urated ligands.[12] Although the $\sigma + \pi$ unit is nearly linear, Mo(2)–C(5)–N = 167.7 (2)°, the C(5)–N–C(31) angle of 135.2 (2)° indicates a change in hybridization at the nitrogen atom away from the linear sp-type normally found for terminally coordinated isocyanide ligands.

Two other compounds in this series which have the $\sigma + \pi$ coordination are $Cp_2Mo_2(CO)_4(NCNMe_2)$[5] and $Et_4N[Cp_2Mo_2(CO)_4CN]$ (V).[7] The former has the nitrile function of the cyanimide ligand σ bonded via the nitrogen atom. In the latter the cyanide ligand is σ bonded via the carbon to one metal atom and π bonded to the other. This molecule was disordered in the crystal, and only crude structural parameters were obtained, but we feel a few useful comparisons can still be made. The π-bonding Mo–C and Mo–N distances in V lie in the range 2.3–2.6 Å and are significantly longer than the corresponding distances in III. One could reasonably infer that the cyanide ligand in V is not as strongly π bonded as the isocyanide in III. This notion is supported by the observation that V is a fluxional molecule which apparently rearranges to an equivalent form in which the σ- and π-bonding modes of the cyanide ligand have been interchanged between the two metal atoms. Intuitively, such a rearrangement would require some degree of metal-ligand bond breaking. Accordingly, we find that the molecules II–IV are not fluxional.

III also contains four terminal carbonyl ligands which could be grouped into pairs. C(1)–O(1) and C(3)–O(3) project toward the adjacent metal atom, Mo(2)–Mo(1)–C(1) = 71.81 (8)° and Mo(2)–Mo(1)–C(2) = 77.50 (8)°, while the other two, C(2)–O(2) and C(4)–O(4), point away from the second metal atom, Mo(2)–Mo(1)–C(2) = 115.15 (8)° and Mo(1)–Mo(2)–C(4) = 109.76 (10)°. We would hesitate to call the former semibridging CO's because the Mo···C distances at approximately 3.2 Å are clearly nonbonding, but the pairing of the environments of the CO ligands might explain the pairing of the resonance shifts of these ligands in the ^{13}C NMR spectra (see above).

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Registry No. I, 56200-27-2; II, 79703-92-7; III, 79703-93-8; IV, 79703-94-9.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

Cleavage of Aryl Carbon–Sulfur Bonds by a Trinuclear Cluster. The Reaction of Alkyl Phenyl Sulfides with $Os_3(CO)_{12}$

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The reactions of the alkyl phenyl sulfides, RSPh (R = Me, *i*-Pr), with $Os_3(CO)_{12}$ have been shown to produce cleavage of the phenyl group from the sulfur atom and yield the molecules $HOs_3(\mu\text{-SR})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ (I, R = Me; II, R = *i*-Pr). I has been analyzed by an X-ray crystallographic analysis: space group $P2_1/n$, at 23 °C, a = 8.697 (2) A, b = 13.442 (5) Å, c = 17.779 (7) Å, β = 99.29 (3)°, V = 2551 (2) Å^3, Z = 4, ρ_{calcd} = 3.07 g/cm^3. For 1999 reflections ($F_o \geq 3.0\sigma(F_o^2)$ R_1 = 0.052 and R_2 = 0.051. I contains an "open" cluster of three osmium atoms with a methanethiolato group bridging the open edge and a triply bridging benzyne, C_6H_4, ligand. In solution I exists as two rapidly equilibrating isomers at room temperature. ^1H DNMR studies have revealed two dynamical processes. A low-energy degenerate process (ΔG^* = 12.7 kcal/mol) which involves a migration of the hydride ligand between the two metal–metal bonds was established through a DNMR study of II. The higher energy isomerization process ($\Delta G^* \cong$ 14.7 kcal/mol) is believed to involve inversions of configuration of the trivalent sulfur atom of the bridging methanethiolato group.

Introduction

A number of workers have shown that triosmium cluster compounds can readily cleave aryl groups from phosphines and other ligands. Frequently, cluster compounds containing benzyne, C_6H_4, ligands are obtained.[1-6] Recently, the cleavage of carbon–sulfur bonds in CS_2 and related ligands by triosmium clusters has been demonstrated,[7] and it occurred to us that such cleavages in alkyl or aryl sulfide molecules might also be possible. Such processes are of fundamental importance to the desulfurization and purification of fossil fuels.[8] Herein we report results of our investigation of the cleavage of carbon–sulfur bonds of alkyl phenyl sulfide molecules by $Os_3(CO)_{12}$. Similar to the reactions with arylphosphines, these reactions also give a number of products. Not all of these have been characterized yet. In this report we will describe the structure and fluxional properties of the family of molecules which

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have the formula $HOs_3(\mu\text{-SR})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$.

