Registry No. 1, 110019-85-7; 2, 110019-86-8; 3, 119693-93-5; 4, 119679-93-5; 5, 119679-94-6; Ph_2CN_2, 883-40-9.

Supplementary Material Available: Table SI, important interplanar angles, Table SII, atomic coordinates for the hydrogen atoms, Table SIII, anisotropic thermal parameters for non-hydrogen atoms, and tables of crystal data, atomic coordinates, anisotropic thermal parameters, orthogonal coordinates, principal axes of the thermal ellipsoid, bond distances and angles, weighted least-squares planes, and interatomic contacts (37 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Crystal Structures of the Clusters $[Os_3H_2(\overline{XCH{=}CHC{=}C})(CO)_9]$ Where X = NMe or S Containing Triply Bridging Ligands Derived from *N*-Methylpyrrole and Thiophene

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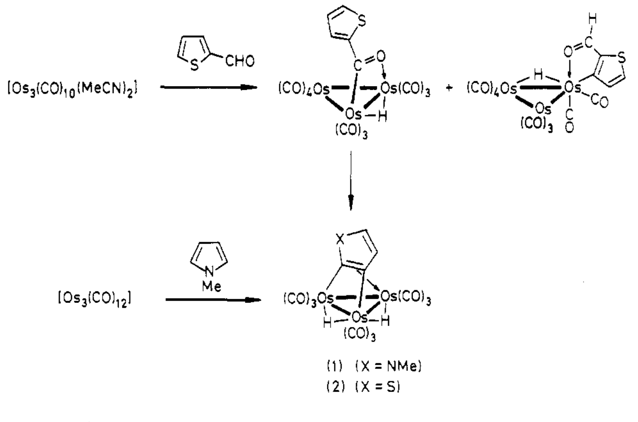
The single-crystal X-ray structures are reported of two complexes containing ligands derived from *N*-methylpyrrole and thiophene respectively: $[Os_3H_2(\overline{XCH{=}CHC{=}C})(CO)_9]$ (1, X = NMe; 2, X = S). Both complexes are structurally related with σ-Os–C bonds at the 2- and 3-positions of the rings and with an η^2-coordination to the third metal atom. Crystals of 1 are triclinic, $P\bar{1}$, with $a = 14.762$ (2) Å, $b = 15.765$ (4) Å, $c = 8.949$ (1) Å, $\alpha = 94.60$ (2)°, $\beta = 99.37$ (1)°, $\gamma = 70.74$ (2)°, $Z = 4$, and $R_w = 0.050$ for 3451 reflections, while those of 2 are monoclinic, $P2_1/c$, with $a = 16.315$ (2) Å, $b = 13.091$ (2) Å, $c = 17.347$ (2) Å, $\beta = 92.05$ (1)°, $Z = 8$, and $R_w = 0.050$ for 2256 reflections. Compound 2 contains two independent molecules in the unit cell, one of which is best modeled by the C_4H_2S ligand disordered in two possible orientations, each 50% populated. Compound 1, likewise, has two independent molecules in the unit cell but without disorder. These structures are compared with that of the benzyne complex $[Os_3H_2(\mu_3,\eta^2\text{-}C_6H_4)(CO)_9]$ (3) which adopts a parallel geometry and with the (diethylamino)ethyne analogue $[Os_3H_2(Et_2NC_2H)(CO)_9]$ (4) in which the ligand is perpendicular to an Os–Os edge. The geometry of 1, and to a lesser extent that in 2, is distorted from the parallel toward the perpendicular type, and the effect of the heteroatom in the organic ring on this distortion is discussed.

Introduction

Furan,[1] thiophene,[2] and pyrrole[2,3] ligands may be introduced into triosmium clusters in dehydrogenated forms as triply bridging ligands. The cluster $[Os_3(CO)_{12}]$ reacts directly with *N*-methylpyrrole (C_4H_4NMe) to give the cluster $[Os_3H_2(C_4H_2NMe)(CO)_9]$ (1) in which the dehydrogenated ligand (C_4H_2NMe) behaves as a four-electron donor[3] and which relates to known alkyne[4-6] or aryne[4,7,8] clusters. A more satisfactory route to such species is from the 2-formyl-substituted derivatives which add oxidatively to $[Os_3(CO)_{10}(MeCN)_2]$ to give acyl clusters.[2] For example,

Scheme I



2-formylthiophene reacts in this way at the formyl function to give $[Os_3H(\overline{SCH{=}CHCH{=}C}CO)(CO)_{10}]$ but also metalates at a ring site to give an isomer, $[Os_3H(\overline{SCH{=}CHC{=}C}CHO)(CO)_{10}]$ (Scheme I). The acyl isomer doubly decarbonylates in refluxing cyclohexane to give a compound that is a subject of this paper, the dihydride

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Table I. Summary of Crystal and Intensity Data

	1	2
formula	$C_{14}H_7NO_9Os_3$	$C_{13}H_4O_9Os_3S$
MW, amu	903.81	906.84
descriptn	yellow plate	yellow platelet
system	triclinic	monoclinic
a, Å	14.762 (2)	16.315 (2)
b, Å	15.765 (4)	13.091 (2)
c, Å	8.949 (1)	17.347 (2)
α, deg	94.60 (2)	
β, deg	99.37 (1)	92.05 (1)
γ, deg	70.74 (2)	
V, Å^3	1939.1	3702.6
space group	$P\bar{1}$	$P2_1/c$
Z	4	8
D_{calcd}, g cm^{-3}	3.10	3.25
cryst size, mm^3	0.55 × 0.45 × 0.25	0.25 × 0.25 × 0.08
μ, cm^{-1} (Mo Kα)	196.8	207.2
λ(Mo Kα), Å (graphite monochromator)	0.710 73	0.710 73
temp, °C	25 (1)	25 (1)
no. of unique data	6808	2802
no. of data with $I_o > 3\sigma(I_0)$	3451	2256
no. of parameters refined	248	231
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.039	0.046
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.050	0.050
largest shift/esd	0.01	0.01
weighting scheme	$1/\sigma(F_o)^2$	$1/\sigma(F_o)^2$
highest peak in final diff map, e Å^{-3}	1.93	1.16

