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Photochemical reactions of 1-ferrocenyl-4-phenyl-1,3-butadiyne with $Fe(CO)_5$ and CO

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ABSTRACT

Photolysis of a hexane solution containing ironpentacarbonyl, 1-ferrocenyl-4-phenyl-1,3-butadiyne at low temperature yields six new products: [$Fe(CO)_2\{\eta^2$:η^2-PhC≡CCC(Fc)C(C≡CPh)C(Fc)$Fe(CO)_3\}$-μ-CO] (**1**), [$Fe_2(CO)_6\{\mu$-η^1:η^1:η^2:η^2-PhC≡CCC(Fc)–C(O)–C(Fc)CC≡CPh}] (**2**), [$Fe_2(CO)_6\{\mu$-η^1:η^1:η^2:η^2-FcCC(C≡C Ph)–C(O)–C(Fc)CC≡CPh}] (**3**), [$Fe_2(CO)_6\{\mu$-η^1:η^1:η^2:η^2-FcC≡CCC(Fc)–C(O)–C(Fc)CC≡CPh}] (**4**), [$Fe(CO)_3\{\mu$-η^2: η^2-[FcCC(C≡CPh)C(C≡CPh)C(Fc)}CO] (**5**) and [$Fe(CO)_3\{\mu$-η^2: η^2-[FcCC(C≡CPh)C(C≡CPh)C(Fc)}CO] (**6**) formed by coupling of acetylenic moieties with CO insertion on metal carbonyl support. In presence of CO, formation of another new product 2,5-bis(ferrocenyl)-3,6-bis(tetracarbonylphenylmaleoyliron)quinone (**7**) was observed which on further reaction with ferrocenylacetyene gave the quinone, 2,5-bis(ferrocenyl)-3,6-bis(ethynylphenyl)quinone (**8**). Structures of **1**–**5** and **8** were established crystallographically.

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1. Introduction

Reactions of ferrocenyl substituted alkynes with cluster carbonyls are of considerable interest due to their applications like multielectron redox catalysts [1,2] and electron storage devices [3]. Intense electronic communication observed in complexes with two or more ferrocenyl units separated by conjugated bridging ligands is also of much interest [4–6]. At the same time, the presence of one or more unsaturated bonds in the molecules of diynes offers additional features for the co-ordination to metal atoms in a cluster and for the formation of carbon–carbon bonds.

As part of our systematic investigation on the reactivity of the alkynes with metal carbonyls and clusters [7–10], we have previously reported the reaction of 1,4-diferrocenyl-1,3-butadiyne with $Ru(CO)_5$ to form [$Ru_2(CO)_6\{C_4Fc_2(C{\equiv}CFc)_2\}_2$], [$Ru_2(CO)_6[\mu$-$\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$-{FcC≡CCC(Fc)–C(O)–C(Fc)CCCFc}]] and [$Ru_2(CO)_6[\mu$-η^1:η^1:η^2:η^2-{FcC≡CCC(Fc)–C(O)–C(–C≡CFc)C(Fc)}]] [11]. When $M_3(CO)_{10}(NCMe)_2$ (M = Os or Ru) react with diynes 1,4-dialkyl-1,3-butadiyne (alkyl = ferrocenyl, Me, Et, Ph, Bu^t, $SiMe_3$) trinuclear or tetranuclear clusters in which only one alkyne group coordinates are formed [12,13]. The free alkyne of cluster can be further used for cluster growth reactions as reported in the formation of the hexanuclear cluster [$Ru_6(\mu_5$-η^1:η^1:η^1:η^2:η^2-$PhCHC_3C_6H_4)(\mu_4$-η^1:η^1:η^2:η^2–$PhCHC_3C_6H_4)(CO)_{15}$] [14]. In the present work, we report the photochemical reactions of the unsymmetrical 1-ferrocenyl-4-phenyl-1,3-butadiyne with $Fe(CO)_5$ and CO at low temperature.

2. Results and discussion

2.1. Photolysis of 1-ferrocenyl-4-phenyl-1,3-butadiyne with $Fe(CO)_5$

Photolysis of a hexane solution of 1-ferrocenyl-4-phenyl-1,3-butadiyne (FcC≡CC≡CPh) and $Fe(CO)_5$ at low temperature (0 °C) yields six new compounds **1**–**6** resulting from the coupling of acetylenic moieties with CO insertion on metal carbonyl framework (Scheme 1). All new compounds were isolated by chromatographic techniques as air stable solids. In solution, slow decomposition was observed in air.

The IR spectra of compounds **1**–**6** show the presence of terminal carbonyls; whereas **1** indicates the presence of semibridging CO in addition to the terminal carbonyls, compounds **2**–**6** show only terminal carbonyls. ^1H and ^{13}C NMR spectra of **1**–**6** confirm the presence of Cp rings and phenyl rings of the FcC≡CC≡CPh and carbonyl groups. Crystals of **1**–**5**, suitable for X-ray analysis, were

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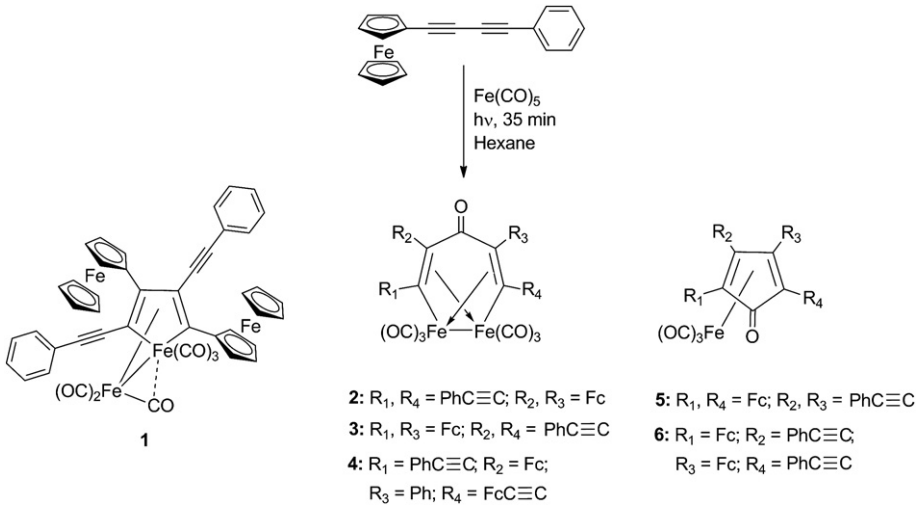


Scheme 1. Reaction of 1-ferrocenyl-4-phenyl-1,3-butadiyne with Fe(CO)5.

grown by slow evaporation of hexane/dichloromethane solutions and their molecular structures are shown in Figs. **1**–**5** respectively (Fig. 6).

