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# Cluster Synthesis. 8. Synthesis and Crystal and Molecular Structures of the Sulfido-Bridged Platinum Osmium Carbonyl Cluster Compounds $PtOs_3(CO)_9L(PPh_3)(\mu_3\text{-}S)_2$ (L = CO, $PPh_3$)

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The sulfido-bridged platinum osmium carbonyl cluster compounds $PtOs_3(CO)_9L(PPh_3)(\mu_3\text{-}S)_2$ (**2**, L = CO; **3**, L = $PPh_3$) have been obtained in yields of 34% and 24%, respectively, from the reaction of $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) with $Pt(PPh_3)_2C_2H_4$ under a nitrogen atmosphere. From the same reaction under a CO atmosphere the yield of **2** is increased to 76% while the yield of **3** is decreased to 3%. Both **2** and **3** have been characterized by single-crystal X-ray diffraction analysis. Crystal data for **2**: space group $P\bar{1}$, $a = 8.944$ (2) Å, $b = 11.312$ (2) Å, $c = 17.058$ (3) Å, $\alpha = 76.20$ (2)°, $\beta = 85.06$ (2)°, $\gamma = 78.41$ (2)°, $Z = 2$, $\rho_{calcd} = 2.78$ g/cm$^3$. The structure was solved by the heavy-atom method and refined (3754 reflections) to the final values of the residuals $R_F = 0.032$ and $R_{wF} = 0.037$. Crystal data for **3**: space group $P2_1/n$, $a = 9.492$ (3) Å, $b = 31.220$ (11) Å, $c = 15.331$ (4) Å, $\beta = 99.34$°, $Z = 4$, $\rho_{calcd} = 2.38$ g/cm$^3$. The structure of **3** was solved by direct methods and refined (3561 reflections) to the final values of the residuals $R_F = 0.038$ and $R_{wF} = 0.038$. Compound **3** is simply a $PPh_3$ derivative of **2**. Both compounds consist of triangular clusters of one platinum and two osmium atoms, with the third osmium atom linked to one of the osmium atoms in the triangular group via a metal–metal bond and the two triply bridging sulfido ligands. The formation of **2** and **3** is believed to occur by insertion of a $PtL_2$ moiety into one of the Os–S bonds in **1** followed by ligand rearrangements.

## Introduction

Research on mixed-metal carbonyl cluster compounds is expanding at an enormous rate.[1-3] Recent studies have shown that the synthesis of these compounds is greatly facilitated by the use of bridging ligands. Of the various types of bridging ligands that have been used, the sulfido ligand has been shown to be especially valuable.[4-10] Sulfido ligands were employed in the synthesis of the first optically resolved chiral cluster compounds.[11]

We have recently shown that sulfido ligands can play an important role in the synthesis of higher nuclearity osmium carbonyl cluster compounds.[12-17] More recently, we have used these reagents to synthesize some new sulfido-bridged mixed-metal cluster compounds.[18,19] In this paper is described the reaction of the bis($\mu$-sulfido) osmium carbonyl cluster $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) with $Pt(PPh_3)_2C_2H_4$.

## Experimental Section

**General Procedures.** Reactions were routinely performed under a dry nitrogen atmosphere, unless otherwise specified. Reagent grade solvents were dried over molecular sieves and deoxygenated by purging with $N_2$ prior to use. CP grade CO gas was obtained from Linde and used without further purification. $Os_3(CO)_9(\mu_3\text{-}S)_2$[20] and $Pt(PPh_3)_2C_2H_4$[21] were prepared by published procedures. Triphenylphosphine was purchased from Aldrich Chemical Co. Precoated silica plates of layer thickness 0.25 mm were obtained from EM Science. Photolyses were carried out by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. IR spectra were recorded on a Nicolet 5-SX FTIR spectrophotometer. A Bruker WM500 FT-NMR spectrometer was used to obtain $^{31}P$ NMR spectra at 203 MHz, using 85% $D_3PO_4$ as the external reference.

**Reactions. $Os_3(CO)_9(\mu_3\text{-}S)_2$ (1) with $Pt(PPh_3)_2C_2H_4$.** In a typical reaction solid $Pt(PPh_3)_2C_2H_4$ (26 mg, 0.0348 mmol) was added to a THF solution (60 mL) of $Os_3(CO)_9(\mu_3\text{-}S)_2$ (30 mg, 0.0339 mmol) at 0 °C under $N_2$. A golden yellow solution resulted after 0.5 h of stirring at 0 °C. The reaction vessel was warmed to room temperature, and stirring was continued for 2 h, yielding an orange-yellow solution. After removal of the solvent in vacuo, the residue was extracted with a minimum quantity of $CH_2Cl_2$ to give an orange solution that was applied to silica TLC plates. Elution with 35% $CH_2Cl_2$ in hexane solution led to the isolation of compounds $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$ (4 mg (11%)), $PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$ (**2**) (16 mg (34%)), $PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$ (**3**) (13 mg (24%)), and 6 mg of an unidentified orange-red compound **4**. IR spectra in the CO stretching region (cm$^{-1}$): for $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$ in hexane, 2082 (s), 2051 (vs), 2023 (s), 2007 (s), 1989 (m), 1981 (w), 1965 (m); for **2** in hexane, 2087 (m), 2083 (w), 2062 (vs), 2050 (s), 2033 (s), 2007 (m), 2003 (sh, w) 1988 (s), 1983 (s), 1969 (w); for **3** in $CHCl_3$, 2067 (s), 2043 (s), 2029 (s), 2000 (m), 1978 (m), 1975 (m), 1969 (m), 1951 (br, w), 1942 (br, w); for **4** in $CHCl_3$, 2061 (vs), 2033 (m), 2022 (m), 1995 (w), 1978 (br, w), 1952 (sh, w) 1939 (sh, w). The $^{31}P$ NMR spectrum of **2** shows a triplet at $\delta$ 14.56 ($J_{Pt-P} = 3033$ Hz).

