Ligand-Assisted Addition Reactions. 1. Alkyne Additions and Couplings in the Unsaturated Cluster Complexes $Os_4(CO)_{11}(\mu_4\text{-}RC_2CO_2Me)(\mu_4\text{-}S)$ (R = H and CO_2Me)

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The reactions of the unsaturated cluster complexes $Os_4(CO)_{11}(\mu_4\text{-}RC_2CO_2Me)(\mu_4\text{-}S)$ (**1a**, R = CO_2Me, and **1b**, R = H) with PhC≡CH have been investigated. The reaction of **1a** with PhC≡CH yields a series of compounds, $Os_4(CO)_{11}(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)[\mu\text{-}SC(Ph)CH]$ (**2**), $Os_4(CO)_{11}[\mu_4\text{-}\eta^5\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**3**), and $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**4**). Compound **2** is formed in 69% yield by reaction at 25 °C. When refluxed in $CHCl_3$, **2** is converted into **3** (25%) and **4** (37%). All the products were characterized by IR, ^1H NMR, elemental, and single-crystal X-ray diffraction analyses. The structure of **2** consists of a spiked triangular cluster of metal atoms with a triply bridging $MeO_2CC{\equiv}CCO_2Me$ ligand and a bridging $HC_2(Ph)S$ ligand formed by the addition of the HC_2Ph molecule to the sulfido ligand, C–S = 1.795 (9) Å. Compound **3** consists of a cluster connected by only three metal–metal bonds. The carbon–sulfur bond was cleaved, and the two alkyne ligands were coupled through formation of a carbon–carbon bond. A four-carbon unsaturated unit bridges three metal atoms, and one of the carboxylate groups is coordinated to the fourth metal atom. Compound **4** consists of a spiked triangular cluster of metal atoms. The coupled alkyne unit formed a metallacyclopentadienyl unit by including one of the metal atoms of the triangular cluster. This unit is π-bonded to another metal atom. The reaction of **1b** with PhC≡CH yields the product $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C_2CO_2Me]$ (**5**), 34% yield by the addition of two formula equivalents of PhC≡CH. Compound **5** was also characterized by IR, ^1H NMR, elemental, and single-crystal X-ray diffraction analyses. The structure of **5** consists of a spiked triangular cluster of metal atoms with a bridging 1-phenylvinyl group extending to the external metal atom of the cluster. A $MeO_2CC_2(H)C_2(Ph)S$ ligand bridges the four metal atoms. This ligand was formed by the removal of the alkynyl hydrogen atom from the MeO_2CC_2H ligand and the addition of one PhC≡CH molecule to the terminal carbon and to the sulfido ligand, C–S = 1.80 (2) Å. Mechanisms are proposed for the formation of all the products. One of the first steps in the PhC≡CH additions is the formation of a carbon–sulfur bond between the alkyne and the sulfido ligand. It is believed that the interactions between electron-rich ligands and unsaturated reagents, in general, may play an important role in the introduction of new ligands into bonding with metal atoms. It is proposed to designate those reactions where these interactions play an important role as ligand-assisted addition reactions and ligand-assisted substitution reactions for addition and substitution reactions, respectively.

Introduction

The discovery that transition-metal complexes can promote carbon–carbon bond formation in the coupling of alkyne molecules has been one of the great successes to emerge from the study of organometallic chemistry.[1] Recently, much interest has been focused on the chemistry of alkyne ligands in polynuclear metal complexes.[2] These studies have demonstrated a variety of new and unusual alkyne ligand transformations.[3,4]

Recent investigations of ligand-bridged cluster complexes with alkynes have revealed a strong tendency of the alkyne ligands to engage in bonding to the bridging ligands.[5-8] It is believed that these interactions may occur very early in the reaction profiles. Indeed, in some cases they may be the first important contacts between the molecules.[5] Such processes could form the basis of a general mechanism for the introduction of unsaturated small molecules into bonding to metal atoms. They have, in some cases, resulted in the formation of unusual new ligands, and these may undergo transformations in new ways. In this report the nature of the reactions of the unsaturated clusters $Os_4(CO)_{11}(\mu_4\text{-}RC_2CO_2Me)(\mu_4\text{-}S)$ (**1a**, R = CO_2Me, and **1b**, R = H) with alkynes is described. These results support the idea that alkyne additions proceed initially via interactions at the sulfido ligand. Coupling of the alkyne ligands occurs in a subsequent step, and this can be influenced by the sulfido ligand. A preliminary report of some of this work has been published.[9]

Experimental Section

General Data. All the reactions were performed under a nitrogen atmosphere. Reagent grade solvents were used without

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further purification. The compounds $Os_4(CO)_{11}(\mu_4\text{-}MeO_2CC\equiv CCO_2Me)(\mu_4\text{-}S)$ (**1a**) and $Os_4(CO)_{11}(\mu_4\text{-}HC\equiv CCO_2Me)(\mu_4\text{-}S)$ (**1b**) were prepared as previously described.[10] ^1H NMR spectra were taken at 300 MHz on a Brüker AM-300 spectrometer or at 80 MHz on an IBM-NR-80 spectrometer. IR spectra were recorded on a Nicolet 5-DXB, FTIR spectrophotometer. Elemental analyses were performed by MIC ANAL, Tucson, AZ.

Reaction between $Os_4(CO)_{11}(\mu_4\text{-}MeO_2CC\equiv CCO_2Me)(\mu_4\text{-}S)$ (1a) and PhC$\equiv$CH. **1a** (8.0 mg, 0.0064 mmol) was dissolved in 10 mL of CH_2Cl_2 solvent. PhC_2H (3.0 μL, 0.027 mmol) was added, and the solution was stirred for 100 min at 25 °C. The solution changed color from yellow to light yellow. The solvent was removed in vacuo, and the residue was chromatographed by TLC on silica gel. A major yellow band was eluted with a 70:30 CH_2Cl_2/hexane solvent mixture, $Os_4(CO)_{11}(\mu\text{-}MeO_2CC\equiv CCO_2Me)[\mu\text{-}SC(Ph)CH]$ (**2**) (6.0 mg, 69%). IR (ν(CO), in hexane): 2098 (s), 2081 (vs), 2057 (vs), 2035 (s), 2022 (s), 2013 (s), 2008 (s), 1993 (m), 1904 (w), 1722 (w). ^1H NMR (δ, in $CDCl_3$ at −15 °C): 8.51 (s, 1 H), 7.38–7.24 (m, 5 H), 3.72 (s, 3 H), 3.17 (s, 3 H). Anal. Calcd: C, 22.31; H, 0.89. Found: C, 22.50; H, 0.68.

Thermolysis of Compound 2. Compound **2** (8.0 mg) was dissolved in 5 mL of $CHCl_3$, and the solution was refluxed for 10 h. The light yellow solution slowly turned to yellow-orange. After removal of the solvent in vacuo, the reaction mixture was separated by TLC on silica gel. Elution with a 70:30 CH_2Cl_2/hexane mixture yielded the following bands: orange $Os_4(CO)_{11}[\mu_4\text{-}\eta^5\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**3**) (2.0 mg, 25%); yellow $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**4**) (3.0 mg, 37%); a trace of unreacted **2**. If the thermolysis was performed in heptane solution (98 °C), compound **4** was obtained in 50% yield and no **3** was obtained. IR (ν(CO), cm^{-1}, in hexane): for **3**, 2101 (m), 2079 (vs), 2059 (s), 2023 (s), 2017 (s), 2013 (s, sh), 2008 (s, sh), 1994 (w), 1979 (vw), 1972 (vw), 1941 (vw), 1737 (vw); for **4**, 2109 (m), 2105 (w, sh), 2082 (s), 2052 (s), 2034 (m), 2007 (s), 1995 (m), 1982 (m), 1948 (vw), 1908 (vw), 1740 (br, w). ^1H NMR (δ, $CDCl_3$): for **3**, 7.4–7.2 (m, C_6H_5), 6.92 (s, CH), 3.77 (s, CH_3), 3.57 (s, CH_3); for **4**, 7.4–7.0 (m, C_6H_5), 6.89 (s, CH), 3.90 (s, CH_3), 3.75 (s, CH_3). Anal. Calcd for **3**: C, 22.31; H, 0.89. Found: C, 22.02; H, 0.72. Calcd for **4**: C, 22.31; H, 0.89. Found: C, 21.96; H, 1.00.

Thermolysis of Compound 3. Compound **3** (4.0 mg) was dissolved in 5 mL of $CHCl_3$. The solution was refluxed for 35 h. During this time, the orange solution slowly changed color to yellow. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and separated on silica gel TLC plates. Elution with a 50:50 CH_2Cl_2/hexane solution yielded two major bands: orange unreacted compound **3** (1.0 mg, 25%); yellow compound **4** (2.0 mg, 50%).

Reaction between $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC\equiv CCO_2Me)$ (1b) and PhC$\equiv$CH. **1b** (10.0 mg, 0.0084 mmol) was dissolved in 10 mL of CH_2Cl_2 solvent at 25 °C. PhC$\equiv$CH (10 μL, 0.091 mmol) was added to the solution. The solution was stirred for 3 h and changed color from yellow to orange. The solvent and unreacted PhC$\equiv$CH were removed in vacuo, and the residue was separated by TLC on silica gel. A major orange band was eluted with a 30:70 CH_2Cl_2/hexane solvent mixture and was identified as $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C_2CO_2Me]$ (**5**) (4.0 mg, 34%). IR (ν(CO), cm^{-1}, in hexane): 2094 (w), 2079 (vs), 2053 (s), 2031 (w), 2019 (m), 2010 (s), 2005 (m), 1990 (w), 1884 (br, vw), 1706 (vw). ^1H NMR (δ, in $CDCl_3$): 8.44 (s, 1 H), 5.77 (d, 1 H, $J_{H\text{-}H}$ = 3.0 Hz), 3.77 (s, 3 H), 3.08 (d, 1 H, $J_{H\text{-}H}$ = 3.0 Hz). Anal. Calcd: C, 26.78; H, 1.1. Found: C, 26.66; H, 1.1.

