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Syntheses of $M_3(\mu\text{-}H)_3(CO)_9(SiXCl_2)_3$ (M = Ru, Os; X = Me, Cl) and Structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiMeCl_2)_3$. Two Conformational Isomers in the Same Crystal

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Reaction of $M_3(CO)_{12}$ (M = Ru, Os) with Cl_2XSiH (X = Me, Cl) in hexane solution, under vacuum at elevated temperatures, gives $M(CO)_4(SiXCl_2)_2$ and $M_3(\mu\text{-}H)_3(CO)_9(SiXCl_2)_3$. The crystal structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiMeCl_2)$ has been determined from three-dimensional X-ray data collected by counter methods. The space group is $P\bar{6}$ with cell dimensions $a = 13.267$ (3) Å, $c = 9.611$ (2) Å, and $Z = 2$. On the basis of 1087 observed reflections, the structure was solved and refined by block-diagonal least-squares methods to $R_F = 0.029$ and $R_{wF} = 0.033$. The unit cell contains two independent molecules, each of $3/m$ symmetry, which differ with respect to the orientation of the methyl and chloro groups. Each molecule has a triangular arrangement of osmium atoms in which each metal–metal bond is presumed bridged by a hydrogen atom; the Os–Os distances (which differ significantly: 3.155 (2) Å, 3.126 (2) Å) are consistent with this view. The Os–Si distances are 2.420 (5) and 2.400 (6) Å. Spectroscopic data indicate the structure in solution is the same as that found in the solid state except that there is rapid rotation about the Os–Si bond.

Introduction

Numerous derivatives of $Os_3(CO)_{12}$, and to a lesser extent $Ru_3(CO)_{12}$, are known in which the triangular skeleton of metal atoms is retained.[1] Many carbonyl complexes that have ligands with group 4B donor atoms bonded to ruthenium or osmium are known.[2] However, with the exception of $[Me_2SiOs(CO)_3]_3$[3] and $[Me_2GeM(CO)_3]_3$ (M = Ru, Os),[4] these do not contain the cluster of transition metals, and even in these cases the compounds are prepared from mononuclear starting materials and not $M_3(CO)_{12}$.

Group 4B ligands are known to exhibit a large trans effect or influence in square-planar complexes.[5] Also, the large trans effect of $SiCl_3$ when bonded to octahedral ruthenium carbonyl molecules has been demonstrated.[6,7] It may be that, once coordinated, the group 4 ligand labilizes the transition metal–metal bonds such that fragmentation of the cluster occurs.

In this paper we report the isolation of $M_3H_3(CO)_9(SiXCl_2)_3$ (X = Me, Cl) from the reaction of the appropriate silane and $M_3(CO)_{12}$. The crystal structure of $Os_3H_3(CO)_9(SiMeCl_2)_3$ reveals the Os_3 cluster intact. It also shows the presence of two conformational isomers resulting from different orientations of the $SiMeCl_2$ group about the osmium–silicon bond.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. The preparations of the compounds were carried out in round-bottom flasks (ca. 80 mL total volume) fitted (via a 10-cm stem) with a Teflon valve. These were immersed to approximately half-volume in oil baths at the desired temperature and the solutions magnetically stirred. Although we have experienced no difficulty in using such vessels, adequate precautions should be taken when low-boiling silanes are heated to temperatures of 135 °C in glass apparatus. Hexane was refluxed over potassium, distilled, and stored over type 4A molecular sieves and under nitrogen before use. The carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ were prepared by literature methods with minor modifications.[8,9] The silanes were commercially available and were used without further purification. Sublimations were carried out on a standard vacuum system at a pressure of less than 5×10^{-3} mmHg.

Infrared spectra were obtained with a Perkin-Elmer 237 spectrometer fitted with an external recorder. The spectra (carbonyl region) were calibrated with carbon monoxide. ^1H and ^{13}C NMR spectra were recorded on a modified Varian XL-100 instrument (operating in the Fourier transform mode). Mass spectra were obtained on a Hewlett-Packard 5985 GC-MS system, which has a mass range of 0–1000. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Analytical and spectroscopic data for the derivatives are given in Table I.

Preparation of $Ru_3H_3(CO)_9(SiCl_3)_3$. Method 1. A flask containing $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) and Cl_3SiH (1.5 mL, 2.0 g, 15 mmol) in hexane (15 mL) was cooled to −196 °C and evacuated. The solution was degassed with one freeze–thaw cycle and then heated, with stirring, to 75 °C for 40 min. The yellow solution was cooled and transferred to a Schlenk flask, and the hexane and excess Cl_3SiH were removed on the vacuum line. The remaining yellow solid (0.53 g) was sublimed at ca. 75 °C onto a probe at −78 °C for 30 h. The sublimate $[Ru(CO)_4(SiCl_3)]_2$ (0.19 g, 36%) was recrystallized from hexane to give the analytical sample as yellow crystals. The material remaining from the sublimation was extracted with hot hexane (20 mL) and the solution filtered. When the solution was cooled to −15 °C, $Ru_3H_3(CO)_9(SiCl_3)_2$ (0.22 g, 46%) was obtained. Although the crystals were spectroscopically and analytically pure, they were very pale yellow (method 2 gave white or colorless crystals).

Method 2. A vessel containing $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) and Cl_3SiH (2.0 mL, 2.7 g, 20 mmol) in hexane (20 mL) was evacuated and the solution degassed as in method 1. The solution was then heated, with stirring, at 70–75 °C for 60 h, at which time an infrared spectrum of the reaction mixture (after removal of Cl_3SiH) showed the absence of $[Ru(CO)_4(SiCl_3)]_2$. The almost colorless solution was cooled and transferred to a Schlenk flask, and hexane and excess Cl_3SiH were removed on the vacuum line. Sublimation of the remaining very pale yellow solid (0.58 g) at 60–65 °C onto a probe at −78 °C for 6 h gave white $Ru(CO)_4(SiCl_3)_2$ (0.34 g, 47%) as a ~1:2 cis–trans mixture. The mixture was identified by its mass and infrared spectrum: *cis*-$Ru(CO)_4(SiCl_3)_2$, ν(CO) 2150 w, 2103 m, 2094 m, 2084 s cm^{-1}; trans isomer, 2089 vs cm^{-1} (in hexane solution). The pure isomers have been prepared previously (by R.K.P.) by alternate methods.[6,10,11] The residue from the sublimation was extracted with

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[1] Some recent examples: (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391. (b) Hanson, B. E.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1852. (c) Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985. (d) Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 91.

