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Cluster Compounds

Activation of Open-Cage Fullerenes with Ruthenium Carbonyl Clusters

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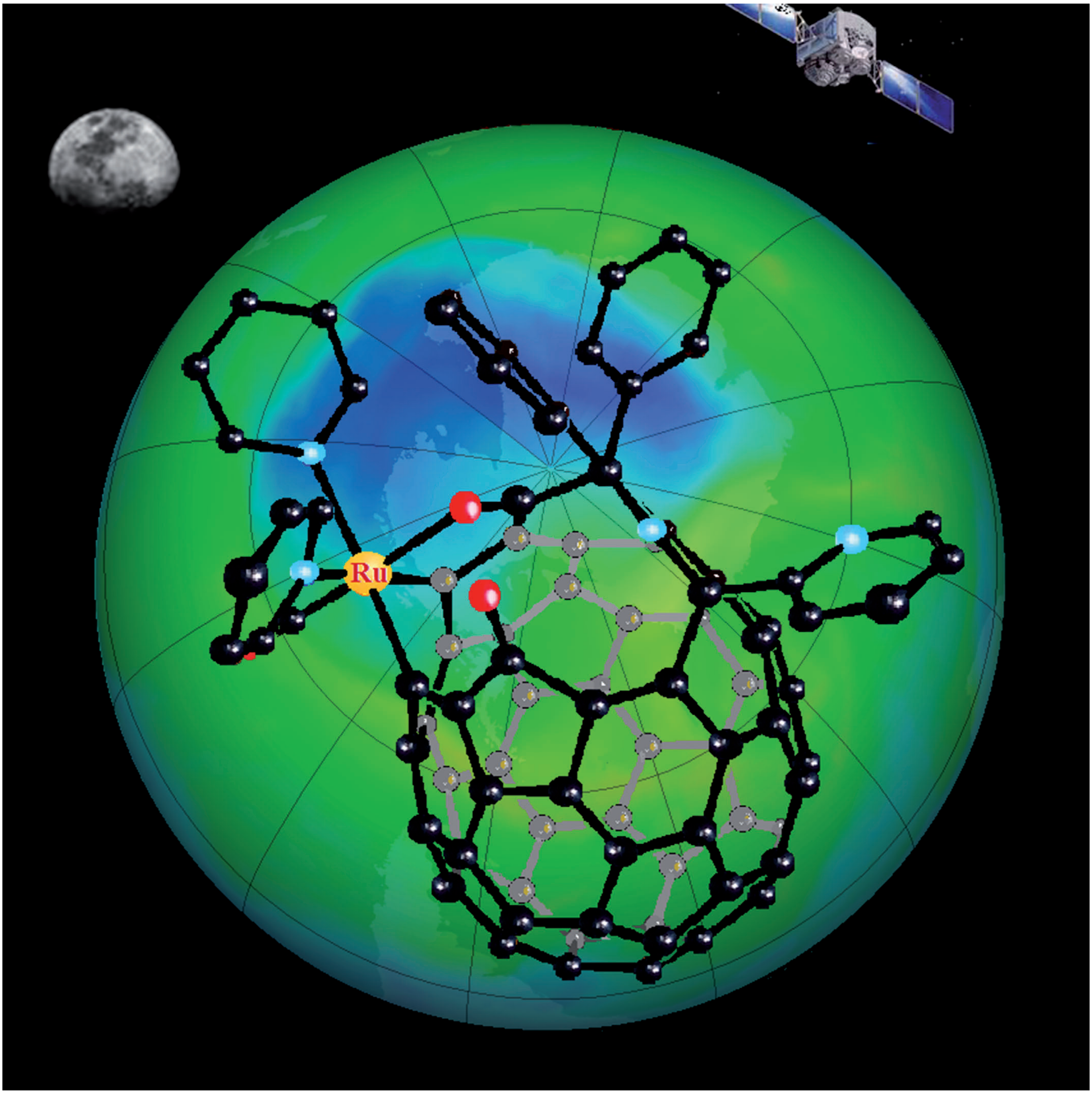
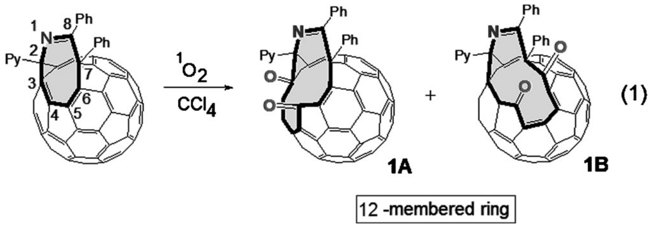
In memory of Duward F. Shriver



