those where no explicit metal–metal bonding is thought to occur, viz., 3.2386 (5) Å in $[Rh_2(CO)_2Cl_2(DPM)_2]$,[11] 3.1520 (8) Å in $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$,[22] and 3.154 (2) Å in $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$.[15] The observed diamagnetism of the complex indicates that at the very least there must be a spin-pairing interaction between the formally 17-electron metal atoms, and the fact that the metal–metal distance is significantly shorter ($\Delta/\sigma = 7.2$) than the $P_1$–$P_2'$ separation within the DPM ligand (3.012 (6) Å) suggests that a metal–metal bond exists. This compression along the metal–metal axis is not the result of constraints of the fluorocarbon bridge since in $[Rh_2(P(OMe)_3)(\mu\text{-}CO)(\mu\text{-}MeO_2CC{=}CCO_2Me)(O_2CMe)(DPM)_2]PF_6$, which contains basically the same bridging ligand and no Rh–Rh bond, the metal–metal distance is 3.386 (1) Å.[8] Also, it should be noted that in $[Rh_2(CNPh)_8]^{2+}$, where a metal–metal bond is required, the metal atoms are separated by 3.193 Å.[18]

The other features of the structure appear normal. Thus the carbon–carbon distances in the phenyl rings range from 1.360 (10) ($C_{141}$–$C_{151}$) to 1.404 (9) Å ($C_{151}$–$C_{161}$) and average 1.382 (8) Å. Also the C–C–C angles average 120.0 (5)° and range from 118.2 (4) ($C_{221}$–$C_{211}$–$C_{261}$) to 121.9 (5)° ($C_{131}$–$C_{121}$–$C_{111}$). The P–F distances in the hexafluorophosphate ion range from 1.490 (7) ($P_3$–$F_6$) to 1.560 (7) Å ($P_3$–$F_5$) and average 1.532 (7) Å. The cis F–P–F angles range from 86.4 (4) to 93.4 (6)° while the trans F–P–F angles are 173.9 (4), 178.1 (4), and 176.8 (4)°. In all respects, therefore, this ion has a normal geometry. The only unusual aspect of the solvent acetone molecule is a rather short $C_{1S}$–$C_{2S}$ distance of 1.40 (1) Å, but this is probably the result of the large thermal motion since no evidence could be found to suggest any positional disorder in any portion of the solvent molecule.

In contrast to the case for $[Rh_2Cl_2(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2]$[9] insertion of carbon monoxide into the metal–metal bond of $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2](PF_6)_2$ does not occur even when it is heated at 60 °C under 2 atm of carbon monoxide for 3 h. This lack of reactivity is probably due in large part to this site being blocked by the isocyanide ligands built on $C_{11}$ and $C_{11}'$ and the phenyl groups built on $C_{112}$ and $C_{112}'$.

## Conclusions

Hexafluorobut-2-yne has been shown to bind to $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ as a cis-dimetalated olefin. The adduct thus formed contains a metal–metal bond that is weaker than that found in related complexes but because of steric constraints does not react with carbon monoxide. The color change from brownish orange to yellow, which is observed when even recrystallized samples of the adduct are treated with carbon monoxide, has been traced to the presence of $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ as an impurity that adds carbon monoxide to yield yellow $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}CO)(DPM)_2](PF_6)_2$.

**Acknowledgment.** We thank the Gulf Oil Foundation and the Tulane University Chemistry Department for financial support. We also thank Dr. Cynthia Day and Crystalytics Co. for their services in providing the data collection and Dr. Charles J. Fritchie, Jr., for the use of his programs and for much helpful discussion and advice.

**Registry No.** $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2{\cdot}2(CH_3)_2CO$, 84848-17-9; Rh, 7440-16-6.

**Supplementary Material Available:** Listings of observed and calculated structure factors (Table II), thermal parameters (Table IV), and idealized hydrogen atom positions (Table V) and a stereoview of the contents of the unit cell (Figure 2) (25 pages). Ordering information is given on any current masthead page.

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# Synthesis and Structure of $Os_3(CO)_{12}(SiCl_3)_2$, a Compound with a Linear $SiOs_3Si$ Backbone. Structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$

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The compounds $Os_3(CO)_{12}(SiXCl_2)_2$ (X = Me, Cl) have been isolated from the reaction of $Os_3(CO)_{12}$ with the appropriate silane, $Cl_2XSiH$, at 140 °C under carbon monoxide pressure (80 atm). The crystal structure of $Os_3(CO)_{12}(SiCl_3)_2$ has been determined by X-ray methods. The space group is $P\bar{1}$ with cell dimensions $a = 11.416$ (3) Å, $b = 9.172$ (4) Å, $c = 8.443$ (4) Å, $\alpha = 123.93$ (3)°, $\beta = 99.87$ (3)°, $\gamma = 98.60$ (3)°, $V = 689.4$ Å$^3$, and $Z = 1$. The structure was solved and refined by block-diagonal least-squares methods for 1989 observed reflections to $R = 0.032$ and $R_w = 0.041$. The molecule has a crystallographic center of symmetry with a linear $SiOs_3Si$ chain (Os–Os = 2.912 (1) Å; Os–Si = 2.377 (3) Å); the carbonyl groups on the terminal Os atoms are staggered with respect to those on the central Os. The spectroscopic properties of $Os_3(CO)_{12}(SiXCl_2)_2$ indicate the linear chain is maintained in solution. The crystal structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$ has also been determined: space group *Pnam*, $a = 17.312$ (2) Å, $b = 17.899$ (3) Å, $c = 9.427$ (2) Å, $V = 2921.1$ Å$^3$, $Z = 4$. The structure was refined to $R = 0.054$ and $R_w = 0.061$ for 923 observed reflections. The molecule has a triangular arrangement of osmium atoms in which each Os–Os bond is presumed bridged by a hydrogen atom (Os–Os = 3.132 (3), 3.133 (3), 3.123 (3) Å). The three Os atoms lie on a crystallographic mirror plane, with the Si atoms also lying in the plane (Os–Si = 2.39 (1), 2.39 (1), 2.37 (1) Å).