**1 with $Pt(PPh_3)_2C_2H_4$ under a CO Atmosphere.** To a CO-saturated THF solution (40 mL) of **1** at 0 °C (22 mg, 0.0248 mmol) was added solid $Pt(PPh_3)_2C_2H_4$ (28 mg, 0.0374 mmol). After the mixture was stirred at 0 °C for 15 min, the reaction vessel was slowly warmed

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**Table I.** Crystallographic Data for X-ray Diffraction Studies

| | 2 | 3 |
|---|---|---|
| | (A) Cell Parameters | |
| formula | $PtOs_3S_2PO_{10}C_{28}H_{15}$ | $PtOs_3S_2P_2O_9C_{45}H_{30}$ |
| temp (±3 °C) | 27 | 26 |
| space group | $P\bar{1}$ | $P2_1/n$ |
| $a$, Å | 8.994 (2) | 9.492 (3) |
| $b$, Å | 11.312 (2) | 31.220 (11) |
| $c$, Å | 17.058 (3) | 15.331 (4) |
| $\alpha$, deg | 76.20 (2) | 90.0 |
| $\beta$, deg | 85.06 (2) | 99.34 (2) |
| $\gamma$, deg | 78.41 (2) | 90.0 |
| $V$, Å$^3$ | 1640.6 (8) | 4483 (4) |
| $M_r$ | 1372.2 | 1606.5 |
| $Z$ | 2 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 2.78 | 2.38 |
| | (B) Measurement of Intensity Data | |
| radiation ($\lambda$, Å) | Mo K$\bar{\alpha}$ (0.710 73) | Mo K$\bar{\alpha}$ (0.710 73) |
| monochromator | graphite | graphite |
| detector aperture, mm | | |
| horiz ($A + B \tan\theta$): $A$, $B$ | 3.0, 1.0 | 3.0, 1.0 |
| vert | 4.0 | 4.0 |
| cryst faces | 001, 00$\bar{1}$, 100, $\bar{1}$00, 02$\bar{1}$, 0$\bar{2}$1 | 010, 0$\bar{1}$0, 021, 0$\bar{2}\bar{1}$, 0$\bar{2}$1, 1$\bar{1}$0, $\bar{1}$10 |
| cryst size, mm | 0.12 × 0.13 × 0.29 | 0.05 × 0.10 × 0.20 |
| crystal orientation directions, deg from $\phi$ axis | normal to 021, 9.9 | $a^*$, 5.8 |
| reflcns measd | $h,\pm k,\pm l$ | $h,k,\pm l$ |
| max 2$\theta$, deg | 48 | 46° |
| scan type | moving-cryst stationary-counter | moving-cryst stationary-counter |
| $\omega$-scan width ($A + 0.347 \tan\theta$), deg | 1.00 | 1.00 |
| bkgd | $^1/_4$ addnl scan at each end of scan | $^1/_4$ addnl scan at each end of scan |
| $\omega$-scan rate (variable), deg/mm: max, min | 10.0, 1.4 | 10.0, 1.5 |
| no. of reflcns measd | 5090 | 4791 |
| data used ($F^2 \geqslant 3.0\sigma(F^2)$) | 3754 | 3561 |
| | (C) Treatment of Data | |
| abs cor coeff, cm$^{-1}$ | 161.2 | 118.5 |
| grid | 8 × 20 × 6 | 14 × 4 × 14 |
| transmissn coeff: max, min | 0.22, 0.13 | 0.60, 0.16 |
| decay cor: max, min | 1.01, 0.97 | |
| $P$ factor | 0.02 | 0.022 |
| final residuals: $R_F$, $R_{wF}$ | 0.032, 0.037 | 0.038, 0.038 |
| esd of unit wt observn | 1.88 | 1.45 |
| largest shift/error value of final cycle | 0.01 | 0.03 |
| largest peak in final diff Fourier, e/Å$^3$ | 1.50 | 1.04 |

**Table II.** Positional and Thermal Parameters and Their Esds for $PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)$ (**2**)

| atom | $x$ | $y$ | $z$ | $B(1,1)$[a] | $B(2,2)$ | $B(3,3)$ | $B(1,2)$ | $B(1,3)$ | $B(2,3)$ | $B_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Pt | 0.07606 (5) | 0.19796 (4) | 0.22584 (3) | 2.59 (2) | 1.93 (2) | 2.98 (2) | 0.03 (2) | −0.21 (2) | −0.45 (2) | 2.58 (1) |
| Os(1) | 0.26711 (5) | −0.05004 (4) | 0.35762 (3) | 2.14 (2) | 2.63 (2) | 2.54 (2) | 0.01 (2) | −0.21 (2) | −0.54 (2) | 2.50 (1) |
| Os(2) | −0.00260 (5) | −0.04192 (4) | 0.27992 (3) | 2.03 (2) | 2.12 (2) | 3.26 (2) | −0.11 (2) | −0.20 (2) | −0.68 (2) | 2.49 (1) |
| Os(3) | 0.22746 (6) | 0.00618 (5) | 0.14387 (3) | 3.07 (2) | 2.69 (2) | 2.48 (2) | 0.10 (2) | −0.13 (2) | −0.83 (2) | 2.80 (1) |
| S(1) | 0.2424 (4) | −0.1657 (3) | 0.2592 (2) | 2.7 (1) | 2.4 (1) | 3.3 (1) | 0.3 (1) | −0.0 (1) | −0.9 (1) | 2.84 (7) |
| S(2) | 0.3289 (4) | 0.1018 (3) | 0.2349 (2) | 2.7 (1) | 2.5 (1) | 3.0 (1) | −0.1 (1) | −0.2 (1) | −0.5 (1) | 2.79 (7) |
| P | 0.1188 (4) | 0.3875 (3) | 0.2412 (2) | 3.2 (1) | 2.0 (1) | 3.1 (1) | −0.1 (1) | −0.1 (1) | −0.5 (1) | 2.83 (8) |