The molecular structure **1** contains a ferracyclopentadiene ring which is formed by a formal coupling of two FcC≡CC≡CPh molecules with an $Fe(CO)_3$ unit. Position 2 and 4 of the ring are occupied by the bulky ferrocenyl groups whereas position 3 and 5 are taken by {PhC≡C} groups. This ferracyclopentadiene ring is η^4-coordinated to another $Fe(CO)_2$ fragment which is also bonded to the ring iron atom (2.498(2)) Å. A sixth carbonyl ligand bridges the metal–metal bond. Within the C_4Fe ring, C(8)–C(27) at 1.451 Å is longer than the corresponding C–C single bond distance of 1.415(6) in the C_4Fe ring of $[Fe_2(CO)_6(C_4H_2Fc_2)]$ and similar to that of 1.455(9) Å in the C_4Ru ring of $[Ru_2(CO)_6\{C_4Fc_2(C{\equiv}CFc)_2\}]$ [11]. The C(7)–C(8) and C(27)–C(28) bond distances of 1.432(7) and 1.455(7) Å, respectively are lengthened from the normal C=C double bond distance due to complexation, and these are also longer than the corresponding distances of the metallocycopentadiene ring of $[Fe_2(CO)_6(C_4H_2Fc_2)]$, $[Ru_2(CO)_6(C_4H_2Fc_2)]$, and $[Ru_2(CO)_6\{C_4Fc_2(C{\equiv}CFc)_2\}]$ [11]. In general, the metallacyclopentadiene ring in **1** is similar to that in $[Fe_2(CO)_6C_4H_2Fc_2]$ [10], $[Ru_2(CO)_6(C_4H_2Fc_2)]$ [15], and $[Ru_2(CO)_6\{C_4Fc_2(C{\equiv}CFc)_2\}_2]$ [11], which are formed in the theromolysis reaction of FcC≡CH and $Fe(CO)_5$, FcC≡CH and $Ru_3(CO)_{12}$ and in the photolysis of FcC≡CC≡CFc and $Ru(CO)_5$ respectively.

The molecular structures of isomers **2**–**4** consist of a diironbicyclo[3.1.1]heptadienone ring. Each iron atom bears three terminal carbonyl ligands and there is η^2-bonding between a double bond of the ring and an iron atom. Two iron atoms of the ring are connected through a direct bond and fulfill its electronic requirements. In **2**, the two bulky ferrocenyl groups are located in the β-position of the ring with respect to the metal atom and the

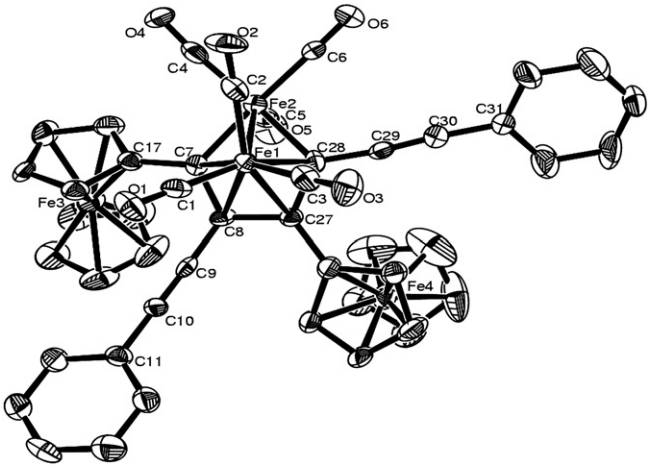


Fig. 1. ORTEP diagram of $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-PhC}{\equiv}CCC(Fc)C(C{\equiv}CPh)CC(Fc)Fe(CO)_3\}\text{-}\mu\text{-CO}]$ (1) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Fe(1)–C(7) = 2.177(5), Fe(1)–C(8) = 2.139(5), Fe(1)–C(27) = 2.188(5), Fe(1)–C(28) = 2.10(5), Fe(2)–C(7) = 1.955(5), Fe(2)–C(28) = 1.961(6), Fe(1)–Fe(2) = 2.498(2), C(7)–C(8) = 1.432(7), C(8)–C(27) = 1.451(7), C(27)–C(28) = 1.455(7), C(7)–C(17) = 1.483(7), C(9)–C(8) = 1.436(7), C(28)–C(29) = 1.424(7), C(27)–C(37) = 1.463(8), C(29)–C(30) = 1.195(7), and C(9)–C(10) = 1.192(7); Fe(2)–C(7)–C(8) = 116.6(4), C(7)–C(8)–C(27) = 114.2(5), C(8)–C(27)–C(28) = 110.1(5), C(27)–C(28)–Fe(2) = 117.5(4), O(2)–C(2)–Fe(1) = 167.7(6), O(1)–C(1)–Fe(1) = 179.3(5), O(3)–C(3)–Fe(1) = 178.3(5).