## Introduction

A number of osmium carbonyl derivatives have the formulation $Os_3(CO)_{12}X_2$, e.g., with X = H,[1] $CH_3$,[2] and halogen.[3] The most probable structures for an $Os_3(CO)_{12}X_2$ compound are shown in **1**–**4**.[4] Spectroscopic evidence suggests that structure **3** is the one commonly adopted. Although structure **4** was thought to pertain to the halogen complexes, subsequent

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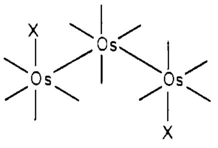
(4) The carbonyl groups are omitted and the structures drawn in an eclipsed conformation, for clarity. All crystallographic studies on these compounds have shown that a staggered arrangement is adopted in the solid state.

0020-1669/83/1322-1162$01.50/0



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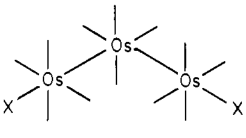

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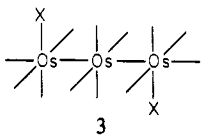

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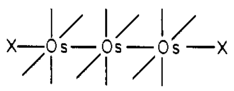

4

work indicated this was probably not the case.[5] This was confirmed for the iodo derivative by a crystal structure determination.[6] Similarly, a compound initially thought to be $Ph_3PAuOs_3(CO)_{12}Cl$ with a linear $AuOs_3Cl$ unit was later shown to be $Os_3(CO)_{10}(AuPPh_3)(Cl)$ with bridging $AuPPh_3$ and Cl ligands.[7]

In our investigation of the mechanism of formation of the $Os_3$ $(\mu\text{-}H)_3(CO)_9(SiXCl_2)_3$ (X = Me, Cl) clusters[8] the compounds $Os_3(CO)_{12}(SiXCl_2)_2$ were isolated. The spectroscopic evidence suggested these complexes were exceptional in that they had a structure of type **4**. Herein we report the details of the preparation and spectroscopic properties of these compounds along with an X-ray diffraction study of $Os_3(CO)_{12}(SiCl_3)_2$ that confirms the linear nature of the $SiOs_3Si$ skeleton. The crystal structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$ is also reported and compared to those of $Os_3(CO)_{12}(SiCl_3)_2$ and the previously described $Os_3(\mu\text{-}H)_3(CO)_9(SiMeCl_2)_3$.

## Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dodecacarbonyltriosmium was prepared by a literature method.[3] The silanes were commercially available and used without further purification. Reactions were carried out in a 200-mL general-purpose bomb from Parr Instrument Co.; it was fitted with a safety disk rated at 3000 psi.

Infrared spectra were obtained with a Perkin-Elmer 237 spectrometer fitted with an external recorder. The spectra (carbonyl region) were calibrated by using carbon monoxide. NMR spectra were obtained on a Bruker 400-MHz instrument. Mass spectra were taken with an Associated Electrical Industries MS-50 spectrometer (regional facility, University of British Columbia); they were obtained by using direct introduction of the solid samples and an ionization voltage of 80 eV. The most abundant peak of the parent ion in the mass spectrum was calculated with use of a computer program obtained from Professor W. A. G. Graham of the University of Alberta. Melting points were obtained with a Gallenkamp instrument on samples sealed in capillaries under nitrogen. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

**Preparation of $Os_3(CO)_{12}(SiCl_3)_2$.** A general-purpose bomb (fitted with a glass liner) was charged with $Os_3(CO)_{12}$ (0.30 g, 0.33 mmol), hexane (20 mL), and $Cl_3SiH$ (2.5 mL, 3.4 g, 25 mmol), pressurized with carbon monoxide (80 atm), and heated in an oil bath at 140 °C for 8 h. (The solution was stirred during this time; the working pressure was ca. 120 atm). After the 8-h period the vessel was allowed to cool to approximately 50 °C, the gases were slowly vented, and the warm solution was transferred to a Schlenk flask. The flask was placed in the refrigerator at −15 °C overnight during which time a white solid precipitated. The mother solution was removed from the solid, which was washed with hexane (2 × 5 mL) and dried on the vacuum line. A coproduct of *trans*-$Os(CO)_4(SiCl_3)_2$[8] ($\nu$(CO) 2081 $cm^{-1}$, hexane solution) was removed from the desired product by sublimation at 65 °C (<0.5 mm) to a probe at −78 °C (this took approximately 5 h). The yield of *trans*-$Os(CO)_4(SiCl_3)_2$ thus isolated was 0.14 g (25%). The crude $Os_3(CO)_{12}(SiCl_3)_2$ (0.18 g, 46%) remaining from the sublimation was recrystallized from hot hexane to give the pure product (0.13 g, 33%) as very pale yellow, almost colorless, crystals. An infrared spectrum of the mother solution revealed the presence of *cis*-$Os(CO)_4(SiCl_3)(H)$[9] ($\nu$(CO) 2150, 2087, 2069 $cm^{-1}$) besides *trans*-$Os(CO)_4(SiCl_3)_2$. There was considerable unreacted starting material when a time period of 2 h was used for the reaction.

