

Coupling reaction between the uncoordinated acetylenic bond of $[\text{Ru}_3(\text{CO})_{10}\{\mu_3\text{-FcC}_2\text{C}\equiv\text{CFc}\}]$ and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ to form $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}_2]$, $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{CCCFc}\}]]$ and $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{-C}\equiv\text{CFc})\text{C}(\text{Fc})\}]]$

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Abstract

Low temperature photolysis of a hexane solution of $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ provides a convenient route to the diyne-bridged cluster $[\text{Ru}_3(\text{CO})_{10}\{\mu_3\text{-FcC}_2\text{C}\equiv\text{CFc}\}]$ (**1**). When a toluene solution containing **1** and diferrocenyldiacetylene was heated at 80 °C three compounds formed: the ruthenacyclopentadiene complex $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}_2]$ (**2**), and two isomers of the diruthenacycloheptadienone complex, $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{CC}\equiv\text{CFc}\}]]$ (**3**), $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{-C}\equiv\text{CFc})\text{C}(\text{Fc})\}]]$ (**4**). Compounds **2–4** have been characterized spectroscopically and their structures established crystallographically. Consistent with structural reports on metallacyclic compounds bearing bulky substituents, in **2** and **3**, the bulkier of the two types of substituents, the $\text{C}\equiv\text{CFc}$ groups are located on the carbon atoms adjacent to the metal atoms, whereas in compound **4**, only one of the two $\text{C}\equiv\text{CFc}$ groups is on the α -carbon atom of the ruthenacyclopentadienone ring.

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1. Introduction

Multinuclear metallocene complexes have 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, biferrrocene 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].

Reactions of ferrocenylacetylene with metal acetylides form ferrocenyl-incorporated mixed-metal clusters and such reactions contrast with others where acetylenes with less bulky substituents are used [13]. Ferrocenylacetylene and $\text{Fe}(\text{CO})_5$ react under photolytic conditions to yield 2,5- and 2,6-diferrocenylquinones [14], and thermolytic reactions of ferrocenylacetylene with $\text{Fe}(\text{CO})_5$ forms $[\text{Fe}(\text{CO})_2\{\eta^5\text{-2,5-Fc}_2\text{C}_5\text{H}_2\text{CO}\}\text{C}(\text{Fc})=\text{CH}]$, $[\text{Fe}(\text{CO})_2\{\eta^2:\eta^2\text{-2,5-Fc}_2\text{C}_4\text{H}_2\text{Fe}(\text{CO})_3\}\mu\text{-CO}]$, $[\text{Fe}(\text{CO})_3\{\eta^2:\eta^2\text{-2,5-Fc}_2\text{C}_4\text{-H}_2\text{CO}\}]$ and 1,2,4-triferrocenylbenzene, or with MCO_6

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(M = Mo, W) in presence of sulfur or selenium powder 2,5-diferrocenylthiophene, and 2,5-diferrocenylselenophene, respectively are formed. Ferrocenyl substituted ruthenium metallacyclic compounds $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-1,4-Fc}_2\text{-C}_5\text{H}_2\text{O}\}]$ and $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-1,5-Fc}_2\text{-C}_5\text{H}_2\text{O}\}]$ have been synthesised when ethynylferrocene was reacted with $\text{Ru}(\text{CO})_5$ under photolytic condition [14b]. Electrochemical studies carried out on these compounds show moderate electronic communication between the two redox active ferrocenyl units via the bridging ligand and which depends upon the orientation and position of the ferrocenyl units. Reactions of polyynes with clusters have attracted considerable interest because the extended carbon chains can show a wide range of coordination modes and can link small clusters together [15,16]. The diynes $\text{RC}\equiv\text{CC}\equiv\text{CR}$ (R = Me, Et, Ph, Bu^t, SiMe₃) react with $\text{M}_3(\text{CO})_{10}(\text{NCMe})_2$ (M = Os or Ru) to give trinuclear or tetranuclear clusters in which only one of the alkynes is coordinated. The free alkyne can be utilized towards cluster growth reactions as demonstrated in the formation of the hexanuclear cluster $[\text{Ru}_6(\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-PhCHC}_3\text{-C}_6\text{H}_4)(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-PhCHC}_3\text{-C}_6\text{H}_4)(\text{CO})_{15}]$ [17].

In this paper, we report on a photolytic preparation of the diyne-bridged cluster $[\text{Ru}_3(\text{CO})_{10}\{\mu_3\text{-FcC}_2\text{C}\equiv\text{CFc}\}]$ and a coupling reaction between its uncoordinated acetylenic bond and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$.

