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Synthesis, structure and electrochemistry of CO incorporated diruthenium metallacyclic compounds $[Ru_2(CO)_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}1,4\text{-}Fc_2C_5H_2O\}]$ and $[Ru_2(CO)_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}1,5\text{-}Fc_2C_5H_2O\}]$

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Abstract

Ferrocenyl substituted ruthenium metallacyclic compounds, $[Ru_2(CO)_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}1,4\text{-}Fc_2C_5H_2O\}]$ (**1**) and $[Ru_2(CO)_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}1,5\text{-}Fc_2C_5H_2O\}]$ (**2**) have been synthesized and structurally characterized. Electrochemical studies for **1** and **2** and the respective quinone derivatives **3** and **4** show weak to no electrochemical coupling at the mixed-valent intermediate state which is dependent on the complex frameworks.

Keywords: Ferrocene; Ruthenium; Metallacycle; Electrochemistry

1. Introduction

Electronic communication between redox active sites in multinuclear metallocene complexes has been extensively studied for potential applications in molecular electronics [1–5]. Several applications like multielectron redox catalysts and electron storage devices have been found for oligomeric ferrocene derivatives [6]. Particular interest has been focused on complexes with reversibly switchable redox active sites which can selectively vary the electronic properties by oxidation or reduction. For example, biferrocene has been one of the most promising materials to be used as a switchable two electron reservoir [7]. An intense electronic communication can be observed in complexes with two or more ferrocenyl units separated by conjugated bridging ligands. This concept has led to the development of ferrocene based molecular wires [8–12].

In recent times we have focused our attention on investigation of reactions of acetylenes with metal acetylides and have found that bulky acetylenes, such as ferrocenylacetylene introduce novel features in reactions with metal acetylides [13]. Under photolytic conditions, reaction between ferrocenylacetylene and $Fe(CO)_5$ yields 2,5- and 2,6-diferrocenylquinones [14], whereas from the reactions of ferrocenylacetylene with mononuclear metal carbonyls $Fe(CO)_5$ and $M(CO)_6$ (M = Mo, W) under thermolytic conditions, $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2CO\}C(Fc){=}CH]$, $[Fe(CO)_2\{\eta^2:\eta^2\text{-}2,5\text{-}Fc_2C_4H_2Fe(CO)_3\}\mu\text{-}CO]$ and $[Fe(CO)_3\{\eta^2:\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$, 1,2,4-triferrocenylbenzene, 2,5-diferrocenylthiophene, and 2,5-diferrocenylselenophene, respectively, have been isolated. Here, we report the synthesis, structural characterization and electrochemical studies of ferrocene based ruthenium metallacyclic compounds and our

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observation on comparison of the electronic coupling between the ferrocenyl sites with different bridges.

2. Results and discussion

Photolysis of a hexane solution of $[Ru_3(CO)_{12}]$ into which carbon monoxide is constantly bubbled, forms $[Ru(CO)_5]$. When we added 1 equiv of ferrocenylacetylene to a freshly prepared hexane solution of $[Ru(CO)_5]$ and carried out photolysis at −10 °C, we observed the formation of two major compounds: $[Ru_2(CO)_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}1,4\text{-}Fc_2C_5H_2O\}]$ (**1**) and $[Ru_2(CO)_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}1,5\text{-}Fc_2C_5H_2O\}]$ (**2**), and trace amounts of the previously reported quinones, 2,5-diferrocenylbenzo-1,4-quinone (**3**) and 2,6-diferrocenylbenzo-1,4-quinone (**4**) [14], as well as 1,2,4-triferrocenylbenzene (**5**) [15] (Scheme 1). When the photolysis was carried out with constant CO bubbling through the solution of $[Ru(CO)_5]$ and ferrocenylacetylene, compounds **3** and **4** constituted the major components of the reaction mixture. Table 1 summarizes the conditions used for the reactions and the yields of the products obtained.