Table II. Selected Bond Lengths (Å) and Angles (deg) for $[Os_3H_2(C_4H_2NMe)(CO)_9]$, Cluster 1

molecule A		molecule B	
Os(1A)–Os(2A)	3.072 (1)	Os(1B)–Os(2B)	3.043 (1)
Os(1A)–Os(3A)	2.779 (1)	Os(1B)–Os(3B)	2.776 (1)
Os(2A)–Os(3A)	2.835 (1)	Os(2B)–Os(3B)	2.828 (1)
Os(1A)–C(1A)	2.06 (2)	Os(1B)–C(1B)	2.07 (2)
Os(2A)–C(2A)	2.15 (2)	Os(2B)–C(2B)	2.15 (2)
Os(3A)–C(1A)	2.56 (2)	Os(3B)–C(1B)	2.50 (2)
Os(3A)–C(2A)	2.24 (2)	Os(3B)–C(2B)	2.24 (2)
N(A)–C(1A)	1.38 (3)	N(B)–C(1B)	1.36 (3)
N(A)–C(4A)	1.36 (3)	N(B)–C(4B)	1.39 (3)
N(A)–C(5A)	1.49 (4)	N(B)–C(5B)	1.45 (4)
C(1A)–C(2A)	1.41 (3)	C(1B)–C(2B)	1.42 (3)
C(2A)–C(3A)	1.42 (3)	C(2B)–C(3B)	1.44 (3)
C(3A)–C(4A)	1.39 (4)	C(3B)–C(4B)	1.36 (4)
Os(2A)–Os(1A)–Os(3A)	57.69 (3)	Os(2B)–Os(1B)–Os(3B)	57.94 (2)
Os(1A)–Os(2A)–Os(3A)	55.96 (3)	Os(1B)–Os(2B)–Os(3B)	56.30 (2)
Os(1A)–Os(3A)–Os(2A)	66.34 (3)	Os(1B)–Os(3B)–Os(2B)	65.76 (3)
Os(2A)–Os(1A)–C(1A)	66.2 (6)	Os(2B)–Os(1B)–C(1B)	67.1 (6)
Os(3A)–Os(1A)–C(1A)	61.7 (5)	Os(3B)–Os(1B)–C(1B)	60.0 (5)
Os(1A)–Os(2A)–C(2A)	65.5 (5)	Os(1B)–Os(2B)–C(2B)	66.4 (6)
Os(3A)–Os(2A)–C(2A)	51.2 (4)	Os(3B)–Os(2B)–C(2B)	51.2 (4)
Os(1A)–Os(3A)–C(1A)	45.1 (4)	Os(1B)–Os(3B)–C(1B)	45.7 (4)
Os(1A)–Os(3A)–C(2A)	70.4 (4)	Os(1B)–Os(3B)–C(2B)	70.9 (5)
Os(2A)–Os(3A)–C(1A)	65.6 (5)	Os(2B)–Os(3B)–C(1B)	66.6 (5)
Os(2A)–Os(3A)–C(2A)	48.5 (6)	Os(2B)–Os(3B)–C(2B)	48.6 (5)
C(1A)–Os(3A)–C(2A)	33.3 (7)	C(1B)–Os(3B)–C(2B)	34.3 (6)
Os(1A)–C(1A)–Os(3A)	73.2 (5)	Os(1B)–C(1B)–Os(3B)	74.3 (5)
Os(1A)–C(1A)–N(A)	141 (2)	Os(1B)–C(1B)–N(B)	139 (1)
Os(1A)–C(1A)–C(2A)	114 (1)	Os(1B)–C(1B)–C(2B)	114 (1)
Os(3A)–C(1A)–N(A)	124 (1)	Os(3B)–C(1B)–N(B)	126 (1)
Os(3A)–C(1A)–C(2A)	61.0 (9)	Os(3B)–C(1B)–C(2B)	62.7 (9)
Os(2A)–C(2A)–Os(3A)	80.3 (6)	Os(2B)–C(2B)–Os(3B)	80.2 (7)
Os(2A)–C(2A)–C(1A)	109 (1)	Os(2B)–C(2B)–C(1B)	109 (1)
Os(2A)–C(2A)–C(3A)	135 (2)	Os(2B)–C(2B)–C(3B)	139 (2)
Os(3A)–C(2A)–C(1A)	86 (1)	Os(3B)–C(2B)–C(1B)	83 (1)
Os(3A)–C(2A)–C(3A)	124 (1)	Os(3B)–C(2B)–C(3B)	124 (1)

$[Os_3H_2(C_4H_2S)(CO)_9]$ (**2**).[2] On the basis of IR and NMR spectroscopic data, we deduced that **1** and **2** have structures akin to that of the benzyne cluster $[Os_3H_2(C_6H_4)(CO)_9]$ (**3**) which contains the μ_3-benzyne ligand bonded through σ-Os–C bonds to two osmium atoms and an η^2-contact with the third.[7] The C–C bond between the two metal-bonded carbon atoms lies essentially parallel to one Os–Os bond. This paper describes the single-crystal X-ray structures of **1** and **2** and discusses factors that lead to such ligands moving out of this parallel geometry.

Experimental Section

The clusters **1** and **2** were prepared as described previously,[2,3] and crystals of each for crystal structure determination were grown by evaporation of hexane solutions.

