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Ligand Substitution Reactons in Electron-Rich Clusters. The Synthesis, Structures, and Bonding of Os$_4$(CO)$_{12}$L(μ_3-S)$_2$ and Os$_4$(CO)$_{11}$L(μ_3-S)$_2$ (L = PMe$_2$Ph and CN-*t*-Bu)

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The compounds Os$_4$(CO)$_{12}$L(μ_3-S)$_2$ (**2a**, L = PMe$_2$Ph; **2b**, L = CN-*t*-Bu) have been synthesized by ligand addition to Os$_4$(CO)$_{12}$(μ_3-S)$_2$ (**1**). Both compounds have been characterized by single-crystal X-ray diffraction analyses. For **2a**: space group $P2_1/a$, a = 17.941 (8) Å, b = 8.957 (3) Å, c = 17.949 (7) Å, β = 99.75 (4)°, Z = 4, ρ_{calcd} = 3.04 g/cm^3. The structure was solved by direct methods and refined (3542 reflections) to the final values for the residuals R_F = 0.041 and R_{wF} = 0.046. For **2b**: space group $P2_1/n$, a = 15.113 (6) Å, b = 10.798 (9) Å, c = 18.659 (6) Å, β = 102.33 (3)°, Z = 4, ρ_{calcd} = 2.87 g/cm^3. The structure was solved by direct methods and refined (1939 reflections) to the final values of the residuals R_F = 0.047 and R_{wF} = 0.050. Both **2a** and **2b** contain open-planar clusters of four osmium atoms with three metal–metal bonds. Triply bridging sulfido ligands are symmetrically disposed on each side of the Os$_4$ plane. When heated to 125 °C, **2a** and **2b** lose CO and are converted in high yield to Os$_4$(CO)$_{11}$L(μ_3-S)$_2$ (**3a**, L = PMe$_2$Ph; **3b**, L = CN-*t*-Bu). **3a** and **3b** were both characterized by single-crystal X-ray diffraction analyses. For **3a**: space group $P\bar{1}$, a = 8.994 (5) Å, b = 10.057 (3) Å, c = 15.048 (7) Å, α = 99.62 (4)°, β = 92.22 (4)°, γ = 92.55 (5)°, Z = 2, ρ_{calcd} = 3.15 g/cm^3. The structure was solved by the heavy-atom method and refined (3110 reflections) to the final values of the residuals R_F = 0.040 and R_{wF} = 0.046. For **3b**: space group *Pbca*, a = 23.819 (15) Å, b = 11.524 (10) Å, c = 18.497 (9) Å, Z = 8, ρ_{calcd} = 3.18 g/cm^3. The structure was solved by direct methods and refined (1815 reflections) to the final values of the residuals R_F = 0.042 and R_{wF} = 0.039. **3a** and **3b** both contain butterfly tetrahedral clusters of four metal atoms with triply bridging sulfido ligands on the two open-triangular faces. In both compounds two of the five metal–metal bonds are elongated, but in **3a** they are nearly equal in length, 2.987 (1) and 3.013 (1) Å, while in **3b** they are significantly different length, 2.965 (1) and 3.115 (1) Å.

Introduction

The ligand substitution reaction represents one of the most basic processes for the introduction of a new molecule into a metal-containing complex.[1] A variety of mechanisms have been established for the reactions of mononuclear metal complexes. For polynuclear metal complexes the mechanistic possibilities are even more diverse.[2] One of the more intriguing of these is that which involves a sequence of a ligand addition accompanied by the cleavage of a metal–metal bond and a ligand elimination followed by a reformation of the metal–metal bond. A number of examples of such reactions in which well-defined intermediates have been isolated and characterized have been reported in recent years.[3-5]

We have recently reported the synthesis and characterization of the electron-rich clusters Os$_4$(CO)$_{12}$(μ_3-S)$_2$,[6] **1**, and Os$_3$W(CO)$_{12}$(PMe$_2$Ph)(μ_3-S)$_2$.[7] Both compounds have some usually long metal–metal bonds, and despite their apparent electron richness, they both exhibit an anomalously high reactivity toward the addition of electron pair donor ligands. In this report are described the synthesis and crystal structure analyses of the compounds Os$_4$(CO)$_{12}$(L)(μ_3-S)$_2$ (**2a**, L = PMe$_2$Ph: **2b**, L = CN-*t*-Bu) formed by the addition of PMe$_2$Ph and CN-*t*-Bu, respectively, to **1** and the crystal structure analyses of the compounds Os$_4$(CO)$_{11}$(L)(μ_3-S)$_2$ (**3a**, L = PMe$_2$Ph; **3b**, L = CN-*t*-Bu) formed by the elimination of CO from **2a** and **2b**, respectively.

Experimental Section

All the products are air stable; however, the reactions were performed under a prepurified nitrogen atmosphere. The solvents were stored over 4-Å molecular sieves and were degassed with a dispersed stream of nitrogen gas before use. Infrared spectra were recorded on a Nicolet 5SX FT-IR spectrophotometer. A Bruker WM 500 FT-NMR spectrometer was used to obtain ^{1}H NMR spectra at 500 MHz. Os$_4$(CO)$_{12}$(μ_3-S)$_2$ was prepared as previously reported.[8] PMe$_2$Ph and CN-*t*-Bu were purchased from Strem Chemicals, Inc., Danvers, MA.

Preparation of Os$_4$(CO)$_{12}$(PMe$_2$Ph)(μ_3-S)$_2$ (2a). A 0.035-g (0.030-mmol) sample of Os$_4$(CO)$_{12}$(μ_3-S)$_2$ was dissolved in 25 mL of CH$_2$Cl$_2$ in a round-bottom flask at room temperature. PMe$_2$Ph (5 μL) was added via syringe, and the mixture was stirred for 2 days at room temperture. The solvent was removed in vacuo, and the residue was dissolved and chromatographed on silica TLC plates with hexane/CH$_2$Cl$_2$ (90/10) solvent. This separated the starting material (0.008 g) from the product Os$_4$(CO)$_{12}$(PMe$_2$Ph)(μ_3-S)$_2$ (**2a**): yield 0.020 g (0.015 mmol, 50%); IR (ν(CO) in hexane) 2101 (w), 2060 (s), 2050 (sh), 2046 (m), 2029 (sh), 2021 (vs), 2015 (m), 1984 (m), 1965 (w) cm^{-1}; ^{1}H NMR (in CD$_2$Cl$_2$) δ 7.49–7.47 (m, 5 H), 2.01 (d, 3 H, $J_{\mathrm{P-H}}$ = 10 Hz), 1.99 (d, 3 H, J = 10 Hz).

Preparation of Os$_4$(CO)$_{11}$(PMe$_2$Ph)(μ_3-S)$_2$ (3a). A 0.020-g (0.015-mmol) sample of Os$_4$(CO)$_{12}$(PMe$_2$Ph)(μ_3-S)$_2$ (**2a**) was refluxed in 30 mL of octane for 3 h. The solvent was removed in vacuo, and the residue was chromatographed on silica TLC plates with hexane/CH$_2$Cl$_2$ (98/2) solvent. The product was recrystallized from hexane/CH$_2$Cl$_2$ (8/2). Os$_4$(CO)$_{11}$(PMe$_2$Ph)(μ_3-S)$_2$ (**3a**): yield 0.018 g (0.014 mmol, 94%); IR (ν(CO) in hexane) 2093 (w), 2060 (vs), 2050 (vs), 2015 (s), 2007 (w), 1994 (w), 1981 (w) cm^{-1}; ^{1}H NMR (in CDCl$_3$) δ 7.74–7.49 (m, 5 H), 2.62 (d, 6 H, $J_{\mathrm{P-H}}$ = 10.5 Hz).

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Table I. Crystallographic Data for X-ray Diffraction Studies

	2a	3a	2b	3b
		(A) Crystal Data		
formula	$Os_4S_2PO_{12}C_{20}H_{11}$	$Os_4S_2PO_{11}C_{19}H_{11}$	$Os_4S_2O_{12}NC_{17}H_9 \cdot 0.5C_6H_{14}$	$Os_4S_2O_{11}NC_{16}H_9$
temp, ± 3 °C	24	22	25	24
space group	$P2_1/a$	$P\bar{1}$	$P2_1/n$, No. 14	$Pbca$, No. 61
a, Å	17.941 (8)	8.994 (5)	15.113 (6)	23.819 (15)
b, Å	8.957	10.057 (3)	10.798 (9)	11.524 (10)
c, Å	17.949 (7)	15.048 (7)	18.659 (6)	18.497 (9)
α, deg	90.00	99.62 (4)	90.0	90.0
β, deg	99.75 (4)	92.22 (4)	102.33 (3)	90.0
γ, deg	90.00	92.55 (5)	90.0	90.0
V, Å^3	2834 (4)	1339 (2)	2975 (5)	5077 (10)
M_r	1299.2	1271.2	1287.3	1216.2
Z	4	2	4	8
ρ_{calcd}, g/cm^3	3.04	3.15	2.87	3.18
		(B) Measurement of Intensity Data		
radiatn	Mo $K\bar{\alpha}$ (0.710 73 Å)	Mo $K\bar{\alpha}$ (0.710 73 Å)	Mo $K\bar{\alpha}$ (0.710 73 Å)	Mo $K\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite	graphite	graphite	graphite
detector aperture, mm horizontal ($A + B \tan \theta$)				
A	3.0	2.6	3.0	3.0
B	1.0	1.2	1.0	1.0
vertical	4.0	4.0	4.0	4.0
cryst faces	001, $00\bar{1}$, 110, $\bar{1}\bar{1}0$, $40\bar{1}$, $\bar{4}01$	010, $0\bar{1}0$, 011, $0\bar{1}\bar{1}$, 001, $0\bar{1}1$, $01\bar{1}$, 100 $\bar{1}00$	$\bar{1}01$, $10\bar{1}$, 201, $\bar{2}0\bar{1}$, 001, $2\bar{2}1$, $\bar{2}2\bar{1}$, $\bar{1}10$	001, $00\bar{1}$, $\bar{1}00$, 100, $\bar{1}\bar{1}0$, 110
cryst size, mm	0.17 × 0.20 × 0.30	0.09 × 0.18 × 0.32	0.12 × 0.14 × 0.18	0.11 × 0.12 × 0.17
cryst orientatn directn, deg from θ axis	normal to $2\bar{1}\bar{1}$; 20.0	a^*; 6.3	b; 2.5	b; 4.9
reflctns measd	$h,k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,+l$
max 2θ, deg	50	48	47	46
scan type	moving crystal-stationary counter	moving crystal-stationary counter	moving crystal-stationary counter	moving crystal-stationary counter
ω scan width (A + 0.347 tan θ), deg	0.95	1.00	1.00	1.00
background	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan
ω scan rate (variable)				
max deg/min	10.0	10.0	10.0	10.00
min deg/min	1.4	1.5	1.5	1.25
no. of reflctns measd	5529	4179	4798	3959
data used ($F^2 \geq 3.0\sigma(F^2)$)	3542	3110	1939	1815
		(C) Treatment of Data		
abs correctn				
coeff cm^{-1}	181.0	192.1	172.5	202.0
grid	14 × 8 × 8	12 × 6 × 12	8 × 12 × 10	8 × 14 × 8
transmissn coeff				
max	0.112	0.23	0.25	0.18
min	0.046	0.03	0.13	0.04
P factor	0.02	0.03	0.03	0.01
final residuals R_F	0.041	0.040	0.047	0.042
R_{wF}	0.046	0.046	0.050	0.039
esd of unit weight observn	2.23	1.92	1.65	1.82
largest shift/error value of final cycle	0.05	0.02	0.10	0.04
largest peak in final diff Fourier, e/Å^3	1.9	3.0	2.3	1.8

Preparation of $Os_4(CO)_{12}$(CN-*t*-Bu)(μ_3-S)$_2$ (2b). A 0.035-g (0.03-mmol) sample of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ was dissolved in 25 mL of CH_2Cl_2 in a round-bottom flask at room temperature. CN-*t*-Bu (35 μL) was added via syringe, and the mixture was stirred for 2 days at room temperature. The solvent was removed in vacuo, and the residue was dissolved and chromatographed on silica TLC plates with hexane/CH_2Cl_2 (90/10). This separated the starting material (0.016 g) from the product $Os_4(CO)_{12}$(CN-*t*-Bu)(μ_3-S)$_2$ (**2b**): yield 0.015 g (0.012 mmol, 40%); IR (ν(CN) in hexane) 2181 (w) cm^{-1}, (ν(CO) in hexane) 2101 (m), 2061 (s), 2048 (m), 2035 (m), 2021 (vs), 2015 (m), 1999 (w), 1987 (m), 1976 (w), 1918 (w) cm^{-1}; ^{1}H NMR (in $CDCl_3$) δ 1.53 (s, 9 H).

