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published in

*J. Organomet. Chem.* 2007, **692**, 819.

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**Photochemical route to unusual tri-tungsten ferrocenylacetylene cluster**

**$[W_3\{\mu-\eta^2, \eta^2-(H)C\equiv CFc\}_2(CO)_{12}]$  and a dimetallacyclodecatetraene**

**$[W_2\{\mu-\eta^2, \eta^2, \eta^2, \eta^2-(Fc)C=C(H)C(H)=C(Fc)C(Fc)=C(H)C(H)=C(Fc)\}(CO)_6]$**

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*Summary: Low temperature photoreaction between tungsten hexacarbonyl and ferrocenylacetylene yielded two unusual metal containing stable compounds, the tritungsten cluster,  $[W_3(\mu-\eta^2, \eta^2-(H)C\equiv CFc)_2(CO)_{12}]$  (**1**) and ditungsten-1,4,5,8-ferrocenylcyclodecatetraene  $[W_2\{\mu-\eta^2, \eta^2, \eta^2, \eta^2-(Fc)C=C(H)C(H)=C(Fc)C(Fc)=C(H)C(H)=C(Fc)\}(CO)_6]$  (**2**). Both compounds were structurally characterized by single crystal X-ray diffraction methods.*

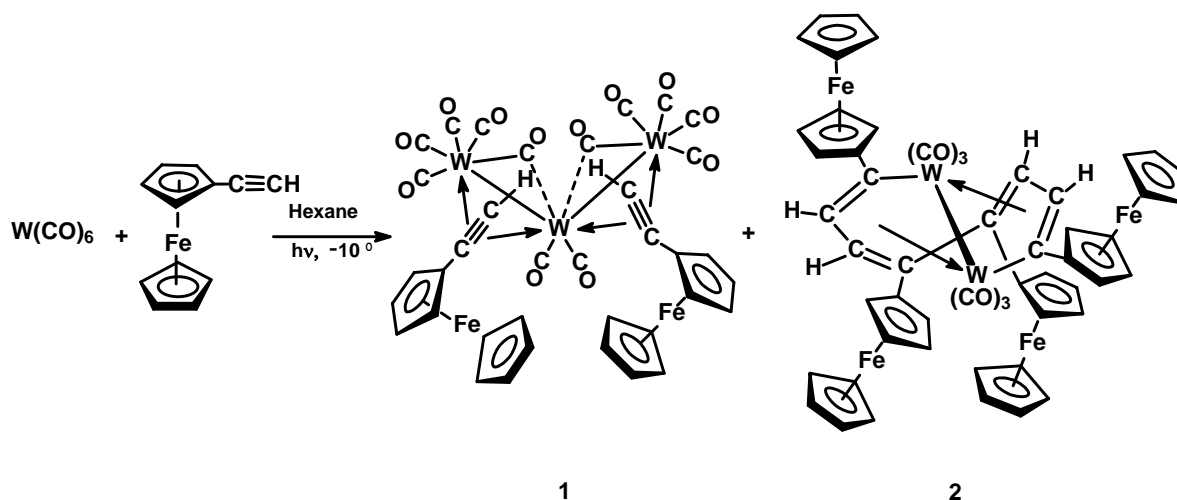
## Introduction

Metal-assisted alkyne oligomerisation reactions have been and continue to be of considerable interest.<sup>1-6</sup> Formation of cyclobutendiones occurs from reactions of a number of alkynes with iron pentacarbonyl in presence of trimethylamine-N-oxide and subsequent oxidation by  $CuCl_2 \cdot 2H_2O$ .<sup>7</sup> Recently, oligomerisations, including co-cyclooligomerisations of ferrocenylacetylenes using metal carbonyls have yielded some

interesting products. For instance, thermal reaction of ferrocenylacetylene with mononuclear  $\text{Fe}(\text{CO})_5$  gave three coupling products  $[\text{Fe}(\text{CO})_2\{\eta^5\text{-2,5-Fc}_2\text{C}_5\text{H}_2\text{CO}\}\text{C}(\text{Fc})=\text{CH}]$ ,  $[\text{Fe}(\text{CO})_2\{\eta^2\text{:}\eta^2\text{-2,5-Fc}_2\text{C}_4\text{H}_2\text{Fe}(\text{CO})_3\}\mu\text{-CO}]$  and  $[\text{Fe}(\text{CO})_3\{\eta^2\text{:}\eta^2\text{-2,5-Fc}_2\text{C}_4\text{H}_2\text{CO}\}]$ .<sup>8</sup> Low temperature photolysis of solutions containing ferrocenylacetylene and iron pentacarbonyl in presence of carbon monoxide forms 2,5- and 2,6-diferrocenylquinones.<sup>9</sup> 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 reaction of ferrocenylacetylene with tungsten hexacarbonyl and 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.