Abstract: Reactions of the open-cage fullerene $C_{63}NO_2(Py)(Ph)_2$ (**1**) with $[Ru_3(CO)_{12}]$ produce $[Ru_3(CO)_8(\mu,\eta^5\text{-}C_{63}NO_2(Py)(Ph)_2)]$ (**2**), $[Ru_2H(CO)_3(\mu,\eta^7\text{-}C_{63}N(Py)(Ph)(C_6H_4))]$ (**3**), and $[Ru(CO)(Py)_2(\eta^3\text{-}C_{63}NO_2(Py)(Ph)_2)]$ (**4**), in which the orifice sizes are modified from 12 to 8, 11, and 15-membered ring, through ruthenium-mediated C–O and C–C bond activation and formation.

The discovery of fullerenes in 1985 marked the beginning of a new field of chemical research,[1] and subsequent work has been extensive thereafter.[2] Apart from fullerene adducts,[3] endofullerenes,[4] and heterofullerenes,[5] open-cage fullerenes present the fourth fundamental research topic of modified fullerenes, whereby one or more bonds are removed chemically to expose an orifice.[6] In this way, it is possible to insert into them atoms or small molecules, such as noble gases (He, Ar, Kr),[7,8] H_2,[7,9] N_2,[7a] H_2O,[10] CO,[7,11] NH_3,[12] and CH_4.[13] Moreover, they have been considered as new spherical molecules with unique properties different from the closed fullerenes and might find applications in photovoltaic components, electronics, biomedicines, and molecular storage.[14] The first open-cage fullerene was reported in 1995 by Wudl and co-workers.[15] Since then, several methods for opening the fullerene cages and expanding the orifice sizes have been developed, which are mainly progressed by organic reactions and chalcogen reagents.[16] Recently, attachment of organometallic fragments to fullerene cores becomes an important area within fullerene chemistry.[17] One of the most fascinating aspects pertaining to organometallic chemistry concerns the activation of organic substrates at metal centers.[18] In particular, transition-metal clusters have attracted increasing attention because of their multimetal center activity in reactions involving substrates, which are not activated by monometallic species.[19] This unique feature should be applicable to tuning the orifice sizes of open-cage fullerenes, too. Herein, we present the reactions of $[Ru_3(CO)_{12}]$ and $C_{63}NO_2(Py)(Ph)_2$ to give mono-, di-, and triruthenium complexes, accompanied by variation of the fullerene cavities.

The elegant open-cage fullerene, $C_{63}NO_2(Py)(Ph)_2$ (**1**), containing a 12-membered heterocyclic ring, was prepared by treating $C_{63}N(Py)(Ph)_2$ with singlet-oxygen ($^1O_2$) according to the method reported by Komatsu and co-workers.[20] Two isomers, **1A** and **1B**, were obtained from cleavage of the C=C double bond at the 3,4- and 5.6-position, respectively [Eq. (1)].



(1)

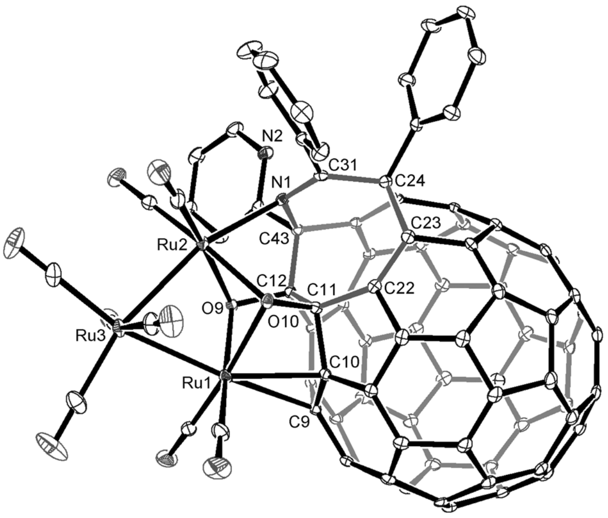


Figure 1. Molecular structure of **2** with thermal elliposids shown at 30%.

