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Coupling reaction between the uncoordinated acetylenic bond of $[Ru_3(CO)_{10}\{\mu_3\text{-}FcC_2C\equiv CFc\}]$ and $FcC\equiv CC\equiv CFc$ to form $[Ru_2(CO)_6\{C_4Fc_2(C\equiv CFc)_2\}_2]$, $[Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{FcC\equiv CCC(Fc)\text{–}C(O)\text{–}C(Fc)CCCFc\}]$ and $[Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{FcC\equiv CCC(Fc)\text{–}C(O)\text{–}C(\text{–}C\equiv CFc)C(Fc)\}]$

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Abstract

Low temperature photolysis of a hexane solution of $[Ru_3(CO)_{12}]$ and $FcC\equiv CC\equiv CFc$ provides a convenient route to the diyne-bridged cluster $[Ru_3(CO)_{10}\{\mu_3\text{-}FcC_2C\equiv CFc\}]$ (**1**). When a toluene solution containing **1** and diferrocenyldiacetylene was heated at 80 °C three compounds formed: the ruthenacyclopentadiene complex $[Ru_2(CO)_6\{C_4Fc_2(C\equiv CFc)_2\}_2]$ (**2**), and two isomers of the diruthenacycloheptadienone complex, $[Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{FcC\equiv CCC(Fc)\text{–}C(O)\text{–}C(Fc)CC\equiv CFc\}]$ (**3**), $[Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\{FcC\equiv CCC(Fc)\text{–}C(O)\text{–}C(\text{–}C\equiv CFc)C(Fc)\}]$ (**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 $C\equiv CFc$ groups are located on the carbon atoms adjacent to the metal atoms, whereas in compound **4**, only one of the two $C\equiv CFc$ groups is on the α-carbon atom of the ruthenacyclopentadienone ring.

Keywords: Ruthenium carbonyl; Cluster; Coupling; Diacetylene; Ferrocenyl

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, 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].

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 $Fe(CO)_5$ react under photolytic conditions to yield 2,5- and 2,6-diferrocenylquinones [14], and thermolytic reactions of ferrocenylacetylene with $Fe(CO)_5$ forms $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2CO\}C(Fc){=}CH]$, $[Fe(CO)_2\{\eta^2:\eta^2\text{-}2,5\text{-}Fc_2C_4H_2Fe(CO)_3\}\mu\text{-}CO]$, $[Fe(CO)_3\{\eta^2:\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$ 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 $[Ru_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}1,4\text{-}Fc_2C_5H_2O\}]$ and $[Ru_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}1,5\text{-}Fc_2C_5H_2O\}]$ have been synthesised when ethynylferroce was reacted with $Ru(CO)_5$ 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 $RC\equiv CC\equiv CR$ (R = Me, Et, Ph, Bu^t, $SiMe_3$,) react with $M_3(CO)_{10}(NCMe)_2$ (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 $[Ru_6(\mu_5\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhCHC_3C_6H_4)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhCHC_3C_6H_4)(CO)_{15}$ [17].

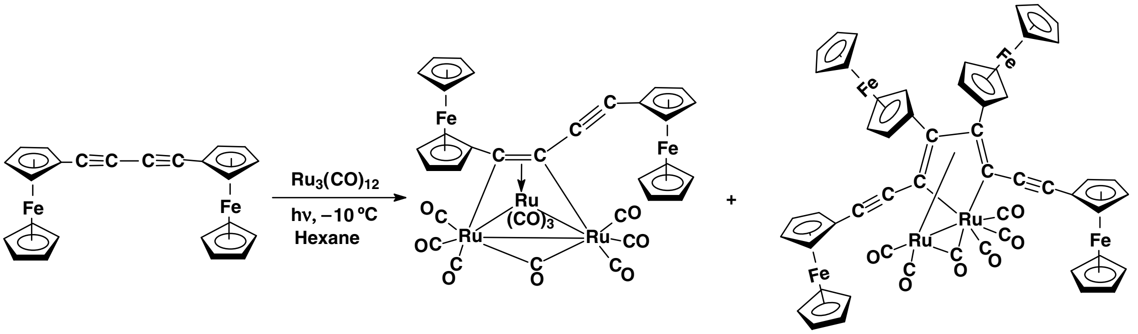
In this paper, we report on a photolytic preparation of the diyne-bridged cluster $[Ru_3(CO)_{10}\{\mu_3\text{-}FcC_2C\equiv CFc\}]$ and a coupling reaction between its uncoordinated acetylenic bond and $FcC\equiv CC\equiv CFc$.

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 $[Ru_3(CO)_{10}\{\mu_3\text{-}FcC_2C\equiv CFc\}]$ (**1**) has been reported to form from the reaction of the labilised cluster $[Ru_3(CO)_{10}(NCMe)_2]$ and $FcC\equiv CC\equiv CFc$ under mild conditions [18]. By contrast the thermolysis reaction of the parent carbonyl $[Ru_3(CO)_{12}]$ and $FcC\equiv CC\equiv CFc$ is reported to form diruthenium complexes, which according to spectroscopic characterization are proposed to be three isomers of $[Ru_2(CO)_6\{C_4Fc_2(C\equiv CFc)_2\}_2]$ and two of the three possible isomers of $[Ru_2(CO)_6\{C_4Fc_2(C\equiv CFc)_2CO\}]$ [19]. During our investigations on the reactions of diacetylenes, we observed that cluster **1** can also be obtained directly from the $[Ru_3(CO)_{12}]$ under photolytic conditions. Low temperature photolysis of a hexane solution containing $[Ru_3(CO)_{12}]$ and $FcC\equiv CC\equiv CFc$ yields **1** as a major product along with a small amount of one of the isomers of the ruthenacyclopentadiene complex $[Ru_2(CO)_6\{C_4Fc_2(C\equiv CFc)_2\}_2]$ (**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 $[Ru_2(CO)_6\{C_4Fc_2(C\equiv CFc)_2\}_2]$ reported earlier.

To establish the identity of **2** unambiguously, we carried out a crystallographic structure determination. Its molecular structure (Fig. 1) comprises a ruthenocyclopentadiene 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 $\{Fc\text{–}C\equiv C\text{–}\}$ groups at 2- and 5-positions of the five membered ring. The ring is η^4-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 C_4Ru 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 C_4Fe ring of $[Fe_2(CO)_6(C_4H_2Fc_2)]$. 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 $[Fe_2(CO)_6(C_4H_2Fc_2)]$ (1.408(6) and 1.412(6) Å).

The metallacyclopentadiene ring in **2** is similar to that observed in the iron compound $[Fe_2(CO)_6(C_4H_2Fc_2)]$; however, the latter is formed by the thermolysis reaction between $Fe(CO)_5$ and ferrocenylacetylene [20]. Another important difference between the iron and the ruthenium compound reported here is the existence of free $\{Fc\text{–}C\equiv C\text{–}\}$ 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 RuC_4 ring is consistent with previous observa-



1 **2**

Scheme 1.