Experimental Section

General Comments. Although these compounds were air stable, the reactions were routinely performed under a prepurified nitrogen atomosphere. Nonane solvent was purified by stirring for 2 days over concentrated sulfuric acid and then allowing to stand overnight over anhydrous sodium carbonate. Hexane solvent was purified by distillation from sodium–benzophenone. Other solvents were stored over 4-Å molecular sieves and degassed with a dispersed stream of nitrogen gas. Osmium carbonyl was prepared from OsO_4.[9] Both phenyl methyl and phenyl isopropyl sulfides were obtained from commercial sources and were used without further purification.

Melting points were determined in evacuated capillary tubes using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX 270.

Preparation of $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ (I). Phenyl methyl sulfide (0.15 mL, 1.28 mmol) was added to $Os_3(CO)_{12}$ (200 mg, 0.221 mmol) in nonane (70 mL). The reaction was maintained at reflux for 20 h. The solvent was removed in vacuo, and the remaining red-brown residue was taken up in a minimal amount of methylene chloride and applied to thin-layer silica plates. Elution with methylene chloride/hexane (10%/90%, v/v) yielded several bands. The product was the third of these. It is yellow in color and follows a red band. It crystallizes from hexane at −20 °C to yield 5.0 mg (2.4%) of yellow crystals, mp 172–174 °C; ^1H NMR (in $CDCl_3$): at 298 K, δ 8.70 (br, C_6H_4), 7.37 (br, C_6H_4), 2.88 (br, Me), −15.95 (OsH); at 213 K, major isomer, δ 8.93 (d, ^3J = 8.5 Hz C_6H_4), 8.48 (d, ^3J = 8.5 Hz C_6H_4), 7.11 (dd, ^3J = 8.5 Hz $^3J'$ = 6.1 Hz, C_6H_4), 6.86 (dd, ^3J = 8.5 Hz, $^3J'$ = 6.1 Hz, C_6H_4), 2.22 (CH_3), −15.97 (OsH); minor isomer, δ 8.89 (d, ^3J = 8.3 Hz, C_6H_4), 8.42 (d, ^3J = 8.3 Hz, C_6H_4), 7.34 (m, C_6H_4), 7.21 (m, C_6H_4), 2.90 (CH_3), −15.67 (OsH). IR (in hexane, $\nu_{CO} \pm 5$ cm^{-1}): 2100 (m), 2076 (vs), 2048 (vs), 2024 (s), 2008 (s), 2001 (s), 1982 (m), 1964 (m) cm^{-1}.

$HOs_3(\mu\text{-S-}i\text{-Pr})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ (II) was prepared and isolated similarly: yield, 5%; mp 142–143 °C. ^1H NMR (in $CDCl)_3$: at 298 K, δ 8.69 (m, C_6H_4), 6.96 (m, C_6H_4), 2.43 (sept, ^3J = 6.7 Hz, C_3H_7), 0.90 (d, ^3J = 6.7 Hz, C_3H_7), −16.05 (OsH). At 213 K, δ 8.90 (d, ^3J = 7.9 Hz, C_6H_4), 8.47 (d, ^3J = 7.9 Hz, C_6H_4), 7.08 (dd, ^3J = 7.9 Hz, ^3J = 5.9 Hz, C_6H_4), 6.83 (dd, ^3J = 7.9 Hz, J' = 5.9 Hz, C_6H_4), 2.33 (m, C_3H_7), 0.90 (d, ^3J = 6.3 Hz, C_3H_7), 0.70 (d, ^3J = 6.2 Hz, C_3H_7), −16.22 (OsH). IR (in hexane, ν_{CO}: 2105 (s), 2080 (vs), 2055 (vs), 2030 (vs), 2017 (vs), 2010 (vs), 1990 (s), 1985 (m), 1970 (s) cm^{-1}.