The new compounds **1** and **2** were characterized by IR and ^{1}H and ^{13}C NMR spectroscopy. Mass spectra of both showed molecular ion peaks and peaks corresponding to successive loss of six carbonyl groups. Based on similarity of spectral features, compounds **1** and **2** were identified as isomers of $[Ru_2(CO)_6\{1,4\text{-}Fc_2C_5H_2O\}]$. Compound **1** has been reported to form in low yield in the thermal reaction between $Ru_3(CO)_{12}$ and ferrocenylacetylene [16]; however, its crystal structure remained unreported. Here, we report the crystallographically determined molecular structure of compounds **1** and **2**.

Single crystals of **1** and **2** were grown from hexane/dichloromethane solvent mixture and single crystal X-ray diffraction analyses of both were carried out. In compound **1**, a pentadienone unit is attached to two ferrocenyl ligands at 1- and 4-carbon position, whereas in **2**, the ferrocenyl ligands are linked to 1- and 5-position of the pentadienone ring. The diferrocenyl pentadienone moiety is linked to $Ru_2(CO)_6$ unit via two sigma and two pi bonds in both the compounds (Figs. 1 and 2).

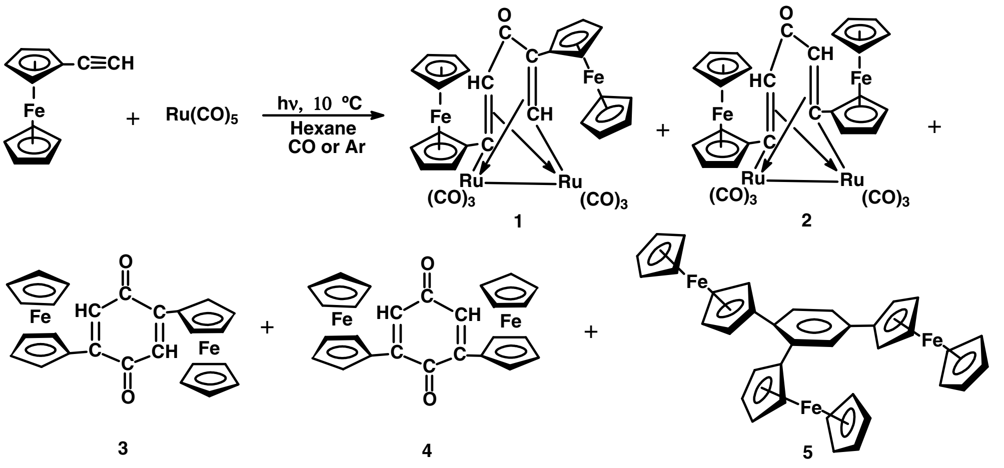
The Ru(1)–Ru(2) distances of 2.7472(9) Å in **1** and 2.716(11) Å in **2** are short for a ruthenium–ruthenium single bond. Values of 2.713(2), 2.735(2) and 2.740(4) Å have been reported in $[Ru_4(CO)_{10}(PPh)(PhC_2PPh_2)]$, $[Cp_2Ru_2(CO)_4]$ and $[(C_{10}H_8)Ru_3(CO)_7]$, respectively [17], but bond lengths near 2.8–2.9 Å are more generally observed [18]. The ethylenic bonds are typically metal-olefinic type (C(8)–C(9) = 1.414(6) Å; C(10)–C(11) = 1.391(5) Å for **1**) and (C(8)–C(9) = 1.401(14) Å; C(10)–C(11) = 1.419(13) Å for **2**) comparable with carbon–carbon bond distances in ruthenium ethylenic units (range 1.37–1.44 Å) [19].

Several examples of cyclodimerization of acetylenes with or without CO have been reported [20]. Various ferroles have been obtained by reacting acetylenes and iron carbonyl in water [21] or in alkaline solutions [22] and by refluxing a solution of $Fe_3(CO)_{12}$ and alkynes in hydrocarbon solvents [23]. Decomplexation reactions of nickel maleoyl complexes $[Ni(bpy)\{C_2R_2(CO)_2\}]$ [24] and of some acyloxy ferrole complexes [25] have led to isolation of cyclobutendiones, $C_2R_2(CO)_2$. Formation of the dimetallacycloheptadienes, **1** and **2** is somewhat unusual since they are usually obtained in the reactions of ruthenium carbonyl with disubstituted acetylenes rather than monosubstituted ones.

