alkyls or alkylidenes. A similar effect could be responsible for the M–N–C inequalities in the amides.

Acknowledgment. The support of this work by the National Science Foundation, Grant CHE85-19289 (J.W.G. and R.E.C.), and by the donors of the Petroleum Research Fund, adminstered by the American Chemical Society, is gratefully acknowledged.

Registry No. $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$, 77357-86-9; $Cp_3UN(C_6H_5)_2$, 98703-43-6; $HN(C_6H_5)_2$, 122-39-4.

Supplementary Material Available: A listing of observed and calculated structure factors for $Cp_3UN(C_6H_5)_2$ (15 pages). Ordering information is given on on any current masthead page.

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(21) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667–7676.

The Coupling of Cumulenes to an Alkyne Ligand in an Osmium Cluster Complex. The Reactions of $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ with Allene and Methyl Isocyanate

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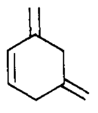
The reactions of $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ (**1**) with allene and methyl isocyanate have been studied. Compound **1** reacts with allene at 25 °C by the addition of 2 mol equiv of allene to yield the new cluster complex $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(CH_2)_2CC(H)C(CO_2Me)](\mu_3\text{-}S)$ (**2**) in 46% yield. Compound **2** was characterized by a single-crystal X-ray diffraction analysis; space group $P\bar{1}$, $a = 15.047$ (3) Å, $b = 11.472$ (2) Å, $c = 9.444$ (2) Å, $\alpha = 103.85$ (2)°, $\beta = 89.10$ (2)°, $\gamma = 77.20$ (1)°, $Z = 2$, $\rho_{calcd} = 2.82$ g/cm^3. The structure was solved by direct methods and was refined (3609 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals, $R = 0.050$ and $R_w = 0.057$. The molecule consists of a group of three osmium atoms joined by metal–metal bonds and bridging ligands. The fourth metal atom is held to the molecule by bridging ligands alone. The bridging ligands include a sulfido ligand, an allene ligand, a carbonyl group, and 1-carbomethoxy-2-allylvinyl group that was formed by addition of an allene molecule to the unsubstituted end of the alkyne ligand in **1**. When reacted with methyl isocyanate at 25 °C, compound **1** adds 1 mol of methyl isocyanate, loses an $Os(CO)_2$ fragment, and forms the product $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (**3**) in 71% yield. Compound **3** was characterized by a single-crystal X-ray diffraction analysis: space group $P2_1/c$, $a = 12.318$ (2) Å, $b = 14.550$ (2) Å, $c = 13.500$ (2) Å, $\beta = 116.482$ (9)°, $Z = 4$, $\rho_{calcd} = 3.05$ g/cm^3. The structure was solved by direct methods and was refined (2947 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals, $R = 0.046$ and $R_w = 0.055$. The molecule consists of an open triangular cluster of three metal atoms with only one metal–metal bond and a triply bridging sulfido ligand. The isocyanate molecule was added to the alkyne ligand at the unsubstituted carbon atom by the formation of a carbon–carbon bond.

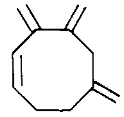
Introduction

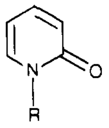
The use of metal complexes to promote the formation of carbon–carbon bonds between unsaturated organic molecules has been one of the greatest triumphs to emerge from the study of organometallic compounds.[1,2] Recently, interest has been focused on the use of metal complexes to activate allenes, A, and heteroallenes, B, X, Y = NR,

$$\underset{A}{R_2C{=}C{=}CR_2} \qquad \underset{B}{X{=}C{=}Y}$$

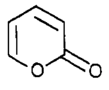
O, or S, which belong to the general class of 1,2-diunsaturated compounds known as cumulenes.[3,4] The metal-catalyzed cooligomerization of alkynes with allenes, alkyl isocyanates, and carbon dioxide yields *exo*-methylenecyclohexene, C, or -cyclooctene, D, derivatives,[5] 2-pyridones, E[6], and pyrones, F,[4] respectively.


C


D



E



F

We have recently synthesized the unsaturated osmium cluster complex $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ (**1**).[7] This complex readily adds donors and unsaturated hydrocarbons. In this report is described the results of our studies of the reactions of compound **1** with allene and methyl isocyanate. A preliminary report has been published.[8]

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(1) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapters 52, 54, 56, 57, 58.

(2) Hegedus, L. S. *J. Organomet. Chem.* **1983**, *245*, 119; **1983**, *283*, 1; **1984**, *298*, 207 and references therein.

(3) Jacobs, T. L. In *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982.

(4) See ref 1, Chapter 50.4.

(5) See ref 1, Chapter 56.3.

(6) Hoberg, H.; Oster, B. W. *Synthesis* **1982**, 324.

(7) Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1272.