Crystallographic Analysis. Crystals of $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ suitable for diffraction measurements were obtained as described above and were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. The unit cell was refined from 25 selected reflections ($2\theta > 31°$) by using the CAD-4 automatic center and least-squares routines. The space group $P2_1/n$ was determined from the systematic absences observed during data collection. Crystal data and data collection parameters are listed in Table I. All data processing was performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. An absorption correction of a Gaussian integration type was applied to all the data. Neutral atom scattering factors were calculated by the standard procedures.[10a] Anomalous dispersion corrections were applied for all nonhydrogen atoms.[10b] The structure was solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions for the benzyne ligand were calculated by assuming idealized sixfold symmetry and C–H distances of 0.95 Å. These hydrogen atom contributions were included in structure factor calculations, but their positions were not refined. Hydrogen atom positions for the methyl group were not observed and were ignored. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$. All atoms heavier than oxygen were refined with anisotropic temperature factors. All other atoms were refined with isotropic temperature factors only. Final fractional atomic coordinates, thermal parameters, and interatomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables II–IV. Structure factor amplitudes are available (see supplementary material).

Table I. Crystallographic Data for X-ray Diffraction Study of $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$

(A) Crystal Data	
formula	$Os_3SO_9C_{16}H_8$
temp, ±5 °C	23
space group	$P2_1/n$
a, Å	8.697 (2)
b, Å	13.442 (5)
c, Å	17.779 (7)
β, deg	99.29 (3)
V, Å^3	2551 (2)
mol wt	946.9
ρ_{calcd}, g/cm^3	3.07
(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite
detector aperture, mm	
horizontal ($A + B \tan \theta$)	
A	3.0
B	1.0
vertical	4.0
cryst faces	$02\bar{1}$, $02\bar{1}$, 001; $00\bar{1}$, $11\bar{1}$, $\bar{1}11$
cryst size, nm	0.16 × 0.15 × 0.09
cryst orientation:	
direction; deg from ϕ axis	normal to 120; 10.8
reflctns measd	$h,k,\pm l$
max 2θ	50°
scan type	moving crystal–stationary counter
ω-scan width, deg	
$A + 0.347 \tan \theta$	$A = 0.85°$
bakgd	one-fourth additional scan at each end of scan
ω-scan rate (variable)	
max, deg/min	6.7°
min, deg/min	1.2°
no of reflctns measd	3934
data used ($F^2 \geq 3.0\sigma(F)^2$)	1999
(C) Treatment of Data	
abs correctn	
coeff, cm^{-1}	198.6
grid	12 × 10 × 8
transmissn coeff	
max	0.26
min	0.07
P factor	0.01
final residuals R	0.052
R_w	0.051
esd of unit wt	2.57
largest shift/error value on final cycle	0.02

Results

The reactions of alkyl phenyl sulfides, RSPh (R = Me, i-Pr) with $Os_3(CO)_{12}$ in refluxing nonane solvent give low yields (<5%) of the molecules $HOs_3(\mu\text{-SR})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ (I, R = Me; II, R = i-Pr) which have been characterized by IR and ^1H DNMR spectroscopies and an X-ray crystallographic analysis of I.

Description of the Structure. The molecular structure of I is shown in Figure 1. The molecule contains an "open" cluster of three osmium atoms with a bridging

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Table II. Final Fractional Atomic Coordinates, Thermal Parameters, and Their Estimated Standard Deviations for $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$

