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Oxidative Cleavage of Metal–Metal Bonds in Heteronuclear Clusters. Reaction of $SnCl_4$ with $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ and the Crystal and Molecular Structures of $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ and $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$

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The reaction of $SnCl_4$ with $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ produces the new compound $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$ formed by the oxidative cleavage of one Ru–Ru bond and the loss of 1 mol of CO from the cluster. The crystal and molecular structures of both $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ and $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$ are reported. For $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ at 23 °C: space group $P2_1/n$; $a = 9.238$ (2) Å, $b = 15.491$ (7) Å, $c = 11.678$ (2) Å; $\beta = 104.98$ (2)°, $V = 1614.4$ (15) Å^3; $Z = 4$; $\rho_{calcd} = 2.42$ g/cm^3. For 1682 reflections, $R_1 = 0.028$ and $R_2 = 0.032$. The molecule contains a triangular cluster of three ruthenium atoms which is capped by a triply bridging inorganic sulfide ligand. For $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$ at 23 °C: space group $P\bar{1}$, $a = 10.093$ (2) Å, $b = 13.346$ (2) Å, $c = 16.832$ (3) Å; $\alpha = 110.20$ (1)°, $\beta = 91.13$ (2)°, $\gamma = 91.61$ (1)°; $V = 2126$ (1) Å^3; $Z = 4$; $\rho_{calcd} = 2.57$ g/cm^3. For 3543 reflections, $R_1 = 0.031$ and $R_2 = 0.031$. This molecule contains a cluster of three ruthenium atoms with only two metal–metal bonds. An inorganic sulfide ligand bridges the three metal atoms and one hydride ligand bridges each metal–metal bond. The "open" edge of the cluster is bridged by a chloride ligand. The trichlorostannyl group is bonded to one of the chloride-bridged metal atoms.

Introduction

Many electron-deficient organometallic complexes spontaneously form polynuclear metal complexes containing metal–metal bonds in order to reduce or remove that electron deficiency. Frequently these metal–metal bonds are the weakest chemical bonds in the molecule. As a result it may be possible to access readily the electron-deficient fragments by simple cleavage of the metal–metal bond. Considerable attention has been focused on the reactivity of metal–metal bonds in dinuclear complexes.[1] It may also be possible to use the mononuclear fragments which are generated as catalysts.

In polynuclear metal complexes containing several metal–metal bonds it may be possible to cleave selectively a limited number of metal–metal bonds in ways that overall would not destroy the polynuclear unit.[1] Under these circumstances it may be possible to utilize cluster compounds as catalysts by using metal–metal bond cleavage processes to produce active sites or activate directly selected substrates or reagents.[2]

With this in mind we have begun a project focused on investigating the reactivity of metal–metal bonds in heteronuclear cluster compounds. The heteroatom in these clusters will be an element from one of the main groups. It is hoped that the bonds between the metal atoms and the heteroatoms will be less reactive than the metal–metal bonds. Thus, the heteroatom will serve to protect the cluster from degradation when the metal–metal bonds are cleaved.[3,4] A variety of chemical agents are known to effect the cleavage of metal–metal bonds in clusters. Herein, we report the results of our investigation of the nature of the metal–metal bond cleavage which occurs when $SnCl_4$[5,6] reacts with the heteronuclear cluster $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$.

Experimental Section

General Data. All reactions and purifications were routinely performed under a prepurified nitrogen atmosphere. Hexane and heptane were purified by distillation from sodium benzophenone. Other solvents were stored over 4-Å molecular sieves and saturated with nitrogen prior to use. Ruthenium carbonyl was obtained from Strem Chemicals Inc. $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$[7] was prepared in essentially quantitative yield through the reaction of $Ru_3(CO)_{12}$ with H_2S (under 1 atm) in refluxing heptane. A similar procedure was used by Deeming to prepare $(\mu\text{-H})_2(\mu_3\text{-S})Os_3(CO)_9$.[8] Anhydrous $SnCl_4$ from Fisher Scientific was used without further purification.

Melting points were determined in evacuated capillary tubes by using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. Fourier transform ^{1}H NMR spectra were obtained at 270 MHz from a Bruker HX270 instrument.

Preparation of $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$. $SnCl_4$ (0.1 mL, 0.855 mmol) was added to a stirred solution of $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ (67.6 mg, 0.115 mmol) in 30 mL of methylene chloride at room temperature. The reaction was stirred for 45 min during which time the solution became noticeably lighter in color. All volatile components were removed under vacuum. The light yellow residue was taken up in methylene chloride, filtered, and crystallized from methylene chloride/hexane to yield light yellow crystals (86.5 mg, 91.5%): mp 299–302 °C dec; IR (in methylene chloride) 2140 (m), 2129 (s), 2080 (m), 2076 (s), 2011 (m) cm^{-1}; ^{1}H NMR (in CD_2Cl_2) δ 13.52 ($^2J = 2.5$ Hz, RuH), 11.98 ($^2J_{^{117,119}Sn-H} = 245$ Hz, $^2J = 2.5$ Hz, RuH).

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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 149–50.

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Table I. Crystallographic Data for X-ray Diffraction Studies

	$Ru_3SO_9C_9H_2$	$Ru_3SnCl_4SO_9C_8H_2$
(A) Crystal Data		
temp, °C (±5 °C)	23	23
space group	$P2_1/n$	$P\bar{1}$
a, Å	9.238 (2)	10.093 (2)
b, Å	15.491 (7)	13.346 (2)
c, Å	11.678 (2)	16.832 (3)
α, deg		110.20 (1)
β, deg	104.98 (2)	91.13 (2)
γ, deg		91.61 (1)
V, Å^3	1614.4 (15)	2126 (1)
mol wt	589.4	821.9
Z	4	4
ρ_{calcd}, g/cm^3	2.42	2.57
ρ_{obsd}, g/cm^3		2.54
(B) Measurement of Intensity Data		
radiation	Mo K$\bar{\alpha}$ (0.71073 Å)	
monochromator	graphite	
detector aperture, mm		
horizontal ($A + B \tan\theta$)°		
A	3.0	3.0
B	1.0	1.0
vertical	4.0	4.0
cryst faces	$00\bar{1}$, 001, $\bar{1}10$, $1\bar{1}0$ $\bar{1}20$, $\bar{1}\bar{1}0$, $0\bar{1}0$	001, $00\bar{1}$, $0\bar{1}1$ 010, $0\bar{1}0$, $1\bar{1}0$, $\bar{1}10$
cryst size	0.17 × 0.12 × 0.14	0.12 × 0.05 × 0.24
cryst orientation: direction, deg from θ axis	normal to 120, 16.0°	a^*, 6.9°
reflctns measd	$h,k,\pm l$	$h,\pm k,\pm l$
max 2θ	48°	45°
scan type	moving crystal-stationary counter	
ω scan width: ($A + 0.347 \tan\theta$)°	0.90	0.90
background	one-fourth additional scan at each end of scan	
ω scan rate (variable)		
max°/min	10.0	10.0
min°/min	1.3	1.3
no. of reflctns measd	2777	5465
data used ($F^2 \geqslant 3.0\sigma(F)^2$)	1682	3543
(C) Treatment of Data		
abs correctn		
coeff, cm^{-1}	27	38
grid		14 × 6 × 8
transmission coeff		
max		0.85
min		0.70
P factor	0.01	0.01
final residuals		
R_1	0.028	0.031
R_2	0.032	0.031
esd of unit weight	2.014	1.65
largest shift/error value on final cycle	0.12	0.07
largest peaks in final diff Fourier, e/Å	0.22	0.46