Reaction of **1A** and equimolar $[Ru_3(CO)_{12}]$ in chlorobenzene at reflux for 30 min gave the cluster complex $[Ru_3(CO)_8(\mu,\eta^5\text{-}C_{63}NO_2(Py)(Ph)_2)]$ (**2**) in 24% yield after purification by TLC (silica gel) and recrystallization from benzene/methanol. Remarkably, the two ketone carbons of **1A** are coupled to generate a vicinal dioxyl species, and the orifice of the open-cage fullerene is changed to an 8-membered ring [Eq. (2)]. Similar coupling of two adjacent carbonyl groups in an open-cage fullerene compound under different conditions has been reported.[9,21] The MALDI mass spectrum of **2** shows the molecular ion peaks around *m/z* 1563, corresponding to combination of **1A** and a $[Ru_3(CO)_8]$ segment. An ORTEP diagram of **2**, depicted in Figure 1, consists of an open triangular $[Ru_3(CO)_8]$ cluster linked to the dioxyl, imine, and one 6:6-ring junction of the modified fullerene. The metal parts contain 50 valence electrons and require only two Ru–Ru bonds to satisfy the 18-electron rule, with Ru1–Ru3 2.7299(5) Å slightly shorter than Ru2–Ru3 2.7614(5) Å. Each ruthenium atom adopts a distorted octahedral coordination. The Ru1 and Ru2 atoms are each associated with two terminal carbonyl ligands *trans* to the bridging oxygen atoms. The Ru–CO distances to Ru1 and Ru2 atoms, averaged 1.851(4) Å, are significantly shorter than those to the Ru3 atom, averaged 1.937(5) Å. This can be ascribed to an enhanced π back-donation from the Ru1 and Ru2 atoms, which are linked to the stronger net electron-donating alkoxyl ligands compared with CO, and/or trans influence of the alkoxyl groups. The C9=C10 ring junction is coordinated to Ru1 atom asymmetrically with Ru1–C9 2.508(3) Å and Ru1–C10 2.299(3) Å. The imine linkage C24-C31-N1-C43 is about planar (±0.02 Å), in which the lone-paired electrons in nitrogen atom

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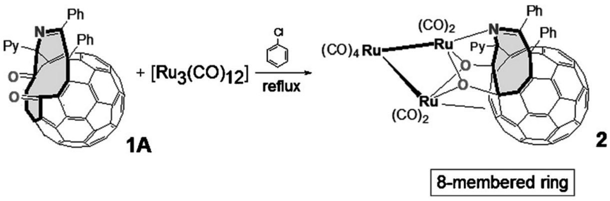
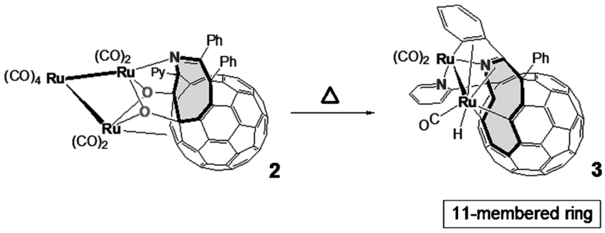
are donated to the Ru2 metal, with N1–Ru2 2.220(3) Å. The Ru2 atom is 1.20 Å away from the imine plane, with the torsional angle C24-C31-N1-Ru2 138.0(4)°. It is important to notice that the C11–C12 distance 1.670(5) Å is unusually long in comparison with normal carbon–carbon single bonds (1.54 Å), likely due to steric constraints of the dioxyl addends to bridge two Ru atoms oppositely.