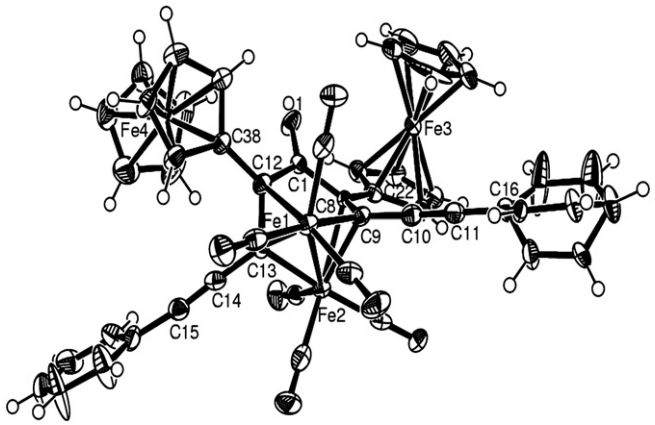


Fig. 2. ORTEP diagram of $[Fe_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-PhC}{\equiv}CC(Fc){-}C(O){-}C(Fc)CC{\equiv}CPh\}]$ (2) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Fe(1)–C(9) = 1.986(7), Fe(1)–C(13) = 2.053(7), Fe(1)–C(12) = 2.188(7), Fe(2)–C(13) = 1.983(7), Fe(2)–C(8) = 2.211(7), Fe(2)–C(9) = 2.056(7), Fe(1)–Fe(2) = 2.528(1), C(9)–C(8) = 1.422(10), C(8)–C(1) = 1.504(9), C(1)–C(12) = 1.50(1), C(12)–C(13) = 1.42(1), C(8)–C(22) = 1.46(1), C(9)–C(10) = 1.42(1), C(13)–C(14) = 1.44(1), C(12)–C(38) = 1.47(1), C(10)–C(11) = 1.21(1), C(14)–C(15) = 1.191(1), and C(1)–O(1) = 1.22(8); Fe(1)–C(13)–C(12) = 75.7(4), Fe(1)–C(12)–C(13) = 65.4(4), C(9)–Fe(1)–C(12) = 83.4(3), C(9)–Fe(1)–C(13) = 88.3(3), C(9)–Fe(2)–C(13) = 83.3(3), C(8)–Fe(2)–C(13) = 83.3(3), Fe(2)–C(8)–C(9) = 64.7(4), Fe(2)–C(9)–C(8) = 76.6(4), C(12)–C(13)–Fe(2) = 115.9(5), C(1)–C(12)–C(13) = 111.0(6), C(8)–C(1)–C(12) = 114.9(6), and C(9)–C(8)–C(1) = 110.7(6).

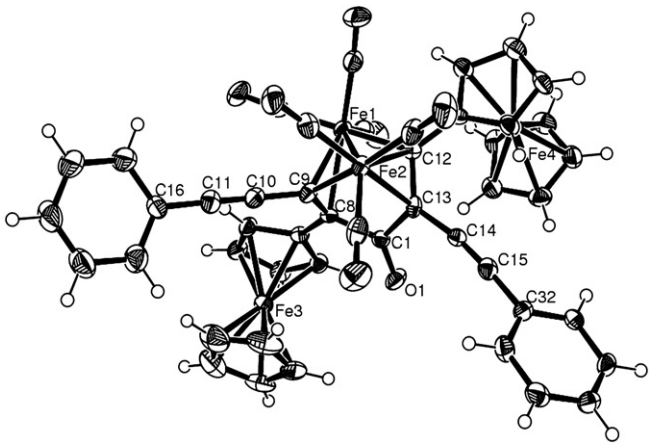


Fig. 3. ORTEP diagram of $[Fe_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhC{\equiv}CCC(Fc){-}C(O){-}C(Fc)CC{\equiv}CPh\}]$ (3) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Fe(1)–C(9) = 2.062(4), Fe(1)–C(8) = 2.202(4), Fe(1)–C(12) = 1.994(3), Fe(2)–C(9) = 1.976(4), Fe(2)–C(12) = 2.140(4), Fe(2)–C(13) = 2.141(4), Fe(1)–Fe(2) = 2.5318(7), C(9)–C(8) = 1.425(5), C(8)–C(1) = 1.502(5), C(1)–C(13) = 1.512(5), C(12)–C(13) = 1.432(5), C(8)–C(22) = 1.484(5), C(9)–C(10) = 1.439(5), C(13)–C(14) = 1.438(5), C(12)–C(38) = 1.469(5), C(10)–C(11) = 1.192(5), C(14)–C(15) = 1.195(5), and C(1)–O(1) = 1.207(4); Fe(1)–C(9)–C(8) = 75.9(2), Fe(1)–C(8)–C(9) = 65.2(2), Fe(1)–C(12)–C(13) = 111.7(3), Fe(2)–C(12)–C(13) = 70.5(2), Fe(2)–C(13)–C(12) = 70.4(2), Fe(2)–C(9)–C(8) = 116.4(3), C(10)–C(9)–C(8) = 112.9(3), C(1)–C(8)–C(9) = 110.3(3), C(8)–C(1)–C(13) = 113.0(3), C(14)–C(13)–C(12) = 127.9(3), C(1)–C(13)–C(12) = 111.8(3), C(13)–C(12)–C(38) = 122.2(3), and C(8)–C(9)–C(10) = 122.9–(3).

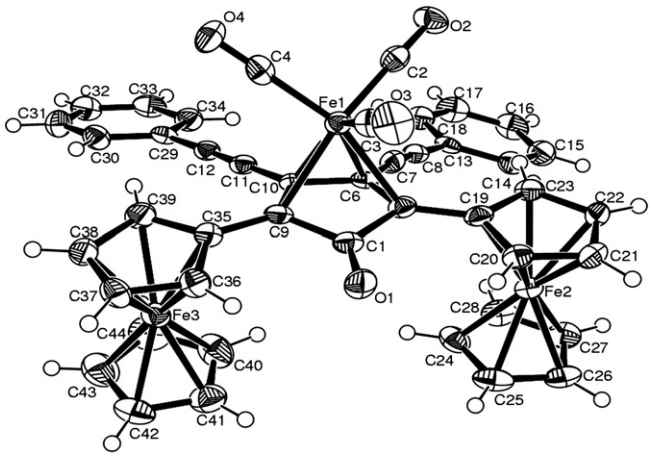


Fig. 5. ORTEP diagram of $[Fe(CO)_3\{\mu\text{-}\eta^2{:}\ \eta^2\text{-}[FcCC(C{\equiv}CPh)C(C{\equiv}CPh)C(Fc)]CO]$ (5) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Fe(1)–C(5) = 2.162(4), Fe(1)–C(6) = 2.097(4), Fe(1)–C(9) = 2.165(4), Fe(1)–C(10) = 2.081(4), C(1)–C(5) = 1.493(6), C(5)–C(6) = 1.441(6), C(6)–C(10) = 1.449(5), C(10)–C(9) = 1.441(6), C(9)–C(1) = 1.479(6), C(5)–C(19) = 1.451(6), C(6)–C(7) = 1.431(6), C(10)–C(11) = 1.432(6), C(9)–C(35) = 1.456(6), C(7)–C(8) = 1.193(5), C(11)–C(12) = 1.197(6), and C(1)–O(1) = 1.226(5); Fe(1)–C(5)–C(6) = 67.8(2), Fe(1)–C(6)–C(10) = 69.1(2), Fe(1)–C(10)–C(9) = 73.4(3), Fe(1)–C(9)–C(10) = 67.0(2), C(9)–C(1)–C(5) = 105.0(4), C(1)–C(5)–C(6) = 106.7(4), C(5)–C(6)–C(10) = 109.1(3), C(6)–C(10)–C(9) = 107.6(4), C(10)–C(9)–C(1) = 108.3(3), C(6)–C(5)–C(19) = 127.1(4), C(5)–C(6)–C(7) = 127.1(4), C(11)–C(10)–C(9) = 128.7(4), C(10)–C(9)–C(35) = 126.5(4), Fe(1)–C(6)–C(5) = 72.6(2), and Fe(1)–C(10)–C(6) = 70.3(2).

