$[Mo_2S_6]^{2-}$ appears to be a convenient route for the synthesis of most known thio anions and may be useful in the synthesis of related, hitherto unknown Mo/S complexes.

Acknowledgment. Financial support of this project by the National Science Foundation (Grant CH-79-0389) is gratefully acknowledged.

Supplementary Material Available: Listings of positional and thermal parameters for $(Ph_4P)_2[MoS(MoS_4)(S_4)]$ and $(Ph_4P)_2[Mo_2S_6/Mo_2S_7]$ (8 pages); listings of structure factors for both compounds (18 pages). Ordering information is given on any current masthead page.

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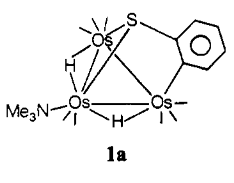
High-Nuclearity Clusters Containing Carbene Ligands. Synthesis, Structural Analyses, and Isomerization of Disulfidohexaosmium Carbonyl Cluster Compounds Containing Secondary (Dimethylamino)carbene Ligands

Sir:

The synthesis in 1964 of the first transition-metal complex to contain a heteronuclear carbene ligand proved to be the beginning of an extensive and exciting new area of transition-metal chemistry.[1,2] Curiously, however, to date there have been very few reports of transition-metal cluster compounds that contain heteronuclear carbene ligands and no examples of complexes where the metal nuclearity is higher than 3.[3-9] We have recently discovered that trimethylamine can serve as a precursor to the formation of secondary (dimethylamino)carbene ligands in triosmium clusters. We have now found that pyrolysis of the trimethylamine complex $Os_3(CO)_8(NMe_3)(\mu_3\text{-}SC_6H_4)(\mu\text{-}H)_2$ (**1**) yields the first examples of hexanuclear cluster compounds that contain heteronuclear carbene ligands.



1a

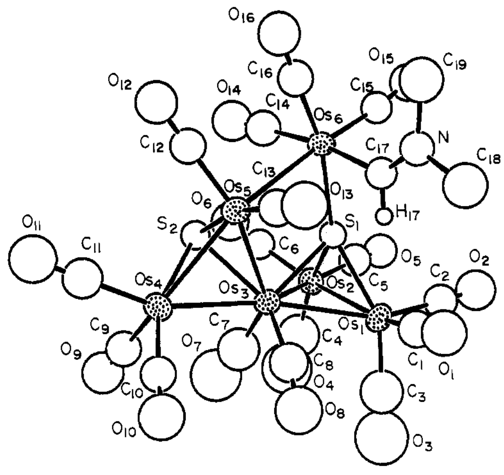


Figure 1. ORTEP diagram of $Os_6(CO)_{16}[C(H)NMe_2](\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2a**) showing 50% probability thermal ellipsoids.

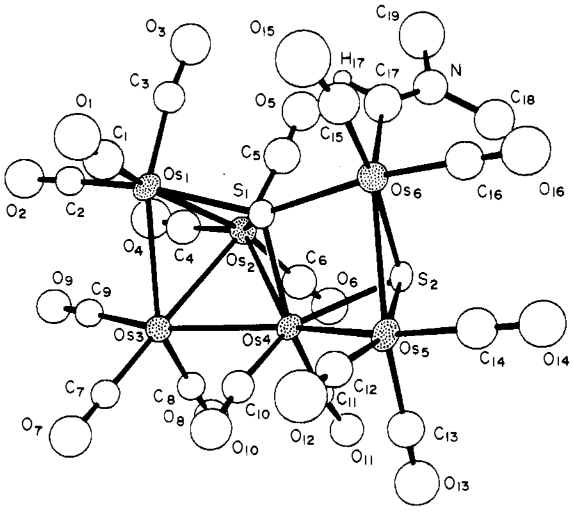
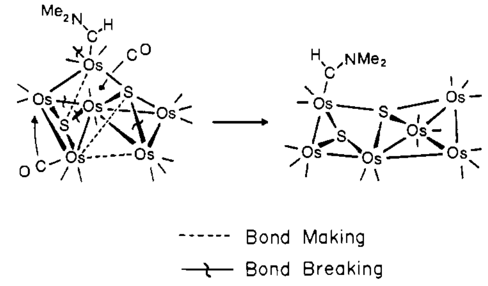


Figure 2. ORTEP diagram of $Os_6(CO)_{16}[C(H)NMe_2](\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2b**) showing 50% probability thermal ellipsoids.