Table I. Crystallographic Data for X-ray Diffraction Studies

	2	3
	(A) Crystal Data	
formula	$Os_4O_{13}C_{24}H_{19}$	$Os_3SO_{12}NC_{15}H_7$
temp, ±3 °C	23	23
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	15.0470 (32)	12.3175 (17)
b, Å	11.4717 (25)	14.5503 (21)
c, Å	9.4436 (23)	13.5001 (18)
α, deg	103.853 (19)	90.0
β, deg	89.101 (17)	116.482 (9)
γ, deg	77.197 (14)	90.0
V, Å^3	1539 (1)	2166 (1)
M_r	1308.1	995.82
Z	2	4
ρ_{calcd}, g/cm^3	2.82	3.05
	(B) Measurement of Intensity Data	
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite
detector aperture, mm		
horizontal	2	2
vertical	2	2
crystal faces	$\bar{1}2\bar{1}$, $\bar{1}00$, 100, 001, $00\bar{1}$, $\bar{1}0\bar{1}$, 010, $0\bar{1}0$, $\bar{1}\bar{1}0$	001, $00\bar{1}$, $\bar{1}\bar{1}1$, $11\bar{1}$, $\bar{1}11$, $1\bar{1}\bar{1}$, 010
crystal size, mm	0.18 × 0.13 × 0.11	0.15 × 0.31 × 0.33
cryst orientation directn, deg from ϕ axis	[120] 13.71	[111] 2.34
reflctns measd	$\pm h,\pm k,+l$	$+h,+k,\pm l$
max 2θ, deg	50	50
scan type	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ)°	1.10	1.10
background (count time, at each end of scan), s	9.0	9.0
ω-scan rate,[a] deg/min	4.0	8.0
no. of reflctns measd	6570	4189
data used ($F^2 \geq 3.0\sigma(F^2)$)	3609	2947
	(C) Treatment of Data	
absorption correctn	applied	applied
coeff, cm^{-1}	175.6	187.6
grid	10 × 10 × 8	16 × 14 × 4
transmissn coeff		
max	0.145	0.087
min	0.076	0.010
no. of variables (refined)	194	289
P factor	0.03	0.03
final residuals		
R_F	0.050	0.046
R_{wF}	0.057	0.055
esd of unit wt obsvn	1.81	2.18
largest shift/error value of final cycle	0.36	0.03
largest peak in final diff Fourier, e/Å^3	1.58	3.28

[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.

Experimental Section

General Data. Although the reaction products are air-stable, all reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were used without further purification. Allene gas was used as purchased from Linde Corp., and methyl isocyanate was used as purchased from Aldrich Chemical Co. $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ (1) was prepared according to the previously reported procedure.[7] IR spectra were recorded on a Nicolet 5-DXB FT-IR spectrophotometer. ^{1}H NMR were recorded on a Brüker AM-300 FT-NMR spectrometer operating at 300 MHz. Elemental microanalyses were performed at MICANAL, Tucson, AZ.

Reaction of 1 with Allene 1 (8 mg, 0.0067 mmol) was dissolved in 10 mL of CH_2Cl_2 solvent at 25 °C. The solution was degassed in vacuo and then saturated with allene (C_3H_4) gas. The reaction solution was stirred for 1.6 h at 25 °C. During this time it slowly changed color from yellow to yellow-orange. After removal of the solvent and excess allene in vacuo, the residue was dissolved in CH_2Cl_2 and was chromatographed on silica gel TLC plates. Elution with a 50/50 CH_2Cl_2/hexane solution yielded an orange band, $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}C(CH_2)_2CHCCO_2Me](\mu_3\text{-}S)$ (2) (4 mg, 0.0031 mmole) in 46% yield. IR [hexane; ν(CO), cm^{-1}]: 2080 (vs), 2053 (s), 2036 (m), 2014 (s), 1999 (s), 1845 (w), 1703 (w). ^{1}H NMR ($CDCl_3$; δ): 6.97 (s, 1 H), 4.66 (s, 1 H), 4.13 (s, 1 H), 3.94 (s, 1 H), 3.68 (d, 1 H), 3.63 (s, 3 H), 3.47 (t, 1 H), 3.12 (s, 1 H), 2.93 (s, 1 H), 2.68 (s, 1 H). Orange crystals of 2 that contain 0.5 mol of hexane/mol of complex were grown from solutions in a 10%, v/v, CH_2Cl_2/hexane solvent mixture at −20 °C. Elemental Anal. Calcd: C, 22.02; H, 1.45. Found: C, 21.05; H, 1.25.