two {PhC≡C–} on the α-carbon of the ring whereas in **3**, the ferrocenyl and {PhC≡C–} groups occupy the alternative positions on the $Fe_2C_5(O)$ ring. Formation of diironbicycloheptadienone ring is a consequence of a formal 2 + 2 + 1 + 1 coupling of two FcC_4Ph, one CO molecule and one $Fe_2(CO)_6$ unit. In **2** and **3**, triple bonds adjacent to bulky ferrocenyl group get coupled in contrast to **4**, in which alternative triple bonds couple to form $Fe_2C_5(O)$ ring and the α-carbons bear the free {FcC≡C–}, {PhC≡C–} groups with respect to metal atoms. The bond parameters of the diironbicycloheptadienone rings of **2, 3**, and **4** are similar. As in the structure of **1**, in **2, 3,** and **4** also, lengthening of the complexed C–C bonds [C(8)–C(9) = 1.42(1) Å; C(12)–C(13) = 1.42(1) Å in 2, C(8)–C(9) = 1.43(5) Å; C(12)–C(13) = 1.43(5) Å in 3, and C(8)–C(9) = 1.42(10) Å; C(13)–C(14) = 1.41(1) Å] in **4**, as compared to the complexed C=C bonds is observed. This is consistent with observations previously made for diruthenabicycloheptadienone ring and for η^4-cyclopentadienone complexes [16–19]. The unbridged Fe–Fe bonds in **2**, **3**, and **4** (2.528(1), 2.532(7), and 2.536(2) Å, respectively) are longer than the CO bridged Fe–Fe bond of **1**(2.498(2) Å).

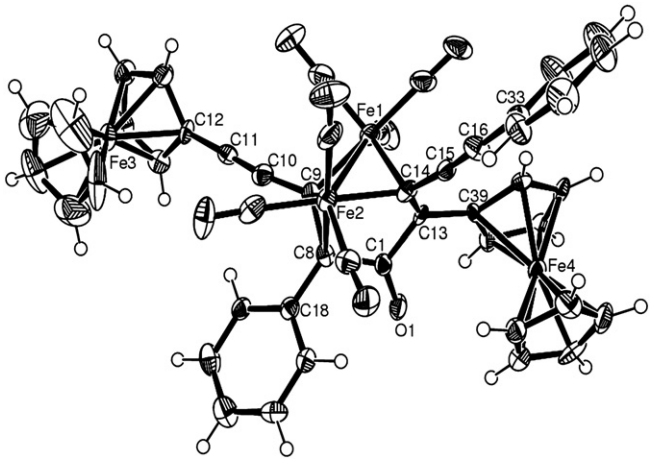


Fig. 4. ORTEP diagram of $[Fe_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}FcC{\equiv}CCC(Fc){-}C(O){-}C(Fc)CC{\equiv}CPh\}]$ (4) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): Fe(1)–C(9) = 1.993(7), Fe(1)–C(14) = 2.070(7), Fe(1)–C(13) = 2.203(7), Fe(2)–C(14) = 1.983(8), Fe(2)–C(9) = 2.099(7), Fe(2)–C(8) = 2.169(7), Fe(1)–Fe(2) = 2.5364(17), C(9)–C(8) = 1.416(10), C(8)–C(1) = 1.498(10), C(1)–C(13) = 1.511(10), C(13)–C(14) = 1.411(10), C(9)–C(10) = 1.44(1), C(8)–C(18) = 1.49(1), C(13)–C(39) = 1.47(1), C(14)–C(15) = 1.42(1), C(15)–C(16) = 1.209(9), C(10)–C(11) = 1.18(1), and C(1)–O(1) = 1.199(8); Fe(1)–C(9)–C(8) = 115.6(5), Fe(1)–C(13)–C(14) = 65.7(4), Fe(1)–C(14)–C(13) = 75.9(4), Fe(2)–C(14)–C(13) = 114.5(5), Fe(2)–C(8)–C(9) = 68.0(4), Fe(2)–C(9)–C(8) = 73.3(4), C(9)–C(8)–C(1) = 109.8(6), C(1)–C(13)–C(14) = 112.2(7), C(8)–C(1)–C(13) = 114.1(6), C(13)–C(14)–C(15) = 125.5(7), C(14)–C(13)–C(39) = 125.2(6), C(9)–C(8)–C(18) = 128.4(7), and C(8)–C(9)–C(10) = 125.9(3).

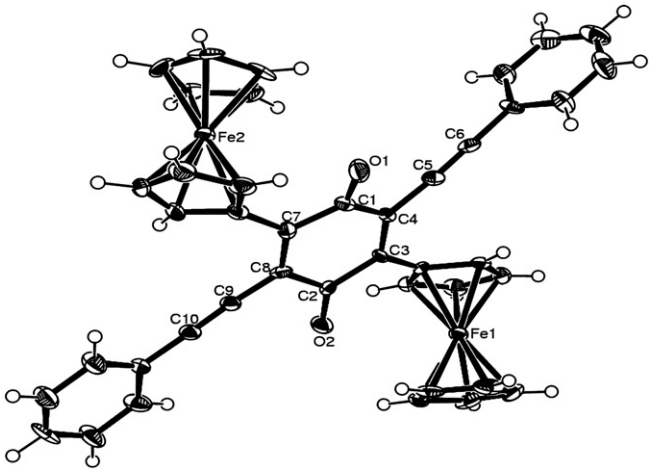
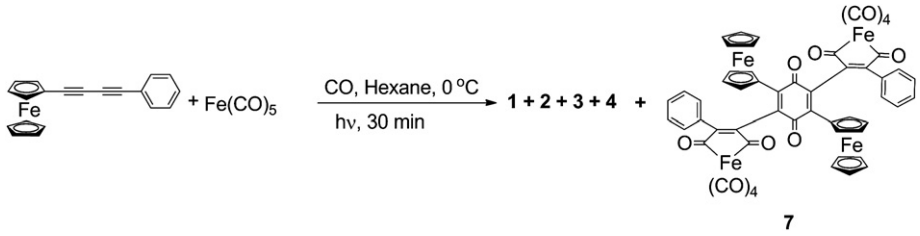