## Results and Discussion

When a hexane solution containing ferrocenylacetylene and a slight excess of tungsten hexacarbonyl was photolysed at  $-10^\circ\text{C}$ , two new compounds formed in approximately equal amounts, and these were identified as  $[\text{W}_3(\mu\text{-}\eta^2,\eta^2\text{-}(\text{H})\text{C}\equiv\text{CFc})_2(\text{CO})_{12}]$  (**1**) and ditungsten-1,4,5,8-ferrocenylcyclodecatetraene  $[\text{W}_2\{\mu\text{-}\eta^2,\eta^2,\eta^2,\eta^2\text{-}(\text{Fc})\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})\text{C}(\text{Fc})=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})\}\text{(CO)}_6]$  (**2**) (Scheme 1). The relative yields of the two products depend on the reactant stoichiometry; using a



### Scheme 1

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).<sup>8</sup>

**Table 1** Amounts of reactants used and yields of products obtained.

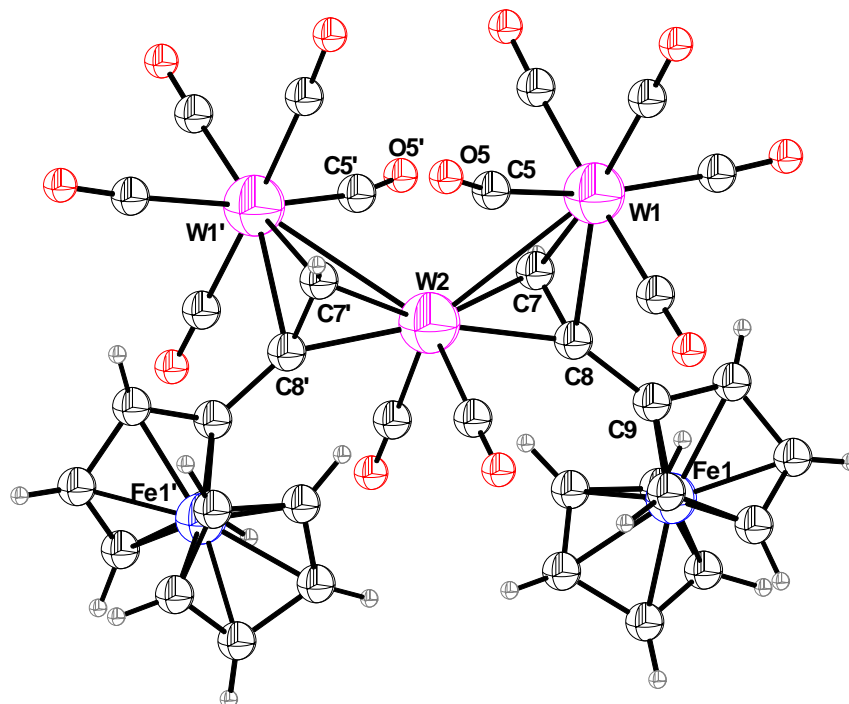
[W(CO) <sub>6</sub> ] [mg (mmol)]	[FcC≡CH] [mg (mmol) (used)] [mg (mmol) (recovered)]	Products obtained	Yield <sup>a</sup> : mg (%)
[110 (0.31)]	[46 (0.22)] [5 (0.02)]	<b>1</b>	48 (37 %)
		<b>2</b>	16 (24 %)
[165 (0.45)]	[32 (0.15)] [5 (0.02)]	<b>1</b>	37 (44 %)
		<b>2</b>	6 (13 %)
[88 (0.25)]	[105 (0.5)] [12 mg (0.06)]	<b>1</b>	40 (14%)
		<b>2</b>	47 (29 %)
		<b>3a+3b</b>	24 (26 %)