Crystallographic Analyses. Crystals of $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ and $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8SnCl_3$ suitable for diffraction measurements were obtained by slow crystallization from hexane solutions and methylene chloride solutions, respectively, cooled to −20 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. For $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ the space group $P2_1/n$ was established from the systematic absences observed in the data. For $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8SnCl_3$ the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. We observed that $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ actually crystallizes in two different modifications. One is that reported here. The other is isomorphous to that found for $(\mu\text{-H})_2(\mu_3\text{-S})Os_3(CO)_9$.[10] Crystal data and data collections 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 (version 16). An absorption correction of a Gaussian integration type was done only for $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8SnCl_3$. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all nonhydrogen 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

The structure of $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ was solved by a combination of Patterson and difference Fourier techniques. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydride ligands were located and refined on coordinates only with fixed thermal parameters of 4.0. Fractional atomic coordinates, 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.

The structure of $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8SnCl_3$ was solved by a combination of direct methods and difference Fourier techniques. The compound crystallizes with two formula equivalents in the asymmetric crystal unit. The six ruthenium and two tin atoms in the asymmetric crystal unit were located

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Table II. Fractional Atomic Coordinates and Their Estimated Standard Deviations for $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$

atom	*x*	*y*	*z*
Ru(1)	−0.01390 (7)	0.10266 (4)	0.24401 (5)
Ru(2)	−0.00594 (6)	0.28829 (4)	0.23621 (5)
Ru(3)	−0.23106 (6)	0.19440 (4)	0.31589 (5)
S	0.0284 (2)	0.1987 (1)	0.4061 (2)
O(1)	0.3040 (6)	0.0401 (4)	0.2471 (5)
O(2)	−0.0812 (8)	−0.0639 (4)	0.3594 (5)
O(3)	−0.1941 (8)	0.0469 (5)	−0.0030 (5)
O(4)	0.3267 (6)	0.3164 (5)	0.2575 (7)
O(5)	−0.0998 (7)	0.3576 (5)	−0.0195 (5)
O(6)	−0.0584 (7)	0.4570 (4)	0.3585 (6)
O(7)	−0.3602 (7)	0.3371 (4)	0.4449 (5)
O(8)	−0.5066 (7)	0.1555 (4)	0.1111 (5)
O(9)	−0.3000 (7)	0.0506 (4)	0.4717 (6)
C(1)	0.1911 (9)	0.0655 (5)	0.2432 (6)
C(2)	−0.0555 (9)	−0.0023 (6)	0.3194 (7)
C(3)	−0.1296 (8)	0.0635 (5)	0.0866 (7)
C(4)	0.2080 (9)	0.3063 (5)	0.2542 (7)
C(5)	−0.0690 (8)	0.3366 (5)	0.0714 (7)
C(6)	−0.0325 (8)	0.3963 (5)	0.3179 (7)
C(7)	−0.3141 (9)	0.2859 (5)	0.3968 (7)
C(8)	−0.4098 (8)	0.1699 (5)	0.1878 (7)
C(9)	−0.2744 (8)	0.1034 (6)	0.4151 (7)
H(1)	0.012 (7)	0.196 (4)	0.181 (5)
H(2)	0.809 (6)	0.267 (4)	0.214 (5)

Table III. Interatomic Distances (Å) with Esds for $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$

Ru(1)-Ru(2)	2.879 (1)	Ru(3)-H(2)	1.75 (5)
Ru(1)-Ru(3)	2.760 (1)	Ru(3)-C(7)	1.966 (7)
Ru(2)-Ru(3)	2.882 (1)	Ru(3)-C(8)	1.958 (7)
Ru(1)-H(1)	1.67 (5)	Ru(3)-C(9)	1.931 (7)
Ru(1)-C(1)	1.918 (7)	Ru(3)-S	2.357 (1)
Ru(1)-C(2)	1.934 (7)	C(1)-O(1)	1.105 (7)
Ru(1)-C(3)	1.968 (7)	C(2)-O(2)	1.115 (7)
Ru(1)-S	2.360 (2)	C(3)-O(3)	1.093 (7)
Ru(2)-H(1)	1.59 (5)	C(4)-O(4)	1.099 (7)
Ru(2)-H(2)	1.69 (4)	C(5)-O(5)	1.076 (7)
Ru(2)-C(4)	1.952 (7)	C(6)-O(6)	1.106 (7)
Ru(2)-C(5)	2.006 (7)	C(7)-O(7)	1.119 (7)
Ru(2)-C(6)	1.973 (7)	C(8)-O(8)	1.112 (7)
Ru(2)-S	2.375 (1)	C(9)-O(9)	1.115 (7)

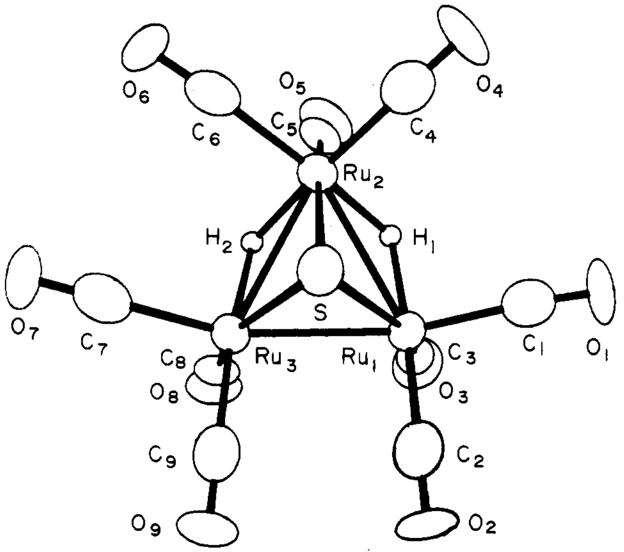

Figure 1. An ORTEP drawing of $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ showing 50% electron density probability ellipsoids. Thermal parameters for the hydride ligands have been artificially reduced.