2.1. Electrochemistry of **1**–**4**

The redox properties of the complexes **1**–**4** have been examined in CH_2Cl_2 solution by cyclic voltammetric and differential pulse voltammetric techniques using a Pt-working electrode. The data are set in Table 2 and the voltammograms are shown in Fig. 3a–d.

Complex **1** exhibits two distinct oxidation couples with a separation in potential of $\Delta E^0 = 267$ mV vs. SCE (Fig. 3a). The observed redox processes are considered to be associated with the iron centers in ferrocenyl units. The separation in potential (ΔE^0) of 267 mV arises primarily due to



Scheme 1.

Table 1
Amounts of reactants used and yields of products obtained

$[Ru_3(CO)_{12}]$ [mg (mmol)]	[Fc(C≡CH)] [mg (mmol) used] [mg (mmol) recovered]	Gas bubbling	Products obtained	Yield[a]: mg (%)
[256 (0.4)]	[210 (1.0)] [22 (0.1)]	Argon	**1**	75 (20%)
			2	82 (22%)
			3	15 (7%)
			4	10 (5%)
			5	15 (8%)
[256 (0.4)]	[210 (1.0)] [24 (0.12)]	Carbon monoxide	**1**	26 (8%)
			2	35 (10%)
			3	45 (22%)
			4	56 (27%)

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

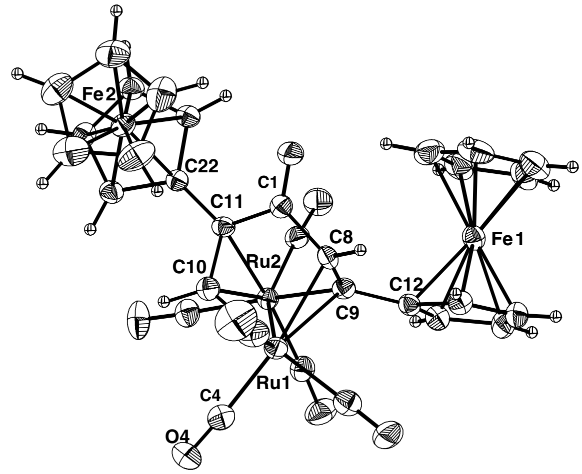


Fig. 1. Molecular structure (ORTEP plot at 50% probability) of $[Ru_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}1,4\text{-}Fc_2C_5H_2O\}]$ (**1**) (Fc = $(\eta^5\text{-}C_5H_5)_2Fe$). Solvent molecule (*n*-hexane) is omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ru(1)–Ru(2) = 2.7472(9), Ru(1)–C(9) = 2.297(4), Ru(1)–C(8) = 2.238(4), Ru(1)–C(10) = 2.062(4), Ru(2)–C(10) = 2.219(4), Ru(2)–C(11) = 2.359(4), Ru(2)–C(9) = 2.081(4), C(8)–C(9) = 1.414(6), C(10)–C(11) = 1.391(5), C(10)–Ru(1)–Ru(2) = 52.65(11), C(8)–C(9)–C(12) = 119.5(3), C(10)–C(11)–C(22) = 122.9(3), C(8)–C(1)–C(11) = 114.1(3).