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Table I. Analytical and Spectroscopic Data

			mol wt		% C		% H				
compd	color	mp, °C[a]	calcd	found[b]	calcd	found	calcd	found	ν(CO), cm^{-1} [c]	^{1}H NMR[d]	^{13}C NMR[e]
$Ru_3H_3(CO)_9(SiCl_3)_3$[f]	white	155–156	961.66	768[g]	11.24	11.28	0.31	0.31	2122 m, 2079 vs	−15.52	189.8,[h] 184.8[i]
$Ru_3H_3(CO)_9(SiMeCl_2)_3$	yellow	121–122	900.40	730[g]	16.01	16.49	1.34	1.41	2110 s, 2066 vs[j]	1.38, −14.88	192.0,[h] 187.3,[i] 20.0[k]
$Os_3H_3(CO)_9(SiCl_3)_3$	white	198–199	1229.05	>1000	8.80	9.17	0.25	0.30	2122 m, 2073 s, 2066 m	−17.20	170.5,[h] 166.0[i]
$Os_3H_3(CO)_9(SiMeCl_2)_3$	pale yellow	158	1167.80	>1000	12.34	12.53	1.04	1.02	2111 m, 2062 s, 2045 m	1.50, −16.59	172.6,[h] 168.8,[i] 19.1[k]
$[Ru(CO)_4(SiCl_3)]_2$	yellow	140–141[l]	695.11	696	13.83	13.93	0.0	0.0	2086 w, 2059 vs[l]		
$Ru(CO)_4(SiMeCl_2)_2$	white	96–97	441.16	442	16.34	16.37	1.37	1.37	2137 m, 2090 m, 2083 m, 2066 s, 2061 vs	1.29, 1.28[m]	*n*
$Os(CO)_4(SiCl_3)_2$[o]	white	182	571.13	572	8.41	8.37	0.0	0.0	2081 vs		*n*
$Os(CO)_4(SiMeCl_2)_2$[o]	white	125	530.29	531	13.59	13.82	1.14	1.16	2093 vw, 2059 vs	1.36	*n*

[a] With decomposition. [b] By mass spectroscopy; most abundant peak of parent ion. [c] Hexane solution. [d] In ppm; $CDCl_3$ solution, Me_4Si internal reference. [e] In ppm; $CDCl_3$ solution, $^{13}CDCl_3$ = 77.0 ppm. [f] Prepared by method 2. By method 1: % C found, 11.60; % H found, 0.34. [g] $(P - SiXCl_2 - 2CO)^+$ (weak); $(P - SiXCl_2 - 3CO)^+$ (strong). [h] Axial CO. [i] Equatorial CO. [j] Broad asymmetric. [k] CH_3. [l] Literature:[24] mp 145–150 °C; ν(CO) 2086 w, 2056 s, 2050 w, sh cm^{-1}. [m] Due to trans isomer.[31] [n] See ref 31. [o] Trans isomer.

hot hexane as before to give $Ru_3H_3(CO)_9(SiCl_3)_3$ (0.23 g, 48%) as white and colorless crystals. Use of higher temperatures in the synthesis gave just *cis*- and *trans*-$Ru(CO)_4(SiCl_3)_2$ with some decomposition.

The Cl_2MeSi analogue, $Ru_3H_3(CO)_9(SiMeCl_2)_3$, was prepared in a similar manner to method 2, only with a reaction time of 24 h and a sublimation temperature of 40 °C. The yields were 0.38 g (57%) of $Ru(CO)_4(SiMeCl_2)_2$ and 0.16 g (35%) of $Ru_3H_3(CO)_9(SiMeCl_2)_3$. Initial attempts to prepare $Ru_3H_3(CO)_9(SiMeCl_2)_3$ by method 1 resulted in extensive decomposition of the cluster at the sublimation step.

The cluster compounds can be handled for short periods in air without apparent decomposition; they are, however, completely decomposed after exposure for 24 h. The mononuclear compounds show signs of decomposition after only 1 h in air.

Preparation of $Os_3H_3(CO)_9(SiMeCl_2)_3$. A flask containing $Os_3(CO)_{12}$ (0.30 g, 0.33 mmol) and Cl_2MeSiH (2.0 mL, 2.2 g, 19 mmol) in hexane (20 mL) was cooled to −196 °C and evacuated on the vacuum line; the solution was degassed by one freeze–thaw cycle. The flask was then placed in an oil bath at 135 °C and the solution stirred for 2 h, during which time there was a change from yellow to almost colorless. The solution was cooled to room temperature and transferred to a Schlenk flask (any crystals which formed at this stage were transferred to the Schlenk flask with the use of warm hexane). Excess Cl_2MeSiH and hexane were removed on the vacuum line, and the resulting solid was sublimed at 60–65 °C for 6 h onto a probe at −78 °C to give $Os(CO)_4(SiMeCl_2)_2$ (0.12 g, 23%) as white crystals. The residue remaining after removal of $Os(CO)_4(SiMeCl_2)_2$ was extracted with boiling hexane (ca. 25 mL), filtered hot, and allowed to stand in the refrigerator at −15 °C, whereupon $Os_3H_3(CO)_9(SiMeCl_2)_3$ (0.24 g, 62%) was obtained as very pale yellow crystals.

The $Os(CO)_4(SiMeCl_2)_2$ obtained in this reaction consists, as determined by ^{1}H NMR spectroscopy, of an approximately 1:3 mixture of the cis and trans isomers. The cis isomer (ν(CO) 2140 m, 2083 m, 2067 m, 2059 s cm^{-1}, hexane solution; ^{1}H NMR δ 1.33, $CDCl_3$ solution) has been separated from the trans isomer by careful sublimation at room temperature by using a water-cooled probe.[10] In this study the pure trans isomer was obtained by first subliming the cis–trans mixture at room temperature (onto a probe at −78 °C) to remove the cis isomer, then subliming the remaining trans isomer at 60 °C, and finally recrystallizing the sublimate from hexane.

