



## Metal carbonyl-promoted reactions of ferrocenylacetylene with sulfur to form thiophene, dithiine, thioketone and vinylthioketone derivatives

Pradeep Mathur<sup>a,b,\*</sup>, Amrendra K. Singh<sup>a</sup>, Saurav Chatterjee<sup>a,1</sup>, Vinay K. Singh<sup>a,2</sup>, Shaikh M. Mobin<sup>b</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India

<sup>b</sup> National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Bombay 400 076, India

### ARTICLE INFO

#### Article history:

Received 7 September 2009

Received in revised form 1 October 2009

Accepted 2 October 2009

Available online 12 October 2009

#### Keywords:

Dithiine

Thioketone

Vinylthioketone

Ferrocenylacetylene

Photolysis

### ABSTRACT

Photolysis of a hexane solution of ferrocenylacetylene and sulfur powder in presence of  $\text{Cr}(\text{CO})_6$  resulted in the formation of 2,6-diferrocenyldithiine and 2,5-diferrocenylthiophene. Similar reactions with  $\text{Mo}(\text{CO})_6$  or  $\text{W}(\text{CO})_6$  gave only the thiophene derivative. Formation of ferrocenyl-substituted thioketone complexes was observed in the reaction of ferrocenylacetylene with water and sulfur, in presence of  $\text{W}(\text{CO})_6$ . Use of  $\text{D}_2\text{O}$  confirmed water as source of protons for the conversion of acetylenic CH to  $\text{CH}_3$ .

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Dithiines are an important class of compounds, identified as one of the components of garlic known to exhibit a number of pharmacological properties [1]. They also find significance in several other areas. For instance, dithieno[3,4-*b*,3',4'-*e*]-[1,4]dithiine is used as a monomer to synthesize polymers suitable for anodically and cathodically colouring applications [2] and some dihydrodithiines have been identified as novel organic conductors [3]. Known methods of synthesis of dithiines include the hydrothiolysis of diphenacylsulfide to form 2,6-diphenyl-1,4-dithiine [4]. Refluxing 1,8-diketones in toluene with Lawesson's Reagent is reported to yield 1,4-dithiines [5]. A series of dithiines have been obtained by cyclisation of 4-(alkylamino)-4-oxobutanoic acids under the action of thionyl chloride [6]. Several dithiines and dithietes have been prepared from the direct reaction of alkynes and sulfur powder under high temperature and pressure [7]. In general, alkynes with bulky substituents give dithietes while those with small substituents give dithiines.

\* Corresponding author. Address: Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India. Tel.: +91 22 25767180; fax: +91 22 25767152.

E-mail address: [mathur@iitb.ac.in](mailto:mathur@iitb.ac.in) (P. Mathur).

<sup>1</sup> Present address: Department of Chemistry, National Institute of Technology, Rourkela 769008, India.

<sup>2</sup> Present address: Department of Chemistry, Faculty of Science, M.S. University of Baroda, Vadodara 390002, India.

There has also been considerable interest in developing methods for obtaining the thiocarbonyl (thione) compounds, a major difficulty being their inherent instability. A wide range of thioketones can be obtained by silyl triflate – promoted sulfuration of ketones by bis(trimethylsilyl)sulfide [8]. The thioketones thus obtained can be trapped *in situ* as the corresponding cycloadducts by reaction with dienes. In order to impart stability to the otherwise unstable thiones, complexes with soft, electron-rich metal centers like tungsten pentacarbonyl have been prepared [9]. Reid and co-workers reported the formation of pentacarbonyltungsten complexes of thioaldehyde and thioketone of trihiapentalenes by the reaction of silver nitrate with triethylammoniumpentacarbonyliodotungstate (0) and trihiapentalenes [10]. Thioketone complexes of tungsten have been obtained from carbene complexes via insertion of sulfur atom into the  $\text{M}=\text{C}$  bonds of carbene complexes [11].