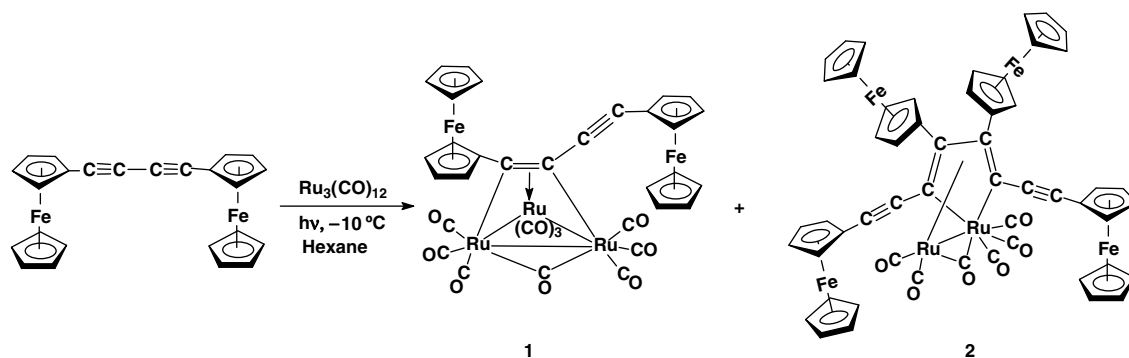
2. Results and discussions

Substitution of carbonyls by labile acetonitrile ligands is a commonly used strategy to minimize fragmentation during investigations of cluster reactions, as it enables use of facile conditions. The diyne-bridged cluster $[\text{Ru}_3(\text{CO})_{10}\{\mu_3\text{-FcC}_2\text{C}\equiv\text{CFc}\}]$ (**1**) has been reported to form from the reaction of the labilised cluster $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$ and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ under mild conditions [18]. By contrast the thermolysis reaction of the parent carbonyl $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ is reported to form diruthenium complexes, which according to spectroscopic characterization are proposed to be three isomers of $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}]$ and two of the three possible isomers of $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\text{CO}\}]$ [19].

During our investigations on the reactions of diacetylenes, we observed that cluster **1** can also be obtained directly from the $[\text{Ru}_3(\text{CO})_{12}]$ under photolytic conditions. Low temperature photolysis of a hexane solution containing $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ yields **1** as a major product along with a small amount of one of the isomers of the ruthenacyclopentadiene complex $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}]$ (**2**) (Scheme 1). Identification of **1** is based on comparison of its infrared and ¹H NMR spectra with that reported earlier while the spectroscopic features of **2** are in good agreement with those of one of the possible isomers of formula $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}]$ reported earlier.

To establish the identity of **2** unambiguously, we carried out a crystallographic structure determination. Its molecular structure (Fig. 1) comprises a ruthenacyclopentadiene ring in which the ruthenium atom bears three terminally bonded carbonyl groups. There are two ferrocenyl ligands at 3- and 4-positions of the ring and two {Fc–C≡C–} groups at 2- and 5-positions of the five membered ring. The ring is η⁴-bonded to a Ru(CO)₂ fragment which is also bonded to the ring ruthenium atom (2.7104(8) Å). A sixth carbonyl ligand bridges the metal–metal bond. Within the C₄Ru ring, C(7)–C(11) at 1.455(9) Å is longer than the corresponding C–C single bond distance of 1.415(6) Å in the C₄Fe ring of $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_2\text{Fc}_2)]$. The C(11)–C(12) and C(7)–C(8) bond distances of 1.427(9) and 1.440(9) Å, respectively are lengthened from the normal C=C double bond distance due to complexation, and these are also longer than the corresponding distances in the metallocyclopentadiene ring of $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_2\text{Fc}_2)]$ (1.408(6) and 1.412(6) Å).

The metallacyclopentadiene ring in **2** is similar to that observed in the iron compound $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_2\text{Fc}_2)]$; however, the latter is formed by the thermolysis reaction between $\text{Fe}(\text{CO})_5$ and ferrocenylacetylene [20]. Another important difference between the iron and the ruthenium compound reported here is the existence of free {Fc–C≡C–} groups in **2** which may be used for further complexation. Isolation of only a single isomer of **2**, in which the two least bulky ligands, the ferrocenyl groups, are furthest from the metal atom of the RuC₄ ring is consistent with previous observa-



Scheme 1.

