Two-Site Reactivity in a Ligand-Bridged Cluster. The Reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$ with Terminal Acetylenes

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Summary: The reaction of the cluster complex $Os_4(CO)_{12}(\mu_3\text{-}S)$, **1**, with PhC≡CH yields two noninterconvertible products, $Os_4(CO)_{12}(\mu_3\text{-}S)[\mu_4\text{-}C{=}C(Ph)H]$, **2a**, in 46% yield and $Os_4(CO)_{12}[\mu_4\text{-}\eta^3\text{-}SC(Ph){=}CH]$, **3a**, in 27% yield. Both products were characterized by IR, ^1H NMR, and X-ray diffraction methods. Compound **2a** consists of a puckered rhombus of four osmium atoms with a triply bridging sulfido ligand and quadruply bridging phenylvinylidene ligand. Compound **3a** consists of a butterfly tetrahedral cluster of four osmium atoms with a novel quadruply bridging SC(Ph)=CH thiolato ligand that was formed by the formation of a carbon-sulfur bond between the sulfido ligand in **1** and the phenyl-substituted carbon atom of the acetylene molecule. The reaction of **1** with $MeO_2CC{\equiv}CH$ yields only the analogue of **3a**.

Interest in the potential of polynuclear transition-metal complexes for use as catalysts continues to be strong,[1,2] and examples that demonstrate the novel reactivity of these complexes are becoming increasingly abundant.[3] We now wish to report on the unusual two-site reactivity of the ligand-bridged cluster compound $Os_4(CO)_{12}(\mu_3\text{-}S)$, 1, toward terminal acetylenes which appears to be nucleophilic in character on the one hand and electrophilic in character on the other.

The reaction of 1,[4,5] with PhC≡CH at 55-60 °C for 12 h in hexane solvent yields two noninterconvertible products. These are a light yellow compound, **2a** (46% yield), and a black compound, **3a** (27% yield). The reaction of 1 with $MeO_2CC{\equiv}CH$ is considerably more facile and yields (50%) of a dark blue compound, **3b**, that appears to be analogous to **3a** and none of the product analogous to **2a**. All the products were characterized by a combination of IR and ^1H NMR spectroscopies. Compounds **2a** and **3a** were also characterized by single-crystal X-ray diffraction analyses and C and H elemental analyses.[6,7]

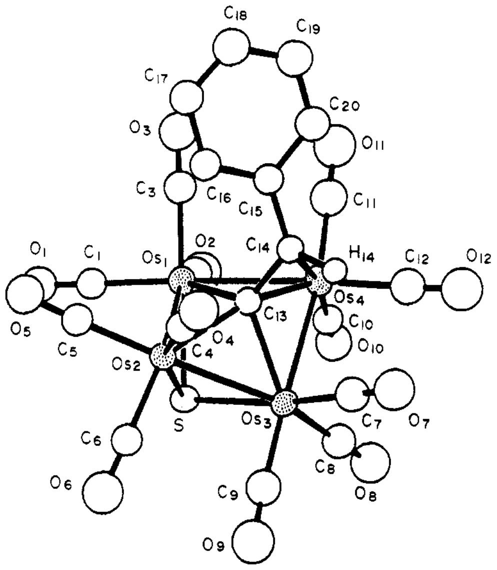

Figure 1. A perspective ORTEP diagram of $Os_4(CO)_{12}(\mu_3\text{-}S)[\mu_4\text{-}C{=}C(Ph)H]$, **2a**, showing 50% thermal ellipsoids.

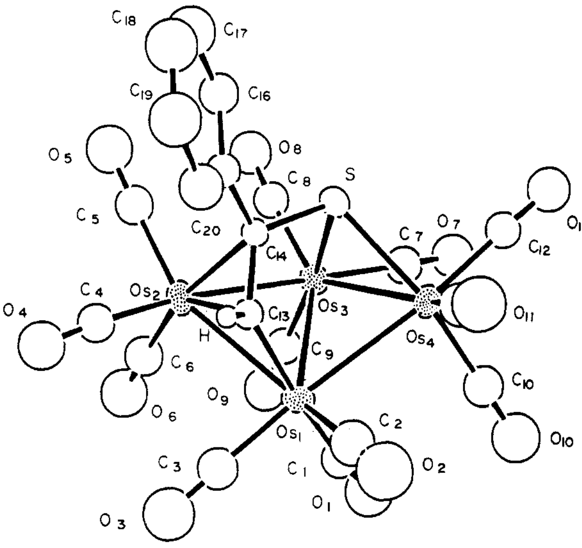

Figure 2. A perspective ORTEP diagram of $Os_4(CO)_{12}(\mu_4\text{-}\eta^3\text{-}SC(Ph){=}CH]$, **3a**, showing 50% probability thermal ellipsoids.