atom	x	y	z	B_{11} [b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	0.3215 (1)	0.19720 (8)	0.05626 (5)	2.80 (4)	2.72 (5)	2.13 (3)	0.00 (5)	0.32 (3)	−0.17 (4)
Os(2)	0.5894 (1)	0.20806 (8)	0.17004 (5)	2.47 (4)	2.42 (4)	2.37 (4)	0.42 (5)	0.47 (3)	0.19 (4)
Os(3)	0.3969 (1)	0.35375 (8)	0.23576 (6)	2.68 (4)	2.57 (4)	2.36 (4)	0.13 (5)	0.59 (3)	−0.29 (4)
S(1)	0.1870 (8)	0.2746 (6)	0.1510 (4)	3.2 (3)	4.1 (4)	3.0 (3)	0.1 (3)	0.0 (3)	−0.6 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.506 (2)	0.091 (2)	−0.053 (1)	5.1 (5)	C(7)	0.313 (3)	0.482 (2)	0.222 (1)	3.4 (6)
O(2)	0.141 (2)	0.006 (2)	0.082 (1)	5.6 (5)	C(8)	0.562 (3)	0.406 (2)	0.306 (1)	3.3 (6)
O(3)	0.094 (2)	0.283 (1)	−0.076 (1)	4.8 (4)	C(9)	0.282 (3)	0.316 (2)	0.317 (1)	3.5 (6)
O(4)	0.815 (2)	0.148 (2)	0.062 (1)	5.4 (5)	C(10)	0.065 (4)	0.380 (2)	0.101 (2)	4.9 (7)
O(5)	0.518 (2)	−0.008 (1)	0.210 (1)	5.0 (5)	C(11)	0.478 (3)	0.317 (2)	0.071 (1)	2.9 (5)
O(6)	0.867 (3)	0.241 (2)	0.296 (1)	6.6 (6)	C(12)	0.521 (3)	0.374 (2)	0.139 (1)	2.5 (5)
O(7)	0.266 (2)	0.564 (2)	0.210 (1)	6.0 (5)	C(13)	0.632 (3)	0.453 (2)	0.145 (1)	3.0 (5)
O(8)	0.669 (2)	0.437 (1)	0.347 (1)	4.9 (4)	C(14)	0.700 (3)	0.481 (2)	0.083 (1)	3.8 (6)
O(9)	0.224 (2)	0.286 (2)	0.366 (1)	5.5 (5)	C(15)	0.672 (3)	0.424 (2)	0.015 (2)	4.6 (7)
C(1)	0.435 (3)	0.128 (2)	−0.012 (1)	3.4 (6)	C(16)	0.567 (3)	0.349 (2)	0.009 (1)	3.2 (5)
C(2)	0.202 (3)	0.075 (2)	0.073 (1)	3.7 (6)	H(13)[a]	0.6617	0.4878	0.1928	5.0
C(3)	0.183 (3)	0.247 (2)	−0.027 (1)	2.8 (5)	H(14)[a]	0.7684	0.5389	0.0853	5.0
C(4)	0.723 (3)	0.167 (2)	0.104 (1)	3.7 (6)	H(15)[a]	0.7269	0.4400	−0.0274	5.0
C(5)	0.543 (3)	0.074 (2)	0.194 (1)	3.2 (6)	H(16)[a]	0.5473	0.3137	−0.0395	5.0
C(6)	0.761 (4)	0.232 (2)	0.249 (2)	4.3 (6)					

[a] Hydrogen atom positions were calculated and not refined. [b] The form of the general temperature factor expression is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

Table III. Interatomic Distances with Esds for $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$

atoms	dist, Å	atoms	dist, Å
Os(1)-Os(2)	2.833 (1)	S(1)-C(10)	1.90 (2)
Os(2)-Os(3)	2.939 (1)	C(11)-C(12)	1.42 (2)
Os(1)···Os(3)	3.791 (1)	C(12)-C(13)	1.43 (2)
Os(1)-S(1)	2.433 (5)	C(13)-C(14)	1.39 (2)
Os(1)-C(1)	1.92 (2)	C(14)-C(15)	1.42 (2)
Os(1)-C(2)	1.99 (2)	C(15)-C(16)	1.35 (2)
Os(1)-C(3)	1.87 (2)	C(16)-C(11)	1.52 (2)
Os(1)-C(11)	2.10 (2)	C(1)-O(1)	1.14 (2)
Os(2)-C(4)	1.86 (2)	C(2)-O(2)	1.09 (2)
Os(2)-C(5)	1.91 (2)	C(3)-O(3)	1.18 (2)
Os(2)-C(6)	1.90 (2)	C(4)-O(4)	1.21 (2)
Os(2)-C(11)	2.37 (2)	C(5)-O(5)	1.18 (2)
Os(2)-C(12)	2.35 (2)	C(6)-O(6)	1.15 (2)
Os(3)-S(1)	2.418 (4)	C(7)-O(7)	1.18 (2)
Os(3)-C(7)	1.87 (2)	C(8)-O(8)	1.14 (2)
Os(3)-C(8)	1.87 (2)	C(9)-O(9)	1.17 (2)
Os(3)-C(9)	1.95 (2)		
Os(3)-C(12)	2.19 (2)	av C-O	1.16 (3)

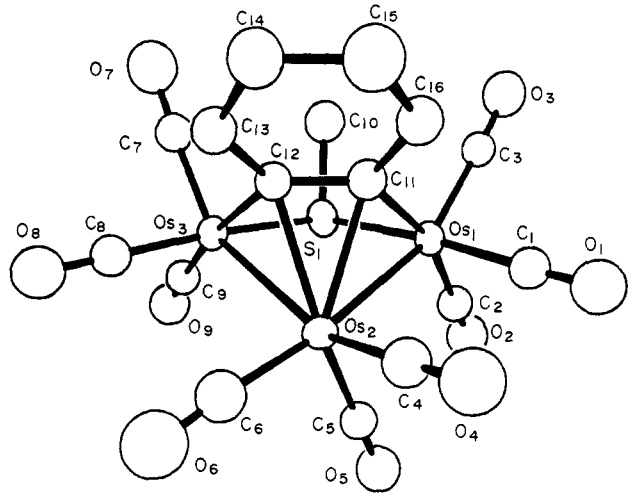

Figure 1. A perspective ORTEP drawing of $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ showing 50% electron density probability ellipsoids.