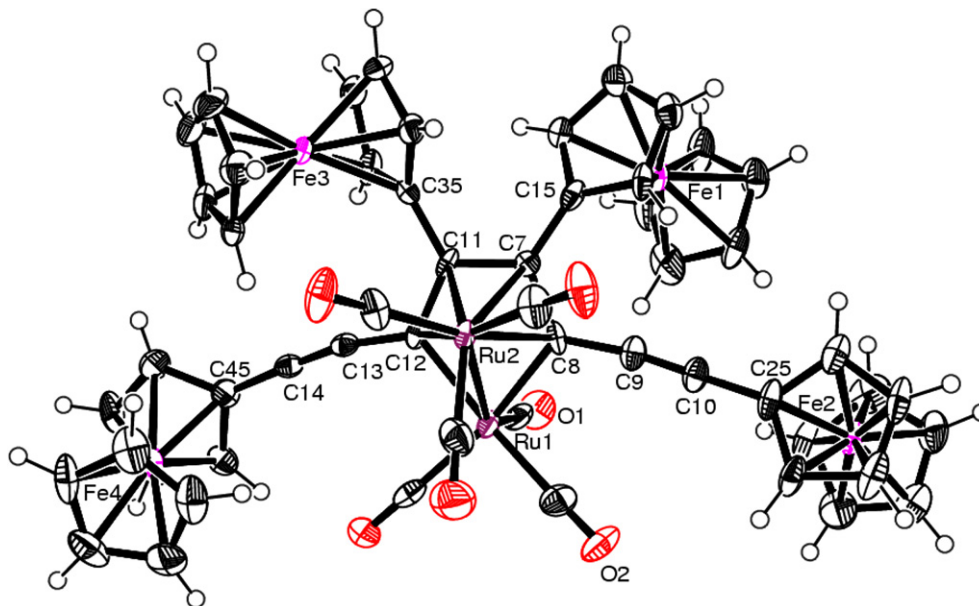
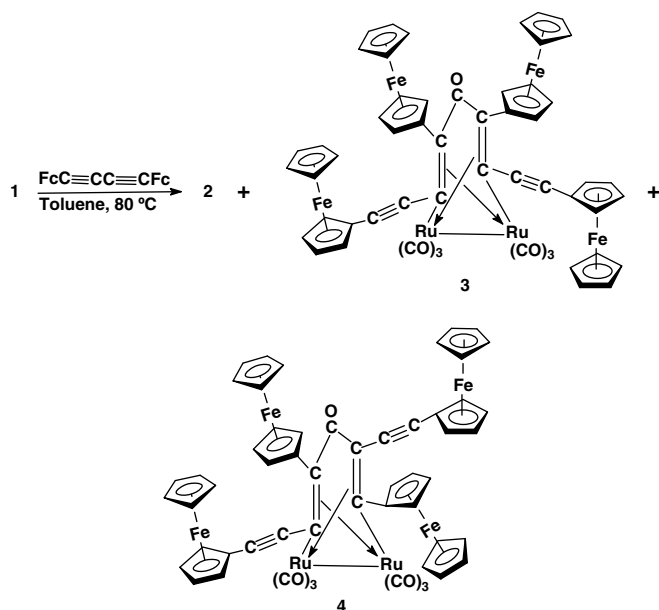


Fig. 1. Molecular structure (ORTEP plot at 50% probability) of $[\text{Ru}(\text{CO})_2\{\eta^2:\eta^2\text{-(Fc}\equiv\text{CCCFC)}_2\text{Ru}(\text{CO})_3\}\mu\text{-CO}]$ (**2**), ($\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$). Selected bond lengths (Å) and bond angles ($^\circ$): $\text{C}(7)\text{--}\text{C}(11) = 1.455(9)$, $\text{C}(7)\text{--}\text{C}(8) = 1.440(9)$, $\text{C}(11)\text{--}\text{C}(12) = 1.427(9)$, $\text{C}(14)\text{--}\text{C}(15) = 1.208(11)$, $\text{C}(9)\text{--}\text{C}(11) = 1.191(10)$.

tions that formation of metallacyclopentadiene ring by dimerisation of acetylenes occurs with the most bulky substituents being preferably located in the α -position with respect to the metal [21].

When a toluene solution containing **1** and diferrocenyldiacetylene was heated at 80°C three compounds formed: **2**, and two isomers of the diruthenacycloheptadienone, $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{CC}\equiv\text{CFc}\}\}]$ (**3**), $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{C}\equiv\text{CFc})\text{C}(\text{Fc})\}\}]$ (**4**) (Scheme 2).