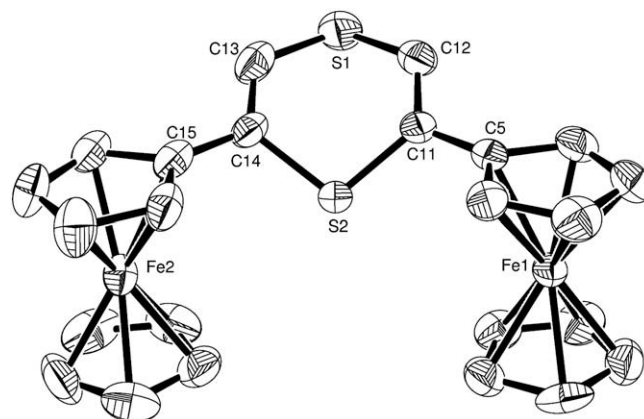
We have been interested, in recent times, on the use of ferrocenylacetylene building block due to its redox chemistry and general robustness under most reaction conditions. Our work in this area has resulted in synthesis of several new ferrocenyl-containing cluster compounds, and also, the use of simple metal carbonyls in facilitating coupling of ferrocenylacetylene with CO has resulted in the synthesis of diferrocenylquinones [12]. As an extension of these coupling reactions, incorporation of small chemical species like sulfur, selenium,  $\text{CS}_2$  and  $\text{NMe}_3$  groups on the carbon chain have also been investigated. These result in the formation of several heterocyclic ligands supported on the metal carbonyl cluster framework [13]. In this paper, we report a single-step  $\text{Cr}(\text{CO})_6$

promoted formation of a dithiine and an unusual reaction of ferrocenylacetylene, sulfur and water with  $W(CO)_6$  to form thioketone derivatives.

## 2. Results and discussions

We have examined the reactions of ferrocenylacetylene, sulfur and  $M(CO)_6$  ( $M = Cr, Mo, W$ ) in dry hexane solvent under photolytic conditions (Scheme 1). In the case of  $M = Cr$ , two products were formed and characterized as the previously reported 2,4-diferrocenylthiophene (**1**) and the new compound 2,6-diferrocenylthiophene (**2**) in 27% and 39% yields, respectively. Serendipitously, we discovered that in presence of trace amounts of moisture in the solvent, in the case of reactions using  $W(CO)_6$  (and not  $Cr(CO)_6$  or  $Mo(CO)_6$ ), two additional compounds **3** and **4** were obtained. These were identified on the basis of spectroscopic characterization and single crystal X-ray structure determination as  $W(CO)_5$  complexes containing ferrocenylethanethione (**3**) and 1,3-diferrocenylbut-2-ene-1-thione (**4**) (Scheme 2).

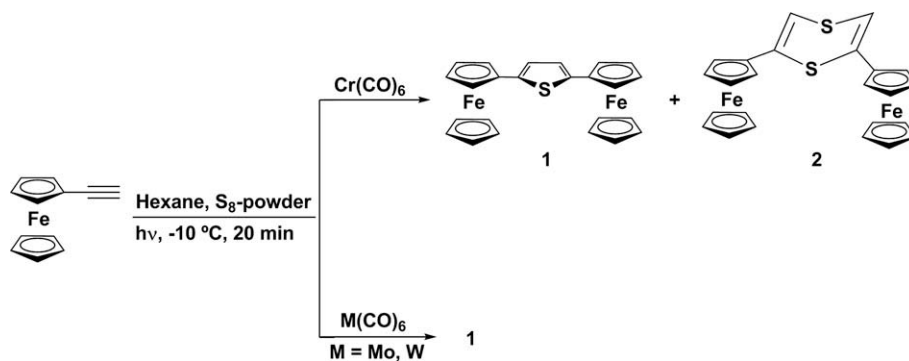
All products were characterized by IR and  $^1H$  and  $^{13}C$  NMR spectroscopy. Compound **1** was identified on the basis of comparison of its spectra with that of 2,4-diferrocenylthiophene reported earlier [13c]. IR spectra of all compounds show the characteristic  $\nu_{(C-S)}$  bands between 1290 and 1296  $cm^{-1}$ .  $^1H$  NMR spectra of **1** and **2** show signals at  $\delta$  6.66 and 6.25 ppm for the CH protons on the thiophene and the 1,4-dithiine rings, respectively; these signals are slightly upfield of those observed in 2,5- and 2,6-diferrocenyl-1,4-quinones [12e]. The spectra also showed a signal for the unsubstituted Cp protons and two signals for the protons of the substituted Cp ring.  $^1H$  NMR spectra of **3** and **4** show signals for Cp protons of ferrocenyl groups as well as methyl groups at  $\delta$  2.78 in **3** and  $\delta$  2.24 in **4**, respectively. The  $^{13}C$  NMR spectra for **1** and **2** display a total of six signals each, four highfield ones for the ferrocenyl carbon atoms and the two downfield signals for the dithiine or the thiophene ring carbon atoms. In order to complete the characterization and establish their molecular structures