Table I. Crystal Data[a]

| | A | B |
|---|---|---|
| | $C_{12}Cl_6O_{12}Os_3Si_2$ | $C_9H_3Cl_9O_9Os_3Si_3$ |
| cryst syst | triclinic | orthorhombic |
| space group | $P\bar{1}$ | *Pnam*[b] |
| *a*, Å | 11.416 (3) | 17.312 (2) |
| *b*, Å | 9.172 (4) | 17.899 (3) |
| *c*, Å | 8.443 (4) | 9.427 (2) |
| $\alpha$, deg | 123.93 (3) | 90.0 |
| $\beta$, deg | 99.87 (3) | 90.0 |
| $\gamma$, deg | 98.60 (3) | 90.0 |
| *V*, $Å^3$ | 689.4 | 2921.1 |
| *Z* | 1 | 4 |
| fw | 1175.96 | 1229.06 |
| $\rho_{calcd}$, g $cm^{-3}$ | 2.832 | 2.794 |
| $\rho_{obsd}$, g $cm^{-3}$ | 2.82[c] | 2.76[c] |
| $\mu$, $cm^{-1}$ | 153.23 | 140.19 |

[a] Esd's of the least significant figures are given in parentheses in this and the succeeding tables. [b] Nonstandard setting of space group *Pnma*. [c] By flotation in $CHBr_3$-hexane.

Table II. Data Collection and Refinement

| | A | B |
|---|---|---|
| scan width, deg[a] | 1.6 | 1.4 |
| background count[b] | 0.4 | 0.25 |
| $2\theta$ max, deg | 50 | 40 |
| total no. of reflns | 2437 | 1484 |
| no. of reflns ($I > 2.3\sigma(I)$) | 1989 | 923 |
| no. of variables | 160 | 162 |
| *R* | 0.032 | 0.054 |
| $R_w$ | 0.041 | 0.061 |

[a] Also corrected for dispersion. [b] Stationary-crystal, stationary-counter background count at each side of the scan, expressed as a fraction of total scan time.

The pale yellow methyldichlorosilyl analogue, $Os_3(CO)_{12}(SiMeCl_2)_2$, was prepared in a similar manner with the exception that a reaction time of 5 h was used; the yield was higher (61% for the crude product). Both compounds appeared reasonably air stable: they showed only superficial etching after 24 h of exposure to air. From the reaction of $ClMe_2SiH$ with $Os_3(CO)_{12}$ under the same conditions, only $Os(CO)_4(SiMe_2Cl)_2$[8] could be isolated. Similarly, $Ru_3(CO)_{12}$ and $Cl_3SiH$, at 90 °C, gave only $[Ru(CO)_4(SiCl_3)]_2$ and $Ru(CO)_4(SiCl_3)_2$.[8]

Anal. Calcd for $C_{12}O_{12}Si_2Cl_6Os_3$: C, 12.26; H, 0.00. Found: C, 12.58; H, 0.00. Mass spectrum (*m/e*): calcd (most abundant peak of the parent ion), 1176; found, 1176. Anal. Calcd for $C_{14}H_6O_{12}Si_2Cl_4Os_3$: C, 14.82; H, 0.53. Found: C, 15.10; H, 0.63. Mass spectrum (*m/e*): calcd, 1136; found, 1136. Spectroscopic and melting point data are recorded in Table VIII.

**X-ray Data Collection for $Os_3(CO)_{12}(SiCl_3)_2$ and $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$.** Crystals of $Os_3(CO)_{12}(SiCl_3)_2$ (A) were obtained by crystallization from a hexane solution as large flat plates. A fragment, 0.054 × 0.182 × 0.242 mm, was cleaved from a large crystal and mounted in a Lindemann capillary for this study. Crystals of $Os_3H_3(CO)_9(SiCl_3)_3$ (B) (also obtained by crystallization from hexane) looked suitable under a microscope. However, X-ray photographs showed that they diffracted very weakly, and most were twinned. Only one crystal (0.090 × 0.112 × 0.228 mm) among those examined gave a single diffraction pattern; this was mounted in a Lindemann capillary and used for data collection.

The data collections for A and B were similar. X-ray photographs taken with Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å) revealed the Laue symmetry (and the systematic absences of B) and gave approximate

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**Table III.** Final Positional Parameters for $Os_3(CO)_{12}(SiCl_3)_2$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Os(1) | 0.29718 (3) | 0.64240 (4) | 0.44619 (5) |
| Os(2) | 0.50000 | 0.50000 | 0.50000 |
| Si | 0.1381 (2) | 0.7724 (4) | 0.4124 (4) |
| Cl(1) | 0.1533 (3) | 0.8659 (5) | 0.2429 (5) |
| Cl(2) | 0.1387 (3) | 0.9998 (4) | 0.6789 (4) |
| Cl(3) | −0.0407 (3) | 0.6027 (5) | 0.2842 (7) |
| C(11) | 0.1752 (9) | 0.3971 (13) | 0.2973 (16) |
| O(11) | 0.1093 (8) | 0.2541 (10) | 0.2062 (14) |
| C(12) | 0.3260 (9) | 0.5816 (13) | 0.1956 (14) |
| O(12) | 0.3430 (8) | 0.5461 (11) | 0.0542 (10) |
| C(13) | 0.4203 (9) | 0.8852 (12) | 0.5964 (13) |
| O(13) | 0.4879 (7) | 1.0236 (9) | 0.6877 (11) |
| C(14) | 0.2752 (9) | 0.6969 (12) | 0.6954 (14) |
| O(14) | 0.2676 (8) | 0.7374 (10) | 0.8448 (11) |
| C(21) | 0.4333 (9) | 0.2822 (12) | 0.2237 (14) |
| O(21) | 0.3978 (8) | 0.1561 (9) | 0.0608 (10) |
| C(22) | 0.5985 (10) | 0.6264 (12) | 0.4187 (15) |
| O(22) | 0.6524 (9) | 0.6964 (10) | 0.3695 (13) |