Crystallographic Analyses. Yellow crystals of **2** and **4** were obtained by slow evaporation benzene/CH_2Cl_2/hexane solutions at 0 °C. Orange crystals of **3** and **5** were grown by cooling CH_2Cl_2/hexane solutions to −20 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the AFC6 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 Equipment Corp. MICROVAX I computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., College Station, TX. Neutral atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[11b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compounds **2**, **4**, and **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed in each case and was confirmed by the successful solution and refinement of the structure. These structures were solved by a combination of Patterson and difference Fourier syntheses. Compound **5** was found to possess a twofold disorder that affected one of the phenyl groups, the methylcarboxylate group, and the oxygen atom O(5) of the semibridging carbonyl ligand. A 50/50 disorder model applied to all the disorder sites converged well upon refinement. However, the molecular dimensions between the disordered groups and the "nondisordered" atoms to which they are directly bonded were in a few cases slightly outside of the normally accepted values (e.g., C(5)–O(5A) = 1.34 (3) Å, C(25)–C(26A) = 1.62 (4) Å, and C(13)–C(14A) = 1.71 (5) Å). These distortions can probably be attributed to a small unresolvable disorder in these "nondisordered" atoms. For compound **2** all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated by assuming idealized geometries. The hydrogen atom H(18) was located in a difference Fourier map. Scattering contributions for the hydrogen atoms were included in the structure factor calculations, but their positions were not refined. One mole of CH_2Cl_2 solvent was found to have cocrystallized with the compound. For compounds **3** and **4** only the metal and sulfur atoms were refined anisotropically. For compound **4**, the hydrogen atom H(18) was located in a difference Fourier synthesis. The hydrogen atom positions on the phenyl group and benzene molecules were calculated by assuming idealized geometries. The hydrogen atoms on the methyl groups were ignored. Due to the complications of the disorder the hydrogen atoms on compound **5** were ignored. The crystals of compound **4** were found to contain 1.5 mol of benzene/mol of complex. One of these benzene molecules lay in a general position. The other was positioned on a center of symmetry.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established uniquely from the systematic absences observed during the collection of data. For this structure the coordinates of the heavy atoms were obtained by direct methods (MULTAN). All remaining non-hydrogen atom were subsequently obtained from difference Fourier syntheses. The hydrogen atom positions were calculated by assuming idealized geometries. Atom H(18) was located in a difference Fourier map. Their scattering contributions were included in the structure factor calculations but their positions were not refined. Only the metal and sulfur atoms were refined with anisotropic thermal parameters.

Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters for compounds **2** and **3**. For compound **5** this material was made available previously.[9]

Results

The unsaturated cluster compound $Os_4(CO)_{11}(\mu_4\text{-}MeO_2CC\equiv CCO_2Me)(\mu_4\text{-}S)$ (**1a**) undergoes reaction by the addition of 1 mol of PhC$\equiv$CH at 25 °C to give a good yield (69%) of the new compound $Os_4(CO)_{11}(\mu\text{-}MeO_2CC\equiv CCO_2Me)(\mu\text{-}SC(Ph)CH]$ (**2**). Compound **2** was characterized by IR and ^1H NMR spectroscopies and elemental and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **2** is shown in Figure

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[10] Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1272.

[11] *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 I. Crystallographic Data for the Structural Analyses for Compounds 2-5[a]

	2	3	4	5
(A) Crystal Data				
formula	$Os_4SO_{15}C_{25}H_{12}\cdot CH_2Cl_2$	$Os_4SO_{15}C_{25}H_{12}$	$Os_4SO_{15}C_{25}H_{12}\cdot 1.5C_6H_6$	$Os_4SO_{13}C_{31}H_{16}$
temp, ±3 °C	23	23	28	28
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	13.900 (3)	12.847 (3)	13.562 (2)	12.706 (4)
b, Å	12.978 (2)	15.068 (3)	14.215 (2)	15.616 (3)
c, Å	9.777 (2)	17.040 (3)	12.731 (2)	10.211 (2)
α, deg	95.80 (2)	90.0	105.48 (1)	90.65 (2)
β, deg	75.36 (2)	111.80 (1)	106.77 (1)	111.51 (2)
γ, deg	110.45 (1)	90.0	115.42 (1)	113.44 (2)
V, Å^3	1599	3063	1893	1700
M_r	1345.1	1345.1	1461.8	1389.2
Z	2	4	2	2
ρ_{calcd}, g/cm^3	2.79	2.92	2.56	2.71
(B) Measurement of Intensity Data				
radiatn	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite	graphite	graphite
detector aperture, mm				
horizontal	2.0	2.0	2.0	2.0
vertical	2.0	2.0	2.0	2.0
crystal faces	$1\bar{1}0,\bar{1}10,100$ $\bar{1}00,\bar{1}0\bar{2},020$	$011,0\bar{1}\bar{1},11\bar{2},01\bar{1}$ $\bar{1}11,\bar{1}\bar{1}1,1\bar{2}2$	$001,00\bar{1},\bar{1}10,1\bar{1}0$ $\bar{1}11,1\bar{1}\bar{1},02\bar{1},0\bar{1}0$	$\bar{1}00,100,0\bar{1}0$ $\bar{1}01,10\bar{1},010$
cryst size, mm	0.03 × 0.10 × 0.38	0.20 × 0.18 × 0.17	0.09 × 0.13 × 0.22	0.04 × 0.15 × 0.55
cryst orientatn: direction; deg from ϕ axis	[102]; 10.24	[210]; 9.9	[111]; 6.4	[102]; 0.82
reflctns measd	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$\pm k,\pm k,+l$
max 2θ, deg	50	50	50	50
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	1.10	1.10	1.10	1.10
bkgd (count time at each end of scan), s	9	9	9	3
ω-scan rate, deg/min	4.0	4.0	4.0	4.0
no. of reflctns measd	5235	5274	5443	7122
data used ($F^2 \geq 3.0\sigma(F^2)$)	3723	3588	4574	4602
(C) Treatment of Data				
absorptn correctn	applied	applied	applied	applied
coeff, cm^{-1}	169	177	143	159
grid	6 × 12 × 12	14 × 8 × 8	14 × 10 × 6	4 × 10 × 20
transmissn coeff				
max	0.61	0.16	0.34	0.42
min	0.13	0.06	0.18	0.09
P factor	0.03	0.03	0.03	0.03
final residuals				
R_F	0.025	0.044	0.032	0.050
R_{wF}	0.029	0.049	0.039	0.057
esd of unit weight observn	1.17	1.66	1.49	2.22
largest shift/error value of final cycle	0.17	0.06	0.16	0.08
largest peak in final diff Fourier, e/Å^3	0.58	2.04	1.17	3.05
no. of variables	406	206	242	266

[a] Rigaku software uses a multiple-scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to first scan etc. A maximum of three scans was permitted per reflection.

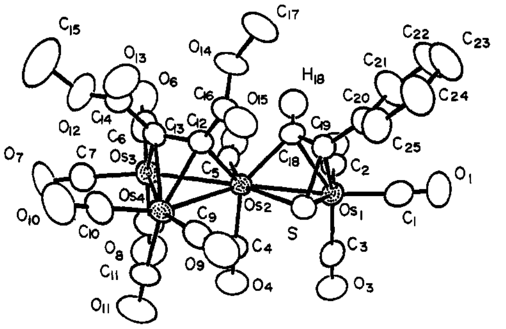

Figure 1. An ORTEP diagram of $Os_4(CO)_{11}(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)[\mu\text{-}SC(Ph)CH]$ (**2**) showing 50% probability thermal ellipsoids.

1. Table II contains final positional parameters. Tables III and IV contain interatomic distances and angles, respectively. Compound **2** consists of a "spiked" triangular cluster of four metal atoms. The osmium–osmium distances in the Os(2), Os(3), Os(4) triangular group vary considerably, Os(2)–Os(3) = 2.9276 (7) Å, Os(2)–Os(4) = 2.8021 (8) Å, and Os(3)–Os(4) = 2.7352 (7) Å. This may be due to the presence of the triply bridging $MeO_2CC{\equiv}CCO_2Me$ ligand that bridges this group in a parallel bonding mode. A similar variation in metal–metal bond lengths was observed in the cluster complex $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ that contains a similarly coordinated alkyne ligand.[12] The Os(1)—Os(2) bond is short at 2.7472 (7) Å, and this bond is bridged by an unusual SC(Ph)=CH ligand that was apparently formed by the addition of the alkyne to the sulfido ligand and two of the metal atoms. The carbon–sulfur bond distance S–C(19) = 1.795 (9) Å is similar to a carbon–sulfur single bond length. The C(18)–C(19) distance of 1.40 (1) Å is indicative of partial multiple bonding. Ligands similar to this one have been observed in the complexes $Fe_2(CO)_6(\mu\text{-}\eta^3\text{-}SC(Ph){=}C(Ph))$][13]

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[12] Pierpont, C. G. *Inorg. Chem.* **1977**, *3*, 636.

Table II. Positional and Thermal Parameters for Compound 2[a]

atom	x	y	z	B(eq), Å^2
Os(1)	0.11446 (3)	0.29228 (3)	−0.07636 (4)	3.04 (2)
Os(2)	0.23600 (3)	0.24316 (3)	0.07211 (4)	2.52 (1)
Os(3)	0.36327 (3)	0.11727 (3)	0.11808 (4)	3.18 (2)
Os(4)	0.38511 (3)	0.32151 (3)	0.23797 (4)	2.86 (2)
S	0.17744 (18)	0.40362 (17)	0.1155 (3)	3.1 (1)
O(1)	−0.0521 (8)	0.3809 (8)	−0.1234 (12)	7.5 (6)
O(2)	0.0223 (7)	0.0727 (6)	−0.2178 (8)	5.7 (4)
O(3)	0.2831 (7)	0.4046 (7)	−0.3349 (9)	5.8 (4)
O(4)	0.4249 (6)	0.3537 (7)	−0.1725 (8)	5.6 (4)
O(5)	0.1763 (6)	0.0180 (6)	−0.0649 (8)	4.9 (4)
O(6)	0.2513 (9)	−0.1290 (6)	0.1082 (12)	8.4 (7)
O(7)	0.5300 (7)	0.0904 (7)	0.2411 (1)	6.7 (5)
O(8)	0.5188 (8)	0.1575 (8)	−0.1760 (10)	7.3 (5)
O(9)	0.3409 (6)	0.5362 (6)	0.3280 (9)	5.1 (4)
O(10)	0.4937 (7)	0.3411 (9)	0.4761 (10)	7.3 (5)
O(11)	0.5927 (6)	0.4194 (7)	0.0243 (9)	6.3 (4)
O(12)	0.3117 (8)	0.0448 (8)	0.4545 (9)	6.7 (5)
O(13)	0.2286 (7)	0.1607 (7)	0.5638 (8)	5.8 (4)
O(14)	0.0498 (5)	0.1470 (6)	0.4297 (7)	4.4 (3)
O(15)	0.1295 (5)	0.3293 (6)	0.4490 (7)	4.3 (3)
C(1)	0.0131 (10)	0.3514 (9)	−0.1104 (12)	4.7 (5)
C(2)	0.0574 (8)	0.1564 (8)	−0.1713 (10)	3.7 (4)
C(3)	0.2191 (9)	0.3601 (8)	−0.2426 (10)	3.9 (5)
C(4)	0.3555 (8)	0.3140 (7)	−0.0799 (11)	3.8 (5)
C(5)	0.2141 (8)	0.0986 (8)	−0.0076 (10)	3.5 (4)
C(6)	0.2931 (10)	−0.0366 (9)	0.1089 (13)	5.0 (6)
C(7)	0.4671 (9)	0.986 (8)	0.1977 (12)	4.3 (5)
C(8)	0.4602 (9)	0.1411 (9)	−0.0692 (13)	4.8 (6)
C(9)	0.3571 (7)	0.4562 (8)	0.2955 (10)	3.6 (4)
C(10)	0.4540 (8)	0.3351 (9)	0.3851 (12)	4.6 (5)
C(11)	0.5164 (8)	0.3830 (8)	0.1038 (12)	4.1 (5)
C(12)	0.2187 (7)	0.2194 (7)	0.2893 (09)	3.0 (4)
C(13)	0.2747 (7)	0.1531 (7)	0.3102 (09)	3.0 (4)
C(14)	0.2666 (8)	0.1213 (8)	0.4588 (11)	3.8 (5)
C(15)	0.3155 (19)	0.0133 (18)	0.5856 (18)	11 (1)
C(16)	0.1311 (7)	0.2417 (8)	0.3991 (10)	3.3 (4)
C(17)	−0.0442 (9)	0.1572 (12)	0.5237 (13)	6.3 (6)
C(18)	0.0713 (7)	0.2001 (7)	−0.1240 (9)	3.1 (4)
C(19)	0.0503 (7)	0.2984 (7)	0.1598 (10)	3.2 (4)
C(20)	−0.0462 (7)	0.3204 (7)	0.2282 (10)	3.3 (4)
C(21)	−0.1425 (9)	0.2532 (10)	0.2022 (15)	5.8 (6)
C(22)	−0.2360 (9)	0.2723 (10)	0.2722 (16)	6.3 (7)
C(23)	−0.2337 (9)	0.3578 (10)	0.3676 (15)	5.8 (6)
C(24)	−0.1393 (10)	0.4238 (10)	0.3926 (14)	5.5 (6)
C(25)	−0.0470 (9)	0.4069 (8)	0.3231 (12)	4.3 (5)
H(18)	0.0177	0.1231	0.1305	5.0

[a] Hydrogen atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + 2ab(\cos\gamma)\beta(1,2) + 2ac(\cos\beta)\beta(1,3) + 2bc(\cos\alpha)\beta(2,3)]$.