Preparation of $Os_4(CO)_{11}$(CN-*t*-Bu)(μ_3-S)$_2$ (3b). A 0.015-g (0.012-mmol) sample of $Os_4(CO)_{12}$(CN-*t*-Bu)(μ_3-S)$_2$ (**3a**) was refluxed in 30 mL of octane for 3 h. The solvent was removed in vacuo, and the residue was chromatographed on silica TLC plates with hexane/CH_2Cl_2 (95/5) solvent. The product was recrystallized from hexane/CH_2Cl_2 (9/1). $Os_4(CO)_{11}$(CN-*t*-Bu)(μ_3-S)$_2$ (**3b**): yield 0.014 g (0.0115 mmol, 96%); IR (ν(CN) in hexane) 2181 cm^{-1}, (ν(CO) in hexane) 2093 (m), 2061 (vs), 2052 (vs), 2031 (w), 2023 (s), 2009 (m), 1995 (m), 1989 (sh), 1984 (m), 1966 (w), cm^{-1}; ^{1}H NMR (in $CDCl_3$) δ 1.53 (s, 9 H).

Crystallographic Analyses. Red crystals of each of the compounds **2a**, **2b**, and **3b** suitable for diffraction analysis were obtained by slow evaporation of solvent from CH_2Cl_2/hexane solutions at 4 °C. Red crystals of **3a** were obtained by slow evaporation of solvent from hexane solutions at 4 °C. 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 each structure. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{\mathrm{raw}})^2 + (PF_o^2)^2]^{1/2}/Lp$.

For **2a** the space group $P2_1/a$ was indicated by the systematic absences in the diffraction pattern. It should be noted, however, that a simple symmetry transform would produce an orthorhombic unit cell of dimensions a = 23.13 Å, b = 27.44 Å, and c = 8.96 Å. This alternative was ruled out because inspection of appropriate sets of symmetry, equivalent reflections under the conditions of orthorhombic symmetry, revealed that the equivalences did not exist. In addition, in the orthorhombic system the systematic absences observed in the monoclinic system were not accounted for. The structure of **2a** was solved by a combination of direct methods and difference Fourier techniques. The coordinates of the four independent osmium atoms were established from the phasing (MULTAN) of 256 reflections ($E_{\min}$ = 1.95). Atoms heavier than oxygen were refined anisotropically. All other non-hydrogen atoms were refined isotropically. Positions of the hydrogen atoms were calculated by assuming idealized geometry. Their contributions were added to the structure factor calculations, but their positions were not refined.

For **3a** the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The coordinates of the metal atoms were obtained from a three-dimensional Patterson function. The coordinates of all remaining non-hydrogen atoms were obtained from a difference Fourier synthesis. Only atoms heavier than oxygen were refined anisotropically. Positions of the hydrogen atoms were calculated. Hydrogen atom contributions were included in structure factor calculations, but they were not refined.

For compound **2b** the unique space group $P2_1/n$ was identified from the systematic absences observed in the data. The coordinates of the metal atoms were obtained from the phasing (MULTAN) of 244 reflections ($E_{\min}$ = 1.54). The coordinates of all remaining non-hydrogen atoms were obtained from difference Fourier calculations. In the later stages of analysis the crystal was found to contain 0.5 mol of hexane solvent cocrystallized per mole of complex. Refinement of the three independent carbon atoms of the centrosymmetrical hexane molecule yielded large thermal parameters for the methylene carbon atoms. This could be due either to high libration of these atoms or an unresolved disorder phenomenon. Only atoms heavier than oxygen were refined anisotropically. Only the hydrogen atoms on the well-refined methyl groups of the isocyanide ligand were calculated.

For compound **3b** the unique space group $Pbca$ was identified from the systematic absences observed in the data. The coordinates of the metal atoms were determined from phasing (MULTAN) of 236 reflections ($E_{\min}$ = 1.89). The coordinates of all remaining non-hydrogen atoms were obtained from difference Fourier calculations. Atoms heavier than oxygen were refined anisotropically. Positions for the hydrogen atoms on the methyl groups were calculated by assuming an idealized threefold symmetry and staggered rotational conformations. See supplementary material for structure factor tables for all four structural analyses.

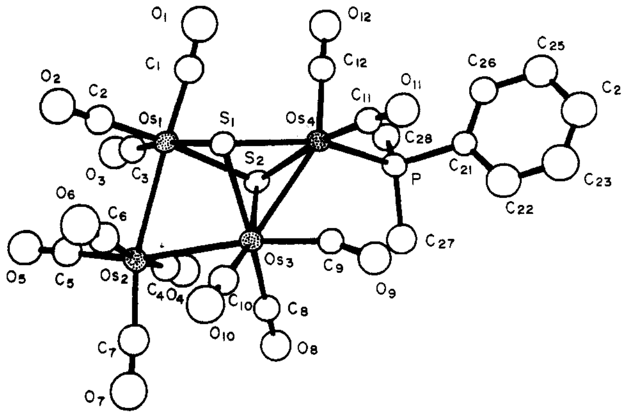

Figure 1. A perspective ORTEP diagram of $Os_4(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$, **2a**, showing 50% probability thermal ellipsoids.

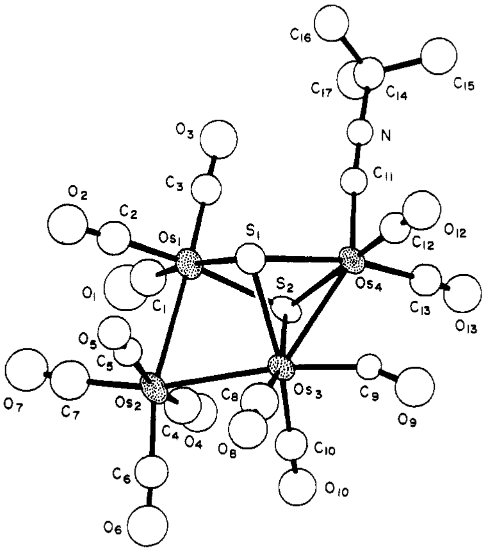

Figure 2. A perspective ORTEP diagram of $Os_4(CO)_{12}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$, **2b**, showing 50% probability thermal ellipsoids.

Results

At room temperature **1** adds 1 mol of either of the electron pair donors PMe_2Ph or CN-*t*-Bu to form the new compounds $Os_4(CO)_{12}(L)(\mu_3\text{-}S)_2$ **2a**, L = PMe_2Ph, or **2b**, L = CN-*t*-Bu, respectively. Both **2a** and **2b** were characterized by single-crystal X-ray diffraction analysis. ORTEP drawings of **2a** and **2b** are shown in Figures 1 and 2, respectively. Final fractional atomic coordinates, interatomic distances, and interatomic angles for **2a** are listed in Tables II–IV, respectively. Final fractional atomic coordinates, interatomic distances, and interatomic angles for **2b** are listed in Tables V–VII, respectively. Both **2a** and **2b** consist of structurally analogous open-planar clusters of four osmium atoms and are very similar to the parent carbonyl cluster $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, **4**.[6] Each contains only three metal–metal bonds. The Os(1)–Os(2) bond distance is 2.915 (1), 2.898 (1), and 2.910 (1) Å in **2a**, **2b**, and **4**, respectively. These distances are very similar to those in $Os_3(CO)_{12}$, 2.877 (3) Å.[10] The Os(2)–Os(3) bond distance is 2.880 (1), 2.867 (1), and 2.897 (1) Å in **2a**, **2b**, and **4**, respectively, and is also very similar to that in $Os_3(CO)_{12}$. However, the doubly sulfur-bridged Os(3)–Os(4) bond in **2a** is considerably shorter at 2.801 (1) Å. This is very similar to the corresponding distance of 2.800 (1) Å in **4**. Short Os–Os bonds of 2.813 (1) Å were also observed for the doubly sulfur-bridged Os–Os bonds in $Os_3(CO)_9(\mu_3\text{-}S)_2$.[11] This shortening can probably be attributed to the contraction effect exerted by the bridging

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[9] "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.

