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Fullerene Complexes

$[Os_3(CO)_6(PMe_3)_3](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$: A Fullerene[60] Coordinated to Two Different Trinuclear Clusters**

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Dedicated to Professor John R. Shapley on the occasion of his 60th birthday

Considerable research effort has been devoted to preparing a variety of [60]fullerene-based (C_{60}) derivatives because of their potential application in the optical, magnetic, electronic, catalytic, and biological areas of materials science.[1] In particular, exohedral metallofullerene chemistry has been intensively studied to investigate new chemical and physical properties of metal–C_{60} coordination. Of special importance are studies on the reactivity and electrochemical properties of these complexes that can lead ultimately to new electronic nanomaterials and nanodevices.[2] Various bonding interactions between metals and C_{60} have been reported, such as η^2,[3] $\mu\text{-}\eta^2{:}\eta^2$,[4] and η^5 types[5] and, particularly, $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$, $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1$, $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2$, and $\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2$ modes for metal clusters.[2a,6] The C_{60} surface can accommodate up to six separate single metal centers through η^2 interactions,[3b] but only 1:1 adducts of C_{60} and metal clusters have been reported to date.[2a,7] However, 2:1 adducts (C_{60} sandwich complexes) are known for $\{Ir_4\}$ and $\{Rh_6\}$ clusters.[6,8] Herein we report the synthesis, characterization, and theoretical studies of three structural isomers of the title complex, $[Os_3(CO)_6(PMe_3)_3](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$—unprecedented 1:2 adducts in which C_{60} is bound to multiple cluster moieties.

An *o*-dichlorobenzene solution of $[Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$[9] and $[Re_3(\mu\text{-}H)_3(CO)_9(MeCN)_3]$[10] (1:1) was heated to reflux for 30 min. After a standard work-up and purification procedure, three isomers of $[Os_3(CO)_6(PMe_3)_3](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$, *cis*-**1** (30%) and *cis*-**2** (a mixture of *cis*-**2A** and *cis*-**2B**, 30%) were produced (Figure 1).

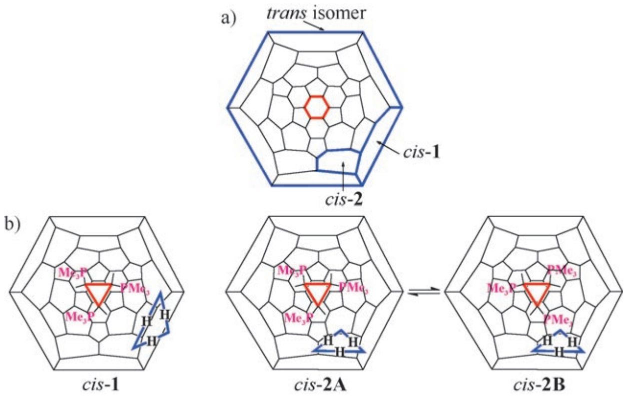

Figure 1. Schlegel diagrams for a) possible isomers of 1:2 adducts; b) *cis*-**1** and *cis*-**2**.

The consideration of $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ binding by one C_{60} to multiple trinuclear cluster moieties is less complicated than that of η^2 binding to multiple mononuclear complex units, as there are only 20 six-membered rings suitable for $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ binding whereas there are 30 6:6 ring-fusion edges suitable for η^2 binding. Moreover, the steric demands of a trinuclear cluster compared to those of a mononuclear unit further restricts the number of possible C_{60} adducts. This situation in turn leads to fewer regioisomers arising from cluster coordination, which simplifies the analysis of such exohedral metallofullerenes in general. Three regioisomers (*trans*-, *cis*-**1**, and *cis*-**2**; Figure 1 a) are expected to be present as double-addition products of trinuclear clusters to C_{60} through $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ bonding (versus eight possible regioisomers through η^2 bonding[2b]). The *trans* isomer, unexpectedly, was not observed. The *cis*-**1** and a mixture of *cis*-**2A** and *cis*-**2B** (Figure 1 b) for the title complex were isolated and fully characterized by spectroscopic methods, X-ray diffraction studies, and a theoretical investigation.