Table III. Intramolecular Distances (Å) for $Os_4(CO)_{11}(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)[\mu\text{-}SC(Ph)CH]$ (2)[a]

Os(1)–C(2)	1.91 (1)	O(1)–C(1)	1.14 (1)
Os(1)–C(1)	1.93 (1)	O(2)–C(2)	1.13 (1)
Os(1)–C(3)	1.93 (1)	O(3)–C(3)	1.13 (1)
Os(1)–C(18)	2.238 (8)	O(4)–C(4)	1.15 (1)
Os(1)–C(19)	2.26 (1)	O(5)–C(5)	1.15 (1)
Os(1)–S	2.402 (2)	O(6)–C(6)	1.14 (1)
Os(1)–Os(2)	2.7472 (6)	O(7)–C(7)	1.10 (1)
Os(2)–C(5)	1.91 (1)	O(8)–C(8)	1.14 (1)
Os(2)–C(4)	1.94 (1)	O(9)–C(9)	1.13 (1)
Os(2)–C(18)	2.09 (1)	O(10)–C(10)	1.14 (1)
Os(2)–C(12)	2.118 (8)	O(11)–C(11)	1.12 (1)
Os(2)–S	2.452 (2)	O(12)–C(14)	1.34 (1)
Os(2)–Os(4)	2.8021 (6)	O(12)–C(15)	1.40 (2)
Os(2)–Os(3)	2.9276 (6)	O(13)–C(14)	1.18 (1)
Os(3)–C(6)	1.90 (1)	O(14)–C(16)	1.35 (1)
Os(3)–C(7)	1.90 (1)	O(14)–C(17)	1.43 (1)
Os(3)–C(8)	1.96 (1)	O(15)–C(16)	1.20 (1)
Os(3)–C(13)	2.08 (1)	C(12)–C(13)	1.40 (1)
Os(3)–Os(4)	2.7352 (5)	C(12)–C(16)	1.50 (1)
Os(4)–C(10)	1.88 (1)	C(13)–C(14)	1.52 (1)
Os(4)–C(11)	1.92 (1)	C(18)–C(19)	1.40 (1)
Os(4)–C(9)	1.92 (1)	C(19)–C(20)	1.45 (1)
Os(4)–C(12)	2.182 (8)		
Os(4)–C(13)	2.247 (8)		
S–C(19)	1.795 (9)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Selected Interatomic Angles (deg) for Compound 2

C(18)–Os(1)–C(19)	36.2 (3)	Os(3)–C(8)–O(8)	178 (1)
C(18)–Os(1)–S	66.1 (2)	Os(4)–C(9)–O(9)	179 (1)
C(18)–Os(1)–Os(2)	48.4 (2)	Os(4)–C(10)–O(10)	178 (1)
C(19)–Os(1)–S	45.2 (2)	Os(4)–C(11)–O(11)	179 (1)
C(19)–Os(1)–Os(2)	67.8 (2)	C(13)–C(12)–C(16)	124.4 (8)
S–Os(1)–Os(2)	56.38 (6)	C(13)–C(12)–Os(2)	112.1 (6)
C(18)–Os(2)–C(12)	85.1 (3)	C(13)–C(12)–Os(4)	74.0 (5)
C(18)–Os(2)–S	67.2 (3)	C(16)–C(12)–Os(2)	120.9 (7)
C(18)–Os(2)–Os(1)	53.0 (2)	C(16)–C(12)–Os(4)	127.5 (6)
C(18)–Os(2)–Os(4)	131.7 (2)	Os(2)–C(12)–Os(4)	81.3 (3)
C(18)–Os(2)–Os(3)	128.2 (2)	C(12)–C(13)–C(14)	119.8 (9)
C(12)–Os(2)–S	93.9 (2)	C(12)–C(13)–Os(3)	110.3 (6)
C(12)–Os(2)–Os(1)	133.5 (3)	C(12)–C(13)–Os(4)	69.0 (5)
C(12)–Os(2)–Os(4)	50.3 (2)	C(14)–C(13)–Os(3)	129.9 (7)
C(12)–Os(2)–Os(3)	67.5 (3)	Os(3)–C(13)–Os(4)	78.4 (3)
S–Os(2)–Os(1)	54.68 (6)	O(13)–C(14)–O(12)	125 (1)
S–Os(2)–Os(4)	94.99 (6)	O(13)–C(14)–C(13)	125 (1)
S–Os(2)–Os(3)	151.89 (6)	O(12)–C(14)–C(13)	110 (1)
Os(1)–Os(2)–Os(4)	147.28 (2)	O(15)–C(16)–C(14)	124.1 (9)
Os(1)–Os(2)–Os(3)	152.76 (2)	O(15)–C(16)–C(12)	126.8 (8)
Os(4)–Os(2)–Os(3)	56.98 (2)	O(14)–C(16)–C(12)	109.1 (8)
C(13)–Os(3)–Os(4)	56.3 (2)	H(18)–C(18)–C(19)	127 (1)
C(13)–Os(3)–Os(2)	69.9 (3)	C(19)–C(18)–Os(2)	106.1 (6)
Os(4)–Os(3)–Os(2)	59.20 (2)	C(19)–C(18)–Os(1)	72.7 (5)
C(12)–Os(4)–C(13)	36.9 (3)	Os(2)–C(18)–Os(1)	78.6 (3)
C(12)–Os(4)–Os(3)	70.7 (2)	C(18)–C(19)–C(20)	131.9 (8)
C(12)–Os(4)–Os(2)	48.3 (2)	C(18)–C(19)–S	104.3 (7)
C(13)–Os(4)–Os(3)	48.1 (2)	C(20)–C(19)–S	123.6 (7)
C(13)–Os(4)–Os(2)	70.5 (2)	C(14)–C(13)–Os(4)	117.3 (6)
Os(3)–Os(4)–Os(2)	63.82 (2)	S–C(19)–Os(1)	71.6 (3)
C(19)–S–Os(1)	63.2 (3)	C(25)–C(20)–C(21)	117 (1)
C(19)–S–Os(2)	81.7 (3)	C(25)–C(20)–C(19)	122.0 (9)
Os(1)–S–Os(2)	68.93 (6)	C(21)–C(20)–C(19)	120.7 (9)
C(14)–O(12)–C(15)	116 (1)	C(20)–C(21)–C(22)	121 (1)
C(16)–O(14)–C(17)	115.4 (9)	C(23)–C(22)–C(21)	120 (1)
Os(1)–C(1)–O(1)	175 (1)	C(21)–C(23)–C(22)	119 (1)
Os(1)–C(2)–O(2)	174.8 (9)	C(23)–C(24)–C(25)	121 (1)
Os(1)–C(3)–O(3)	176 (1)	C(24)–C(25)–C(20)	122 (1)
Os(2)–C(4)–O(4)	178 (1)	C(18)–C(19)–Os(1)	71.0 (5)
Os(2)–C(5)–O(5)	159.3 (9)	C(20)–C(19)–S	123.6 (7)
Os(3)–C(6)–O(6)	178 (1)	C(20)–C(19)–Os(1)	125.1 (7)
Os(3)–C(7)–O(7)	178 (1)	Os(3)···C(5)–O(5)	121 (1)

and $Os_4(CO)_{12}[\mu_4\text{-}\eta^3\text{-}SC(Ph){=}CH]$.[5] Overall, the compound contains 64 valence electrons, and with four metal-metal bonds it is electron-precise. Formally, however, the Os(2)–Os(3) bond would be regarded as a donor–acceptor bond from Os(2) to Os(3). As is common with such formulations, one of the carbonyl ligands (C(5)–O(5)) has adopted a semibridging bonding mode, Os(3)···C(5) = 2.60 (1) Å.[14] All of the remaining carbonyl ligands are of a terminal type. The hydrogen atom H(18) was observed structurally as shown in Figure 1. This was supported further by its characteristic low-field ^{1}H NMR shift, δ 8.51.[5]

When refluxed in a $CHCl_3$ solution for 10 h, compound **2** was transformed into the two new compounds $Os_4(CO)_{11}[\mu_4\text{-}\eta^5\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**3**) in 25% yield and $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**4**) in 37% yield. When compound **2** was heated to reflux in a heptane solution, only compound **4** was formed (50% yield). Compound **3** can be converted into **4** when refluxed in $CHCl_3$ solvent over a prolonged period (35 h). Compounds **3** and **4** were both characterized

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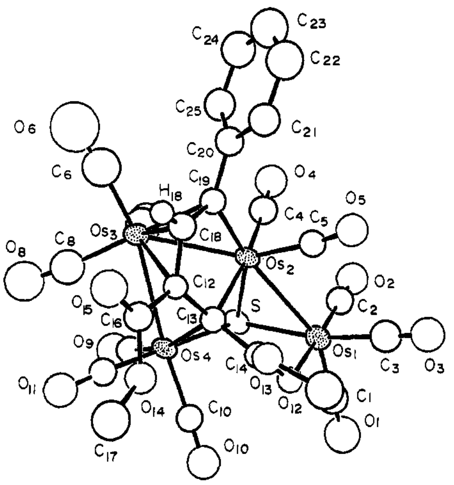