Fig. 6. ORTEP diagram of 2,4-diferrocenyl-3,6-bis(phenylethynyl) cyclohexa-2,5-diene-1,4-dione (8) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): C(3)–C(4) = 1.362(8), C(5)–C(6) = 1.195(9), C(7)–C(8) = 1.361(8), C(10)–C(9) = 1.194(8), C(1)–O(1) = 1.238(7), C(2)–O(2) = 1.212(7); C(3)–C(4)–C(5) = 123.5(6) and C(7)–C(8)–C(9) = 124.0(6).



Scheme 2. Reaction of 1-ferrocenyl-4-phenyl-1,3-butadiyne with $Fe(CO)_5$ and CO.

The molecular structure of **5** consists of an $Fe(CO)_3$ unit coordinated to cyclopentadienone ring with a $Fe(CO)_3$ unit η^4 bonded to it, formally resulting from a 2 + 2 + 1 coupling of two FcC_4Ph molecules with one CO molecule. In contrast to **1**, the ferrocenyl groups attached to the cyclopentadienone ring at α-carbons and are "*syn*", opposite to the $Fe(CO)_3$ unit. The two free {PhC≡C−} groups are located at the β-positions of the ring with respect to ring CO. The cyclopentadineone ring is not planar, and the =CO group is out of the plane with an angle of ~15° in cyclopentadienone ring [10]. The bond distances C(5)–C(6) (1.44 (2) Å), C(6)–C(10) (1.45(5) Å), and C(9)–C(10) (1.44(2) Å) are indicative of delocalization of 4–π electrons over these four carbon atoms.

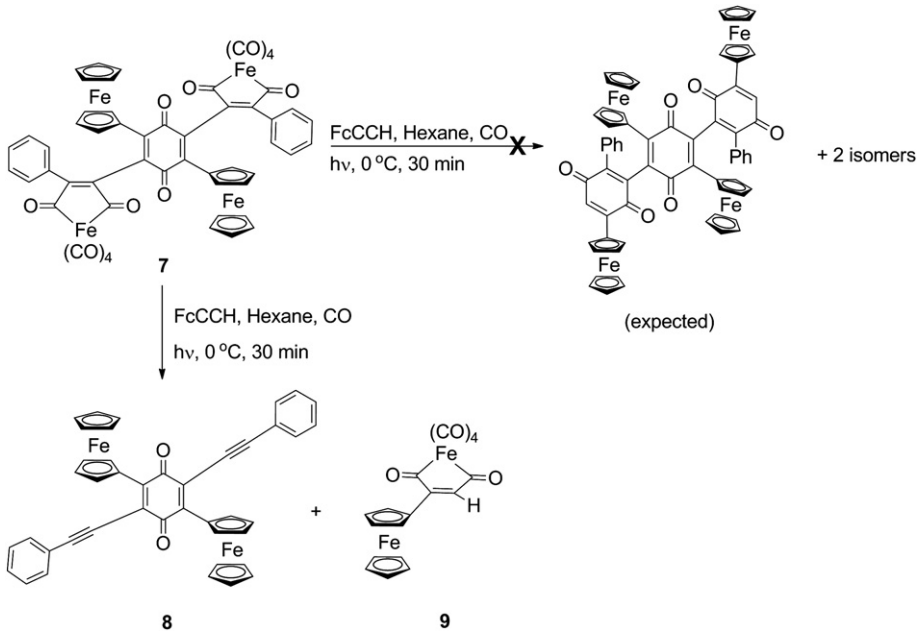
Based on the similarity in the spectroscopic data of **6** with that of **5**, molecular structure for compound **6** can be proposed as a cyclopentadienone ring derivative [$Fe(CO)_3\{\mu\text{-}\eta^2$: η^2-[FcCC(C≡CPh)C(C≡CPh)C(Fc)}CO] which is an isomer of compound **5**.

2.2. Photolysis of 1-ferrocenyl-4-phenyl-1,3-butadiyne with $Fe(CO)_5$ and CO

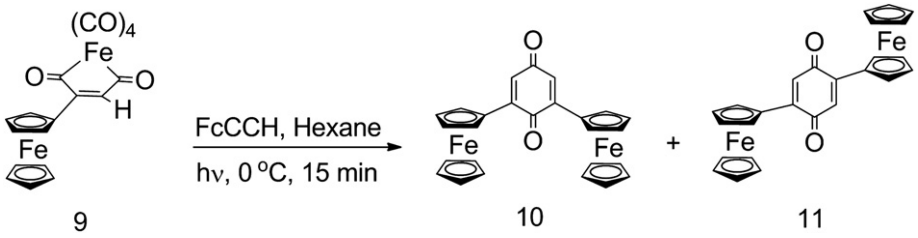
In order to isolate other possible isomers, the photolytic reaction of 1-ferrocenyl 4-phenyl 1,3-butadiyne with $Fe(CO)_5$ and CO was carried at low temperature. A new green compound **7** was obtained along with compounds **1**–**4** (Scheme 2).

The IR spectrum of compound **7** shows the presence of terminal carbonyls and peak at 1670 cm^{-1} indicates the presence of aliphatic carbonyl group. ^1H and ^{13}C NMR spectra of compound **7** confirm the presence of Cp rings, phenyl rings of FcC≡CC≡CPh and carbonyl groups. Mass spectrum of compound **7** shows a peak centered at m/z 1096, for [M–CO]. All attempts to grow suitable crystal for single-crystal X-ray structure determination were unsuccessful. However, based on the spectroscopic data **7**, can be identified as a biferrole derivative of quinone. To substantiate this, its reaction with ferrocenylacetylene was investigated. The reaction yields the quinone **8** and compound **9** (Scheme 3). Compound **8** was identified crystallographically (Fig. 6). When compound **9** was photolyzed with ferrocenyleneacetylene compounds **10** and **11** were obtained and this reaction is similar to that of FcCCH and $Fe(CO)_5$ reported earlier (Scheme 4) [20].