Crystal Structure Determinations. Suitable crystals of each compound, **1** and **2**, were examined by using similar procedures. The crystal was attached to a glass fiber mounted in a brass pin in a goniometer head and optically centered on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of 22 reflections ($5 \leq \theta \leq 14°$) for **1** and 25 reflections ($3 \leq \theta \leq 9°$) for **2**. Details of the crystal data for both compounds are given in Table I. The lack of systematic absences for **1** and systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, for **2** and subsequent least-squares refinement confirmed the choice of their respective space groups. Data for each compound were collected by using the ω–2θ scan technique with variable scan rates of 1.3–8.3° min^{-1} in ω to a maximum 2θ angle of 50° for **1** and 40° for **2** and variable scan ranges calculated by the following: θ scan width = $0.8 + 0.350 \tan \theta°$. Background measurements using the moving crystal–moving counter technique were made at the beginning and end of each scan. Two standard reflections monitored every 120 min during data collection showed only a very small loss of intensity: however, a decay correction was applied as was an empirical absorption correction based on a series of ψ scans. Relative transmission coefficients ranged from 0.454 to 0.999 for **1** and 0.221 to 0.997 for **2**. Lorentz and polarization corrections were also applied to each data set.

The structures were solved by standard Patterson and difference Fourier techniques. Final refinement for each included anisotropic thermal parameters for osmium atoms and isotropic thermal parameter for all other atoms. Only those reflections with $I_o > 3\sigma(I_o)$ were used in the final full-matrix, least-squares refinements. Scattering factors were taken from Cromer and Waber,[9] and anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[10] The highest peaks in the difference Fouriers were positioned near to or within the osmium rings. No attempt was made to locate hydrogen atoms on the pyrrole or thiophene rings. The final refinement parameters are given in Table I and selected bond lengths and angles in Tables II and III.

All calculations were carried out on a DEC MicroVax computer using the SDP/VAX system of programs.[11] Atomic positional parameters for compounds **1** and **2** are listed in Tables IV and V, respectively. Anisotropic thermal parameters (Tables S1 and S2), structure factors (Tables S3 and S4), and least-squares planes (Tables S5 and S6) have been deposited as supplementary material.

Results and Discussion

X-ray Structure of $[Os_3H_2(C_4H_2NMe)(CO)_9]$ (1). We have synthesized the clusters $[Os_3H_2(C_4H_2NR)(CO)_9]$ where N = H or Me.[2,3] The compound with R = H readily isomerizes with hydrogen atom transfer (via the metal atoms) from N to C to give the N-coordinated form $[Os_3H_2(\overline{N{=}CHCH{=}CHC})(CO)_9]$ and was consequently difficult to isolate pure and crystallize satisfactorily. Hence we decided to determine the single-crystal X-ray structure of the N-methylated compound **1** which cannot isomerize in this way and is easier to get in good crystalline form.

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Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Os_3H_2(C_4H_2S)(CO)_9]$, Cluster 2

molecule A		molecule B	
Os(1A)–Os(2A)	2.898 (1)	Os(1B)–Os(2B)	2.899 (1)
Os(1A)–Os(3A)	2.882 (1)	Os(1B)–Os(3B)	2.860 (1)
Os(2A)–Os(3A)	2.858 (1)	Os(2B)–Os(3B)	2.836 (1)
Os(1A)–C(1A)	2.14 (2)	Os(1B)–C(1B)	2.16 (2)
Os(2A)–C(2A)	2.13 (2)	Os(2B)–C(2B)	2.17 (2)
Os(3A)–C(1A)	2.43 (2)	Os(3B)–C(1B)	2.46 (2)
Os(3A)–C(2A)	2.31 (2)	Os(3B)–C(2B)	2.23 (2)
S(1A)–C(1A)	1.65 (2)	S(1B)–C(1B)	1.72 (2)
S(1A)–C(4A)	1.49 (4)	S(1B)–C(4B)	1.73 (3)
C(1A)–C(2A)	1.38 (3)	C(1B)–C(2B)	1.38 (3)
C(2A)–S(2A)	1.69 (2)	C(2B)–C(3B)	1.56 (3)
S(2A)–C(4A)	1.44 (4)	C(3B)–C(4B)	1.30 (3)
Os(2A)–Os(1A)–Os(3A)	59.28 (3)	Os(2B)–Os(1B)–Os(3B)	59.01 (2)
Os(1A)–Os(2A)–Os(3A)	60.08 (3)	Os(1B)–Os(2B)–Os(3B)	59.80 (2)
Os(1A)–Os(3A)–Os(2A)	60.64 (3)	Os(1B)–Os(3B)–Os(2B)	61.18 (3)
Os(2A)–Os(1A)–C(1A)	68.5 (4)	Os(2B)–Os(1B)–C(1B)	68.4 (5)
Os(3A)–Os(1A)–C(1A)	55.5 (5)	Os(3B)–Os(1B)–C(1B)	56.6 (5)
Os(1A)–Os(2A)–C(2A)	69.5 (6)	Os(1B)–Os(2B)–C(2B)	69.8 (5)
Os(3A)–Os(2A)–C(2A)	52.8 (6)	Os(3B)–Os(2B)–C(2B)	50.7 (6)
Os(1A)–Os(3A)–C(1A)	46.5 (5)	Os(1B)–Os(3B)–C(1B)	47.1 (5)
Os(1A)–Os(3A)–C(2A)	67.7 (5)	Os(1B)–Os(3B)–C(2B)	69.9 (6)
Os(2A)–Os(3A)–C(1A)	66.0 (4)	Os(2B)–Os(3B)–C(1B)	66.2 (4)
Os(2A)–Os(3A)–C(2A)	47.2 (6)	Os(2B)–Os(3B)–C(2B)	48.8 (5)
C(1A)–Os(3A)–C(2A)	33.6 (7)	C(1B)–Os(3B)–C(2B)	33.9 (7)
Os(1A)–C(1A)–Os(3A)	78.0 (7)	Os(1B)–C(1B)–Os(3B)	76.3 (6)
Os(1A)–C(1A)–S(1A)	142 (1)	Os(1B)–C(1B)–S(1B)	140 (1)
Os(1A)–C(1A)–C(2A)	111 (1)	Os(1B)–C(1B)–C(2B)	112 (1)
Os(3A)–C(1A)–S(1A)	119.2 (9)	Os(3B)–C(1B)–S(1B)	120 (1)
Os(3A)–C(1A)–C(2A)	68 (1)	Os(3B)–C(1B)–C(2B)	64 (1)
Os(2A)–C(2A)–Os(3A)	80.0 (8)	Os(2B)–C(2B)–Os(3B)	80.4 (8)
Os(2A)–C(2A)–C(1A)	110 (1)	Os(2B)–C(2B)–C(1B)	108 (1)
Os(2A)–C(2A)–S(2A)	138 (1)	Os(2B)–C(2B)–C(3B)	139 (1)
Os(3A)–C(2A)–C(1A)	78 (1)	Os(3B)–C(2B)–C(1B)	82 (1)
Os(3A)–C(2A)–S(2A)	118 (1)	Os(3B)–C(2B)–C(3B)	120 (1)