Figure 2. An ORTEP diagram of $Os_4(CO)_{11}[\mu_4\text{-}\eta^5\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (**3**) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters for $Os_4(CO)_{11}[\mu_4\text{-}\eta^5\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (3)

atom	x	y	z
Os(1)	0.71288 (6)	0.04411 (5)	0.93047 (4)
Os(2)	0.83960 (6)	0.19829 (5)	0.99725 (4)
Os(3)	0.82865 (6)	0.37235 (5)	1.05855 (5)
Os(4)	0.61086 (6)	0.27202 (5)	0.99317 (4)
S	0.6572 (4)	0.1923 (3)	0.8860 (3)
O(1)	0.4976 (16)	−0.0526 (12)	0.8338 (11)
O(2)	0.7865 (14)	0.0361 (10)	0.7826 (10)
O(3)	0.8369 (12)	−0.1243 (10)	1.0143 (9)
O(4)	0.9562 (14)	0.2314 (11)	0.8742 (10)
O(5)	0.9923 (12)	0.0440 (9)	1.0789 (8)
O(6)	1.011 (2)	0.5067 (16)	1.1421 (15)
O(7)	0.7794 (15)	0.4193 (12)	0.8760 (12)
O(8)	0.6667 (16)	0.5185 (13)	1.0652 (11)
O(9)	0.4793 (14)	0.3938 (11)	0.8465 (10)
O(10)	0.4282 (13)	0.1406 (10)	0.9788 (9)
O(11)	0.5353 (12)	0.3744 (9)	1.1144 (9)
O(12)	0.6773 (9)	0.0508 (7)	1.0444 (7)
O(13)	0.7708 (10)	0.0809 (8)	1.1786 (7)
O(14)	0.6807 (10)	0.2362 (8)	1.2206 (7)
O(15)	0.8397 (12)	0.3075 (9)	1.2948 (8)
C(1)	0.5800 (19)	−0.0144 (15)	0.8706 (14)
C(2)	0.7572 (17)	0.0389 (13)	0.8374 (12)
C(3)	0.7912 (18)	−0.0628 (14)	0.9833 (13)
C(4)	0.9094 (17)	0.2167 (13)	0.9192 (12)
C(5)	0.9286 (15)	0.0990 (12)	1.0412 (11)
C(6)	0.947 (2)	0.4527 (18)	1.1099 (16)
C(7)	0.8021 (20)	0.4045 (16)	0.9471 (15)
C(8)	0.723 (2)	0.4591 (16)	1.0637 (14)
C(9)	0.5264 (17)	0.3496 (13)	0.9025 (12)
C(10)	0.4980 (16)	0.1895 (12)	0.9826 (11)
C(11)	0.5695 (15)	0.3336 (12)	1.0707 (11)
C(12)	0.8136 (14)	0.2552 (10)	1.1563 (10)
C(13)	0.7476 (14)	0.1957 (11)	1.0850 (10)
C(14)	0.7273 (14)	0.1065 (11)	1.1005 (10)
C(15)	0.7696 (19)	−0.0137 (15)	1.1980 (13)
C(16)	0.7805 (15)	0.2708 (12)	1.2307 (11)
C(17)	0.6462 (19)	0.2351 (14)	1.2938 (13)
C(18)	0.9223 (15)	0.2781 (11)	1.1662 (11)
C(19)	0.9581 (14)	0.2650 (11)	1.0979 (10)
C(20)	1.0788 (16)	0.2726 (12)	1.1112 (11)
C(21)	1.1555 (17)	0.2190 (12)	1.1757 (12)
C(22)	1.267 (2)	0.2203 (15)	1.1895 (14)
C(23)	1.303 (2)	0.2726 (16)	1.1410 (15)
C(24)	1.235 (2)	0.3238 (16)	1.0771 (14)
C(25)	1.1221 (18)	0.3226 (14)	1.0618 (12)

Table VI. Selected Intramolecular Distances (Å) for $Os_4(CO)_{11}[\mu_4\text{-}\eta^5\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (3)[a]

Os(1)–C(1)	1.85 (2)	O(4)–C(4)	1.16 (2)
Os(1)–C(2)	1.87 (2)	O(5)–C(5)	1.17 (2)
Os(1)–C(3)	1.94 (2)	O(6)–C(6)	1.14 (3)
Os(1)–O(12)	2.16 (1)	O(7)–C(7)	1.16 (2)
Os(1)–S	2.381 (5)	O(8)–C(8)	1.16 (3)
Os(1)–Os(2)	2.822 (1)	O(9)–C(9)	1.14 (2)
Os(2)–C(5)	1.86 (2)	O(10)–C(10)	1.14 (2)
Os(2)–C(4)	1.88 (2)	O(11)–C(11)	1.17 (2)
Os(2)–C(19)	2.08 (2)	O(12)–C(14)	1.26 (2)
Os(2)–C(13)	2.22 (2)	O(13)–C(14)	1.30 (2)
Os(2)–S	2.407 (4)	O(13)–C(15)	1.47 (2)
Os(2)–Os(3)	2.846 (1)	O(14)–C(16)	1.33 (2)
Os(3)–C(7)	1.87 (2)	O(14)–C(17)	1.47 (2)
Os(3)–C(6)	1.89 (3)	O(15)–C(16)	1.21 (2)
Os(3)–C(8)	1.91 (3)	C(12)–C(18)	1.39 (2)
Os(3)–C(19)	2.24 (2)	C(12)–C(13)	1.49 (2)
Os(3)–C(18)	2.28 (2)	C(12)–C(16)	1.50 (2)
Os(3)–Os(4)	3.007 (1)	C(13)–C(14)	1.41 (2)
Os(4)–C(11)	1.85 (2)	C(18)–H(18)	0.92
Os(4)–C(10)	1.87 (2)	C(18)–C(19)	1.41 (2)
Os(4)–C(9)	1.92 (2)	Os(2)···Os(4)	3.118 (1)
Os(4)–C(13)	2.19 (2)	Os(3)···C(12)	2.484 (2)
Os(4)–S	2.438 (4)	Os(2)···C(18)	2.931 (2)
O(1)–C(1)	1.16 (2)	Os(1)···Os(4)	3.961 (1)
O(2)–C(2)	1.13 (2)	Os(4)···C(12)	3.033 (2)
O(3)–C(3)	1.12 (2)	Os(2)···C(12)	2.978 (2)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Selected Interatomic Angles (deg) for Compound 3

O(12)–Os(1)–S	96.0 (3)	Os(1)–C(1)–O(1)	179 (2)
O(12)–Os(1)–Os(2)	83.2 (3)	Os(1)–C(2)–O(2)	178 (2)
S–Os(1)–Os(2)	54.3 (1)	Os(1)–C(3)–O(3)	180 (2)
C(19)–Os(2)–C(13)	82.1 (6)	Os(2)–C(4)–O(4)	176 (2)
C(19)–Os(2)–S	150.2 (5)	Os(2)–C(5)–O(5)	170 (2)
C(19)–Os(2)–Os(1)	150.0 (5)	Os(3)–C(6)–O(6)	173 (3)
C(19)–Os(2)–Os(3)	51.2 (5)	Os(3)–C(7)–O(7)	175 (2)
C(13)–Os(2)–Os(1)	83.4 (4)	Os(3)–C(8)–O(8)	173 (2)
C(13)–Os(2)–S	85.6 (4)	Os(4)–C(9)–O(9)	177 (2)
C(13)–Os(2)–Os(3)	70.0 (4)	Os(4)–C(10)–O(10)	177 (2)
S–Os(2)–Os(1)	53.4 (1)	Os(4)–C(11)–O(11)	174 (2)
S–Os(2)–Os(3)	99.1 (1)	C(18)–C(12)–C(13)	119 (1)
Os(1)–Os(2)–Os(3)	143.78 (3)	C(18)–C(12)–C(16)	117 (1)
C(19)–Os(3)–C(18)	36.5 (6)	C(13)–C(12)–C(16)	122 (1)
C(19)–Os(3)–Os(2)	46.4 (4)	C(14)–C(13)–C(12)	120 (1)
C(19)–Os(3)–Os(4)	103.5 (4)	C(14)–C(13)–Os(4)	119 (1)
C(18)–Os(3)–Os(2)	68.8 (4)	C(14)–C(13)–Os(2)	109 (1)
C(18)–Os(3)–Os(4)	97.2 (4)	C(12)–C(13)–Os(4)	109 (1)
Os(2)–Os(3)–Os(4)	64.32 (3)	C(12)–C(13)–Os(2)	105 (1)
C(13)–Os(4)–S	85.5 (4)	Os(4)–C(13)–Os(2)	89.8 (6)
C(13)–Os(4)–Os(3)	67.1 (4)	O(12)–C(14)–O(13)	119 (1)
S–Os(4)–Os(3)	94.2 (1)	O(12)–C(14)–C(13)	125 (2)
Os(1)–S–Os(2)	72.2 (1)	O(13)–C(14)–C(13)	116 (1)
Os(1)–S–Os(4)	110.6 (2)	O(15)–C(16)–O(14)	123 (2)
Os(2)–S–Os(4)	80.1 (1)	O(15)–C(16)–C(12)	124 (2)
C(14)–O(12)–Os(1)	120 (1)	O(14)–C(16)–C(16)	113 (1)
C(14)–O(13)–C(15)	119 (1)	H(18)–C(18)–C(12)	105 (2)
C(16)–O(14)–C(17)	118 (1)	H(18)–C(18)–C(19)	136 (2)
C(12)–C(18)–C(19)	119 (2)	C(18)–C(19)–Os(2)	113 (1)
C(12)–C(18)–Os(3)	81 (1)	C(18)–C(19)–Os(3)	73 (1)
C(19)–C(18)–Os(3)	70 (1)	C(20)–C(19)–Os(2)	124 (1)
C(18)–C(19)–C(20)	120 (2)	C(20)–C(19)–Os(3)	127 (1)
		Os(2)–C(19)–Os(3)	82.4 (6)

by IR and ^1H NMR spectroscopies and by elemental and single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of **3** is shown in Figure 2. Final positional parameters are listed in Table V. Intramolecular distances and selected interatomic angles are listed in Tables VI and VII, respectively. In this compound the four metal atoms are connected by only three metal–metal bonds. The distances Os(1)–Os(2) = 2.822 (1) Å and Os(2)–Os(3) = 2.846 (1) Å are of normal lengths. The Os(3)–Os(4) distance of 3.007 (1) Å is unusually and inexplicably long. A triply bridging sulfido ligand is bonded to the metal atoms Os(1), Os(2), and Os(4). The most interesting ligand is the group $(MeO_2C)CC(CO_2Me)C(H)C(Ph)$ that was formed through