Reaction of 1 with Methyl Isocyanate. 1 (10 mg, 0.0084 mmol) was dissolved in 6 mL of methyl isocyanate at 25 °C. The mixture was stirred for 70 min, and the CH_3NCO was then removed in vacuo. The light yellow residue was dissolved in CH_2Cl_2 and was chromatographed on silica gel TLC plates. A yellow band was eluted with a 50/50 CH_2Cl_2/hexane solution which yielded 6.0 mg of $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3) (0.006 mmol, 71% yield). IR [CH_2Cl_2, ν(CO), cm^{-1}]: 2109 (s), 2088 (vs), 2065 (s), 2011 (br, s), 1706 (br, w), 1678 (br, w), 1608 (vw). ^{1}H NMR ($CDCl_3$ δ): 4.18 (1 H, CH), 3.94 (3 H, CH_3), 3.80 (3 H, CH_3). Anal. Calcd: C, 18.08; H, 0.70; N, 1.40. Found: C, 18.30; H, 0.57; N, 1.65.

Crystallographic Analyses. Orange platelets of 2 suitable for X-ray diffraction measurements were grown by cooling hexane/CH_2Cl_2 (90/10, v/v) solutions to −20 °C. Yellow platelets

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(8) Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1274.

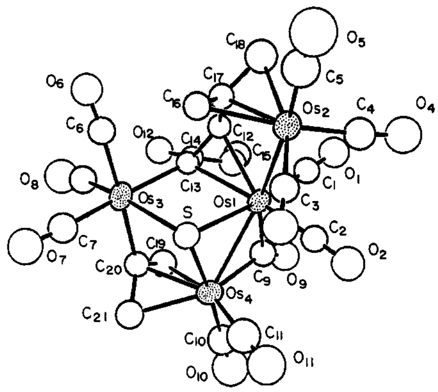

Figure 1. An ORTEP diagram of $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(CH_2)_2CC(H)C(CO_2Me)](\mu_3\text{-}S)$ (2) showing 50% probability thermal ellipsoids.

of 3 were grown by slow evaporation of solvent from solutions in a 5/5/90 benzene/CH_2Cl_2/hexane mixture at 5 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic four-circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the diffractometer 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. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 2 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. All atoms heavier than oxygen were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were not determined and were subsequently ignored. Toward the end of the refinement a molecule of hexane, evidently obtained from the crystallization solvent, was found positioned about a crystallographic center of symmetry. The carbon atoms were included in the final refinements of the analysis, but large temperature factors and slightly abnormal molecular dimensions suggested that the hexane molecule contained a significant degree of disorder. However, a good disorder model could not be refined and the final results include the initial poorly refined hexane molecule.

Compound 3 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the systematic absences observed in the data. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were not located in the structure determination and were subsequently ignored in the analysis. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. A table of observed and calculated structure factor amplitudes for compound 3 is available (see supplementary material). The corresponding information for compound 2 was published previously.[8]

Table II. Positional Parameters for $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}MeO_2CC{=}C(H)C(CH_2)_2](\mu_3\text{-}S)$ (2)

atom	x	y	z	B(eq), Å^2
Os(1)	−0.22731 (05)	−0.03726 (07)	−0.26709 (08)	2.9
Os(2)	−0.18597 (06)	0.19797 (08)	−0.11644 (09)	3.7
Os(3)	−0.21724 (06)	−0.19782 (08)	0.02965 (09)	3.3
Os(4)	−0.14769 (06)	−0.29633 (08)	−0.34941 (09)	3.7
S	−0.1145 (03)	−0.1465 (05)	−0.1378 (06)	3.1
O(1)	−0.3823 (11)	0.1138 (15)	−0.3981 (18)	5.6
O(2)	−0.0942 (11)	−0.0044 (15)	−0.4942 (18)	5.3
O(3)	0.0143 (11)	0.0658 (14)	−0.1956 (17)	4.9
O(4)	−0.2304 (12)	0.2992 (17)	−0.384 (02)	6.3
O(5)	−0.1339 (15)	0.427 (02)	0.055 (02)	8.6
O(6)	−0.2533 (10)	0.0092 (14)	0.3125 (17)	4.7
O(7)	−0.0627 (12)	−0.3381 (17)	0.1749 (20)	6.2
O(8)	−0.3534 (13)	−0.3156 (18)	0.149 (02)	7.1
O(9)	−0.3041 (11)	−0.1979 (15)	−0.5268 (18)	5.3
O(10)	−0.1574 (15)	−0.502 (02)	−0.618 (02)	8.5
O(11)	0.0290 (14)	−0.2755 (18)	−0.497 (02)	7.1
O(12)	−0.4439 (10)	−0.1548 (14)	−0.0433 (17)	4.6
O(13)	−0.4349 (10)	−0.0801 (14)	−0.2359 (17)	4.6
C(1)	−0.3237 (14)	0.0551 (19)	−0.349 (02)	3.6
C(2)	−0.1448 (14)	−0.0151 (18)	−0.410 (02)	3.4
C(3)	−0.0596 (14)	0.1148 (19)	−0.170 (02)	3.5
C(4)	−0.2141 (16)	0.255 (02)	−0.287 (03)	4.8
C(5)	−0.1602 (18)	0.339 (03)	−0.005 (03)	5.8
C(6)	−0.2363 (14)	−0.0625 (19)	0.205 (02)	3.6
C(7)	−0.1216 (16)	−0.288 (02)	0.117 (02)	4.4
C(8)	−0.3077 (15)	−0.264 (02)	0.110 (02)	4.2
C(9)	−0.2546 (15)	−0.1884 (20)	−0.433 (02)	3.9
C(10)	−0.1529 (17)	−0.424 (02)	−0.513 (03)	5.1
C(11)	−0.0353 (19)	−0.281 (02)	−0.437 (03)	5.7
C(12)	−0.3229 (13)	0.0540 (17)	−0.057 (02)	2.8
C(13)	−0.3120 (13)	−0.0771 (17)	−0.0742 (20)	2.8
C(14)	−0.4046 (14)	−0.1079 (18)	−0.116 (02)	3.3
C(15)	−0.5236 (17)	−0.095 (02)	−0.275 (03)	5.2
C(16)	−0.1909 (13)	0.1336 (18)	0.091 (02)	3.2
C(17)	−0.2799 (13)	0.1457 (18)	0.026 (02)	3.1
C(18)	−0.3240 (17)	0.268 (02)	0.016 (03)	5.2
C(19)	−0.2669 (16)	−0.368 (02)	−0.256 (02)	4.4
C(20)	−0.1976 (14)	−0.3540 (19)	−0.159 (02)	3.5
C(21)	−0.1067 (15)	−0.435 (02)	−0.216 (02)	4.2
C(22)	0.469 (04)	0.517 (05)	0.211 (06)	6.7
C(24)	0.480 (11)	0.495 (15)	0.458 (16)	16.4
C(25)	0.514 (06)	0.529 (08)	0.346 (10)	12.5