Scheme I



Compound **1** was obtained as a mixture of two slowly interconverting isomers, **1a** (21% yield) and **1b** (10% yield), from the reaction of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ with an excess of Me_3NO in refluxing CH_2Cl_2 for 3 h.[10] When 26 mg of **1a** was refluxed in heptane solvent for 20 min, it was transformed into a mixture of three new hexaosmium clusters that are all isomers with the

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(10) Compounds **1a** and **1b** are yellow products that were isolated by TLC on silica gel plates by using a 20% CH_2Cl_2/80% hexane solvent mixture. IR (ν(CO), in hexane, cm^{-1}): for **1a**, 2086 m, 2048 s, 2036 s, 2005 s, 1995 m, 1972 m; for **1b**, 2085 m, 2049 s, 2035 s, 2007 s, 1990 m, 1970 m. ^1H NMR (δ, in $CDCl_3$): for **1a**, 7.51-6.22 (m, 4 H), 3.35 (s, 9 H), -13.51 (s, 1 H), -21.46 (s, 1 H); for **1b**, 7.40-6.30 (m, 4 H), 3.13 (s, 9 H), -13.03 (s, 1 H), -22.00 (s, 1 H). Compounds **1a** and **1b** isomerize to a 4/1 **1a**/**1b** equilibrium in a $CHCl_3$ solution. This takes a period of several days at 25 °C. Compound **1a** was also characterized by a single-crystal X-ray diffraction analysis. Compound **1a** contains a triply bridging orthometalated benzenethiolato ligand on the face of a triosmium cluster. A trimethylamine ligand is coordinated to one of the sulfur-bridged metal atoms. Additional details will be provided in the full report on this work. Satisfactory elemental analyses (C, H, N) have been obtained: Anal. Calcd (found) for **1a**: C, 21.17 (21.29); H, 1.56 (1.38); N, 1.45 (1.43). Calcd (found) for **1b**: C, 21.17 (21.43); H, 1.56 (1.46); N, 1.45 (1.43).

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formula $Os_6(CO)_{16}[C(H)NMe_2](\mu_3\text{-}S)(\mu_4\text{-}S)(\mu\text{-}H)_2$ (**2**). These products can be separated by TLC on silica gel. In order of elution they are as follows: yellow **2a**, 2.5 mg (11%), red **2b**, 8.8 mg (38%), and orange **2c**, 6.0 mg (26%).[11] Compounds **2a** and **2b** have been characterized by single-crystal X-ray diffraction analyses.[12,13]

An ORTEP diagram of the molecular structure of **2a** is shown in Figure 1.[14] The molecule consists of two triangular triosmium groupings Os(1)–Os(2)–Os(3) and Os(3)–Os(4)–Os(5) that share the atom Os(3). Each triangle is bridged by a sulfido ligand. A sixth osmium atom Os(6) bridges the two triangular groups through a metal–metal bond to Os(5) and a coordinate bond to S(1). Os(6) contains a terminally coordinated secondary (dimethylamino)carbene ligand, C(17), N, C(18), C(19). The Os(6)–C(17) distance of 2.05 (2) Å is similar to the osmium–carbon (carbene) distances of 2.026 (15) Å [2.04 (2) Å] observed in $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**3**).[3] Compound **2a** contains two bridging hydride ligands (^1H NMR, $\delta = -18.90$ and -27.00). These were not located crystallographically. There are 16 linear terminal carbonyl ligands distributed as shown in Figure 1.