Although preparation of **3** and **4** by a thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 2 equiv. of diferrocenyldiacetylene, and their spectroscopic characterization have been reported earlier, we carried out molecular structure determinations of **3** and **4** by single crystal X-ray diffraction methods. Their molecular structures (Figs. 2 and 3, respectively) consist of a diruthenabicyclo[3.1.1]hepta-1,4-dienone ring. Each ruthenium atom bears three terminal carbonyl groups and η^2 -bonding between a double bond of the ring and a ruthenium atom completes the electronic requirements of each ruthenium atom. In **3**, the two bulky ferrocenyl groups are located in the β -positions of the ring with respect to the metal atoms and the $\{\text{Fc}\text{--}\text{C}\equiv\text{C}\text{--}\}$ on the α -carbon atoms of the ring, whereas in **4**, the ferrocenyl and $\{\text{Fc}\text{--}\text{C}\equiv\text{C}\text{--}\}$ groups occupy alternate positions on the $\text{Ru}_2\text{C}_5(\text{O})$ ring. We did not detect formation of the third possible isomer with both ferrocenyl groups on the α positions. A compound related to **3**, $[\text{Ru}_2(\text{CO})_6\{\text{Fc}\text{--}\text{C}\equiv\text{CCC}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})\text{C}\equiv\text{CFc}\}]$ has been reported earlier. It has been isolated from a thermolytic reaction between $\text{PhC}_2\text{C}_2\text{Ph}$ and $\text{Ru}_3(\text{CO})_{12}$ [22]. The bond parameters within the diruthenabicycloheptadienone rings of **3** and **4** are similar. As in the structure of **2**, in **3** and **4** too there is a lengthening of the complexed $\text{C}=\text{C}$ bonds ($\text{C}(8)\text{--}\text{C}(9) = 1.420(4)$ Å; $\text{C}(12)\text{--}\text{C}(13) = 1.418(4)$ Å in **3** and $\text{C}(8)\text{--}\text{C}(9) = 1.424(5)$ Å; $\text{C}(12)\text{--}\text{C}(13) = 1.417(4)$ Å). This is consistent with observations previously made for η^4 -cyclopentadienone complexes that on η^4 -coordination, there is a loss of localized single and double bonding seen in free cyclopentadienones [23]. The unbridged $\text{Ru}\text{--}\text{Ru}$ bonds in **3** and **4** (2.7417(4) and 2.7248(8) Å, respectively) are longer than the CO-bridged $\text{Ru}\text{--}\text{Ru}$ bond in **2** (2.7104(8) Å). All three compounds display shorter than usual $\text{Ru}\text{--}\text{Ru}$ bond distances. Though



Scheme 2.

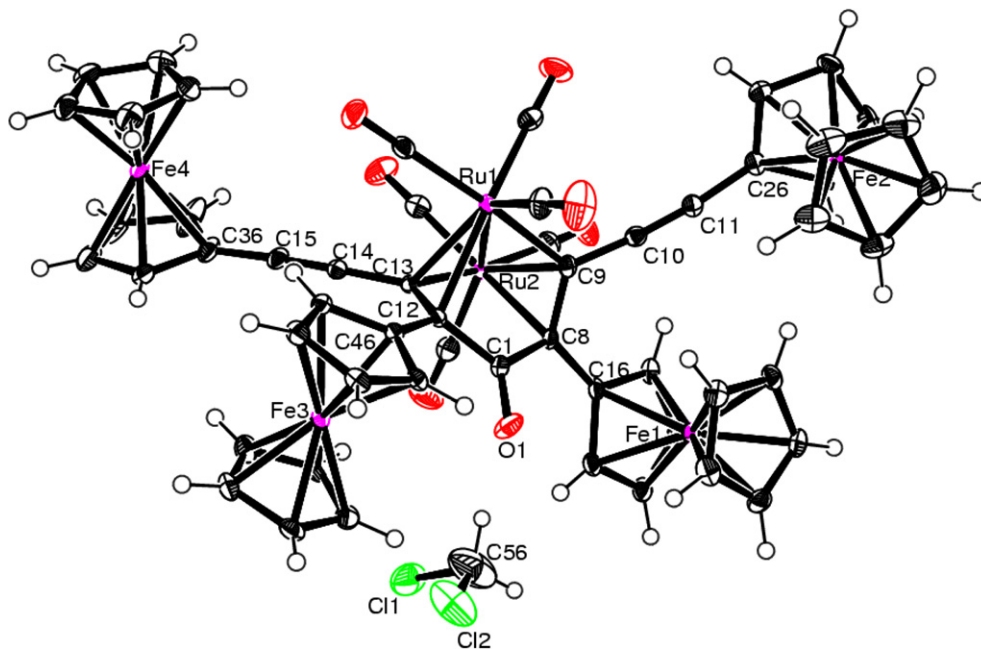


Fig. 2. Molecular structure (ORTEP plot at 50% probability) of $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{Fc}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{CC}\equiv\text{CFc}\}]\cdot\text{CH}_2\text{Cl}_2$ ($3 \cdot \text{CH}_2\text{Cl}_2$). Selected bond lengths (Å) and bond angles (°): C(8)–C(9) = 1.420(4), C(10)–C(11) = 1.211(4), C(12)–C(13) = 1.418(4), C(14)–C(15) = 1.207(4), Ru(1)–Ru(2) = 2.7417(4), C(13)–C(14)–C(15) = 171.5(3), C(1)–C(12)–C(13) = 111.3(2).