in an electron density map based on the phasing (MULTAN) of 196 reflections ($E_{\min} \geq 1.90$). The remaining atoms including hydride ligands were obtained from difference Fourier syntheses. All atoms heavier than oxygen were refined with anisotropic temperature factors. All other nonhydrogen atoms were refined with isotropic temperature factors only. Hydride ligands were refined on their coordinates with fixed thermal parameters of 4.0. Final fractional atomic coordinates, interatomic distances, and angles are listed in Tables V–VII. Structure factor amplitudes and thermal parameters are available for both structures (see supplementary material).

Results

For comparative purposes we have performed a crystal structure analysis of our starting material $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$. Its molecular structure is shown in Figure 1. The molecule contains a triangular cluster of three mutually bonded ruthenium atoms which is capped by a triply bridging sulfide ligand. Hydride ligands, which were located and refined, bridge two of the three metal–metal bonds on the side of the cluster opposite the sulfide ligand. The hydride-bridged metal–metal bonds are slightly longer

Table IV. Interatomic Angles (Deg) with Esds for $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$

Ru(2)-Ru(1)-Ru(3)	61.43 (2)	Ru(1)-Ru(2)-H(2)	77 (2)	Ru(1)-Ru(3)-H(2)	90 (1)
Ru(1)-Ru(2)-Ru(3)	57.26 (2)	Ru(3)-Ru(2)-S	52.20 (4)	Ru(2)-Ru(3)-S	52.76 (4)
Ru(1)-Ru(3)-Ru(2)	61.30 (2)	Ru(3)-Ru(2)-C(5)	116.3 (2)	Ru(2)-Ru(3)-C(7)	101.3 (2)
Ru(2)-Ru(1)-S	52.80 (4)	Ru(3)-Ru(2)-C(4)	146.3 (2)	Ru(2)-Ru(3)-C(8)	112.8 (2)
Ru(2)-Ru(1)-C(1)	104.9 (2)	Ru(3)-Ru(2)-C(6)	94.7 (2)	Ru(2)-Ru(3)-C(9)	147.2 (2)
Ru(2)-Ru(1)-C(2)	149.7 (2)	Ru(3)-Ru(2)-H(1)	81 (2)	Ru(2)-Ru(3)-H(2)	32 (1)
Ru(2)-Ru(1)-C(3)	106.9 (2)	Ru(3)-Ru(2)-H(2)	34 (2)	S-Ru(3)-C(7)	104.1 (2)
Ru(2)-Ru(1)-H(1)	27 (2)	S-Ru(2)-C(4)	94.6 (2)	S-Ru(3)-C(8)	155.1 (2)
Ru(3)-Ru(1)-S	54.14 (4)	S-Ru(2)-C(5)	164.3 (2)	S-Ru(3)-C(9)	95.6 (2)
Ru(3)-Ru(1)-C(1)	157.1 (2)	S-Ru(2)-C(6)	95.7 (2)	S-Ru(3)-H(2)	85 (1)
Ru(3)-Ru(1)-C(2)	92.8 (2)	S-Ru(2)-H(1)	79 (2)	C(7)-Ru(3)-C(8)	98.6 (3)
Ru(3)-Ru(1)-C(3)	100.4 (2)	S-Ru(2)-H(2)	86 (2)	C(7)-Ru(3)-C(9)	94.1 (3)
Ru(3)-Ru(1)-H(1)	83 (2)	Ru(1)-H(1)-Ru(2)	124 (3)	C(7)-Ru(3)-H(2)	92 (1)
S-Ru(1)-C(1)	103.1 (2)	Ru(2)-H(2)-Ru(3)	114 (3)	C(8)-Ru(3)-C(9)	93.0 (3)
S-Ru(1)-C(2)	100.1 (2)	C(4)-Ru(2)-C(5)	94.9 (3)	C(8)-Ru(3)-H(2)	84 (2)
S-Ru(1)-C(3)	151.8 (2)	C(4)-Ru(2)-C(6)	94.3 (3)	C(9)-Ru(3)-H(2)	173 (2)
S-Ru(1)-H(1)	78 (2)	C(4)-Ru(2)-H(1)	88 (2)	Ru(1)-C(1)-O(1)	175.3 (6)
C(1)-Ru(1)-C(2)	93.5 (3)	C(4)-Ru(2)-H(2)	176 (1)	Ru(1)-C(2)-O(2)	177.7 (6)
C(1)-Ru(1)-C(3)	101.3 (2)	C(5)-Ru(2)-C(6)	96.1 (3)	Ru(1)-C(3)-O(3)	175.7 (6)
C(1)-Ru(1)-H(1)	90 (2)	C(5)-Ru(2)-H(1)	89 (2)	Ru(2)-C(4)-O(4)	176.0 (6)
C(2)-Ru(1)-C(3)	92.4 (3)	C(5)-Ru(2)-H(2)	84 (2)	Ru(2)-C(5)-O(5)	175.2 (7)
C(2)-Ru(1)-H(1)	176 (2)	C(6)-Ru(2)-H(1)	174 (2)	Ru(2)-C(6)-O(6)	174.6 (7)
C(3)-Ru(1)-H(1)	88 (2)	C(6)-Ru(2)-H(2)	90 (2)	Ru(3)-C(7)-O(7)	178.6 (6)
Ru(1)-Ru(2)-S	52.31 (4)	H(1)-Ru(2)-H(2)	88 (2)	Ru(3)-C(8)-O(8)	176.3 (6)
Ru(1)-Ru(2)-C(4)	99.9 (2)	Ru(1)-Ru(3)-S	54.22 (4)	Ru(3)-C(9)-O(9)	179.5 (7)
Ru(1)-Ru(2)-C(5)	113.6 (2)	Ru(1)-Ru(3)-C(7)	157.2 (2)	Ru(1)-S-Ru(2)	74.89 (4)
Ru(1)-Ru(2)-C(6)	145.6 (2)	Ru(1)-Ru(3)-C(8)	101.8 (2)	Ru(1)-S-Ru(3)	71.64 (4)
Ru(1)-Ru(2)-H(1)	29 (2)	Ru(1)-Ru(3)-C(9)	95.0 (2)	Ru(2)-S-Ru(3)	75.04 (4)