<sup>a</sup> Based on amount of FcC≡CH consumed

The two new compounds, **1** and **2** were characterised by IR and <sup>1</sup>H and <sup>13</sup>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<sup>-1</sup>, indicating the presence of semibridging carbonyl. <sup>1</sup>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

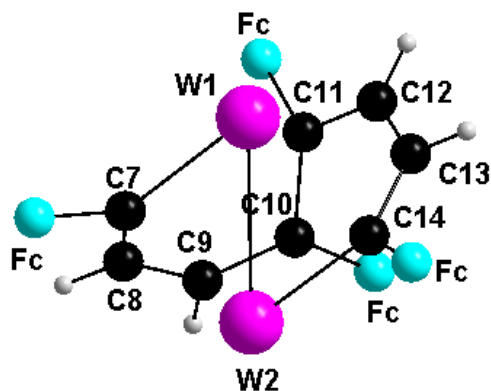
for compound **1** show a peak at  $\delta$  6.96 whereas, for compound **2** peaks at  $\delta$  5.69 (doublet) and  $\delta$  7.33 (doublet) corresponding to olefinic protons have been observed.  $^{13}\text{C}$  NMR spectra show the presence of terminal carbonyl carbons and acetylenic carbons along 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** (Figure 1) consists of a bent tungsten chain bearing a total of twelve terminally bonded carbonyls, 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 semibridging character ( $\text{W}(1)\text{-C}(5)\text{-O}(5) = 165.3(6)^\circ$ ), consistent with the presence of donor – acceptor metal - metal bonds (*vide infra*). Two ferrocenylacetylene molecules straddle the W-W bonds by means of  $\eta^2, \eta^2$  bonding in a similar fashion to that observed in  $[\text{Pt}_3\{\mu_2(\eta^2\text{-PhC}_2\text{Ph})_2(\text{Et}_3\text{P})_4\}]$ .<sup>15</sup> The average W-W bond distance (3.1 Å) is longer than that of W-W bond in  $[\text{W}_2(\text{OPr}^i)_6(\text{py})(\mu\text{-C}_2\text{H}_2)]$  (2.567(1) Å),<sup>10</sup>  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_2(\mu\text{-NPh})(\mu\text{-C}_2\text{Et}_2)]$  (2.5923(5) Å),<sup>11</sup>  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_3(\text{PMe}_3)(\mu\text{-Cl})(\mu\text{-C}_2\text{Et}_2)]$  (2.814(2) Å),<sup>11</sup>  $[\text{W}_2(\mu\text{-PhC}_2\text{AuPPh}_3)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (2.958(1) Å)<sup>12</sup> and  $[\text{Cp}^*\text{W}_2\text{Fe}_2(\text{CO})_6(\text{O})_2(\mu\text{-O})(\mu_3\text{-S})_2(\eta^2\text{-CC}(\text{Me})\text{C}=\text{CH}_2)]$  (2.8535(7) Å),<sup>13</sup> but comparable to that in complex  $[\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\text{C}_2\text{ToI}_2)]$  (3.087 Å (av)).<sup>14</sup> 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:  $[\text{Pt}_3\{\mu_2(\eta^2\text{-PhC}_2\text{Ph})_2(\text{Et}_3\text{P})_4\}]$  (1.34(3) Å),<sup>15</sup>  $[\text{Mo}_2(\mu\text{-}\eta^2\text{-HC}_2\text{Ph})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1.354(5) Å),<sup>16</sup>  $[\text{Co}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-PPh}_2\text{C}\equiv\text{CSiMe}_3)(\text{dppm})]$  (1.344(9) Å),<sup>17</sup>  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_3(\text{PMe}_3)(\mu\text{-Cl})(\mu\text{-C}_2\text{Et}_2)]$  (2.814(2) Å),<sup>11</sup>  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_2(\mu\text{-NPh})(\mu\text{-C}_2\text{Et}_2)]$  (1.36(1) Å)<sup>11</sup> and  $[\text{W}_2(\text{OPr}^i)_6(\text{py})(\mu\text{-C}_2\text{H}_2)]$  (1.39(2) Å).<sup>10</sup> Electron counting rules are satisfied if one assumes that the two W-W bonds are of donor-acceptor type.