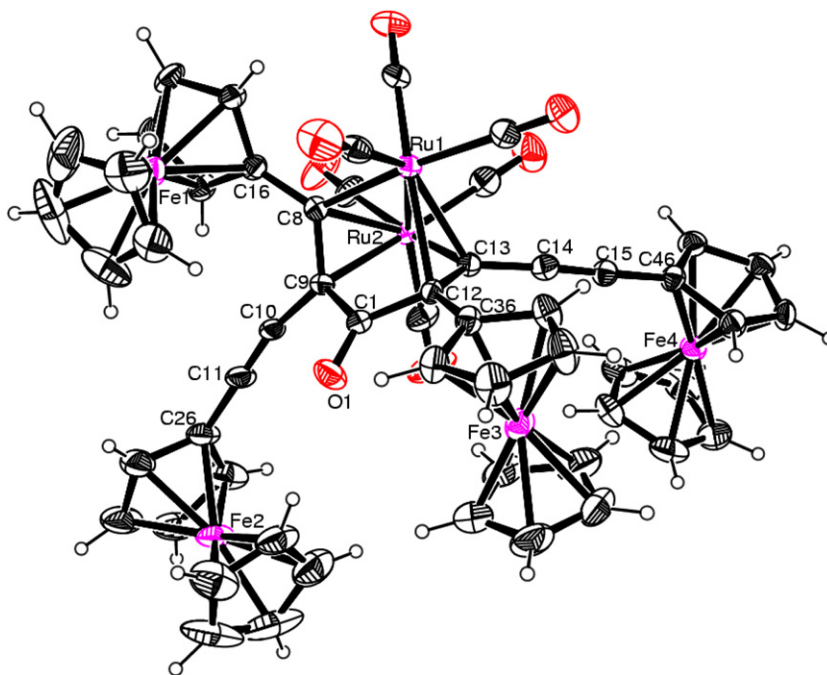


Fig. 3. Molecular structure (ORTEP plot at 50% probability) of $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{Fc}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{-C}\equiv\text{CFc})\text{C}(\text{Fc})\}]]$ (**4**). Selected bond lengths (Å) and bond angles (°): C(8)–C(9) = 1.424(5), C(10)–C(11) = 1.190(5), C(12)–C(13) = 1.417(4), C(14)–C(15) = 1.194(5), Ru(1)–Ru(2) = 2.7248(8), C(13)–C(14)–C(15) = 169.2(4), C(1)–C(12)–C(13) = 111.8(3).

bond distances of 2.713(2) Å, 2.735(2) Å and 2.740(4) Å have been reported in $[\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)(\text{PhC}_2\text{PPh}_2)]$, $[\text{Cp}_2\text{-Ru}_2(\text{CO})_4]$ and $[(\text{C}_{10}\text{H}_8)\text{Ru}_3(\text{CO})_7]$, respectively [24], bond lengths near 2.8–2.9 Å are more generally observed [25]. The ethylenic bonds in all three compounds are typically metal-olefinic type (C(7)–C(8) = 1.441(10) Å, C(12)–C(13) =

1.427(11) Å for **2**, C(8)–C(9) = 1.421(6) Å; C(12)–C(13) = 1.418(8) Å for **3** and C(8)–C(9) = 1.425(15) Å; C(13)–C(12) = 1.417(13) Å for **4**) comparable with carbon–carbon bond distances in ruthenium ethylenic units (range 1.37–1.44 Å) [26]. Although the reaction of $[\text{Ru}_3(\mu_3\text{-PhC}_2\text{C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_8]$ with $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ yields a com-

pound presumed to be formed by addition of the two diynes to diruthenium unit, its instability prevented its complete identification. However, the thermolytic reaction of $[\text{Ru}_3(\mu_3\text{-PhC}_2\text{C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_8]$ with $\text{SiMe}_3\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3$ forms several compounds, one of which has been identified as $[\text{Ru}_2\{\mu\text{-C}(\text{C}\equiv\text{CPh})\text{CPhC}(\text{SiMe}_3)\text{C}(\text{C}\equiv\text{CSiMe}_3)\}(\mu\text{-dppm})(\text{CO})_4]$ [27], analogous to our compound **4**.

Formation of compounds **2**, **3** and **4** has also been observed in relatively low yields when $[\text{Ru}(\text{CO})_5]$ and diferrocenyldiacetylene are photolysed at low temperature.