The overall molecular structures of *cis*-**1** and *cis*-**2B** are illustrated in Figure 2. For *cis*-**1**, two enantiomers (*cis*-**1** and

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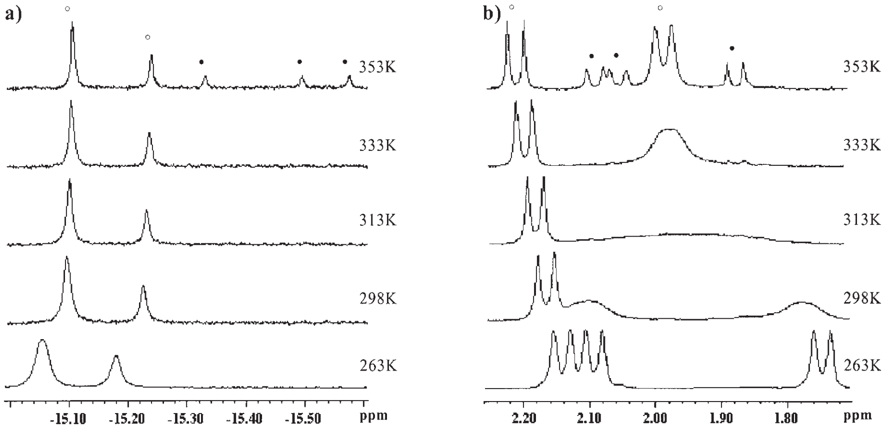

Figure 3. a) Hydride and b) PMe_3 regions in ^1H NMR spectra of *cis*-**1** (○) in $C_6D_4Cl_2$. Resonances arising from *cis*-**2** are denoted with ● at 353 K.

cis-**1′**) are present in the crystallographic asymmetric unit. Only *cis*-**2B** was observed crystallographically, although *cis*-**2B** is less stable than *cis*-**2A** because of steric repulsion between one PMe_3 ligand on the osmium center and the trirhenium moiety (Figure 1b). The general structural features of both *cis*-**1** and *cis*-**2B**·$2CS_2$ are the same except for the position of the trirhenium cluster at C_{60} (the C_6 ring of C46–C58 for *cis*-**1** and that of C27–C47 for *cis*-**2B**). The three equatorial PMe_3 ligands on the osmium atoms in both complexes are arranged as remote from one another as possible, with a distorted C_3 symmetry as observed in $[Os_3(CO)_6(PMe_3)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ (**3**).[9] The axial carbonyl ligands are positioned in a propeller-like configuration as reported in structurally characterized triruthenium and triosmium $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ complexes.[7,2a] However, the trirhenium moiety in both isomers has an almost idealized C_{3v} local symmetry owing to the elongated Re−H−Re bonds (av. 3.184 Å vs 3.02 Å in $[Re_2(CO)_{10}]$[11]), which allows for some steric relief. These values compare with an average Os−Os bond length of 2.932 Å. The bridging hydride ligands could not be located in the structural analyses.

The variable temperature (VT) ^1H NMR spectra of *cis*-**1** are provided in Figure 3. The spectrum at 298 K reveals two singlets at $\delta = -15.10$ and -15.23 ppm in a 2:1 ratio for the three bridging hydrides. The three inequivalent PMe_3 ligands give rise to three doublets ($^2J_{HP} = 10.0$ Hz) at $\delta = 2.14$, 2.09, and 1.75 ppm in a ratio of 1:1:1 at 263 K. As the temperature increases, the two resonances at $\delta = 2.09$ and 1.75 ppm coalesce ($T_c = (313 \pm 3)$ K, $\Delta G^{\ddagger}_c = (18.5 \pm 0.2)$ kcal mol^{-1}) and sharpen into a doublet ($^2J_{HP} = 10.0$ Hz) at $\delta = 1.99$ ppm at 353 K. These spectral data indicate that the three PMe_3 ligands undergo coupled restricted rotation at each osmium center (Scheme 1).[9] Consequently, *cis*-**1** adopts a C_s symmetry through fast exchange between the two enantiomers, *cis*-**1** and *cis*-**1′**.