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Table II. Positional and Thermal Parameters and Their Esds for $Os_4(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (2a)[a]

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	B_{eqv}, Å^2
Os(1)	0.23591 (4)	0.22717 (8)	0.76368 (4)	2.34 (2)	2.89 (3)	2.34 (2)	−0.28 (2)	0.43 (2)	−0.44 (2)	2.52 (1)
Os(2)	0.18613 (4)	0.24089 (8)	0.60061 (4)	2.91 (3)	3.44 (3)	2.22 (2)	−0.25 (3)	0.91 (2)	−0.05 (2)	2.80 (1)
Os(3)	0.06938 (4)	0.11332 (8)	0.67283 (3)	2.24 (2)	2.52 (3)	1.89 (2)	−0.04 (2)	0.38 (2)	−0.05 (2)	2.21 (1)
Os(4)	0.07463 (4)	0.03319 (7)	0.82447 (3)	2.41 (2)	2.18 (3)	1.85 (2)	0.02 (2)	0.52 (2)	−0.17 (2)	2.13 (1)
S(1)	0.1050 (2)	0.2809 (5)	0.7796 (2)	2.8 (2)	2.0 (2)	2.6 (1)	−0.1 (1)	0.7 (1)	−0.4 (1)	2.45 (8)
S(2)	0.1732 (2)	−0.0185 (5)	0.7513 (2)	2.3 (2)	2.4 (2)	2.6 (2)	0.3 (1)	0.3 (1)	−0.4 (1)	2.44 (8)
P	0.0505 (3)	−0.2241 (5)	0.8292 (2)	3.6 (2)	2.3 (2)	2.5 (2)	0.1 (2)	0.8 (1)	−0.2 (2)	2.73 (9)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.2863 (8)	0.208 (2)	0.9337 (8)	5.9 (4)	C(11)	−0.0137 (9)	0.083 (2)	0.8623 (9)	2.7 (3)
O(2)	0.2746 (8)	0.556 (2)	0.7606 (8)	5.3 (3)	C(12)	0.1323 (9)	0.021 (2)	0.9205 (9)	3.1 (3)
O(3)	0.3874 (8)	0.127 (2)	0.7308 (7)	5.4 (3)	C(21)	−0.0213 (9)	−0.279 (2)	0.8830 (8)	2.6 (3)
O(4)	0.2576 (8)	−0.072 (2)	0.6007 (8)	5.5 (3)	C(22)	−0.0984 (11)	−0.297 (2)	0.8477 (11)	4.9 (5)
O(5)	0.3318 (8)	0.373 (2)	0.5651 (8)	5.6 (3)	C(23)	−0.1526 (12)	−0.335 (3)	0.8892 (12)	5.3 (5)
O(6)	0.1299 (8)	0.558 (2)	0.6259 (8)	6.3 (4)	C(24)	−0.1360 (12)	−0.354 (3)	0.9629 (11)	5.1 (5)
O(7)	0.0987 (8)	0.226 (2)	0.4369 (8)	6.0 (4)	C(25)	−0.0599 (11)	−0.338 (2)	1.0022 (11)	4.7 (4)
O(8)	0.0596 (7)	−0.121 (1)	0.5478 (7)	4.2 (3)	C(26)	−0.0045 (9)	−0.297 (2)	0.9594 (9)	3.3 (4)
O(9)	−0.0819 (7)	−0.004 (1)	0.7001 (7)	4.3 (3)	C(27)	0.0216 (11)	−0.315 (2)	0.7373 (10)	4.2 (4)
O(10)	−0.0269 (8)	0.354 (2)	0.5836 (7)	5.2 (3)	C(28)	0.1334 (10)	−0.332 (2)	0.8697 (10)	3.7 (4)
O(11)	−0.0701 (7)	0.110 (1)	0.8826 (7)	4.4 (3)	H(271)	−0.0217	−0.2687	0.7155	5.00
O(12)	0.1670 (7)	0.008 (1)	0.9809 (7)	4.5 (3)	H(272)	0.0615	−0.3139	0.7140	5.00
C(1)	0.2645 (10)	0.212 (2)	0.8691 (10)	3.9 (4)	H(273)	0.0099	−0.4177	0.7520	5.00
C(2)	0.2618 (10)	0.429 (2)	0.7623 (10)	3.7 (4)	H(281)	0.1554	−0.2925	0.9218	5.00
C(3)	0.3292 (10)	0.169 (2)	0.7419 (10)	3.7 (4)	H(282)	0.1210	−0.4349	0.8803	5.00
C(4)	0.2303 (10)	0.046 (2)	0.5996 (10)	3.9 (4)	H(283)	0.1726	−0.3310	0.8422	5.00
C(5)	0.2763 (11)	0.322 (2)	0.5793 (10)	4.2 (4)	H(22)	−0.1147	−0.2768	0.7995	5.00
C(6)	0.1497 (10)	0.435 (2)	0.6178 (10)	3.9 (4)	H(23)	−0.2041	−0.3497	0.8703	5.00
C(7)	0.1297 (11)	0.228 (2)	0.5007 (11)	4.3 (4)	H(24)	−0.1749	−0.3776	0.9941	5.00
C(8)	0.0617 (9)	−0.032 (2)	0.5934 (9)	3.0 (3)	H(25)	−0.0464	−0.3569	1.0566	5.00
C(9)	−0.0206 (9)	0.034 (2)	0.7039 (8)	2.7 (3)	H(26)	0.0475	−0.2841	0.9858	5.00
C(10)	0.0091 (9)	0.263 (2)	0.6163 (9)	3.3 (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 $Os_4(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (2a)

Os(1)-Os(2)	2.915 (1)	P-C(21)	1.805 (11)
Os(2)-Os(3)	2.880 (1)	P-C(27)	1.834 (13)
Os(3)-Os(4)	2.801 (1)	P-C(28)	1.818 (13)
Os(1)-S(1)	2.460 (3)	C(1)-O(1)	1.159 (14)
Os(1)-S(2)	2.465 (3)	C(2)-O(2)	1.164 (15)
Os(3)-S(1)	2.432 (3)	C(3)-O(3)	1.158 (14)
Os(3)-S(2)	2.441 (3)	C(4)-O(4)	1.161 (15)
Os(4)-S(1)	2.454 (3)	C(5)-O(5)	1.164 (14)
Os(4)-S(2)	2.419 (3)	C(6)-O(6)	1.173 (15)
Os(4)-P	2.349 (3)	C(7)-O(7)	1.185 (15)
Os(1)-C(1)	1.880 (13)	C(8)-O(8)	1.140 (13)
Os(1)-C(2)	1.870 (14)	C(9)-O(9)	1.141 (12)
Os(1)-C(3)	1.856 (13)	C(10)-O(10)	1.142 (13)
Os(2)-C(4)	1.919 (14)	C(11)-O(11)	1.157 (12)
Os(2)-C(5)	1.871 (14)	C(12)-O(12)	1.160 (13)
Os(2)-C(6)	1.900 (14)	C(21)-C(22)	1.429 (17)
Os(2)-C(7)	1.908 (14)	C(22)-C(23)	1.365 (19)
Os(3)-C(8)	1.917 (12)	C(23)-C(24)	1.318 (18)
Os(3)-C(9)	1.932 (1)	C(24)-C(25)	1.433 (19)
Os(4)···C(9)	2.519 (11)	C(25)-C(26)	1.404 (16)
Os(3)-C(10)	1.901 (12)	C(26)-C(21)	1.363 (15)
Os(4)-C(11)	1.881 (11)	Os(1)···Os(4)	3.695 (1)
Os(4)-C(12)	1.858 (12)	S(1)···S(2)	3.026 (4)

sulfur ligands.[12] In **2b**, however, the Os(3)–Os(4) bond is significantly longer at 2.878 (1) Å. The reason for this could be due to a structural trans effect produced by the isocyanide ligand. A similar bond lengthening effect was observed in derivatives of $Os_3(CO)_9(\mu_3\text{-}S)_2$ that contained a strong σ-donating ligand trans to the osmium–osmium bond.[11] The nonbonding Os(1)···Os(4) distances 3.695 (1)°, 3.689 (1), and 3.659 (1) Å for **2a**, **2b**, and **4**, respectively, are very similar.

Each compound contains two triply bridging sulfido ligands, S(1) and S(2), bonded to the metal atoms Os(1), Os(3), and Os(4), which are symmetrically displaced on opposite sides of the Os_4 plane. The Os–S distances in **4** range from 2.402 (4) to 2.473 (4) Å. All the Os–S distances in **2a** and **2b** lie within this range. Similar Os–S distances were observed for the triosmium clusters $Os_3(CO)_9(\mu_3\text{-}S)_2$ and $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$.[11] **2a** and **2b** both have 12 carbonyl ligands. These are arranged such that Os(1) contains three, Os(2) contains four, Os(3) contains three, and Os(4) contains two. All are of a linear terminal type except C(9)–O(9), which is a semibridging ligand to Os(4). A similar semibridge was also observed for **4**.[6] A sensitive indicator of the variation in semibridging character is the very weakly bonding Os(4)···C(9) internuclear separation. This distance decreased smoothly from 2.61 (2) to 2.519 (11) Å and finally to 2.44 (2) Å for **4**, **2a**, and **2b**, respectively. This change is significant and apparently can be explained by the "charge-equalizing" effect through which an excess of charge on one metal atom is reduced by an interaction with a CO ligand on a neighboring metal atom. **2a** and **2b** both differ from **4** in that they have poorer electron withdrawing, PMe_2Ph or CN-*t*-Bu ligands on Os(4) in place of a CO ligand. This should result in an increase in electron density on Os(4) compared to that in **4**. As a result, the semibridging interaction of C(9)–O(9) is greater in both **2a** and **2b** than in **4**. Interestingly, the semibridging interaction in **2b** is greater than in **2a**. This could be due to the fact that isocyanides are generally poorer π acceptors than phosphines[14] but might also be related to the geometric location of the isocyanide ligand in **2b**. Specifically, the isocyanide ligand in **2b** is positioned directly opposite the semibridging carbonyl ligand. The C(9)···Os(4)–C(11) angle is 169.5 (9)°. From this position

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(12) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261.

(13) (a) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. (b) Cotton, F. A.; Troup, J. *J. Am. Chem. Soc.* **1974**, *96*, 1233.

(14) See ref 1, Chapter 3.

Table IV. Interatomic Angles (deg) with Esds for Os$_4$(CO)$_{12}$(PMe$_2$Ph)(μ_3-S)$_2$ (2a)