Table III. Selected Interatomic Distances (Å) for $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C{=}C(H)C(CH_2)](\mu_3\text{-}S)$ (2)[a]

Os(1)–C(1)	1.89 (2)	Os(4)–C(19)	2.37 (2)
Os(1)–C(2)	1.91 (2)	Os(4)–S	2.442 (5)
Os(1)–C(9)	2.16 (2)	C(1)–O(1)	1.16 (2)
Os(1)–C(12)	2.31 (2)	C(2)–O(2)	1.14 (2)
Os(1)–C(13)	2.40 (2)	C(3)–O(3)	1.12 (2)
Os(1)–S	2.408 (5)	C(4)–O(4)	1.15 (3)
Os(1)–Os(4)	2.856 (1)	C(5)–O(5)	1.18 (3)
Os(1)–Os(2)	2.937 (1)	C(6)–O(6)	1.13 (2)
Os(2)–C(5)	1.83 (3)	C(7)–O(7)	1.17 (2)
Os(2)–C(4)	1.90 (3)	C(8)–O(8)	1.12 (3)
Os(2)–C(3)	1.93 (2)	C(9)–O(9)	1.17 (2)
Os(2)–C(17)	2.20 (2)	C(10)–O(10)	1.18 (3)
Os(2)–C(16)	2.26 (2)	C(11)–O(11)	1.13 (3)
Os(2)–C(18)	2.29 (2)	C(14)–O(13)	1.31 (2)
Os(3)–C(7)	1.90 (2)	C(14)–O(12)	1.19 (2)
Os(3)–C(8)	1.92 (2)	C(15)–O(13)	1.43 (3)
Os(3)–C(6)	1.95 (2)	C(12)–C(17)	1.43 (3)
Os(3)–C(20)	2.17 (2)	C(12)–C(13)	1.44 (3)
Os(3)–C(13)	2.17 (2)	C(13)–C(14)	1.55 (3)
Os(3)–S	2.452 (5)	C(16)–C(17)	1.47 (3)
Os(4)–C(10)	1.87 (3)	C(17)–C(18)	1.44 (3)
Os(4)–C(11)	1.93 (3)	C(19)–C(20)	1.40 (3)
Os(4)–C(9)	2.09 (2)	C(20)–C(21)	1.48 (3)
Os(4)–C(20)	2.23 (2)	Os(1)···Os(3)	3.692 (1)
Os(4)–C(21)	2.25 (2)	Os(3)···Os(4)	3.551 (1)

[a] Estimated standard deviations are given in parentheses.

Results

Compound 1 reacted with allene by the addition of 2 mol of allene/mol of complex to yield the complex $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}C(CH_2)_2)C(H)CCO_2Me](\mu_3\text{-}S)$ (2) in 46% yield. The compound was characterized by IR and ^1H NMR spectroscopies and by elemental and single-

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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.