Table V. Fractional Atomic Coordinates and Their Estimated Standard Deviations for $(\mu\text{-H})_2(\mu_3\text{-S})(\mu_2\text{-Cl})Ru_3(SnCl_3)(CO)_8$

atom	*x*	*y*	*z*
Sn(1)	0.41955 (7)	−0.03970 (5)	0.25512 (4)
Sn(2)	0.90467 (7)	0.35776 (6)	0.24800 (4)
Ru(1)	0.25427 (8)	0.23026 (6)	0.49613 (5)
Ru(2)	0.53954 (9)	0.28661 (6)	0.53596 (5)
Ru(3)	0.51222 (8)	0.13933 (6)	0.36053 (5)
Ru(4)	1.24961 (8)	0.29118 (7)	0.05365 (5)
Ru(5)	1.02827 (8)	0.26497 (6)	−0.06910 (5)
Ru(6)	0.91486 (8)	0.25559 (6)	0.08678 (5)
Cl(1)	0.5775 (3)	−0.1672 (2)	0.1898 (2)
Cl(2)	0.3030 (3)	−0.0388 (2)	0.1334 (2)
Cl(3)	0.2642 (3)	−0.1407 (2)	0.3020 (2)
Cl(4)	0.9098 (3)	0.2542 (3)	0.3360 (2)
Cl(5)	1.0786 (3)	0.4841 (3)	0.3090 (2)
Cl(6)	0.7224 (3)	0.4634 (2)	0.3055 (2)
Cl(7)	0.2938 (3)	0.2127 (2)	0.3488 (1)
Cl(8)	1.1228 (3)	0.1834 (2)	0.1191 (2)
S(1)	0.4333 (3)	0.1134 (2)	0.4861 (2)
S(2)	1.0541 (2)	0.3949 (2)	0.0678 (2)
O(1)	0.0787 (8)	0.4189 (6)	0.5079 (5)
O(2)	0.1931 (9)	0.2374 (7)	0.6710 (5)
O(3)	0.0453 (8)	0.0494 (6)	0.4284 (5)
O(4)	0.6302 (8)	0.5151 (7)	0.5589 (5)
O(5)	0.5064 (8)	0.3480 (6)	0.7261 (5)
O(6)	0.8291 (8)	0.2270 (6)	0.5454 (4)
O(7)	0.7613 (8)	0.0289 (6)	0.3721 (5)
O(8)	0.5938 (7)	0.2076 (6)	0.2129 (4)
O(9)	1.3808 (8)	0.4154 (6)	0.2262 (5)
O(10)	1.4601 (7)	0.1205 (6)	0.0151 (4)
O(11)	1.3971 (8)	0.4232 (6)	−0.0305 (5)
O(12)	1.0267 (8)	0.0510 (6)	−0.2179 (5)
O(13)	1.1703 (8)	0.3984 (6)	−0.1580 (5)
O(14)	0.7681 (8)	0.3452 (6)	−0.1128 (4)
O(15)	0.6544 (7)	0.3456 (6)	0.0638 (4)
O(16)	0.7779 (8)	0.0495 (6)	0.0863 (4)
C(1)	0.139 (1)	0.3454 (8)	0.5038 (6)
C(2)	0.220 (1)	0.2379 (9)	0.6058 (7)
C(3)	0.120 (1)	0.1210 (8)	0.4538 (6)
C(4)	0.594 (1)	0.4295 (9)	0.5515 (7)
C(5)	0.518 (1)	0.3221 (9)	0.6538 (7)
C(6)	0.720 (1)	0.2486 (8)	0.5430 (6)
C(7)	0.666 (1)	0.0746 (8)	0.3667 (6)
C(8)	0.568 (1)	0.1821 (8)	0.2693 (6)
C(9)	1.331 (1)	0.3703 (9)	0.1607 (7)
C(10)	1.385 (1)	0.1856 (8)	0.0269 (6)
C(11)	1.344 (1)	0.3730 (9)	0.0045 (7)
C(12)	1.024 (1)	0.1329 (9)	−0.1641 (6)
C(13)	1.118 (1)	0.3443 (9)	−0.1275 (6)
C(14)	0.865 (1)	0.3126 (8)	−0.0985 (6)
C(15)	0.756 (1)	0.3107 (8)	0.0709 (6)
C(16)	0.827 (1)	0.1285 (8)	0.0879 (6)
H(1)	0.372 (7)	0.323 (6)	0.522 (4)
H(2)	0.571 (7)	0.266 (6)	0.428 (4)
H(3)	1.196 (7)	0.220 (6)	−0.032 (4)
H(4)	0.934 (7)	0.182 (6)	−0.023 (4)

(0.12 Å) than the unbridged metal–metal bond. Six carbonyl ligands lie essentially in the plane of the Ru_3 triangle while the remaining three are essentially perpendicular to it. Interatomic distances and angles are listed in Table III and IV. Overall the molecular structure is very similar to that of the osmium analogue which has been studied by the combined X-ray and neutron diffraction technique.[10]

The reaction of $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ with $SnCl_4$ produced only one product as monitored by ^1H NMR spectroscopy (91% isolated yield). This product showed metal–hydride resonances at δ 11.98 and 13.52 which were coupled to each other J_{HH} = 2.5 Hz. The lower field resonance was also coupled to the tin atom J_{Sn-H} = 245 Hz. The IR spectrum had five CO absorptions 2140 (m), 2129 (s), 2080 (m), 2076 (s) and 2011 (m) cm^{-1} which are indicative of a polynuclear metal carbonyl complex. The molecular formula $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$ was established with the aid of an X-ray crystallographic analysis, and the molecular structure of one of two crystallographically independent molecules in the asymmetric crystal unit is shown in Figure 2. The two independent molecules are essentially identical structurally. Interatomic distances and angles are listed in Tables VI and VII. This compound consists of a cluster of three metal atoms having only two metal–metal bonds. Each metal–metal bond contains one bridging hydride ligand while a sulfide ligand bridges all three metal atoms. The hydride-bridged