Os(1)-Os(2)-Os(3)	69.75 (2)	Os(2)-Os(3)-C(8)	84.3 (3)	Os(1)-S(1)-Os(3)	85.24 (8)
Os(2)-Os(3)-Os(4)	129.18 (2)	Os(2)-Os(3)-C(9)	169.7 (3)	Os(1)-S(1)-Os(4)	97.52 (10)
Os(2)-Os(1)-S(1)	88.38 (6)	Os(2)-Os(3)-C(10)	82.7 (3)	Os(1)-S(2)-Os(3)	84.95 (9)
Os(2)-Os(1)-S(2)	83.67 (6)	Os(4)-Os(3)-S(1)	55.38 (7)	Os(1)-S(2)-Os(4)	98.33 (10)
Os(2)-Os(1)-C(1)	177.4 (4)	Os(4)-Os(3)-S(2)	54.43 (6)	Os(3)-S(1)-Os(4)	69.95 (7)
Os(2)-Os(1)-C(2)	88.9 (4)	Os(4)-Os(3)-C(8)	122.4 (3)	Os(3)-S(2)-Os(4)	70.39 (7)
Os(2)-Os(1)-C(3)	86.2 (4)	Os(4)-Os(3)-C(9)	61.1 (3)	Os(1)-C(1)-O(1)	175 (1)
S(1)-Os(1)-S(2)	75.81 (9)	Os(4)-Os(3)-C(10)	128.4 (3)	Os(1)-C(2)-O(2)	177 (1)
S(1)-Os(1)-C(1)	90.1 (4)	S(1)-Os(3)-S(2)	76.75 (9)	Os(1)-C(3)-O(3)	177 (1)
S(1)-Os(1)-C(2)	93.2 (4)	S(1)-Os(3)-C(8)	168.6 (3)	Os(2)-C(4)-O(4)	179 (1)
S(1)-Os(1)-C(3)	172.4 (4)	S(1)-Os(3)-C(9)	97.0 (3)	Os(2)-C(5)-O(5)	179 (1)
S(2)-Os(1)-C(1)	93.9 (4)	S(1)-Os(3)-C(10)	92.1 (4)	Os(2)-C(6)-O(6)	176 (1)
S(2)-Os(1)-C(2)	166.9 (4)	S(2)-Os(3)-C(8)	93.0 (4)	Os(2)-C(7)-O(7)	175 (1)
S(2)-Os(1)-C(3)	98.3 (4)	S(2)-Os(3)-C(9)	104.3 (3)	Os(3)-C(8)-O(8)	177 (1)
C(1)-Os(1)-C(2)	93.3 (6)	S(2)-Os(3)-C(10)	163.3 (4)	Os(3)-C(9)-O(9)	159 (1)
C(1)-Os(1)-C(3)	95.1 (5)	C(8)-Os(3)-C(9)	90.4 (5)	Os(3)-C(10)-O(10)	179 (1)
C(2)-Os(1)-C(3)	91.9 (6)	C(8)-Os(3)-C(10)	96.7 (5)	Os(4)-C(11)-O(11)	176 (1)
Os(1)-Os(2)-C(4)	85.1 (4)	C(9)-Os(3)-C(10)	89.2 (5)	Os(4)-C(12)-O(12)	177 (1)
Os(1)-Os(2)-C(5)	95.3 (4)	Os(3)-Os(4)-S(1)	54.67 (6)	Os(4)-P-C(21)	116.1 (4)
Os(1)-Os(2)-C(6)	86.0 (4)	Os(3)-Os(4)-S(2)	55.19 (7)	Os(4)-P-C(27)	115.4 (5)
Os(1)-Os(2)-C(7)	164.8 (4)	Os(3)-Os(4)-C(11)	113.5 (3)	Os(4)-P-C(28)	113.0 (4)
Os(3)-Os(2)-C(4)	88.6 (4)	Os(3)-Os(4)-C(12)	147.0 (3)	C(21)-P-C(27)	104.0 (6)
Os(3)-Os(2)-C(5)	165.0 (4)	Os(3)-Os(4)-P	108.9 (7)	C(21)-P-C(28)	104.6 (5)
Os(3)-Os(2)-C(6)	89.6 (4)	S(1)-Os(4)-S(2)	76.77 (9)	C(27)-P-C(28)	102.3 (6)
Os(3)-Os(2)-C(7)	95.1 (4)	S(1)-Os(4)-C(11)	98.6 (3)	P-C(21)-C(22)	121.2 (9)
C(4)-Os(2)-C(5)	88.7 (6)	S(1)-Os(4)-C(12)	103.8 (4)	P-C(21)-C(26)	121.0 (9)
C(4)-Os(2)-C(6)	171.0 (5)	S(1)-Os(4)-P	162.13 (9)	C(21)-C(22)-C(23)	120.8 (13)
C(4)-Os(2)-C(7)	95.2 (6)	S(2)-Os(4)-C(11)	168.4 (3)	C(22)-C(23)-C(24)	121.3 (15)
C(5)-Os(2)-C(6)	90.7 (6)	S(2)-Os(4)-C(12)	98.5 (3)	C(23)-C(24)-C(25)	121.0 (14)
C(5)-Os(2)-C(7)	99.9 (6)	S(2)-Os(4)-P	89.31 (10)	C(24)-C(25)-C(26)	117.4 (12)
C(6)-Os(2)-C(7)	93.7 (6)	C(11)-Os(4)-C(12)	92.9 (5)	C(25)-C(26)-C(21)	121.7 (11)
Os(2)-Os(3)-S(1)	89.73 (7)	C(11)-Os(4)-P	92.9 (4)	C(26)-C(21)-C(22)	117.8 (11)
Os(2)-Os(3)-S(2)	84.83 (7)	C(12)-Os(4)-P	89.2 (4)		

Table V. Positional and Thermal Parameters and Their Esds for Os$_4$(CO)$_{12}$(CN-*t*-Bu)(μ_3-S)$_2$·0.5C$_6$H$_{14}$ (2b)[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	B_{eqv}, Å^2
Os(1)	1.02602 (8)	0.4285 (1)	0.83590 (6)	2.67 (5)	4.50 (7)	3.07 (4)	0.02 (8)	0.54 (4)	0.43 (7)	3.43 (3)
Os(2)	1.14826 (8)	0.4169 (2)	0.73575 (6)	2.02 (5)	4.15 (7)	4.43 (5)	0.12 (8)	0.80 (4)	0.27 (7)	3.52 (3)
Os(3)	0.96446 (7)	0.4123 (1)	0.65449 (6)	2.20 (4)	3.37 (6)	3.08 (4)	−0.09 (7)	1.05 (3)	0.02 (6)	2.81 (2)
Os(4)	0.80482 (7)	0.4166 (2)	0.70594 (6)	2.08 (4)	3.39 (6)	3.37 (4)	−0.04 (7)	0.96 (4)	0.02 (6)	2.89 (3)
S(1)	0.9295 (5)	0.5636 (9)	0.7434 (4)	3.0 (3)	4.2 (5)	3.3 (3)	−0.2 (4)	0.9 (3)	0.2 (3)	3.4 (2)
S(2)	0.9314 (5)	0.2816 (8)	0.7514 (4)	2.8 (3)	3.1 (4)	3.9 (3)	0.7 (3)	1.4 (3)	0.8 (3)	3.1 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	1.151 (2)	0.246 (3)	0.930 (1)	9.3 (8)	C(9)	0.850 (2)	0.400 (3)	0.588 (1)	2.4 (6)
O(2)	1.146 (2)	0.636 (2)	0.906 (1)	5.8 (6)	C(10)	1.007 (2)	0.281 (3)	0.604 (1)	4.0 (7)
O(3)	0.907 (2)	0.440 (2)	0.945 (1)	6.0 (6)	C(11)	0.751 (2)	0.409 (3)	0.791 (1)	2.9 (6)
O(4)	1.135 (2)	0.133 (3)	0.759 (1)	6.7 (7)	C(12)	0.728 (2)	0.545 (3)	0.664 (1)	3.4 (7)
O(5)	1.132 (1)	0.701 (2)	0.730 (1)	3.6 (6)	C(13)	0.722 (2)	0.289 (3)	0.662 (2)	4.1 (8)
O(6)	1.235 (2)	0.398 (3)	0.604 (1)	6.1 (6)	C(14)	0.658 (2)	0.417 (4)	0.893 (1)	4.1 (7)
O(7)	1.316 (2)	0.428 (3)	0.861 (1)	7.3 (7)	C(15)	0.553 (2)	0.414 (4)	0.852 (2)	5.3 (8)
O(8)	1.025 (1)	0.612 (2)	0.562 (1)	4.9 (5)	C(16)	0.676 (2)	0.536 (3)	0.938 (2)	4.9 (9)
O(9)	0.803 (1)	0.407 (3)	0.531 (1)	5.6 (5)	C(17)	0.679 (3)	0.300 (4)	0.942 (2)	6.2 (10)
O(10)	1.033 (2)	0.195 (2)	0.577 (1)	5.7 (6)	C(18)	0.983 (3)	0.107 (5)	0.151 (2)	8.4 (12)
O(12)	0.685 (1)	0.626 (2)	0.636 (1)	4.9 (5)	C(19)	0.969 (5)	0.096 (8)	0.073 (3)	17.6 (25)
O(13)	0.681 (2)	0.208 (2)	0.639 (1)	6.0 (6)	C(20)	1.000 (6)	0.012 (9)	0.032 (3)	19.6 (31)
N	0.711 (1)	0.415 (3)	0.837 (1)	2.7 (4)	H(151)	0.5419	0.3409	0.8244	6.00
C(1)	1.104 (3)	0.321 (4)	0.895 (2)	5.7 (9)	H(152)	0.5170	0.4167	0.8879	6.00
C(2)	1.100 (2)	0.560 (3)	0.881 (2)	4.3 (7)	H(153)	0.5411	0.4845	0.8213	6.00
C(3)	0.956 (2)	0.434 (3)	0.902 (1)	3.8 (7)	H(161)	0.7371	0.5397	0.9635	6.00
C(4)	1.140 (2)	0.243 (4)	0.747 (2)	5.7 (9)	H(162)	0.6619	0.6058	0.9069	6.00
C(5)	1.139 (2)	0.600 (3)	0.735 (1)	2.9 (6)	H(163)	0.6378	0.5380	0.9735	6.00
C(6)	1.198 (2)	0.413 (4)	0.651 (1)	4.1 (7)	H(171)	0.7411	0.302[illegible]	0.9664	6.00
C(7)	1.260 (2)	0.426 (4)	0.813 (2)	6.1 (9)	H(172)	0.6420	0.3006	0.9770	6.00
C(8)	1.002 (2)	0.542 (3)	0.599 (2)	5.0 (9)	H(173)	0.6674	0.2294	0.9121	6.00

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

there may be an even greater concentration of electron density on Os(4) in the vicinity of C(9), and this may lead to an even stronger semibridging interaction than that in **2b**.

When solutions of **2a** or **2b** are heated to reflux in octane solvent for 3 h they lose 1 mol of CO and are converted in high yield to the products Os$_4$(CO)$_{11}$(L)(μ_3-S)$_2$, **3a**, L = PMe$_2$Ph, or **3b**, L = CN-*t*-Bu. Both **3a** and **3b** have been characterized by single-crystal X-ray diffraction methods. ORTEP diagrams of **3a** and **3b** are shown in Figures 3 and 4, respectively. Final fractional atomic coordinates, interatomic distances, and interatomic angles for **3a** are listed in Tables VIII–X. Final fractional atomic coordinates, interatomic distances, and interatomic angles for **3b** are

Table VI. Interatomic Distances (Å) with Esds for $Os_4(CO)_{12}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$ (2b)

Os(1)-Os(2)	2.898 (1)	Os(4)-C(13)	1.93 (3)
Os(2)-Os(3)	2.867 (1)	C(1)-O(1)	1.17 (3)
Os(3)-Os(4)	2.878 (1)	C(2)-O(2)	1.10 (3)
Os(1)-S(1)	2.482 (7)	C(3)-O(3)	1.22 (3)
Os(1)-S(2)	2.466 (7)	C(4)-O(4)	1.21 (4)
Os(3)-S(1)	2.465 (8)	C(5)-O(5)	1.10 (3)
Os(3)-S(2)	2.429 (7)	C(6)-O(6)	1.16 (2)
Os(4)-S(1)	2.448 (8)	C(7)-O(7)	1.10 (3)
Os(4)-S(2)	2.411 (7)	C(8)-O(8)	1.14 (3)
Os(1)-C(1)	1.84 (3)	C(9)-O(9)	1.15 (2)
Os(1)-C(2)	1.89 (3)	C(10)-O(10)	1.16 (3)
Os(1)-C(3)	1.79 (2)	C(11)-N	1.17 (2)
Os(2)-C(4)	1.90 (4)	C(12)-O(12)	1.15 (3)
Os(2)-C(5)	1.98 (3)	C(13)-O(13)	1.10 (3)
Os(2)-C(6)	1.89 (2)	N-C(14)	1.45 (3)
Os(2)-C(7)	1.97 (3)	C(14)-C(15)	1.60 (3)
Os(3)-C(8)	1.89 (3)	C(14)-C(16)	1.53 (4)
Os(3)-C(9)	1.90 (2)	C(14)-C(17)	1.55 (4)
Os(4)···C(9)	2.44 (2)	C(18)-C(19)	1.43 (6)
Os(3)-C(10)	1.89 (3)	C(19)-C(20)	1.33 (9)
Os(4)-C(11)	1.92 (2)	Os(1)···Os(4)	3.689 (1)
Os(4)-C(12)	1.87 (3)	S(1)···S(2)	3.05 (1)