The trichlorosilicon analogues were prepared by the same method with the exception that the reaction was allowed to proceed for 3 h. Although an infrared spectrum of the solution after 2 h indicated that the reaction was essentially complete, the solution was pale yellow and gave a pale yellow product for $Os_3H_3(CO)_9(SiCl_3)_3$. Allowing the reaction to proceed for an additional 1 h resulted in an essentially colorless solution from which white or colorless crystals of $Os_3H_3(CO)_9(SiCl_3)_3$ were obtained. The yields were 0.11 g (19%) of $Os(CO)_4(SiCl_3)_2$ and 0.25 g (68%) of $Os_3H_3(CO)_9(SiCl_3)_3$. The $Os(CO)_4(SiCl_3)_2$ was isolated as the trans isomer . If the reaction was carried out at 115 °C for 24 h, significant amounts of the cis isomer were formed (ν(CO) 2152 w, 2095 m, 2080 vs cm^{-1}, hexane solution). The preparation of the cis form and its isomerization to the trans compound at 120 °C have been described.[11]

The yield of $Os_3H_3(CO)_9(SiCl_3)_3$ did not appear to be significantly increased by removing the CO (after 20, 50, 80, and 100 min) from the reaction flask. The yield was only slightly decreased, with a concomitant increase in the yield of $Os(CO)_4(SiCl_3)_2$, when a reaction time of 24 h was used. However, for the Cl_2MeSi derivatives there was complete reaction of the cluster after 24 h. When the reaction was followed by infrared spectroscopy (in hexane solution), carbonyl absorptions (at 2096 and 2060 cm^{-1} for X = Cl and 2091 and 2056 cm^{-1} for X = Me, plus, in both cases, bands coincident with those of $Os_3(CO)_{12}$) were observed which could not be assigned to either starting materials or products. These bands were not due to the $[Os(CO)_4(SiXCl_2)]_2$ species, which have been prepared by other means.[12] No attempt was made to isolate the intermediates in these complex mixtures.

The osmium clusters are more robust than their ruthenium analogues: they showed no apparent decomposition after exposure to air for 24 h, although several days of exposure did cause yellowing of the crystals.

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Table II. Crystal Data[a]

$C_{12}H_{12}Cl_6O_9Os_3Si_3$
crystal system: hexagonal
space group: $P\bar{6}$
$a = 13.267$ (3) Å
$c = 9.611$ (2) Å
$V = 1465.0$ Å^3
$Z = 2$
fw = 1167.81
$\rho_c = 2.647$ g cm^{-3}
$\rho_o = 2.61$ g cm^{-3}
$\mu = 137.0$ cm^{-1}

[a] Esd's of the least significant figures are given in parentheses in this and the succeeding tables.

The $M_3H_3(CO)_9(SiXCl_2)_3$ clusters are more soluble in hexane than the parent carbonyls, $M_3(CO)_{12}$.

Attempts to prepare (at various temperatures) $M_3H_3(CO)_9(SiMe_2Cl)_3$ gave only $M(CO)_4(SiMe_2Cl)_2$, as identified by infrared spectroscopy: *cis*-$Ru(CO)_4(SiMe_2Cl)_2$, ν(CO) 2117, 2073, 2051, 2037 cm^{-1}; *cis*- and *trans*-$Os(CO)_4(SiMe_2Cl)_2$, ν(CO) 2120 w, 2061 w, 2047 sh, 2033 s cm^{-1}, hexane solution.[10]

X-ray Data Collection for $Os_3H_3(CO)_9(SiMeCl_2)_3$

A section (0.098 × 0.092 × 0.176 mm) of a well-formed needle was mounted in a sealed Lindemann capillary under nitrogen. X-ray photographs taken with Cu Kα radiation revealed hexagonal $\bar{6}$ Laue symmetry and extinctions $000l$, $l = 2n + 1$, which suggested the space groups $P6_3$ or $P6_3/m$ (but see below).

Cell dimensions were obtained by least-squares analysis from the setting angles of 18 reflections $25° < 2\theta < 31°$ centered on a Picker FACS-1 four-circle diffractometer with monochromated Mo Kα radiation ($\lambda = 0.709\,30$ Å). Crystal data are given in Table II. The peak profiles of 1514 unique reflections $4° \leq 2\theta \leq 60°$ were measured with a θ–2θ scan running at 2° min^{-1}. A scan width of $(1.3 + 0.692 \tan \theta)°$ was used for reflections $4° \leq 2\theta \leq 45°$ and of $(1.1 + 0.692 \tan \theta)°$ for $45° \leq 2\theta \leq 60°$. Stationary-crystal stationary-counter background counts of 10% of scan time were taken on each side of the scan. Peak profile analyses using the method of Grant and Gabe[13] were performed on all reflections to derive the intensities and their associated errors, $\sigma(I)$. Three standards were measured after every 75 reflections but showed no indication of decomposition. A total of 1087 reflections with $I > 2.5\,\sigma(I)$ were regarded as observed and used in the structure solution and refinement.

Determination and Refinement of the Structure

Solution of the three-dimensional Patterson synthesis was first attempted in $P6_3$, but it quickly became evident that this space group was incorrect and that $P\bar{6}$ should be used. The apparent absences $000l$, $l = 2n + 1$, were therefore accidental although almost precise (see later). The coordinates of two independent Os atoms, each on a mirror plane, were determined from the Patterson map. Full-matrix least-squares refinement of these atoms with individual isotropic temperature factors yielded $R_F = 0.16$.[14] A difference-Fourier synthesis phased by this model revealed all remaining nonhydrogen atoms, and refinement led to $R_F = 0.079$. At this stage an analytic absorption correction was applied to the data ($T = 0.332 - 0.196$) with further refinement resulting in $R_F = 0.061$. Inversion of configuration ($x, y, z \rightarrow -x, -y, z$) lowered R_F to 0.054, and refinement using these coordinates and anisotropic temperature factors converged to $R_F = 0.030$.

The H atoms could not be located in an inner-data difference map. The coordinates of the methyl H atoms were calculated by assuming staggered conformations with $\angle$Si–C–H = 109.5° and $r_{C-H} = 0.95$ Å.[15] These atoms were incorporated in the structure factor calculations but were not refined. The ^{1}H NMR spectrum of the compound indicates the presence of bridging hydrogen ligands. Reasonable coordinates for these nuclei[16] can be estimated by assuming symmetrical bridges in the plane of the osmium atoms, with $r_{Os-H} = 1.83$ Å.[17] These are shown in Figure 1. The bridging hydrogen atoms were not included in the structure factor calculations as the positions required in an X-ray structure analysis are those of maximum electron density, which lie somewhere in the OsHOs triangles.[18] These sites can sometimes be determined by extending the trans vectors,[19] but

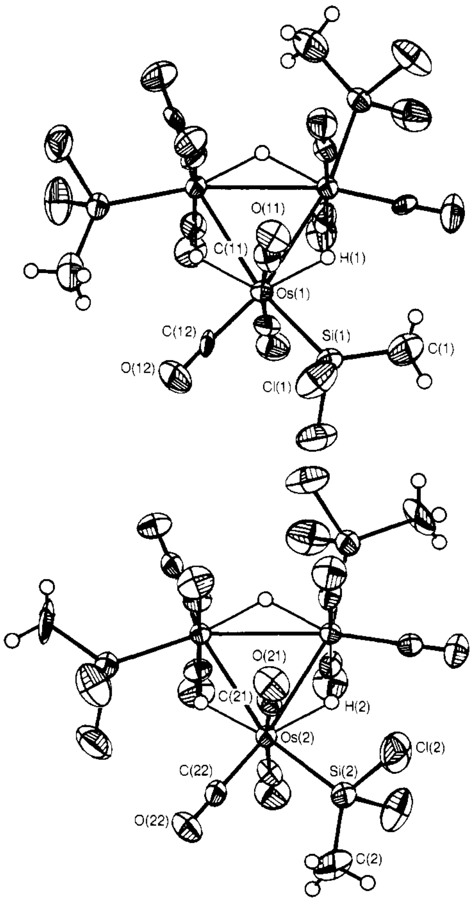

Figure 1. Projected views of molecule 1 (top) and molecule 2 (bottom), showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms are drawn as small circles at their calculated positions.