(2)

Compound **2** is robust enough to remain intact by heating at reflux in chlorobenzene for several hours. A well thermal reaction was achieved by pyrolyzing solid **2** at 350 °C under vacuum for 30 min, from which the dinuclear complex $[Ru_2H(CO)_3(\mu,\eta^7\text{-}C_{63}N(Py)(Ph)(C_6H_4))]$ (**3**) was isolated in 40% yield after purification [Eq. (3)].



(3)

It is interesting that the two C(cage)–O bonds of **2** have been cleaved, and the cage reformation from **1 A** to **3** is reminiscent to the McMurry reaction.[22] The phenyl group connected to the imine carbon has undergone an *ortho*-metalation reaction on one Ru atom. Most strikingly, the other Ru atom is inserted into the pentagon facing the imine group to generate an eleven-membered ring. Insertion of a cobalt or an osmium atom into one pentagon ring of the bisfulleroid $C_{64}H_4$ was previously described.[16a,23] The MALDI MS spectrum of **3** displays the molecular ions around *m/z* 1288, with the isotope distribution matching a Ru_2 pattern. The IR spectrum displays three carbonyl stretches at $\tilde{\nu}=2032$, 1996, and 1971 cm^{-1}. The ^1H NMR spectrum shows a complicated set of signals in the range $\delta=9.20\text{–}7.05$ ppm for the phenyl and pyridyl protons, and one upfield resonance at $\delta=-6.89$ ppm for the terminal hydride. The ORTEP diagram of **3** is shown in Figure 2. The coordination around the Ru1 atom can be described as a distorted octahedron, which is linked to the Ru2 atom, two terminal carbonyls, a pyridine, an imine, and a phenyl ring. The Ru1–Ru2 bond length, 2.790(2) Å, is slightly longer than those measured for **2**. Three terminal carbonyls are linked to the ruthenium metals with Ru1–C1 1.87(2), Ru1–C2 1.92(2), and Ru2–C3 1.90(2) Å. The hydride ligand, which occupies a coordination site, was not located but is believed to bind the Ru2 atom to satisfy the 18-electron rule. Therefore, the coordination around the Ru2 atom can be viewed as a four-legged piano stool (including the hydride ligand) by considering the (Ru1, N2, C10, C11, C12) unit as a metala-heterocyclopentadienyl ring to bind the Ru2 atom in an η^5-fashion, with Ru2–N2 2.16(1), Ru2–C10 2.20(1), Ru2–C11 2.40(1), and Ru2–C12 2.46(1) Å. The coordinated imine C10–N2 distance 1.35(2) Å is elongated by 0.09 Å in comparison with the C31–N1 bond in **2**, and the phenyl C11–C12 bond lengths 1.46(2) Å is 0.12 Å longer than the C13–C14 and C15–C16 bonds (averaging 1.34(2) Å), likely due to back donation from the Ru2 metal to the π^* orbitals of the ligands.

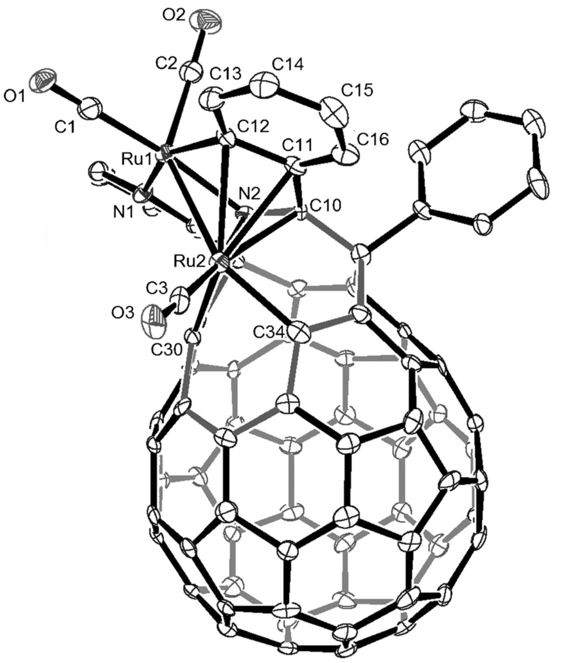


Figure 2. Molecular structure of **3** with thermal elliposids shown at 30%.