Table VIII. Positional and Thermal Parameters (B(eq)) for $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (4)

atom	x	y	z	B(eq), Å^2
Os(1)	−0.42111 (4)	0.23716 (4)	−0.10598 (4)	3.8
Os(2)	−0.23065 (4)	0.23638 (4)	0.04709 (4)	3.4
Os(3)	−0.08884 (4)	0.25771 (4)	0.27939 (4)	3.9
Os(4)	−0.04287 (4)	0.18756 (4)	0.08684 (4)	4.6
S	−0.0175 (3)	0.3699 (2)	0.1784 (3)	3.8
O(1)	−0.6109 (9)	0.1221 (9)	−0.0235 (9)	5.3
O(2)	−0.5511 (9)	0.0057 (9)	−0.3306 (10)	5.8
O(3)	−0.5781 (10)	0.3087 (9)	−0.2432 (10)	6.2
O(4)	−0.3952 (8)	0.1078 (7)	0.1462 (8)	4.1
O(5)	−0.3327 (8)	−0.0085 (7)	−0.1425 (8)	4.0
O(6)	−0.2154 (9)	0.0303 (9)	0.2978 (9)	5.2
O(7)	0.1640 (9)	0.3403 (9)	0.4659 (9)	5.4
O(8)	−0.1291 (9)	0.3913 (9)	0.4783 (10)	5.7
O(9)	0.0165 (10)	0.1828 (9)	−0.1277 (10)	6.1
O(10)	−0.1471 (10)	−0.0657 (10)	0.0331 (10)	6.0
O(11)	0.2138 (10)	0.2531 (9)	0.2395 (10)	6.2
O(12)	−0.1980 (8)	0.4811 (8)	0.3031 (8)	4.3
O(13)	−0.3981 (8)	0.3393 (8)	0.1914 (8)	4.2
O(14)	−0.2923 (8)	0.5586 (7)	−0.0356 (8)	4.1
O(15)	−0.3289 (9)	0.5425 (9)	0.1187 (10)	5.6
C(1)	−0.5404 (11)	0.1663 (11)	−0.0546 (11)	3.5
C(2)	−0.5021 (11)	0.0929 (11)	−0.2455 (12)	3.7
C(3)	−0.5198 (11)	0.2787 (11)	−0.1952 (12)	3.7
C(4)	−0.3153 (10)	0.1619 (10)	0.1266 (10)	2.8
C(5)	−0.2756 (10)	0.0856 (10)	−0.0619 (11)	2.9
C(6)	−0.1642 (12)	0.1179 (11)	0.2917 (12)	3.9
C(7)	0.0658 (12)	0.3092 (11)	0.3972 (12)	4.0
C(8)	−0.1159 (12)	0.3441 (12)	0.3995 (13)	4.3
C(9)	−0.0134 (11)	0.1821 (11)	−0.0503 (12)	3.8
C(10)	−0.1086 (12)	0.0319 (12)	0.0519 (12)	4.0
C(11)	0.1141 (13)	0.2273 (12)	0.1806 (13)	4.5
C(12)	−0.2679 (9)	0.4253 (9)	0.0240 (10)	2.5
C(13)	−0.2712 (9)	0.3632 (9)	0.0936 (10)	2.5
C(14)	−0.2858 (10)	0.4040 (10)	0.2076 (10)	2.8
C(15)	−0.4196 (15)	0.3708 (14)	0.2998 (15)	6.0
C(16)	−0.2987 (11)	0.5141 (10)	0.0429 (11)	3.4
C(17)	−0.3306 (13)	0.6417 (13)	−0.0298 (14)	5.1
C(18)	−0.2436 (10)	0.3857 (9)	−0.0777 (10)	2.7
C(19)	−0.2272 (9)	0.2925 (9)	−0.0895 (9)	2.2
C(20)	−0.1889 (9)	0.2615 (9)	−0.1862 (10)	2.5
C(21)	−0.0872 (10)	0.3510 (10)	−0.1820 (11)	3.2
C(22)	−0.0481 (11)	0.3301 (11)	−0.2702 (12)	3.9
C(23)	−0.1113 (12)	0.2184 (11)	−0.3646 (12)	4.0
C(24)	−0.2118 (11)	0.1278 (11)	−0.3698 (12)	3.8
C(25)	−0.2505 (10)	0.1495 (10)	−0.2817 (10)	3.0
C(26)	0.6318 (16)	0.3033 (16)	0.5692 (17)	6.6
C(27)	0.6584 (16)	0.4087 (16)	0.6174 (17)	6.9
C(28)	0.5659 (17)	0.4292 (17)	0.5920 (18)	7.1
C(29)	0.4499 (16)	0.3388 (16)	0.5173 (17)	6.5

a combination of the original two alkyne molecules. This ligand is bonded to all four metal atoms. The ends of the four-carbon chain C(13)–C(12)–C(18)–C(19) are bonded to Os(2), Os(2)–C(13) = 2.22 (2) Å and Os(2)–C(19) = 2.08 (2) Å. Only C(13) is bonded to Os(4), Os(4)–C(13) = 2.19 (2) Å. The three carbon atoms C(12), C(18), and C(19) are bonded to Os(3) in a π-allylic fashion, Os(3)–C(12) = 2.48 (2) Å, Os(3)–C(18) = 2.28 (2) Å, and Os(3)–C(19) = 2.24 (2) Å, although the longer Os(3)–C(12) distance indicates that this bond is considerably weaker than the other two. The oxygen atom O(12) of one of the carboxylate groups is bonded to Os(1), Os(1)–O(12) = 2.16 (1) Å. Similar coordination of the oxygen atoms of carboxylate groups has been observed previously in osmium cluster complexes.[10,15] The two alkyne ligands were joined by formation of the carbon–carbon bond C(12)–C(18) = 1.39 (2) Å. This bond and the bond C(18)–C(19) of length 1.41 (2) Å appear to contain partial multiple-bonding character. The C(12)–C(13) bond at 1.49 (2) Å is closer to a single bond. There are 11 terminally coordinated carbonyl ligands that are distributed about the molecules as shown in Figure 2.

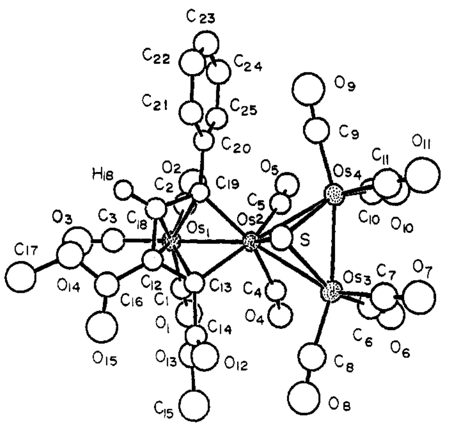

Figure 3. An ORTEP diagram of $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (4) showing 50% probability thermal ellipsoids.

Table IX. Intramolecular Bond Distances (Å) for $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (4)[a]

Os(1)–C(2)	1.89 (1)	O(3)–C(3)	1.15 (1)
Os(1)–C(3)	1.89 (1)	O(4)–C(4)	1.17 (1)
Os(1)–C(1)	1.90 (1)	O(5)–C(5)	1.17 (1)
Os(1)–C(12)	2.26 (1)	O(6)–C(6)	1.17 (1)
Os(1)–C(18)	2.26 (1)	O(7)–C(7)	1.16 (1)
Os(1)–C(13)	2.29 (1)	O(8)–C(8)	1.16 (2)
Os(1)–C(19)	2.32 (1)	O(9)–C(9)	1.17 (1)
Os(1)–Os(2)	2.7572 (8)	O(10)–C(10)	1.18 (1)
Os(2)–C(4)	1.91 (1)	O(11)–C(11)	1.17 (1)
Os(2)–C(5)	1.92 (1)	O(12)–C(14)	1.20 (1)
Os(2)–C(13)	2.09 (1)	O(13)–C(14)	1.31 (1)
Os(2)–C(19)	2.10 (1)	O(13)–C(15)	1.49 (2)
Os(2)–S	2.359 (3)	O(14)–C(16)	1.32 (1)
Os(2)–Os(4)	2.8608 (7)	O(14)–C(17)	1.47 (2)
Os(2)–Os(3)	2.8769 (9)	O(15)–C(16)	1.19 (1)
Os(3)–C(7)	1.86 (1)	C(12)–C(13)	1.40 (1)
Os(3)–C(6)	1.88 (1)	C(12)–C(18)	1.46 (1)
Os(3)–C(8)	1.92 (1)	C(12)–C(16)	1.47 (2)
Os(3)–S	2.371 (3)	C(13)–C(14)	1.52 (2)
Os(3)–Os(4)	2.7391 (8)	C(18)–C(19)	1.41 (1)
Os(4)–C(11)	1.85 (1)	Os(3)···C(4)	2.57 (1)
Os(4)–C(10)	1.86 (1)	Os(4)···C(5)	2.61 (1)
Os(4)–C(9)	1.89 (1)		
Os(4)–S	2.364 (3)		
O(1)–C(1)	1.14 (1)		
O(2)–C(2)	1.15 (1)		

[a] Estimated standard deviations are given in parentheses.

An ORTEP drawing of the molecular structure of compound 4 is shown in Figure 3. Final positional parameters are listed in Table VIII. Intramolecular bond distances and angles are listed in Tables IX and X. The molecular formula is $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$. The four metal atoms are arranged in the form of the spiked triangle. The triangular group Os(2), Os(3), Os(4) is bridged by the sulfido ligand. The Os(3)–Os(4) bond at 2.7391 (8) Å is significantly shorter than the other two, Os(2)–Os(3) = 2.8769 (9) Å and Os(2)–Os(4) = 2.8608 (7) Å. The external osmium–osmium bond Os(1)–Os(2) is also short, 2.7572 (8) Å. This bond is bridged by the coupled alkyne unit $(MeO_2C)CC(CO_2Me)C(H)C(Ph)$. The ends of the four-carbon chain C(13)–C(12)–C(18)–C(19) bridge the bond, but atoms C(12) and C(18) are bonded to the metal atom Os(1) only. Combined with Os(2), the four carbon atoms and the metal atom could be viewed as a metallacyclopendienyl unit that is π-bonded to Os(1). Similar groupings formed by the coupling of two alkynes and their coordination to a metal atom have been

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(15) Einstein, F. W. B.; Nussbaum, S.; Sutton, D.; Willis, A. C. *Organometallics* **1984**, *5*, 568.