Table III. Final Positional Parameters[a] for $[Os_3H_3(CO)_9(SiMeCl_2)_3]$

atom	x	y	z
Os(1)	−0.00449 (6)	−0.13948 (6)	0.0000 (0)
Si(1)	0.1325 (5)	−0.2096 (5)	0.0000 (0)
Cl(1)	0.1035 (5)	−0.3187 (5)	0.1686 (6)
C(1)	0.2929 (27)	−0.1105 (27)	0.0000 (0)
C(11)	0.0067 (12)	−0.1336 (11)	0.2004 (16)
O(11)	0.0197 (10)	−0.1272 (9)	0.3206 (12)
C(12)	−0.1211 (14)	−0.2987 (17)	0.0000 (0)
O(12)	−0.1903 (16)	−0.3985 (13)	0.0000 (0)
Os(2)	0.57554 (6)	0.39855 (6)	0.5000 (0)
Si(2)	0.6276 (5)	0.5998 (5)	0.5000 (0)
Cl(2)	0.7354 (5)	0.6864 (4)	0.3324 (6)
C(2)	0.5162 (30)	0.6436 (27)	0.5000 (0)
C(21)	0.5794 (10)	0.4059 (12)	0.2954 (14)
O(21)	0.5829 (10)	0.4110 (11)	0.1811 (11)
C(22)	0.4143 (17)	0.3558 (16)	0.5000 (0)
O(22)	0.3208 (12)	0.3327 (15)	0.5000 (0)
H(C1)1	0.3135	−0.0640	0.0807
H(C1)2	0.3290	−0.1568	0.0000
H(C2)1	0.4680	0.6142	0.4193
H(C2)2	0.5515	0.7270	0.5000

[a] See ref 16 for calculated coordinates of H(1) and H(2).

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(14) $R_F = \sum||F_o| - |F_c|| / \sum|F_o|$.

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(16) H(1) = (0.1350, −0.0045, 0.0); H(2) = (0.7331, 0.4924, 0.5).

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Table IV. Anisotropic Thermal Parameters[a] for $[Os_3H_3(CO)_9(SiMeCl_2)_3]$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os(1)	2.99 (3)	2.62 (3)	3.64 (3)	1.46 (3)	0.00 (0)	0.00 (0)
Si(1)	4.1 (3)	3.5 (3)	4.4 (3)	2.3 (2)	0.0 (0)	0.0 (0)
Cl(1)	10.5 (4)	9.3 (4)	7.5 (3)	7.6 (3)	2.5 (3)	3.5 (3)
C(1)	7.1 (9)	7.0 (18)	11.7 (29)	5.0 (15)	0.0 (0)	0.0 (0)
C(11)	4.4 (7)	3.4 (6)	5.3 (8)	1.8 (6)	−0.3 (7)	1.4 (7)
O(11)	6.8 (7)	5.5 (6)	4.6 (6)	2.8 (6)	−0.5 (6)	0.5 (5)
C(12)	1.3 (7)	4.0 (10)	5.8 (13)	1.5 (7)	0.0 (0)	0.0 (0)
O(12)	6.2 (11)	3.0 (8)	11.9 (17)	1.0 (8)	0.0 (0)	0.0 (0)
Os(2)	2.78 (3)	2.72 (3)	3.33 (3)	1.38 (3)	0.00 (0)	0.00 (0)
Si(2)	3.7 (3)	3.5 (3)	5.7 (4)	2.0 (2)	0.0 (0)	0.0 (0)
Cl(2)	9.7 (4)	5.2 (3)	8.4 (4)	2.2 (2)	2.7 (3)	2.2 (3)
C(2)	9.0 (23)	6.2 (18)	25.0 (52)	7.0 (19)	0.0 (0)	0.0 (0)
C(21)	2.9 (6)	4.6 (7)	3.7 (6)	1.6 (6)	−0.2 (6)	−0.4 (6)
O(21)	7.0 (8)	8.3 (9)	3.8 (6)	3.8 (7)	0.1 (6)	0.7 (6)
C(22)	3.9 (10)	2.5 (9)	5.4 (13)	1.3 (8)	0.0 (0)	0.0 (0)
O(22)	3.4 (7)	7.4 (11)	5.3 (10)	2.7 (8)	0.0 (0)	0.0 (0)
H(C1)1	8.0					
H(C1)2	8.0					
H(C2)1	14.6					
H(C2)2	14.6					

[a] The thermal parameters are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{23}klb^*c^*)]$. The U_{ij} values have been multiplied by 100.

Table V. Interatomic Distances (A) and Angles (Deg)[a]

Distances

molecule 1		molecule 2		molecule 1		molecule 2	
Os(1)-Os(1)^a	3.155 (2)	Os(2)-Os(2)^d	3.125 (2)	Si(1)-Cl(1)	2.076 (6)	Si(2)-Cl(2)	2.078 (6)
Os(1)-Si(1)	2.420 (5)	Os(2)-Si(2)	2.400 (6)	Si(1)-C(1)	1.85 (3)	Si(2)-C(2)	1.84 (2)
Os(1)-C(11)	1.93 (2)	Os(2)-C(21)	1.97 (1)	C(11)-O(11)	1.17 (2)	C(21)-O(21)	1.10 (2)
Os(1)-C(12)	1.89 (2)	Os(2)-C(22)	1.92 (2)	C(12)-O(12)	1.18 (2)	C(22)-O(22)	1.11 (2)