3. Conclusions

This study reports the low temperature photolysis of $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ as a facile method for synthesis of $[\text{Ru}_3(\text{CO})_{10}\{\mu_3\text{-FcC}_2\text{C}\equiv\text{CFc}\}]$ (**1**). Thermolysis of toluene solution of **1** and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ yields a mixture of the ruthenacyclopentadiene complex $[\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2\}_2]$ (**2**) and two of the three possible isomers of the diruthenacycloheptadienone complex, $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{CC}\equiv\text{CFc}\}]]$ (**3**) and $[\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{C}\equiv\text{CFc})\text{C}(\text{Fc})\}]]$ (**4**). Although **1** has been reported earlier, our synthesis avoids the necessity of activating $[\text{Ru}_3(\text{CO})_{12}]$ prior to its reaction with the diacetylene. Compounds **2–4** have been structurally characterized. Structures of **2** and **3** have the bulky ($\text{C}\equiv\text{CFc}$) groups adjacent to the metal atoms in the metalacyclopentadiene and dimetalacycloheptadienone rings, respectively while in **4** only one of the two ($\text{C}\equiv\text{CFc}$) groups is adjacent to the ring metal atom. We did not observe the isomer in which both ($\text{C}\equiv\text{CFc}$) groups are located on the β -carbons of the ring with respect to the metal.

While the availability of free $\text{C}\equiv\text{C}$ functionality in the metal–alkyne complex **1** should provide opportunity of building up larger clusters by further interaction of the ligand with other metal ligand fragments, our studies reported here demonstrate the utility of the uncoordinated alkyne to engage in coupling reactions with free alkynes to

form metal–ligand systems of the type seen in compounds **2–4**.

3.1. Experimental

3.1.1. General procedures

All reactions and manipulations were carried out under an inert atmosphere of dry, pre-purified argon or nitrogen using standard Schlenk line techniques. Solvents were purified, dried and distilled under an argon atmosphere prior to use. Photolysis reactions were carried out in a double-walled quartz vessel having a 125 W immersion type mercury lamp operating at 366 nm. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path lengths NaCl cell and NMR spectra on a 400 MHz Varian Mercury Plus spectrometer in CDCl_3 . TLC plates (20 × 20 cm, Silica gel 60 F₂₅₄) were purchased from Merck. $\text{Ru}_3(\text{CO})_{12}$ was purchased from Strem Chemicals as used as such. $\text{FcC}\equiv\text{CH}$ [28] and $\text{Fc}_2(\text{C}\equiv\text{C})_2$ [29] were prepared following reported procedures. Table 1 summarizes important conditions used in the preparations of **1–4**.

3.1.2. Photolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with diferrocenyldiacetylene

A hexane solution (10 ml) of diferrocenyldiacetylene (167 mg, 0.4 mmol) was added to the hexane solution of $[\text{Ru}_3(\text{CO})_{12}]$ (256 mg, 0.4 mmol) and photolysed 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 reddish-brown compound $[\text{Ru}_3(\text{CO})_{10}\{\mu_3\text{-FcC}_2\text{C}\equiv\text{CFc}\}]$ (**1**) (133 mg, 38%) and brown $[\text{Ru}(\text{CO})_2\{\eta^2\text{:}\eta^2\text{-}(\text{FcC}\equiv\text{CCCFC})_2\text{Ru}(\text{CO})_3\}\mu\text{-CO}]$ (**2**) (25 mg, 12%).

Compound **1**: IR ($\nu(\text{CO})$, cm^{-1} , *n*-hexane): 2093, 2063, 2054, 2030, 1872. ^1H NMR (δ , CDCl_3): 4.26 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.31 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.28–4.73 (m, 8H, $\eta^5\text{-C}_5\text{H}_4$). Anal. Calc. for **1**: C, 40.76; H, 1.79. Found: C, 41.10; H, 1.93%. Anal. Calc. for **2**: C, 53.65; H, 2.98.

Table 1
Reaction conditions for preparation of **1–4** and their yields

[mg (mmol)]	$[\text{Fc}_2(\text{C}\equiv\text{C})_2]$ [mg (mmol) used] [mg (mmol) recovered]	Reaction conditions	Products obtained	Yield ^a : mg (%)
$[\text{Ru}_3(\text{CO})_{12}]$ [256 (0.4)]	[167 (0.4)] [22 (0.05)]	hv, -10°C , Hexane	1	133 (38)
			2	25 (12)
$[\text{Ru}_3(\text{CO})_{12}]$ [256 (0.4)]	[334 (0.8)] [25 (0.06)]	80°C , Toluene	2	102 (23)
			3	123 (28)
			4	98 (22)
1 [200 (0.2)]	[84 (0.2)]	80°C , Toluene	2	38 (32)
			3	28 (23)
			4	31 (25)
$\text{Ru}(\text{CO})_5$ [(0.6)]	[167 (0.4)] [30 (0.07)]	hv, -10°C , Hexane	1	40 (12)
			2	16 (8)
			3	19 (9)
			4	18 (9)

^a Based on amount of $\text{Fc}_2(\text{C}\equiv\text{C})_2$ consumed.

