Fullerene Complexes

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# $[(\mu\text{-H})_3Re_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}Sc_2C_2@C_{3v}(8)\text{-}C_{82})]$: Face-Capping Cluster Complex of an Endohedral Fullerene**

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Fullerenes with atoms, ions, or clusters in their inner space are referred to as endohedral fullerenes. These spherical molecules have unique properties that can be very different from those of the empty fullerenes.[1,2] Among these hybrid molecules, endohedral metallofullerenes (EMFs) have attracted great attention because substantial charge transfer from encaged metal atoms or clusters to the fullerene cage occurs, and this property may find application in catalysis, photovoltaic components, electronics, and biomedicines.[3] Not only conventional metal atoms (usually one or two),[4] but a wide variety of metallic species have been encapsulated in fullerenes. Fullerenes encapsulating a metal nitride ($M_3N$),[5] a metal-carbide cluster ($M_2C_2/M_3C_2/M_4C_2$),[6] a metal oxide ($M_2O/M_4O_2/M_4O_3$),[7] a metal cyanide ($M_3NC$),[8] and even a metal sulfide ($M_2S$)[9] were all successfully obtained and structurally characterized. The functionalization of EMFs with organic adducts has also attracted much interest, because the resulting EMFs could have more useful properties, including perhaps higher solubility and stability, than those of pristine EMFs.[10] However, to our knowledge, the coordination chemistry of EMFs has not been described. Several interesting questions await an answer in this unexplored field: 1) Will the metals add regiospecifically to the EMF surface? 2) How will the geometry and properties of the EMF be affected by the bonded metals? 3) Will the encapsulated species interact with the coordinated metals? Our continuing interest in fullerene chemistry[11] led us to prepare the scandium carbide endofullerene $Sc_2C_2@C_{3v}(8)\text{-}C_{82}$ (**1**) and investigate its complexation with a $Re_3$ cluster.

Compound **1** was synthesized by modifying a previously described method.[12] Graphite rods filled with $Sc_2O_3$ were annealed at 1000 °C for 12 h and then evaporated by arc discharge under a flow of $He/N_2$. The soot was subjected to Soxhlet extraction with $CS_2$ and then purified by a multiple-stage HPLC separation process. The pure compound **1** (>99%; 0.7 mg obtained from the evaporation of 16 composite graphite rods) was treated with $[(\mu\text{-H})_3Re_3(CO)_{11}(NCMe)]$ (2 equiv) in chlorobenzene at reflux for 3.5 h. After purification of the reaction products by HPLC (with a Buckyprep-M column and toluene as the eluent) and recrystallization from $CS_2$/*n*-hexane, $[(\mu\text{-H})_3Re_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}Sc_2C_2@C_{3v}(8)\text{-}C_{82})]$ (**2**; 57%) was obtained as an air-stable, greenish-brown crystalline solid. The molecular-ion peaks around *m*/*z* 1914 in the MALDI mass spectrum of **2** (Figure 1) match the isotope distribution calculated for **2**. The $^1H$ NMR spectrum displayed only one singlet signal at $\delta = -16.00$ ppm, which indicated the presence of bridging hydride ligands.

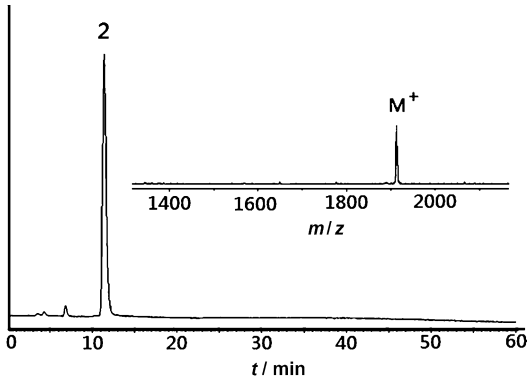


***Figure 1.*** HPLC chromatogram for the final stage of the separation of **2** and MALDI mass spectrum of **2**.

Crystals of **2** suitable for an X-ray diffraction study were grown from $CH_2Cl_2/CS_2$/*n*-hexane in a capillary tube at ambient temperature over several weeks. The identification of three $Sc_2$ pairs in different positions indicated rotation of the Sc atoms inside the $C_{82}$ cage.[13] The ORTEP drawing of **2** displays the $Sc_2C_2$ moiety with 50% occupancy (Figure 2).

There is a crystallographic symmetry imposed on the complex (Figure 3). The hexagon perpendicular to the symmetry plane is coordinated to the $Re_3$ cluster in an $\eta^2,\eta^2,\eta^2$ bonding fashion. The three hydride ligands were not located directly, but are believed to lie on the $Re_3$ plane in such an arrangement that each H atom spans one Re–Re edge, as determined for $[(\mu\text{-H})_3Re_3(CO)_8(CNCH_2Ph)(\eta^2,\eta^2,\eta^2\text{-}C_{60})]$.[14] The trimetallic moiety is based on an isosceles triangle, in which the Re1–Re2 distance (3.176(2) Å) is slightly shorter than the Re1–Re1A distance (3.201(2) Å). Each Re atom is associated with three terminal carbonyl groups. The Re–CO distances range from 1.91(4) to 2.01(3) Å, C–O bond lengths range from 1.06(4) to 1.17(5) Å, and Re-C-O angles are in the range 163(3)–177(3)°. The $Re_3$ triangle is positioned over the three 6:6 junctions of the hexagon; the two planes are essentially parallel (0.5(8)°). The