**Table IV.** Final Positional Parameters for $Os_3H_3(CO)_9(SiCl_3)_3$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Os(1) | 0.34705 (10) | 0.49434 (10) | 0.25000 |
| Os(2) | 0.17760 (10) | 0.43300 (10) | 0.25000 |
| Os(3) | 0.20696 (11) | 0.60514 (9) | 0.25000 |
| Si(1) | 0.4204 (8) | 0.3813 (8) | 0.2500 |
| Cl(11A)[a] | 0.5329 (19) | 0.3885 (16) | 0.2500 |
| Cl(11B)[b] | 0.3633 (31) | 0.2839 (28) | 0.2500 |
| Cl(12A)[a] | 0.4000 (13) | 0.3175 (12) | 0.0812 (26) |
| Cl(12B)[b] | 0.4938 (24) | 0.3697 (23) | 0.0847 (53) |
| Si(2) | 0.0404 (8) | 0.4165 (8) | 0.2500 |
| Cl(21) | −0.0200 (9) | 0.5120 (10) | 0.2500 |
| Cl(22) | −0.0001 (6) | 0.3597 (9) | 0.0834 (17) |
| Si(3) | 0.2752 (9) | 0.7197 (7) | 0.2500 |
| Cl(31) | 0.2129 (10) | 0.8137 (7) | 0.2500 |
| Cl(32) | 0.3504 (7) | 0.7313 (6) | 0.0848 (13) |
| C(11) | 0.4393 (33) | 0.5538 (31) | 0.2500 |
| O(11) | 0.4962 (22) | 0.5822 (21) | 0.2500 |
| C(12) | 0.3494 (17) | 0.4894 (17) | 0.0494 (32) |
| O(12) | 0.3488 (12) | 0.4846 (14) | −0.0746 (25) |
| C(21) | 0.1761 (30) | 0.3266 (29) | 0.2500 |
| O(21) | 0.1841 (22) | 0.2615 (18) | 0.2500 |
| C(22) | 0.1721 (16) | 0.4355 (13) | 0.0560 (37) |
| O(22) | 0.1704 (13) | 0.4366 (13) | −0.0685 (25) |
| C(31) | 0.1154 (28) | 0.6618 (25) | 0.2500 |
| O(31) | 0.0528 (19) | 0.6903 (17) | 0.2500 |
| C(32) | 0.2081 (17) | 0.6063 (15) | 0.0621 (44) |
| O(32) | 0.2073 (14) | 0.6103 (12) | −0.0764 (31) |

[a] Occupancy 0.65. [b] Occupancy 0.35.

**Table V.** Interatomic Distances (Å) and Angles (deg) for $[Os_3(CO)_{12}(SiCl_3)_2]$

| | | | |
|---|---|---|---|
| Os(1)–Os(2) | 2.9120 (9) | Si–Cl(1) | 2.055 (4) |
| Os(1)–Si | 2.377 (3) | Si–Cl(2) | 2.040 (4) |
| Os(1)–C(11) | 1.972 (10) | Si–Cl(3) | 2.043 (4) |
| Os(1)–C(12) | 1.968 (10) | C(11)–O(11) | 1.121 (12) |
| Os(1)–C(13) | 1.960 (9) | C(12)–O(12) | 1.110 (12) |
| Os(1)–C(14) | 1.945 (9) | C(13)–O(13) | 1.101 (11) |
| Os(2)–C(21) | 1.936 (9) | C(14)–O(14) | 1.123 (12) |
| Os(2)–C(22) | 1.960 (10) | C(21)–O(21) | 1.134 (11) |
| | | C(22)–O(22) | 1.109 (12) |
| Os(2)–Os(1)–Si | 177.39 (7) | Os(1)–Os(2)–Os(1)[a] | 180.0 |
| Os(2)–Os(1)–C(11) | 90.9 (3) | Os(1)–Os(2)–C(21) | 91.2 (3) |
| Os(2)–Os(1)–C(12) | 88.0 (3) | Os(1)–Os(2)–C(22) | 89.8 (3) |
| Os(2)–Os(1)–C(13) | 88.3 (3) | Os(1)–Os(2)–C(21)[a] | 88.8 (3) |
| Os(2)–Os(1)–C(14) | 89.1 (3) | Os(1)–Os(2)–C(22)[a] | 90.2 (3) |
| Si–Os(1)–C(11) | 91.7 (3) | C(21)–Os(2)–C(22) | 90.0 (4) |
| Si–Os(1)–C(12) | 92.4 (3) | C(21)–Os(2)–C(21)[a] | 180.0 |
| Si–Os(1)–C(13) | 89.1 (3) | C(21)–Os(2)–C(22)[a] | 90.0 (4) |
| Si–Os(1)–C(14) | 90.6 (3) | C(22)–Os(2)–C(22)[a] | 180.0 |
| C(11)–Os(1)–C(12) | 90.5 (4) | Os(2)–C(21)–O(21) | 177.8 (10) |
| C(11)–Os(1)–C(13) | 179.1 (4) | Os(2)–C(22)–O(22) | 178.7 (10) |
| C(11)–Os(1)–C(14) | 89.4 (4) | Os(1)–Si–Cl(1) | 113.78 (15) |
| C(12)–Os(1)–C(13) | 89.9 (4) | Os(1)–Si–Cl(2) | 113.50 (15) |
| C(12)–Os(1)–C(14) | 177.1 (4) | Os(1)–Si–Cl(3) | 116.11 (15) |
| C(13)–Os(1)–C(14) | 90.2 (4) | Cl(1)–Si–Cl(2) | 103.2 (2) |
| Os(1)–C(11)–O(11) | 176.5 (10) | Cl(1)–Si–Cl(3) | 104.2 (2) |
| Os(1)–C(12)–O(12) | 179.2 (8) | Cl(2)–Si–Cl(3) | 104.7 (2) |
| Os(1)–C(13)–O(13) | 177.0 (8) | | |
| Os(1)–C(14)–O(14) | 176.2 (8) | | |