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0.196 (1) | −0.2654 (9) | 0.4885 (6) | 4.9 (2) | C(10) | −0.125 (2) | 0.256 (1) | 0.2018 (8) | 3.9 (3) |
| O(2) | 0.145 (1) | 0.1298 (9) | 0.4648 (6) | 4.8 (2) | C(11) | 0.223 (1) | 0.382 (1) | 0.3293 (7) | 3.2 (3) |
| O(3) | 0.600 (1) | −0.0927 (10) | 0.3976 (7) | 6.4 (3) | C(12) | 0.370 (2) | 0.309 (1) | 0.3399 (8) | 3.8 (3) |
| O(4) | −0.247 (1) | 0.0021 (10) | 0.1581 (7) | 6.9 (3) | C(13) | 0.447 (2) | 0.304 (1) | 0.4057 (9) | 4.6 (3) |
| O(5) | −0.086 (1) | −0.2792 (9) | 0.3819 (6) | 4.8 (2) | C(14) | 0.385 (2) | 0.369 (1) | 0.4634 (9) | 4.5 (3) |
| O(6) | −0.193 (1) | 0.1086 (9) | 0.3905 (6) | 4.7 (2) | C(15) | 0.242 (2) | 0.439 (1) | 0.4538 (9) | 4.5 (3) |
| O(7) | 0.056 (1) | −0.1281 (10) | 0.0583 (7) | 6.4 (3) | C(16) | 0.163 (2) | 0.445 (1) | 0.3876 (8) | 3.8 (3) |
| O(8) | 0.181 (1) | 0.2380 (9) | 0.0076 (6) | 5.4 (2) | C(21) | 0.221 (1) | 0.472 (1) | 0.1559 (8) | 3.3 (3) |
| O(9) | 0.529 (1) | −0.1012 (9) | 0.0727 (6) | 5.2 (2) | C(22) | 0.183 (2) | 0.474 (1) | 0.0798 (9) | 4.2 (3) |
| O(10) | −0.255 (1) | 0.2861 (9) | 0.1858 (6) | 5.5 (2) | C(23) | 0.246 (2) | 0.546 (2) | 0.0119 (10) | 5.9 (4) |
| C(1) | 0.221 (1) | −0.182 (1) | 0.4399 (7) | 3.0 (2) | C(24) | 0.355 (2) | 0.609 (1) | 0.0235 (9) | 5.3 (4) |
| C(2) | 0.192 (1) | 0.064 (1) | 0.4228 (8) | 3.5 (3) | C(25) | 0.392 (2) | 0.610 (1) | 0.0959 (10) | 5.6 (4) |
| C(3) | 0.472 (2) | −0.078 (1) | 0.3827 (9) | 4.8 (3) | C(26) | 0.326 (2) | 0.537 (1) | 0.1646 (9) | 4.2 (3) |
| C(4) | −0.152 (2) | −0.020 (1) | 0.2055 (9) | 4.8 (3) | C(31) | −0.061 (1) | 0.492 (1) | 0.2518 (7) | 2.7 (2) |
| C(5) | −0.056 (1) | −0.190 (1) | 0.3427 (8) | 3.3 (3) | C(32) | −0.099 (1) | 0.608 (1) | 0.1994 (8) | 3.5 (3) |
| C(6) | −0.121 (1) | 0.055 (1) | 0.3467 (7) | 3.1 (3) | C(33) | −0.242 (2) | 0.680 (1) | 0.2075 (10) | 5.2 (4) |
| C(7) | 0.122 (2) | −0.075 (1) | 0.0885 (9) | 4.4 (3) | C(34) | −0.341 (2) | 0.642 (1) | 0.2654 (10) | 5.6 (4) |
| C(8) | 0.194 (1) | 0.153 (1) | 0.0614 (8) | 3.7 (3) | C(35) | −0.309 (2) | 0.530 (1) | 0.3182 (9) | 5.2 (4) |
| C(9) | 0.412 (2) | −0.059 (1) | 0.0986 (8) | 3.7 (3) | C(36) | −0.167 (1) | 0.452 (1) | 0.311 (1) | 3.9 (3) |

[a] The form of the anisotropic thermal parameter is $\exp[^1/_4[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

**Table III.** Interatomic Distances (Å) with Esds for $Os_3Pt(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$ (2)

| | | | |
|---|---|---|---|
| Os(1)-Os(2) | 2.826 (1) | Os(3)-C(7) | 1.883 (12) |
| Os(1)···Os(3) | 3.585 (1) | Os(3)-C(8) | 1.895 (10) |
| Os(2)-Os(3) | 2.990 (1) | Os(3)-C(9) | 1.849 (9) |
| Os(1)···Pt | 3.401 (1) | Pt-C(10) | 1.831 (11) |
| Os(2)-Pt | 2.858 (1) | P-C(11) | 1.816 (10) |
| Os(3)-Pt | 2.905 (1) | P-C(21) | 1.824 (10) |
| Os(1)-S(1) | 2.409 (2) | P-C(31) | 1.818 (9) |
| Os(2)-S(1) | 2.399 (2) | C(1)-O(1) | 1.140 (11) |
| Os(3)-S(1) | 2.405 (2) | C(2)-O(2) | 1.147 (11) |
| Os(1)-S(2) | 2.471 (2) | C(3)-O(3) | 1.169 (12) |
| Os(3)-S(2) | 2.417 (2) | C(4)-O(4) | 1.172 (13) |
| Pt-S(2) | 2.305 (2) | C(5)-O(5) | 1.142 (10) |
| S(1)···S(2) | 3.196 (6) | C(6)-O(6) | 1.147 (10) |
| Pt-P | 2.330 (2) | C(7)-O(7) | 1.146 (12) |
| Os(1)-C(1) | 1.879 (9) | C(8)-O(8) | 1.153 (11) |
| Os(1)-C(2) | 1.889 (10) | C(9)-O(9) | 1.158 (11) |
| Os(1)-C(3) | 1.863 (12) | C(10)-O(10) | 1.184 (11) |
| Os(2)-C(4) | 1.862 (12) | C-$C_{av}$(11-16) | 1.37 (2) |
| Os(2)-C(5) | 1.884 (10) | C-$C_{av}$(21-26) | 1.37 (4) |
| Os(2)-C(6) | 1.882 (10) | C-$C_{av}$(31-36) | 1.38 (3) |

**Table IV.** Selected Interatomic Angles (deg) with Esds for $Os_3Pt(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$ (2)

| | | | |
|---|---|---|---|
| Os(1)-Os(2)-Os(3) | 76.03 (1) | S(1)-Os(2)-C(6) | 145.2 (3) |
| Os(1)-Os(2)-Pt | 73.50 (1) | Os(2)-Os(3)-C(7) | 86.6 (3) |
| Os(3)-Os(2)-Pt | 59.50 (1) | Os(2)-Os(3)-C(8) | 120.9 (3) |
| Os(2)-Os(3)-Pt | 57.99 (1) | Os(2)-Os(3)-C(9) | 144.5 (3) |
| Os(2)-Pt-Os(3) | 62.51 (1) | Pt-Os(3)-C(7) | 123.1 (3) |
| Os(1)-S(1)-Os(2) | 72.00 (6) | Pt-Os(3)-C(8) | 75.0 (3) |
| Os(1)-S(1)-Os(3) | 96.24 (8) | Pt-Os(3)-C(9) | 144.0 (3) |
| Os(2)-S(1)-Os(3) | 76.98 (7) | S(1)-Os(3)-S(2) | 83.01 (8) |
| Os(1)-S(2)-Os(3) | 94.34 (8) | S(1)-Os(3)-C(7) | 90.2 (3) |
| Os(1)-S(2)-Pt | 90.76 (8) | S(1)-Os(3)-C(8) | 172.0 (3) |
| Os(3)-S(2)-Pt | 75.89 (7) | S(1)-Os(3)-C(9) | 93.2 (3) |
| Os(1)-Os(2)-S(1) | 54.16 (6) | S(2)-Os(3)-C(7) | 169.4 (3) |
| Os(2)-Os(1)-S(1) | 53.85 (5) | S(2)-Os(3)-C(8) | 94.0 (3) |
| Os(2)-Os(3)-S(1) | 51.41 (5) | S(2)-Os(3)-C(9) | 97.5 (3) |
| Os(3)-Os(2)-S(1) | 51.60 (6) | Os(2)-Pt-C(10) | 86.8 (3) |
| Pt-Os(2)-S(1) | 98.81 (6) | Os(3)-Pt-C(10) | 113.9 (3) |
| Os(2)-Os(1)-S(2) | 82.81 (6) | Os(2)-Pt-P | 155.13 (6) |
| Os(2)-Os(3)-S(2) | 85.40 (6) | Os(3)-Pt-P | 137.01 (6) |
| Os(2)-Pt-S(2) | 87.78 (6) | S(2)-Pt-C(10) | 167.6 (3) |
| Os(3)-Pt-S(2) | 53.79 (6) | S(2)-Pt-P | 95.04 (8) |
| Os(2)-Os(1)-C(1) | 90.2 (3) | C(10)-Pt-P | 94.6 (3) |
| Os(2)-Os(1)-C(2) | 99.9 (3) | Pt-P-C(11) | 115.9 (3) |
| Os(2)-Os(1)-C(3) | 162.1 (4) | Pt-P-C(21) | 114.7 (3) |
| S(1)-Os(1)-S(2) | 81.80 (8) | Pt-P-C(31) | 110.7 (3) |
| S(1)-Os(1)-C(1) | 89.2 (3) | C(11)-P-C(21) | 105.0 (4) |
| S(1)-Os(1)-C(2) | 153.7 (3) | C(11)-P-C(31) | 104.5 (4) |
| S(1)-Os(1)-C(3) | 108.9 (4) | C(21)-P-C(31) | 105.1 (4) |
| Os(3)-Os(2)-C(4) | 89.7 (4) | Os(1)-C(1)-O(1) | 177.8 (9) |
| Os(3)-Os(2)-C(5) | 132.1 (3) | Os(1)-C(2)-O(2) | 177.1 (9) |
| Os(3)-Os(2)-C(6) | 134.5 (3) | Os(1)-C(3)-O(3) | 178.3 (11) |
| Os(1)-Os(3)-C(4) | 165.5 (4) | Os(2)-C(4)-O(4) | 175.2 (11) |
| Os(1)-Os(2)-C(5) | 98.3 (3) | Os(2)-C(5)-O(5) | 178.5 (8) |
| Os(1)-Os(2)-C(6) | 91.8 (3) | Os(2)-C(6)-O(6) | 176.7 (9) |
| Pt-Os(2)-C(4) | 97.0 (4) | Os(3)-C(7)-O(7) | 176.8 (11) |
| Pt-Os(2)-C(5) | 164.7 (3) | Os(3)-C(8)-O(8) | 174.8 (9) |
| Pt-Os(2)-C(6) | 75.0 (3) | Os(3)-C(9)-O(9) | 177.9 (10) |
| S(1)-Os(2)-C(4) | 118.5 (4) | Pt-C(10)-O(10) | 176.1 (10) |
| S(1)-Os(2)-C(5) | 86.1 (3) | | |