We then investigated the coordination reaction of **1 B**. It is surprising that **1 B** displays a very different reactivity from **1 A**, despite that their structures are closely resembling. Heating **1 B** and $[Ru_3(CO)_{12}]$ at reflux in chlorobenzene led to a dark brown solid, which was extracted with pyridine, purified by TLC (silica gel, eluting with pyridine/CH_2Cl_2), and crystallized from pyridine/*n*-hexane to give black crystals of $[Ru(CO)(C_5H_5N)_2(\eta^3\text{-}C_{63}NO_2(Py)(Ph)_2)]$ (**4**) in 46% yield [Eq. (4)]. In this reaction, the Ru_3 cluster is fragmented to become a mononuclear complex, and the Ru atom is inserted into the pentagon far away from the imine group, forming an orifice with a 15-membered ring. The IR spectrum of **4** in CH_2Cl_2 displays an absorption at $\tilde{\nu}=1936$ cm^{-1} for the terminal carbonyl, and two absorptions at 1736 and 1605 cm^{-1} corresponding to the free and coordinated ketone stretch, respectively. The ORTEP diagram of **4** is depicted in Figure 3. The coordination around the Ru1 atom can be described as a distorted octahedron, which is bonded to a terminal carbonyl, two pyridines, and a ketone and two carbon atoms of the fullerene cage. The ketone con-

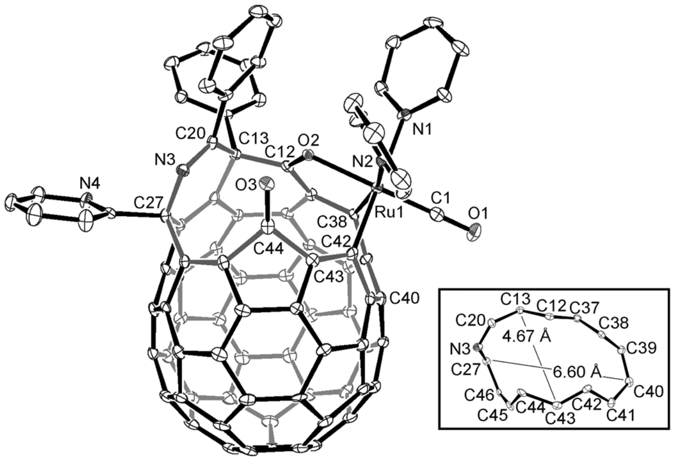


Figure 3. Molecular structure of **4** with thermal elliposids shown at 30 %.

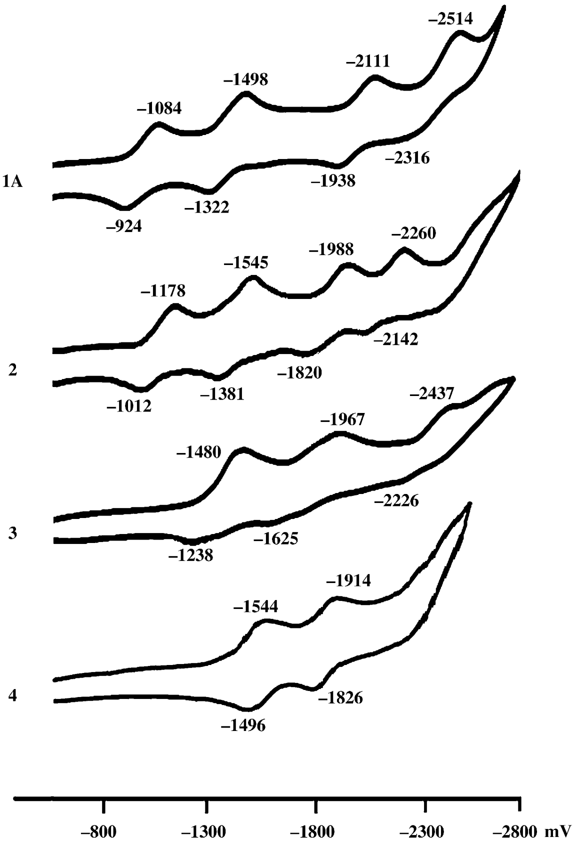
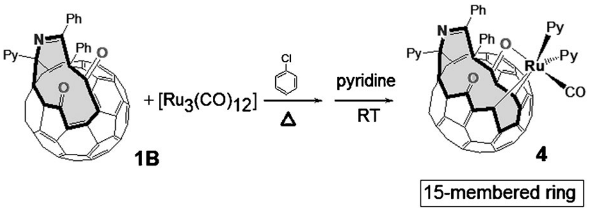