Compound **2a** has been formulated as $Os_4(CO)_{12}(\mu_3\text{-}S)[\mu_4\text{-}C{=}C(Ph)H]$, and an ORTEP diagram of its structure is shown in Figure 1.[8] The cluster consists of a puckered rhombus of four osmium atoms. The four osmium-osmium bonds are not unusual and range from 2.787 (1) to 2.866 (1) Å in length.[9] Each metal atom contains three

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[6] The products were separated by tlc on silica gel. For **2a**: IR (ν(CO) in hexane) 2104 (vw), 2074 (s), 2069 (s), 2051 (m), 2041 (w), 2017 (s), 2000 (m), 1995 (sh), 1987 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.703 (H), 7.0-7.5 (Ph). Anal. Calcd: C, 19.50; H, 0.49. Found: C, 19.57; H, 0.50. For **3a**: IV (ν(CO) in hexane) 2097 (w), 2068 (vs), 2041 (s), 2017 (w), 2008 (w), 1996 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.406, 7.0-8.0 (Ph). For **3b**: IR (ν(CO) in hexane) 2101 (w), 2070 (vs), 2045 (s), 2021 (m), 2011 (w), 1998 (w), 1971 (vw), 1710 (w, br); ^1H NMR ($CDCl_3$) δ 8.491 (H), 3.741 (CH_3). Anal. Calcd: C, 15.83; H, 0.33. Found: C, 16.54; H, 0.38. Compound **2a** was recovered unchanged after treatment at 125 °C for 18 h. Compound **3a** is transformed at 125 °C into several new compounds which are currently under investigation, but no compound **2a** is formed.

[7] X-ray diffraction data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer. All programs used in the structure solutions and refinements were from the Enraf-Nonius SDP library. All calculations were performed on a Digital Equipment Corp. PDP 11/60 computer. Absorption corrections were performed for both structure analyses.

[8] Yellow crystals of **2a** were grown from CH_2Cl_2/hexane (10/90, v/v) solvent by slow evaporation at -20 °C. The crystals belong to the monoclinic crystal system, space group $P2_1/n$, with a = 12.669 (3) Å, b = 13.098 (3) Å, c = 14.929 (3) Å, β = 94.23 (2)°, Z = 4, and ρ_{calcd} = 3.31 g/cm³. The structure was solved by the heavy-atom method and refined with 2484 reflections ($F^2 \geq 3.0\sigma(F^2)$) to final values for the residuals R_F = 0.027 and R_{wF} = 0.034.

[9] Selected interatomic distances (Å) and angles (deg) for **2a** are as follows: Os(1)-Os(2) = 2.850 (1), Os(2)-Os(3) = 2.787 (1), Os(3)-Os(4) = 2.866 (1), Os(1)-Os(4) = 2.859 (1), Os(1)-S = 2.426 (3), Os(2)-S = 2.413 (3), Os(3)-S = 2.433 (3), Os(1)-C(1) = 2.222 (11), Os(2)-C(13) = 2.167 (11), Os(3)-C(13) = 2.187 (12), Os(4)-C(13) = 2.122 (11), Os(1)-C(14) = 2.227 (11), Os(1)···Os(3) = 3.567 (1), Os(2)···Os(4) = 4.152 (1); Os(2)-Os(1)-Os(4) = 93.29 (2), Os(1)-Os(2)-Os(3) = 78.74 (2), Os(2)-Os(3)-Os(4) = 94.51 (2), Os(3)-Os(4)-Os(1) = 77.32 (2).

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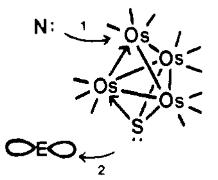
Scheme I



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linear terminal carbonyl ligands. There is a triply bridging sulfido ligand linked to the triosmium group Os(1), Os(2), and Os(3) and a quadruply bridging phenylvinylidene on the opposite side of the rhombus from the sulfido ligand. The vinylidene hydrogen atom H(14) was characterized by direct observation in a difference Fourier synthesis and by its ^{1}H NMR signal at δ 6.703. Carbon atom C(13) is bonded to all four metal atoms while C(14) is bonded only to Os(4). The C(13)–C(14) distance of 1.446 (16) Å is indicative of partial multiple bonding. Similarly, coordinated vinylidene ligands have been observed in other cluster complexes; in fact, the formation of vinylidene ligands by 1,2-hydrogen shifts is a characteristic feature of the reactivity terminal acetylene ligands.[10]

Compound **3a** has been formulated as $Os_4(CO)_{12}[\mu_4\text{-}\eta^3\text{-}SC(Ph)CH]$ and an ORTEP diagram of its molecular structure is shown in Figure 2.[11] The molecule consists of a butterfly tetrahedral cluster of four osmium atoms. The five osmium–osmium bonding distances are normal and range from 2.7640 (7) to 2.8490 (7) Å. Each metal atom has three linear terminal carbonyl ligands.[12] The most unusual ligand is the thiolato ligand SC(Ph)=CH, which to our knowledge has an unprecedented form. It was apparently formed by the formation of a carbon–sulfur bond between the phenyl-substituted carbon atom of the acetylene and the sulfido ligand. The C(14)–S bond length 1.817 (11) Å is characteristic of a carbon–sulfur single bond. The sulfur atom bridges metal atoms Os(3) and Os(4) while the acetylenic portion (C(13) and C(14)) is coordinated in a σ, π fashion to Os(1) and Os(2). The C(13)–C(14) separation at 1.400 (15) Å indicates that considerable multiple-bond character is still present. The hydrogen atom on C(13) was observed in a difference Fourier synthesis, and its very low-field ^{1}H NMR shift (δ 9.406) is characteristic of coordinated terminal acetylenes.[13] The formation of carbon–sulfur bonds is quite unusual but has been observed previously in metal complexes containing sulfido[14] and thiolato[15] ligands.