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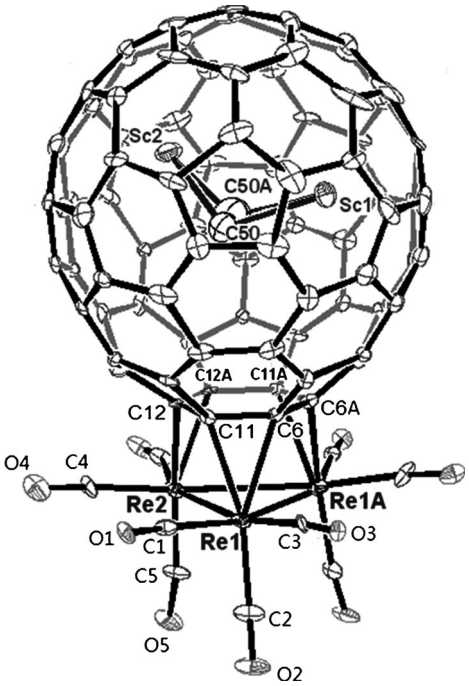


***Figure 2.*** Molecular structure of **2**. Thermal elliposids are shown at 30% probability. The Re atoms and the $Sc_2C_2$ moiety are disordered at their sites; the ORTEP diagram displays the Re atoms with 95% and the $C_2Sc_2$ moiety with 50% occupancy. Selected bond distances [Å]: Re1–Re2 3.176(2), Re1–Re1A 3.201(2), Re1–C1 2.01(3), Re1–C2 1.98(4), Re1–C3 1.95(4), Re1–C6 2.33(2), Re1–C11 2.31(2), Re2–C4 1.96(3), Re2–C5 1.91(4), Re2–C12 2.33(2), Sc1–C50 2.2(1), Sc2–C50 2.6(1), C50–C50A 1.20(2). Selected bond angles [°]: Re1-Re2-Re1A 60.52(5), Re2-Re1-Re1A 59.74(3), Sc1-C50-Sc2 109(5), Sc1-C50-C50A 74.3(10), Sc2-C50-C50A 76.8(6), C50-Sc1-C50A 31(2), C50-Sc2-C50A 26(1).

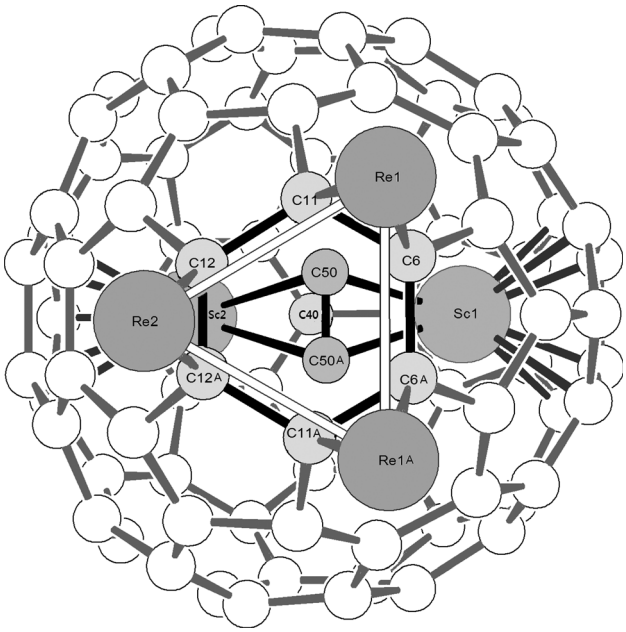


***Figure 3.*** Highlighted configuraton of **2**. A plane of symmetry passes through the Re2, Sc2, C40, and Sc1 atoms. The Sc1 and Sc2 atoms show interactions with the fullerene core. The C–C bonds within the coordinated hexagon are localized, with the distances [Å]: C6–C6A 1.48(4), C6–C11 1.43(3), C11–C12 1.52(4), and C12–C12A 1.32(5).

Re atoms are bonded to the ring carbon atoms about equally (2.31(2)–2.33(2) Å), and the average Re–$C_{ring}$ distance of 2.32 Å is comparable to that measured for $[(\mu\text{-H})_3Re_3(CO)_8(CNCH_2Ph)(\eta^2,\eta^2,\eta^2\text{-}C_{60})]$ (average: 2.31 Å).[14] The C–C bonds within the coordinated hexagon are localized and range from 1.32(5) to 1.52(4) Å in length. Shorter and longer bonds appear to alternate around the ring. The $C_6$ ring is pulled out of the fullerene sphere. This distortion of the regular fullerene structure is consistent with the change in hybridization of these $C_6$ ring atoms to $sp^3$[15] and is reflected by lengthening of the distances from the tip C40 atom to the ring C6, C11, and C12 atoms (8.61–8.63 Å; average: 8.62 Å). These distances are approximately 0.15 Å longer than those measured for pristine **1** (8.43–8.50 Å; average: 8.47 Å).[13]