Table IV. Selected Interatomic Angles (deg) for $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C{=}C(H)C(CH_2)_2](\mu_3\text{-}S)$ (2)[a]

Os(4)–Os(1)–Os(2)	141.22 (4)	C(13)–C(12)–C(17)	135 (2)
S–Os(1)–Os(2)	90.5 (1)	Os(1)–C(12)–C(17)	105 (2)
S–Os(1)–Os(4)	54.5 (1)	Os(1)–C(12)–C(13)	75 (1)
S–Os(4)–Os(1)	53.4 (1)	Os(3)–C(13)–C(12)	128 (1)
Os(1)–S–Os(4)	72.2 (1)	C(14)–C(13)–C(12)	107 (2)
Os(1)–S–Os(3)	98.9 (2)	Os(1)–C(13)–C(12)	69 (1)
Os(4)–S–Os(3)	93.0 (2)	Os(3)–C(13)–C(14)	119 (1)
Os(1)–C(1)–O(1)	179 (2)	Os(1)–C(13)–C(14)	114 (1)
Os(1)–C(2)–O(2)	178 (2)	Os(1)–C(13)–Os(3)	107.7 (7)
Os(2)–C(3)–O(3)	177 (2)	O(12)–C(14)–O(13)	124 (2)
Os(2)–C(4)–O(4)	174 (2)	O(12)–C(14)–C(13)	121 (2)
Os(2)–C(5)–O(5)	172 (3)	O(13)–C(14)–C(13)	116 (2)
Os(3)–C(6)–O(6)	172 (2)	C(14)–O(13)–C(15)	119 (2)
Os(3)–C(7)–O(7)	177 (2)	C(17)–C(16)–Os(2)	69 (1)
Os(3)–C(8)–O(8)	171 (2)	C(12)–C(17)–C(18)	112 (2)
Os(4)–C(9)–O(9)	140 (2)	C(12)–C(17)–C(16)	131 (2)
Os(1)–C(9)–O(9)	135 (2)	Os(2)–C(17)–C(12)	111 (1)
Os(4)–C(9)–Os(1)	84.4 (8)	C(16)–C(17)–C(18)	116 (2)
Os(4)–C(10)–O(10)	178 (2)	C(19)–C(20)–C(21)	114 (2)
Os(4)–C(11)–O(11)	176 (2)	Os(3)–C(20)–C(19)	121 (2)
Os(2)–C(17)–C(18)	74 (1)	Os(4)–C(20)–C(19)	78 (1)
Os(2)–C(18)–C(17)	68 (1)	Os(3)–C(20)–C(21)	123 (1)
Os(2)–C(17)–C(16)	73 (1)	Os(4)–C(20)–C(21)	71 (1)
Os(4)–C(19)–C(20)	67 (1)	Os(4)–C(20)–Os(3)	107.7 (8)
		Os(4)–C(21)–C(20)	70 (1)

[a] Estimated standard deviations are given in parentheses.

crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of 2 is shown in Figure 1. Atomic positional parameters are listed in Table II. Intramolecular bond distances and angles are listed in Table III and IV, respectively.

The molecule contains four osmium atoms consisting of a group of three, Os(1), Os(2), annd Os(4), that are linked by metal–metal bonds, Os(1)–Os(2) = 2.937 (1) Å and Os(1)–Os(4) = 2.856 (1) Å, and the fourth, Os(3), that is tied to the cluster by bridging ligands only, Os(1)···Os(3) = 3.692 (1) Å and Os(3)···Os(4) = 3.551 (1) Å. There is a triply bridging sulfido ligand that bridges the Os(1)–Os(4) bond and Os(3). An allene ligand bridges the nonbonded pair of metal atoms Os(3)···Os(4). This ligand is π-bonded through all three of its carbon atoms to Os(4). The central carbon atom C(20) is σ-bonded to Os(3), Os(3)–C(20) = 2.17 (2) Å. The carbon–carbon bond distances, C(19)–C(20) = 1.40 (3) Å and C(20)–C(21) = 1.48 (3) Å, are longer than those in free allene (C–C = 1.308 Å).[10] A similarly coordinated allene ligand is found in the complex $Os_3(CO)_{11}(\mu_2\text{-}\eta^3\text{-}C_3H_4)$.[11] The most interesting ligand is a 1-carbomethoxy-2-allylvinyl group that was apparently formed by the addition of the second mole of allene to the alkyne ligand of 1 through the formation of a carbon–carbon bond, C(12)–C(17), between the central carbon atom of the allene and the unsubstituted end of the alkyne. The allyl group is π-bonded to Os(2). The alkenyl group, C(12)–C(13), is π-bonded to Os(1), but atom C(13) serves as a bridge to Os(3) through an Os–C σ-bond, Os(3)–C(13) = 2.17 (2) Å. The carbon–carbon bond distances throughout the ligand are all similar in length, C(12)–C(13) = 1.44 (3) Å, C(12)–C(17) = 1.43 Å, C(16)–C(17) = 1.47 (3) Å, and C(17)–C(18) = 1.44 (3) Å, and suggest the existence of considerable electron delocalization. Overall, there are 11 carbonyl ligands. All are of a linear terminal type except C(9)–O(9) which bridges the Os(1)–Os(4) bond, ν(CO) = 1845 cm^{-1}. The allylvinyl ligand serves as a six-electron donor, and the allene and sulfido ligands serve as four-electron donors. Compound 2 contains a total of 68 valence electrons, and with only two metal–metal bonds, it is, therefore, electron-precise. The ^{1}H NMR spectrum shows nine resonances of intensity 1 that can be assigned the protons on the allene ligand, the allyl group, and atom C(12), although more specific assignments cannot be made at this time. Most of these resonances are broad due to unresolved long-range coupling interactions with other protons.