methanethiolato group, a triply bridging benzyne ligand, C_6H_4, and a bridging hydride ligand. The Os(2)–Os(3) distance at 2.939 (1) Å is 0.106 Å longer than the Os(1)–Os(3) distance of 2.833 (1) Å. Although both distances are similar to those observed in $Os_3(CO)_{12}$ (i.e., 2.877 (3) Å),[11] the elongation of the one bond is significant and is a feature which is characteristic of the presence of bridging hydride ligands.[12] Spectroscopic measurements confirm the presence of a bridging hydride ligand in these molecules (vide infra) and accordingly, we conclude that the bridging hydride ligand straddles the Os(2)–Os(3) bond although this was not confirmed by "direct" observation in the crystallographic analysis. The Os(1)···Os(3) distance at 3.791 (1) Å is clearly too large to allow any significant direct metal–metal bonding.

The "open" edge of the cluster contains the bridging methanethiolato group which serves formally as a three-electron donor. Being tricoordinate and also containing a lone pair of electrons, the sulfur atom has a pyramidal structure, and as expected, the Os(1)–S–Os(3), Os(1)–S–C(10), and Os(3)–S–C(10) angles of 102.8 (2), 106.6 (6), and 105.9 (6)°, respectively, are approximately tetrahedral.

A triply bridging benzyne ligand, C_6H_4, is coordinated to one face of the cluster. Atom C(11) is asymmetrically bonded to Os(1) and Os(2), Os(1)–C(11) = 2.10 (2) Å and Os(2)–C(11) = 2.37 (2) Å, and atom C(12) is asymmetrically bonded to Os(3) and Os(2), Os(3)–C(12) = 2.19 (2) Å and Os(2)–C(12) = 2.35 (2) Å, although the asymmetry for C(12) is not as large as for C(11). The benzyne ligand serves formally as a four-electron donor, and the bonding can be viewed as σ bonds to Os(1) and Os(3) and a π-donor bond to Os(2). There does not appear to be any systematic pattern of long and short C–C bond alternations within the benzyne ring. The ring is planar and is inclined at an angle of 71.5° from the Os_3 plane. Similar incline angles have been found in other triosmium cluster compounds containing benzyne ligands.[1,2,4]

There are nine linear terminal carbonyl ligands. The average C–O bond distance is 1.16 (3) Å. The osmium–carbon distances which are trans to osmium–benzyne σ

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Table IV. Interatomic Angles with Esds for $HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$

