The Coordination and Structure of a Thiolate-Terminated “Molecular-Scale Wire” Linked to a Triosmium Cluster

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The molecule (*p,p*)-$HSC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ has been attached to a triosmium cluster and characterized crystallographically. The complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_6H_4\text{-}C{\equiv}CC_6H_4C{\equiv}CC_6H_5)$ (**1**) was obtained in 49% yield from the reaction of the thiol $HSC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ with $Os_3(CO)_{10}(NCMe)_2$. The sulfur atom bridges two metal atoms on the edge of a triangular cluster of three osmium atoms. The three aryl rings are nearly coplanar. The ligand is 18.27(2) Å in length from the sulfur atom to the *para*-carbon atom of the third aryl ring. This compound may serve as a model for the coordination of thiol-terminated molecular wires to metallic probe surfaces.

Future computational systems will eventually consist of logic devices that are ultra dense, ultra fast, and ultra small[1][2][3]. The slow step in existing computational architectures is not usually the switching time, but the time it takes for an electron to travel through the circuit. By using molecular-scale electronic interconnects[4], electronic transmission times will be minimized and the resulting computational operations will occur at far greater speeds than those attainable from conventional patterned architectural arrays[1].

Although it is well documented that bulk conjugated organic materials can be semiconducting or even conducting when doped[5], recent studies have shown that oriented thiol-terminated conjugated rigid-rod molecules[6] can conduct electrons through a single undoped conjugated molecule, “molecular-scale wire”, to and from a metallic surface[7]. However, initial studies have indicated the presence of a transmission barrier at the metal-organic interface[8]. A detailed knowledge of the bonding of thiols to metallic surfaces will be crucial to developing an understanding of electron-transport mechanisms and the constuction of devices involving the metal-organic interfaces. The metal-thiol linkage is usually regarded to be a single metal−sulfur bond with transfer of the hydrogen atom to the metal surface. Therefore, we have undertaken a study to determine the nature of the structures and modes of attachment of some thiol-terminated molecular wires to metal clusters serving as models for metal surfaces.

The complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_6H_4C{\equiv}CC_6H_4\text{-}C{\equiv}CC_6H_5)$ (**1**) was obtained in 49% yield from the reaction of (*p,p*)-$HSC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ with $Os_3(CO)_{10}(NCMe)_2$. Crystals of **1**, suitable for X-ray crystallographic analysis, were obtained by slow evaporation of solvent from a solution in CH_2Cl_2 solvent at 25°C. An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. The molecule consists of a linear $SC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ ligand linked to the triosmium cluster by the sulfur atom bridging two of the three osmium atoms. The reaction has produced cleavage of the thiol sulfur−hydrogen bond and transfer of the hydrogen atom to the osmium cluster to become a hydride ligand. The position of the hydride ligand was located and refined crystallographically. It bridges the Os(1)−Os(2) bond of a triangular cluster of three osmium atoms, Os(1)−H(1) = 1.9(1) Å and Os(2)−H(1) = 1.81(8) Å, and exhibits the characteristic high-field resonance shift in the ^1H-NMR spectrum, $\delta = -17.04$. The sulfur atom bridges the same two metal atoms on the other side of the Os_3 plane, Os(1)−S = 2.423(3) Å and Os(2)−S = 2.421(4) Å. These values are similar to those found for other bridging thiolate−triosmium linkages that have been structurally characterized previously[9]. The alkyne C−C bonds are short, C(46)−C(47) = 1.16(2), C(54)−C(55) = 1.19(2) Å as expected for C−C triple bonds, and the alkyne groups are linear. The sulfur−carbon distance, S−C(40) = 1.82(1) Å, is typical of a carbon−sulfur single bond. The overall length of the ligand is an interesting feature. The distance from S to C(59) is 18.27(2) Å. Although the central aryl ring is twisted approximately 10° away from the planes of the two other rings, the three aryl rings are nearly coplanar. This is a feature that would facilitate electron transmission through the π-orbital network.

Figure 2 shows the packing of the molecules in the crystal. All aryl rings are nearly coplanar. The intermolecular spacings between the rings of the different molecules are determined largely by the size of the cluster.

Studies have shown that bis(phenylethynyl)arenes exhibit strong fluorescence and are effective receptors for chemilumescence processes[10]. We have found that **1** exhibits a single strong UV absorption at 332 nm ($\varepsilon = 48500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$)