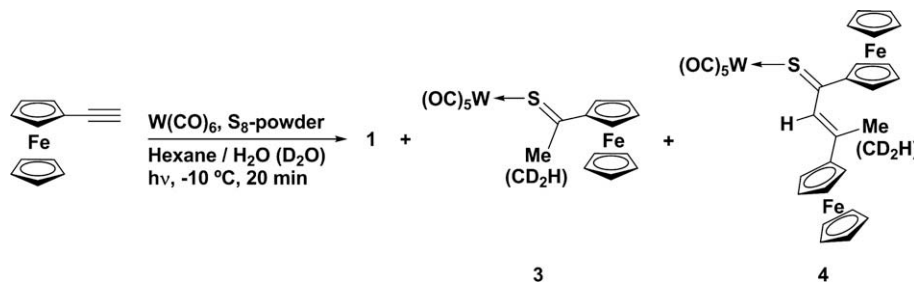
**Fig. 1.** Molecular structure of **2** (ORTEP plot at 50% probability). Selected bond lengths (Å) and bond angles ( $^\circ$ ): S(1)–C(12) = 1.748(8), S(1)–C(13) = 1.756(9), S(2)–C(11) = 1.758(7), S(2)–C(14) = 1.774(7), C(11)–C(12) = 1.323(10), C(13)–C(14) = 1.305(10), C(12)–S(1)–C(13) = 100.4(4), C(11)–S(2)–C(14) = 101.9(3), C(12)–C(11)–S(2) = 121.8(6), C(11)–C(12)–S(1) = 124.1(6), C(13)–C(14)–S(2) = 121.0(6), C(14)–C(13)–S(1) = 125.0(6).

of the three new compounds, single crystal X-ray structure determinations of **2–4** were carried out.

ORTEP diagram of **2** is shown in Fig. 1. The structure of **2** consists of a puckerd 1,4-dithiine ring with ferrocenyl groups attached at 2 and 6 positions in *syn* orientation, similar to that observed in the structure of 2,6-diferrocenylquinone [12e]. The average C=C bond distance (1.314 Å) is slightly shorter than the average C=C bond distance in 2,6-diferrocenylquinone (1.356 Å). Sulfur forms marginally longer bonds to the carbon atoms which bear the ferrocenyl groups (average 1.768 Å) as compared to the other pair in the molecule (average 1.752 Å); however, both distances are longer than typical C=S double bond distance ( $\sim 1.6$  Å) and closer to the C–S single bond distances which range from  $\sim 1.72$  to 1.81 Å [14].