[a] Atoms are related to those given in Table III by the transformation $1-x, 1-y, 1-z$.

unit cell dimensions. The crystals were then transferred to a Picker FACS-I four-circle automated diffractometer where graphite-monochromatized Mo K$\alpha_1$ radiation ($\lambda = 0.709\,30$ Å) was used. Accurate cell dimensions were obtained by least squares from the setting angles of reflections widely separated in reciprocal space, which were accurately centered on the detector: 20 with $27° < 2\theta < 34°$ for A and 24 with $22° < 2\theta < 27°$ for B. Crystal data for A and B are given in Table I. The intensities of a unique data set were collected in each case by using a $\theta$–$2\theta$ scan running at 2° min$^{-1}$. Details of the data collections are given in Table II. Two standards were measured after every 75 reflections to check stability. For B there was no indication of decomposition, but for A the standards showed an approximate 3% linear decrease in intensity over the time of the data collection, and so the data were scaled appropriately. Reflections where $I > 2.3\sigma(I)$ were regarded as observed and used in the structure solution and refinement. Analytic absorption corrections were applied to each data set ($T$ = 0.441–0.126 for A, 0.288–0.233 for B).

**Determination and Refinement of the Structures.** In both structures the coordinates of the Os atoms were determined from the three-dimensional Patterson map. Fourier maps phased by these atoms revealed all remaining (non-hydrogen) atoms. All atoms in A were refined with anisotropic temperature factors. For B a difference-Fourier map, which was calculated after several cycles of least squares, revealed that the Cl atoms about Si(1) were disordered. A reasonable approximation to the observed electron density was obtained by assuming that there were two orientations of the Cl atoms, one of occupancy 0.65 and the other 0.35. The temperature factors of these atoms were kept isotropic in all further refinement. The remaining atoms were assigned anisotropic temperature factors, but upon refinement, C(11), C(21), and C(31) gave nonpositive-definite determinants and so were constrained to be isotropic. The hydride atoms were not located.[10] In each case the structure was refined to completeness (all shift:error ratios <0.15).

Refinement was by block-diagonal (Gauss–Siedel) least-squares analysis minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma(F))^2 + 0.0009F^2]^{-1}$. Neutral-atom scattering factors with anomalous dispersion corrections[11] were used throughout. Computer programs[12] were run on a PDP-8e computer.

Final positional parameters for A and B are reported in Tables III and IV, respectively. Bond length and angle data for $Os_3(CO)_{12}(SiCl_3)_2$ are given in Table V and for $Os_3H_3(CO)_9(SiCl_3)_3$ in Table VI.

## Results and Discussion

Reaction of a hexane solution of $Os_3(CO)_{12}$ with $Cl_2XSiH$ (X = Me, Cl) at 140 °C under carbon monoxide (80 atm) gave $Os_3(CO)_{12}(SiXCl_2)_2$ and *trans*-$Os(CO)_4(SiXCl_2)_2$ after 5–8 h. The products were separated by sublimation of the mononuclear compound. Trinuclear derivatives were not observed in the corresponding reactions of $Os_3(CO)_{12}$ and $ClMe_2SiH$ (product $Os(CO)_4(SiMe_2Cl)_2$) or of $Ru_3(CO)_{12}$ with $Cl_3SiH$ (products $Ru(CO)_4(SiCl_3)_2$ and $[Ru(CO)_4(SiCl_3)]_2$). Prolonged reaction (at higher temperatures) of $M_3(CO)_{12}$ (M = Ru, Os) with $Cl_2XSiH$ under CO pressure gives exclusively $M(CO)_4(SiXCl_2)_2$.[13] It is probable, therefore, that the reaction under CO pressure proceeds with

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(10) If it is assumed that each hydrogen atom forms a symmetric bridge between two osmium atoms with $r_{Os-H}$ = 1.83 Å, then they are located at (0.2817, 0.4139, 0.25), (0.1382, 0.5277, 0.25), and (0.3117, 0.5904, 0.25).

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**Table VI.** Interatomic Distances (A) and Angles (deg) for $[Os_3H_3(CO)_9(SiCl_3)_3]$

