The W–W distances, assigned formal oxidation states of the W atoms, and the number of d electrons available per W–W interaction are shown in Table I for $W_3S_8^{2-}$ and related ions. There is a trend of decreasing W–W bond distance with increase in the number of d electrons available per W–W bond. This trend is consistent with the results of a recent ab initio calculation carried out on $Mo_3S_9^{2-}$, where donation of electron density from the central Mo atom to the terminal ones is suggested.[16]

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 83-08076). S.B. acknowledges with gratitude leave from Alchemie Research Centre, Thane 400601, India.

Supplementary Material Available: Table II, a list of positional parameters (1 page). Ordering information is given on any current masthead page.

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Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Sumit Bhaduri
James A. Ibers*

Received June 18, 1985

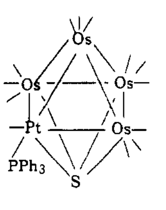
Synthesis of Square-Pyramidal Platinum–Osmium Clusters by Metal–Metal Exchange. Isolation and Structural Characterization of a Hexanuclear Intermediate

Sir:

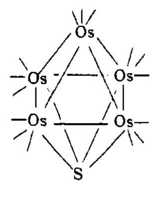
The discovery that some metal alloys have catalytic properties far superior to those of their individual components has been a significant advance to the area of heterogeneous catalysis[1] and has also been a major stimulus for the study of heteronuclear (mixed-metal) cluster compounds.[2] Systematic routes for the synthesis of heteronuclear metal cluster compounds are now beginning to emerge. The metal–metal exchange reaction, e.g. (1),

$$M_nL_x + M'L'_y \rightarrow M_{n-1}M'L_{x-a}L'_{y-b} + ML_aL_b \tag{1}$$

has been prominent among these, but this reaction is complicated mechanistically both by ligand exchange processes and by the sequence of metal-addition and -elimination steps that are frequently unobserved.[3,4] In this report we describe the synthesis of the square-pyramidal heteronuclear cluster $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**1**) from the reaction of the square pyramidal homonuclear cluster $Os_5(CO)_{15}(\mu_4\text{-}S)$ (**2**) with $Pt(PPh_3)_2C_2H_4$. From this reaction we have also isolated the hexanuclear adduct



1



2

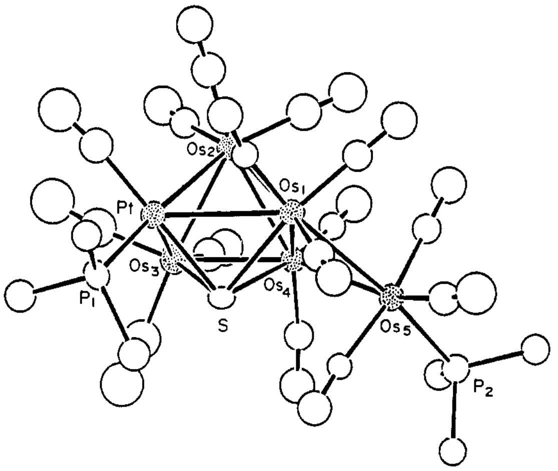


Figure 1. ORTEP diagram of $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**3**) showing 50% probability thermal motion ellipsoids. For clarity only carbon atoms directly attached to the phenyl rings have been included.

$PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**3**) and have shown that it is a precursor to **1**.

$Os_5(CO)_{15}(\mu_4\text{-}S)$[5] (**2**) (30 mg, 21 μmol) was mixed with $Pt(PPh_3)_2C_2H_4$ (15.5 mg, 21 μmol) in THF solvent at 0 °C and stirred for 0.5 h. After the mixture was warmed to 25 °C and stirred for an additional 2 h, the solvent was removed and the dark brown residue was separated on silica TLC plates with CH_2Cl_2/hexane, 35/65 v/v, solvent. Six bands were separated. In order of elution these were unreacted **2** (10%), brown **1** (6%), orange-red $Os_5(CO)_{14}PPh_3(\mu_4\text{-}S)$ (**4**)[6] (9%), green-brown **5**, brown **6**, and purple **3** (7%).[7] Compounds 5 and 6 are still under investigation. Compounds **1** and **3** have been characterized by IR and ^{31}P NMR spectroscopies,[7] elemental analyses,[8] and single-crystal X-ray diffraction analyses.[9] Compound **1** was found to be a structural analogue of **2** in which a $Pt(PPh_3)CO$ moiety was exchanged for one of the $Os(CO)_3$ units of the square base.[10,11]