Table VI. Interatomic Distances (Å) with Esds for $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$

molecule 1		molecule 2	
Ru(1)–Ru(2)	2.959 (1)	Ru(4)–Ru(5)	2.942 (1)
Ru(1)· · ·Ru(3)	3.458 (1)	Ru(4)· · ·Ru(6)	3.481 (1)
Ru(2)–Ru(3)	2.931 (1)	Ru(5)–Ru(6)	2.924 (1)
Ru(1)–Cl(7)	2.450 (2)	Ru(4)–Cl(8)	2.443 (2)
Ru(1)–S(1)	2.391 (2)	Ru(4)–S(2)	2.411 (2)
Ru(1)–C(1)	1.921 (9)	Ru(4)–C(9)	1.90 (1)
Ru(1)–C(2)	1.85 (1)	Ru(4)–C(10)	1.934 (9)
Ru(1)–C(3)	1.90 (1)	Ru(4)–C(11)	1.84 (1)
Ru(1)–H(1)	1.64 (6)	Ru(4)–H(3)	1.51 (6)
Ru(2)–S(1)	2.384 (2)	Ru(5)–S(2)	2.361 (2)
Ru(2)–C(4)	1.90 (1)	Ru(5)–C(12)	1.927 (8)
Ru(2)–C(5)	1.89 (1)	Ru(5)–C(13)	1.90 (1)
Ru(2)–C(6)	1.914 (9)	Ru(5)–C(14)	1.90 (1)
Ru(2)–H(1)	1.81 (6)	Ru(5)–H(3)	1.97 (6)
Ru(2)–H(2)	1.77 (6)	Ru(5)–H(4)	1.82 (6)
Ru(3)–Sn(1)	2.571 (1)	Ru(6)–Sn(2)	2.588 (1)
Ru(3)–Cl(7)	2.469 (2)	Ru(6)–Cl(8)	2.462 (2)
Ru(3)–S(1)	2.404 (2)	Ru(6)–S(2)	2.411 (2)
Ru(3)–C(7)	1.81 (1)	Ru(6)–C(15)	1.833 (9)
Ru(3)–C(8)	1.903 (9)	Ru(6)–C(16)	1.901 (9)
Ru(3)–H(2)	1.76 (6)	Ru(6)–H(4)	1.78 (6)
Sn(1)–Cl(1)	2.361 (2)	Sn(2)–Cl(4)	2.351 (3)
Sn(1)–Cl(2)	2.346 (2)	Sn(2)–Cl(5)	2.355 (2)
Sn(1)–Cl(3)	2.358 (2)	Sn(2)–Cl(6)	2.363 (2)
C(1)–O(1)	1.16 (1)	C(9)–O(9)	1.16 (1)
C(2)–O(2)	1.14 (1)	C(10)–O(10)	1.14 (1)
C(3)–O(3)	1.15 (1)	C(11)–O(11)	1.16 (1)
C(4)–O(4)	1.15 (1)	C(12)–O(12)	1.15 (1)
C(5)–O(5)	1.16 (1)	C(13)–O(13)	1.14 (1)
C(6)–O(6)	1.15 (1)	C(14)–O(14)	1.13 (1)
C(7)–O(7)	1.18 (1)	C(15)–O(15)	1.16 (1)
C(8)–O(8)	1.15 (1)	C(16)–O(16)	1.14 (1)

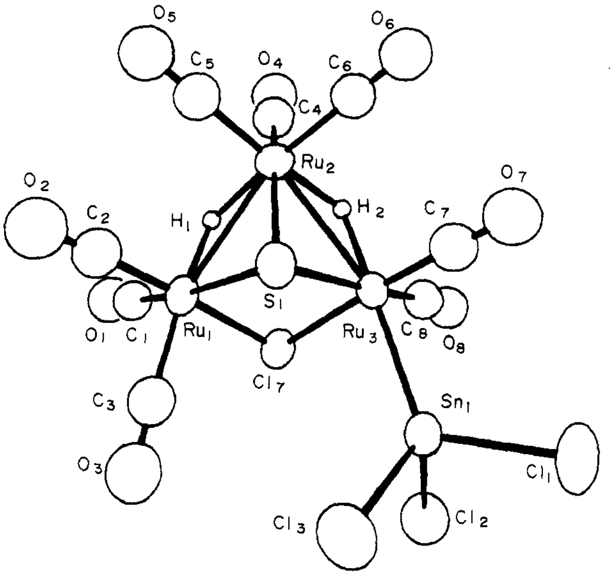

Figure 2. An ORTEP drawing of one of the two independent molecules of $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8SnCl_3$ in the crystal showing 50% electron density probability ellipsoids. Thermal parameters for the hydride ligands have been artificially reduced.

Table VII. Interatomic Angles (Deg) with Esds for $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$