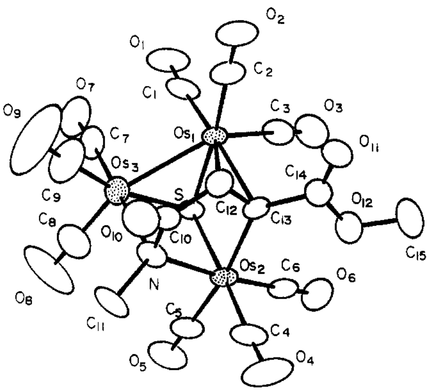

Figure 2. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and B(eq) for $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3)

atom	X	Y	Z	B(eq), Å^2
Os(1)	0.72384 (06)	0.11394 (04)	0.67911 (05)	2.1
Os(2)	0.81605 (06)	−0.11744 (04)	0.73589 (06)	2.1
Os(3)	0.58554 (06)	0.00584 (05)	0.75908 (06)	3.3
S	0.6341 (04)	−0.0352 (03)	0.6131 (04)	2.2
O(1)	0.4942 (13)	0.2231 (09)	0.5445 (14)	4.4
O(2)	0.8337 (14)	0.2964 (09)	0.7869 (15)	5.2
O(3)	0.7967 (16)	0.1235 (11)	0.4922 (14)	6.7
O(4)	1.0469 (14)	−0.2108 (10)	0.9066 (13)	4.6
O(5)	0.6688 (14)	−0.2975 (10)	0.6868 (14)	4.8
O(6)	0.8947 (12)	−0.1643 (10)	0.5567 (12)	4.4
O(7)	0.3476 (13)	0.1031 (12)	0.6196 (13)	6.3
O(8)	0.4372 (17)	−0.1613 (18)	0.755 (02)	13.2
O(9)	0.596 (02)	0.106 (02)	0.9621 (19)	13.7
O(10)	0.8622 (12)	0.0229 (09)	1.0132 (10)	3.5
O(11)	1.0464 (11)	0.1296 (08)	0.7832 (12)	3.3
O(12)	1.0307 (12)	−0.0025 (09)	0.6946 (13)	5.8
N	0.7575 (13)	−0.0694 (10)	0.8578 (12)	3.4
C(1)	0.5787 (17)	0.1800 (12)	0.5985 (18)	2.9
C(2)	0.7922 (17)	0.2296 (13)	0.7490 (17)	3.7
C(3)	0.7735 (18)	0.1220 (12)	0.5638 (13)	3.2
C(4)	0.9622 (18)	−0.1748 (11)	0.8482 (15)	2.7
C(5)	0.7245 (17)	−0.2307 (12)	0.7078 (16)	3.2
C(6)	0.8636 (16)	−0.1478 (11)	0.6231 (15)	2.4
C(7)	0.4418 (18)	0.0686 (16)	0.6724 (19)	5.9
C(8)	0.498 (02)	−0.0978 (19)	0.762 (03)	9.1
C(9)	0.5919 (20)	0.0679 (20)	0.8892 (17)	6.1
C(10)	0.8294 (15)	0.0090 (11)	0.9156 (15)	3.6
C(11)	0.7518 (20)	−0.1390 (15)	0.9390 (18)	6.4
C(12)	0.8749 (14)	0.0649 (12)	0.8495 (15)	2.7
C(13)	0.8921 (13)	0.0185 (11)	0.7670 (715)	2.6
C(14)	0.9962 (16)	0.0565 (13)	0.7471 (17)	3.8
C(15)	1.134 (02)	0.0265 (17)	0.677 (03)	8.5

The reaction of 1 with CH_3NCO proceeds smoothly at 25 °C when CH_3NCO is used as the reaction solvent to give a good yield (71%) of the new compound $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3). Compound 3 has been characterized by IR and ^{1}H 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. Atomic positional parameters are listed in Table V. Intramolecular bond distances and angles are listed in Tables VI and VII, respectively.

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(10) Maki, A. G.; Toth, R. A. *J. Mol. Spectrosc.* **1965**, *17*, 136.
(11) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1982**, *231*, C65.