given in Tables XI–XIII. Both compounds consist of butterfly tetrahedral clusters of four osmium atoms and have a triply bridging sulfido ligand across each open-triangular face. Both are structurally similar to the parent carbonyl cluster $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, **1**.[6] An interesting feature of the structure of **1** is that two of the five metal–metal bonds are unusually long, that is, greater than 3.00 Å in length although they are also decidedly inequivalent 3.002 (1) vs. 3.091 (1) Å. Similar distortions in the metal–metal bonding are observed in both **3a** and **3b**. In **3a**, the two bonds, Os(1)–Os(3) = 2.987 (1) Å and Os(2)–Os(4) = 3.013 (1) Å, are significantly longer than the others, Os(1)–Os(2) = 2.925 (1) Å, Os(2)–Os(3) = 2.921 (1) Å, and Os(3)–Os(4) = 2.893 (1) Å, but unlike those in **1** the two long bonds are nearly equal in length. The short metal–metal bonds in **3a** are very similar to those in **1**. In **3b** bonds Os(1)–Os(3) = 2.965 (1) Å and Os(2)–Os(4) = 3.115 (1) Å are also significantly longer than the remaining three, but in this case they are highly inequivalent and even more inequivalent than in **1**. The three shorter bonds in **3b** are nearly identical with those in **3a**. The reason for the selective lengthening of two of the five metal–metal bonds is not clear, but it occurs that each of the three short bonds has a ligand positioned approximately trans to it, while the long bonds do not. The explanation for the large inequivalence between the two long bonds in **1** and **3b** is also unclear, but the cause might be as simple as crystal packing effects. The internuclear separations between the wingtip metal atoms Os(1) and Os(4) are 3.535 (1) and 3.535 (1) Å for **3a** and **3b** are indicative of nonbonding interactions. The Os–S distances in **3a** and **3b** are similar to those in **1** with the distances to the wingtip metal atoms being approximately 0.04 Å longer than those to the hinge metal atoms in all cases.

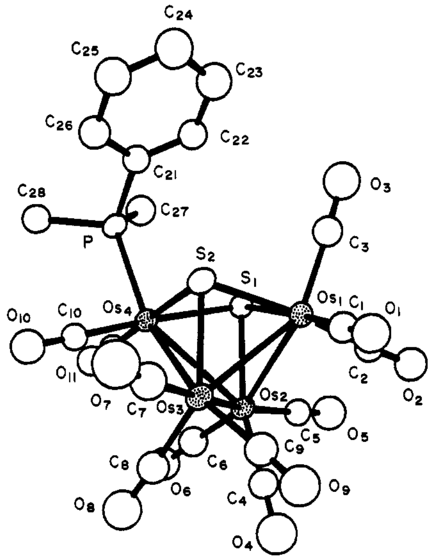

Figure 3. A perspective ORTEP diagram of $Os_4(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)_2$, **3a**, showing 50% probability thermal ellipsoids.

Table VII. Interatomic Angles (deg) with Esds for $Os_4(CO)_{12}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$ (2b)

Os(1)-Os(2)-Os(3)	70.28 (3)	Os(2)-Os(3)-S(1)	87.45 (16)	S(2)-Os(4)-C(13)	96.4 (8)
Os(2)-Os(3)-Os(4)	129.14 (4)	Os(2)-Os(3)-S(2)	86.93 (16)	C(11)-Os(4)-C(12)	92.0 (10)
Os(2)-Os(1)-S(1)	86.44 (15)	Os(2)-Os(3)-C(8)	84.7 (9)	C(11)-Os(4)-C(13)	88.1 (11)
Os(2)-Os(1)-S(2)	85.55 (15)	Os(2)-Os(3)-C(9)	171.2 (6)	C(12)-Os(4)-C(13)	93.7 (10)
Os(2)-Os(1)-C(1)	87.0 (9)	Os(2)-Os(3)-C(10)	83.2 (8)	Os(1)-S(1)-Os(3)	84.24 (26)
Os(2)-Os(1)-C(2)	85.5 (8)	Os(4)-Os(3)-S(1)	55.24 (17)	Os(1)-S(1)-Os(4)	96.87 (30)
S(1)-Os(1)-S(2)	76.06 (21)	Os(4)-Os(3)-S(2)	54.62 (16)	Os(1)-S(2)-Os(3)	85.35 (24)
S(1)-Os(1)-C(1)	172.9 (10)	Os(4)-Os(3)-C(8)	123.9 (9)	Os(1)-S(2)-Os(4)	98.30 (27)
S(1)-Os(1)-C(2)	94.1 (9)	Os(4)-Os(3)-C(9)	59.4 (6)	Os(3)-S(1)-Os(4)	68.95 (22)
S(1)-Os(1)-C(3)	96.5 (8)	Os(4)-Os(3)-C(10)	127.0 (8)	Os(3)-S(2)-Os(4)	70.16 (19)
S(2)-Os(1)-C(1)	100.6 (10)	S(1)-Os(3)-S(2)	77.06 (21)	Os(1)-C(1)-O(1)	176 (3)
S(2)-Os(1)-C(2)	167.1 (8)	S(1)-Os(3)-C(8)	90.5 (9)	Os(1)-C(2)-O(2)	178 (3)
S(2)-Os(1)-C(3)	96.6 (8)	S(1)-Os(3)-C(9)	100.7 (7)	Os(1)-C(3)-O(3)	178 (2)
C(1)-Os(1)-C(2)	88.2 (13)	S(1)-Os(3)-C(10)	168.1 (8)	Os(2)-C(4)-O(4)	175 (2)
C(1)-Os(1)-C(3)	90.1 (13)	S(2)-Os(3)-C(8)	165.3 (9)	Os(2)-C(5)-O(5)	176 (2)
C(2)-Os(1)-C(3)	92.8 (11)	S(2)-Os(3)-C(9)	98.2 (7)	Os(2)-C(6)-O(6)	172 (3)
Os(1)-Os(2)-C(4)	84.8 (9)	S(2)-Os(3)-C(10)	95.0 (8)	Os(2)-C(7)-O(7)	172 (3)
Os(1)-Os(2)-C(5)	84.6 (6)	C(8)-Os(3)-C(9)	91.7 (11)	Os(3)-C(8)-O(8)	174 (2)
Os(1)-Os(2)-C(6)	164.4 (7)	C(8)-Os(3)-C(10)	95.9 (10)	Os(3)-C(9)-O(9)	153 (2)
Os(1)-Os(2)-C(7)	95.5 (8)	C(9)-Os(3)-C(10)	89.2 (11)	Os(3)-C(10)-O(10)	174 (2)
Os(3)-Os(2)-C(4)	87.9 (9)	Os(3)-Os(4)-S(1)	55.81 (16)	Os(4)-C(11)-N	171 (2)
Os(3)-Os(2)-C(5)	87.5 (7)	Os(3)-Os(4)-S(2)	55.23 (15)	Os(4)-C(12)-O(12)	175 (2)
Os(3)-Os(2)-C(6)	94.3 (7)	Os(3)-Os(4)-C(11)	146.1 (6)	Os(4)-C(13)-O(13)	174 (3)
Os(3)-Os(2)-C(7)	165.7 (8)	Os(3)-Os(4)-C(12)	112.4 (8)	C(11)-N-C(14)	177 (3)
C(4)-Os(2)-C(5)	169.4 (10)	Os(3)-Os(4)-C(13)	112.2 (8)	N-C(14)-C(15)	107 (2)
C(4)-Os(2)-C(6)	95.6 (13)	S(1)-Os(4)-S(2)	77.72 (22)	N-C(14)-C(16)	110 (2)
C(4)-Os(2)-C(7)	92.0 (14)	S(1)-Os(4)-C(11)	103.0 (8)	N-C(14)-C(17)	109 (2)
C(5)-Os(2)-C(6)	93.3 (12)	S(1)-Os(4)-C(12)	90.7 (8)	C(15)-C(14)-C(16)	108 (2)
C(5)-Os(2)-C(7)	90.1 (13)	S(1)-Os(4)-C(13)	168.0 (8)	C(15)-C(14)-C(17)	109 (3)
C(6)-Os(2)-C(7)	100.0 (11)	S(2)-Os(4)-C(11)	97.3 (8)	C(16)-C(14)-C(17)	112 (2)
		S(2)-Os(4)-C(12)	166.5 (8)	C(18)-C(19)-C(20)	129 (7)