Compound **3** is a hexanuclear species and its molecular structure is shown in the ORTEP diagram in Figure 1.[9,12] The cluster of

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(6) The identity of **4** was confirmed by an independent synthesis from the reaction of **2** with PPh_3. Anal. Calcd: C, 23.47; H, 0.92. Found: C, 23.60; H, 0.96.

(7) IR spectra were obtained on a Nicolet 5DXB FT-IR spectrometer in CH_2Cl_2 solvent. (CO) positions (cm^{-1}) are as follows: for **1**, 2087.4 (w), 2051.5 (s), 2019.7 (m), 1997.1 (w), 1972.9 (w); for **3**, 2064.5 (m), 2048.1 (s), 2035.9 (s), 2028.8 (s), 2017.1 (m), 1994.1 (m), 1971.9 (m), 1901.4 (w); for **4**, 2090.7 (s), 2055.8 (s), 2044.9 (s), 2028.9 (s), 2011.8 (s), 1996.4 (m), 1979.0 (m), 1977.0 (w), 1951.4 (w); for **5**, 2093.0 (w), 2086.6 (w), 2061.5 (s), 2050.9 (s), 2028.8 (s), 2021.8 (s), 2001.7 (w), 1792.7 (w); for **6**, 2076.3 (s), 2043.3 (s), 2029.4 (s), 2015.0 (s), 1986.1 (m), 1963.1 (m), 1903.9 (w), 1784.4 (w). ^{31}P NMR spectra in CD_2Cl_2 (δ vs. H_3PO_4): for **1**, 43.86 (t, J_{Pt-P} = 2601 Hz); for **3** 26.23 (t, J_{Pt-P} = 2442 Hz), 5.31 (s); for **4**, 35.34 (s).

(8) Elemental analyses were performed by MicAnal, Tucson, AZ. Anal. Cacld for **1**: C, 23.06; H, 0.93. Found: C, 22.95; H, 0.77. Calcd for **3**: C, 28.85; H, 1.41. Found: C, 29.12; H, 1.23. Calcd for **4**: C, 23.47; H, 0.92. Found: C, 23.6; H, 0.96.

(9) Intensity data were collected on an Enraf-Nonius CAD4 diffractometer by the Molecular Structure Corp., College Station, TX. Structure solutions and refinements were performed on a Digital Equipment Corp. VAX 11/782 computer by using the Enraf-Nonius program library SDP-Plus at the University of South Carolina. Diffraction data were corrected for the effects of absorption.

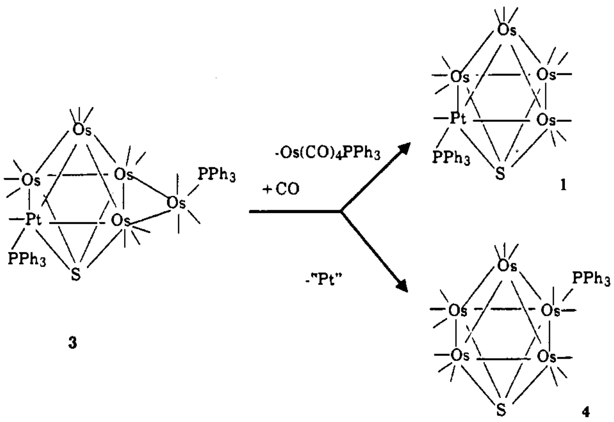
(10) Crystals of **1** were grown by slow evaporation of solvent from solutions in a CH_3OH/CH_2Cl_2 solvent mixture. The crystals belong to the triclinic space group $P\bar{1}$, No. 2, with a = 13.116 (4) Å, b = 9.655 (3) Å, c = 14.669 (4) Å, α = 89.68 (3)°, β = 104.79 (2)°, γ = 89.11 (3)°, Z = 2, and ρ_{calcd} = 2.99 g/cm³. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined by using 4505 reflections ($F^2 \geq 3.0\sigma(F^2)$) to the final residuals R = 0.044 and R_w = 0.052.