to room temperature, and stirring was continued for 2 h under a CO atmosphere. Chromatography of the golden yellow reaction solution on silica TLC plates using hexane/$CH_2Cl_2$ (75/25) separated trace amounts of unreacted $Os_3(CO)_9(\mu_3\text{-}S)_2$ from $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$ (3 mg (11%)), **2** (26 mg (76%)), and **3** (ca. 1 mg (3%)).

**2 with PPh$_3$.** A mixture of **2** (68 mg, 0.0495 mmol) and $PPh_3$ (19 mg, 0.0725 mmol) in hexane solution (100 mL) was refluxed for 3 h to yield a golden yellow solution. Chromatography of the mixture on silica TLC plates using hexane/$CH_2Cl_2$ (5/1) separated the unreacted **2** (25 mg (37%)) from $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$ (9 mg (17%)) and **3** (32 mg (40%)).

**2 with CO Gas.** No reaction occurred between compound **2** and CO gas at room temperature or in refluxing hexane temperature. A 20-mL solution of **2** (12 mg, 0.0087 mmol) in toluene was refluxed under an atmosphere of CO for 4.5 h. Chromatography of the resultant solution on silica TLC plates yielded $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$ (3 mg (31%)), $Os_3(CO)_9(\mu_3\text{-}S)_2$ (2 mg (26%)), and the unreacted **2** (ca. 1 mg (8%)) as the only isolable products.

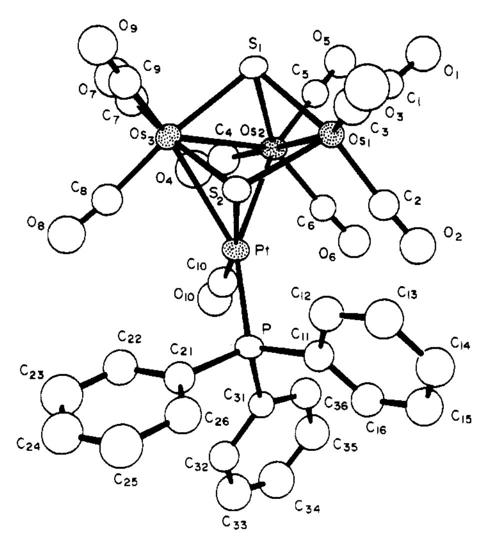

**Figure 1.** ORTEP diagram of $PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$ (**2**) showing 50% probability thermal ellipsoids.

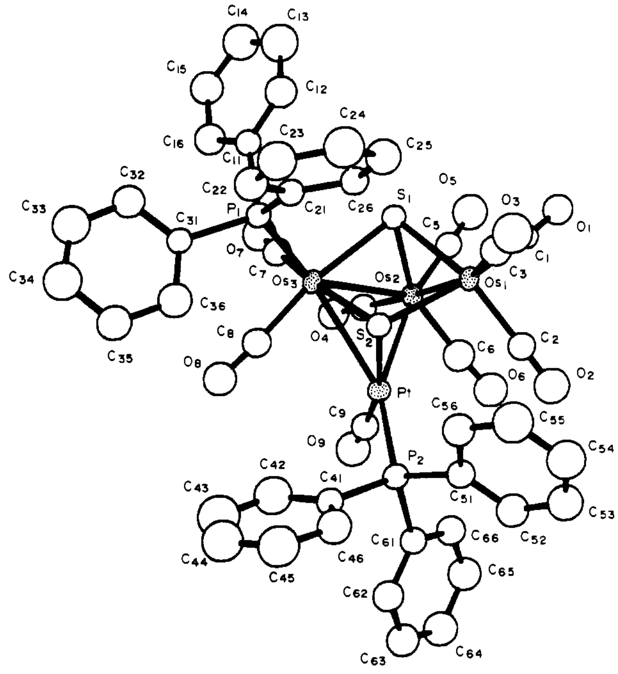

**Figure 2.** ORTEP diagram of $PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$ (**3**) showing 50% probability thermal ellipsoids.