Table VIII. Positional and Thermal Parameters and Their Esds for $Os_4(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)_2$ (3a)[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	B_{eqv}, Å^2
Os(1)	0.23720 (7)	0.28211 (7)	0.39872 (4)	2.71 (3)	2.10 (3)	1.95 (2)	0.03 (2)	0.02 (2)	0.45 (2)	2.25 (1)
Os(2)	−0.02562 (7)	0.14398 (7)	0.29760 (4)	2.31 (2)	2.27 (3)	2.28 (2)	0.07 (2)	0.40 (2)	0.65 (2)	2.25 (1)
Os(3)	0.25205 (7)	0.00350 (7)	0.29412 (4)	2.95 (3)	1.92 (3)	2.60 (2)	0.55 (2)	0.61 (2)	0.92 (2)	2.40 (1)
Os(4)	0.20521 (7)	0.17801 (6)	0.16216 (4)	2.30 (2)	1.79 (2)	1.92 (2)	0.13 (2)	0.31 (2)	0.56 (2)	1.97 (1)
S(1)	0.0980 (5)	0.3472 (4)	0.2724 (2)	2.9 (2)	2.0 (2)	2.2 (1)	0.1 (1)	0.2 (1)	0.6 (1)	2.37 (8)
S(2)	0.4013 (4)	0.2003 (4)	0.2800 (2)	2.5 (2)	2.6 (2)	2.7 (1)	0.2 (2)	0.3 (1)	1.0 (1)	2.52 (8)
P	0.3154 (5)	0.3416 (4)	0.0899 (2)	3.0 (2)	2.2 (2)	2.3 (1)	0.3 (2)	0.5 (1)	1.0 (1)	2.42 (8)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.426 (1)	0.166 (1)	0.5372 (8)	4.6 (3)	C(11)	0.049 (2)	0.166 (2)	0.0757 (9)	2.7 (3)
O(2)	0.013 (1)	0.362 (1)	0.5422 (8)	4.3 (3)	C(21)	0.489 (2)	0.419 (2)	0.1415 (10)	2.9 (3)
O(3)	0.393 (2)	0.560 (2)	0.4324 (8)	5.1 (3)	C(22)	0.495 (2)	0.521 (2)	0.2134 (10)	3.1 (3)
O(4)	−0.114 (2)	−0.097 (2)	0.3869 (9)	6.5 (4)	C(23)	0.628 (2)	0.575 (2)	0.2568 (12)	4.5 (4)
O(5)	−0.259 (2)	0.317 (2)	0.3907 (8)	5.4 (3)	C(24)	0.760 (2)	0.526 (2)	0.2254 (12)	4.8 (4)
O(6)	−0.251 (1)	0.040 (2)	0.1442 (8)	4.8 (3)	C(25)	0.756 (2)	0.420 (2)	0.1540 (12)	4.3 (4)
O(7)	0.542 (2)	−0.123 (2)	0.2469 (10)	6.7 (4)	C(26)	0.627 (2)	0.364 (2)	0.1122 (10)	3.5 (3)
O(8)	0.052 (2)	−0.223 (2)	0.1859 (9)	5.5 (3)	C(27)	0.200 (2)	0.481 (2)	0.0823 (11)	4.0 (4)
O(9)	0.233 (2)	−0.117 (2)	0.4638 (8)	5.2 (3)	C(28)	0.353 (2)	0.283 (2)	−0.0270 (10)	3.3 (3)
O(10)	0.361 (1)	−0.051 (1)	0.0505 (7)	4.1 (3)	H(22)	0.4031	0.5604	0.2347	5.00
O(11)	−0.044 (1)	0.160 (1)	0.0193 (7)	4.0 (3)	H(23)	0.6268	0.6458	0.3104	5.00
C(1)	0.349 (2)	0.210 (2)	0.4850 (10)	3.1 (3)	H(24)	0.8566	0.5653	0.2567	5.00
C(2)	0.091 (2)	0.330 (2)	0.4855 (10)	3.2 (3)	H(25)	0.8488	0.3817	0.1325	5.00
C(3)	0.336 (2)	0.454 (2)	0.4220 (10)	3.4 (3)	H(26)	0.6301	0.2897	0.0619	5.00
C(4)	−0.079 (2)	−0.004 (2)	0.3525 (11)	3.5 (4)	H(271)	0.1702	0.5202	0.1410	5.00
C(5)	−0.171 (2)	0.248 (2)	0.3554 (10)	3.1 (3)	H(272)	0.2499	0.5479	0.0558	5.00
C(6)	−0.166 (2)	0.085 (2)	0.2017 (11)	3.9 (4)	H(273)	0.1099	0.4498	0.0460	5.00
C(7)	0.427 (2)	−0.082 (2)	0.2633 (12)	4.3 (4)	H(281)	0.4156	0.2085	−0.0315	5.00
C(8)	0.128 (2)	−0.135 (2)	0.2299 (11)	3.8 (4)	H(282)	0.2625	0.2559	−0.0612	5.00
C(9)	0.239 (2)	−0.067 (2)	0.3998 (11)	3.7 (4)	H(283)	0.4025	0.3541	−0.0514	5.00
C(10)	0.301 (2)	0.035 (2)	0.0923 (9)	2.7 (3)					

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

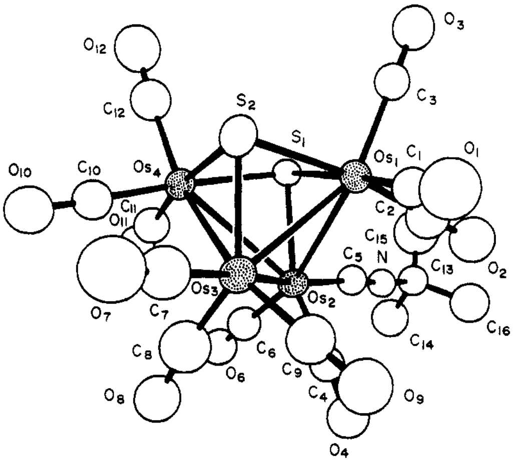

Figure 4. A perspective ORTEP diagram of $Os_4(CO)_{11}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$, **3b**, showing 50% probability thermal ellipsoids.

Table IX. Interatomic Distances (Å) with Esds for $Os_4(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)_2$ (3a)

Os(1)–Os(2)	2.925 (1)	P–C(21)	1.81 (1)
Os(1)–Os(3)	2.987 (1)	P–C(27)	1.80 (2)
Os(1)–S(2)	2.423 (3)	P–C(28)	1.81 (1)
Os(1)–S(1)	2.431 (3)	C(1)–O(1)	1.17 (1)
Os(2)–Os(3)	2.921 (1)	C(2)–O(2)	1.14 (1)
Os(2)–Os(4)	3.013 (1)	C(3)–O(3)	1.15 (2)
Os(2)–S(1)	2.376 (3)	C(4)–O(4)	1.19 (2)
Os(3)–Os(4)	2.893 (1)	C(5)–O(5)	1.16 (2)
Os(3)–S(2)	2.386 (3)	C(6)–O(6)	1.15 (2)
Os(4)–S(2)	2.428 (3)	C(7)–O(7)	1.16 (2)
Os(4)–S(1)	2.430 (3)	C(8)–O(8)	1.19 (2)
Os(4)–P	2.325 (3)	C(9)–O(9)	1.16 (1)
Os(1)–C(1)	1.88 (1)	C(10)–O(10)	1.15 (1)
Os(1)–C(2)	1.91 (1)	C(11)–O(11)	1.16 (1)
Os(1)–C(3)	1.88 (2)	C(21)–C(22)	1.36 (2)
Os(2)–C(4)	1.87 (1)	C(21)–C(26)	1.43 (2)
Os(2)–C(5)	1.86 (1)	C(22)–C(23)	1.38 (2)
Os(2)–C(6)	1.88 (1)	C(23)–C(24)	1.38 (2)
Os(3)–C(7)	1.86 (2)	C(24)–C(25)	1.38 (2)
Os(3)–C(8)	1.86 (2)	C(25)–C(26)	1.36 (2)
Os(3)–C(9)	1.85 (1)	Os(1)···Os(4)	3.535 (1)
Os(4)–C(10)	1.89 (1)	S(1)···S(2)	3.167 (8)
Os(4)–C(11)	1.86 (1)		

3a and **3b** each contain eleven linear terminal carbonyl ligands. In **3a** the PMe_2Ph ligand is located on the wingtip metal Os(4)–P = 2.325 (3) Å. Although the methyl groups on the phosphine ligand are inequivalent due to the lack of a symmetry plane in **3a**, this inequivalence is not observed in the ^1H NMR spectrum even at −90 °C. However a slight repositioning of the CO ligands on the hinge atoms Os(2) and Os(3), accompanied by an interchange of the long and short metal–metal bonds between the hinge and wingtip metal atoms, could lead to a dynamic averaging, which is rapid even at −90 °C. In contrast to **3a** the ligand substituent CN-*t*-Bu in **3b** is found on a hinge metal atom Os(2).

Discussion

Through a stepwise sequence of ligand addition and CO elimination the PMe_2Ph and CN-*t*-Bu derivatives **3a** and **3b** of **1** have been prepared. The intermediates **2a** and **2b** have been isolated and structurally characterized. The addition of CO to **1** has been reported previously.[6] In all cases ligand addition to **1** leads to open clusters analogous to **2a** and **2b**. In **1** each metal atom contains three CO ligands. In **2a** and **2b** the metal atom Os(2) has four CO ligands while the metal atom Os(4) has only two. This implies that a CO ligand shift has occurred in the course of the addition of the donor. It is well-known that CO ligands can readily migrate between metal atoms in polynuclear metal carbonyl complexes.[15] However, facile

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(15) Band, E.; Muetterties, E. L. *Chem. Rev.* 1978, *78*, 639.

Table X. Interatomic Angles (deg) with Esds for $Os_4(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)_2$ (3a)

Os(2)-Os(1)-Os(3)	59.22 (2)	Os(3)-Os(2)-C(5)	153.3 (3)	S(1)-Os(4)-S(2)	81.37 (10)
Os(1)-Os(2)-Os(3)	61.45 (2)	Os(3)-Os(2)-C(6)	116.8 (4)	S(1)-Os(4)-P	92.20 (11)
Os(1)-Os(2)-Os(4)	73.06 (2)	Os(4)-Os(2)-C(4)	131.0 (4)	S(2)-Os(4)-P	93.96 (10)
Os(3)-Os(2)-Os(4)	58.31 (1)	Os(4)-Os(2)-C(5)	136.5 (4)	Os(2)-Os(4)-C(10)	125.0 (4)
Os(1)-Os(3)-Os(2)	59.33 (2)	Os(4)-Os(2)-C(6)	89.2 (4)	Os(2)-Os(4)-C(11)	87.4 (3)
Os(1)-Os(3)-Os(4)	73.91 (2)	S(1)-Os(2)-C(4)	160.3 (4)	Os(3)-Os(4)-C(10)	79.3 (3)
Os(2)-Os(3)-Os(4)	62.43 (2)	S(1)-Os(2)-C(5)	88.2 (4)	Os(3)-Os(4)-C(11)	127.4 (4)
Os(2)-Os(4)-Os(3)	59.26 (1)	S(1)-Os(2)-C(6)	108.6 (4)	S(1)-Os(4)-C(10)	170.8 (3)
Os(2)-Os(1)-S(1)	51.67 (7)	C(4)-Os(2)-C(5)	92.5 (6)	S(1)-Os(4)-C(11)	95.9 (4)
Os(2)-Os(1)-S(2)	92.62 (7)	C(4)-Os(2)-C(6)	91.1 (6)	P-Os(4)-C(10)	93.5 (4)
Os(3)-Os(1)-S(1)	89.64 (7)	C(5)-Os(2)-C(6)	88.1 (6)	P-Os(4)-C(11)	86.7 (4)
Os(3)-Os(1)-S(2)	51.04 (8)	Os(1)-Os(3)-S(2)	59.33 (2)	C(10)-Os(4)-C(11)	91.5 (5)
S(1)-Os(1)-S(2)	81.45 (10)	Os(2)-Os(3)-S(2)	93.47 (7)	Os(4)-P-C(21)	115.6 (4)
Os(2)-Os(1)-C(1)	124.0 (4)	Os(4)-Os(3)-S(2)	53.74 (7)	Os(4)-P-C(27)	113.4 (5)
Os(2)-Os(1)-C(2)	80.8 (4)	Os(1)-Os(3)-C(7)	125.1 (5)	Os(4)-P-C(28)	114.5 (5)
Os(2)-Os(1)-C(3)	139.7 (4)	Os(1)-Os(3)-C(8)	140.1 (4)	C(21)-P-C(27)	104.4 (6)
Os(3)-Os(1)-C(1)	82.4 (4)	Os(1)-Os(3)-C(9)	90.1 (5)	C(21)-P-C(28)	105.2 (6)
Os(3)-Os(1)-C(2)	122.8 (4)	Os(2)-Os(3)-C(7)	166.4 (4)	C(27)-P-C(28)	102.4 (6)
Os(3)-Os(1)-C(3)	143.3 (4)	Os(2)-Os(3)-C(8)	81.0 (4)	P-C(21)-C(22)	122 (1)
S(1)-Os(1)-C(1)	171.9 (4)	Os(2)-Os(3)-C(9)	99.9 (4)	P-C(21)-C(26)	119 (1)
S(1)-Os(1)-C(2)	95.9 (4)	Os(4)-Os(3)-C(7)	105.3 (4)	C(23)-C(24)-C(25)	119 (1)
S(1)-Os(1)-C(3)	89.8 (4)	Os(4)-Os(3)-C(8)	92.8 (4)	C(24)-C(25)-C(26)	122 (1)
S(2)-Os(1)-C(1)	92.4 (4)	Os(4)-Os(3)-C(9)	160.4 (4)	C(21)-C(26)-C(25)	119 (1)
S(2)-Os(1)-C(2)	173.1 (4)	S(2)-Os(3)-C(7)	82.4 (5)	Os(1)-C(1)-O(1)	177 (1)
S(2)-Os(1)-C(3)	92.7 (4)	S(2)-Os(3)-C(8)	143.4 (4)	Os(1)-C(2)-O(2)	174 (1)
C(1)-Os(1)-C(2)	89.7 (5)	S(2)-Os(3)-C(9)	124.2 (4)	Os(1)-C(3)-O(3)	177 (1)
C(1)-Os(1)-C(3)	95.6 (5)	C(7)-Os(3)-C(8)	94.6 (6)	Os(2)-C(4)-O(4)	179 (1)
C(2)-Os(1)-C(3)	93.7 (6)	C(7)-Os(3)-C(9)	93.1 (6)	Os(2)-C(5)-O(5)	178 (1)
Os(1)-Os(2)-S(1)	53.39 (7)	C(8)-Os(3)-C(9)	92.4 (6)	Os(2)-C(6)-O(6)	175 (1)
Os(3)-Os(2)-S(1)	92.31 (7)	Os(2)-Os(4)-S(1)	50.38 (7)	Os(3)-C(7)-O(7)	174 (1)
Os(4)-Os(2)-S(1)	51.97 (7)	Os(2)-Os(4)-S(2)	90.39 (7)	Os(3)-C(8)-O(8)	177 (1)
Os(1)-Os(2)-C(4)	107.2 (4)	Os(2)-Os(4)-P	141.17 (8)	Os(3)-C(9)-O(9)	177 (1)
Os(1)-Os(2)-C(5)	98.6 (4)	Os(3)-Os(4)-S(1)	91.92 (7)	Os(4)-C(10)-O(10)	179 (1)
Os(1)-Os(2)-C(6)	160.1 (4)	Os(3)-Os(4)-S(2)	52.40 (7)	Os(4)-C(11)-O(11)	177 (1)
Os(3)-Os(2)-C(4)	78.4 (4)	Os(3)-Os(4)-P	144.93 (8)		