(11) Selected interatomic distances (Å) for **1** are Pt–Os(1) = 2.900 (1), Pt–Os(3) = 2.875 (1), Pt–Os(4) = 2.749 (1), Os(1)–Os(2) = 2.799 (1), Os(1)–Os(4) = 2.802 (1), Os(2)–Os(3) = 2.770 (1), Os(2)–Os(4) = 2.911 (1), Os(3)–Os(4) = 2.862 (1), Pt–S = 2.326 (3), Os(1)–S = 2.477 (3), Os(2)–S = 2.445 (4), and Os(3)–S = 2.499 (4).

0020-1669/86/1325-0004$01.50/0

3 is similar to that of **1**, consisting of a square-pyramidal $PtOs_4$ group with the platinum atom in the square base and the square base bridged by a sulfido ligand.[13] However, **3** contains in addition an $Os(CO)_3PPh_3$ group bridging one of the osmium–osmium bonds in the base of the square pyramid. This group was clearly formed by the extrusion of one of the $Os(CO)_3$ groups from the cluster in **2**. It was stabilized in the bridging site by the addition of a PPh_3 ligand. This is supported by the observation that the yield of **3** is increased to 18% when the reaction is performed in the presence of 1 equiv of PPh_3. All the osmium atoms have three carbonyl ligands except Os(4), which has only two. The platinum atom contains one carbonyl ligand acquired presumably by migration from the osmium atoms. Although all details of the formation of **3** are not yet clear, the formation of platinum–sulfur bonding must be accompanied by a platinum insertion into an osmium–osmium bond.

It is easy to envisage the formation of **1** from **3** by the removal of the *edge*-bridging $Os(CO)_3PPh_3$ moiety. This was accomplished in 45% yield by treatment of **3** with CO. The formation of **1** was accompanied by formation of a corresponding amount of $Os(CO)_4PPh_3$. Surprisingly, this reaction also produced large amounts of **4**, indicating that the extrusion of the platinum moiety was also facile even though it had been incorporated into the main body of the cluster. The platinum-containing product from the latter reaction has not been identified. The existence of platinum–sulfur bonding in **3** provides further support for the notion that bridging ligands can play important roles in metal–metal-exchange reactions.[3,4]



Acknowledgment. This research was supported by the National Science Foundation under Grant No. CHE-8416460.

Supplementary Material Available: ORTEP drawings and tables of final fractional atomic coordinates, bond distances, and bond angles for both structural analyses (17 pages). Ordering information is given on any current masthead page.

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(12) Crystals of **3** were grown from CH_2Cl_2/hexane solutions under a CO atmosphere at −30 °C. The crystals belong to the triclinic space group $P\bar{1}$, No. 2, with $a = 12.538$ (2) Å, $b = 15.908$ (2) Å, $c = 18.061$ (2) Å, $\alpha = 63.008$ (9), $\beta = 76.629$ (9)°, $\gamma = 65.68$ (1)°, $Z = 2$, and $\rho_{calcd} = 2.414$ g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined by using 4976 reflections ($F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals $R = 0.052$ and $R_w = 0.074$.