**Crystallographic Analyses.** Golden yellow crystals of compounds **2** and **3** suitable for diffraction analysis were obtained from solutions in $CH_2Cl_2$/methanol at room temperature and $CH_2Cl_2$/hexane solvent by cooling to −10 °C, respectively. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital PDP 11/45 computer by using the Enraf-Nonius SDP program library (version 18). Absorption corrections of a Gaussian integration type were done for both structures. Neutral-atom scattering factors were calculated by the standard procedures.[22a] Anomalous

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[22] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Table V. Positional and Thermal Parameters and Their Esds for $PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$ (3)

| atom | *x* | *y* | *z* | *B*(1,1)[a] | *B*(2,2) | *B*(3,3) | *B*(1,2) | *B*(1,3) | *B*(2,3) | $B_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Pt | 0.75008 (7) | 0.08137 (2) | 0.18209 (4) | 1.85 (3) | 1.75 (3) | 3.08 (3) | 0.12 (3) | 0.88 (2) | −0.07 (3) | 2.18 (1) |
| Os(1) | 1.00252 (7) | 0.10085 (2) | 0.05914 (4) | 2.15 (3) | 2.02 (3) | 2.47 (3) | −0.19 (3) | 0.57 (2) | −0.32 (3) | 2.19 (1) |
| Os(2) | 0.70892 (7) | 0.09211 (2) | −0.00681 (4) | 1.72 (3) | 1.74 (3) | 2.58 (3) | 0.23 (3) | 0.58 (2) | −0.15 (3) | 1.99 (1) |
| Os(3) | 0.71961 (7) | 0.16815 (2) | 0.11349 (4) | 2.19 (3) | 2.08 (3) | 2.45 (3) | −0.11 (3) | 0.61 (2) | 0.16 (3) | 2.21 (1) |

| atom | *x* | *y* | *z* | *B*, Å$^2$ | atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| S(1) | 0.8459 (5) | 0.1567 (2) | −0.0091 (3) | 2.43 (9) | C(22) | 1.037 (2) | 0.2793 (7) | 0.237 (1) | 3.9 (4) |
| S(2) | 0.9270 (5) | 0.1325 (2) | 0.1928 (3) | 2.37 (9) | C(23) | 1.182 (2) | 0.2881 (8) | 0.259 (1) | 5.0 (5) |
| P(1) | 0.7980 (5) | 0.2388 (2) | 0.1392 (3) | 2.36 (9) | C(24) | 1.279 (2) | 0.2658 (8) | 0.219 (1) | 5.4 (5) |
| P(2) | 0.8454 (5) | 0.0494 (2) | 0.3160 (3) | 2.64 (10) | C(25) | 1.236 (2) | 0.2348 (7) | 0.157 (1) | 4.3 (5) |
| O(1) | 1.063 (1) | 0.0750 (4) | −0.1220 (7) | 3.9 (3) | C(26) | 1.087 (2) | 0.2256 (6) | 0.136 (1) | 2.9 (4) |
| O(2) | 1.072 (1) | 0.0106 (5) | 0.1252 (8) | 5.2 (3) | C(31) | 0.720 (2) | 0.2681 (6) | 0.226 (1) | 2.4 (4) |
| O(3) | 1.302 (2) | 0.1340 (5) | 0.1232 (9) | 5.9 (4) | C(32) | 0.672 (2) | 0.3099 (7) | 0.215 (1) | 3.9 (4) |
| O(4) | 0.385 (1) | 0.0983 (5) | −0.0459 (8) | 4.6 (3) | C(33) | 0.624 (2) | 0.3290 (8) | 0.286 (1) | 5.3 (5) |
| O(5) | 0.718 (2) | 0.0878 (5) | −0.2013 (9) | 6.0 (4) | C(34) | 0.629 (2) | 0.3105 (8) | 0.363 (1) | 5.3 (5) |
| O(6) | 0.721 (1) | −0.0046 (5) | 0.0180 (8) | 5.5 (4) | C(35) | 0.678 (2) | 0.2681 (7) | 0.376 (1) | 4.4 (5) |
| O(7) | 0.459 (1) | 0.1953 (5) | −0.0146 (8) | 5.2 (3) | C(36) | 0.726 (2) | 0.2465 (7) | 0.305 (1) | 4.4 (5) |
| O(8) | 0.537 (1) | 0.1658 (5) | 0.2592 (7) | 4.6 (3) | C(41) | 0.826 (2) | 0.0811 (6) | 0.413 (1) | 2.7 (4) |
| O(9) | 0.471 (1) | 0.0352 (5) | 0.1537 (8) | 5.4 (4) | C(42) | 0.701 (2) | 0.1035 (8) | 0.413 (1) | 5.6 (5) |
| C(1) | 1.039 (2) | 0.0831 (6) | −0.054 (1) | 2.5 (3) | C(43) | 0.680 (3) | 0.1271 (8) | 0.487 (1) | 6.6 (6) |
| C(2) | 1.051 (2) | 0.0445 (6) | 0.103 (1) | 3.1 (4) | C(44) | 0.789 (2) | 0.1294 (8) | 0.556 (1) | 6.0 (6) |
| C(3) | 1.188 (2) | 0.1212 (7) | 0.097 (1) | 3.7 (4) | C(45) | 0.915 (2) | 0.1097 (8) | 0.557 (1) | 5.8 (6) |
| C(4) | 0.510 (2) | 0.0957 (6) | −0.031 (1) | 3.3 (4) | C(46) | 0.934 (2) | 0.0846 (7) | 0.485 (1) | 4.2 (5) |
| C(5) | 0.712 (2) | 0.0881 (6) | −0.127 (1) | 3.3 (4) | C(51) | 1.035 (2) | 0.0358 (6) | 0.329 (1) | 3.0 (4) |
| C(6) | 0.711 (2) | 0.0325 (7) | 0.010 (1) | 4.6 (5) | C(52) | 1.083 (2) | −0.0058 (7) | 0.336 (1) | 4.1 (5) |
| C(7) | 0.556 (2) | 0.1856 (7) | 0.036 (1) | 3.5 (4) | C(53) | 1.230 (2) | −0.0131 (7) | 0.340 (1) | 4.6 (5) |
| C(8) | 0.610 (2) | 0.1655 (7) | 0.205 (1) | 3.5 (4) | C(54) | 1.322 (2) | 0.0190 (8) | 0.338 (1) | 5.3 (5) |
| C(9) | 0.581 (2) | 0.0519 (6) | 0.162 (1) | 3.3 (4) | C(55) | 1.279 (2) | 0.0606 (8) | 0.335 (1) | 5.8 (6) |
| C(11) | 0.760 (2) | 0.2723 (6) | 0.041 (1) | 2.6 (4) | C(56) | 1.134 (2) | 0.0699 (7) | 0.330 (1) | 3.8 (4) |
| C(12) | 0.860 (2) | 0.2834 (7) | −0.010 (1) | 4.0 (4) | C(61) | 0.760 (2) | −0.0021 (6) | 0.334 (1) | 2.9 (4) |
| C(13) | 0.825 (2) | 0.3025 (8) | −0.092 (1) | 5.7 (6) | C(62) | 0.722 (2) | −0.0125 (7) | 0.414 (1) | 3.8 (4) |
| C(14) | 0.686 (2) | 0.3150 (8) | −0.120 (1) | 5.5 (5) | C(63) | 0.658 (2) | −0.0517 (7) | 0.423 (1) | 4.4 (5) |
| C(15) | 0.584 (2) | 0.3069 (7) | −0.071 (1) | 4.7 (5) | C(64) | 0.635 (2) | −0.0795 (8) | 0.355 (1) | 5.2 (5) |
| C(16) | 0.615 (2) | 0.2844 (7) | 0.008 (1) | 4.0 (4) | C(65) | 0.672 (2) | −0.0691 (7) | 0.272 (1) | 4.9 (5) |
| C(21) | 0.989 (2) | 0.2483 (6) | 0.174 (1) | 2.6 (4) | C(66) | 0.733 (2) | −0.0303 (7) | 0.263 (1) | 3.7 (4) |