Ru(1)-Ru(2)-Ru(3)	71.91 (2)	S(1)-Ru(3)-Sn(1)	96.48 (6)	C(12)-Ru(5)-H(3)	87 (2)
Ru(2)-Ru(1)-Cl(7)	88.78 (5)	S(1)-Ru(3)-C(7)	91.8 (3)	C(12)-Ru(5)-H(4)	81 (2)
Ru(2)-Ru(1)-S(1)	51.60 (5)	S(1)-Ru(3)-C(8)	171.2 (3)	C(13)-Ru(5)-C(14)	89.0 (4)
Ru(2)-Ru(1)-C(1)	116.9 (3)	S(1)-Ru(3)-H(2)	86 (2)	C(13)-Ru(5)-H(3)	92 (2)
Ru(2)-Ru(1)-C(2)	93.1 (3)	Sn(1)-Ru(3)-C(7)	88.5 (3)	C(13)-Ru(5)-H(4)	175 (2)
Ru(2)-Ru(1)-C(3)	147.8 (3)	Sn(1)-Ru(3)-C(8)	90.4 (3)	C(14)-Ru(5)-H(3)	177 (2)
Ru(2)-Ru(1)-H(1)	32 (2)	Sn(1)-Ru(3)-H(2)	176 (2)	C(14)-Ru(5)-H(4)	88 (2)
Cl(7)-Ru(1)-S(1)	87.30 (7)	C(7)-Ru(3)-C(8)	93.8 (4)	H(3)-Ru(5)-H(4)	90 (3)
Cl(7)-Ru(1)-C(1)	88.8 (3)	C(7)-Ru(3)-H(2)	94 (2)	Ru(5)-Ru(6)-Cl(8)	89.38 (5)
Cl(7)-Ru(1)-C(2)	177.4 (3)	C(8)-Ru(3)-H(2)	87 (2)	Ru(5)-Ru(6)-S(2)	51.44 (5)
Cl(7)-Ru(1)-C(3)	87.5 (3)	Ru(3)-Sn(1)-Cl(1)	116.13 (7)	Ru(5)-Ru(6)-Sn(2)	143.21 (3)
Cl(7)-Ru(1)-H(1)	86 (2)	Ru(3)-Sn(1)-Cl(2)	118.37 (7)	Ru(5)-Ru(6)-C(15)	94.9 (3)
S(1)-Ru(1)-C(1)	167.9 (3)	Ru(3)-Sn(1)-Cl(3)	118.89 (6)	Ru(5)-Ru(6)-C(16)	120.4 (3)
S(1)-Ru(1)-C(2)	92.4 (3)	Cl(1)-Sn(1)-Cl(2)	98.94 (9)	Ru(5)-Ru(6)-H(4)	36 (2)
S(1)-Ru(1)-C(3)	96.2 (3)	Cl(1)-Sn(1)-Cl(3)	102.38 (8)	Cl(8)-Ru(6)-S(2)	85.63 (7)
S(1)-Ru(1)-H(1)	83 (2)	Cl(2)-Sn(1)-Cl(3)	98.69 (9)	Cl(8)-Ru(6)-Sn(2)	86.42 (5)
C(1)-Ru(1)-C(2)	92.0 (4)	Ru(1)-C(1)-O(1)	175.0 (8)	Cl(8)-Ru(6)-C(15)	175.7 (3)
C(1)-Ru(1)-C(3)	95.0 (4)	Ru(1)-C(2)-O(2)	175.8 (9)	Cl(8)-Ru(6)-C(16)	87.7 (3)
C(1)-Ru(1)-H(1)	85 (2)	Ru(1)-C(3)-O(3)	174.8 (8)	Cl(8)-Ru(6)-H(4)	89 (2)
C(2)-Ru(1)-C(3)	90.0 (4)	Ru(4)-Ru(5)-Ru(6)	72.80 (2)	S(2)-Ru(6)-Sn(2)	91.78 (5)
C(2)-Ru(1)-H(1)	96 (2)	Ru(5)-Ru(4)-Cl(8)	89.31 (6)	S(2)-Ru(6)-C(15)	96.4 (3)
C(3)-Ru(1)-H(1)	174 (2)	Ru(5)-Ru(4)-S(2)	51.17 (5)	S(2)-Ru(6)-C(16)	169.5 (3)
Ru(1)-Ru(2)-S(1)	51.81 (5)	Ru(5)-Ru(4)-C(9)	148.4 (3)	S(2)-Ru(6)-H(4)	88 (2)
Ru(1)-Ru(2)-C(4)	116.4 (3)	Ru(5)-Ru(4)-C(10)	118.6 (3)	Sn(2)-Ru(6)-C(15)	89.7 (3)
Ru(1)-Ru(2)-C(5)	93.1 (3)	Ru(5)-Ru(4)-C(11)	90.5 (3)	Sn(2)-Ru(6)-C(16)	96.0 (3)
Ru(1)-Ru(2)-C(6)	151.8 (3)	Ru(5)-Ru(4)-H(3)	37 (2)	Sn(2)-Ru(6)-H(4)	176 (2)
Ru(1)-Ru(2)-H(1)	29 (2)	Cl(8)-Ru(4)-S(2)	86.04 (7)	C(15)-Ru(6)-C(16)	90.8 (4)
Ru(1)-Ru(2)-H(2)	92 (2)	Cl(8)-Ru(4)-C(9)	89.9 (3)	C(15)-Ru(6)-H(4)	94 (2)
Ru(3)-Ru(2)-S(1)	52.56 (5)	Cl(8)-Ru(4)-C(10)	89.2 (6)	C(16)-Ru(6)-H(4)	84 (2)
Ru(3)-Ru(2)-C(4)	116.4 (3)	Cl(8)-Ru(4)-C(11)	179.6 (3)	Ru(6)-Sn(2)-Cl(4)	116.58 (7)
Ru(3)-Ru(2)-C(5)	152.4 (3)	Cl(8)-Ru(4)-H(3)	89 (2)	Ru(6)-Sn(2)-Cl(5)	116.15 (7)
Ru(3)-Ru(2)-C(6)	90.9 (3)	S(2)-Ru(4)-C(9)	97.3 (3)	Ru(6)-Sn(2)-Cl(6)	120.86 (7)
Ru(3)-Ru(2)-H(1)	86 (2)	S(2)-Ru(4)-C(10)	168.7 (3)	Cl(4)-Sn(2)-Cl(5)	101.2 (1)
Ru(3)-Ru(2)-H(2)	34 (2)	S(2)-Ru(4)-C(11)	93.6 (3)	Cl(4)-Sn(2)-Cl(6)	99.2 (1)
S(1)-Ru(2)-C(4)	164.1 (3)	S(2)-Ru(4)-H(3)	89 (2)	Cl(5)-Sn(2)-Cl(6)	99.30 (9)
S(1)-Ru(2)-C(5)	99.9 (3)	C(9)-Ru(4)-C(10)	93.0 (4)	Ru(4)-C(9)-O(9)	177.9 (9)
S(1)-Ru(2)-C(6)	100.0 (3)	C(9)-Ru(4)-C(11)	90.1 (4)	Ru(4)-C(10)-O(10)	175.1 (8)
S(1)-Ru(2)-H(1)	81 (2)	C(9)-Ru(4)-H(3)	174 (2)	Ru(4)-C(11)-O(11)	175.5 (9)
S(1)-Ru(2)-H(2)	86 (2)	C(10)-Ru(4)-C(11)	91.2 (4)	Ru(2)-C(4)-O(4)	177.8 (9)
C(4)-Ru(2)-C(5)	91.0 (4)	C(10)-Ru(4)-H(3)	81 (2)	Ru(2)-C(5)-O(5)	177.3 (9)
C(4)-Ru(2)-C(6)	91.1 (4)	C(11)-Ru(4)-H(3)	91 (2)	Ru(2)-C(6)-O(6)	178.0 (8)
C(4)-Ru(2)-H(1)	88 (2)	Ru(4)-Ru(5)-S(2)	52.71 (5)	Ru(3)-C(7)-O(7)	176.4 (8)
C(4)-Ru(2)-H(2)	83 (2)	Ru(4)-Ru(5)-C(12)	114.8 (3)	Ru(3)-C(8)-O(8)	176.1 (8)
C(5)-Ru(2)-C(6)	92.6 (4)	Ru(4)-Ru(5)-C(13)	93.4 (3)	Ru(1)-S(1)-Ru(2)	76.59 (6)
C(5)-Ru(2)-H(1)	91 (2)	Ru(4)-Ru(5)-C(14)	149.4 (3)	Ru(1)-S(1)-Ru(3)	92.31 (7)
C(5)-Ru(2)-H(2)	174 (2)	Ru(4)-Ru(5)-H(3)	28 (2)	Ru(2)-S(1)-Ru(3)	75.48 (7)
C(6)-Ru(2)-H(1)	176 (2)	Ru(4)-Ru(5)-H(4)	91 (2)	Ru(1)-H(1)-Ru(2)	118 (3)
C(6)-Ru(2)-H(2)	85 (2)	Ru(6)-Ru(5)-S(2)	53.01 (5)	Ru(2)-H(2)-Ru(3)	112 (3)
H(1)-Ru(2)-H(2)	91 (3)	Ru(6)-Ru(5)-C(12)	116.3 (3)	Ru(5)-C(12)-O(12)	175.6 (8)
Ru(2)-Ru(3)-Cl(7)	89.09 (5)	Ru(6)-Ru(5)-C(13)	149.5 (3)	Ru(5)-C(13)-O(13)	175.1 (8)
Ru(2)-Ru(3)-S(1)	51.96 (5)	Ru(6)-Ru(5)-C(14)	90.0 (3)	Ru(5)-C(14)-O(14)	176.8 (8)
Ru(2)-Ru(3)-Sn(1)	148.40 (3)	Ru(6)-Ru(5)-H(3)	87 (2)	Ru(6)-C(15)-O(15)	177.4 (8)
Ru(2)-Ru(3)-C(7)	91.5 (3)	Ru(6)-Ru(5)-H(4)	35 (2)	Ru(6)-C(16)-O(16)	176.8 (8)
Ru(2)-Ru(3)-C(8)	120.1 (3)	S(2)-Ru(5)-C(12)	163.7 (3)	Ru(4)-S(2)-Ru(5)	76.12 (6)
Ru(2)-Ru(3)-H(2)	34 (2)	S(2)-Ru(5)-C(13)	96.8 (3)	Ru(4)-S(2)-Ru(6)	92.42 (7)
Cl(7)-Ru(3)-S(1)	86.62 (7)	S(2)-Ru(5)-C(14)	96.7 (3)	Ru(5)-S(2)-Ru(6)	75.55 (6)
Cl(7)-Ru(3)-Sn(1)	87.24 (5)	S(2)-Ru(5)-H(3)	80 (2)	Ru(4)-H(3)-Ru(5)	114 (3)
Cl(7)-Ru(3)-C(7)	175.2 (3)	S(2)-Ru(5)-H(4)	88 (2)	Ru(5)-H(4)-Ru(6)	108 (3)
Cl(7)-Ru(3)-C(8)	88.3 (3)	C(12)-Ru(5)-C(13)	94.2 (4)		
Cl(7)-Ru(3)-H(2)	90 (2)	C(12)-Ru(5)-C(14)	95.5 (4)		