atoms	angles, deg	atoms	angles, deg	atoms	angles, deg
Os(1)-Os(2)-Os(3)	82.09 (3)	C(4)-Os(2)-C(6)	90.8 (8)	Os(3)-S(1)-C(10)	105.9 (6)
Os(2)-Os(1)-S(1)	85.2 (1)	C(4)-Os(2)-C(11)	86.7 (6)	Os(1)-C(11)-Os(2)	78.4 (5)
Os(2)-Os(1)-C(1)	91.6 (5)	C(4)-Os(2)-C(12)	107.2 (7)	Os(1)-C(11)-C(12)	127 (1)
Os(2)-Os(1)-C(2)	109.0 (5)	C(5)-Os(2)-C(6)	99.5 (7)	Os(1)-C(11)-C(16)	121 (1)
Os(2)-Os(1)-C(3)	153.6 (5)	C(5)-Os(2)-C(11)	132.3 (6)	Os(2)-C(11)-C(12)	71.5 (8)
Os(2)-Os(1)-C(11)	55.1 (4)	C(5)-Os(2)-C(12)	153.3 (6)	Os(2)-C(11)-C(16)	121 (1)
S(1)-Os(1)-C(1)	175.2 (5)	C(6)-Os(2)-C(11)	128.1 (7)	Os(2)-C(12)-Os(3)	80.6 (5)
S(1)-Os(1)-C(2)	86.0 (5)	C(6)-Os(2)-C(12)	98.6 (7)	Os(2)-C(12)-C(11)	73.4 (9)
S(1)-Os(1)-C(3)	94.2 (5)	C(11)-Os(2)-C(12)	35.1 (5)	Os(2)-C(12)-C(13)	123 (1)
S(1)-Os(1)-C(11)	87.6 (5)	Os(2)-Os(3)-S(1)	83.1 (1)	Os(3)-C(12)-C(11)	120 (1)
C(1)-Os(1)-C(2)	91.7 (7)	Os(2)-Os(3)-C(7)	142.9 (5)	Os(3)-C(12)-C(13)	117 (1)
C(1)-Os(1)-C(3)	90.3 (7)	Os(2)-Os(3)-C(8)	95.1 (5)	C(11)-C(12)-C(13)	123 (1)
C(1)-Os(1)-C(11)	93.6 (7)	Os(2)-Os(3)-C(9)	120.9 (5)	C(12)-C(13)-C(14)	121 (1)
C(2)-Os(1)-C(3)	97.2 (7)	Os(2)-Os(3)-C(12)	52.0 (4)	C(13)-C(14)-C(15)	119 (2)
C(2)-Os(1)-C(11)	163.4 (6)	S(1)-Os(3)-C(7)	94.9 (5)	C(14)-C(15)-C(16)	119 (2)
C(3)-Os(1)-C(11)	98.6 (6)	S(1)-Os(3)-C(8)	175.6 (5)	C(15)-C(16)-C(11)	125 (2)
Os(1)-Os(2)-C(4)	93.6 (5)	S(1)-Os(3)-C(9)	85.5 (5)	C(16)-C(11)-C(12)	112 (1)
Os(1)-Os(2)-C(5)	86.2 (5)	S(1)-Os(3)-C(12)	89.0 (4)	Os(1)-C(1)-O(1)	177 (2)
Os(1)-Os(2)-C(11)	46.5 (4)	C(7)-Os(3)-C(8)	89.0 (7)	Os(1)-C(2)-O(2)	177 (2)
Os(1)-Os(2)-C(12)	74.5 (4)	C(7)-Os(3)-C(9)	95.7 (8)	Os(1)-C(3)-O(3)	176 (2)
Os(3)-Os(2)-C(4)	154.5 (6)	C(7)-Os(3)-C(12)	91.1 (7)	Os(2)-C(4)-O(4)	174 (2)
Os(3)-Os(2)-C(5)	112.6 (5)	C(8)-Os(3)-C(9)	92.0 (7)	Os(2)-C(5)-O(5)	178 (1)
Os(3)-Os(2)-C(6)	91.5 (6)	C(8)-Os(3)-C(12)	93.1 (7)	Os(2)-C(6)-O(6)	176 (2)
Os(3)-Os(2)-C(11)	72.0 (4)	C(9)-Os(3)-C(12)	171.6 (7)	Os(3)-C(7)-O(7)	176 (2)
Os(3)-Os(2)-C(12)	47.4 (4)	Os(1)-S(1)-Os(3)	102.8 (2)	Os(3)-C(8)-O(8)	173 (2)
C(4)-Os(2)-C(5)	92.1 (8)	Os(1)-S(1)-C(10)	106.6 (6)	Os(3)-C(9)-O(9)	177 (2)

bonds (i.e., C(2)–O(2) and C(9)–O(9)) are noticeably longer than others (see Table III). The shortest intermolecular contact was between the carbonyl oxygen atoms O(1) and O(5) at 3.00 (2) Å.

Dynamical Behavior and Solution Structures of I and II. At −60 °C of the ^{1}H NMR spectrum of I shows two resonances δ −15.67 and −15.97 of unequal intensity (ratio 1:5) which can be assigned to bridging hydride ligands. There are two methyl resonances with the same ratio of intensities for the bridging methanethiolato group. On this basis we conclude that I exists in solution as two inequivalent isomers one of which is probably the same isomer A as found in the solid state (see Scheme I).

We have not been able to establish unambiguously the structure of the second isomer in solution, but we consider structures B and C to be likely candidates, and on the basis of an analysis of the dynamical behavior we believe B is more probable than C. B differs from A only by an inversion of configuration at the pyramidal sulfur atom. C differs from A in the orientation of the benzyne ligand. In A, the benzyne ligand bridges the nonbonded osmium atoms via its osmium–carbon σ bonds. In C it bridges a pair of bonded osmium atoms. Interestingly, the molecule $Os_3(\mu_3\text{-PEt})(\mu_3\text{-}C_6H_4)(CO)_9$ was recently shown to have its benzyne ligand coordinated in a manner analogous to that in C.[4]

There are prominent doublets at 8.98 and 8.48 ppm of equal intensity and two apparent triplets (actually doublets of doublets) of equal intensity at 7.11 and 6.86 ppm. Low intensity doublets were observed near the prominent ones, but the expected low intensity triplets of the minor isomer were not clearly resolved. In A the protons of the benzyne ligand should appear in an ABCD pattern. The prominent doublets can be assigned to the A and D protons where the AC, AD, and BD couplings are approximately zero and the AB and CD couplings are equal (8.5 Hz), and the triplets can be assigned to the B and C protons where AC and BD couplings are zero, and the AB and CD couplings are 8.5 Hz, and the BC coupling is 6.1 Hz.