[a] The form of the anisotropic thermal parameter is $\exp[{}^1/_4[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

Table VI. Interatomic Distances (Å) with Esds for $PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$ (3)

| | | | |
|---|---|---|---|
| Os(1)–Os(2) | 2.819 (1) | S(1)···S(2) | 3.158 (9) |
| Os(1)···Os(3) | 3.612 (1) | C(1)–O(1) | 1.130 (4) |
| Os(2)–Os(3) | 2.998 (1) | C(2)–O(2) | 1.116 (18) |
| Os(1)···Pt | 3.336 (1) | C(3)–O(3) | 1.169 (18) |
| Os(2)–Pt | 2.878 (1) | C(4)–O(4) | 1.174 (16) |
| Os(3)–Pt | 2.904 (1) | C(5)–O(5) | 1.154 (15) |
| Os(1)–S(1) | 2.417 (4) | C(6)–O(6) | 1.167 (20) |
| Os(1)–S(2) | 2.484 (4) | C(7)–O(7) | 1.144 (16) |
| Os(2)–S(1) | 2.403 (4) | C(8)–O(8) | 1.171 (16) |
| Os(3)–S(1) | 2.414 (3) | C(9)–O(9) | 1.154 (17) |
| Os(3)–S(2) | 2.411 (4) | P(1)–C(11) | 1.818 (15) |
| Pt–S(2) | 2.304 (4) | P(1)–C(21) | 1.826 (14) |
| Os(1)–C(1) | 1.906 (13) | P(1)–C(31) | 1.864 (14) |
| Os(1)–C(2) | 1.915 (18) | P(2)–C(41) | 1.813 (15) |
| Os(1)–C(3) | 1.870 (18) | P(2)–C(51) | 1.828 (16) |
| Os(2)–C(4) | 1.868 (16) | P(2)–C(61) | 1.839 (16) |
| Os(2)–C(5) | 1.848 (15) | C–C$_{av}$(11–16) | 1.37 (3) |
| Os(2)–C(6) | 1.879 (20) | C–C$_{av}$(21–26) | 1.39 (2) |
| Os(3)–C(7) | 1.875 (17) | C–C$_{av}$(31–36) | 1.38 (4) |
| Os(3)–C(8) | 1.876 (15) | C–C$_{av}$(41–46) | 1.38 (2) |
| Pt–C(9) | 1.836 (17) | C–C$_{av}$(51–56) | 1.38 (3) |
| Os(3)–P(1) | 2.342 (4) | C–C$_{av}$(61–66) | 1.37 (2) |
| Pt–P(2) | 2.330 (4) | | |

dispersion corrections were applied to all non-hydrogen atoms.[22b] Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

For the analysis of **2**, all atoms heavier than oxygen were refined anisotropically and all other non-hydrogen atoms were refined isotropically. Positions of the hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. Because of the large size of **3** only the metal atoms were refined anisotropically.

Compound **2** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and subsequently confirmed by the successful solution and refinement of the structure. The structure was solved by the heavy-atom method. The results of the final refinement are given in Table I. Final fractional atomic coordinates for the non-hydrogen atoms are given in Table II. Interatomic distances and selected angles are given in Tables III and IV. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement.

For compound **3** the space group $P2_1/n$ was indicated by the systematic absences observed during the data collection. The structure of **3** was solved by a combination of direct methods and difference Fourier analysis. The coordinates of the metal atoms were obtained from an *E* map produced by the phasing (MULTAN) of 212 reflections ($E_{min} = 2.16$). The results of the final refinement are given in Table I. Fractional atomic coordinates for the non-hydrogen atoms are given in Table V. Interatomic distances and selected angles are listed in Tables VI and VII. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. Tables of structure factor amplitudes and positional parameters of the hydrogen atoms for both structural analyses are given in the supplementary material.

## Results

The reaction of $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) with $Pt(PPh_3)_2C_2H_4$ under a nitrogen atmosphere at room temperture yielded four isolable products. The two principal products have been identified as the new mixed-metal cluster compounds $PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$ (**2**) (34% yield) and $PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$ (**3**) (24% yield) on the basis of single-crystal

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(23) The identity of this compound as $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$ was established by a crystal structure analysis (space group $P2_1/c$, $a = 10.459$ (5) Å, $b = 9.705$ (7) Å, $c = 29.20$ (3) Å, $\beta = 94.50$ (5)°) and by an independent synthesis from the reaction of **1** with $PPh_3$.

**Table VII.** Selected Interatomic Angles (deg) with Esds for $PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$ (3)