The corresponding VT ^1H NMR spectra of *cis*-**2** are shown in Figure 4. The spectra taken at low temperatures

Scheme 1. Coupled restricted rotation at each of the three osmium centers.

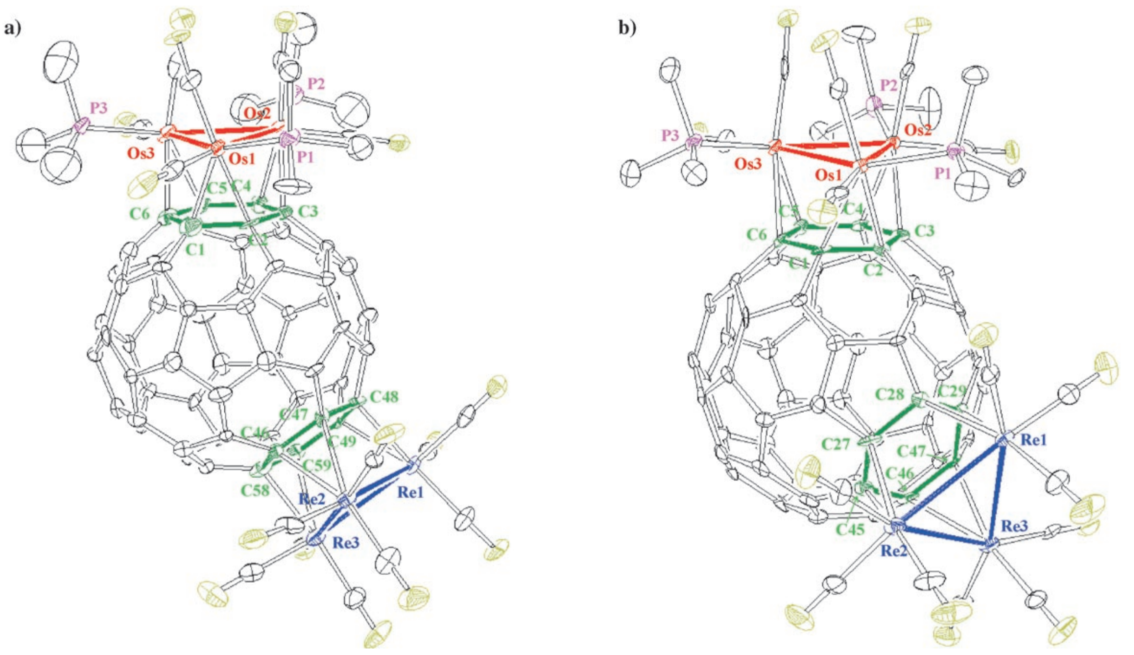

Figure 2. Molecular structures and atom labeling schemes for a) *cis*-**1** and b) *cis*-**2B**.

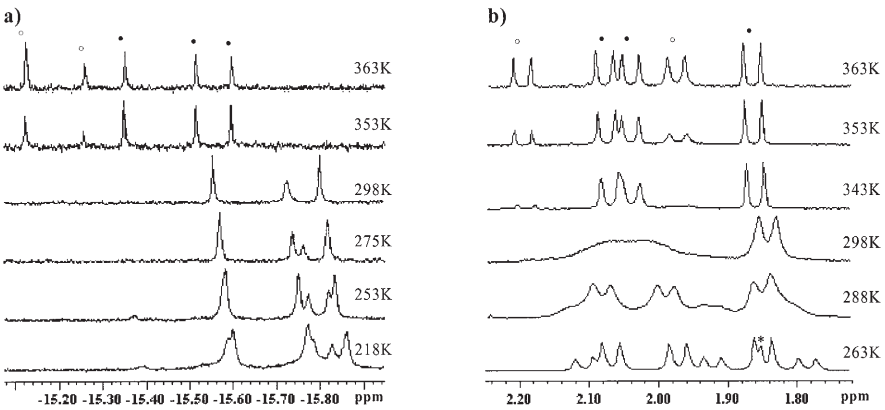

Figure 4. a) Hydride and b) PMe_3 regions in ^1H NMR spectra of *cis*-**2** (●) in $C_6D_4Cl_2$ (spectra of the hydride region below 353 K were obtained in $CDCl_3$). Resonances arising from *cis*-**1** are denoted with ○ at 353 K; signal arising from water is marked with *.