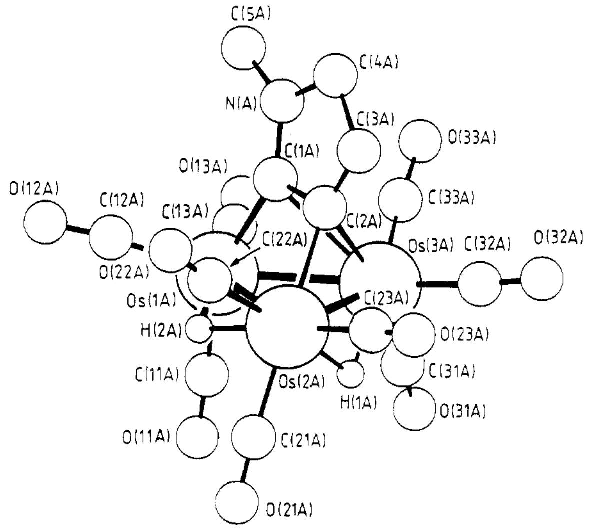

Figure 1. Molecular structure of molecule A of the cluster $[Os_3H_2(MeNCH{=}CHC{=}C)(CO)_9]$ (1). The independent molecule (B) is very similar. The atoms are represented as spheres with sizes proportional to their covalent radii (PLUTO program, SDP/VAX).

Table IV. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $[Os_3H_2(C_4H_2NMe)(CO)_9]$, Cluster 1[a]

atom	x	y	z	B, Å^2
Os(1A)	0.16274 (6)	0.29800 (6)	0.09290 (9)	3.31 (2)
Os(2A)	0.27661 (5)	0.34257 (5)	–0.13102 (9)	2.76 (2)
Os(3A)	0.33464 (5)	0.17654 (5)	0.01651 (9)	2.69 (2)
O(11A)	0.257 (2)	0.377 (2)	0.372 (3)	10.0 (7)*
O(12A)	–0.044 (1)	0.424 (1)	0.072 (2)	6.6 (4)*
O(13A)	0.130 (1)	0.158 (1)	0.270 (3)	7.7 (5)*
O(21A)	0.346 (1)	0.499 (1)	0.009 (2)	7.6 (5)*
O(22A)	0.112 (1)	0.453 (1)	–0.361 (2)	5.1 (4)*
O(23A)	0.421 (1)	0.288 (1)	–0.352 (2)	6.4 (4)*
O(31A)	0.447 (1)	0.165 (1)	0.335 (2)	6.6 (4)*
O(32A)	0.274 (1)	0.016 (1)	0.059 (2)	5.3 (4)*
O(33A)	0.499 (1)	0.072 (1)	–0.155 (2)	6.6 (5)*
N(A)	0.113 (1)	0.172 (1)	–0.192 (2)	3.6 (3)*
C(1A)	0.158 (1)	0.228 (1)	–0.111 (2)	3.0 (3)*
C(2A)	0.232 (1)	0.226 (1)	–0.195 (2)	2.6 (3)*
C(3A)	0.225 (1)	0.174 (1)	–0.330 (2)	3.9 (4)*
C(4A)	0.148 (2)	0.142 (1)	–0.324 (3)	4.3 (5)*
C(5A)	0.035 (2)	0.147 (2)	–0.138 (3)	5.4 (6)*
C(11A)	0.214 (2)	0.346 (2)	0.274 (3)	5.9 (6)*
C(12A)	0.035 (2)	0.379 (2)	0.079 (3)	4.5 (5)*
C(13A)	0.140 (2)	0.214 (2)	0.205 (3)	5.6 (6)*
C(21A)	0.320 (2)	0.441 (2)	–0.043 (3)	4.9 (5)*
C(22A)	0.176 (1)	0.411 (1)	–0.275 (2)	3.8 (4)*
C(23A)	0.369 (1)	0.308 (1)	–0.269 (2)	3.9 (4)*
C(31A)	0.407 (1)	0.169 (1)	0.211 (2)	3.8 (4)*
C(32A)	0.298 (1)	0.078 (1)	0.045 (2)	3.6 (4)*
C(33A)	0.437 (1)	0.114 (1)	–0.089 (2)	3.3 (4)*
Os(1B)	0.20520 (6)	–0.17806 (6)	0.62166 (9)	3.43 (2)
Os(2B)	0.28159 (5)	–0.16948 (5)	0.32922 (9)	3.01 (2)
Os(3B)	0.34673 (5)	–0.32266 (5)	0.51125 (9)	2.87 (2)
O(11B)	0.349 (1)	–0.093 (1)	0.804 (3)	7.9 (5)*
O(12B)	0.006 (2)	–0.043 (1)	0.646 (3)	7.8 (5)*
O(13B)	0.195 (2)	–0.288 (2)	0.877 (3)	8.7 (6)*
O(21B)	0.372 (1)	–0.020 (1)	0.412 (2)	7.0 (5)*
O(22B)	0.118 (1)	–0.061 (1)	0.100 (2)	5.8 (4)*
O(23B)	0.395 (1)	–0.252 (1)	0.071 (2)	6.1 (4)*
O(31B)	0.503 (1)	–0.333 (1)	0.777 (2)	6.5 (4)*
O(32B)	0.288 (1)	–0.467 (1)	0.637 (2)	6.1 (4)*
O(33B)	0.475 (1)	–0.451 (1)	0.304 (2)	7.6 (5)*
N(B)	0.105 (1)	–0.311 (1)	0.420 (2)	3.9 (4)*
C(1B)	0.166 (1)	–0.261 (1)	0.451 (2)	2.6 (3)*
C(2B)	0.220 (1)	–0.276 (1)	0.328 (2)	3.3 (4)*
C(3B)	0.186 (2)	–0.335 (1)	0.220 (3)	4.1 (4)*
C(4B)	0.118 (2)	–0.357 (2)	0.283 (3)	4.4 (5)*
C(5B)	0.041 (2)	–0.321 (2)	0.520 (3)	5.5 (6)*
C(11B)	0.294 (2)	–0.129 (2)	0.746 (3)	5.8 (6)*
C(12B)	0.087 (2)	–0.094 (2)	0.640 (3)	5.0 (5)*
C(13B)	0.201 (2)	–0.244 (2)	0.783 (4)	6.9 (7)*
C(21B)	0.340 (2)	–0.075 (2)	0.382 (3)	4.9 (5)*
C(22B)	0.180 (2)	–0.103 (2)	0.187 (3)	4.5 (5)*
C(23B)	0.351 (2)	–0.220 (2)	0.169 (3)	4.4 (5)*
C(31B)	0.443 (2)	–0.328 (2)	0.675 (3)	4.5 (5)*
C(32B)	0.312 (1)	–0.414 (1)	0.583 (2)	3.8 (4)*
C(33B)	0.424 (2)	–0.402 (2)	0.384 (3)	4.8 (5)*