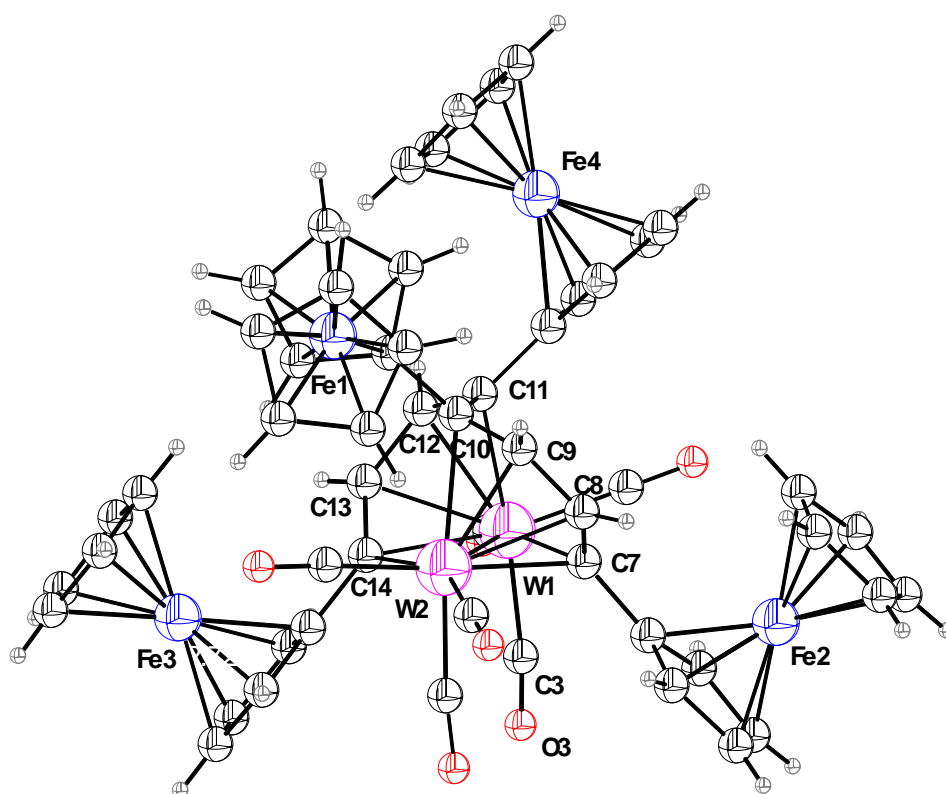


**Figure 1** Molecular structure (ORTEP plot at 50 % probability) of  $[W_3(\mu-C_2HFc)_2(CO)_{12}]$  (**1**) ( $Fc = (\eta^5-C_5H_5)_2Fe$ ). Selected bond lengths (Å) and bond angles (deg):  $W(1)-W(2) = 3.1017(3)$ ,  $W(2)-C(7) = 2.117(6)$ ,  $W(2)-C(8) = 2.173(6)$ ,  $W(1)-C(7) = 2.372(6)$ ,  $W(1)-C(8) = 2.474(6)$ ,  $C(7)-C(8) = 1.326(8)$ ,  $C(8)-C(9) = 1.463(8)$ ,  $W(1)-W(2)-W(1') = 110.012(14)$ ,  $W(1)-C(7)-W(2) = 87.2(2)$ ,  $W(1)-C(8)-W(2) = 83.5(2)$ ,  $C(7)-C(8)-C(9) = 135.7(6)$ ,  $C(8)-W(2)-C(8') = 162.3(3)$ ,  $W(1)-C(5)-O(5) = 165.3(6)$

The core structure of **2** consists of a spirocyclic tetraferrocenyldimetalacyclodecatetraene unit (Figure 2). Each tungsten atom bears three terminal carbonyls and is attached to the rest of the ring by means of a single C-W sigma bond and two  $\eta^2$ -interactions with the olefinic components of the ring, thereby satisfying the 18-electron rule (Figure 3). The W-C, C-C single and double bond distances are within the expected ranges for such bonds and require no further comment.