Figure 4. Cyclic voltammograms for **1 A**-**4** in *o*-dichlorbenezene. The potentials are versus the Fc/Fc$^+$ couple.

nected to the ruthenium atom has the bond lengths O2–Ru1 2.124(5) and O2–C12 1.279(8) Å, whereas the uncoordinated ketone O3–C44 bond lengths is 1.200(8) Å. The C38–C42 edge has been broken by oxidative insertion of the ruthenium atom with Ru1–C38 1.971(7) and Ru1–C42 2.040(7) Å, and the non-bonding C38···C42 distance is 2.56(6) Å. The 15-membered ring orifice traverses 6.60 Å from C27 to C40 atoms, which is close to the diameter of C_{60} (7.1 Å)[2a] and 4.67 Å from C13 to C43 atoms.



(4)

The electrochemical properties of **1 A**-**4** were studied by cyclic voltammetry (CV) in dry, oxygen-free *o*-dichlorobenzene solution at 27 °C (Figure 4). Within the solvent cutoff, C_{60}, $C_{63}N(Py)(Ph)_2$, **1 A**, and **1 B** exhibited four quasi-reversilbe redox waves in the negative scan upon CV.[24] Complex **2** also displays four reduction waves at $E_{1/2} = -1095$, -1463, -1904, and -2201 mV (vs. Fc/Fc$^+$ couple), which are shifted anodically by approximately 200 mV compared to $C_{63}N(Py)(Ph)_2$ (the parent compound having a similar eight-membered ring; see [Eq. (1)]) and may be ascribed to the presence of two electron-withdrawing oxyl addends and/or delocalization of negative charges to the Ru_3 cluster, making the fullerene cage more ease to reduce. In contrast, complexes **3** and **4** have a ruthenium atom inserted into the fullerene rim to form metallofullerenes with distinct skeletons. Their LUMO might carry some Ru characters and are different from **2**, thus, presenting dissimilar CV profiles.

Modern organic syntheses often involve several transition-metal-catalyzed steps.[25] Frequently, the functionalized organic substrates are released from metal by numerous methods, such as β-elimination and oxidative cleavage at the last stage.[22] Our preliminary studies revealed that treating complexes **2**–**4** with H_2O_2 or I_2 can result in decomposition of the ruthenium complexes and release new open-cage fullerenes. Characterization of these fullerene derivatives is in progress and will be described elsewhere.

In conclusion, three new ruthenium complexes of open-cage fullerenes were prepared and structurally characterized. The transformation from **1** to **4** is of interest within the context of the chemistry of fullerenes and of the ability of transition-metal clusters to promote fullerene-cage modification. It may provide an attractive general strategy for tuning the orifice sizes of open-cage fullerenes. Recently, preparation of endohedral fullerenes encapsulating transition metals in isolable and stable form remains great challenges to chemists. Traditional metal/graphite laser and arc evaporation methods are limited in the fullerene size and low product yield.[26] An alternative approach by opening the fullerene cages, followed by metal complexation and insertion, might provide a promising pathway, in which the orifice size is an important factor. We are currently investigating the activity of **2**–**4** with an aim to include ruthenium atom(s) inside the fullerene cages.

Experimental Section

Details on the reaction procedures, characterization data, and structural determination for **2**–**4** are given in the Supporting Information. CCDC-957056 (**2**), CCDC-957057 (**3**), and CCDC-957058 (**4**) 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.

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Keywords: C–C activation · cluster compounds · fullerenes · ruthenium · structure elucidation

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