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

The molecular structure of 1 is shown in Figure 1, and selected bond lengths and angles are in Table II. The structure is essentially as depicted in Scheme I. There are two independent molecules in the asymmetric unit, and, since there is very little difference between them, only one of these, A, is illustrated. Only non-hydrogen atoms were located and the two bridging hydride ligands are placed in positions given by energy-minima calculations (using the program HYDEX[12]) which effectively place the atoms in the least crowded sites consistent with normal Os–H bond lengths. More qualitative considerations, such as Os–Os distances (which are longest for the bridged edges) and Os–Os–CO angles, also place the hydrides along the Os(1)–Os(2) and Os(2)–Os(3) edges. Note that the HYDEX program positions the hydride H(1) in the metal plane along the Os(1)–Os(2) edge while H(2) bridges Os(2) and Os(3) well below the metal plane. We would expect therefore that H(1) would have the most effect on opening the Os–Os–C angles of the equatorial CO ligands and H(2) likewise on the axial CO ligands. Consistent with this, the axial CO ligands on the Os(2)–Os(3) edge give Os–Os–C angles in the range 117.5–121.2° (average 118.7°) compared

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[12] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

Table V. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $[Os_3H_2(C_4H_2S)(CO)_9]$, Cluster 2[a]

atom	x	y	z	B, Å^2
Os(1A)	0.33014 (5)	0.27397 (7)	−0.04471 (5)	2.59 (2)
Os(2A)	0.50283 (5)	0.26264 (7)	−0.07751 (5)	2.42 (2)
Os(3A)	0.38216 (5)	0.20644 (7)	−0.19333 (4)	2.41 (2)
S(1A)	0.321	0.466	−0.192	8.0*
S(2A)	0.464	0.445	−0.228	8.0*
O(11A)	0.316 (1)	0.072 (2)	0.048 (1)	5.9 (4)*
O(12A)	0.164 (1)	0.286 (2)	−0.099 (1)	5.7 (4)*
O(13A)	0.312 (1)	0.425 (2)	0.094 (1)	6.5 (4)*
O(21A)	0.560 (1)	0.090 (2)	0.037 (1)	6.9 (5)*
O(22A)	0.574 (1)	0.435 (2)	0.021 (1)	5.3 (4)*
O(23A)	0.640 (1)	0.264 (2)	−0.190 (1)	6.4 (4)*
O(31A)	0.342 (1)	−0.018 (2)	−0.180 (1)	6.1 (4)*
O(32A)	0.231 (1)	0.251 (2)	−0.286 (1)	6.4 (4)*
O(33A)	0.478 (1)	0.199 (2)	−0.343 (1)	5.6 (4)*
C(1A)	0.360 (1)	0.374 (2)	−0.137 (1)	2.1 (4)*
C(2A)	0.440 (1)	0.361 (2)	−0.157 (1)	2.9 (4)*
C(3A)	0.463	0.445	−0.228	3.5*
C(4A)	0.387 (2)	0.497 (3)	−0.245 (2)	7.7 (8)*
C(5A)	0.321	0.466	−0.192	3.5*
C(11A)	0.319 (1)	0.153 (2)	0.017 (1)	2.9 (4)*
C(12A)	0.227 (2)	0.281 (2)	−0.078 (2)	4.7 (6)*
C(13A)	0.318 (1)	0.368 (2)	0.040 (1)	2.2 (4)*
C(21A)	0.540 (1)	0.157 (2)	−0.005 (1)	3.3 (4)*
C(22A)	0.545 (1)	0.365 (2)	−0.015 (1)	3.8 (5)*
C(23A)	0.587 (1)	0.261 (2)	−0.143 (1)	3.9 (5)*
C(31A)	0.353 (1)	0.073 (2)	−0.186 (1)	4.3 (5)*
C(32A)	0.291 (1)	0.234 (2)	−0.251 (1)	2.8 (4)*
C(33A)	0.438 (1)	0.201 (2)	−0.288 (1)	2.3 (4)*
Os(1B)	0.83083 (5)	0.24665 (7)	−0.30419 (4)	2.53 (2)
Os(2B)	1.00217 (5)	0.28723 (7)	−0.33092 (5)	2.63 (2)
Os(3B)	0.87916 (5)	0.34990 (7)	−0.44056 (5)	2.52 (2)
S(1B)	0.8353 (4)	0.0810 (6)	−0.4726 (4)	4.7 (1)*
O(11B)	0.798 (1)	0.428 (2)	−0.192 (1)	5.7 (4)*
O(12B)	0.666 (1)	0.237 (2)	−0.370 (1)	5.2 (4)*
O(13B)	0.820 (1)	0.067 (2)	−0.187 (1)	5.9 (4)*
O(21B)	1.054 (1)	0.436 (2)	−0.194 (1)	7.1 (5)*
O(22B)	1.079 (1)	0.096 (2)	−0.263 (1)	7.2 (5)*
O(23B)	1.136 (1)	0.345 (2)	−0.436 (1)	5.8 (4)*
O(31B)	0.816 (1)	0.554 (2)	−0.389 (1)	5.1 (4)*
O(32B)	0.735 (1)	0.309 (2)	−0.544 (1)	6.3 (4)*
O(33B)	0.976 (1)	0.414 (2)	−0.584 (1)	5.8 (4)*
C(1B)	0.871 (1)	0.168 (2)	−0.405 (1)	2.3 (4)*
C(2B)	0.947 (1)	0.203 (2)	−0.427 (1)	3.0 (4)*
C(3B)	0.975 (1)	0.144 (2)	−0.500 (1)	3.4 (4)*
C(4B)	0.921 (1)	0.079 (2)	−0.528 (1)	4.4 (5)*
C(11B)	0.809 (1)	0.357 (2)	−0.230 (1)	3.0 (4)*
C(12B)	0.729 (1)	0.238 (2)	−0.345 (1)	3.6 (5)*
C(13B)	0.823 (1)	0.138 (2)	−0.231 (1)	2.9 (4)*
C(21B)	1.035 (1)	0.374 (2)	−0.243 (1)	3.8 (5)*
C(22B)	1.052 (1)	0.174 (2)	−0.287 (1)	3.6 (5)*
C(23B)	1.086 (1)	0.322 (2)	−0.392 (1)	3.9 (5)*
C(31B)	0.839 (1)	0.472 (2)	−0.408 (1)	3.4 (4)*
C(32B)	0.792 (1)	0.324 (2)	−0.504 (1)	3.1 (4)*
C(33B)	0.939 (1)	0.389 (2)	−0.529 (1)	4.0 (5)*