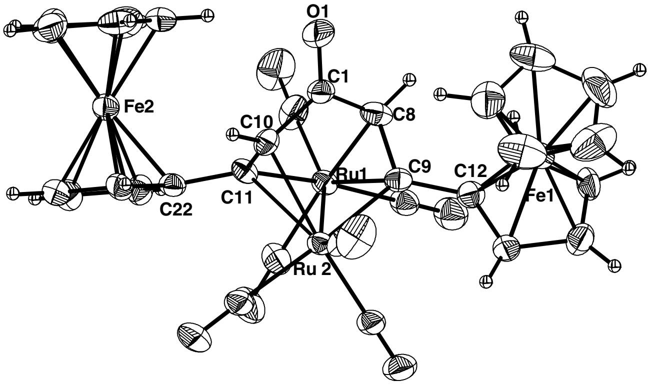


Fig. 2. Molecular structure (ORTEP plot at 50% probability) of $[Ru_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}1,5\text{-}Fc_2C_5H_2O\}]$ (**2**) (Fc = $(\eta^5\text{-}C_5H_5)_2Fe$). Selected bond lengths (Å) and bond angles (°): Ru(1)–Ru(2) = 2.7161(11), Ru(1)–C(8) = 2.272(10), Ru(1)–C(9) = 2.311(10), Ru(2)–C(9) = 2.072(10), Ru(2)–C(11) = 2.311(10), Ru(2)–C(10) = 2.259(10), Ru(1)–C(11) = 2.092(10), C(8)–C(9) = 1.401(14), C(10)–C(11) = 1.419(13), C(1)–C(8) = 1.453(16), C(1)–C(10) = 1.479(15), Ru(1)–C(2) = 1.924(13), C(9)–C(12) = 1.450(15), C(11)–C(22) = 1.460(14), Ru(2)–C(9)–Ru(1) = 76.4(3), C(9)–Ru(2)–Ru(1) = 55.8(3), C(11)–Ru(2)–Ru(1) = 48.4(2), C(10)–Ru(2)–Ru(1) = 71.9(3), C(1)–C(10)–Ru(2) = 104.5(7), C(9)–C(8)–Ru(1) = 73.7(6).

the effect of two chemically non-equivalent ferrocene centers in **1** and due to the bridging function mediated electrochemical coupling at the intermediate mixed valent Fe(II)/Fe(III) centers, if any [26]. This separation of 267 mV translates to the comproportionation constant (K_c) value of 3.35×10^4 (calculated using the equation, $RT\ln K_c = nF\Delta E^0$) [27]. However, two chemically equivalent ferrocene centers in **2** show two closely spaced iron based oxidation processes (Fig. 3b) with separation in potential of 143 mV. The resultant K_c value of 2.65×10^2 implies weak intermetallic electrochemical coupling between the intermediate mixed valent iron centers in **2**.

Complex **3** with two ferrocenyl units linked to the *p*-benzoquinone bridging ligand at the 2- and 5-positions, displays two ferrocenyl based oxidation processes with a separation in potential of 252 mV (Fig. 3c). The cathodic wave of the oxidation processes appears to be distorted and consequently the current height is much higher than that of the corresponding anodic waves possibly due to electro-adsorption [28]. The K_c value of 1.87×10^4 in the mixed valent $Fe^{II}Fe^{III}$ state of **3** reveals that the ferrocenyl moieties are moderately electrochemically coupled via the involvement of the quinone unit. However, the corresponding isomeric complex **4** with two ferrocenyl units bonded to the *p*-benzoquinone ligand at 2- and 6-positions displays simultaneous two electron oxidation process associated with the ferrocenyl moieties, implying no electrochemical coupling between the terminal ferrocenyl units. Thus, the extent of *p*-benzoquinone mediated electrochemical coupling between the chemically equivalent terminal ferrocenyl units is related to the positional linkage of the ferrocenyl units with respect to the quinone based spacer. Instability of the electrogenerated oxidized species at the coulometric time scale has precluded any further studies on the intermediate mixed valent Fe(II)Fe(III) species.

The quinone based expected successive two one-electron reductions (Quinone $\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$ Semiquinone $\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$ Catecholate) in **3** and **4** have also been observed (Table 2).