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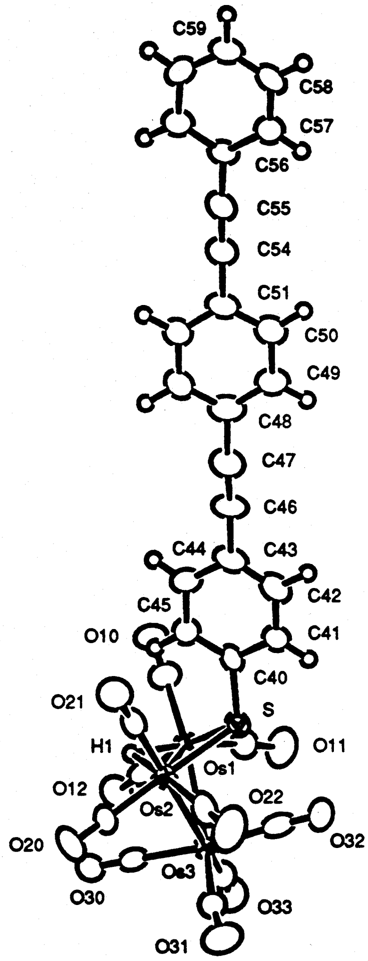
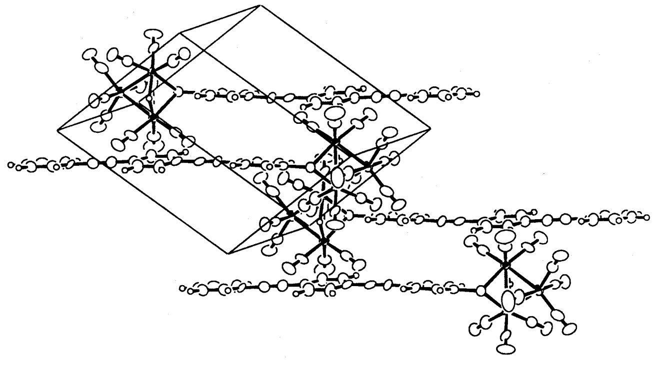
Figure 1. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_6H_4C\equiv CC_6H_4C\equiv CC_6H_5)$ (**1**)[a]



[a] Selected interatomic distances [Å] and angles [°] are: Os(1)−Os(2) = 2.8765(8), Os(1)−Os(3) = 2.8565(7), Os(2)−Os(3) = 2.8626(8), Os(1)−S = 2.423(3), Os(2)−S = 2.421(4), Os(1)−H(1) = 1.9(1), Os(2)−H(1) = 1.81(8), S−C(40) = 1.82(1), C(46)−C(47) = 1.16(2), C(54)−C(55) = 1.19(2), S···C(59) = 18.27(2); Os(1)−S−C(40) = 113.5(4), Os(2)−S−C(40) = 111.6(5).

Figure 2. Packing diagram of compound **1** showing the stacking of the $HSC_6H_4C\equiv CC_6H_4C\equiv CC_6H_5$ ligand in the solid state



and a series of emissions at 348, 362, and 377 nm (λ_{ex} = 300 nm) which can be attributed to the $SC_6H_4C\equiv CC_6H_4C\equiv CC_6H_5$ ligand.

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Experimental Section

The reaction was performed under nitrogen. 24.0 mg of $HSC_6H_4C\equiv CC_6H_4C\equiv CC_6H_5$[6b] (0.0773 mmol), dissolved in 4 ml of CH_2Cl_2, was added to a solution of 75.0 mg of $Os_3(CO)_{10}(NCMe)_2$ (0.0804 mmol) in 50 ml of CH_2Cl_2. After stirring for 2 h at 25°C, the solvent was removed and the residue separated by TLC (in air) on silica gel by using a hexane/CH_2Cl_2 (3:1) solvent mixture. This yielded a yellow band containing 44.1 mg of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_6H_4C\equiv CC_6H_4C\equiv CC_6H_5)$ (**1**) (49%). − IR (νCO in hexane, cm^{-1}): 2110 (m), 2069 (vs), 2060 (m), 2026 (vs), 2020 (m), 2003 (m), 1992 (w), 1987 (w). − ^1H NMR (δ in $CDCl_3$): 7.52−7.25 (m, 13 H, Ph), −17.04 (s, 1 H, Os-H). − $C_{32}H_{14}O_{10}Os_3S$ (1161.12): calcd. C 33.10, H 1.22; found 32.98, 1.37.

Crystal Data: Space group = $P\bar{1}$, a = 15.019(3), b = 13.831(2), c = 9.299(1) Å, α = 90.21(1), β = 72.67(2), γ = 114.77°, Z = 2; 3221 reflections, R = 0.035. Diffraction measurements at 20°C were made on a Rigaku AFC6S four-circle diffractometer using Mo-K_α radiation. The structure solution and refinement were made by using the TEXSAN MOTIF structure-solving program library (v. 1.8) of the Molecular Structure Corp., The Woodlands, TX on a Silicon Graphics Indigo^2 computer. An absorption correction (DIFABS) was applied. − Crystallographic Data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101062. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: int code + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk).

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[4] “Molecular electronics” is a poorly defined term since some authors refer to it as any molecular-based system such as a film or a liquid-crystalline array. Other authors, including us, have preferred to reserve the term “molecular electronics” for single-molecule tasks, such as single-molecule-based devices or single-molecular wires. Due to this confusion, we have chosen here to follow the Petty et al. [M. C. Petty, M. R. Bryce, D. Bloor (Eds.) in *Introduction to Molecular Electronics*, Oxford Univ. Press, New York, **1995**] terminology by using two subcategories, namely “molecular materials for electronics” for bulk applications and “molecular-scale electronics” for single-molecule applications.

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