Table XI. Positional and Thermal Parameters and Their Esds for $Os_4(CO)_{11}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$ (3b)[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$	B_{eqv}, Å^2
Os(1)	0.59285 (4)	0.2756 (1)	0.74676 (7)	2.52 (4)	3.45 (5)	2.84 (4)	0.17 (5)	0.28 (5)	0.24 (6)	2.94 (2)
Os(2)	0.69055 (5)	0.2293 (1)	0.65559 (6)	2.38 (4)	2.97 (5)	3.25 (5)	0.21 (5)	0.15 (5)	−0.10 (6)	2.87 (2)
Os(3)	0.57852 (5)	0.1786 (1)	0.59946 (6)	3.02 (5)	3.05 (6)	3.46 (5)	−0.17 (5)	−0.49 (5)	−0.11 (5)	3.18 (3)
Os(4)	0.61656 (5)	0.4164 (1)	0.58015 (6)	3.03 (5)	3.00 (6)	2.94 (5)	0.22 (5)	0.09 (5)	0.31 (5)	2.99 (2)
S(1)	0.6606 (3)	0.4142 (6)	0.6981 (4)	3.4 (3)	2.4 (3)	2.9 (3)	−0.1 (3)	0.5 (3)	−0.1 (3)	2.9 (2)
S(2)	0.5360 (3)	0.3483 (7)	0.6484 (4)	3.3 (3)	3.9 (4)	3.9 (4)	−0.1 (3)	0.5 (3)	1.0 (4)	3.7 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.5015 (9)	0.103 (2)	0.783 (1)	6.9 (6)	C(8)	0.617 (1)	0.135 (3)	0.526 (2)	7.1 (10)
O(2)	0.6695 (9)	0.158 (2)	0.854 (1)	7.0 (6)	C(9)	0.570 (1)	0.034 (3)	0.636 (2)	5.3 (8)
O(3)	0.5584 (8)	0.451 (2)	0.861 (1)	5.1 (5)	C(10)	0.582 (1)	0.402 (3)	0.494 (2)	4.3 (7)
O(4)	0.6957 (9)	−0.033 (2)	0.652 (1)	5.6 (5)	C(11)	0.684 (1)	0.446 (3)	0.530 (2)	4.9 (8)
O(6)	0.7822 (8)	0.242 (2)	0.546 (1)	5.7 (5)	C(12)	0.599 (1)	0.577 (3)	0.585 (2)	5.3 (8)
O(7)	0.7252 (7)	0.473 (2)	0.501 (1)	5.0 (5)	C(13)	0.830 (1)	0.248 (3)	0.825 (1)	4.6 (7)
O(8)	0.5541 (8)	0.388 (2)	0.440 (1)	5.5 (5)	C(14)	0.887 (1)	0.226 (3)	0.786 (2)	7.9 (10)
O(9)	0.5864 (9)	0.671 (2)	0.593 (1)	6.9 (6)	C(15)	0.829 (2)	0.352 (4)	0.861 (2)	11.2 (14)
O(10)	0.4722 (9)	0.144 (2)	0.513 (1)	7.1 (6)	C(16)	0.821 (1)	0.144 (3)	0.876 (2)	7.5 (10)
O(11)	0.5660 (9)	−0.060 (2)	0.662 (1)	6.2 (6)	H(141)	0.8887	0.1406	0.7812	5.00
O(12)	0.6505 (8)	0.098 (2)	0.478 (1)	6.0 (6)	H(142)	0.9160	0.2227	0.8320	5.00
N	0.7855 (8)	0.236 (2)	0.772 (1)	3.6 (5)	H(151)	0.8594	0.3906	0.8652	5.00
C(1)	0.537 (1)	0.162 (2)	0.770 (1)	3.5 (6)	H(161)	0.7773	0.0840	0.8652	5.00
C(2)	0.641 (1)	0.206 (3)	0.811 (2)	6.2 (9)	H(143)	0.8905	0.2864	0.7473	5.00
C(3)	0.569 (1)	0.384 (3)	0.818 (1)	3.5 (7)	H(152)	0.8116	0.3515	0.9093	5.00
C(4)	0.693 (1)	0.065 (2)	0.653 (1)	4.0 (6)	H(153)	0.8034	0.4110	0.8345	5.00
C(5)	0.749 (1)	0.238 (3)	0.731 (1)	3.7 (6)	H(162)	0.8200	0.1645	0.9254	5.00
C(6)	0.745 (1)	0.238 (3)	0.586 (1)	4.5 (7)	H(163)	0.8515	0.0885	0.8689	5.00
C(7)	0.515 (1)	0.160 (3)	0.543 (2)	5.5 (8)					

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

migratory behavior for phosphine ligands has not yet been reported, and thus one can probably safely conclude from the observation of the phosphine ligand on Os(4) that atom Os(4) is the site where the addition occurred. It was previously speculated that the site of addition to 1 was one of the hinge metal atoms.[6] The present results can be rationalized better by addition to one of the wingtip metal atoms, accompanied by a CO ligand shift, a sulfido ligand shift, and the cleavage of the two elongated metal–metal bonds; see Scheme I. The addition of PMe_2Ph to the isoelectronic mixed-metal cluster $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ seems to proceed similarly.[7] Indeed, all

Scheme I

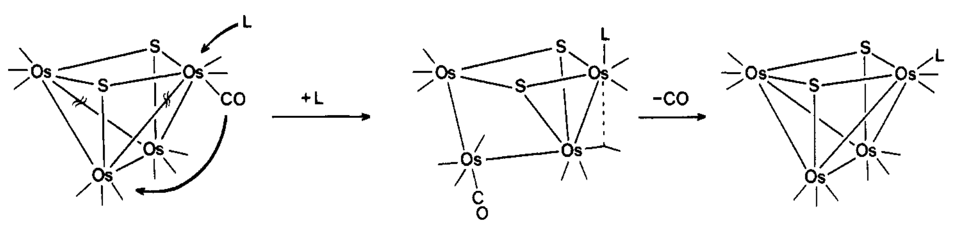

Table XII. Interatomic Distances (Å) with Esds for $Os_4(CO)_{11}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$ (3b)

Os(1)-Os(2)	2.923 (1)	Os(4)-C(10)	1.80 (3)
Os(1)-Os(3)	2.965 (1)	Os(4)-C(11)	1.89 (3)
Os(2)-Os(3)	2.922 (1)	Os(4)-C(12)	1.90 (3)
Os(2)-Os(4)	3.115 (1)	C(1)-O(1)	1.12 (2)
Os(3)-Os(4)	2.909 (1)	C(2)-O(2)	1.17 (3)
Os(1)-S(1)	2.443 (5)	C(3)-O(3)	1.13 (2)
Os(2)-S(1)	2.381 (6)	C(4)-O(4)	1.14 (2)
Os(4)-S(1)	2.421 (5)	C(5)-N	1.17 (2)
Os(1)-S(2)	2.417 (6)	C(6)-O(6)	1.16 (2)
Os(3)-S(2)	2.381 (6)	C(7)-O(7)	1.17 (2)
Os(4)-S(2)	2.428 (6)	C(8)-O(8)	1.27 (2)
S(1)···S(2)	3.199 (8)	C(9)-O(9)	1.19 (2)
Os(1)-C(1)	1.91 (2)	C(10)-O(10)	1.20 (2)
Os(1)-C(2)	1.85 (3)	C(11)-O(11)	1.15 (3)
Os(1)-C(3)	1.90 (2)	C(12)-O(12)	1.13 (2)
Os(2)-C(4)	1.89 (2)	N-C(13)	1.45 (2)
Os(2)-C(5)	1.96 (2)	C(13)-C(14)	1.55 (3)
Os(2)-C(6)	1.83 (2)	C(13)-C(15)	1.38 (4)
Os(3)-C(7)	1.86 (2)	C(13)-C(16)	1.54 (3)
Os(3)-C(8)	1.72 (2)	Os(1)···Os(4)	3.535 (1)
Os(3)-C(9)	1.81 (2)		

nucleophilic additions to 1 could proceed by attack at the wingtip metal atoms.