An ORTEP diagram of the molecular structure of **2b** is shown in Figure 2.[15] The molecule contains a cluster of six osmium atoms. The group Os(1)–Os(2)–Os(3)–Os(4) is arranged in the form of a butterfly tetrahedron. Atoms Os(5) and Os(6) extend from the wing-tip atom Os(4). Sulfido ligand S(1) bridges the Os(1)–Os(2)–Os(4) open triangular group of the butterfly tetrahedron and is linked to Os(6). Sulfido ligand S(2) bridges the open triangular group Os(4)–Os(5)–Os(6). A secondary (dimethylamino)carbene ligand is terminally coordinated to Os(6). The Os(6)–C(17) distance of 2.04 (3) Å is equivalent to those in **3** and in **2a**. Compound **2b** contains two bridging hydride ligands (^1H NMR, $\delta = -13.67$ and -15.25). These were not located crystallographically, but they are beleived to bridge the two elongated osmium–osmium bonds Os(1)–Os(3) = 2.991 (1) Å and Os(5)–Os(6) = 2.981 (1) Å. There are 16 terminal carbonyl ligands distributed shown in Figure 2. Compound **2b** is structurally very similar to its carbonyl homologue $Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)_2$.[16]

When refluxed in octane solvent under an atmosphere of carbon monoxide, compound **2a** is converted into **2b** (16% yield) and $Os_5(CO)_{14}(\mu_3\text{-}S)_2(\mu\text{-}H)_2$ (13% yield).[17] The latter is formed by the removal of the carbene-containing osmium atom Os(6). The transformation of **2a** into **2b** is dependent on the CO atmosphere, and little or no **2b** is formed in its absence. A transformation pathway of **2a** into **2b** is shown in Scheme I. This is clearly a multistep process that cannot be delineated at this time, but it is believed that the shift of a CO ligand from Os(6) to Os(3) in **2a** is of pivotal importance. Although this could be accomplished by a sequence of bridge/terminal rearrangements, the importance of the CO atmosphere suggests a dissociation/readdition process as shown in Scheme I.

Compounds **2b** and **2c** equilibrate slowly in solution at 25 °C. The equilibrium mixture **2b**/**2c** is 1.00/0.89 in $CDCl_3$ solvent. Structural studies of **2c** are currently in progress.

The transformation of **1** into the **2a**–**c** mixture of isomers represents another example of the arene elimination/cluster condensation sequence that was observed for $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$;[18] however, the most interesting features demonstrated by this reaction are the transformation of a coordinated trimethylamine ligand into a secondary (dimethylamino)carbene ligand in a high-nuclearity cluster and its stability in the presence of major framework rearrangements in the cluster. It is believed that tertiary amines containing methyl groups may provide a general route to secondary aminocarbenes in polynuclear metal complexes.

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy. We wish to thank Johnson-Matthey for a loan of osmium tetraoxide.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and selected interatomic distances and angles for **2a** and **2b** (14 pages); tables of observed and calculated structure factor amplitudes for both structural analyses (36 pages). Ordering information is given on any current masthead page.

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(11) IR (ν(CO), in hexane, cm^{-1}): for **2a**, 2097 w, 2079 s, 2072 s, 2053 s, 2020 s, 2012 m, 2008 s, 1969 w, 1941 w; for **2b**, 2099 w, 2080 s, 2069 s, 2046 m, 2037 w, 2029 s, 2020 w, 2003 m, 1991 w, 1987 w, 1973 w, br; for **2c** (in CH_2Cl_2 solvent), 2098 w, 2080 s, 2066 s, 2045 s, 2029 s, 1997 m, br, 1986 m, br. ^1H NMR (δ, in CD_2Cl_2: for **2a**, 10.00 (s, 1 H), 3.80 (s, 3 H), 3.73 (s, 3 H), −18.90 (s, 1 H), −27.00 (s, 1 H); for **2b**, 11.56 (s, 1 H), 3.75 (s, 3 H), 3.69 (s, 3 H), −13.67 (s, 1 H), −15.25 (s, 1 H); for **2c**, 9.98 (s, 1 H), 3.53 (s, 3 H), 3.45 (s, 3 H), −13.49 (s, 1 H), −15.28 (s, 1 H). Satisfactory elemental analyses have been obtained: Anal. Calcd (found) for **2a**: C, 13.32 (13.41); H, 0.53 (0.58); N, 0.82 (0.86). Calcd for **2b**: C, 13.32 (13.68); H, 0.53 (0.61); N, 0.82 (0.84). The latter was crystallized in the absence of benzene solvent.