Angles

molecule 1		molecule 2		molecule 1		molecule 2	
Os(1)^a-Os(1)-Os(1)^b	60.0 (-)	Os(2)^d-Os(2)-Os(2)^e	60.0 (-)	C(11)-Os(1)-C(11)^c	172.4 (6)	C(21)-Os(2)-C(21)^g	175.1 (5)
Os(1)^a-Os(1)-Si(1)	167.8 (1)	Os(2)^d-Os(2)-Si(2)	160.1 (1)	C(11)-Os(1)-C(12)	92.8 (4)	C(21)-Os(2)-C(22)	90.7 (4)
Os(1)^a-Os(1)-C(11)	91.7 (4)	Os(2)^d-Os(2)-C(21)	92.0 (4)	Os(1)-Si(1)-Cl(1)	110.8 (2)	Os(2)-Si(2)-Cl(2)	110.5 (2)
Os(1)^a-Os(1)-C(12)	106.6 (5)	Os(2)^d-Os(2)-C(22)	110.6 (6)	Os(1)-Si(1)-C(1)	122.8 (9)	Os(2)-Si(2)-C(2)	121.5 (11)
Os(1)^b-Os(1)-Si(1)	107.8 (1)	Os(2)^e-Os(2)-Si(2)	100.1 (1)	Cl(1)-Si(1)-Cl(1)^c	102.6 (3)	Cl(2)-Si(2)-Cl(2)^f	101.7 (4)
Os(1)^b-Os(1)-C(11)	87.9 (4)	Os(2)^e-Os(2)-C(21)	89.7 (4)	Cl(1)-Si(1)-C(1)	103.9 (6)	Cl(2)-Si(2)-C(2)	105.4 (7)
Os(1)^b-Os(1)-C(12)	166.6 (5)	Os(2)^e-Os(2)-C(22)	170.6 (6)	Os(1)-C(11)-O(11)	176.4 (12)	Os(2)-C(21)-O(21)	179.2 (12)
Si(1)-Os(1)-C(11)	87.6 (4)	Si(2)-Os(2)-C(21)	87.6 (4)	Os(1)-C(12)-O(12)	177.6 (16)	Os(2)-C(22)-O(22)	178.9 (18)
Si(1)-Os(1)-C(12)	85.6 (5)	Si(2)-Os(2)-C(22)	89.3 (6)				

[a] Atoms are related to those given in Table III by the following transformations: (a) $y - x, -x, z$; (b) $-y, x - y, z$; (c) $x, y, -z$; (d) $1 - y, x - y, z$; (e) $1 + y - x, 1 - x, z$; (f) $x, y, 1 - z$.

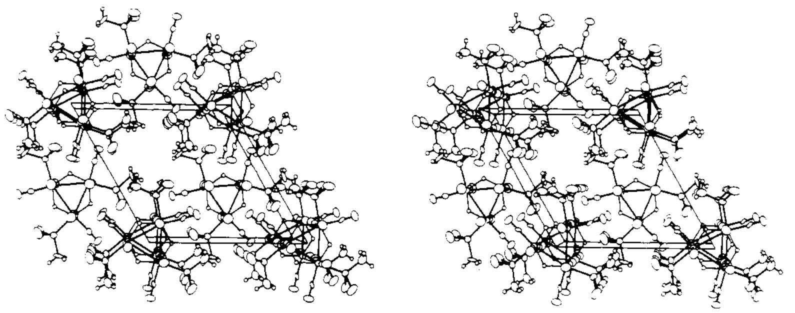

Figure 2. Molecular packing in the unit cell. The view is down *c*, with *a* across the page.

on this occasion the results were not sensible. The structure was refined to completeness (all shift/error ratios <0.1), the final residuals being $R_F = 0.029$, $R_{wF} = 0.033$, and GOF = 1.004.[20] Refinement was by least-squares analysis, minimizing the function $\sum w(|F_o| - |F_c|)^2$. In the early stages the least-squares analysis was full matrix with unit weights. For the final cycles it was block diagonal (Gauss–Siedel) with the weighting scheme $w = 1/[(\sigma(F))^2 + 0.0004F^2]$. Neutral-atom scattering factors were used, with anomalous dispersion corrections applied to the nonhydrogen atoms.[21] Computer programs[22] were run on an in-house PDP-8e computer.

The atomic coordinates are listed in Table III, the associated thermal parameters in Table IV, and bond lengths and angles in Table V. Figure 1 shows the conformation of each of the molecules and also the atomic labeling scheme. Figure 2 is a stereoview showing

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(20) $R_{wF} = (\sum w(|F_o| - |F_c|)^2/\sum F_o^2)^{1/2}$; GOF = $(\sum w(|F_o| - |F_c|)^2/(n - m))^{1/2}$, where n = number of observations and m = number of variables.

(21) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99, 149.

(22) Gabe, E. J.; Larsen, A. C.; Lee, F. L.; Wang, Y. "The NSERC PDP-8e Crystal Structure System"; NSERC: Ottawa, 1979.

the molecular packing within the unit cell.

Results and Discussion

The reaction of excess Cl_2XSiH (X = Me, Cl) with $Os_3(CO)_{12}$ in hexane at 135 °C in an evacuated, sealed flask gave $Os_3H_3(CO)_9(SiXCl_2)_3$ and $Os(CO)_4(SiXCl_2)_2$. The mononuclear compound was readily separated from the cluster by sublimation. Analytical data and physical and spectroscopic properties of these and the corresponding ruthenium derivatives are reported in Table I.

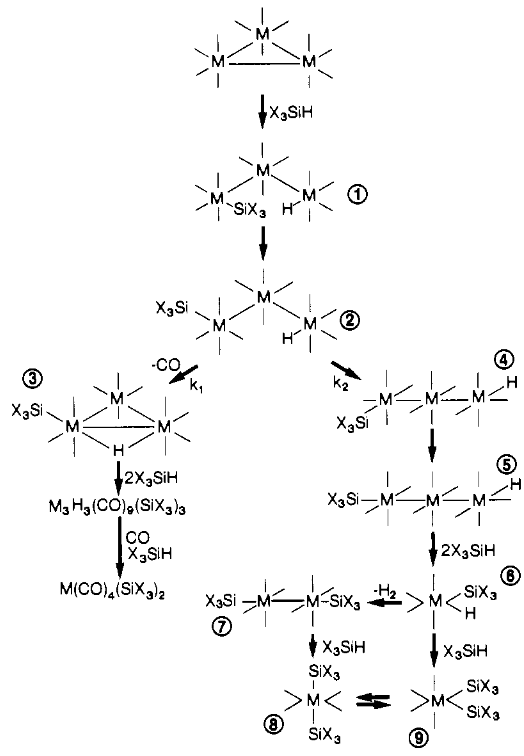
A similar reaction of Cl_2XSiH with $Ru_3(CO)_{12}$ at 70 °C gave, after 40 min, $Ru_3H_3(CO)_9(SiXCl_2)_3$ and $[Ru(CO)_4(SiXCl_2)]_2$. The isolation of $[Ru(CO)_4(SiCl_3)]_2$ from the reaction of Cl_3SiH and $Ru_3(CO)_{12}$ has appeared in the literature.[23] In the present study it was found that, for X = Cl, the dimer could be separated from the cluster by careful sublimation, but for X = Me, there was extensive decomposition of the cluster when sublimation at elevated temperatures was attempted. If the reaction was allowed to proceed for longer periods, however, the $[Ru(CO)_4(SiXCl_2)]_2$, together with some of the cluster, was converted to $Ru(CO)_4(SiXCl_2)_2$. As in the osmium case, this could be readily separated from the trinuclear species.