| | | | | | |
|---|---|---|---|---|---|
| Os(1)-Os(2) | 3.132 (3) | Os(2)-Os(3) | 3.123 (3) | Os(3)-Os(1) | 3.133 (3) |
| Os(1)-Si(1) | 2.389 (12) | Os(2)-Si(2) | 2.394 (14) | Os(3)-Si(3) | 2.367 (13) |
| Os(1)-C(11) | 1.92 (6) | Os(2)-C(21) | 1.91 (5) | Os(3)-C(31) | 1.88 (5) |
| Os(1)-C(12) | 1.89 (3) | Os(2)-C(22) | 1.83 (3) | Os(3)-C(32) | 1.77 (4) |
| Si(1)-Cl(11A) | 1.95 (3) | Si(2)-Cl(21) | 2.00 (2) | Si(3)-Cl(31) | 2.00 (2) |
| Si(1)-Cl(12A) | 1.99 (3) | Si(2)-Cl(22) | 2.00 (2) | Si(3)-Cl(32) | 2.04 (1) |
| Si(1)-Cl(11B) | 2.00 (5) | | | | |
| Si(1)-Cl(12B) | 2.02 (5) | | | | |
| C(11)-O(11) | 1.11 (7) | C(21)-O(21) | 1.17 (6) | C(31)-O(31) | 1.20 (6) |
| C(12)-O(12) | 1.17 (4) | C(22)-O(22) | 1.17 (4) | C(32)-O(32) | 1.31 (5) |
| Os(3)-Os(1)-Os(2) | 59.79 (6) | Os(1)-Os(2)-Os(3) | 60.11 (6) | Os(2)-Os(3)-Os(1) | 60.09 (6) |
| Os(3)-Os(1)-Si(1) | 161.4 (4) | Os(1)-Os(2)-Si(2) | 166.6 (4) | Os(2)-Os(3)-Si(3) | 159.4 (4) |
| Os(3)-Os(1)-C(11) | 107.0 (17) | Os(1)-Os(2)-C(21) | 111.3 (16) | Os(2)-Os(3)-C(31) | 113.2 (14) |
| Os(3)-Os(1)-C(12) | 92.7 (9) | Os(1)-Os(2)-C(22) | 92.3 (8) | Os(2)-Os(3)-C(32) | 90.8 (9) |
| Os(2)-Os(1)-Si(1) | 101.6 (4) | Os(3)-Os(2)-Si(2) | 106.4 (4) | Os(1)-Os(3)-Si(3) | 99.3 (4) |
| Os(2)-Os(1)-C(11) | 166.8 (17) | Os(3)-Os(2)-C(21) | 171.4 (16) | Os(1)-Os(3)-C(31) | 173.3 (14) |
| Os(2)-Os(1)-C(12) | 90.2 (9) | Os(3)-Os(2)-C(22) | 89.1 (7) | Os(1)-Os(3)-C(32) | 89.9 (8) |
| Si(1)-Os(1)-C(11) | 91.6 (11) | Si(2)-Os(2)-C(21) | 82.1 (16) | Si(3)-Os(3)-C(31) | 87.3 (15) |
| Si(1)-Os(1)-C(12) | 87.1 (9) | Si(2)-Os(2)-C(22) | 87.2 (9) | Si(3)-Os(3)-C(32) | 89.1 (10) |
| C(11)-Os(1)-C(12) | 90.5 (9) | C(21)-Os(2)-C(22) | 91.3 (8) | C(31)-Os(3)-C(32) | 90.2 (8) |
| C(12)-Os(1)-C(12)[a] | 174.1 (13) | C(22)-Os(2)-C(22)[a] | 173.4 (13) | C(32)-Os(3)-C(32) | 178.1 (14) |
| Os(1)-Si(1)-Cl(11A) | 118.4 (11) | Os(2)-Si(2)-Cl(21) | 114.4 (8) | Os(3)-Si(3)-Cl(31) | 117.4 (8) |
| Os(1)-Si(1)-Cl(12A) | 113.1 (7) | Os(2)-Si(2)-Cl(22) | 114.2 (6) | Os(3)-Si(3)-Cl(32) | 114.0 (5) |
| Cl(11A)-Si(1)-Cl(12A) | 102.4 (9) | Cl(21)-Si(2)-Cl(22) | 104.6 (8) | Cl(31)-Si(3)-Cl(32) | 105.0 (6) |
| Cl(12A)-Si(1)-Cl(12A)[a] | 106.1 (11) | Cl(22)-Si(2)-Cl(22)[a] | 103.7 (9) | Cl(32)-Si(3)-Cl(32) | 99.5 (8) |
| Os(1)-Si(1)-Cl(11B) | 118.3 (16) | | | | |
| Os(1)-Si(1)-Cl(12B) | 114.9 (13) | | | | |
| Cl(11B)-Si(1)-Cl(12B) | 102.7 (16) | | | | |
| Cl(12B)-Si(1)-Cl(12B)[a] | 100.9 (19) | | | | |
| Os(1)-C(11)-O(11) | 174 (5) | Os(2)-C(21)-O(21) | 172 (5) | Os(3)-C(31)-O(31) | 173 (4) |
| Os(1)-C(12)-O(12) | 178 (3) | Os(2)-C(22)-O(22) | 178 (3) | Os(3)-C(32)-O(32) | 177 (2) |

[a] Atoms are related to those given in Table IV by the transformation $x$, $y$, $^1/_2 - z$.

stepwise metal–metal bond cleavage and that the products isolated depend on the relative rate constants for M–M bond breaking in the various $Cl_{3-x}Me_xSi[M(CO)_4]_nSiMe_xCl_{3-x}$ ($x$ = 0–2; $n$ = 3, 2) intermediates. The results also suggest that the $SiMe_2Cl$ ligand labilizes the metal–metal bonds to a greater extent than $SiXCl_2$.

There was no evidence for hydrides of the type $(H)[M(CO)_4]_n(SiMe_xCl_{3-x})$ ($n$ = 3, 2), and it is assumed that under the conditions the M–H bond is rapidly converted to M–$SiMe_xCl_{3-x}$. However, as we have previously reported, if the same reaction is carried out in the absence of CO pressure, the products are $M_3H_3(CO)_9(SiXCl_2)_3$ and $M(CO)_4(SiXCl_2)_2$.[8] At that time it was suggested that the initial step in the formation of the cluster compound involved the cleavage of an osmium–osmium bond to give $(H)Os_3(CO)_{12}(SiXCl_2)$ (of structural type **1**) rather than CO dissociation to give $Os_3(CO)_{11}(SiCl_3)(H)$. The isolation of the trinuclear products, $Os_3(CO)_{12}(SiXCl_2)_3$, from the corresponding reactions under CO pressures supports this supposition. That CO dissociation is partly involved in the rate-determining step cannot be completely ruled out since the reactions did appear to be slightly impeded by CO pressure, although this may have been due to slightly different experimental conditions in the two cases. The failure to observe trinuclear ruthenium compounds in the reactions carried out under CO pressure may be due to cleavage of the ruthenium–ruthenium bonds by carbon monoxide. It is known that $Ru_3(CO)_{12}$ reacts with CO to give $Ru(CO)_5$ at elevated temperatures and pressures.[13,14]

**Crystal Structure of $Os_3(CO)_{12}(SiCl_3)_2$.** An ORTEP view of the molecule is shown in Figure 1; a view down the $SiOs_3Si$ axis showing the staggered arrangement is depicted in Figure 2. Bond length and angle data are recorded in Table V. The compound represents a rare example of a metal–carbonyl compound that contains a linear five-member chain of metal, or metalloid, atoms. (There are a few examples of metal-carbonyl compounds in the literature that have pentametallic chains,[15] but in no case does the geometry of the unit appear