metal–metal bonds Ru(1)–Ru(2) = 2.959 (1) Å, Ru(2)–Ru(3) = 2.931 (1) Å, Ru(4)–Ru(5) = 2.942 (1) Å, and Ru(5)–Ru(6) = 2.924 (1) Å are slightly longer than those in $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ (Ru(1)–Ru(2) = 2.879 (1) Å and Ru(2)–Ru(3) = 2.882 (1) Å). The remaining metal–metal interactions Ru(1)···Ru(3) = 3.458 (1) Å and Ru(4)···Ru(6) = 3.481 (1) Å are clearly nonbonding, and in place of the metal–metal bond is a bridging chlorine atom.

Two of the ruthenium atoms contain three terminal carbonyl ligands while the third contains two carbonyl ligands and a trichlorostannyl group. The latter lies on the sulfur-bridged side of the Ru_3 plane nearly trans to the bridging hydride ligand. The Ru–Sn bond distances Ru(3)–Sn(1) = 2.571 (1) Å and Ru(6)–Sn(2) = 2.588 (1) Å are similar to those found for the trichlorostannyl groups in the molecules $(\mu\text{-Cl})_3Ru_2(CO)_6(SnCl_3)$, Ru–Sn = 2.565 (4) Å,[5] and $Ru(CO)(PPh_3)_2(O{=}CMe_2)(SnCl_3)$, Ru–Sn = 2.5935 (9) Å.[11]

The hydride ligands were located and refined (coordinates only) in both molecules of $(\mu\text{-H})(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$. They lie on the side of the Ru_3 plane which is opposite to the bridging sulfide ligand. Interestingly, they lie essentially in the planes defined by the ruthenium atoms which they bridge and the two carbonyl ligands on those atoms which are most perpendicular to the Ru_3 plane (cf. Table VIII). As a result, these carbonyl ligands are pushed away from the metal–metal bonds. The effects of

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[11] Gould, R. O.; Sime, W. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1978**, 76.

Table VIII. Unit-Weighted Least-Squares Planes for $(\mu\text{-H})_2(\mu_3\text{-S})\mathrm{Ru}_3(\mathrm{CO})_9$ and $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})\mathrm{Ru}_3(\mathrm{CO})_8(\mathrm{SnCl}_3)$