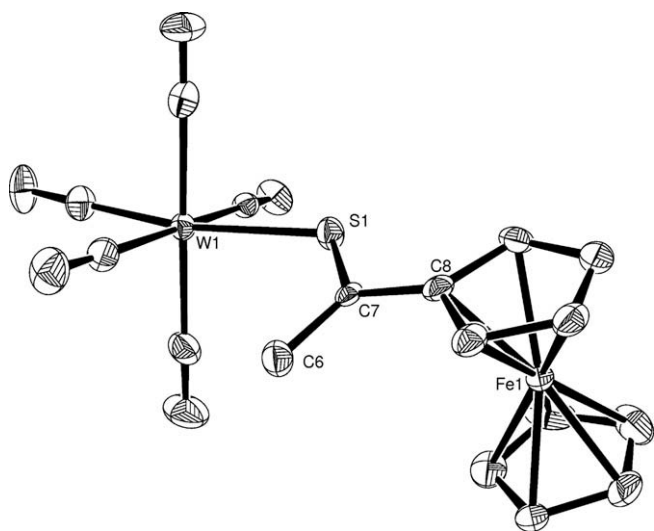
**Scheme 1.**



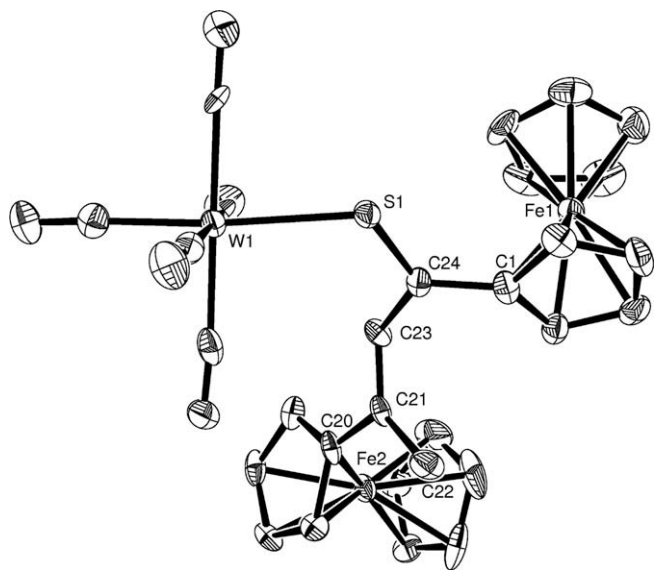
**Scheme 2.**

ORTEP diagrams of **3** and **4** are shown in Figs. 2 and 3, respectively. Molecules of both **3** and **4** contain a  $W(CO)_5$  group attached to the S atom of a thioketone. Compound **3** contains a ferrocenylethanethione unit while **4** has a 1,3-diferrocenylbut-2-ene-1-thione unit attached to the metal center. The S–C bond distances in thione unit of **3**, 1.640(4) Å (S(1)–C(7), Fig. 2) and **4**, 1.672(9) Å (S(1)–C(24), Fig. 2) are in good agreement with thioketone metal complexes reported earlier 1.618(8) Å in  $Me_2CSCr(CO)_5$  [15] and 1.647(4) Å in C-allylcyclopentene-1-thione complex of  $W(CO)_5$  [9]. Similarly, the distances C(7)–C(8) = 1.449(6) Å in **3** and C(1)–C(24) = 1.464(10) Å in **4** match with the corresponding bond distance in pentacarbonylchromium complex of ferrocenylphenylthioketone [16].

Water is the source of two of the three methyl protons in the formation of **3** and **4**. This is substantiated by the observation that



**Fig. 2.** Molecular structure of **3** (ORTEP plot at 50% probability). Selected bond lengths (Å) and bond angles ( $^\circ$ ): S(1)–C(7) = 1.640(4), C(6)–C(7) = 1.501(6), C(7)–C(8) = 1.449(6), W(1)–S(1) = 2.5266(11), C(7)–S(1)–W(1) = 119.55(15), C(8)–C(7)–S(1) = 119.2(3), C(8)–C(7)–C(6) = 117.4(4), C(6)–C(7)–S(1) = 123.4(3).



**Fig. 3.** Molecular structure of **4** (ORTEP plot at 50% probability). Selected bond lengths (Å) and bond angles ( $^\circ$ ): W(1)–S(1) = 2.5350(19), S(1)–C(24) = 1.672(9), C(1)–C(24) = 1.464(10), C(23)–C(24) = 1.454(11), C(21)–C(23) = 1.351(11), C(20)–C(21) = 1.461(11), C(21)–C(22) = 1.495(10), C(24)–S(1)–W(1) = 115.5(3), C(23)–C(24)–S(1) = 120.7(6).

use of solvent carefully dried over sodium-benzophenone does not give compounds **3** and **4** in the reaction of ferrocenylacetylene with  $W(CO)_6$  and sulfur powder. Further,  $^1H$  NMR spectra of **3** and **4** obtained from reaction of ferrocenylacetylene,  $W(CO)_6$ , sulfur powder and  $D_2O$  in hexane solvent reveals a much diminished signal for the methyl protons in both cases. Compounds **3** and **4** are unusually stable; even on extended reaction times we did not observe transformation of **3** and **4** into any other products. Conversion of **3** or **4** into **1** or **2** were not observed.