Table 2
Electrochemical data in CH_2Cl_2

Compound	Electrochemical data			
	Metal oxidation E^0, V (ΔE_p, mV)	$\Delta E/\text{mV} = E_2^0 - E_1^0$	K_c[a]	Ligand reduction E^0, V (ΔE_p, mV)
1	$E_1^0 = 0.441$ (120), $E_2^0 = 0.708$ (120)	0.267	3.35×10^4	–
2	$E_1^0 = 0.582$ (120), $E_2^0 = 0.725$ (120)	0.143	2.65×10^2	–
3	$E_1^0 = 0.349$ (120), $E_2^0 = 0.601$ (120)	0.252	1.87×10^4	−0.622(120), −1.17(150)
4	0.595 (150)	–		−0.671(150), −1.14(130)

[a] $K_c = 10^{\Delta E/0.059}$.

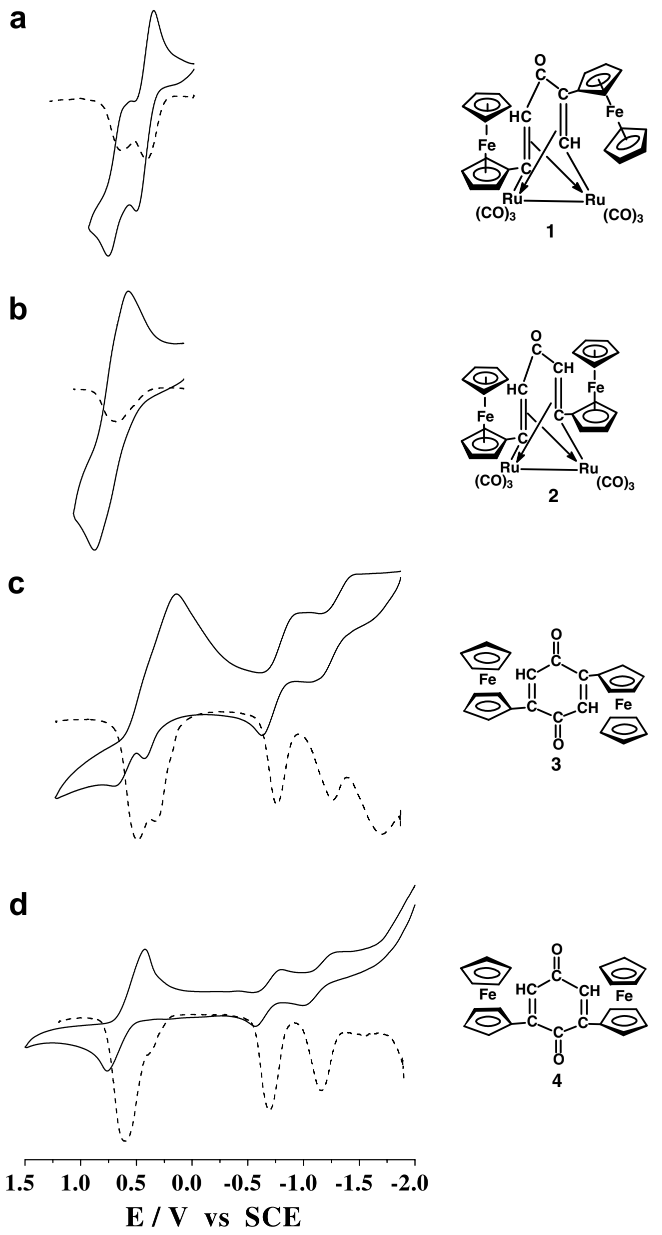


Fig. 3. Cyclic voltammograms (—) and differential pulse voltammograms (---) of **1**–**4** in CH_2Cl_2.