When the temperature is raised, the resonances of the benzyne ligand in both isomers broaden, coalesce, and average, doublets with doublets and triplets with triplets, $\Delta G_{228\,K}^* = 12.7$ kcal/mol[13] (coalescence temperature is approximately −10 °C)), but at −10 °C, the methyl and hydride resonances have not changed and remain sharp. As the temperature is raised still further, these resonances begin to broaden (hydrides and methyls to approximately the same extent), coalesce (30 °C, methyls; 20 °C, hydrides), and reform as singlets: $\Delta G_{263\,K}^* = 14.7$ kcal/mol (minor isomer to major isomer) and $\Delta G_{273\,K}^* = 15.3$ kcal/mol[13] (major isomer to minor isomer). Clearly two processes are operative. The lowest energy process, (1), produces a plane of symmetry in the benzyne ligand of both isomers. For the low-energy process the two most plausible mechanisms are as follows: (1a), a 180° rotation of benzyne ligand (this process has been observed in other triosmium clusters containing triply bridging benzyne ligands);[3,4] or (1b), an exchange of the hydride ligand between the metal–metal bonds (see Scheme I). Evidence which distinquishes between these mechanisms was obtained from a ^{1}H DNMR analysis of II. At −60 °C the ^{1}H NMR spectrum of II is consistent with the presence of only one isomer. The resonances of the benzyne ligand are similar to those in I. As expected for a structure of the type A, the isopropyl methyl groups are diastereotopic and appear as two doublets. As the temperature is raised, the resonances of the benzyne ligand are averaged in a manner analogous to those in I, but most importantly the isopropyl methyl doublets are also averaged at the same rate: $\Delta G_{223\,K}^* = 12.4$ kcal/mol.[13,15] This latter observation rules out mechanism (1a) and implies (1b).

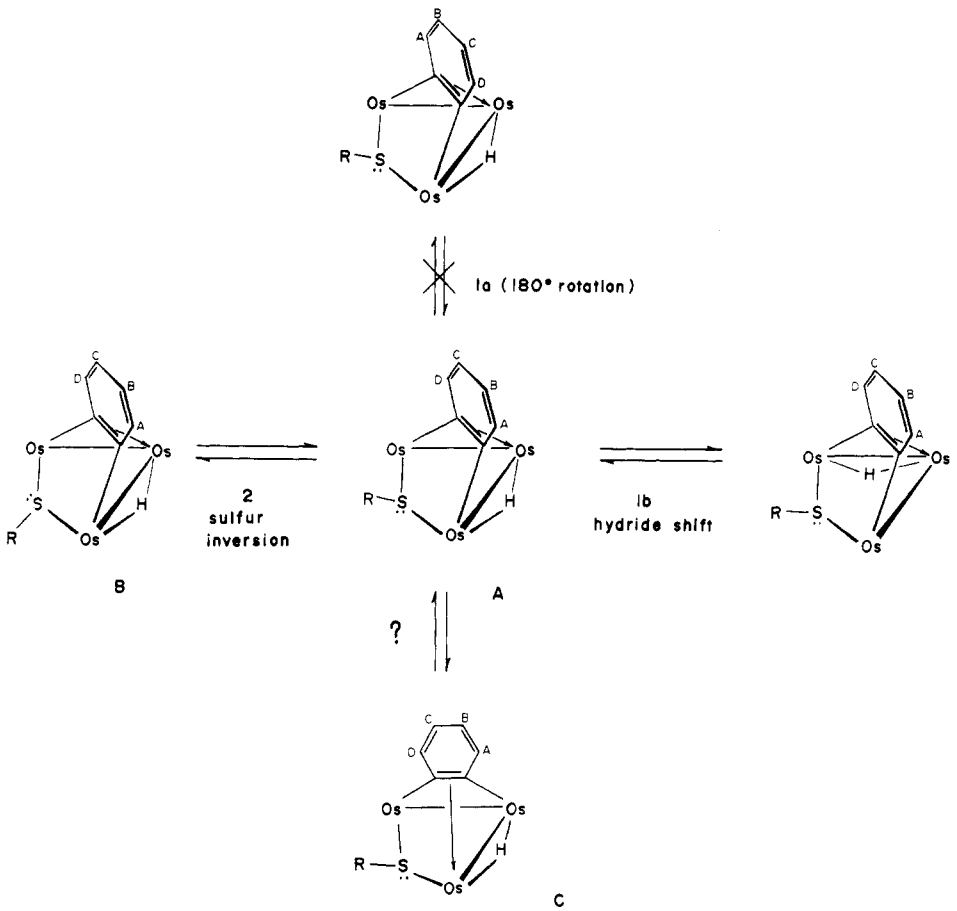
Since the resonances of the benzyne ligand in the minor isomer of I are averaged similarly to those of the major isomer, we believe their structures must be similar too. As a result we prefer the structure B for the minor isomer since hydride shifts will produce a pairwise averaging of