Photolytic synthesis of diferrocenyldithiines described here represents a marked improvement over the previously reported syntheses of dithiines as it is a convenient single-step process. This contrasts with the general high temperature/pressure conditions required in the dithiine preparation reported in literature [9]. Secondly, in the method described here, a dithiine with bulky substituents has been obtained. This contrasts with the previously reported general observation that with bulky substituents, dithiines are preferentially formed; smaller substituents being a requirement for obtaining dithiines. The exact role of chromium carbonyl in our reactions is not known presently. It may be proposed that initial coordination of two ferrocenylacetylene molecules to the chromium center is followed by incorporation of S during cyclisation on metal leading to compounds **1** and **2**. Formation of a chromium disulfide unit followed by insertion of the ferrocenylacetylene into the S–S bond of the disulfide unit can also be a possible mechanism for the formation of **1** and **2**. However, without further detailed investigations, these remain unsubstantiated ideas only. The significance of water in the formation of unusual ligand systems bound to metal centers is revealed by the formation of **3** and **4**. To the best of our knowledge compound **4** is the first known thione complex in which both the substituents on the C=S group are bulky and contain ferrocenyl units.

### 3. Experimental details

#### 3.1. General procedure

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. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path length NaCl cell and NMR spectra on a Varian Mercury 400 MHz spectrometer in  $CDCl_3$ . 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>).  $FcC\equiv CH$  was prepared using a reported method [17].  $Cr(CO)_6$ ,  $Mo(CO)_6$  and  $W(CO)_6$  were purchased from Strem, and used without further purification. Photochemical reactions were carried out using double-walled quartz vessel having a 125 W immersion type mercury lamp manufactured by Applied Photophysics Ltd.

#### 3.2. Photolytic reaction of $M(CO)_6$ ( $M = Cr, Mo, W$ ) with ferrocenylacetylene and sulfur

In a typical reaction, a hexane solution of ferrocenylacetylene (105 mg, 0.5 mmol),  $M(CO)_6$  (0.5 mmol) and sulfur powder (256 mg, 1 mmol) was subjected to UV irradiation for 20 min at  $-10^\circ C$  in an argon atmosphere. Removal of the solvent in vacuo and chromatographic work-up of the residue on a silica gel column using dichloromethane/hexane (20:80 v/v) solvent mixture as eluant gave the unreacted ferrocenylacetylene ( $M = Cr$ , 18 mg,  $Mo$ , 23 mg,  $W$ , 21 mg) followed by the products **1** ( $M = Cr$ , 25 mg, 27%;  $Mo$ , 36 mg, 41%;  $W$ , 32 mg, 35%;) and **2** ( $M = Cr$ , 39 mg, 39%).

**Table 1**  
Crystallographic data and structure refinement parameters for **2–4**.

	2	3	4
Empirical formula	C <sub>24</sub> H <sub>20</sub> Fe <sub>2</sub> S <sub>2</sub>	C <sub>17</sub> H <sub>12</sub> FeO <sub>5</sub> SW	C <sub>29</sub> H <sub>22</sub> Fe <sub>2</sub> O <sub>5</sub> SW
Formula weight	484.22	568.03	778.08
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
a (Å)	10.525(4)	6.7733(2)	13.0685(5)
b (Å)	9.924(3)	12.2808(14)	10.9881(3)
c (Å)	19.346(3)	21.357(3)	19.8769(8)
α (°)	90	90	90
β (°)	103.349(16)	96.539(8)	108.627(4) °
γ (°)	90	90	90°
V (Å <sup>3</sup> )	1966.1(9)	1764.9(3)	2704.77(17)
Z	4	4	4
D <sub>calc</sub> (mg m <sup>-3</sup> )	1.636	2.138	1.911
Abs. coefficient (mm <sup>-1</sup> )	1.695	7.476	5.416
F(0 0 0)	992	1080	1512
Crystal size (mm <sup>3</sup> )	0.25 × 0.10 × 0.10	0.33 × 0.26 × 0.21	0.11 × 0.08 × 0.06
θ Range (°)	2.03–25.00	3.07–25.00	2.92–25.00
Index ranges	0 ≤ h ≤ 12, -11 ≤ k ≤ 0, -22 ≤ l ≤ 22	-8 ≤ h ≤ 8, -14 ≤ k ≤ 14, -18 ≤ l ≤ 25	-15 ≤ h ≤ 15, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected/unique	3648/3449 [R <sub>int</sub> = 0.0571]	13 833/3094 [R <sub>int</sub> = 0.0422]	22 984/4754 [R <sub>int</sub> = 0.0936]
Data/restraints/parameters	3449/0/253	3094/0/227	4754/0/344
Goodness-of-fit (GOF) on F <sup>2</sup>	0.993	1.192	1.048
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0598, wR <sub>2</sub> = 0.1251	R <sub>1</sub> = 0.0204, wR <sub>2</sub> = 0.0465	R <sub>1</sub> = 0.0421, wR <sub>2</sub> = 0.0821
R indices (all data)	R <sub>1</sub> = 0.1642, wR <sub>2</sub> = 0.1567	R <sub>1</sub> = 0.0264, wR <sub>2</sub> = 0.0573	R <sub>1</sub> = 0.0712, wR <sub>2</sub> = 0.0969
Largest diff peak/hole (e Å <sup>-3</sup> )	0.454 and -0.651	0.920 and -0.788	1.922 and -1.250