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

Table VI. IR Data for Clusters of the Type $[Os_3H_2(\mu_3,\eta^2\text{-ligand})(CO)_9]$

μ_3, η^2-ligand	ν(CO),[a] cm^{-1}	ref
$\overline{\text{MeNCH=CHC=C}}$	2104 m, 2074 vs, 2048 vs, 2025 vs, 2022 sh, 1998 vs, 1989 m, 1976 m, 1945 w	2, 3
$\overline{\text{SCH=CHC=C}}$	2108 m, 2081 vs, 2054 vs, 2033 vs, 2024 s, 2008 vs, 1999 s, 1985 m, 1973 mw, 1958 w	2
$\overline{\text{OCH=CHC=C}}$	2108 m, 2084 vs, 2058 vs, 2036 vs, 2028 s, 2010 s, 2000 m, 1992 m, 1977 w	2
Et_2NC_2H	2098 m, 2068 vs, 2041 vs, 2015 s, 2012 s, 1996 ms, 1979 m, 1975 m, 1965 m	14
$EtOC_2H$	2106 m, 2078 vs, 2052 vs, 2025 vs, 2007 s, 2002 s, 1995 s, 1982 m	13
C_6H_4	2109 m, 2082 s, 2056 vs, 2035 s, 2025 m, 2010 s, 2000 m, 1987 sh, 1984 m	4

[a] All data for cyclohexane solutions.

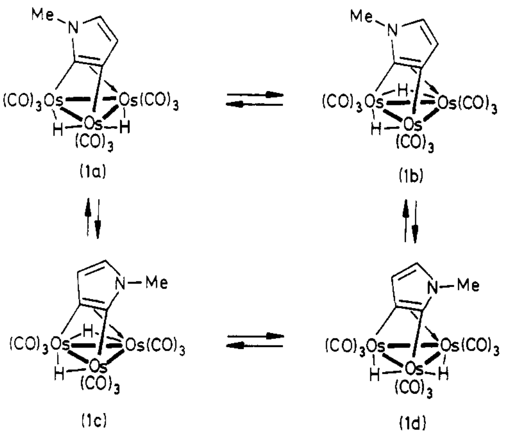

Figure 2. Possible isomers of 1: **1a** and **1c** are enantiomers and are diastereomerically related to the other enantiomeric pair **1b** and **1d**.

with related angles on the other edges of 95.4–109.9° (average 100.0°). Likewise Os–Os–C angles for the equatorial CO ligands at the Os(1)–Os(2) edge are 102.1–114.2° (average 109.4°) with related angles at the other edges 91.8 to 98.7° (average 95.9°). Clearly it is these specific increases in Os–Os–C angles that result in the HYDEX program selecting the hydride positions shown. The calculated positions are convincing because these are directly trans to CO ligands with each metal atom adopting a closely octahedral arrangement. The related benzyne cluster $[Os_3H_2(C_6H_4)(CO)_9]$ has a similar structure, but in solution one hydride ligand rapidly migrates between two Os–Os edges to give a time-averaged symmetry plane bisecting the C_6H_4 ligand. Motions of this kind (Figure 2) would interconvert two diastereoisomers, **1a** and **1b**, and their corresponding enantiomers, **1c** and **1d**. Rotation of the μ_3-ligand would be necessary to interconvert enantiomers. Only one diastereoisomer, **1a**, is in the crystal, and only one set of ^1H NMR resonances is observed in solution even at low temperatures. Either only one enantiomeric pair, **1a** and **1c**, is present in solution or the diastereomers are in rapid equilibrium giving a coalesced NMR spectrum. We believe that the former is the case.

The *N*-methylpyrrolic ligand has the C(1)–C(2) edge approximately parallel to the Os(1)–Os(2) edge but distortions from this arrangement will be discussed later.