Table X. Intramolecular Bond Angles (deg) for $Os_4(CO)_{11}[\mu\text{-}\eta^4\text{-}(MeO_2C)CC(CO_2Me)C(H)C(Ph)](\mu_3\text{-}S)$ (4)

C(2)–Os(1)–C(3)	90.2 (5)	C(8)–Os(3)–S	108.1 (4)
C(2)–Os(1)–C(1)	89.4 (5)	C(8)–Os(3)–Os(4)	162.3 (4)
C(2)–Os(1)–C(12)	154.8 (5)	C(8)–Os(3)–Os(2)	106.8 (4)
C(2)–Os(1)–C(18)	117.2 (5)	S–Os(3)–Os(4)	54.54 (7)
C(2)–Os(1)–C(13)	148.7 (4)	S–Os(3)–Os(2)	52.34 (7)
C(2)–Os(1)–C(19)	93.7 (4)	Os(4)–Os(3)–Os(2)	61.19 (2)
C(2)–Os(1)–Os(2)	101.1 (4)	C(11)–Os(4)–C(10)	91.5 (6)
C(3)–Os(1)–C(1)	90.4 (5)	C(11)–Os(4)–C(9)	91.3 (6)
C(3)–Os(1)–C(12)	92.7 (5)	C(11)–Os(4)–S	99.2 (4)
C(3)–Os(1)–C(18)	93.7 (5)	C(11)–Os(4)–Os(3)	96.5 (4)
C(3)–Os(1)–C(13)	121.1 (5)	C(11)–Os(4)–Os(2)	150.6 (4)
C(3)Os(1)–C(19)	122.4 (4)	C(10)–Os(4)–C(9)	98.1 (6)
C(3)–Os(1)–Os(2)	165.2 (4)	C(10)–Os(4)–S	152.9 (4)
C(1)–Os(1)–C(12)	115.6 (5)	C(10)–Os(4)–Os(3)	99.5 (4)
C(1)–Os(1)–C(18)	153.0 (5)	C(10)–Os(4)–oS(2)	110.6 (4)
C(1)–Os(1)–C(13)	91.8 (4)	C(9)–Os(4)–S	106.4 (4)
C(1)–Os(1)–C(19)	146.9 (4)	C(9)–Os(4)–Os(3)	160.5 (4)
C(1)–Os(1)–Os(2)	99.2 (3)	C(9)–Os(4)–Os(2)	103.9 (4)
C(12)–Os(1)–C(18)	37.6 (4)	S–Os(4)–Os(3)	54.77 (7)
C(12)–Os(1)–C(13)	35.9 (4)	S–Os(4)–Os(2)	52.63 (7)
C(12)–Os(1)–C(19)	63.8 (4)	Os(3)–Os(4)–Os(2)	61.78 (2)
C(12)–Os(1)–Os(2)	73.0 (3)	Os(2)–S–Os(4)	74.57 (9)
C(18)–Os(1)–C(13)	63.4 (4)	Os(2)–S–Os(3)	74.94 (8)
C(18)–Os(1)–C(19)	35.8 (4)	Os(4)–S–Os(3)	70.69 (8)
C(18)–Os(1)–Os(2)	72.7 (3)	C(14)–O(13)–C(15)	117 (1)
C(13)–Os(1)–C(19)	69.2 (4)	C(16)–O(14)–C(17)	117 (1)
C(13)–Os(1)–Os(2)	47.8 (2)	O(1)–C(1)–Os(1)	178 (1)
C(19)–Os(1)–Os(2)	48.0 (2)	O(2)–C(2)–Os(1)	180 (1)
C(4)–Os(2)–C(5)	87.9 (5)	O(3)–C(3)–Os(1)	176 (1)
C(4)–Os(2)–C(13)	90.1 (4)	O(4)–C(4)–Os(2)	161 (1)
C(4)–Os(2)–C(19)	151.7 (4)	O(5)–C(5)–Os(2)	162 (1)
C(4)–Os(2)–S	112.4 (3)	O(6)–C(6)–Os(3)	177 (1)
C(4)–Os(2)–Os(1)	96.9 (3)	O(7)–C(7)–Os(3)	176 (1)
C(4)–Os(2)–Os(4)	101.7 (3)	O(8)–C(8)–Os(3)	174 (1)
C(4)–Os(2)–Os(3)	61.1 (3)	O(9)–C(9)–Os(4)	173 (1)
C(5)–Os(2)–C(13)	150.4 (4)	O(10)–C(10)–Os(4)	178 (1)
C(5)–Os(2)–C(19)	90.8 (4)	O(11)–C(11)–Os(4)	179 (1)
C(5)–Os(2)–S	114.6 (3)	C(13)–C(12)–C(18)	114 (1)
C(5)–Os(2)–Os(1)	96.6 (3)	C(13)–C(12)–C(16)	124 (1)
C(5)–Os(2)–Os(4)	62.5 (3)	C(13)–C(12)–Os(1)	73.5 (6)
C(5)–Os(2)–Os(3)	100.2 (3)	C(18)–C(12)–C(16)	122 (1)
C(13)–Os(2)–C(19)	77.4 (4)	C(18)–C(12)–Os(1)	71.4 (6)
C(13)–Os(2)–S	93.5 (3)	C(16)–C(12)–Os(1)	118.5 (7)
C(13)–Os(2)–Os(1)	54.4 (3)	C(12)–C(13)–C(14)	118 (1)
C(13)–Os(2)–Os(4)	146.3 (3)	C(12)–C(13)–Os(2)	117.5 (7)
C(13)–Os(2)–Os(3)	104.5 (3)	C(12)–C(13)–Os(1)	70.6 (6)
C(19)–Os(2)–S	93.8 (3)	C(14)–C(13)–Os(2)	124.1 (7)
C(19)–Os(2)–Os(1)	55.2 (3)	C(14)–C(13)–Os(1)	128.8 (7)
C(19)–Os(2)–Os(4)	102.8 (3)	Os(2)–C(13)–Os(1)	77.8 (3)
C(19)–Os(2)–Os(3)	146.4 (3)	O(12)–C(14)–O(13)	126 (1)
S–Os(2)–Os(1)	137.05 (7)	O(12)–C(14)–C(13)	120 (1)
S–Os(2)–Os(4)	52.81 (7)	O(13)–C(14)–C(13)	113 (1)
S–Os(2)–Os(3)	52.72 (7)	O(15)–C(16)--O(14)	122 (1)
Os(1)–Os(2)–Os(4)	151.13 (2)	O(15)–C(16)–C(12)	125 (1)
Os(1)–Os(2)–Os(3)	151.44 (2)	O(14)–C(16)–C(12)	113 (1)
Os(4)–Os(2)–Os(3)	57.03 (2)	C(19)–C(18)–C(12)	115 (1)
C(7)–Os(3)–C(6)	92.3 (5)	C(19)–C(18)–Os(1)	74.5 (6)
C(7)–Os(3)–C(8)	92.0 (6)	C(12)–C(18)–Os(1)	71.0 (6)
C(7)–Os(3)–S	96.5 (4)	C(18)–C(19)–C(20)	114.3 (9)
C(7)–Os(3)–Os(4)	93.4 (4)	C(18)–C(19)–Os(2)	116.0 (7)
C(7)–Os(3)–Os(2)	147.0 (4)	C(18)–C(19)–Os(1)	69.7 (6)
C(6)–Os(3)–C(8)	95.9 (6)	C(20)–C(19)–Os(2)	128.9 (7)
C(6)–Os(3)–S	154.0 (4)	C(20)–C(19)–Os(1)	130.5 (7)
C(6)–Os(3)–Os(4)	100.7 (4)	Os(2)–C(19)–Os(1)	76.9 (3)
C(6)–Os(3)–Os(2)	111.8 (4)		

Table XI. Positional and Thermal Parameters for Compound 5

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.11063 (7)	0.22485 (5)	0.22011 (7)	3.9
Os(2)	0.02910 (6)	0.23221 (4)	−0.06812 (6)	2.9
Os(3)	0.00042 (7)	0.36887 (4)	−0.25934 (7)	3.3
Os(4)	−0.18103 (6)	0.18815 (4)	−0.32922 (6)	2.7
S	−0.0741 (4)	0.1058 (3)	0.0336 (4)	3.7
O(1)	−0.0305 (18)	0.3189 (12)	0.2994 (19)	7.4
O(2)	0.345 (2)	0.3989 (16)	0.399 (3)	10.5
O(3)	0.135 (2)	0.1077 (15)	0.458 (2)	9.7
O(4)	0.074 (2)	0.1237 (15)	−0.278 (2)	10.1
O(5)′	0.253 (3)	0.4258 (18)	0.036 (3)	4.4
O(5)	0.188 (3)	0.4392 (18)	0.082 (3)	4.4
O(6)	0.123 (2)	0.5749 (14)	−0.100 (2)	9.0
O(7)	−0.1406 (14)	0.4190 (9)	−0.5298 (15)	5.0
O(8)	0.1859 (19)	0.3657 (12)	−0.3847 (20)	7.8
O(9)	−0.4115 (18)	0.2002 (12)	−0.5420 (19)	7.2
O(10)	−0.1029 (16)	0.1377 (10)	−0.5578 (17)	6.0
O(11)	−0.3324 (15)	−0.0153 (11)	−0.3143 (16)	5.8
O(12)′	−0.351 (4)	0.300 (3)	−0.178 (5)	7.3
O(12)	−0.339 (4)	0.312 (2)	−0.224 (4)	3.9
O(13)	−0.196 (3)	0.4493 (19)	−0.246 (3)	5.0
O(13)′	−0.282 (3)	-0.3839 (17)	−0.337 (3)	4.2
C(1)	0.022 (2)	0.2811 (14)	0.264 (2)	5.0
C(2)	0.258 (3)	0.3304 (18)	0.334 (3)	6.1
C(3)	0.124 (2)	0.1542 (17)	0.367 (3)	6.1
C(4)	0.052 (2)	0.1719 (16)	−0.209 (2)	5.6
C(5)	0.148 (3)	0.3634 (20)	−0.017 (3)	7.7
C(6)	0.077 (3)	0.4951 (18)	−0.163 (3)	6.2
C(7)	−0.0888 (18)	0.3992 (12)	−0.4280 (20)	3.7
C(8)	0.121 (2)	0.3736 (14)	−0.333 (2)	4.8
C(9)	−0.322 (2)	0.1922 (13)	−0.467 (2)	4.4
C(10)	−0.1364 (19)	0.1561 (13)	−0.472 (2)	3.9
C(11)	−0.2736 (18)	0.0626 (12)	−0.3129 (19)	3.6
C(12)	−0.1359 (16)	0.2505 (11)	−0.1078 (17)	2.8
C(13)	−0.1478 (17)	0.3157 (11)	−0.1938 (18)	3.3
C(14)	−0.220 (4)	0.370 (3)	−0.221 (3)	2.7
C(14)′	−0.285 (5)	0.325 (3)	−0.236 (4)	3.0
C(15)	−0.428 (5)	0.353 (3)	−0.266 (5)	5.9
C(15)′	−0.399 (4)	0.395 (3)	−0.383 (4)	4.5
C(16)	−0.2197 (18)	0.1976 (12)	−0.0351 (19)	3.6
C(17)	−0.2048 (17)	0.1272 (11)	0.0276 (18)	3.1
C(18)	−0.283 (2)	0.0684 (14)	0.099 (2)	4.6
C(19)	−0.358 (3)	0.0990 (17)	0.137 (3)	6.4
C(20)	−0.435 (3)	0.0379 (19)	0.207 (3)	7.3
C(21)	−0.429 (3)	−0.039 (2)	0.234 (3)	7.8
C(22)	−0.362 (3)	−0.0764 (19)	0.199 (3)	7.4
C(23)	−0.281 (3)	−0.0211 (17)	0.125 (3)	6.4
C(24)	0.1861 (18)	0.1377 (12)	0.1315 (19)	3.7
C(25)	0.1962 (18)	0.2164 (12)	0.0605 (19)	3.5
C(26)	0.322 (4)	0.261 (3)	0.065 (4)	3.7
C(26)′	0.333 (4)	0.304 (3)	0.100 (4)	3.7
C(27)	0.427 (4)	0.280 (3)	0.190 (4)	3.3
C(27)′	0.433 (4)	0.318 (3)	0.230 (4)	4.0
C(28)′	0.554 (5)	0.377 (4)	0.243 (6)	6.8
C(28)	0.547 (4)	0.327 (3)	0.188 (5)	4.7
C(29)	0.559 (6)	0.348 (4)	0.065 (6)	7.3
C(29)′	0.565 (6)	0.428 (4)	0.137 (6)	7.2
C(30)′	0.465 (4)	0.418 (3)	0.008 (5)	5.2
C(30)	0.457 (4)	0.327 (3)	−0.059 (4)	4.3
C(31)′	0.346 (4)	0.354 (2)	−0.007 (4)	3.5
C(31)	0.340 (4)	0.287 (3)	−0.057 (4)	4.2

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + 2ab(\cos\gamma)\beta(1,2)$ p $2ac(\cos\beta)\beta(1,3) + 2bc(\cos\alpha)\beta(2,3)]$.

observed previously.[16] In accord with this it was observed that the C(12)–C(13) and C(18)–C(19) distances of 1.40 (1) and 1.41 (1) Å, respectively, are significantly shorter than the C(12)–C(18) distance of 1.46 (1) Å. Like compound **2**, compound **4** is also electron-precise, but formally one of two metal–metal bonds Os(2)–Os(3) or Os(2)–Os(4) would be regarded as a donor–acceptor bond. Through resonance, however, this bond would be distributed equally. Accordingly, both carbonyl ligands on Os(2) adopt semibridging modes, one to each of the other osmium atoms, Os(3)···C(4) = 2.57 (1) Å and Os(4)···C(5) = 2.61 (1) Å.