**1**: M.P. 199–201 °C. IR (ν(CS), cm<sup>-1</sup>, *n*-hexane): 1290(s). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 6.66 (s, 2H, {Fc-CC(H)C(H)C(Fc)}), 4.15 (s, 10H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 4.35 (t, 4H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 4.64 (t, 4H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C NMR: 66.54 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 69.07 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 70.46 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 81.64 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 122.66 (s, C-C), 141.7 (s, C-S). Mass (*m/z*): 451.83 (M<sup>+</sup>).

**2**: M.P. 119–121 °C. IR (ν(CS), cm<sup>-1</sup>, *n*-hexane): 1296(m). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 6.25 (s, 2H, {Fc-CC(H)S}<sub>2</sub>), 4.56 (t, 4H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 4.27 (t, 4H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 4.24 (s, 10H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): 67.45 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 69.48 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 69.84 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 83.54 (s, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 113.23 (s, Fc-C-S), 138.52 (s, Fc-C-C-S). Mass (*m/z*): 483.80 (M<sup>+</sup>).

### 3.3. Photolytic reaction of W(CO)<sub>6</sub> with ferrocenylacetylene and sulfur in wet hexane

A wet hexane (0.5% H<sub>2</sub>O v/v) solution of ferrocenylacetylene (105 mg, 0.5 mmol), W(CO)<sub>6</sub> (176 mg, 0.5 mmol) and sulfur powder (256 mg, 0.5 mmol) was subjected to UV irradiation for 20 min at -10 °C in an argon atmosphere. 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 gave the unreacted ferrocenylacetylene (18 mg) followed by the products **1** (27 mg, 29%), **3** (48 mg, 20%) and **4** (25 mg, 16%).

**3**: M.P. = 135 °C (decomp.). Anal. Calc.: C, 35.93; H, 2.11. Found: C, 36.24; H, 2.19%. IR (ν(CO), cm<sup>-1</sup>, *n*-hexane): 2068(s), 1941(vs), 1928(s), 1262(m). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 5.03 (t, 2H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 4.94 (t, 2H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 4.26 (s, 5H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 2.78 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): 192 (CO), 69.9–71.7 (Cp carbon).

**4**: M.P. = 128–130 °C. Anal. Calc.: C, 44.76; H 2.83. Found: C, 44.92; H 2.95%. IR (ν(CO), cm<sup>-1</sup>, *n*-hexane): 2063(s), 1942(vs), 1923(s), 1261.8(m). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 5.91 (s, 1H, CH), 4.58–4.12 (m, 8H, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>), 4.19 (s, 5H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 4.26 (s, 5H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 2.24 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): 192, 194 (CO), 69.8–70.2 (m, Cp carbon).

### 3.4. Crystal structure determination for **2–4**

Suitable X-ray quality crystals of **2–4** 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 **3** (0.33 × 0.26 × 0.21) mm<sup>3</sup> and **4** (0.11 × 0.08 × 0.06) 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 **3** and **4**) were applied. The structures were solved by direct methods (SHELXL-XS) and refined by full matrix least squares against F<sup>2</sup> using SHELXL-97 software [18]. 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 1.

### Acknowledgements

P.M. is grateful to the Department of Science and Technology, Government of India. AKS and SC are grateful to Council of Scientific and Industrial Research, New Delhi for research fellowships.

### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.003.