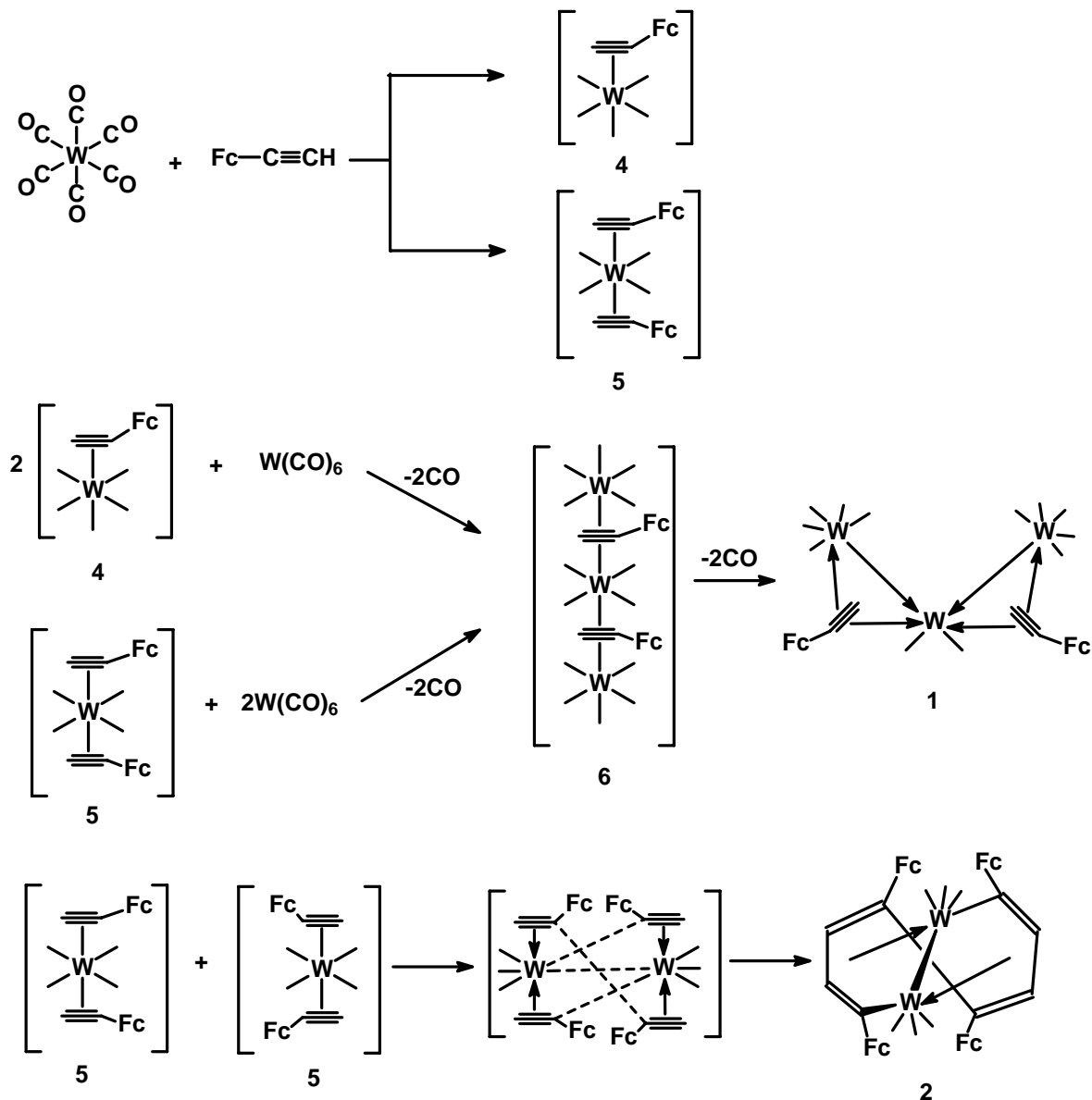


**Figure 2** Core structure of compound **2**



**Figure 3** Molecular structure (ORTEF plot at 50 % probability) of  $[\text{W}_2(\mu\text{-C}_8\text{H}_4\text{Fc}_4)(\text{CO})_6]$  (**2**) ( $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ ). Solvent molecule ( $\text{CH}_2\text{Cl}_2$ ) is omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and bond angles (deg):  $\text{W}(1)\text{-W}(2) = 2.911(6)$ ,  $\text{W}(1)\text{-C}(7) = 2.237(2)$ ,  $\text{W}(2)\text{-C}(7) = 2.330(4)$ ,  $\text{W}(2)\text{-C}(8) = 2.327(0)$ ,  $\text{W}(2)\text{-C}(9) = 2.292(1)$ ,  $\text{W}(2)\text{-C}(10) = 2.396(6)$ ,  $\text{W}(1)\text{-C}(11) = 2.396(2)$ ,  $\text{W}(1)\text{-C}(12) = 2.303(2)$ ,  $\text{W}(1)\text{-C}(13) = 2.329(1)$ ,  $\text{W}(1)\text{-C}(14) = 2.364(3)$ ,  $\text{W}(2)\text{-C}(14) = 2.228(0)$ ,  $\text{C}(14)\text{-C}(13) = 1.398(4)$ ,  $\text{C}(14)\text{-W}(2)\text{-W}(1) = 52.76(0)$ ,  $\text{C}(7)\text{-W}(1)\text{-W}(2) = 51.83(0)$ .

Although our attempts to isolate the mono- and the bis-acetylene derivatives,  $[\text{W}(\text{CO})_5\text{Fc}]$  (**4**) and  $[\text{W}(\text{CO})_4\text{Fc}_2]$  (**5**) have been unfruitful, we believe these to be key intermediates in the overall mechanism of formation of **1** and **2** (Scheme 2). Reaction of two molecules of **4** with one of  $\text{W}(\text{CO})_6$  would form the tungsten intermediate,  $[\{\text{W}(\text{CO})_5\}_2\text{W}(\text{CO})_4\text{Fc}_2]$  (**6**) which on decarbonylation would give **1**. Intermediate **6** can also be thought to arise from initial formation of the bis-substituted intermediate **5**, one molecule of which may react with two units of  $[\text{W}(\text{CO})_4]$  (from photolytic decarbonylation of  $\text{W}(\text{CO})_6$ ). Intermediate **5** may also undergo dimerisation of the type shown in Scheme 2, thus providing the basic foundation for a 2-W, 8-C product. Subsequent decarbonylation, W-W bond formation and coupling of the four ferrocenylacetylene molecules would form compound **2**. Thus, use of an excess amount of tungsten hexacarbonyl in the reaction is likely to form greater proportion of **4** relative to **5** and therefore give **1** as