Although there was infrared evidence for intermediates in the reaction of $Os_3(CO)_{12}$ with Cl_2XSiH, these were not $[Os(CO)_4(SiXCl_2)]_2$, which have been synthesized by other routes.[12] In both the ruthenium and osmium cases, prolonged reaction periods, or higher temperatures, resulted in conversion of the cluster to $M(CO)_4(SiXCl_2)_2$ with only traces of decomposition.[24] Presumably, since the reactions were carried out in sealed vessels, there is recombination with the liberated carbon monoxide to give the tetracarbonyl compound.

As is generally observed with metal clusters, the third-row transition-metal compound is more stable than its second-row congener. We have found that the action of carbon monoxide on the present clusters also follows this trend and that the trichlorosilicon clusters are more stable than the Cl_2MeSi analogues.[12] Somewhat surprisingly, the clusters are more soluble in nonpolar organic solvents than the parent carbonyls.

Stone and co-workers have reported the reactions of silanes, including Me_3SiH, with $M_3(CO)_{12}$.[23,25] They did not observe any species corresponding to $M_3H_3(CO)_9(SiR_3)_3$. Similarly, we found that the only product of the reaction of $M_3(CO)_{12}$ and $ClMe_2SiH$ was $M(CO)_4(SiMe_2Cl)_2$. A weak band in the infrared spectrum near 2095 cm^{-1}, detected in the initial stages of the reaction, could have been due to the cluster compound, but it disappeared as the reaction progressed. It may be that the $M_3H_3(CO)_9(SiMe_2Cl)_3$ clusters are less stable and are rapidly converted to the monomeric derivatives, or the route by which $M_3(CO)_{12}$ and Cl_3SiH initially give $M(CO)_4(SiCl_3)_2$ is the exclusive pathway by which the reaction of $ClMe_2SiH$ with $M_3(CO)_{12}$ proceeds.

Scheme I



A reasonable mechanism that accounts for these results is shown in the Scheme I. The reaction of I_2 with $Os_3(CO)_{12}$ gives $Os_3(CO)_{12}I_2$, which has a structure analogous to **4**.[26] This molecule contains a linear Os_3 chain, which must involve an isomerization at the central osmium atom during its formation from $Os_3(CO)_{12}$. A plausible intermediate to the formation of such a compound is one analogous to **2**. However, in the present case, the strong trans effect of the $SiXCl_2$ group could labilize the trans carbonyl in **2** and allow the formation of the hydrogen bridge before isomerization can occur. Repeating this process would give the observed cluster product. It has been found that the carbonyls trans to the $SiCl_3$ groups in the mononuclear compounds $M(CO)_4(SiCl_3)_2$ are labile.[11] Initial studies[27] have also shown that, in some monomeric ruthenium carbonyl derivatives, the trans effect of $SiMeCl_2$ is at least as great as that of $SiCl_3$. Since $M(CO)_4(SiXCl_2)_2$ or $[M(CO)_4(SiXCl_2)]_2$ is formed together with the cluster, it is assumed that the rates k_1 and k_2 are comparable for the case of Cl_3SiH and Cl_2MeSiH. The trans-labilizing effects of the $SiCl_3$ and $SiMe_3$ ligands have not been compared; it may be weaker in the latter.[28] If this were the case, k_2 would be much greater than k_1 and the cluster compound would not be observed. Alternatively, the metal–metal bonds in the $SiCl_3$ intermediates may be more resistant to attack by silane than the corresponding $SiMe_3$ compounds. The ruthenium–ruthenium bond in $[Ru(CO)_4(SiCl_3)]_2$ was found to be more resistant to attack by iodine than that in $[Ru(CO)_4(SiMe_3)]_2$.[30]

Cis–trans isomerization readily occurs in the monomeric derivatives $M(CO)_4(SiMe_{3-x}Cl_x)_2$ (x = 0–3), with the ease of isomerization increasing with increasing methyl substitution.[31] Therefore, the isomerization of **4** to **5** with the SiX_3 group trans to a metal–metal bond is entirely reasonable (this bonding situation is present in the $[M(CO)_4(SiX_3)]_2$ derivatives[32]). In **5** the high trans effect of the SiX_3 group could

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[23] Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 2559.

[24] The $M(CO)_4(SiXCl_2)_2$ compounds are best prepared by the action of Cl_2XSiH on $M_3(CO)_{12}$ at 180 °C under 80 atm of carbon monoxide. The reaction is complete after 18 h.[10]

[25] Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3147.

[26] Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

[27] Xiang, H.; Chalk, K. L.; Pomeroy, R. K., unpublished results.

[28] The CO stretching frequencies of *cis*-$Ru(CO)_4(SiCl_3)_2$ are extremely high (2150, 2103, 2094, 2084 cm^{-1})[6] and are consistent with the $SiCl_3$ ligand being a good π-acceptor ligand. Those of the trimethylsilicon analogue are much lower (2094, 2031, 2015, 2009 cm^{-1}),[23] which indicate the $SiMe_3$ group has poorer π-acceptor properties. In square-planar complexes, good π-acceptor ligands usually have high trans effects.[29] The available[2] $M-ECl_3$ bond lengths (M = Fe, Ru; E = Si, Ge, Sn) are shorter than similar $M-EMe_3$ bond lengths, again consistent with more double-bond character in the former linkage.

[29] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1201.

[30] Ash, M. J.; Brookes, A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 458.

[31] Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407.

[32] Howard, J. A. K.; Kellett, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2332.

weaken the metal–metal bonds so that further fragmentation readily occurs, which, as mentioned in the Introduction, could account for why so few clusters exist with these ligands. The molecule **5** could react with further X_3SiH in a number of ways, some of which could give the products **7** and **9** directly. We favor the initial formation of the hydride **6**. It has been isolated in some instances in the reaction of $M_3(CO)_{12}$ and X_3SiH.[7,25,27] It is known[12,25] (in some cases) to give the dimeric product **7** on pyrolysis and can thus account for why, in the reaction of Me_3SiH and $Ru_3(CO)_{12}$, $[Ru(CO)_4(SiMe)]_2$ is formed in 90% yield.[23] Compound **6** is also known[7,25] to react with excess X_3SiH to give the monomeric derivatives although this may go via the dimeric compound **7**, especially in the case of ruthenium. However, in the reaction of $Os_3(CO)_{12}$ and Cl_3SiH at 115 °C, it is difficult to account for the formation of *cis*-$Os(CO)_4(SiCl_3)_2$ if the reaction goes via $[Os(CO)_4(SiCl_3)]_2$. This compound would be expected to give the trans isomer and the cis–trans equilibrium lies almost exclusively in favor of the trans isomer at 120 °C.[11]