Table VI. Intramolecular Distances (Å) for $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3)

Os(1)–C(1)	1.89 (2)	O(1)–C(1)	1.15 (2)
Os(1)–C(3)	1.91 (2)	O(2)–C(2)	1.11 (2)
Os(1)–C(2)	1.93 (2)	O(3)–C(3)	1.12 (2)
Os(1)–C(13)	2.33 (1)	O(4)–C(4)	1.12 (2)
Os(1)–C(12)	2.33 (2)	O(5)–C(5)	1.15 (2)
Os(1)–S	2.419 (4)	O(6)–C(6)	1.15 (2)
Os(1)–Os(3)	2.861 (1)	O(7)–C(7)	1.17 (2)
Os(2)–C(6)	1.91 (2)	O(8)–C(8)	1.17 (3)
Os(2)–C(5)	1.94 (2)	O(9)–C(9)	1.11 (3)
Os(2)–C(4)	1.95 (2)	O(10)–C(10)	1.21 (2)
Os(2)–C(13)	2.15 (2)	O(11)–C(14)	1.22 (2)
Os(2)–N	2.19 (2)	O(12)–C(14)	1.30 (2)
Os(2)–S	2.426 (4)	O(12)–C(15)	1.46 (2)
Os(3)–C(8)	1.86 (3)	N–C(10)	1.44 (2)
Os(3)–C(7)	1.87 (2)	N–C(11)	1.52 (2)
Os(3)–C(9)	1.94 (2)	C(10)–C(12)	1.49 (2)
Os(3)–N	2.22 (1)	C(12)–C(13)	1.40 (2)
Os(3)–S	2.378 (4)	C(13)–C(14)	1.53 (2)
Os(1)···Os(2)	3.526 (1)	Os(2)···Os(3)	3.488 (1)
		Os(3)···C(10)	2.80 (2)
		Os(2)···C(10)	2.99 (2)

[a] Estimated standard deviations are given in parentheses.

The structure of 3 contains only three osmium atoms. Os(1) and Os(3) are bonded at a length of 2.861 (1) Å. Os(2) is linked to the cluster by bridging ligands alone. There is a triply bridging sulfido ligand with Os–S distances with normal lengths. The most interesting ligand consists of the chain of atoms C(13)–C(12)–C(10)–N. This could be viewed as a derivative of acrylamide and was formed by a combination of one mole of CH_3NCO with the alkyne ligand of 1. The two molecules have been joined through the formation of a carbon–carbon bond, C(10)–C(12) = 1.49 (2) Å, between the carbon atom of the isocyanate and the unsubstituted end of the alkyne. The nitrogen atom bridges the metal atoms Os(2) and Os(3), Os(2)–N = 2.19 (2) Å and Os(3)–N = 2.22 (1) Å. The unsaturated group, C(12)–C(13) (1.40 (2) Å), is π-bonded to Os(1) and σ-bonded through C(13) to Os(2), Os(1)–C(13) = 2.33 (1) Å vs. Os(2)–C(13) = 2.15 (2) Å. Atom C(10) is not bonded to a metal atom. The closest approaches are Os(2)···C(10) = 2.99 (2) Å and Os(3)···C(10) = 2.80 (2) Å. A similar ligand was found to be bridging two metal atoms in the complex $(C_5H_5)_2Rh_2[\mu\text{-}\eta^3\text{-}C(CF_3)C(CF_3)C(CF_3)C(O)NPh]$.[12]

Discussion

The addition of the cumulenes, allene and methyl isocyanate, to 1 proceeds in good yield under mild conditions. It is believed that the facile addition can be attributed to the fact that 1 is a 62-electron cluster that is formally electron-deficient.[7] In both of the addition reactions described in this report, it was found that one cumulene molecule had been joined between the unsubstituted end of the alkyne ligand in 1 and the central atom of the cumulene through the formation of a carbon–carbon bond. This would appear to be a logical first step in the known catalytic cooligomerization reactions of alkynes with allenes[5] and alkyl isocyanates.[6] Chisholm has recently reported examples of carbon–carbon bond formation between allene ligands and alkylidyne ligands in the synthesis of a series of complexes of the type $W_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)[RCH(CHR)CCSiMe_3]$ (R = H or Me).[13] Dickson has recently reported an example of the coupling of an isocyanate molecule to the coordinated alkyne ligand in the complex $(C_5H_5)_2Rh_2(CO)(\mu\text{-}CF_3C_2CF_3)$ by formation of a carbon–carbon bond to the isocyanate carbon atom.[12]

Table VII. Intramolecular Bond Angles (deg) for $Os_3(CO)_9[\mu_3\text{-}\eta^2MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3).