In this paper we have reported the low temperature photochemical reaction of $Fe(CO)_5$ and FcC≡CC≡CPh. Photolysis of FcC≡CC≡CPh and $Fe(CO)_5$ yields a mixture of ferracyclopentadiene complex [$Fe(CO)_2\{\eta^2$:η^2-PhC≡CCC(Fc)C(C≡CPh)CC(Fc)Fe$(CO)_3$}-μ-CO] (**1**), three of ten possible isomers of the diferracycloheptadienone complex, [$Fe_2(CO)_6\{\mu\text{-}\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$-PhC≡CC(Fc)–C(O)–C(Fc)CC≡CPh}] (**2**), [$Fe_2(CO)_6\{\mu\text{-}\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$-PhC≡CCC(Fc)–C(O)–C(Fc)CC≡CPh}] (**3**), [$Fe_2(CO)_6\{\mu\text{-}\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$-FcC≡CCC(Fc)–C(O)–C(Fc)CC≡CPh}] (**4**), and two of three possible isomers of cyclopentadienone complex, [$Fe(CO)_3\{\mu\text{-}\eta^2$: η^2-[FcCC(C≡CPh)C(C≡CPh)C(Fc)}CO] (**5**), [$Fe(CO)_3\{\mu\text{-}\eta^2$: η^2-[FcCC(C≡CPh)C(Fc)C(C≡CPh)}CO] (**6**). Compounds **1**–**6** have been structurally characterized. It is observed that between the FcC≡C– and the PhC≡C– units, it is the former which involves in the addition to form the



Scheme 3. Formation of the quinone **8** and the ferrole **9**.



Scheme 4. Conversion of the ferrole **9** to the quinones **10** and **11**.

$Fe_2C_5(O)$ rings. The PhC≡C– unit remains pendent, either in the α- or β-position with respect to the Fe atom.

3. Experimental Section

3.1. General procedure

All reactions and manipulations were performed using standard Schlenk line techniques under an inert atmosphere of prepurified argon or nitrogen. Solvents were purified, dried, and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer as hexane solutions in 0.1 mm path length NaCl cells and NMR spectra on a Varian VXRO-300S spectrometer in $CDCl_3$. Iron pentacarbonyl and ferrocene were purchased from Fluka and Spectrochem, respectively, and these were used without further purification. Phenylacetylene was purchased from Aldrich and used without further purification. TLC plates were purchased from Merck (20 × 20 cm silica gel 60 F_{254}). Photochemical reactions were carried out using double-walled quartz vessels and a 125 W immersion type mercury lamp operating at 366 nm, manufactured by Applied Photophysics Ltd. FcC≡CH [21] and FcC≡C–C≡CPh [22] were prepared following reported procedures.

3.2. Photolysis of $Fe(CO)_5$ with 1-ferrocenyl-4-phenyl-1,3-butadiyne

1-ferrocenyl-4-phenyl-1,3-butadiyne (105 mg, 0.34 mmol) and ironpentacarbonyl (0.3 ml, 22.2 mmol) was added to the hexane solution (60 ml) and photolyzed for 35 min at 0 °C under argon atmosphere. The solvent was removed in vacuo, the residue was dissolved in dichloromethane and subjected to chromatographic work-up using TLC plates. Elution with a dichloromethane/hexane mixture (35:65 v/v) gave the orange red compound [$Fe(CO)_2\{\eta^2$:η^2-PhC≡CCC(Fc)C(C≡CPh)CC(Fc)$Fe(CO)_3\}$-μ-CO] (**1**), Pink compound [$Fe_2(CO)_6\{\mu$-η^1:η^1:η^2:η^2-PhC≡CC(Fc)–C(O)–C(Fc)CC≡CPh}] (**2**), Grey compound [$Fe_2(CO)_6\{\mu$-η^1:η^1:η^2:η^2-PhC≡CCC(Fc)–C(O)–C(Fc)CC≡CPh}] (**3**), Blackish grey compound [$Fe_2(CO)_6\{\mu$-η^1:η^1:η^2:η^2-FcC≡CCC(Fc)–C(O)–C(Fc)CC≡CPh}] (**4**), Pink [$Fe(CO)_3\{\mu$-η^2:η^2-[FcCC(C≡CPh)C(C≡CPh)C(Fc)}CO] (**5**) and maroon compound [$Fe(CO)_3\{\mu$-η^2:η^2-[FcCC(C≡CPh)C(Fc)C(C≡CPh)}CO] (**6**)

1: Yield: 21 mg (18%). IR (cm^{-1}, ν_{CO}): 2066 (s), 2036 (vs), 2001 (s, br). ^1H NMR ($CDCl_3$): δ 7.36–7.63 (m, 10H, C_6H_5), 3.98–4.29 (m, 18H, η^5-C_5H_5, η^5-C_5H_4). ^{13}C NMR ($CDCl_3$): δ 68.65–73.93 (sub Cp carbons), 69.07 (unsub Cp carbon), 95.03 (Ph**C**≡CC), 97.91 (PhC≡**C**C), 135.18 (PhC≡C**C**Fe), 127.55–131.73 (phenylcarbons), 211.81, 212.17 (Fe–**C**O). MS (m/z, ES+): 901, 900, 816, 765. M. P. 120–122 °C

2: Yield: 18 mg (15%). IR (cm^{-1}, ν_{CO}): 2074 (w), 2049 (vs), 2018 (s, br), 1650 (br). ^1H NMR ($CDCl_3$): δ 7.42–7.46 (m, 6H, C_6H_5), 7.57–7.59 (m, 4H, C_6H_5), 4.22–4.37 (m, 14H, η^5-C_5H_5, η^5-C_5H_4), 5.06–5.07 (m, 4H, η^5-C_5H_4). ^{13}C NMR ($CDCl_3$): δ 66.01–84.51 (sub Cp carbons), 70.09 (unsub Cp carbon), 98.28 (Ph**C**≡CC), 99.38 (PhC≡**C**C), 113.44 (PhC≡C**C**Fe), 123.52–130.87 (phenylcarbons), 152.85 (Fc**C**C(O)), 192.79, 198.63, 207.01, 208.99 (Fe–**C**O). MS (m/z, ES+): 929, 928. M. P. 181–183 °C