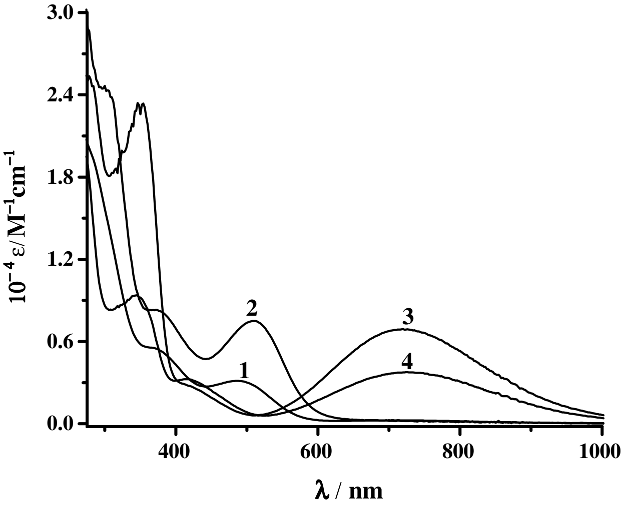


Fig. 4. Electronic spectra of **1**–**4**.

2.2. Electronic spectra of *1–4*

The electronic spectral features of the complexes (**1**–**4**) in CH_2Cl_2 are given in Fig. 4 and Table 3. All the four complexes (**1**–**4**) exhibit intense π–π* transitions in the UV-region. Compounds **1** and **2** show moderately intense charge-transfer bands in the visible region at 489 and 509 nm, respectively, which are believed to be ferrocene based transitions. Free ferrocene also displays one CT band at 443 nm in CH_2Cl_2. However, complexes **3** and **4** involving the *p*-benzoquinone bridging unit exhibit one reasonably intense low energy transition each at 721 and 730 nm, respectively, in addition to ferrocene based transition at 424 and 419 nm. The low-energy transitions near 700 nm may be considered to be associated with the quinone moiety [29].

We were unable to check the spectral properties of the complexes at the mixed valent intermediate Fe(II)/Fe(III) state due to the instability of the electrogenerated oxidized species which indeed restricted any further correlation to be made between the observed electrochemical features and the extent of electronic coupling. Moreover, in the absence

Table 3
Electronic spectral data for **1**–**4**

Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})
1	489(3151), 367(5482), 283(19564)
2	509(7515), 372(8343), 300(24457)
3	721(6917), 424(sh), 352(23321), 276(25209)
4	730(3680), 419(3151), 343(9325), 262(22050)

of calculated MO energies a tentative assignment of the transitions in the native state of the complexes has not been possible.

3. Experimental details

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. Carbon monoxide (99.95% purity) of BOC India Limited was used as supplied. 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 Plus spectrometer in $CDCl_3$. UV–vis spectral studies were performed on Perkin Elmer Lambda 950 spectrophotometer. Cyclic voltammetric, differential pulse voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was the supporting electrolyte, and the solution concentration of the analyte was ca. 10^{-3} M; the scan rate used was $50\ mV\ s^{-1}$. A platinum gauze working electrode was used in the coulometric experiments. All electrochemical experiments were carried out under a dinitrogen atmosphere. The elemental analysis was carried out with a Perkin–Elmer 240 C elemental analyzer. Electrospray mass spectra were recorded on a Micromass Q-ToF mass spectrometer. TLC plates (20 × 20 cm, Silica gel 60 F_{254}) were purchased from Merck. $Ru_3(CO)_{12}$ [30] and $FcC{\equiv}CH$ [31] were prepared following reported procedures.

3.2. Preparation of [Ru(CO)$_5$]

A 30 ml hexane solution of $Ru_3(CO)_{12}$ (256 mg, 0.4 mmol) was photolyzed with constant stirring and CO bubbling for 20 min at −10 °C. A pale yellow solution of $[Ru(CO)_5]$ was obtained which was reacted further as soon as prepared.

3.3. Photolysis of [Ru(CO)$_5$] with ferrocenylacetylene

An hexane solution (10 ml) of ferrocenylacetylene (209 mg, 1 mmol) was added to the hexane solution of freshly prepared $[Ru(CO)_5]$ and photolyzed for 20 min at −10 °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 (30:70 v/v) gave the following four compounds in order of elution: unreacted yellow ferrocenylacetylene, yellow 1,2,4-triferrocenylbenzene (**5**), green 2,5-diferrocenyl quinone (**3**), brown $[Ru_2(CO)_6\{FcC{=}CH(CO)FcC{=}CH\}]$ (**1**), green 2,6-diferrocenyl quinone (**4**) and $[Ru_2(CO)_6\{FcC{=}CH(CO)CH{=}CFc\}]$ (**2**).