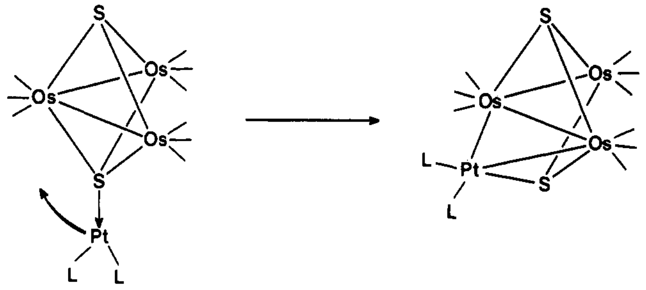
| | | | |
|---|---|---|---|
| Os(1)–Os(2)–Os(3) | 76.70 (2) | Pt–Os(2)–C(5) | 166.4 (5) |
| Os(2)–Os(3)–Pt | 58.36 (2) | Pt–Os(2)–C(6) | 75.5 (5) |
| Os(3)–Os(2)–Pt | 59.18 (2) | S(1)–Os(2)–C(4) | 118.6 (5) |
| Os(2)–Pt–Os(3) | 62.46 (2) | S(1)–Os(2)–C(5) | 87.0 (5) |
| Os(2)–Os(1)–S(1) | 53.97 (9) | S(1)–Os(2)–C(6) | 147.2 (6) |
| Os(2)–Os(1)–S(2) | 86.20 (9) | Os(2)–Os(3)–C(7) | 84.2 (5) |
| Os(1)–Os(2)–S(1) | 54.42 (9) | Os(2)–Os(3)–C(8) | 117.2 (5) |
| Os(3)–Os(2)–S(1) | 51.67 (8) | Pt–Os(3)–C(7) | 121.6 (5) |
| Pt–Os(2)–S(1) | 97.29 (8) | Pt–Os(3)–C(8) | 74.0 (5) |
| Os(2)–Os(3)–S(2) | 83.60 (9) | Os(2)–Os(3)–P(1) | 145.90 (9) |
| Pt–Os(3)–S(2) | 50.34 (10) | Pt–Os(3)–P(1) | 163.91 (10) |
| Os(2)–Os(3)–S(1) | 51.34 (10) | S(2)–Os(3)–C(7) | 167.8 (5) |
| Pt–Os(3)–S(1) | 96.37 (10) | S(2)–Os(3)–C(8) | 96.4 (5) |
| Os(2)–Pt–S(2) | 88.26 (9) | S(1)–Os(3)–C(7) | 90.8 (5) |
| Os(3)–Pt–S(2) | 53.68 (10) | S(1)–Os(3)–C(8) | 168.4 (5) |
| Os(1)–S(2)–Os(3) | 95.08 (12) | S(2)–Os(3)–P(1) | 97.97 (14) |
| Os(1)–S(2)–Pt | 88.25 (13) | S(1)–Os(3)–P(1) | 94.96 (13) |
| Os(3)–S(2)–Pt | 75.98 (12) | Os(2)–Pt–C(9) | 85.3 (4) |
| Os(1)–S(1)–Os(2) | 71.61 (11) | Os(3)–Pt–C(9) | 112.0 (5) |
| Os(1)–S(1)–Os(3) | 96.80 (13) | Os(2)–Pt–P(2) | 155.05 (11) |
| Os(2)–S(1)–Os(3) | 76.98 (11) | Os(3)–Pt–P(2) | 136.09 (11) |
| S(1)–Os(1)–S(2) | 80.22 (12) | S(2)–Pt–C(9) | 165.6 (5) |
| S(1)–Os(3)–S(2) | 81.75 (12) | S(2)–Pt–P(2) | 93.42 (14) |
| Os(2)–Os(1)–C(1) | 87.8 (4) | Os(3)–P(1)–C(11) | 112.8 (5) |
| Os(2)–Os(1)–C(2) | 101.9 (5) | Os(3)–P(1)–C(21) | 118.3 (5) |
| Os(2)–Os(1)–C(3) | 165.6 (5) | Os(3)–P(1)–C(31) | 115.5 (5) |
| S(2)–Os(1)–C(1) | 170.6 (5) | Pt–P(2)–C(41) | 114.2 (5) |
| S(2)–Os(1)–C(2) | 99.1 (6) | Pt–P(2)–C(51) | 115.6 (5) |
| S(2)–Os(1)–C(3) | 89.5 (5) | Pt–P(2)–C(61) | 112.8 (5) |
| S(1)–Os(1)–C(1) | 90.4 (5) | Os(1)–C(1)–O(1) | 175.9 (14) |
| S(1)–Os(1)–C(2) | 155.8 (5) | Os(1)–C(2)–O(2) | 175.0 (16) |
| S(1)–Os(1)–C(3) | 111.7 (5) | Os(1)–C(3)–O(3) | 178.0 (14) |
| Os(1)–Os(2)–C(4) | 166.8 (5) | Os(2)–C(4)–O(4) | 179.5 (10) |
| Os(1)–Os(2)–C(5) | 101.0 (5) | Os(2)–C(5)–O(5) | 175.9 (15) |
| Os(1)–Os(2)–C(6) | 93.4 (6) | Os(2)–C(6)–O(6) | 174.8 (17) |
| Os(3)–Os(2)–C(4) | 90.3 (5) | Os(3)–C(7)–O(7) | 176.5 (15) |
| Os(3)–Os(2)–C(5) | 131.4 (5) | Os(3)–C(8)–O(8) | 176.2 (15) |
| Os(3)–Os(2)–C(6) | 134.5 (5) | Pt–C(9)–O(9) | 175.4 (14) |
| Pt–Os(2)–C(4) | 99.9 (4) | | |

X-ray diffraction analyses. One minor product has been identified as $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$,[23] a $PPh_3$ derivative of $Os_3(CO)_9(\mu_3\text{-}S)_2$. Due to an inability to obtain single crystals, a fourth compound, **4**, has not been completely characterized yet. Since **3** is simply a $PPh_3$ derivative of **2**, the structures of both compounds will be described jointly.

ORTEP diagrams of the molecular structures of **2** and **3** are shown in Figures 1 and 2, respectively. Final fractional atomic coordinates and interatomic distances and angles for **2** are listed in Tables II–IV. Final fractional atomic coordinates and interatomic distances and angles for **3** are listed in Tables V–VII.

Both compounds consist of open tetranuclear clusters containing one platinum and three osmium atoms. The platinum and two osmium atoms Os(2) and Os(3) form a triangular group of three, with the third osmium Os(1) bonded to only Os(2) of this group. The platinum–osmium bonds are slightly unequal: Pt–Os(2) = 2.858 (1) Å [2.878 (1) Å] vs. Pt–Os(3) = 2.905 (1) Å [2.904 (1) Å]. Here and in all cases that follow, the value within brackets is the corresponding value for compound **3**. These distances are slightly longer than those observed in the tetrahedral $PtOs_3$ clusters in the compounds $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$, which ranged from 2.740 (1) to 2.853 (1) Å,[19] and $H_2PtOs_3(CO)_{10}[P(C_6H_{11})_3]$, 2.791 and 2.832 (1) Å.[24] The two osmium–osmium distances are considerably different. The shorter bond, Os(1)–Os(2) = 2.826 (1) Å [2.819 (1) Å], is very similar to that observed in compound **1**, 2.813 (1) Å.[25] The longer bond, Os(2)–Os(3) = 2.990 (1) Å [2.998 (1) Å], is significantly longer than that found in $Os_3(CO)_{12}$, 2.877 (3) Å,[26] but is not as long as the unusually long osmium–osmium bonds, 3.002 (1) and 3.091 (1) Å, found in the electron-rich cluster $Os_4(CO)_{12}(\mu_3\text{-}S)_2$.[27] The significant difference between the Os(1)–Os(2) and Os(2)–Os(3) bond lengths in **2** and **3** may be a result of steric crowding effects. Specifically, the crowding between Os(1), which is six-coordinate, and Os(2), which is seven-coordinate, should be considerably less than that between Os(2) and Os(3), which are both seven-coordinate. The Os(1)···Os(3) and Os(1)···Pt distances, 3.585 (1) Å [3.612 (1) Å] and 3.401 (1) Å [3.336 (1) Å], are probably completely nonbonding. Osmium Os(1) is further tied to the rest of the cluster via the bridging sulfido ligands S(1) and S(2). S(1) serves as a triple bridge across the three osmium atoms, while S(2) serves as a triple bridge across the Os(1), Os(3), and Pt atoms. The Os(1)–S(2) distance, 2.471 (2) Å [2.484 (4) Å], is significantly longer than all the remaining Os–S distances that span the narrow range 2.399 (2)–2.417 (2) Å in both **2** and **3**. Nevertheless, these distances are not greatly different from those found in **1**.[25] As expected, the platinum–sulfur distance, 2.305 (2) Å [2.304 (4) Å], is significantly shorter than the osmium–sulfur distances.[28]

**Scheme I**



The platinum atom contains one $PPh_3$ ligand, Pt–P = 2.330 (2) Å [2.330 (4) Å]. In **3** a second $PPh_3$ ligand is coordinated to osmium Os(3), Os(3)–P(1) = 2.342 (1) Å. Compound **2** has 10 linear terminal carbonyl ligands, while compound **3** has only nine.