The endohedral $Sc_2C_2$ cluster assumes a butterfly shape, which is positioned in such a way that neither of the two Sc atoms is close to the *exo* $Re_3$ cluster. The shortest cage–Sc contacts (2.08 Å to Sc1 and 2.25 Å to Sc2) are not much changed from those in **1** (1.99–2.22 Å).[13] The hinge C50–C50A distance (1.20(2) Å), typical of a C≡C triple bond, and the Sc···Sc separation (3.95 Å) are comparable with those in **1**, whereas the mean Sc–$C_{carbide}$ distance in **2** (2.40 Å) is 0.19 Å longer than that in **1** (2.21 Å). This difference gives rise to a smaller dihedral angle between the two $ScC_2$ planes in **2** (114.3°) in comparison with **1** (130°). Apparently, the change in the $Sc_2C_2$ skeleton is caused by elongation of the $C_{82}$ core and charge-density redistribution upon complexation to the $Re_3$ cluster.

The electronic structure of **1** has been described as $(Sc_2C_2)^{4+}C_{82}^{4-}$ as a result of four-electron transfer from $Sc_2C_2$ to $C_{82}$.[16] Therefore, **1** should act as a more efficient electron donor than neutral fullerenes, such as $C_{60}$. This hypothesis is supported by the carbonyl region of the IR spectrum of **2**, the absorption pattern of which is identical to that of $[(\mu\text{-H})_3Re_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}C_{60})]$,[14] except that the CO stretches for **2** are all red-shifted by 2 $cm^{-1}$ in agreement with the increase in π back-donation from the more electron rich $Re_3$ center of **2**. The $^1H$ NMR spectrum is also consistent with an electron-rich fullerene: the bridging hydride resonance of **2** at $\delta = -16.00$ ppm is shielded by 0.68 ppm with respect to that of $[(\mu\text{-H})_3Re_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}C_{60})]$ (−15.32 ppm).

The visible/near-infrared (Vis/NIR) absorption spectra of compounds **1** and **2** in $CS_2$ are shown in Figure 4 for comparison. It is well-established that the electronic absorptions of fullerenes are predominantly due to π→π* carbon-cage transitions and depend on the structure and charge state of the carbon cage.[1] The onsets in the spectrum of **2** are blue-shifted relative to those in the spectrum of **1**, which suggests that the HOMO–LUMO gaps for **2** are larger than for **1**. These shifts can be ascribed to the difference in the amount of negative charge on the $C_{82}$ core.[17] Theoretical calculations showed that the HOMO of $Sc_2C_2@C_{3v}(8)\text{-}C_{82}$ was delocalized not only over the $Sc_2C_2$ cluster but also over the $C_{82}$ cage.[18,19] Presumably, the donation of six electrons from the $C_{82}$ core to the $Re_3$ cluster leads to stablization of the HOMO levels.

The $C_{3v}(8)\text{-}C_{82}$ core consists of 31 hexagons and 12 pentagons.[20] Only one $C_6$ ring is surrounded by three

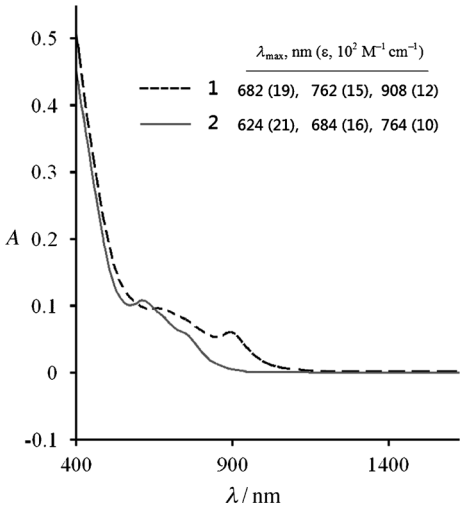


***Figure 4.*** Vis/NIR absorption spectra of compounds **1** and **2** in $CS_2$.

hexagons and three pentagons (see Figure 3). This $C_6$ ring apparently has more ring strain and less conjugation energy than the other $C_6$ rings (surrounded by four or five hexagons). Since no other isomers of **2** were isolated or detected, the regiospecific complexation of the $Re_3$ cluster with this unique hexagon to yield **2** may be governed by both steric and electronic effects.

In summary, in the first investigation of the coordination chemistry of EMFs, a $Re_3$ cluster was added regiospecifically to one hexagon of the $Sc_2C_2@C_{3v}(8)$-$C_{82}$ core. The geometry and electronic properties of $Sc_2C_2@C_{3v}(8)$-$C_{82}$ were altered by the coordinated Re atoms, although no obvious interactions between the endohedral $Sc_2C_2$ species and the exohedral $Re_3$ cluster were observed. Further studies of metal complexes of other EMFs are under way.

## Experimental Section

Details of the reaction procedures, characterization data, and details of the structural determination of **2** are given in the Supporting Information. CCDC 898771 contains 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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