### References

- [1] (a) E.B. Kuettner, R. Hingenfeld, M.S. Weiss, J. Biol. Chem. 277 (2002) 46402; (b) G. Siegel, E. Walter, S. Engel, A. Walker, F. Michel, Wien. Med. Wochenschr. 149 (1999) 217; (c) E. Block, Angew. Chem., Int. Ed. Engl. 31 (1992) 1135; (d) Y. Tsai, L.L. Cole, L.E. Davis, S.J. Lockwood, V. Simmons, G.C. Wild, Planta Med. 51 (1985) 460; (e) K.C. Agarwal, Med. Res. Rev. 16 (1996) 111.
- [2] E. Sahin, P. Camerlu, L. Toppare, Synth. Met. 156 (2006) 1073.
- [3] T. Imakubo, T. Shirahata, K. Herve, L. Ouhab, J. Mater. Chem. 16 (2006) 162.
- [4] L.G. Shagun, L.P. Ermolyuk, I.A. Dorofeev, L.N. Il'icheva, M.G. Voronkov, Chem. Heterocycl. Compd. 40 (2004) 1216.
- [5] T. Ozturk, Tetrahedron Lett. 37 (1996) 2821.
- [6] F. Zentz, R. Labia, D. Sirot, O. Faure, R. Grillot, A. Valla, Farmaco 60 (2005) 944.
- [7] K.S. Choi, I. Akiyama, M. Hoshino, J. Nakayama, Bull. Chem. Soc. Jpn. 66 (1993) 623.
- [8] A. Degl'Innocenti, A. Capperucci, A. Mordini, G. Reginato, A. Ricci, F. Cerreta, Tetrahedron Lett. 34 (1993) 873.
- [9] H.-P. Wu, R. Aumann, S. Venne-Dunker, P. Saarenketo, Eur. J. Org. Chem. (2000) 3463.
- [10] P.J. Pogorzelec, D.H. Reid, Chem. Commun. (1983) 289.

- [11] (a) H. Fischer, *J. Organomet. Chem.* 219 (1981) C34;  
(b) H. Fischer, K. Treier, U. Gerbing, *J. Organomet. Chem.* 433 (1992) 127;  
(c) J.U. Koehler, J. Lewis, P.R. Raithby, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 993.
- [12] (a) P. Mathur, A. Das, S. Chatterjee, S.M. Mobin, *J. Organomet. Chem.* 693 (2008) 1919;  
(b) P. Mathur, S. Chatterjee, A. Das, S.M. Mobin, *J. Organomet. Chem.* 692 (2007) 819;  
(c) P. Mathur, S. Chatterjee, A. Das, G.K. Maji, S. Lahiri, S.M. Mobin, *J. Organomet. Chem.* 692 (2007) 1601;  
(d) P. Mathur, V.K. Singh, S.M. Mobin, C. Srinivasu, R. Trivedi, A.K. Bhunia, V.G. Puranik, *Organometallics* 24 (2005) 367;  
(e) P. Mathur, A.K. Bhunia, S.M. Mobin, V.K. Singh, C. Srinivasu, *Organometallics* 23 (2004) 3694.
- [13] (a) P. Mathur, A.K. Singh, J.R. Mohanty, S. Chatterjee, S.M. Mobin, *Organometallics* 27 (2008) 5094;  
(b) P. Mathur, V.K. Singh, A.K. Singh, S.M. Mobin, C. Thöne, *J. Organomet. Chem.* 691 (2006) 3336;  
(c) P. Mathur, A.K. Singh, V.K. Singh, P. Singh, R. Rahul, S.M. Mobin, C. Thöne, *Organometallics* 24 (2005) 4793.
- [14] (a) A.E. Pullen, R.M. Olk, S. Zeltner, E. Hoyer, K.A. Abboud, J.R. Reynolds, *Inorg. Chem.* 36 (1997) 958;  
(b) H.J. Nam, H.-J. Lee, D.-Y. Noh, *Polyhedron* 23 (2004) 115;  
(c) J. Dai, M. Munakata, L.-P. Wu, T. Kuroda-Sowa, Y. Suenaga, *Inorg. Chim. Acta* 258 (1997) 65;  
(d) M.G.B. Drew, J.M. Kisenyi, R.V. Parish, *J. Chem. Soc., Dalton Trans.* (1987) 1605.
- [15] B.A. Karcher, R.A. Jacobson, *J. Organomet. Chem.* 132 (1977) 387.
- [16] J.C. Barnes, W. Bell, C. Glidewell, R.A. Howie, *J. Organomet. Chem.* 385 (1990) 369.
- [17] G. Doisneau, G. Balavoine, T.F. Khan, *J. Organomet. Chem.* 425 (1992) 113.
- [18] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112.