(13) ΔG^* was estimated at the temperature where the limiting spectrum at slow exchange was just attained.[14]

(14) Faller, J. W., In "Transition Metal Olefin and Acetylene Complexes"; Bennett, M. A., Ed.; Wiley: New York, in press.

(15) We observed that the collapse of the two isopropyl methyl doublets is noticeably asymmetric near coalescence. We believe this could be caused by small amounts of a minor isomer (not significantly populated in the slow exchange region) which averages with the major isomer.

Scheme I



the resonances of the benzyne ligand. This would not occur in C. It is conceivable that the benzyne ligand resonances of an isomer like C could be averaged by 180° rotations,[3,4] but it is difficult to imagine a mechanism that would not involve A as an intermediate, and the spectra show that such isomerization does not occur in this temperature range.

The higher energy process interconverts the two isomers of I. If A and B are the correct structures, the isomerization involves only the inversion of configuration of the sulfur atom. While such inversions at trivalent sulfur are generally of fairly high energy when the three substituents are alkyl groups,[16] it has been shown that barrier can be reduced considerably when one of the substituents is a metal atom.[17]

In 1973 Deeming reported the preparation and dynamical behavior of the complexes $HOs_3(EMe_2)(C_6H_4)(CO)_9$ (E = P or As) and $HOs_3(PMe_2)(C_6H_4)(CO)_8PMe_2Ph$.[3] Structurally, he assumed that the triosmium clusters contained three metal–metal bonds. Thus, in order to maintain satisfactory electron configurations, he proposed that the benzyne ligand served as a two-electron donor. Although the benzyne ligand can serve as a two-electron donor in trosmium clusters,[6] in view of our present results, we propose to reformulate Deeming's complexes as "open" clusters containing benzyne ligands serving as four-electron donors.[18] The dynamical activity in his molecules showed a pairwise averaging of the benzyne ligand resonances which could also be explained by hydride shifts. The observation of phosphorus coupling to the hydride ligand in the fast exchange region[3] indicates that the hydride shift occurs by an intramolecular process in these molecules.

In summary, we found that triosmium clusters can readily cleave aryl groups from alkyl aryl sulfide molecules. We have characterized a new class of triosmium cluster which contains a triply bridging benzyne ligand serving as a four-electron donor. These molecules are dynamically active via two processes. A lower energy process involves rapid shifts of the hydride ligand between the metal–metal bonds, and a higher energy process appears to involve inversion of configuration of the sulfur atom of the bridging methanethiolato ligands.

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Registry No. I, 79435-97-5; II, 79435-98-6; $Os_3(CO)_{12}$, 15696-40-9; MeSPh, 100-68-5; *i*-PrSPh, 3019-20-3.

Supplementary Material Available: A listing of structure factor amplitudes for the X-ray structural analysis (9 pages). Ordering Information is given on any current masthead page.

(16) Darwish D.; Tomilson, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 5938.
(17) (a) Abel, E. W.; Ahmed, A. K. S.; Farrow, G. W.; Orrell, K. G.; Sik, G. *J. Chem. Soc., Dalton Trans.* **1977**, 47. (b) Abel, E. W.; Farrow, G. W.; Orrell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1977**, 42. (c) Abel, E. W.; Farrow, G. W.; Orrell, K. G. *Ibid.* **1976**, 1160. (d) Abel, E. W.; Khan, A. R.; Kite, K.; Orrell, K. G.; Sik, V. *J. Organomet. Chem.* **1978**, *145*, C18.

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