the major product and this is indeed observed in our synthesis. On the other hand, use of an excess amount of ferrocenylacetylene would form larger amounts of the bis-substituted derivative, **5**, from which both **1** and **2** are obtainable, again consistent with our findings. Our final observation on the formation of triferrocenylbenzene as a cyclooligomerisation product is consistent with the use of a large excess of ferrocenylacetylene.



**Scheme 2** Proposed mechanism for formation of **1** and **2**.

In spite of the presence of two  $\{\text{W(CO)}_5\}$  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  $\text{W}_2(\text{CO})_6$  group of **2** in our attempts to obtain  $\text{Fc}_4\text{C}_8\text{H}_4$  or  $\text{Fc}_5\text{C}_{10}\text{H}_5$ . We are presently looking at ways to produce other ferrocenyl-containing spirocyclic compounds like **2** as possible precursors to novel poly-ferrocenyl-substituted compounds.



## Experimental Details

### *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<sub>3</sub>. Elemental analyses were performed on a Carlo-Erba automatic analyser. TLC plates were purchased from Merck (20x20 cm, Silica gel 60 F<sub>254</sub>). FcC≡CH was prepared using a reported method.<sup>18</sup> W(CO)<sub>6</sub>, purchased from Strem, was used without further purification.

### *Photolytic reaction of tungsten hexacarbonyl with ferrocenylacetylene*

In a typical reaction, a hexane solution of ferrocenylacetylene and W(CO)<sub>6</sub> was subjected to UV irradiation for 25 minutes at -10°C in presence of argon. Removal of the solvent in vacuo and chromatographic work-up of the residue on a silica gel column using dichloromethane/hexane mixture (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 °C (decomp.). Analytical: calculated (found): C, 33.06 (33.47); H, 1.54 (1.62). IR( $\nu$ (CO), cm<sup>-1</sup>, n-hexane): 2069, 2007, 1996.5, 1956. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 4.26 (s, 10H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 4.0-4.88 (m, 8H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>), 6.96 (s, 2H, C≡CH). <sup>13</sup>C NMR( $\delta$ , CDCl<sub>3</sub>): 192 (CO), 106 (Fc-C≡), 83 (≡CH), 69.9-71.7 (Cp carbon).