Stone and co-workers have reached similar conclusions to those outlined in the scheme regarding the fate of $Os(CO)_4(SiMe_3)(H)$.[25] We have verified that the hydrides $M(CO)_4(SiXCl_2)(H)$ do not give the clusters on heating.[12]

An alternative mechanism for the formation of the cluster compounds is the initial dissociation of CO from the parent carbonyl followed by oxidative addition of the silane at the vacant site. Repetition of this process could give the $M_3H_3(CO)_9(SiXCl_2)_3$ derivatives without metal–metal bond cleavage. A preliminary study of the reaction of $Os_3(CO)_{12}$ and Cl_2MeSiH (in hexane at 135–140 °C), under carbon monoxide (80 atm), has been carried out. It was found that the $Os_3(CO)_{12}$ was completely consumed after 2 h; the products were $Os(CO)_4(SiMeCl_2)(H)$, $Os(CO)_4(SiMeCl_2)_2$, $[Os(CO)_4(SiMeCl)]_2$, and one tentatively identified as $(Cl_2MeSi)Os_3(CO)_{12}(SiMeCl_2)$. There was no evidence for $Os_3H_3(CO)_9(SiMeCl_2)_3$. The products obtained are consistent with a mechanism that involves the initial breaking of an osmium–osmium bond. In a similar reaction with Cl_3SiH (to yield analogous products), the carbon monoxide did appear to partially suppress the reaction and some $Os_3(CO)_{12}$ was recovered unchanged after 2 h. A route involving CO dissociation cannot, therefore, be completely ruled out, especially as CO substitution in $Ru_3(CO)_{12}$[33] and $Os_3(CO)_{12}$[34] occurs at the temperatures used to prepare the present clusters. However, it is difficult to see, if the major route to the clusters does involve CO dissociation from $M_3(CO)_{12}$, why $ClMe_2SiH$ does not yield a cluster analogous to $M_3H_3(CO)_9(SiMeCl_2)_3$.

Also, it should not be forgotten that other products besides the $M_3H_3(CO)_9(SiXCl_2)_3$ compounds were obtained that must have arisen from metal–metal cleavage in the parent carbonyl.

Crystal Structure of $Os_3(\mu_2H)_3(CO)_9(SiMeCl_2)_3$. The crystal structure of $Os_3H_3(CO)_9(SiMeCl_2)_3$ consists of two independent molecules, each possessing crystallographically imposed $3/m$ (C_{3h}) symmetry. The ORTEP diagrams of the two molecules are shown in Figure 1. The structure presented an interesting crystallographic oddity since the apparent systematic absences did not correctly indicate the alternative possible space groups. With two molecules of identical compositions located on mirror planes precisely half a cell apart in *c*, the only contributions to the $000l$, $l = 2n + 1$, reflections come from the very small differences in the *z* components of the non-mirror-plane atoms. Consequently these reflections are very weak rather than "systematically" absent.

The presence of bridging hydrogen ligands is clearly indicated from the ^1H NMR spectrum and is also required if each osmium atom is to satisfy the 18-electron rule. The bridging hydrogens were, however, not directly located in this study. The question of bridging hydride ligands and their effect on the associated metal–metal distances has been thoroughly discussed by Churchill and co-workers.[19] The presence of a singly μ_2-bridging hydride would be expected to cause an elongation of the Os–Os vector over what is found in $Os_3(CO)_{12}$ (mean Os–Os distance = 2.877 (3) Å).[35] The osmium–osmium bond lengths found in the present molecules (3.155 (2), 3.126 (2) Å) are among the longest distances observed for such bonds and are consistent with the presence of bridging hydride atoms. (That the bond lengths are still longer than those found for other OsHOs systems probably reflects the large trans influence of the $SiMeCl_2$ ligand.) The hydride ligands as displayed in Figure 1 were calculated by assuming symmetric bonding to the adjacent osmium atoms although we have no direct evidence to support this. Studies on $Ru_3H(CO)_9(C_6H_9)$[36] and $Mn_3H_3(CO)_{12}$[37] showed M–H distances that were essentially equal, but in compounds in which the metals were not equivalent, asymmetric bonding was observed.[17] In $Os_3H_3(CO)_9(SiMeCl_2)_3$ the hydrides are trans to a carbonyl on one side but trans to the silyl group on the other, so slight asymmetry of the Os–H–Os bonds is possible.

A symmetric M_3H_3 unit has been found in $Mn_3H_3(CO)_{12}$.[37] In $Ru_3H_3(CMe)(CO)_9$ the hydrogen atoms are below the Ru_3 plane on the side opposite to the CMe ligand.[38] The osmium analogue is presumably isostructural although the bridging hydrogens were not directly located.[39] Another structure with which the current one may be compared is $Os_3(\mu\text{-}H)_2(CO)_{10}[Re(CO)_5]_2$.[40] This molecule may be considered as arising from the replacement of two carbonyls in $Os_3(CO)_{12}$ by two $H\text{–}M'L_n$ units whereas the present molecule has three carbonyl groups replaced by such units. We are unaware of any other structure containing Os–Si bonds that would allow direct comparison of bond lengths. The mean Os–Si distance (2.410 Å) is considerably shorter than the terminal Ru–Si bond length in $[(Me_3Si)(OC)_3Ru(SiMe_2)]_2$ (2.507 Å)[41] and in $Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$ (2.452 Å).[42] The covalent radii of Ru(0) (1.427 Å) and Os(0) (1.439 Å), as adjudged from the M–M distances in $M_3(CO)_{12}$, are similar.[43] The shortening in the Os–Si bond, therefore, may be attributed to the increased π-acceptor character of the $SiMeCl_2$ ligand.[44]

The most novel feature of the present structural determination is the existence of two conformational isomers in the same crystal. This results from different orientations of the $SiMeCl_2$ group about the Os–Si bond. In one molecule (hereafter referred to as M1) the methyl of the $SiMeCl_2$ ligand is anti to the equatorial carbonyl whereas in the other molecule (M2) it is syn (Figure 1). The effects of this minor variation on the other parameters within a given molecule are quite noticeable. Both the Os–Os and Os–Si distances in M1 (3.155 (2) and 2.420 (5) Å) are significantly longer than in M2 (3.126

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(33) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2094.

(34) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 897.

(35) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(36) Catti, M.; Gervasio, G.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2260.

(37) Kirtley, S. W.; Olsen, J. P.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 4532.

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(40) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3546.

(41) Crozat, M. M.; Watkins, S. F. *J. Chem. Soc., Dalton Trans.* **1972**, 2512.