Compound **1**: IR (ν(CO), cm^{-1}, *n*-hexane): 2086, 2063, 2026, 1721. ^1H NMR (δ, $CDCl_3$): 4.24 (s, 5H, η^5-C_5H_5), 4.13 (s, 5H, η^5-C_5H_5), 4.12–4.90 (m, 8H, η^5-C_5H_4), 5.19 (s, 1H, C=C*H*), 8.70 (s, 1H, C=C*H*). ^{13}C NMR (δ, $CDCl_3$): 69.2–72.1 (m, Cp), 109.2 (s, C=*C*H), 127.6 (s, C=*C*H), 144 (s, Fc*C*=CH), 151.5 (s, Fc*C*=CH), 191.9 (*C*O), 210, 214 (Ru–*C*O). Anal. Calc.: C, 45.49; H, 2.46. Found: C, 46.10; H, 2.53%. Mass spectra (*m*/*z*): 818.4, 790.5, 762.5, 734.5.

Compound **2:** IR (ν(CO), cm^{-1}, *n*-hexane): 2085.9, 2064, 2024.5, 1892.9, 1724. ^1H NMR (δ, $CDCl_3$): 4.23 (s, 10H, η^5-C_5H_5), 4.47–4.78 (m, 8H, η^5-C_5H_4), 5.17 (s, 2H, C=C*H*). ^{13}C NMR (δ, $CDCl_3$): 69.6–71.7 (m, Cp), 120.3 (s, C=*C*H), 139.8 (s, Fc*C*=CH), 192.5 (CO). Anal. Calc.: C, 45.49; H, 2.46. Found: C, 44.97; H, 2.61%. Mass spectra (*m*/*z*): 818.7, 791.5, 763.6, 735.6, 707.6, 679.7.

Compound **3:** IR (ν(CO), cm^{-1}, *n*-hexane): 1780, 1670, 1643. ^1H NMR (δ, $CDCl_3$): 4.16 (s, 10H, η^5-C_5H_5), 4.61 (s, 4H, η^5-C_5H_4), 4.99 (s, 4H, η^5-C_5H_4), 6.83 (s, 2H, C=C*H*). ^{13}C NMR (δ, $CDCl_3$): 69.8–72.2 (m, Cp), 127.6 (s, C=*C*H), 147.8 (Fc*C*=CH), 185.9 (CO). Anal. Calc.: C, 65.58; H, 4.23. Found: C, 65.28; H, 4.54%.

Compound **4:** IR (ν(CO), cm^{-1}, *n*-hexane): 1778, 1737, 1618. ^1H NMR (δ, $CDCl_3$): 4.18 (s, 10H, η^5-C_5H_5), 4.63 (s, 4H, η^5-C_5H_4), 4.97 (s, 4H, η^5-C_5H_4), 6.83 (s, 2H, C=C*H*). ^{13}C NMR (δ, $CDCl_3$): 69.8–72.0 (m, Cp), 127.2 (s, C=*C*H), 148.8 (Fc*C*=CH), 186.5 (CO). Anal. Calc.: C, 65.58; H, 4.23. Found: C, 65.94; H, 4.47%.

Compound **5:** ^1H NMR (δ, $CDCl_3$): 4.05–4.16 (m, 15H, η^5-C_5H_5), 4.37 (t, 6H, η^5-C_5H_4), 4.72 (t, 6H, η^5-C_5H_4), 7.88 (d, $^4J_{HH} = 1.6$ Hz, 1H, aromatic CH), 7.65 (d, $^3J_{HH} = 8$ Hz, 1H, aromatic CH), 7.35 (dd, $^4J_{HH} = 1.6$ Hz, $^3J_{HH} = 8$ Hz, 1H, aromatic CH).