C(1)–Os(1)–C(3)	93.7 (9)	C(5)–Os(2)–C(4)	92.4 (7)
C(1)–Os(1)–C(2)	86.1 (7)	C(5)–Os(2)–C(13)	170.7 (7)
C(1)–Os(1)–C(13)	173.7 (7)	C(5)–Os(2)–N	93.5 (7)
C(1)–Os(1)–C(12)	149.0 (8)	C(5)–Os(2)–S	90.4 (5)
C(1)–Os(1)–S	94.9 (5)	C(4)–Os(2)–C(13)	94.1 (6)
C(1)–Os(1)–Os(3)	85.8 (6)	C(4)–Os(2)–N	93.0 (7)
C(3)–Os(1)–C(2)	96.7 (8)	C(4)–Os(2)–S	173.4 (5)
C(3)–Os(1)–C(13)	85.2 (7)	C(13)–Os(2)–N	79.6 (6)
C(3)–Os(1)–C(12)	114.6 (7)	C(13)–Os(2)–S	82.5 (4)
C(3)–Os(1)–S	90.8 (5)	N–Os(2)–S	81.0 (4)
C(3)–Os(1)–Os(3)	143.2 (5)	C(8)–Os(3)–C(7)	91 (1)
C(2)–Os(1)–C(13)	100.1 (6)	C(8)–Os(3)–C(9)	99 (1)
C(2)–Os(1)–C(12)	78.6 (7)	C(8)–Os(3)–N	89.8 (9)
C(2)–Os(1)–S	172.4 (6)	C(8)–Os(3)–S	100 (1)
C(2)–Os(1)–Os(3)	119.9 (6)	C(8)–Os(3)–Os(1)	154 (1)
C(13)–Os(1)–C(12)	34.8 (6)	C(7)–Os(3)–C(9)	89 (1)
C(13)–Os(1)–S	79.0 (4)	C(7)–Os(3)–N	178.3 (8)
C(13)–Os(1)–Os(3)	91.4 (4)	C(7)–Os(3)–S	97.0 (7)
C(12)–Os(1)–S	97.0 (4)	C(7)–Os(3)–Os(1)	93.0 (6)
C(12)–Os(1)–Os(3)	78.9 (4)	C(9)–Os(3)–N	92.5 (7)
S–Os(1)–Os(3)	52.7 (1)	C(9)–Os(3)–S	160.3 (8)
C(6)–Os(2)–C(5)	90.4 (8)	C(9)–Os(3)–Os(1)	107.1 (8)
C(6)–Os(2)–C(4)	90.9 (8)	N–Os(3)–S	81.3 (4)
C(6)–Os(2)–C(13)	96.1 (7)	N–Os(3)–Os(1)	85.9 (4)
C(6)–Os(2)–N	174.4 (6)	S–Os(3)–Os(1)	54.0 (1)
C(6)–Os(2)–S	95.0 (5)	Os(3)–S–Os(1)	73.2 (1)
Os(3)–S–Os(2)	93.1 (1)	O(9)–C(9)–Os(3)	177 (3)
Os(1)–S–Os(2)	93.4 (1)	O(10)–C(10)–N	123 (2)
C(14)–O(12)–C(15)	115 (2)	O(10)–C(10)–C(12)	122 (2)
C(10)–N–C(11)	111 (2)	N–C(10)–C(12)	114 (2)
C(10)–N–Os(2)	109 (1)	C(13)–C(12)–C(10)	116 (1)
C(10)–N–Os(3)	97 (1)	C(13)–C(12)–Os(1)	72 (1)
C(11)–N–Os(2)	118 (1)	C(10)–C(12)–Os(1)	114 (1)
C(11)–N–Os(3)	115 (1)	C(12)–C(13)–C(14)	114 (1)
Os(2)–N–Os(3)	104.6 (6)	C(12)–C(13)–Os(2)	113 (1)
O(1)–C(1)–Os(1)	175 (2)	C(12)–C(13)–Os(1)	73 (1)
O(2)–C(2)–Os(1)	177 (2)	C(14)–C(13)–Os(2)	129 (1)
O(3)–C(3)–Os(1)	176 (2)	C(14)–C(13)–Os(1)	109 (1)
O(4)–C(4)–Os(2)	175 (2)	Os(2)–C(13)–Os(1)	103.8 (6)
O(5)–C(5)–Os(2)	177 (2)	O(11)–C(14)–O(12)	124 (2)
O(6)–C(6)–Os(2)	178 (2)	O(11)–C(14)–C(13)	124 (2)
O(7)–C(7)–Os(3)	175 (2)	O(12)–C(14)–C(13)	111 (1)
O(8)–C(8)–Os(3)	175 (3)		

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

The formation of 3 was accompanied by a loss of a unit consisting of one osmium atom and two carbonyl ligands from 1. The fate of this eliminated unit was not established.

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Supplementary Material Available: A table of anisotropic thermal parameters for compound 3 (1 page); a listing of structure factor amplitudes for compound 3 (21 pages). See any current masthead page for ordering information.

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[12] Dickson, R. S.; Nesbit, R. J.; Pateras, H.; Baimbridge, W. *Organometallics* **1985**, *4*, 2128.

[13] Chisholm, M. H.; Folting, K.; Heppert, J. A.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1755.