(42) Howard, J. A. K.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 59.

(43) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(44) The Ru–Si distance of 2.414 Å found in $Ru(SiMe_3)(CO)_2[C_8H_8(SiMe_3)]$[45] is not trans to a metal–metal bond as in the molecules under discussion. The shortness of this bond can probably be attributed to the trans influence of the $C_8H_8(SiMe_3)$ ligand.

(45) Harris, P. J.; Howard, J. A. K.; Knox, S. A. R.; McKinney, R. J.; Phillips, R. P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 403.

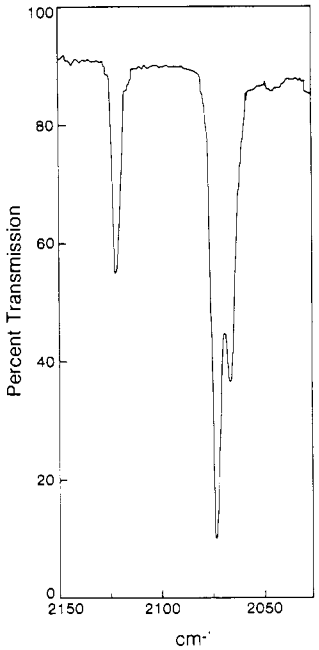

Figure 3. Carbonyl stretching region of the infrared spectrum of $Os_3H_3(CO)_9(SiCl_3)_3$ in hexane solution.

(2) and 2.400 (6) Å). This is curious as usually the bond trans to a lengthened bond tends to be short. It could result from the repulsive interaction between H(1) and the methyl group, which is evidenced by the widening of the Os–Os–Si angle in M1 to 107.8 (1)° compared to 100.1 (1)° in M2, where this interaction is not present. The Os–C distances in M1 are about 1 esd shorter than those in M2. This is hardly conclusive but is consistent with increased back-donation from the metal to carbon because of decreased $d\pi$–$d\pi$ bonding in the long Os–Si bond of this molecule.

Solution Studies. The spectroscopic evidence indicates that the structure adopted by the cluster compounds in solution is the same as that found for $Os_3H_3(CO)_9(SiMeCl_2)_3$ in the solid state, except that there is rapid rotation about the osmium–silicon bond. The very simple infrared spectra exhibited by these compounds in the carbonyl region (e.g., Figure 3) are consistent with molecular C_{3h} symmetry and the local symmetry about each metal atom, i.e., a *mer*-$M(CO)_3A_2B$ system. Bridging hydrogen ligands typically exhibit ^1H NMR resonances at higher fields than terminal hydrides.[46] The present group of compounds is no exception. For $Ru(CO)_4(SiCl_3)(H)$[7] the resonance is at δ −7.35 compared to −15.52 for $Ru_3H_3(CO)_9(SiCl_3)_3$. For $Os(CO)_4(SiXCl_2)(H)$[12] the hydride signal is at δ −7.94 (X = Cl) and −8.34 (X = Me). The corresponding resonances for the appropriate cluster compounds are −17.20 and −16.59, respectively. The resonances found for the hydrido-cluster complexes are in the region found for other such derivatives.[46] The two signals, in the ratio of 2:1, observed in the carbonyl region of the ^{13}C NMR spectra of the cluster compounds are assigned to the axial and equatorial carbonyls, respectively. It also indicates a static structure, on the NMR time scale, for the carbonyl groups. As in the monomeric derivatives $M(CO)_4(SiXCl_2)_2$, the resonance due to the equatorial carbonyl group comes at a higher field than that due to the axial CO groups, and, also, the signals of the ruthenium derivatives are at higher field to those of osmium.[31] The resonance, in both the ^1H and ^{13}C NMR spectra, due to the methyl group in $Os_3H_3(CO)_9(SiMeCl_2)_3$ remained a singlet even at −120 °C (in $CFCl_2H$ solution), indicative of rapid rotation about the Os–Si bond in solution.

The compound $(\eta\text{-}C_5H_5)Fe(CO)_2(SiMeCl_2)$ shows a doubling of the carbonyl stretching bands in the solution infrared spectrum compared to the two observed for the trichlorosilicon analogue. This is attributed to the presence of two conformational isomers existing in solution.[47] The present dichloromethylsilicon compounds show no such overt splitting although the absorptions are significantly broadened compared to those of the $SiCl_3$ analogues. This suggests that in the iron compound there are two possible configurations of the $SiMeCl_2$ group with a relatively large barrier between them. This might arise from steric interaction of the substituents on the silicon with the cyclopentadienyl ring. In the $M_3H_3(CO)_9(SiMeCl_2)_3$ compounds, on the other hand, it is possible that the barrier between the two conformations found in the solid state is small, perhaps due to the flexible nature of the carbonyl groups. This could lead to intermediate configurations having significant populations in solution and, hence, to the observed general broadening of the carbonyl adsorptions. Similar arguements can be applied to the $M(CO)_4(SiMeCl_2)_2$ derivatives. It is evident, from the bond lengths and angles found in the two conformers of $Os_3H_3(CO)_9(SiMeCl_2)_3$, that there probably is considerable motion in the other parts of the molecule as the $SiMeCl_2$ group rotates.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and to the B.C. Provincial Government for a grant (to G.N.v.B).

Registry No. $Ru_3H_3(CO)_9(SiCl_3)_3$, 79357-01-0; $Ru_3H_3(CO)_9(SiMeCl_2)_3$, 79329-39-8; $Os_3H_3(CO)_9(SiMeCl_2)_3$, 79329-40-1; $Os_3H_3(CO)_9(SiCl_3)_3$, 79329-41-2; $[Ru(CO)_4(SiCl_3)]_2$, 25929-57-1; *cis*-$Ru(CO)_4(SiCl_3)_2$, 36570-60-2; *trans*-$Ru(CO)_4(SiCl_3)_2$, 36570-62-4; *cis*-$Ru(CO)_4(SiMeCl_2)_2$, 58894-92-1; *trans*-$Ru(CO)_4(SiMeCl_2)_2$, 58957-81-6; *cis*-$Os(CO)_4(SiMeCl_2)_2$, 58957-84-9; *trans*-$Os(CO)_4(SiMeCl_2)_2$, 58919-94-1; *cis*-$Os(CO)_4(SiCl_3)_2$, 36570-61-3; *trans*-$Os(CO)_4(SiCl_3)_2$, 58957-82-7; *cis*-$Ru(CO)_4(SiMe_2Cl)_2$, 58894-91-0; *trans*-$Ru(CO)_4(SiMe_2Cl)_2$, 79389-92-7; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; Cl_3SiH, 10025-78-2; Cl_2MeSiH, 75-54-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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