## Discussion

The two principal products obtained from the reaction of **1** with $Pt(PPh_3)_2C_2H_4$ are the mixed-metal cluster compounds **2** and **3**. The cluster cores can be formed simply by the insertion of a $PtL_2$ moiety, formed by the loss of $C_2H_4$ from $Pt(PPh_3)_2C_2H_4$, into an osmium–sulfur bond to the central osmium atom in the cluster of **1** (Scheme I). This may be preceded by an initial coordinative interaction between the lone pair of electrons on the sulfido ligand and the unsaturated $PtL_2$ moiety. In contrast, when solutions of **1** and $Os(CO)_5$ are photolyzed, the compound $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ is formed by insertion of an $Os(CO)_4$ group into one of the metal–metal bonds in **1**.[15] In both **2** and **3** the platinum atom contains a CO ligand and only one $PPh_3$ ligand. The loss of one $PPh_3$ ligand from the platinum atom may be induced by increased steric interaction in the initial product. The addition of the CO ligand to the platinum atom could occur by a ligand shift from one of the osmium atoms (e.g., Os(3)). Addition of $PPh_3$ or CO to the osmium atom could then yield **3** or **2**, respectively. Adventitious CO should be produced in the reaction of **1** with $PPh_3$, which leads to the formation of the minor product,

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$Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$. Indeed, when the reaction is performed under a CO atmosphere, the yield of **2** is greatly increased. The tendency to form mixed-metal clusters in the reaction of **1** with $Pt(PPh_3)_2C_2H_4$ is to be contrasted with the reaction of $Os_3(CO)_{12}$ with $Pt(PR_3)_4$ compounds, which yields only the phosphine-substituted derivatives $Os_3(CO)_{12-x}(PR_3)_x$ ($x = 1, 2$).[29]

Although the reaction of iron chalcogenide analogues of **1**, $Fe_3(CO)_9(\mu_3\text{-}E)_2$ (E = S, Te), does yield mixed-metal clusters upon reaction with $Pt(PPh_3)_2C_2H_4$, in these cases the iron cluster undergoes fragmentation and yields the diiron complexes $Fe_2(CO)_6(\mu_3\text{-}E)_2Pt(PPh_3)_2$.[30]

Compounds **2** and **3** are both 64-electron clusters. Thus, for all the metal atoms to obey the effective atomic number rule the cluster should contain only four metal–metal bonds, as is observed. In contrast, however, the isoelectronic compounds $Os_4(CO)_{12}(\mu_3\text{-}S)_2$[27] and $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$[18] both contain butterfly clusters of four metal atoms that have five metal–metal bonds. These compounds alternatively adhere to the bonding requirements of the polyhedral skeletal electron pair (PSEP) theory. Compounds **2** and **3** could adopt analogous structures that obey the PSEP theory simply by forming a bond between osmium Os(1) and the platinum atom but instead opt for the more open electron-precise structure that is observed.

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**Registry No.** **1**, 72282-40-7; **2**, 92763-25-2; **3**, 93403-89-5; $Pt(PPh_3)_2C_2H_4$, 12120-15-9; $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$, 93403-90-8; Os, 7440-04-2; Pt, 7440-06-4.

**Supplementary Material Available:** Tables of structure factor amplitudes and hydrogen atom parameters for both structure analyses (34 pages). Ordering information is given on any current masthead page.

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# Synthesis and Structure of New Trinuclear Cluster Compounds $[M_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (M = Mo, W). Comparison of Mo and W Bond Radii as a Function of M–M Bond Order

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The autoclave reaction at 160 °C of butyric acid with either $W(CO)_6$ or $Mo_2(O_2CMe)_4$ leads, after suitable workup, to compounds containing the trinuclear cluster cations $[M_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (M = W, Mo). The compounds have been fully characterized by spectroscopic methods as well as by a crystal structure determination. $[W_3O_2(O_2CC_3H_7)_6(H_2O)_3](CF_3SO_3)_2\cdot 2H_2O$ (**1**) is monoclinic, with $C2/c$, $a = 24.434$ (4) Å, $b = 23.628$ (5) Å, $c = 20.790$ (4) Å, $\beta = 124.61$ (1)°, and $Z = 8$. Crystals of $[Mo_3O_2(O_2CC_3H_7)_6(H_2O)_3](ClO_4)_2\cdot 3H_2O$ (**2**) are cubic, with $P2_13$, $a = 16.272$ (3) Å, and $Z = 4$. Bond distances and angles in both compounds along with those determined on similar compounds establish that there is a consistent difference of 0.016 [3] Å between the W–W and Mo–Mo bond lengths, with the W–W bonds being the shorter ones. This bond radius relationship, $r(Mo)/r(W) > 1$, is probably general for long (ca. 2.70 Å) M–M bonds and for single M–X bonds, whereas for M–M triple and quadruple bonds the ratio is <1. The value of unity is apparently encountered in the range 2.70–2.50 Å.

## Introduction

As part of our continuing investigation of triangular trinuclear cluster compounds of molybdenum and tungsten,[2] we are always interested in preparative methods that allow preparation of new compounds or the preparation of known compounds more efficiently. As a general proposition, the use of an autoclave (pressure bomb) to contain a mixture of a carboxylic acid and some lower valent compound of the metal seemed to have practical advantages. For example, if the metal carbonyl, $Mo(CO)_6$ or $W(CO)_6$, is to be used as a starting material, an open, refluxing system is very messy to operate since the volatile carbonyl must be mechanically (manually) returned to the pot at frequent intervals. While the problem is tractable with a lower boiling acid (e.g., acetic acid (118 °C) or propionic acid (141 °C)), it becomes very bothersome with higher boiling acids. Actually, the use of a sealed reaction container for reactions with $W(CO)_6$ was first described in 1971,[3] but the results were inconclusive because the proper workup procedures employing cation-exchange resins were not then in use. Indeed, a secondary goal in the present work was to show that a representative compound reported in ref 3, when suitably worked up, is a $[W_3O_2(O_2CR)_6L_3]^{2+}$ compound. We have also further tested the possibility of using $Mo_2(O_2CCH_3)_4$ rather than $Mo(CO)_6$ as a starting material[4] with only the carboxylic acid as the oxidizing agent to obtain the $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ ion. Finally, with the additional structural results available from this work, we have examined how the ratio of bond radii for molybdenum and tungsten varies with the lengths of the bonds.

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