3: Yield: 16 mg (13%). IR (cm^{-1}, ν_{CO}): 2074 (w), 2049 (s, br), 2017 (s, br), 1681 (br). ^1H NMR ($CDCl_3$): δ 7.41–7.46 (m, 6H, C_6H_5), 7.60–7.66 (m, 4H, C_6H_5), 4.23–4.36 (m, 13H, η^5-C_5H_5, η^5-C_5H_4), 4.56–4.71 (m, 2H, η^5-C_5H_4), 5.13–5.3 (m, 3H, η^5-C_5H_4). ^{13}C NMR ($CDCl_3$): δ 65.84–84.24 (sub Cp carbons), 69.01–75.96 (unsub Cp carbon), 90.75 (Ph**C**≡CC), 93.76 (PhC≡**C**C), 112.83 (PhC≡C**C**Fe), 97.40 (FcC≡C**C**), 98.58 (PhC≡C**C**C(O)), 123.53–131.66 (phenyl carbons), 152.62 (Fc**C**C(O)), 194.51, 195.13, 206.46 (Fe–**C**O). MS (m/z, ES+): 929, 928, 340. M. P. 145–147 °C.

4: Yield: 15 mg (13%). IR (cm^{-1}, ν_{CO}): 2180 (br), 2074 (w), 2051 (s), 2020(s) 1683 (br). ^1H NMR ($CDCl_3$): δ 7.36–7.64 (m, 10H, C_6H_5), 4.09–4.22(m, 18H, η^5-C_5H_5, η^5-C_5H_4). ^{13}C NMR ($CDCl_3$): δ 64.48–71.64 (unsub Cp carbons), 83.6–84.06 (sub Cp carbons), 96.29 (Ph**C**≡CC), 97.99 (PhC≡**C**C), 98.06 (PhC≡C**C**), 113.87 (PhC≡C**C**Fe), 118.02 (FcC≡C**C**Fe), 123.66–138.24 (phenyl carbons), 152.62 (Fc**C**C(O)), 165.25 (Ph**C**(O)), 195.56, 209.06, 214.21 (Fe–**C**O). MS (m/z, ES+): 929, 928, 356. M. P. 171–172 °C.

5: Yield: 2 mg (2%). IR (cm^{-1}, ν_{CO}): 2063 (s, br), 2011(s, br), 1674 (br). ^1H NMR ($CDCl_3$): δ 7.47–7.49 (m, 6H, C_6H_5), 7.71–7.44 (m, 6H, C_6H_5), 4.21–4.44 (m, 18H, η^5-C_5H_5, η^5-C_5H_4). MS (m/z, ES+): 790, 789, 788. M. P. 169–172 °C.

6: Yield: 16 mg (16%). IR (cm^{-1}, ν_{CO}): 2066 (s), 2012 (s, br), 1673 (br). ^1H NMR ($CDCl_3$): δ 7.78–7.81 (m, 2H, C_6H_5), 7.65–7.67 (m, 2H, C_6H_5), 7.54–7.56 (m, 3H, C_6H_5), 7.39–7.45 (m, 3H, C_6H_5), 5.52–5.58 (m, 2H, η^5-C_5H_4), 5.27–5.29 (m, 2H, η^5-C_5H_4), 4.40–4.56 (m, 4H, η^5-C_5H_4), 4.16–4.27 (m, 10H, η^5-C_5H_5). ^{13}C NMR ($CDCl_3$): δ 66.85–75.97 (sub Cp carbons), 69.63 (unsub Cp carbons), 128.69–131.97 (phenyl carbons), 97.03 (Ph**C**≡CC), 98.19 (PhC≡**C**C), 123.11 (PhC≡C**C**), 167.25 (**C**O), 207.01 (Fe–**C**O). MS (m/z, ES+): 790, 789, 788. M. P. 176–178 °C.

3.3. Photolysis of $Fe(CO)_5$ with CO and 1-ferrocenyl-4-phenyl-1,3-butadiyne

1-ferrocenyl-4-phenyl-1,3-butadiyne (105 mg, 0.34 mmol) and ironpentacarbonyl (0.3 ml, 22.2 mmol) was added to the hexane solution (60 ml) and photolyzed for 35 min at 0 °C under continuous bubbling of CO. The solvent was removed in vacuo, the residue was subjected to chromatographic work-up using TLC plates. Elution with a dichloromethane/hexane mixture (35:65 v/v) gave a green band **7** along with the compounds **1**–**4**. The green compound **7** was again photolyzed with ferrocenylacetylene (21 mg, 0.1 mmol) and hexane at 0 °C for 30 min under constant CO bubbling. The solvent was removed in vacuo, the residue was dissolved in dichloromethane and subjected to chromatographic work-up using TLC plates. Elution with a dichloromethane/hexane mixture (30:70 v/v) gave the olive green compound 2,5-diferrocenyl-3,6-bis(phenylethynyl)cyclohexa-2,5-diene-1,4-dione (**8**).

7: Yield: 21 mg (20%). IR (cm^{-1}, ν_{CO}): 2109 (b), 2052 (s, br), 2028 (s), 1670 (b); ^1H NMR ($CDCl_3$): δ 4.19 (s, 10 H, η^5-C_5H_5), 4.67 (m, 4 H,

Table 1
Crystal Data and Structure Refinement Parameters for **1**–**5** and **8**.