A	*B*	*C*	*D*	atoms	dist from plane, Å
		(A) $(\mu\text{-H})_2(\mu_3\text{-S})\mathrm{Ru}_3(\mathrm{CO})_9$			
		Plane 1[a]			
−0.3521	−0.0167	−0.9358	−2.2981	Ru(1)	0.0
				Ru(2)	0.0
				Ru(3)	0.0
				S[b]	−1.702 (2)
				H(1)[b]	0.49 (6)
				H(2)[b]	0.82 (6)
		Plane 2			
−0.0516	0.0078	−0.9986	−2.7235	Ru(1)	−0.058 (1)
				Ru(2)	0.058 (1)
				C(1)	0.045 (7)
				C(4)	−0.044 (8)
				H(1)[b]	0.68 (6)
		Plane 3			
0.9756	−0.1133	−0.1879	−1.6475	Ru(1)	0.106 (1)
				Ru(2)	−0.108 (1)
				C(3)	−0.071 (8)
				C(5)	0.073 (8)
				H(1)[b]	0.49 (6)
		Plane 4			
0.4768	−0.8306	−0.2876	−4.9205	Ru(2)	0.078 (1)
				Ru(3)	−0.078 (1)
				C(5)	−0.050 (8)
				C(8)	0.050 (8)
				H(2)[b]	−0.36 (6)
		Plane 5			
−0.4598	0.2775	−0.8435	−0.7024	Ru(2)	0.047 (1)
				Ru(3)	−0.048 (1)
				C(6)	−0.039 (8)
				C(7)	0.040 (8)
				H(2)	0.92 (6)
		(B) $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})\mathrm{Ru}_3(\mathrm{CO})_8(\mathrm{SnCl}_3)$			
		Plane 1[a]			
−0.1027	0.9434	−0.3153	−2.5352	Ru(1)	0.0
				Ru(2)	0.0
				Ru(3)	0.0
				S(1)[b]	−1.557 (3)
				Cl(7)[b]	1.275 (3)
				Sn(1)[b]	−1.064 (1)
				H(1)[b]	0.78 (8)
				H(2)[b]	0.83 (8)
		Plane 2			
0.1515	0.1409	−0.9784	−7.3431	Ru(1)	0.055 (1)
				Ru(2)	−0.056 (1)
				C(1)	−0.04 (1)
				C(4)	0.04 (1)
				H(1)[b]	−0.01 (7)
		Plane 3			
−0.9468	0.3103	−0.0850	−5.3388	Ru(2)	−0.047 (1)
				Ru(3)	0.049 (1)
				C(4)	0.03 (1)
				C(8)	−0.03 (1)
				H(2)[b]	−0.13 (8)
		Plane 4			
0.1343	−0.9353	−0.3275	−1.9421	Ru(4)	0.0
				Ru(5)	0.0
				Ru(6)	0.0
				S(2)[b]	−1.561 (3)
				Cl(8)[b]	1.194 (3)
				Sn(2)[b]	−1.256 (3)
				H(3)[b]	0.80 (8)
				H(4)[b]	0.92 (8)
		Plane 5			
0.5186	0.6948	−0.4983	8.5784	Ru(4)	−0.044 (1)
				Ru(5)	0.043 (1)
				C(10)	0.03 (1)
				C(11)	−0.03 (1)
				H(3)[b]	0.06 (8)

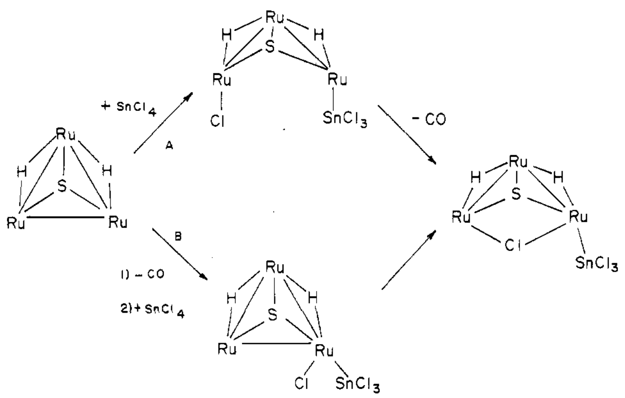
Table VIII (*Continued*)

Plane 6

−0.8731	0.3891	−0.2938	−7.1820	Ru(5)	0.041 (1)
				Ru(6)	−0.042 (1)
				C(12)	−0.02 (1)
				C(16)	0.03 (1)
				H(4)[b]	0.11 (7)

[a] Equations of the planes are of the form $Ax + By + Cz = D$. [b] These atoms were not used in defining the plane.

Scheme I



such bridging hydride ligands on the ligand structure of polynuclear metal complexes have been described in detail by Churchill.[12] It is not clear why the hydrides lie in these planes since moving out of the planes would clearly lead to a decrease in steric interactions, but if one neglects the metal–metal interactions, each metal atom contains six ligands which lie arranged in fairly regular octahedral configurations. The bonding in $(\mu\text{-H})_2(\mu_3\text{-S})Os_3(CO)_9$ has been described similarly, and the hydride bridges were described as "open" three-center two-electron bonds with little direct Os–Os bonding.[10] However, this concept is somewhat difficult to embrace[12] since the bridged Ru–Ru distances in $(\mu\text{-H})_2(\mu_3\text{-S}(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$ are barely 0.10 Å longer than those found in $Ru_3(CO)_{12}$ (Ru–Ru = 2.85–2.86 Å) where full Ru–Ru single bonds can be tnticipated.[13] A similar relationship also exists between $(\mu\text{-H})_2(\mu_3\text{-S})Os_3(CO)_9$ and $Os_3(CO)_{12}$.

Discussion

The reaction of $SnCl_4$ with $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$ leads to the addition of one formula equivalent of $SnCl_4$ to the cluster while at the same time 1 mol of CO is expelled. One Sn–Cl bond in $SnCl_4$ and one Ru–Ru bond in the cluster are cleaved. The cleaved Ru–Ru bond is replaced with a bridging chloride ligand. The expelled CO ligand is replaced with a trichlorostannyl group.

It has been reported previously that $SnCl_4$ will cleave one Ru–Ru bond in $Ru_3(CO)_{12}$ at room temperature to yield $Ru_3(CO)_{12}Cl(SnCl_3)$[5] which probably contains a linear chain of metal atoms like $Os_3(CO)_{12}I_2$.[14] However, at 100 °C all the metal–metal bonds are cleaved and $(\mu\text{-Cl})_3Ru_2(CO)_5SnCl_3$ is formed.[5]

Mechanistically, the two most plausible routes to $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8(SnCl_3)$ are shown in Scheme I. Via route **A** the $SnCl_4$ oxidatively cleaves one Ru–Ru bond. This may occur in a sequence of steps (not shown) which could involve electron transfers, Cl^+ addition followed by $SnCl_3^-$, or spontaneous fission. These processes have been implicated in halogen cleavages.[15-17] Subsequent CO loss accompanied by a shift of the chloride ligand into a bridging position could complete the reaction.

Alternatively, one could imagine initial CO loss accompanied by a rapid oxidative addition of $SnCl_4$ to a single ruthenium atom (route B). Subsequent opening of the Ru–Ru bond and movement of the chloride ligand into the bridging position would complete the process. If the reaction between $SnCl_4$ and $Ru_3(CO)_{12}$ can be used as a guide to what is happening in the present reaction, route A is probably the correct one.[5]

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Registry No. $(\mu\text{-H})_2(\mu_3\text{-S})(\mu\text{-Cl})Ru_3(CO)_8SnCl_3$, 79084-24-5; $(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9$, 32574-35-9; $SnCl_4$, 7646-78-8.

Supplementary Material Available: Structure factor amplitudes and thermal parameters for both structures are available (27 pages). Ordering information is given on any current masthead page.

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