**2**: M.P = 128-130 °C. Analytical: calculated (found): C, 47.16 (47.52); H 2.91 (3.05). IR( $\nu$ (CO), cm<sup>-1</sup>, n-hexane): 2022.9, 1995, 1989. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 5.69 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz, FcC=CH), 7.33 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, FcC=CH), 4.0 (s, 10H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 4.19

(s, 10H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 3.84-4.52 (m, 16H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR( $\delta$ , CDCl<sub>3</sub>): 192, 194 (C=O), 73.0, 68.2 (C=CH), 112.0, 94.2 ((Fc)C=C), 69.8-70.2 (m, Cp carbon).

**3a** : <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 4.05-4.16 (m, 27H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> and  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>), 7.44 (s, 3 H, aromatic CH).

**3b** : <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 4.05-4.16 (m, 15H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 4.37 (t, 6H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>), 4.72 (t, 6H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>), 7.88 (d, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1H, aromatic CH), 7.65 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1H, aromatic CH), 7.35 (dd, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1H, aromatic CH).

### *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 °C, and X-ray crystallographic data were recorded from single-crystal samples of **1** (0.33 x 0.21 x 0.16) mm<sup>3</sup> and **2** (0.16 x 0.10 x 0.01) mm<sup>3</sup>, 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 (for **1** and **2**) were applied. The structures were solved by direct methods (SHELXLXS) and refined by full matrix least squares against F<sup>2</sup> using SHELXL-97 software.<sup>19</sup> 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 summarized in Table 2.

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

	<b>1</b>	<b>2.CH<sub>2</sub>Cl<sub>2</sub></b>
Empirical formula	C <sub>36</sub> H <sub>20</sub> Fe <sub>2</sub> O <sub>12</sub> W <sub>3</sub>	C <sub>55</sub> H <sub>42</sub> Cl <sub>2</sub> Fe <sub>4</sub> O <sub>6</sub> W <sub>2</sub>
Formula weight	1307.77	1460.89
Crystal system	Monoclinic	Monoclinic,
Space group	<i>I</i> 2/a	<i>P</i> 2 <sub>1</sub> /n
<i>a</i> , Å	11.8654(9)	16.2846(11)
<i>b</i> , Å	27.5344(13)	14.026(2)
<i>c</i> , Å	13.535(3)	20.809(2)
$\alpha$ deg	90	90
$\beta$ deg	110.609(11)°	95.357(7)
$\gamma$ deg	90	90
<i>V</i> , Å <sup>3</sup>	4139.0(8)	4732.2(9)
<i>Z</i>	4	4
D <sub>calcd</sub> , Mg m <sup>-3</sup>	2.099	2.051
abs coeff, mm <sup>-1</sup>	9.045	6.202
F(000)	2424	2824
Cryst size, mm	0.33 x 0.21 x 0.16	0.16 x 0.10 x 0.01
$\theta$ range, deg	3.18 to 25.00	2.90 to 25.00
index ranges	-14 ≤ <i>h</i> ≤ 14, -32 ≤ <i>k</i> ≤ 32, -16 ≤ <i>l</i> ≤ 15	-19 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 16, -24 ≤ <i>l</i> ≤ 24
reflections collected/ unique	11233 / 3600 [R(int)= 0.0247]	34611 / 8287 [R(int) = 0.0475]
data/ restraints / parameters	3600 / 0 / 240	8287 / 0 / 622
goodness-of-fit on F <sup>2</sup>	1.101	0.966
Final R indices	R1 = 0.0292	R1 = 0.0341,
[I > 2σ(I)]	wR2 = 0.0720	wR2 = 0.0732
R indices	R1 = 0.0376	R1 = 0.0522,
(all data)	wR2 = 0.0746	wR2 = 0.0776
largest diff peak and hole, eÅ <sup>-3</sup>	2.574 -0.811	2.545 -2.370

**Acknowledgement.** P.M. is grateful to the Department of Science and Technology, Government of India, for research funding and S.C. is grateful to the Council of Scientific and Industrial Research, Government of India, for fellowship.

**Supporting Information Available:** CIF tables for the structural analyses of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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