	1	2	3	4	5	8
Formula	$C_{46}H_{28}Fe_4O_6$	$C_{47}H_{28}Fe_4O_6$	$C_{47}H_{28}Fe_4O_6$	$C_{47}H_{28}Fe_4O_6$	$C_{44}H_{28}Fe_3O_4$	$C_{42}H_{28}Fe_2O_2$
Mol. wt	900.08	928.11	928.09	928.09	788.21	676.34
Temp, K	150(2)	150(2)	150(2)	150(2)	150(2)	120(2)
Cryst syst	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\,2_1\,2_1\,2_1$
a, Å	10.876(4)	13.6121(11)	13.9695(14)	11.800(3)	13.6811(16)	10.1208(18)
b, Å	13.044(4)	17.568(3)	10.376(2)	12.338(3)	10.5966(13)	12.0741(16)
c, Å	15.098(5)	16.480(16)	27.919(3)	15.350(3)	23.370(4)	24.888(5)
α, deg	104.24(3)	90	90	68.12(2)	90	90
β, deg	97.17(3)	10.3166(9)	98.576(9)	68.34(2)	94.029(14)	90
γ, deg	113.61(3)	90	90	85.88(2)	90	90
V, Å^3	1841.2(10)	3837.5(8)	4001.5(10)	1921.9(8)	3379.7(8)	3041.3(9)
Z	2	4	4	2	4	4
D (calcd), Mg/m^{-3}	1.624	1.606	1.541	1.604	1.549	1.477
Abs coeff, mm^{-1}	1.597	1.537	1.474	1.534	1.317	0.992
F (000)	912	1880	1880	940	1608	1392
Cryst size, mm	0.27 × 0.23 × 0.18	0.80 × 0.23 × 0.18	0.23 × 0.18 × 0.15	0.34 × 0.28 × 0.22	0.33 × 0.26 × 0.21	0.23 × 0.18 × 0.13
θ range, deg	3.11–25.00	3.07–25.00	2.95–25.00	2.95–25.00	2.93–25.00	2.98–25.00
Index ranges	$-12 \le h \ge 12$	$-16 \le h \ge 16$	$-13 \le h \ge 16$	$-14 \le h \ge 13$	$-16 \le h \ge 16$	$-12 \le h \ge 12$
	$-15 \le k \ge 15$	$-20 \le k \ge 20$	$-12 \le k \ge 12$	$-14 \le k \ge 14$	$-12 \le k \ge 12$	$-14 \le k \ge 14$
	$-17 \le l \ge 17$	$-19 \le l \ge 19$	$-33 \le l \ge 30$	$-18 \le l \ge 18$	$-27 \le l \ge 27$	$-29 \le l \ge 29$
No. of rflns collected/unique	13921/6394	28427/6738	18977/7029	15854/6727	28798/5940	24227/5333
	[R(int) = 0.0821	[R(int) = 0.0580	[R(int) = 0.0562	[R(int) = 0.1021	[R(int) = 0.1137	[R(int) = 0.1849]
No. of data/restraints/param.	6394/0/505	6738/0/542	7029/0/523	6727/0/523	5940/0/460	5333/0/415
Goodness-of-fit on F^2	0.868	1.353	0.983	0.98	0.917	0.918
final R indices ([I > 2σ(I)])	$R_1 = 0.0544$	$R_1 = 0.0788$	$R_1 = 0.0393$	$R_1 = 0.0663$	$R_1 = 0.0436$	$R1 = 0.0640$
	$wR_2 = 0.0900$	$wR_2 = 0.1616$	$wR_2 = 0.0803$	$wR_2 = 0.15$	$wR_2 = 0.0850$	wR2 = 0.1053
R indices (all data)	$R_1 = 0.1289$	$R_1 = 0.0945$	$R_1 = 0.0744$	$R_1 = 0.1369$	$R_1 = 0.940$	$R1 = 0.1037$
	$wR_2 = 0.1063$	$wR_2 = 0.1658$	$wR_2 = 0.0957$	$wR_2 = 0.1759$	$wR_2 = 0.1029$	wR2 = 0.1172
Largest diff peak and hole, eÅ^{-3}	0.69 and −0.406	0.64 and −0.572	0.395 and −0.398	0.895 and −0.692	0.647 and −0.722	0.547 and −0.397

η^5-C_5H_4), 5.41–5.42 (m, 4H, η^5-C_5H_4), 7.40–7.42 (m, 6H, C_6H_5), 7.61–7.64 (m 4H, C_6H_5),^{13}C NMR ($CDCl_3$): δ 128.83–131.76 (phenyl carbons), δ 70.59–84.95 (sub Cp carbons), δ 71.27 (unsub Cp carbons), δ 123.05 (Ph**C**=C-), δ 111.75 (PhC=**C**-), δ 147. 93 (FcC=C–), δ 198.93, 199.11, 202.35 (Fe–CO), δ 171.85 (CO) MS (m/z, ES+): 1096 [M–CO], M. P. 135–137 °C.

8: Yield: 4.5 mg (21%). IR (cm^{-1}, ν_{CO}): 1658 (s, br), ^{1}H NMR ($CDCl_3$): δ 7.65–7.68 (m, 4H, C_6H_5), 7.40–7.42 (m, 4H, C_6H_5), 5.49–5.48 (m, 2H, C_6H_5), 4.24 (s, 10H, η^5-C_5H_5, η^5-C_5H_5), 4.75–5.49 (m, 8H, η^5-C_5H_5, η^5-C_5H_4). ^{13}C NMR ($CDCl_3$): δ 128.79–131.89 (phenyl carbons), δ 56.80–73.05 (sub Cp carbons), δ 69.12 (unsub Cp carbons), δ 107.97 (Ph**C**=C-), δ 104.72 (PhC=**C**–), δ 180.03 (Fc**C**=C), δ 153.79 (FcC=**C**), δ 177.51 (**C**O) MS (m/z, ES+): 676, M. P. 163–165 °C.

3.4. Crystal structure determination of compounds *1*–*5* and *8*

Suitable x-ray quality crystals of **1**–**5** and **8** were grown by slow evaporation of dichloromethane/n-hexane solvent mixture in the temperature variation of 25 °C to −5 °C and X-ray diffraction studies were undertaken. Relevant crystallographic data and details of measurements are given in Table 1. X-ray crystallographic data were collected from Single-crystal samples of **1** (0.27 × 0.23 × 0.18 mm^3), **2** (0.8 × 0.23 × 0.18 mm^3), **3** (0.23 × 0.18 × 0.15 mm^3), **4** (0.34 × 0.28 × 0.22 mm^3), **5** (0.33 × 0.26 × 0.21 mm^3) and **8** (0.23 × 0.18 × 0.13 mm^3) mounted on a Oxford Diffraction XCALIBUR-S CCD system equipped with graphite-monochromated Mo Kα radiation (0.71070 Å). The data were collected by the ω-2θ scan mode, and absorption correction was applied by using Multi-Scan. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares against F^2 using SHELXL-97 software [23]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and refined using a riding model.

Acknowledgements

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 732846, 732845, 732848, 732849, 732847 and 764199 for compound **1**–**5** and **8**. Copies of this information may 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 http://www.ccdc.cam.ac.uk).

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