Found: C, 54.05; H, 2.59%. IR ($\nu(\text{CO})$, cm^{-1} , *n*-hexane): 2074, 2044, 2009, 1969, 1865. ^1H NMR (δ , CDCl_3): 4.34 (s, 10H, $\eta^5\text{-C}_5\text{H}_5$), 4.26 (s, 10H, $\eta^5\text{-C}_5\text{H}_5$), 4.65–4.22 (m, 16H, $\eta^5\text{-C}_5\text{H}_4$). ^{13}C NMR (δ , CDCl_3): 68.6–71.98 (m, Cp), 65.7 (FcC–CFc), 75.2 (FcC \equiv CC), 86.0 (FcC \equiv CC), 91.6 (FcC \equiv CC), 94.0 (FcC \equiv CC), 100.9 (FcC \equiv CC), 185.2 (Ru–CO–Ru), 194.7 (Ru–CO), 198.4 (Ru–CO).

3.1.3. Thermal reaction of **1** with diferrocenyldiacetylene

A toluene solution of diferrocenyldiacetylene (84 mg, 0.2 mmol) and **1** (200 mg, 0.2 mmol) was heated to 80 °C in argon atmosphere for 2 h. After the reaction the solvent was evaporated to dryness and the solid mixture was dissolved in dichloromethane for further work-up. The following compounds were separated by chromatographic workup (TLC) using dichloromethane/hexane solvent mixture (30:70 v/v) in the order of elution: brown $[\text{Ru}(\text{CO})_2\{\eta^2:\eta^2\text{-(FcC}\equiv\text{CCFc)}_2\text{Ru}(\text{CO})_3\}\mu\text{-CO}]$ (**2**) (38 mg, 32%), red $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{-CC}\equiv\text{CFc}\}\}]$ (**3**) (28 mg, 23%) and red $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{-C}\equiv\text{CFc})\text{C}(\text{Fc})\}\}]$ (**4**) (31 mg, 25%).

Anal. Calc. for **3**: C, 53.40; H, 2.91. Found: C, 54.06; H, 3.23%. IR ($\nu(\text{CO})$, cm^{-1} , *n*-hexane): 2084, 2063, 2045, 2020, 1654. ^1H NMR (δ , CDCl_3): 4.27 (s, 10H, $\eta^5\text{-C}_5\text{H}_5$), 4.26 (s, 10H, $\eta^5\text{-C}_5\text{H}_5$), 4.20–5.01 (m, 16H, $\eta^5\text{-C}_5\text{H}_4$). ^{13}C NMR (δ , CDCl_3): 68.2–71.63 (m, Cp), 65.1 (FcC–CFc), 149.8.0 (FcC \equiv CC), 87.1 (FcC \equiv CC), 93.7 (FcC \equiv CC), 94.2

(FcC \equiv CC), 99.6 (FcC \equiv CC), 179.5 (CO), 198.7 (Ru–CO), 198.4 (Ru–CO).

Anal. Calc. for **4**: C, 53.40; H, 2.91. Found: C, 54.24; H, 3.15%. IR ($\nu(\text{CO})$, cm^{-1} , *n*-hexane): 2085, 2063, 2022, 2003, 1695. ^1H NMR (δ , CDCl_3): 4.35 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.32 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.29 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.28 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.23–5.09 (m, 16H, $\eta^5\text{-C}_5\text{H}_4$). ^{13}C NMR (δ , CDCl_3): 65.06–73.88 (m, Cp), 151.8 (FcC–Ru), 113.9 (FcC \equiv CCRu), 95.9 (FcC–C(O)), 94.6 (FcC \equiv CC), 92.75 (FcC \equiv CCRu), 90.6 (FcC \equiv CC(CO)), 88.56 (FcC \equiv CCRu), 87.0 (FcC \equiv CC(CO)), 186.9 (CO), 195.9, 195.5, 194.5, 193.7 (Ru–CO).

3.1.4. Thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with diferrocenyldiacetylene

A toluene solution of diferrocenyldiacetylene (334 mg, 0.8 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (256 mg, 0.4 mmol) was heated to 80 °C in argon atmosphere for 2 h. After the reaction the solvent was evaporated to dryness and the solid mixture was dissolved in dichloromethane for further work-up. The following compounds were separated by TLC using dichloromethane/hexane solvent mixture (30:70 v/v) in the order of elution: unreacted $\text{Ru}_3(\text{CO})_{12}$ (trace), unreacted FcC \equiv CC \equiv CFc (trace), $[\text{Ru}(\text{CO})_2\{\eta^2:\eta^2\text{-(FcC}\equiv\text{CCFc)}_2\text{-Ru}(\text{CO})_3\}\mu\text{-CO}]$ (**2**), $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{Fc})\text{-CC}\equiv\text{CFc}\}\}]$ (**3**) and $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CCC}(\text{Fc})\text{-C}(\text{O})\text{-C}(\text{-C}\equiv\text{CFc})\text{C}(\text{Fc})\}\}]$ (**4**).

