



Synthesis and characterization of face-capping triruthenium cluster complexes of pentamethylfullerenes



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ABSTRACT

Reaction of the pentamethylhydrofullerene $C_{60}HMe_5$ (**1**) with $Ru_3(CO)_{12}$ in refluxing toluene affords the face-capping cluster complex $Ru_3(CO)_9(\eta^2, \eta^2, \eta^2-C_{60}HMe_5)$ (**2**). Elution of **1** on TLC plates (silica gel) leads to hydroxyepoxidation of the cyclopentadiene group to generate $C_{60}Me_5(O)(OH)$ (**3**) and $C_{60}Me_5(O)_2(OH)$ (**4**). Reaction of **3** with $Ru_3(CO)_{12}$ in refluxing toluene gives the face-capping complex $Ru_3(CO)_9(\eta^2, \eta^2, \eta^2-C_{60}Me_5(O)(OH))$ (**5**). The structures of **2**, **3**, and **5** have been determined by a single-crystal X-ray diffraction study.

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1. Introduction

The discovery of fullerenes in 1985 marked the beginning of a new field of chemical research [1]. Attachment of organometallic complexes to fullerenes is an important area within fullerene chemistry, due to its potential application in biological, magnetic, electronic, catalytic and optical devices [2–11]. With the development of an extensive organic chemistry of fullerenes, it is now possible to construct a variety of modified fullerenes that incorporate metal-binding groups into their structures [5,12–15]. The syntheses of such fullerene derivatives offer the potential to exploit the chemical reactivity, redox and electron-acceptor characteristics, photochemical behavior, electron-withdrawing properties, and novel structural features that a fullerene group provides. Remarkably, the pentamethylhydrofullerene $C_{60}HMe_5$ (**1**) was prepared by Nakamura and coworkers through selective multiaddition of organocopper reagents to C_{60} [16]. Compound **1** contains an isolated cyclopentadiene unit. It has been demonstrated that deprotonation of **1** generates the species $C_{60}Me_5^-$, which behaves like a Cp^- anion and can form a variety of metal complexes in an η^5 -bonding fashion [17,18]. Most interestingly, thermolysis of **1** and $Cp_2Fe_2(CO)_4$ was found to afford the sandwich complex $CpFe(\eta^5-C_{60}Me_5)$ [19]. We recently described the reaction of the bisfulleroid

$C_{64}H_4$ with an Os_3 cluster to generate a diene complex, which carried out a C–H bond activation to give $(\mu-H)Os_3(CO)_9(\eta^4-C_{64}H_3)$ [20]. On the other hand, C_{60} reacted with $M_3(CO)_{12}$ ($M = Ru, Os$) to give $M_3(CO)_9(\eta^2, \eta^2, \eta^2-C_{60})$ through coordination of one hexagon ring [8,21]. It is therefore of interest to investigate if a metal cluster is preferably bonded to the isolated cyclopentadiene site or to one six-membered ring of **1**. In our continuing interest in metal-fullerene chemistry [22–24], herein we present the complexation reaction of $Ru_3(CO)_{12}$ with **1** and $C_{60}Me_5(O)(OH)$.

2. Results and discussion

2.1. Reactions

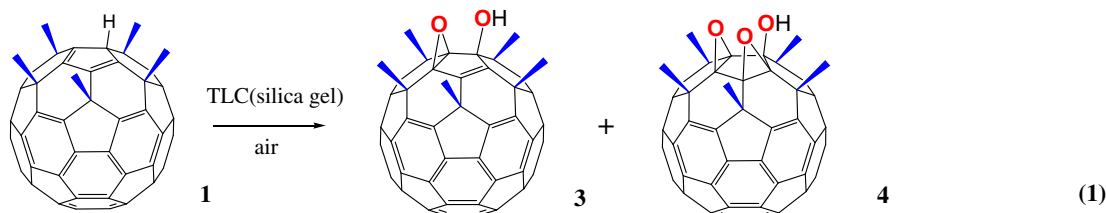
Compound **1** and $Ru_3(CO)_{12}$ were dissolved in toluene, and the solution was heated to reflux for 8 h under dinitrogen. After purification of the products by TLC (silica gel), the complex $Ru_3(CO)_9(\eta^2, \eta^2, \eta^2-C_{60}HMe_5)$ (**2**) was obtained in 16% yield. The analogous face-capping cluster complex $Ru_3(CO)_9(\eta^2, \eta^2, \eta^2-C_{60})$ has been prepared in 16% yield by heating $Ru_3(CO)_{12}$ and C_{60} in refluxing chlorobenzene for 1.5 h [8,10]. It appears that the five methyl addends hinder the bulky triruthenium cluster from accessing the isolated cyclopentadiene unit of **1**, making one removed hexagonal ring more feasible for metal complexation.