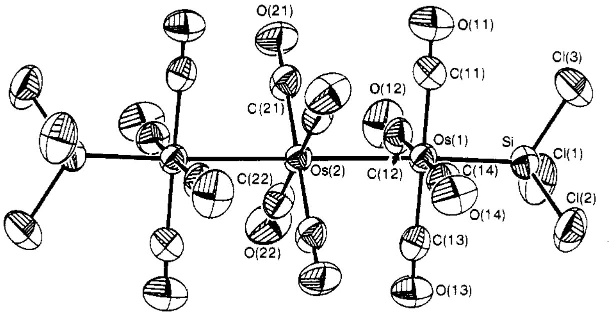

**Figure 1.** Projection of the $Os_3(CO)_{12}(SiCl_3)_2$ molecule, showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels.

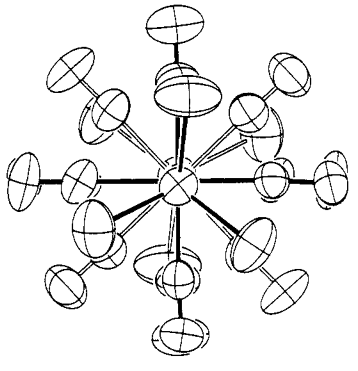

**Figure 2.** View of the $Os_3(CO)_{12}(SiCl_3)_2$ molecule down the $Os_3$ axis. Bonds in the closest $Os(CO)_4$ and $SiCl_3$ units are blocked in. The view, with respect to Figure 1, is from right to left.

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**Table VII.** Selected Bond Length and Angle Data for Some Iron and Ruthenium (M)–Group 4 (E) Complexes

| compd | M–E bond length(s), Å | range of the MEX[a] angle, deg | range of the XEX angle, deg |
|---|---|---|---|
| *cis*-$Fe(CO)_4(SiMe_3)_2$[b] | 2.456 (2) | 110.3 (2)–114.4 (2) | 106.2 (3)–108.3 (3) |
| *trans*-$Fe(CO)_4(SiCl_3)_2$[c] | 2.326 (2) | 113.3 (1)–115.1 (1) | 103.9 (1)–105.6 (1) |
| $(C_5H_5)Fe(CO)(SiCl_3)_2(H)$[d] | 2.252 (3) | 112.2 (1)–116.7 (1) | 102.7 (2)–104.3 (2) |
| $(C_7H_6SiMe_3)Ru_2(CO)_5(SiMe_3)$[e] | 2.452 (3) | 111.4 (5)–114.6 (4) | 104.5 (7)–106.5 (8) |
| $(C_8H_8SiMe_3)Ru(CO)_2(SiMe_3)$[f] | 2.414 (2) | 112.1 (3)–113.1 (3) | 105.4 (5)–107.4 (5) |
| $[(Me_3Si)Ru(CO)_3(SiMe_2)]_2$[g] | 2.507 (8) | 110.7 (6)–118.8 (9) | 104 (1)–106 (1) |
| $(Bu_2C_6H_4)Ru(CO)(SiCl_3)_2$[h] | 2.338 (1)<br>2.340 (1) | 110.7 (4)–120.1 (1) | 99.6 (1)–103.8 (1) |
| $[Ru(CO)_4(SnMe_3)]_2$[i] | 2.691 (1) | 109.6 (2)–113.4 (2) | 106.0 (3)–107.4 (3) |
| $[(Me_3Sn)Ru(CO)_3(SnMe_2)]_2$[j] | 2.686 (2) | 108 (1)–120 (1) | 104 (1)–109 (1) |
| $(\mu\text{-}Cl)_3Ru_2(CO)_5(SnCl_3)$[k] | 2.565 (4) | 113.0 (4)–119.7 (4) | 98.2 (5)–103.7 (5) |
| $(C_6H_6)Ru(CH_3)(L)(SnCl_3)$[l] | 2.543 (1) | 116.2 (1)–124.9 (4) | 96.0 (2)–97.8 (1) |
| $(\mu\text{-}H)(\mu\text{-}S)(\mu\text{-}Cl)Ru_3(CO)_8(SnCl_3)$[m] | 2.571 (1)<br>2.588 (1) | 116.1 (1)–120.9 (1) | 98.7 (1)–102.4 (1) |

[a] X = C or Cl. [b] Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* **1977,** *16,* 897. [c] Whitla, W. A.; Graham, W. A. G., unpublished results. [d] Manojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970,** *9,* 447. [e] Howard, J.; Woodward, P. *J. Chem. Soc. Dalton Trans.* **1975,** 59. [f] Harris, P. J.; Howard, J. A. K.; Knox, S. A. R.; McKinney, R. J.; Phillips, R. P.; Stone, F. G. A.; Woodward, P. *Ibid.* **1978,** 403. [g] Crozat, M. M.; Watkins, S. F. *Ibid.* **1972,** 2512. [h] Einstein, F. W. B.; Jones, T. *Inorg. Chem.* **1982,** *21,* 987. [i] Watkins, S. F. *J. Chem. Soc. A* **1969,** 1552. [k] Elder, M.; Hall, D. *Ibid.* **1970,** 245. [l] L = $Ph_2PNHCH(CH_3)Ph$; ref 27a. [m] Adams, R. D.; Katahira, D. A. *Organometallics* **1982,** *1,* 53.