(12) Crystals of **2a** and **2b** were grown by slow evaporation of solvent from CH_2Cl_2/hexane/benzene solutions at −20 °C. Compound **2a** crystallizes in the triclinic crystal system, space group $P\bar{1}$, with $a = 15.652$ (3) Å, $b = 9.587$ (2) Å, $c = 10.768$ (4) Å, $\alpha = 99.70$ (2)°, $\beta = 95.92$ (2)°, $\gamma = 92.80$ (2)°, $Z = 2$, and $\rho_{calcd} = 3.58$ g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined (3412 reflections) to the final values of the residuals $R = 0.040$ and $R_w = 0.044$. The carbonyl ligand C(8)–O(8) was found to be partially disordered. Two sites were satisfactorily refined. Compound **2b** crystallizes in the monoclinic crystal system with $^1/_2$ mol of C_6H_6/mol of complex in space group $P2_1/c$, with $a = 16.070$ (4) Å, $b = 12.054$ (5) Å, $c = 18.387$ (13) Å, $\beta = 107.08$ (4)°, $Z = 4$, and $\rho_{calcd} = 3.41$ g/cm^3. The structure of **2b** was solved by direct methods (MULTAN) and was refined (2820 reflections) to the final values of the residuals $R = 0.044$ and $R_w = 0.045$.

(13) Diffraction measurements for **2a** were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation. Diffraction measurements for **2b** were made on an Enraf-Nonius CAD-4 automatic diffractometer. The structure solution and refinements were performed on a Digital Equipment Corp. VAX 11/782 computer by using the Enraf-Nonius SDP program library. Diffraction data were corrected for the effects of absorption.

(14) Selected interatomic distances (Å) and angles (deg) for **2a** are as follows: Os(1)–Os(2) = 2.808 (1), Os(1)–Os(3) = 2.819 (1), Os(2)–Os(3) = 2.838 (1), Os(3)–Os(4) = 2.808 (1), Os(3)–Os(5) = 2.884 (1), Os(4)–Os(5) = 2.877 (2), Os(5)–Os(6) = 2.864 (1), Os(1)–S(1) = 2.338 (5), Os(2)–S(1) = 2.338 (5), Os(3)–S(1) = 2.381 (5), Os(3)–S(2) = 2.399 (5), Os(4)–S(2) = 2.370 (5), Os(5)–S(2) = 2.384 (6), Os(6)–S(1) = 2.459 (5), Os(6)–C(17) = 2.05 (2), C(17)–N = 1.30 (2); Os(6)–C(17)–N = 135 (1).

(15) Selected interatomic distances (Å) and angles (deg) for **2b** are as follows: Os(1)–Os(2) = 2.815 (1), Os(1)–Os(3) = 2.991 (1), Os(2)–Os(3) = 2.844 (1), Os(2)–Os(4) = 2.868 (1), Os(3)–Os(4) = 2.823 (1), Os(4)–Os(5) = 2.802 (1), Os(5)–Os(6) = 2.981 (1), Os(1)–S(1) = 2.365 (5), Os(2)–S(1) = 2.397 (5), Os(4)–S(1) = 2.334 (5), Os(6)–S(1) = 2.434 (5), Os(4)–S(2) = 2.443 (5), Os(5)–S(2) = 2.371 (6), Os(6)–S(2) = 2.442 (5), Os(6)–C(17) = 2.04 (3), C(17)–N = 1.31 (3); Os(6)–C(17)–N = 134 (2).

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Synthesis of a New Family of Water-Soluble Clusters: $Ru_3(CO)_{12-x}L_x$ (x = 1-3), $Os_3(CO)_{10}L_2$, and $Ir_4(CO)_9L_3$ (L = Trisodium Salt (Hydrated) of Tris(*m*-sulfonatophenyl)phosphine)

Sir:

The synthesis of water-soluble clusters is of interest for their possible use as homogeneous catalysts in this solvent. There are several advantages for carrying out catalytic reactions in water: easy recovery of the costly transition metal in a biphasic system (e.g. in hydroformylation of olefins with rhodium),[1,2] use of water