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[16] (a) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982, Chapter 31.4.2.2.4. (b) Dodge, R. P.; Shomaker, V. *J. Organomet. Chem.* **1965**, *3*, 274. (c) Ferraris, G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1974**, 1813. (d) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221.

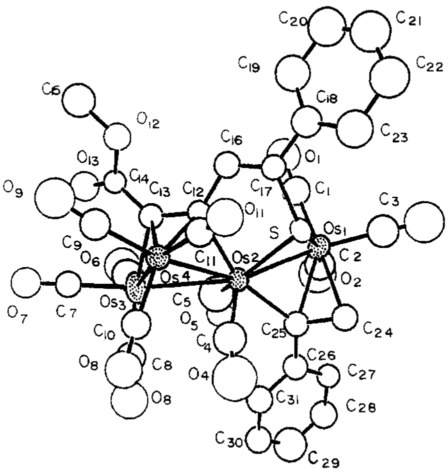


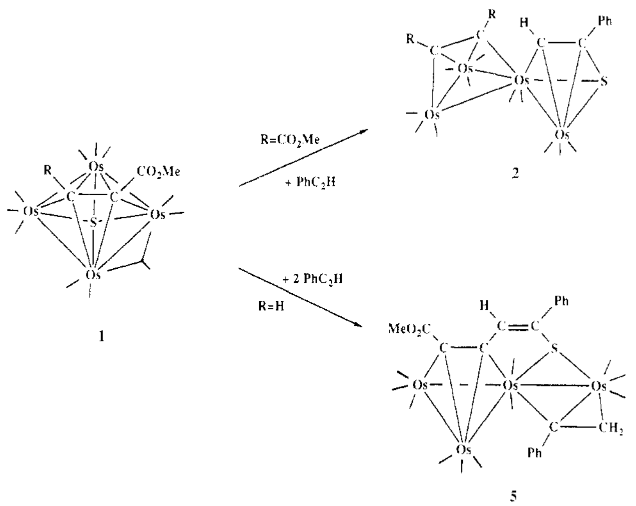
Figure 4. An ORTEP diagram of $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C{\equiv}CCO_2Me]$ (**5**) showing 50% probability thermal ellipsoids.

Table XII. Intramolecular Distances (Å) for $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C{\equiv}CCO_2Me]$ (5)[a]

Os(1)–C(1)	1.85 (2)	C(2)–O(2)	1.14 (3)
Os(1)–C(2)	1.87 (3)	C(3)–O(3)	1.19 (3)
Os(1)–C(3)	1.87 (2)	C(4)–O(4)	1.19 (3)
Os(1)–C(24)	2.29 (2)	C(5)–O(5)	1.20 (4)
Os(1)–C(25)	2.29 (2)	C(6)–O(6)	1.20 (3)
Os(1)–S	2.400 (4)	C(7)–O(7)	1.13 (2)
Os(1)–Os(2)	2.759 (1)	C(8)–O(8)	1.18 (2)
Os(2)–C(4)	1.88 (2)	C(9)–O(9)	1.17 (2)
Os(2)–C(5)	1.92 (3)	C(10)–O(10)	1.18 (2)
Os(2)–C(12)	2.12 (2)	C(11)–O(11)	1.14 (2)
Os(2)–C(25)	2.16 (2)	C(14)–O(12)	1.41 (6)
Os(2)–S	2.384 (4)	C(15)–O(12)	1.45 (6)
Os(2)–Os(4)	2.826 (1)	C(14)–O(13)	1.21 (4)
Os(2)–Os(3)	2.948 (1)	C(12)–C(13)	1.37 (2)
Os(3)–C(7)	1.87 (2)	C(12)–C(16)	1.50 (2)
Os(3)–C(6)	1.88 (3)	C(13)–C(14)	1.44 (3)
Os(3)–C(8)	1.91 (2)	C(16)–C(17)	1.32 (2)
Os(3)–C(13)	2.09 (2)	C(17)–C(18)	1.48 (3)
Os(3)–Os(4)	2.713 (1)	C(18)–C(19)	1.38 (3)
Os(4)–C(9)	1.85 (2)	C(18)–C(23)	1.43 (3)
Os(4)–C(10)	1.88 (2)	C(19)–C(20)	1.48 (3)
Os(4)–C(11)	1.89 (2)	C(20)–C(21)	1.26 (3)
Os(4)–C(12)	2.22 (2)	C(21)–C(22)	1.34 (3)
Os(4)–C(13)	2.21 (2)	C(22)–C(23)	1.51 (3)
S–C(17)	1.80 (2)	C(24)–C(25)	1.42 (2)
C(1)–O(1)	1.18 (2)	C(25)–C(26)	1.44 (4)
C(26)–C(27)	1.39 (5)	C(29)–C(30)	1.35 (7)
C(26)–C(31)	1.38 (5)	C(30)–C(31)	1.38 (5)
C(27)–C(28)	1.41 (5)	Os(3)···C(5)	2.527 (2)
C(28)–C(29)	1.35 (6)	Os(4)···C(4)	2.882 (2)
C(5)–O(5)′	1.34 (3)	C(26)′–C(27)′	1.40 (5)
C(14)′–O(13)′	1.15 (6)	C(26)′–C(31)′	1.37 (5)
C(14)′–O(12)′	1.39 (4)	C(27)′–C(28)′	1.40 (7)
C(15)′–O(12)′	1.47 (5)	C(28)′–C(29)′	1.36 (7)
C(13)–C(14)′	1.71 (5)	C(29)′–C(30)′	1.41 (7)
C(25)–C(26)′	1.62 (4)	C(30)′–C(31)′	1.39 (6)

[a] Estimated standard deviations are given in parentheses.

Scheme I



The reaction of **1b** with PhC≡CH proceeds by addition at 25 °C. The product identified as $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)CC(CO_2Me)]$ (**5**) was obtained in 34% yield after 3 h. This compound was characterized by IR and ^1H NMR spectroscopies and by elemental and single-crystal X-ray diffraction analyses. An ORTEP drawing of **5** is shown in Figure 4. Final positional parameters are listed in Table XI. Intramolecular bond distances and angles are listed in Tables XII and XIII. The four metal atoms in **5** are arranged in the form of a spiked triangular cluster that is very similar to that of compound **2**. The metal–metal bonds exhibit similar variations in their lengths and range from 2.713 (1) to 2.948 (1) Å. The external metal–metal bond Os(1)–Os(2) is also short, 2.759 (1) Å. There is a 1-phenylvinyl group that bridges the Os(1)–Os(2) bond in the commonly observed σ,π-bonding mode.[17] The hydrogen atoms on C(24) were not observed crystallographically but were confirmed by the observation of their ^1H NMR signals δ 5.77 and 3.08 and have the characteristically small geminal coupling constant $J_{H\text{-}H}$ = 3.08 Hz.[18] The most interesting ligand in **5** consists of the chain C(13), C(12), C(16), C(17), and S. Carbons C(12) and C(13) bridge the triangular group of metal atoms. Carbon atoms C(16) and C(17) are not bonded to any metal atoms, but C(17) is bonded to the sulfur atom through a single bond, C(17)–S = 1.80 (2) Å. The C(12)–C(13) bond length of 1.37 (2) Å indicates a multiple-bond character. This group could be regarded as a triply bridging acetylenic unit.[12] The C(16)–C(17) bond length of 1.32 (2) Å is indicative of a carbon–carbon double bond. The C(12)–C(16) bond (1.50 (2) Å) is single. The hydrogen atom on atom C(16) was not observed crystallographically but was confirmed spectroscopically: ^1H NMR δ 8.44 (s, 1 H). Compound **5** contains 64 valence electrons and is electron-precise. However, as in compound **2** the Os(2)–Os(3) bond in **5** is formally a donor–acceptor bond, and the carbonyl ligand C(5)–O(5) has adopted a semibridging bonding mode, Os(3)···C(5) = 2.527 (2) Å.[14] A twofold rotational disorder of the carbomethoxy group was observed in the crystal of **5**. The second conformation (not shown in Figure 4) is rotated by 35° relative to the one that is shown. The phenyl group bonded to atom C(25) and the carbonyl group C(5)–O(5) also exhibited a twofold disorder, but only the disorder of oxygen atom of the latter could be resolved.

Discussion

Compounds **1a,b** undergo facile addition of PhC≡CH to form the products **2** and **5**, respectively, which contain opened (spiked triangular) clusters of metal atoms; see Scheme I. It is important and believed to be mechanistically significant that in both cases a bond has been formed between the sulfido ligand in the cluster and the phenyl-substituted carbon atom of the PhC≡CH molecule.

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(17) (a) Orpen, A. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2466. (b) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

(18) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1966; p 714.

