvent in vacuo and chromatographic work-up of the residue on TLC plates using dichloromethane/hexane (20:80 v/v) solvent mixture as eluant separated the following in order of elution: tungsten hexacarbonyl, unreacted yellow ferrocenylacetylene, orange **1**, yellow **3** (formed when a large excess of ferrocenylacetylene was used) and green **2**. Amounts of reactants used and yields of the products obtained are given in Table 1.

1: M.P. $= 192\,^{\circ}\mathrm{C}$ (decomp.). Analytical: calculated (found): C, 33.06 (33.47); H, 1.54 (1.62). IR(v(CO), cm^{-1}, n-hexane): 2069, 2007, 1996.5, 1956. ^{1}H NMR (δ, CDCl$_3$): 4.26 (s, 10H, η^{5}-C$_5$H$_5$), 4.0–4.88 (m, 8H, η^{5}-C$_5$H$_4$), 6.96 (s, 2H, C≡CH). ^{13}C NMR(δ, CDCl$_3$): 192 (*CO*), 106 (Fc-*C*≡), 83 (≡*C*H), 69.9–71.7 (Cp carbon).

2: M.P $= 128$–$130\,^{\circ}\mathrm{C}$. Analytical: calculated (found): C, 47.16 (47.52); H 2.91 (3.05). IR(v(CO), cm^{-1}, n-hexane): 2022.9, 1995, 1989. ^{1}H NMR (δ, CDCl$_3$): 5.69 (d, 2H, $^{3}J_{\mathrm{HH}} = 5.5$ Hz, FcC=CH), 7.33 (d, 2H, $^{3}J_{\mathrm{HH}} = 5.2$ Hz, FcC=CH), 4.0 (s, 10H, η^{5}-C$_5$H$_5$), 4.19 (s, 10H, η^{5}-C$_5$H$_5$), 3.84–4.52 (m, 16H, η^{5}-C$_5$H$_4$). ^{13}C NMR(δ, CDCl$_3$): 192, 194 (*CO*), 73.0, 68.2 (C=*C*H), 112.0, 94.2 ((Fc)*C*=C), 69.8–70.2 (m, Cp carbon).

3a: ^{1}H NMR (δ, CDCl$_3$): 4.05–4.16 (m, 27H, η^{5}-C$_5$H$_5$ and η^{5}-C$_5$H$_4$), 7.44 (s, 3 H, aromatic CH) [8a].

3b: ^{1}H NMR (δ, CDCl$_3$):4.05–4.16 (m, 15H, η^{5}-C$_5$H$_5$), 4.37 (t, 6H, η^{5}-C$_5$H$_4$), 4.72 (t, 6H, η^{5}-C$_5$H$_4$), 7.88 (d, $^{4}J_{\mathrm{HH}} = 1.6$ Hz, 1H, aromatic CH), 7.65 (d,$^{3}J_{\mathrm{HH}} = 8$ Hz, 1H, aromatic CH), 7.35 (dd, $^{4}J_{\mathrm{HH}} = 1.6$ Hz, $^{3}J_{\mathrm{HH}} = 8$ Hz, 1H, aromatic CH).

3.3. Crystal structure determination for **1** and **2**

Suitable X-ray quality crystals of **1** and **2** were grown by slow evaporation of dichloromethane/*n*-hexane solvent mixture at $0\,^{\circ}\mathrm{C}$, and X-ray crystallographic data were recorded from single-crystal samples of **1** ($0.33 \times 0.21 \times 0.16$) mm^3 and **2** ($0.16 \times 0.10 \times 0.01$) mm^3, mounted on glass fibers. Oxford diffraction XCALIBUR-S CCD was used for the cell determination and intensity data. Appropriate empirical absorption corrections using the programs multi-scan were applied. The structures were solved by direct methods (SHELXLXS) and refined by full matrix least squares against F^2 using SHELXL-97 software [19]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine a riding model. Crystallographic details are summarised in Table 2.

Appendix A. Supplementary material

CCDC 622005 and 622006 contain the supplementary crystallographic data (excluding structure factors) for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from

Table 2
Crystal data and structure refinement parameters for **1** and **2**

Compound	**1**	**2** · CH$_2$Cl$_2$
Empirical formula	C$_{36}$H$_{20}$Fe$_2$O$_{12}$W$_3$	C$_{55}$H$_{42}$Cl$_2$Fe$_4$O$_6$W$_2$
Formula weight	1307.77	1460.89
Crystal system	Monoclinic	Monoclinic
Space group	*I*2/*a*	*P*2$_1$/*n*
a (Å)	11.8654(9)	16.2846(11)
b (Å)	27.5344(13)	14.026(2)
c (Å)	13.535(3)	20.809(2)
α (°)	90	90
β (°)	110.609(11)	95.357(7)
γ (°)	90	90
V (Å^3)	4139.0(8)	4732.2(9)
Z	4	4
D_{calc} (Mg m^{-3})	2.099	2.051
Absolute coefficient (mm^{-1})	9.045	6.202
F(000)	2424	2824
Crystal size (mm)	$0.33 \times 0.21 \times 0.16$	$0.16 \times 0.10 \times 0.01$
θ Range (°)	3.18–25.00	2.90–25.00
Index ranges	$-14 \leqslant h \leqslant 14$, $-32 \leqslant k \leqslant 32$, $-16 \leqslant l \leqslant 15$	$-19 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 16$, $-24 \leqslant l \leqslant 24$
Reflections collected/unique [R_{int}]	11233/3600 [0.0247]	34611/8287 [0.0475]
Data/restraints/parameters	3600/0/240	8287/0/622
Goodness-of-fit on F^2	1.101	0.966
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0292$, $wR_2 = 0.0720$	$R_1 = 0.0341$, $wR_2 = 0.0732$
R indices (all data)	$R_1 = 0.0376$, $wR_2 = 0.0746$	$R_1 = 0.0522$, $wR_2 = 0.0776$
Largest difference peak and hole (e Å^{-3})	2.574 and -0.811	2.545 and -2.370

the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.022.

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