X-ray Structure of $[Os_3H_2(C_4H_2S)(CO)_9]$ (2). This crystal also contains two independent molecules, A and B, in the unit cell, the structures of which are shown in Figure 3 and selected bond lengths and angles are in Table III. However, molecule A is disordered. Refinement of the structure proceeded normally except for the temperature factors associated with S(1A) and carbon atoms C(3A) and C(4A). Satisfactory refinement was achieved with the atoms labeled S(1A) and S(2A) each given a 50% population of S and C atoms, that is with the thiophenic ligands orientated in the two possible directions with equal probability. Molecule B refined quite satisfactorily and all atom temperature factors were normal: our discussion of the structure is based on this molecule. As with cluster 1 the hydride ligands are shown in calculated positions, and as for 1 these positions are consistent with which one would expect from qualitative considerations. The

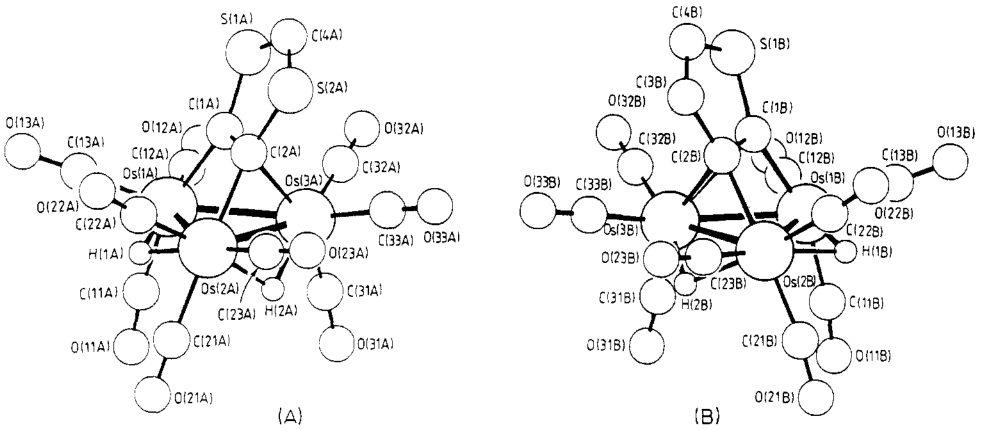

Figure 3. Molecular structures of molecules A and B of the cluster $[Os_3H_2(\overline{SCH{=}CHC{=}C})(CO)_9]$. Molecule A is disordered with S(1A) and S(2A) representing 50% populations of S and C atoms. The atoms are represented as spheres with sizes proportional to their covalent radii (PLUTO program, SDP/VAX).

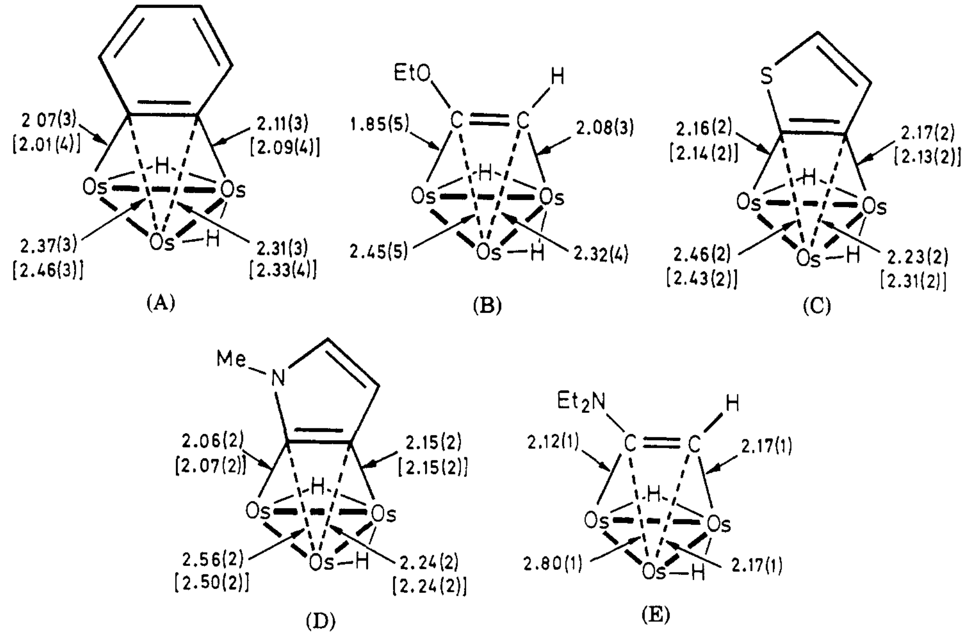

Figure 4. Various clusters of the general type $[Os_3H_2(\mu_3,\eta^2\text{-ligand})(CO)_9]$ where L = C_6H_4 (A), $EtOC_2H$ (B), C_4H_2S (C), C_4H_2NMe (D), and Et_2NC_2H (E) showing the variations in Os–C bond lengths. Where there are two independent molecules in the unit cell, two sets of data are given.

structures of 1 and 2 are very similar.