We believe it is significant that **2a** and **3a** can not be interconverted.[6] In fact, this observation strongly suggests that they were formed by different mechanisms. The structure of **1** could be viewed as a triangular cluster of three $Os(CO)_3$ groups bridged by a "capping" $Os(CO)_3$ group and a triply bridging sulfido ligand.[5] The electron-deficient character of $Os(CO)_3$ "capping" groups was recognized several years ago.[16] These sites permit nucleophilic ligand additions through the cleavage of a metal–metal bond, path 1; see Scheme I. This could be the first step in the formation of compound **2a**. The greater yield of the product **3b** for the more electron-deficient acetylene $MeO_2CC{\equiv}CH$ suggests a nucleophilic character of the cluster, path 2. Thus, a reaction proximate to the electron-rich sulfido ligand might be favored, and this could lead to the formation of products **3a** and **3b**.

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Registry No. **1**, 82080-90-8; **2a**, 97919-65-8; **3a**, 97919-66-9; **3b**, 97919-67-0; $MeO_2CC{\equiv}CH$, 922-67-8; $PhC{\equiv}CH$, 536-74-3.

Supplementary Material Available: Tables of structure factor amplitudes, final fractional atomic coordinates and thermal parameters, interatomic distances, and selected bond angles for compounds **2a** and **3a** (33 pages). Ordering information is given on any current masthead page.

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[11] Black crystals of **3a** were grown by slow evaporation of hexane solvent at 0 °C. Crystals of **3a** belong to the monoclinic crystal system, space group $P2_1/c$, with $a = 8.923$ (1) Å, $b = 10.315$ (1) Å, $c = 27.868$ (6) Å, $\beta = 97.09$ (1)°, $Z = 4$, and $\rho_{calcd} = 3.21$ g/cm^3. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. Full-matrix least-squares refinement on 2770 reflections ($F^2 \geq 3.0\sigma(F^2)$) yielded the final residuals $R_F = 0.033$ and $R_{wF} = 0.034$.

[12] Selected interatomic distances (Å) and angles (deg) are as follows: Os(1)–Os(2) = 2.7840 (7), Os(1)–Os(3) = 2.8490 (7), Os(1)–Os(4) = 2.8442 (7), Os(2)–Os(3) = 2.8132 (7), Os(3)–Os(4) = 2.7640 (7), Os(3)–S = 2.391 (3), Os(4)–S = 2.370 (3), Os(1)–C(13) = 2.124 (11), Os(2)–C(13) = 2.198 (12), Os(2)–C(14) = 2.366 (11), C(14)–S = 1.817 (11), C(13)–C(14) = 1.400 (15); Os(2)–Os(1)–Os(4) = 103.75 (2), Os(2)–Os(3)–Os(4) = 105.10 (2), Os(3)–S–Os(4) = 70.98 (9), Os(3)–S–C(14) = 100.7 (4), Os(4)–S–C(14) = 109.7 (4), S–C(14)–C(13) = 116.3 (7), Os(2)–C(14)–S = 102.0 (5).

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Application of Pentacarbonylchromium Carbenes in β-Lactam Synthesis: Preparation and X-ray Crystallographic Study of (1-Methyl-4-phenyl-3(*E*)-(phenylmethylene)-azetidinylidene)pentacarbonylchromium

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Summary: The reaction of the tetramethylammonium salt of (1-hydroxyethylidene)pentacarbonylchromium (**1c**) with toluene-4-sulfonyl chloride and *N*-benzylidenemethylamine (**7a**) gave the title azetidine complex **8a** (25%), whose structure was confirmed by a crystal structure determination. Subsequent oxidation with pyridine *N*-oxide gave 1-methyl-4-(phenylmethylene)-2-azetidinone **9a** (96%). These reactions were extended to *N*-(3-methylbenzylidene)methylamine and *N*-(4-methylbenzylidene)-methylamine.

In 1974 Fischer reported an intriguing observation on the dehydration of (1-hydroxyethylidene)pentacarbonylchromium (**1a**). Thus reaction of **1a** with dicyclohexylcarbodiimide (**2**) in dichloromethane solution gave the iminoazetidinylidene complex **4** (47%).[1] It is possible but by no means certain that **4** was produced via the formal [2 + 2] cycloaddition[2] reaction between excess **2** and the

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