Table 2
Crystal data and structure refinement parameters for compounds **2–4**

	2 · C ₆ H ₁₄	3 · CH ₂ Cl ₂	4
Empirical formula	C ₅₄ H ₃₆ Fe ₄ O ₆ Ru ₂	C ₅₆ H ₃₈ Cl ₂ Fe ₄ O ₇ Ru ₂	C ₅₅ H ₃₆ Fe ₄ O ₇ Ru ₂
Formula weight	1206.37	1319.30	1234.38
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	22.5321(8)	11.1579(6)	10.664(3)
<i>b</i> (Å)	7.3909(2)	14.840(4)	12.086(4)
<i>c</i> (Å)	26.3356(9)	16.1613(14)	21.047(4)
α (°)	90	69.191(14)	99.33(2)
β (°)	95.820(3)	82.380(6)	98.65(2)
γ (°)	90	77.233(10)	113.01(3)
<i>V</i> (Å ³)	4363.1(2)	2435.4(6)	2394.5(11)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.837	1.799	1.712
Absorption coefficient (mm ⁻¹)	2.024	1.929	1.848
<i>F</i> (000)	2400	1312	1228
Crystal size (mm ³)	0.18 × 0.11 × 0.08	0.31 × 0.27 × 0.21	0.36 × 0.31 × 0.27
θ Range (°)	2.98–25.00	2.94–25.00	2.99–25.00
Index ranges	–24 ≤ <i>h</i> ≤ 26, –8 ≤ <i>k</i> ≤ 8, –31 ≤ <i>l</i> ≤ 30	–13 ≤ <i>h</i> ≤ 13, –17 ≤ <i>k</i> ≤ 17, –19 ≤ <i>l</i> ≤ 19	–12 ≤ <i>h</i> ≤ 12, –14 ≤ <i>k</i> ≤ 14, –25 ≤ <i>l</i> ≤ 25
Reflections collected/unique [<i>R</i> _{int}]	38432/7671 [0.0949]	22882/8549 [0.0220]	22951/8419 [0.0376]
Data/restraints/parameters	7671/0/595	8549/0/640	8419/0/613
Goodness-of-fit on <i>F</i> ²	1.053	1.072	0.905
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0508, <i>wR</i> ₂ = 0.0966	<i>R</i> ₁ = 0.0247, <i>wR</i> ₂ = 0.0564	<i>R</i> ₁ = 0.0308, <i>wR</i> ₂ = 0.0588
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0969, <i>wR</i> ₂ = 0.1172	<i>R</i> ₁ = 0.0304, <i>wR</i> ₂ = 0.0592	<i>R</i> ₁ = 0.0601, <i>wR</i> ₂ = 0.0657
Largest difference in peak and hole (e Å ⁻³)	1.217 –0.533	1.398 –1.013	0.490 –0.380

3.1.5. Photolysis of $[Ru(CO)_5]$ with diiferrocenyldiacetylene

A hexane solution (10 ml) of diiferrocenyldiacetylene (167 mg, 0.4 mmol) was added to the hexane solution of $[Ru(CO)_5]$ (0.6 mmol) and photolysed 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 compound $[Ru_3(CO)_{10}\{\mu_3\text{-FcCCC}\equiv\text{CFc}\}]$ (**1**), $[Ru(CO)_2\{\eta^2:\eta^2\text{-}(\text{FcC}\equiv\text{CCCFc})_2\text{Ru(CO)}_3\mu\text{-CO}\}]$ (**2**), $[Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CC}(\text{Fc})\text{-C(O)-C(Fc)CC}\equiv\text{CFc}\}]]$ (**3**) and $[Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{\text{FcC}\equiv\text{CC}(\text{Fc})\text{-C(O)-C(-C}\equiv\text{CFc)C(Fc)}\}]]$ (**4**).

3.1.6. Crystal structure determination for 2–4

Suitable X-ray quality crystals of **2–4** were grown from dichloromethane/*n*-hexane solvent mixture at 0°C , and X-ray crystallographic data were recorded from single-crystal samples of **2** ($0.18 \times 0.11 \times 0.08$) mm^3 , **3** ($0.31 \times 0.27 \times 0.21$) mm^3 and **4** ($0.36 \times 0.31 \times 0.27$) mm^3 mounted on glass fibers. Relevant crystallographic data and structure refinement details are listed in Table 2. 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. Appropriate empirical absorption corrections using the programs multi-scan were applied. The structures for all the three compounds were solved by direct methods (SHELXLXS) and refined by full matrix least squares against F^2 using SHELXL-97 software [30]. 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 676207, 676208 and 676209 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.02.021](https://doi.org/10.1016/j.jorganchem.2008.02.021).

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