Ligand elimination from the open clusters proceeds by the loss of a CO ligand and yields the closed clusters 3 that are structurally analogous 1. The microscopic reverse of the ligand addition to 1 would lead to loss of L and the regeneration of 1. At present, there is no evidence for the occurrence of this process, and the loss of CO that leads to the compounds 3 in high yield might occur by an elimination directly from the carbonyl-rich $Os(CO)_4$ group. The fact that the isocyanide ligand in **3b** is located on the hinge atom Os(2) could be explained by a subsequent interchange of the isocyanide and a CO ligand between atoms Os(4) and Os(2).[15]

The structural analyses of compounds 3 provide further evidence concerning their unusual bonding. Like 1, compounds 3 are 64-electron clusters. To obey the effective atomic number rule these clusters should have only four metal–metal bonds.[16] These compounds do, however, contain five significant Os–Os interactions. The significant elongations of two of the five metal–metal bonds may be an alternative via a partial delocalization to the complete cleavage of one bond. The reason for the inequivalence of the two long bonds in 1 and **3b** is not apparent at this time. Other 64-electron tetranuclear cluster compounds that have five metal–metal bonds also exhibit significant bond lengthening effects on some of their metal–metal bonds.[16-18] It should be pointed out that the electronic structures of 1 and 3 can be rationalized within the

Table XIII. Interatomic Angles (deg) with Esds for $Os_4(CO)_{11}(CN\text{-}t\text{-}Bu)(\mu_3\text{-}S)_2$ (3b)

Os(2)-Os(1)-Os(3)	59.51 (3)	Os(3)-Os(2)-C(4)	79.4 (7)	Os(2)-Os(4)-C(12)	140.9 (7)
Os(1)-Os(2)-Os(4)	71.44 (3)	Os(3)-Os(2)-C(5)	154.9 (6)	Os(3)-Os(4)-S(2)	52.05 (15)
Os(1)-Os(2)-Os(3)	60.95 (3)	Os(3)-Os(2)-C(6)	114.2 (6)	Os(3)-Os(4)-C(10)	83.1 (7)
Os(1)-Os(3)-Os(2)	59.54 (3)	S(1)-Os(2)-C(4)	155.4 (7)	Os(3)-Os(4)-C(11)	119.6 (7)
Os(1)-Os(3)-Os(4)	73.84 (3)	S(1)-Os(2)-C(5)	86.1 (7)	Os(3)-Os(4)-C(12)	147.6 (7)
Os(3)-Os(2)-Os(4)	57.50 (3)	S(1)-Os(2)-C(6)	113.4 (8)	S(2)-Os(3)-C(7)	87.9 (8)
Os(2)-Os(3)-Os(4)	64.58 (3)	C(4)-Os(2)-C(5)	92.8 (10)	S(2)-Os(3)-C(8)	140.3 (8)
Os(2)-Os(4)-Os(3)	57.92 (3)	C(4)-Os(2)-C(6)	91.1 (10)	S(2)-Os(3)-C(9)	124.3 (10)
Os(2)-Os(1)-S(1)	51.73 (13)	C(5)-Os(2)-C(6)	89.6 (8)	C(7)-Os(3)-C(8)	87.4 (12)
Os(2)-Os(1)-S(2)	94.31 (14)	Os(2)-Os(3)-S(2)	95.11 (15)	C(7)-Os(3)-C(9)	90.5 (11)
Os(2)-Os(1)-C(1)	123.8 (6)	Os(2)-Os(3)-C(7)	166.0 (8)	C(8)-Os(3)-C(9)	95.2 (12)
Os(2)-Os(1)-C(2)	78.1 (8)	Os(2)-Os(3)-C(8)	81.6 (9)	Os(1)-S(1)-Os(2)	74.58 (17)
Os(2)-Os(1)-C(3)	139.4 (6)	Os(2)-Os(3)-C(9)	99.0 (8)	Os(1)-S(1)-Os(4)	93.01 (19)
Os(3)-Os(1)-S(1)	89.07 (13)	Os(4)-Os(3)-S(1)	90.83 (14)	Os(2)-S(1)-Os(4)	80.90 (17)
Os(3)-Os(1)-S(2)	51.30 (15)	Os(4)-Os(3)-S(2)	53.52 (14)	Os(1)-S(2)-Os(4)	93.48 (20)
Os(3)-Os(1)-C(1)	82.4 (6)	Os(4)-Os(3)-C(7)	107.3 (8)	Os(1)-S(2)-Os(3)	76.31 (18)
Os(3)-Os(1)-C(2)	120.0 (8)	Os(4)-Os(3)-C(8)	90.8 (10)	Os(3)-S(2)-Os(4)	74.43 (17)
Os(3)-Os(1)-C(3)	147.9 (6)	Os(4)-Os(3)-C(9)	161.6 (8)	Os(1)-C(1)-O(1)	174 (2)
S(1)-Os(1)-S(2)	82.31 (19)	S(1)-Os(4)-S(2)	82.57 (19)	Os(1)-C(2)-O(2)	176 (2)
S(1)-Os(1)-C(1)	171.3 (6)	S(1)-Os(4)-C(10)	174.0 (7)	Os(1)-C(3)-O(3)	175 (2)
S(1)-Os(1)-C(2)	96.3 (8)	S(1)-Os(4)-C(11)	94.5 (7)	Os(2)-C(4)-O(4)	178 (2)
S(1)-Os(1)-C(3)	91.4 (7)	S(1)-Os(4)-C(12)	93.5 (8)	Os(2)-C(5)-N	174 (2)
S(2)-Os(1)-C(1)	91.0 (6)	S(2)-Os(3)-C(7)	87.9 (8)	Os(2)-C(6)-O(6)	176 (2)
S(2)-Os(1)-C(2)	171.1 (8)	S(2)-Os(3)-C(8)	140.3 (10)	Os(3)-C(7)-O(7)	174 (2)
S(2)-Os(1)-C(3)	97.0 (6)	S(2)-Os(3)-C(9)	124.3 (8)	Os(3)-C(8)-O(8)	172 (2)
C(1)-Os(1)-C(2)	89.5 (10)	C(7)-Os(3)-C(8)	87.4 (12)	Os(3)-C(9)-O(9)	177 (2)
C(1)-Os(1)-C(3)	94.9 (9)	C(7)-Os(3)-C(9)	90.5 (11)	Os(4)-C(10)-O(10)	174 (2)
C(2)-Os(1)-C(3)	91.8 (10)	C(8)-Os(3)-C(9)	95.2 (12)	Os(4)-C(11)-O(11)	174 (2)
Os(1)-Os(2)-S(1)	53.69 (13)	Os(1)-Os(3)-S(2)	52.39 (14)	Os(4)-C(12)-O(12)	175 (2)
Os(1)-Os(2)-C(4)	102.4 (7)	Os(1)-Os(3)-C(7)	131.0 (8)	C(5)-N-C(13)	173 (3)
Os(1)-Os(2)-C(5)	98.3 (6)	Os(1)-Os(3)-C(8)	141.2 (9)	N-C(13)-C(14)	108 (2)
Os(1)-Os(2)-C(6)	163.9 (7)	Os(1)-Os(3)-C(9)	90.8 (8)	N-C(13)-C(15)	113 (3)
Os(4)-Os(2)-S(1)	50.11 (13)	Os(2)-Os(4)-S(1)	48.99 (13)	N-C(13)-C(16)	104 (2)
Os(4)-Os(2)-C(4)	134.2 (7)	Os(2)-Os(4)-S(2)	89.44 (14)	C(14)-C(13)-C(15)	113 (3)
Os(4)-Os(2)-C(5)	132.8 (7)	Os(2)-Os(4)-C(10)	126.5 (7)	C(14)-C(13)-C(16)	107 (2)
Os(4)-Os(2)-C(6)	92.9 (7)	Os(2)-Os(4)-C(11)	82.1 (7)	C(15)-C(13)-C(16)	111 (2)
Os(3)-Os(2)-S(1)	91.31 (13)				

framework of the polyhedral skeletal electron pair theory.[19] According to this theory the Os_4S_2 core of the compounds would have the form of a nido pentagonal bipyramid. This polyhedron would possess eight cluster valence orbitals into which 16 electrons could be placed. In fact, according to this theory compounds 1 and 3 do contain exactly 16 cluster valence electrons. Although the PSEP theory thus predicts a stable structure with five metal–metal bonds, it does not indicate where selective bond lengthening should occur. As indicated above, this may be a natural consequence of further considerations that include the effects of the ligand dispositions.

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Supplementary Material Available: Tables of structure factor amplitudes for all four structural analyses are available (47 pages). Ordering information is given on any current masthead page.

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Carbon–Palladium(II) Complexes of Dialkyl Malonates: Synthesis, ^1H and ^{13}C NMR Spectroscopy, and Single-Crystal Structure Analyses[1,2]

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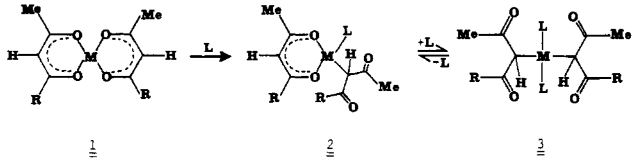
Novel square-planar palladium(II) complexes [PdL(dialkyl malonato)$_2$] having Pd–C(malonato) σ bonds were prepared by the intermolecular exchange of chloro ligands with dialkyl malonate. The bidentate ligand (L) is 2,2′-bipyridine, 1,10-phenanthroline, 2,2-bis(2-pyridyl)-1,3-dioxolane, di-2-pyridylmethane, or 1,2-bis(2-pyridyl)ethane, whereas dialkyl malonate behaves as a unidentate ligand coordinating through the central carbon atom. Treatment of bis metalated complexes with 1,3-dibromopropane under basic conditions did not result in the expected cyclization via C–C bond formation, but rather one of the malonates is replaced by bromide. The ^1H and ^{13}C NMR and IR spectra, novel chemistry, and structural aspects of ring size in the organometallics are discussed. Single-crystal X-ray structure analyses were conducted on bis(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II), $PdC_{27}H_{34}N_2O_{10}$, and bromo(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II), $PdBrC_{20}H_{23}N_2O_6$. Both the crystals are monoclinic and crystallize in space group $P2_1/c$. The cell constants for the former are a = 9.837 (2) Å, b = 21.647 (4) Å, c = 14.089 (2) Å, β = 95.45 (1)°, and Z = 4. Bond lengths involving palladium average 2.110 (3) Å for Pd–N and 2.095 (4) Å for Pd–C bonds. For the latter compound the cell constants are a = 8.982 (1) Å, b = 14.318 (3) Å, c = 17.368 (4) Å, β = 101.71 (2)°, and Z = 4. Bond lengths in the coordination sphere average 2.086 (4) Å for Pd–N, 2.107 (4) Å for Pd–C, and 2.404 (1) Å for Pd–Br bonds. All the pyridine rings are planar and produce an intramolecular dihedral angle of 72.6° in former and 67.3° in the latter. The palladium coordination is slightly tetrahedrally distorted from square-planar geometry.

Introduction

Usually β-dicarbonyl ligands, e.g., acetylacetonate anion, O,O-coordinate a metal ion to form a six-membered chelate ring (1). Rearrangement of the bidentate O ligands to an unidentate central carbon atom bond with Pd(II) and Pt(II) has been reported by Okeya et al.[3] and others.[4,5] Thus, the bis(acetylacetonate)palladium(II) complex on treatment with Lewis bases such as pyridine, triphenylphosphine, or diethylamine afford the C–Pd complexes 2 and 3. C-Metalated complexes of ethyl acetoacetate have been obtained in a similar manner, via the rearrangement of the corresponding O,O′-bonded chelate complexes.[3-5]

Scheme I



R = Me or OEt; M = Pd(II) or Pt(II); L = Py, PPh_3, HNR_2 etc.

Since dialkyl malonates do not exist in appreciable amounts as the enol tautomer[6] and due to the limited number of established examples of their C-bonded organometallics, we synthesized a series of unidentate (malonate-*C*)palladium(II) complexes.[7,8] We herein expand

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