3.4. Photolysis of [Ru(CO)$_5$] with ferrocenylacetylene in presence of CO

An hexane solution of ferrocenylacetylene (209 mg, 1 mmol) and $[Ru(CO)_5]$ (~1 mmol) was subjected to photolysis for 20 min at −10 °C in presence of constant CO-bubbling. The solvent was evaporated in vacuo and the dried mixture was dissolved in dichloromethane for further work-up. The following compounds were separated by chromatographic separation by TLC using dichloromethane/hexane solvent mixture (30:70 v/v) in the order of elution: unreacted yellow ferrocenylacetylene, green 2,5-diferrocenyl quinone (**3**), brown $[Ru_2(CO)_6\{FcC{=}CH(CO)FcC{=}CH\}]$ (**1**), green 2,6-diferrocenyl quinone (**4**) and $[Ru_2(CO)_6$-$\{FcC{=}CH(CO)CH{=}CFc\}]$ (**2**).

Table 4
Crystal data and structure refinement parameters for **1** and **2**

	1 · C_6H_{14}	**2**
Empirical formula	$C_{34}H_{27}Fe_2O_7Ru_2$	$Fe_2Ru_2O_7C_{31}H_{20}$
Formula weight	861.40	818.31
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	10.0504(6)	22.648(3)
b (Å)	11.0738(8)	15.9120(16)
c (Å)	15.840(5)	18.457(3)
α (°)	97.190(13)	90
β (°)	94.590(11)	111.535(11)
γ (°)	112.582(6)	90
V (Å^3)	1599.2(5)	6187.1(14)
Z	2	8
D_{calc} (Mg m^{-3})	1.789	1.757
Absorption coefficient (mm^{-1})	1.863	1.921
$F(000)$	854	3216
Crystal size (mm)	0.21 × 0.11 × 0.08	0.35 × 0.30 × 0.30
θ Range (°)	3.02–30.00	1.60–24.97
Index ranges	$-13 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 15$, $-20 \leqslant l \leqslant 22$	$-26 \leqslant h \leqslant 24$, $-18 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 21$
Reflections collected/ unique	20387/9260 [R(int) = 0.0405]	5574/5391 [R(int) = 0.0288]
Data/restraints/ parameters	9260/0/407	5391/0/379
Goodness-of-fit on F^2	0.880	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0446$, $wR_2 = 0.0989$	$R_1 = 0.0676$, $wR_2 = 0.1754$
R indices (all data)	$R_1 = 0.0826$, $wR_2 = 0.1093$	$R_1 = 0.1341$, $wR_2 = 0.2071$
Largest diff peak and hole (e Å^{-3})	1.644, −0.659	3.176, −0.816

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

Suitable X-ray quality crystals of **1** and **2** were grown from dichloromethane/*n*-hexane solvent mixture at 0 °C, and X-ray crystallographic data were recorded from single-crystal samples of **1** $(0.21 \times 0.11 \times 0.08)\ mm^3$ and **2** $(0.35 \times 0.30 \times 0.30)\ mm^3$ mounted on glass fibers. Relevant crystallographic data and structure refinement details are listed in Table 4. Oxford diffraction XCALIBUR-S CCD area detector diffractometer equipped with an LN-2 low-temperature attachment was used for the cell determination and intensity data collection for **1**. Appropriate empirical absorption corrections using the programs multi-scan were applied (**1**). A Nonius MACH3 diffractometer was used for the cell determination and intensity data collection of **2**. Monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used for the measurements. Unit cell parameters were derived and refined by using randomly selected 25 reflections in the θ range 5.2800–12.3300° (**2**). Appropriate empirical absorption correction using the program psi-scan (for **2**) was applied. The structures for both the compounds were solved by direct methods (SHELXLXS) and refined by full matrix least squares against F^2 using SHELXL-97 software [32]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine a riding model.

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Appendix A. Supplementary material

CCDC 627228 and 627229 contain the supplementary crystallographic data for **1** and **2**. The data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from 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.2006.12.017.

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