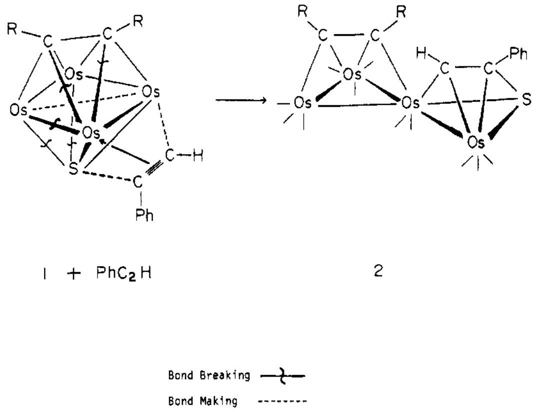
Table XIII. Selected Interatomic Angles (deg) for $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C{\equiv}CCO_2CH_3)]$ (5)

Os(1)–Os(2)–Os(3)	139.70 (4)	Os(4)–C(9)–O(9)	173 (2)	C(17)–C(18)–C(19)	120 (2)
Os(1)–Os(2)–Os(4)	145.91 (3)	Os(4)–C(10)–O(10)	177 (2)	C(17)–C(18)–C(23)	118 (2)
Os(3)–Os(2)–Os(4)	56.00 (3)	Os(4)–C(11)–O(11)	175 (2)	C(18)–C(19)–C(20)	118 (2)
Os(2)–Os(4)–Os(3)	64.28 (4)	C(13)–C(12)–C(16)	128 (2)	C(19)–C(20)–C(21)	119 (3)
Os(2)–Os(3)–Os(4)	59.72 (3)	Os(2)–C(12)–C(13)	113 (1)	C(20)–C(21)–C(22)	127 (3)
S–Os(1)–Os(2)	54.5 (1)	Os(4)–C(12)–C(13)	72 (1)	C(21)–C(22)–C(23)	118 (2)
S–Os(2)–Os(1)	55.1 (1)	Os(2)–C(12)–C(16)	119 (1)	C(18)–C(23)–C(22)	115 (2)
S–Os(2)–Os(4)	95.8 (1)	Os(4)–C(12)–C(16)	119 (1)	Os(1)–C(24)–C(25)	72 (1)
S–Os(2)–Os(3)	145.7 (1)	Os(2)–C(12)–Os(4)	81.1 (5)	C(24)–C(25)–C(26)	120 (2)
C(12)–Os(4)–C(13)	36.0 (5)	C(12)–C(13)–C(14)	134 (2)	Os(2)–C(25)–C(24)	120 (1)
Os(2)–S–C(17)	102.4 (5)	Os(4)–C(13)–C(12)	72 (1)	Os(1)–C(25)–C(24)	72 (1)
Os(1)–S–C(17)	107.1 (6)	Os(3)–C(13)–C(14)	113 (2)	Os(2)–C(25)–C(26)	120 (1)
Os(1)–S–Os(2)	70.4 (1)	Os(4)–C(13)–C(14)	129 (2)	Os(1)–C(25)–C(26)	113 (2)
C(14)–O(12)–C(15)	115 (3)	Os(3)–C(13)–Os(4)	78.1 (6)	Os(1)–C(25)–Os(2)	76.5 (6)
Os(1)–C(1)–O(1)	177 (2)	O(12)–C(14)–O(13)	120 (3)		
Os(1)–C(2)–O(2)	175 (2)	C(13)–C(14)–O(13)	131 (3)		
Os(1)–C(3)–O(3)	178 (2)	C(13)–C(14)–O(12)	109 (3)		
Os(2)–C(4)–O(4)	167 (2)	C(12)–C(16)–C(17)	120 (2)		
Os(2)–C(5)–O(5)	152 (3)	C(16)–C(17)–C(18)	125 (2)		
Os(3)–C(6)–O(6)	178 (2)	S–C(17)–C(16)	117 (1)		
Os(3)–C(7)–O(7)	179 (2)	S–C(17)–C(18)	118 (1)		
Os(3)–C(8)–O(8)	172 (2)	C(19)–C(18)–C(23)	122 (2)		

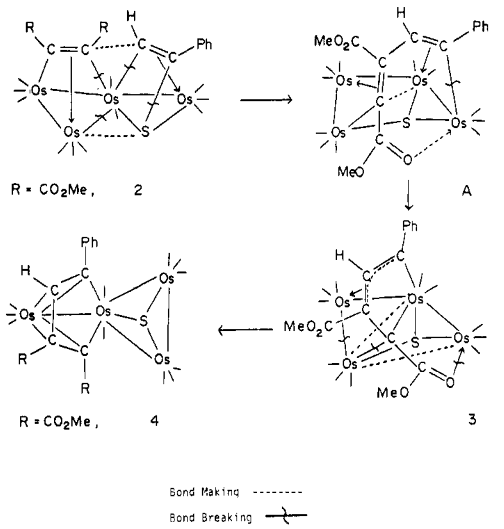
A similar result was observed in the formation of the compound $Os_4(CO)_{12}[\mu_4\text{-}\eta^3\text{-}SC(Ph){=}CH]$ (**6**) from the reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$ with PhC≡CH.[5] Compound **5** is a terminal product, but both **2** and **6** undergo further transformations in which the carbon–sulfur bond is cleaved. This suggests that the carbon–sulfur bonding interactions occur at a very early stage in the addition reactions, possibly, even before any significant interactions between the metal atoms and the PhC≡CH molecule. This is consistent with the fact that the compounds **1a**,**b** do not contain vacant coordination sites, even though they are formally unsaturated.[10]

It is well-established that sulfido ligands can form bonding interactions to coordinatively unsaturated metal complexes by employing their residual lone pair of electrons.[19] Similarly, it is conceivable that the lone pair of electrons on the sulfido ligand could form bonding interactions to unsaturated organic molecules, such as PhC≡CH. It has been shown that the sulfido molydenum dimers $[(CH_3)_nC_5H_{5-n}MoS(\mu\text{-}S)]_2$ undergo facile addition of alkenes and alkynes to yield products in which the alkenes and alkynes are bonded exclusively to the sulfido ligands.[6] Favorable interactions between a sulfido ligand and an unsaturated organic molecule could play a key role in facilitating the entry of the new molecule into the coordination sphere of the metal atom. A generalized mechanism could be envisaged through which any ligand that contains a lone pair of electrons or could readily produce a lone pair of electrons[20] could interact with any unsaturated molecule by the formation of a donor–acceptor bond. The added molecule may or may not be ultimately transferred wholly or in part into the coordination sphere of a metal atom. In cases where bonding between a metal atom and the added molecule does develop, it is proposed to designate the reaction as a *ligand-assisted addition*. If a ligand is displaced from a metal by an incoming molecule, the reaction would be designated as a *ligand-assisted substitution*. The reactions that lead to the formation of **1a**,**b** would be of the latter type.[5,10,23] The reactions that lead to the formation of **2** and **6** would be of the former type.

Scheme II



Scheme III



Scheme II shows one mechanism for the addition of PhC≡CH to **1a**. Not all of the essential bond-making and

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(19) (a) Adams, R. D.; Horvath, I. T.; Wang, S. *Inorg. Chem.* **1985**, *24*, 1728. (b) Winter, A.; Jibril, I.; Huttner, G. *J. Organomet Chem.* **1983**, *242*, 259. (c) Adams, R. D.; Babin, J. E.; Natarajan, K. *J. Am. Chem. Soc.* **1986**, *108*, 3518. (d) Adams, R. D.; Mannig, D.; Segmuller, B. E. *Organometallics* **1983**, *2*, 149.

(20) Certain iron cluster compounds that contain triply bridging phosphinidene ligands, μ_3-PR, undergo facile additions of alkynes.[8d,21] These additions could occur by a transformation that first converts the triply bridging phosphinidene ligand into a doubly bridging phosphinidene ligand that would contain a lone pair of electrons. Such a transformation has been advanced to explain the facile addition of metal carbonyl units to clusters containing phosphinidene ligands.[22]

(21) Knoll, K.; Orama, O.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 976.

(22) Colbran, S. B.; Johnson, B. F. G.; Lewis, J.; Sorrell, R. M. *J. Chem. Soc., Chem. Commun.* **1986**, 525.

(23) Adams, R. D.; Wang, S. *J. Am. Chem. Soc.* **1987**, *109*, 924.

-breaking steps are shown and other processes are possible, but the alkyne–sulfur interaction is believed to be one of the first important contacts, and this leads to the formation of a carbon–sulfur bond. Scheme III shows a proposed transformation of **2** into **3** via an unobserved intermediate A. The most important steps in this transformation are the cleavage of the carbon–sulfur bond and the formation of a carbon–carbon bond between the two alkyne ligands. The latter step could occur by a simple reductive-elimination process since the appropriate carbon atoms are both bonded to the same metal atom, Os(2). Cleavage of the carbon–sulfur bond would yield a sulfido ligand that could induce the cleavage of a metal–metal bond as it shifts to become a triply bridging ligand. The addition of the carboxylate oxygen atom to Os(1) would permit the four-carbon unsaturated unit to shift into its final position on atoms Os(2), Os(3), and Os(4) in **3**. The transformation of **3** into **4** requires only minor reorganization of the cluster framework that would be facilitated by the cleavage of the metal–oxygen bond to the carboxylate group.

The formation of **5** requires the addition of 2 mol of PhC≡CH. Since no intermediates were observed in this reaction, it is more difficult to predict the course of events, but the reaction of **1a** with PhC≡CH could be a useful guide. A product analogous to **2** would be a logical first step. A key transformation is the cleavage of the acetylenic C—H bond in the $MeO_2CC{\equiv}CH$ ligand. Such transformations have been observed previously in cluster complexes that contain monosubstituted alkyne ligands.[24] The hydrogen atom probably shifts to the metal atoms to become a hydride ligand. The remainder of the $MeO_2CC{\equiv}CH$ ligand becomes an acetylide, $MeO_2CC{\equiv}C$, ligand. Unlike compound **2**, carbon–sulfur bond cleavage does not occur in the formation of **5**. However, a carbon–carbon bond formation does occur. The PhC=CH grouping is released from metal coordination but remains bound to the molecule through the carbon–carbon bond C(12)–C(16) and the carbon–sulfur bond. To complete the formation of **5** a second PhC≡CH molecule adds to the cluster and inserts into the metal–hydride bond to yield the 1-phenylvinyl ligand. Such insertions have been observed previously in hydride-containing cluster complexes.[25] Although it is believed that interactions between the sulfido ligand in **1a,b** and the entering alkyne molecule play a key role in the addition process, these interactions alone are not necessarily sufficient to ensure that the addition will proceed to completion. Another important feature of the compounds **1a,b** is that they are electronically unsaturated by the amount of two electrons.[10] Thus, the addition of a donating ligand will yield stable, electron-precise clusters such as the compounds **2**–**4** are.

The reactions described here serve to demonstrate the rich and varied nature of ligand transformations that can occur for transition-metal cluster compounds, but more importantly they show the importance of interactions between entering molecules and existing ligands in addition reactions. It is believed that such interactions may serve as the basis for a general mechanism of ligand addition and substitution in metal complexes that has not been fully appreciated or recognized in the past. It is proposed that reactions of this type should be referred to as ligand-assisted addition reactions and ligand-assisted substitution reactions, respectively.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Johnson Matthey Inc. for a loan of osmium tetroxide. The Brüker AM-300 NMR spectrometer was purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

Registry No. **1a**, 106799-87-5; **1b**, 102110-06-5; **2**, 106799-86-4; **3**, 106820-89-7; **4**, 106799-89-7; **5**, 102233-91-0; PhC≡CH, 536-74-3.

Supplementary Material Available: Tables of anisotropic thermal parameters for compounds 2–4 (3 pages); listings of structure factor amplitudes for the structural analyses of compounds 2–4 (83 pages). For compound 5 this information was published previously.[9] Ordering information is given on any current masthead page.

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[24] (a) Schnering, C.; Albiez, T.; Bernhardt, W.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 479. (b) Roland, E.; Vahrenkamp, H., *J. Mol. Catal.* **1983**, *21*, 233. (c) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

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