Comparison of Structures 1 and 2 and Related Published Structures. In Figure 4 we have summarized structural features of the Os_3–ligand systems for a series of clusters of the type $[Os_3H_2(\mu_3,\eta^2\text{-ligand})(CO)_9]$ where the ligand is a four-electron donor bonded through two carbon atoms. The structure of the C_6H_4 compound seems to be the only one of this type determined for a symmetrical ligand but even then the symmetry of the ligand is lost in the cluster because of the hydride positions which give the molecule C_1 symmetry. One of the two independent molecules of the C_6H_4 cluster in the unit cell seems to be refined more satisfactorily than the other so the data for this one are used here. On passing through the series in the order C_6H_4,[7] $EtOC_2H$,[13] $\overline{SCH{=}CHC{=}C}$, $Me\overline{NCH{=}CHC{=}C}$, and Et_2NC_2H,[14] the μ_3-ligands become increasingly more distorted out of the idealized parallel geometry. Noting particularly the Os–C bond lengths in the η^2 interaction with the front osmium atom, these are quite close for the C_6H_4 complex [2.37 (3) and 2.31 (3) Å] but very different for the (diethylamino)ethyne cluster [2.80 (1) and 2.17 (1) Å]. The distance 2.80 (1) Å is too long to be considered a bonding distance, and the ligand is in the perpendicular mode. Figure 5 shows two extreme descriptions, A and B, for the bonding of alkynes. The perpendicular form B is normally higher in energy than the parallel form A, but a π-donor substituent X might reverse this by stabilizing the carbene bond by introducing contributions from form C. All the examples in Figure 4, except the C_6H_4 case, have heteroatoms X that could operate in this way. A contribution from C would build up

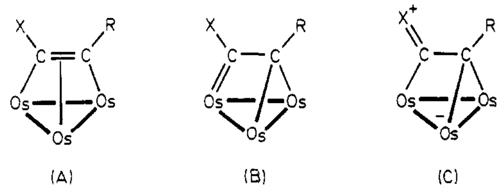

Figure 5. Possible forms of $M_3(XC_2R)$: (A), parallel, (B) and (C), perpendicular.

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(13) Boyar, E.; Deeming, A. J.; Felix, M. B. S.; Kabir, S. E.; Adiata, T.; Bhusate, R.; Powell, H. R.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1989**, 5.

(14) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717.

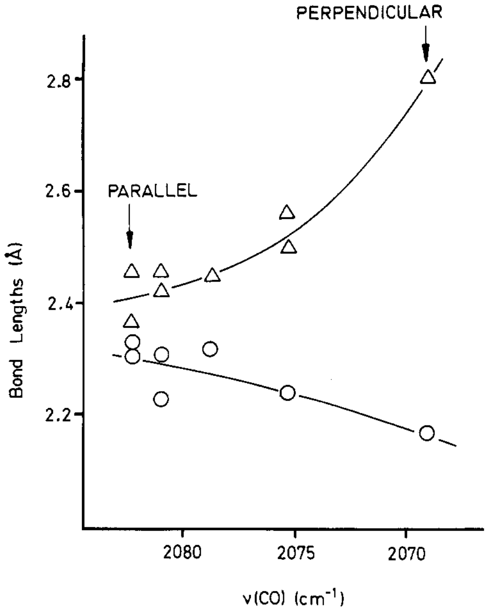

Figure 6. Plot of the bond lengths (Å) in the η^2-interactions in the clusters in Figure 4 against ν(CO) (cm^{-1}), the average of the three ν(CO) absorptions of highest wavenumber for each compound. These three absorptions are easy to identify and to relate to each other.

negative charge at the metal atoms and give lower ν(CO) wavenumbers. The Et_2NC_2H compound has ν(CO) values about 10 cm^{-1} lower than those for the benzyne cluster (Table IV). This is consistent with about 0.2 of a negative charge at the metal atoms based on a shift of about 50 cm^{-1} on introducing a full negative charge, which might be achieved, for example, by deprotonation.

If the π-donor effect of X leads to the distortion from the parallel geometry, there ought to be a relation between ν(CO) and these bond distances. Figure 6 shows the relation between the distances in the η^2-contact and ν(CO) (using an average of the three highest wavenumber ν(CO) absorptions). There are quite small differences in these values leading to considerable scatter, but it seems that the lower the wavenumber the greater is the difference in bond lengths. Figure 6 shows that the geometry of cluster 1 is closer to that of the Et_2NC_2H cluster while the Os–C distances in cluster 2 are much closer to those of the C_6H_4 compound. Pyrrole is only weakly basic and π-donation from the N atom in 1 should be much less than in the (diethylamino)ethyne cluster. An extreme form of cluster 1 related to C in Figure 5 would contain a tetrahedral carbon atom and aromaticity would be grossly diminished or lost altogether. This would not be too disturbing because we have shown that the unsubstituted analogue $[Os_3H_2(NHCH{=}CHC{=}C)(CO)_9]$ readily converts to a more stable isomer with a tetrahedral ring atom (Figure 7). Nonetheless it does seem that the aromaticity of the pyrrole ring operates against the adoption of the perpendicular geometry. The limited extent of π-donation from the N atom in 1 is even greater than that from the S atom in 2, which is not significantly different structurally from the C_6H_4 cluster.

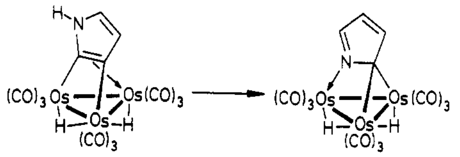

Figure 7. Thermal isomerization of the unsubstituted form of cluster 1 into its nonaromatic N-bonded isomer.[2]

The plane of the μ_3-ligand is expected to change from tilted to vertical as the ligand rotates from parallel to perpendicular. The C_6H_4 ligand makes an angle of 63.9° to the Os_3 plane,[7] whereas in the Et_2NC_2H cluster the C_2NCC set of atoms is planar with the plane of these atoms at 89.9° to the metal plane. The *N*-methylpyrrole ring in 1 is tilted to the metal plane by 74.0 (5) and 71.9 (5)° for molecules A and B and the thiophene ring in 2 by 64.3 (8) and 65.8 (8)° for the two molecules. As expected compound 1 is closer to the Et_2NC_2H cluster and compound 2 closer to the C_6H_4 cluster in this respect. We predict that any increase in π-donation from the heteroatom should twist the ligand and make it more closely vertical and one way to do this would be to protonate at the metal atoms. We are currently trying to grow crystals of the species $[Os_3H_3(MeNCH{=}CHC{=}C)(CO)_9][BF_4]$ to establish its crystal structure to test this prediction.

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Registry No. 1, 119946-96-2; 2, 109464-88-2.

Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares planes (6 pages); listings of structure factor amplitudes (78 pages). Ordering information is given on any current masthead page.