Previously, Taylor and coworkers reported the synthesis of $C_{60}Me_6$ from $C_{60}Cl_6$. From the reaction mixture, the hydroxyepoxy pentamethylfullerenes $C_{60}Me_5(O)(OH)$ (**3**) and $C_{60}Me_5(O)_2(OH)$ (**4**)

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were also obtained in low yields, while the origin of their formation was unclear [25,26]. During the preparation of **1**, we found that applying **1** on TLC (silica gel) and eluting the plates with CS₂/CH₂Cl₂ (4:1, v/v) led to isolation of compounds **3** and **4** in 24% and 21% yield, respectively (Eq. (1)). Moreover, compound **3** and **4** could be generated (detected with ¹H NMR) by vigorously stirring the benzene solution of **1** under air for several hours. Since solid **1** is stable, we suggest that hydroxyepoxidation of the cyclopentadiene group of **1** in solution is caused by the dissolved oxygen and water molecules.



The reactions of metal complexes with epoxides were known [27]. We then moved to investigate if the epoxide or hydroxy groups of **3** could bind with a metal carbonyl cluster. However, treating compound **3** with Ru₃(CO)₁₂ in refluxing toluene was found to produce Ru₃(CO)₉(η²,η²,η²-C₆₀Me₅(O)(OH)) (**5**) in 22% yield, where the Ru₃ triangle is face-capped by one hexagon of the fullerene. Again, the steric factors seem to play an important role in determining the coordination sites of **3**.

2.2. Characterization of the products

The ¹H NMR spectral data of **3** and **4** are in close agreement with those reported in the literature [25]. Compound **3** is

asymmetric which presents five methyl proton resonances in the range 2.35–2.14 ppm and the OH resonance at 3.56 ppm, while compound **4** has a C_s symmetry to display three methyl proton resonances at 2.32, 2.17, and 2.07 ppm in a 1:2:2 ratio and the OH resonance at 4.34 ppm. Compounds **2** and **5** are each forming an air-stable, dark orange–red crystalline solid. Their IR spectrum in the carbonyl region presents an identical absorption pattern as that of Ru₃(CO)₉(η²,η²,η²-C₆₀) [8]. The ESI mass spectra of **2** and **5** show the molecular ion peaks at *m/z* 1354 and 1386 (¹⁰²Ru), respectively. The ¹H NMR spectrum of **2** displays three signals at 4.60, 4.52, and 4.47 ppm in a 2:2:1 ratio for the methynyl proton resonances and thirteen signals in the range 2.59–2.21 ppm for the methyl proton resonances, suggesting the existence of three isomers. This can be rationalized by the configurations drawn in Fig. 1, where the methynyl proton can be distributed in three different sites. On the other hand, the ¹H NMR spectrum of **5** exhibits five signals at 3.66, 3.65, 3.64, 3.61, and 3.55 ppm for the hydroxyl proton resonances and a set of complicated signals in the range 2.51–2.05 ppm for the methyl proton resonances, in agreement with five plausible isomers for **5** shown in Fig. 2.

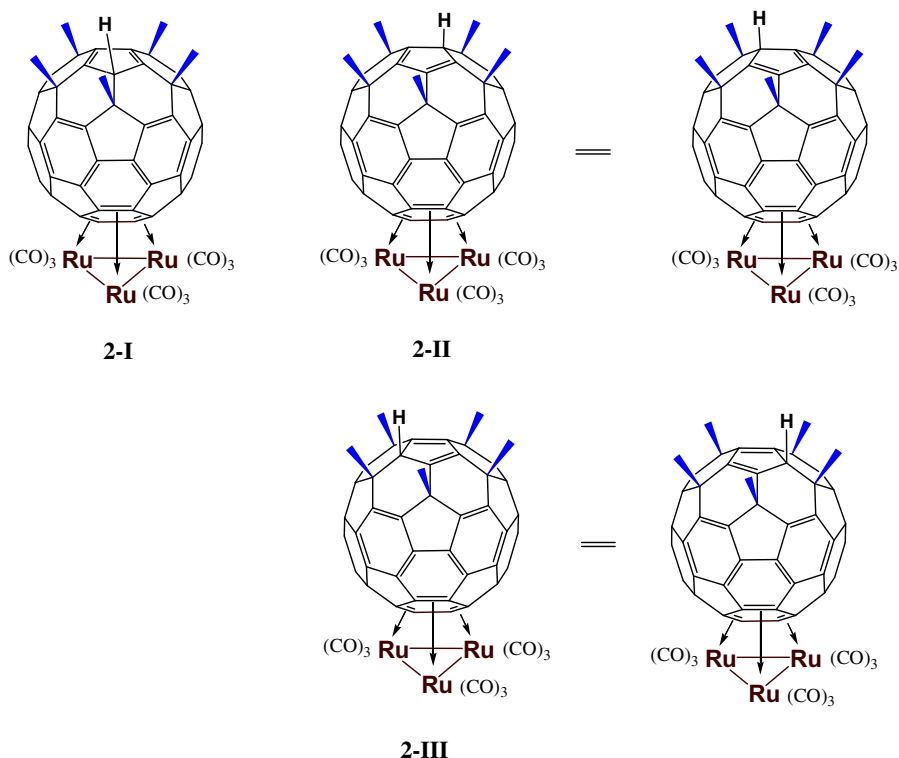


Fig. 1. Plausible isomers for compound **2**.

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