exhibit six singlet resonances for hydride and six doublet resonances for PMe_3, which correspond exactly to what is expected for the presence of both *cis*-**2A** and *cis*-**2B** at a slow exchange rate. As the temperature increases, the two sets of six signals coalesce as pairs to give three singlets for the hydrides and three doublets for the PMe_3 ligands at a fast exchange rate. Based on the same fluxional process for *cis*-**2** as in *cis*-**1**, the two structural isomers, *cis*-**2A** and *cis*-**2B**, equilibrate with a simultaneous fast exchange to their respective enantiomers. The more-stable *cis*-**2A** exists in a ratio of 65:35 relative to the less-stable *cis*-**2B**. The resonances arising from *cis*-**1** and *cis*-**2** are seen in both spectra at 363 K, which implies that they interconvert at high temperatures by changing the coordination sites of the trinuclear clusters on C_{60} with $K_{eq}([cis\text{-}\mathbf{2}]/[cis\text{-}\mathbf{1}]) = 1.1$ at 353 K.

Density functional theory (DFT) was used to investigate the electronic structure and relative stability of the four possible isomers: *cis*-**1** is the most stable followed by *cis*-**2A** (+0.8), *cis*-**2B** (+0.9), and *trans* (+1.9 kcal mol^{-1}) isomers (see Supporting Information). The regiochemistry for the formation of the isomers can be understood from the frontier-orbital interaction between the highest occupied molecular orbital (HOMO) of **3** and the lowest unoccupied molecular orbital (LUMO) of the $\{Re_3(\mu\text{-}H)_3(CO)_9\}$ fragment (see Supporting Information). In the HOMO diagrams of **3**, the active orbital lobes in C_{60} are mainly distributed around the $[Os_3(CO)_6(PMe_3)_3]$ cluster and gradually decrease further away from the cluster moiety, thus resulting in a negligibly small contribution at the *trans* position. This unfavorable frontier-orbital interaction and the instability arising from the relatively high energy in the *trans* isomer clearly accounts for the absence of this isomer; this isomer is also the least likely to form statistically ($^1/_6$ relative to other isomers).

Data from cyclic voltammograms (CVs) and half-wave potentials of *cis*-**1**, *cis*-**2**, **3**, $[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ (**4**), and free C_{60} are provided in the Supporting Information. The general features of the CVs of *cis*-**1** and *cis*-**2** are very similar, although the corresponding half-wave potential of *cis*-**1** reveals a slight cathodic shift relative to that for *cis*-**2**. The CVs of *cis*-**1** and *cis*-**2**, apparently, are not a simple addition of those of **3** and **4**. The data in the Supporting Information suggest that both *cis*-**1** and *cis*-**2** undergo reversible one-electron C_{60}-localized electrochemical reactions[8b] up to hexa-anionic species within the chlorobenzene potential window.

In conclusion, we have prepared and fully characterized C_{60} compounds with twp-cluster moieties (1:2 adducts: *cis*-**1**, *cis*-**2A**, and *cis*-**2B**) that are unprecedented in C_{60} metal-cluster chemistry. Interestingly, the sterically least congested *trans* isomer has not been observed because of an unfavorable frontier orbital interaction and the higher energy of this isomer, as determined by DFT calculations. A detailed kinetic, spectroscopic, electrochemical, and theoretical investigation of these isomers is currently under way.

Experimental Section

Synthetic procedures and characterization data for *cis*-**1** and *cis*-**2** are given in the Supporting Information. CCDC-620159 (*cis*-**1**) and CCDC-620160 (*cis*-**2B**) 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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