(13) Selected interatomic distances (Å) for **3** are Pt–Os(1) = 3.031 (1), Pt–Os(2) = 2.762 (1), Pt–Os(3) = 2.818 (1), Os(1)–Os(2) = 2.877 (1), Os(1)–Os(4) = 2.791 (1), Os(1)–Os(5) = 2.984(1), Os(2)–Os(3) = 2.896 (1), Os(2)–Os(4) = 2.823 (1), Os(3)–Os(4) = 2.719 (1), and Os(4)–Os(5) = 2.761 (1).

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

Richard D. Adams*
James E. Babin
Rahina Mahtab
Suning Wang

Received August 19, 1985

Mixed-Metal Gold Clusters. Synthesis and X-ray Structural Characterization of $[Au_5Re(H)_4(PPh_3)_7](PF_6)_2$ and $[Au_3Rh(H)(CO)(PPh_3)_5](PF_6)$

Sir:

There has been much recent interest in the synthesis and structural characterization of mixed transition metal gold clusters.[1-7] These compounds are important because of their potential use as bimetallic catalysts[8,9] and because of their intrinsically novel structures. The synthetic routes to these compounds have generally included (i) the combination of a carbonyl metalate with $AuPR_3X$, e.g. $[Os_4H_3(CO)_{12}]^- + AuClPPh_3 \rightarrow [Os_4H_3(CO)_{12}AuPPh_3]$,[11] and (ii) the replacement of metal hydrides by $AuPR_3$ units, e.g. $[(NO_3)Ir(PPh_3)_2H(AuPPh_3)_2]^+ + AuNO_3PPh_3 \rightarrow [(NO_3)Ir(PPh_3)_2(AuPPh_3)_3]^+$.[12] The structures of many of these clusters illustrate a close structural similarity between the hydride ligand and the $AuPR_3$ unit.[4,13]

It has become clear from the growing number of mixed-metal gold clusters that for many metals the transition metal to gold bond is thermodynamically favorable. In addition, bonds between gold atoms are favorable, as seen by the large number of stable gold phosphine clusters such as $[Au_9(PPh_3)_8]^{3+}$.[1,10] Gold clusters of this type have been synthesized by the reduction of $Au(PR_3)^+$ units; for example, the reaction of $AuNO_3PPh_3$ with $NaBH_4$ gives $[Au_9(PPh_3)_8](NO_3)_3$ in good yield.[10] Gold is partially reduced from +1 to $+^1/_3$ in this reaction. It therefore should be possible to synthesize large mixed-metal gold clusters by reaction of a coordinatively unsaturated mononuclear transition-metal hydride with a mononuclear gold(I) complex. In effect, the transition-metal hydride can reduce gold(I) and promote gold cluster growth. The coordinatively unsaturated transition-metal moiety that is produced by hydride loss or ligand dissociation can either trap a gold cluster fragment or participate directly in cluster growth, thereby forming a mixed-metal cluster. We have been successful with this conceptual approach and suggest that it is general for the synthesis of a large variety of mixed-metal gold clusters.

The reaction of 6 equiv of $AuNO_3PPh_3$ with a CH_2Cl_2 solution of $ReH_7(PPh_3)_2$[14] at −60 °C immediately gave a yellow solution. The addition of ethanol, removal of the CH_2Cl_2, and the addition of NH_4PF_6 yielded a precipitate. Yellow crystals of $[Au_5Re(H)_4(PPh_3)_7](PF_6)_2$ (**1**) were obtained in ca. 60% yield from a CH_2Cl_2–$(C_2H_5)_2O$ solvent mixture. The reaction of $RhH(CO)(PPh_3)_3$[15] with 1 equiv of $AuNO_3(PPh_3)$ in toluene solution at −78 °C yielded an orange-brown solid after gentle stirring for 12 h at 25 °C. A microcrystalline product was formed upon dissolving this solid in methanol and adding 2 equiv of KPF_6. Larger orange-brown crystals of $[Au_3Rh(H)(CO)(PPh_3)_5]PF_6$ (**2**) were obtained in 50% yield from a CH_2Cl_2–$(C_2H_5)_2O$ solvent mixture. All of the above manipulations were carried out under

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