to have been established.) The staggered conformation is typical and has previously been found in such molecules as $Os_3(CO)_{12}I_2$[6] and $[Mn_3(CO)_{14}]^-$.[16] It has also been observed, in compounds of this type, that the equatorial carbonyl ligands on the terminal metal atoms are bent inward toward the central atom.[6,16] This has been attributed to a bonding interaction between the $\pi^*$ orbitals of the carbonyl groups and the filled d orbitals on the opposite metal atom.[16] On the other hand, in monomeric derivatives of formula $M(CO)_nX$, it is often found (e.g., $Mn(CO)_5(SiMe_3)$, $Co(CO)_4(SiCl_3)$) that the equatorial carbonyls are bent toward X.[17] This, in turn, is thought to be due to an interaction of the $2p_z$ orbital on the carbonyl with the valence s and $p_z$ orbitals on X.[7] In the present molecule, there may be a balance between the two bonding modes since there is no significant bending of the carbonyl substituents on the terminal osmium atoms in either direction. This is true even for the carbonyl (C(11)–O(11)) that is eclipsed (Figure 2) by a chlorine atom on the trichlorosilyl ligand (the Os(2)–Os(1)–C(11) angle is 90.9 (3)°). In contrast, the corresponding Os–Si–Cl angle has opened up to 116.11 (15)°, compared to a mean value of 113.64° for the Os–Si–Cl angles for the noneclipsed chlorines.

The Os–Os distance (2.912 (1) Å) in $Os_3(CO)_{12}(SiCl_3)_2$ is somewhat longer than usual unbridged Os–Os bond lengths; e.g., in $Os_3(CO)_{12}$ the mean value is 2.877 (13) Å.[18] However, it is comparable to the corresponding distance in $Os_3(CO)_{12}I_2$ (2.935 (2) Å)[6] and the Os–Os vectors involving the central osmium atom in $Os_5(CO)_{19}$.[19] In the latter molecule, two $Os_3$ triangles share an apex (in a "bow-tie" arrangement). The four Os–Os lengths to the central atom (mean 2.930 Å) are significantly longer than the two external Os–Os distances (2.851 Å). The lengthening, therefore, of the Os–Os bond in these molecules appears to be a reflection of the trans influence of the other osmium carbonyl group.

**Nature of the Os–Si Bond.** MacDiarmid and co-workers have analyzed the nature of the bonding between silicon and cobalt tetracarbonyl in silylcobalt tetracarbonyls.[17] Results from molecular structure data, mass spectral studies, and molecular orbital calculations, they concluded, were consistent with the presence of partial double-bond character in the Co–Si linkage. Similarly, Graham and co-workers have concluded that the $SiCl_3$ ligand has strong $\pi$-acceptor properties in first-row transition-metal carbonyl complexes[20] and in $Ru(CO)_4(SiCl_3)_2$.[21] A review of complexes with silicon–transition-metal bonds agrees with these ideas.[22]

The results of this study are also consistent with this view. A normal covalent Os–Si bond length of 2.59 Å may be estimated from the Si–Si distance (2.30 Å) in $Si_2Cl_6$[23] and the Os–Os vector (2.877 Å) in $Os_3(CO)_{12}$.[17,24] The observed bond length of 2.377 (3) Å is more than 0.2 Å shorter than this value, in agreement with some multiple bonding between the osmium and silicon atoms.

We have previously rationalized the fact that the trans isomer is thermodynamically the most stable isomer of $Os(CO)_4(SiCl_3)_2$ in terms of the $\pi$-acceptor properties of the $SiCl_3$ ligand.[25] Thus most compounds of the type $M(CO)_4X_2$ (M = Fe, Ru, Os) exist as the cis isomer since this avoids, as far as possible, the strong $\pi$-acceptor carbonyl ligands competing for the same $\pi$-electron density on the central metal. However, if the $SiCl_3$ group, when bonded to osmium, has $\pi$-acceptor properties comparable to those of CO, then neither geometry would be preferred on electronic grounds. In such a situation steric factors would dictate the geometry, and hence the trans configuration is the one observed since it minimizes the steric interactions between the bulkier trichlorosilyl substituents. Similar arguments may be applied to the present molecule to explain why the $SiCl_3$ groups are exceptional in adopting positions that are trans to the Os–Os bonds. Models show that there is a close approach of the chlorine atoms of the $SiCl_3$ ligand to the carbonyls on the central osmium atom if the silyl moieties are placed cis to the $Os_3$ chain.

The angles about the silicon atoms in $Os_3(CO)_{12}(SiCl_3)_2$ differ significantly from the tetrahedral value: those involving the transition metal are greater than 109.5° (113.50 (15),

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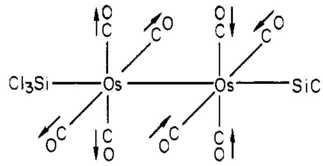
(24) A slightly longer value (2.61 Å) is obtained if the covalent radius of osmium is calculated from the Os–Os length (2.912 Å) actually found in $Os_3(CO)_{12}(SiCl_3)_2$.

(25) Pomeroy, R. K.; Wijesekera, K. S. *Inorg. Chem.* **1980,** *19,* 3729.

113.78 (15), 116.11 (15)°). This is generally observed in complexes with group 4 ligands; some examples pertinent to this discussion are given in Table VII.[26] Previous explanations of this effect have invoked the ideas of Bent: that there is more p character in bonds to the more electronegative substituents (X); i.e., there is more s character in the metal (M) to group 4 element (E) bond.[27] However, the XEX angles would also be expected to close if the M–E bond had significant double-bond character. The correlation between the M–E bond lengths and MEX angles are consistent with these ideas: the more electronegative substituents are expected to cause greater contraction of the d orbitals on E, which results in increased $\pi$-overlap with the d orbitals on M and a shorter M–E bond. These arguments are similar to those applied to phosphorus donor ligands.[28] Various differences in spectroscopic properties and structural parameters of complexes with such ligands have been attributed to the $\pi$-acceptor properties of the ligand. For example, it is generally accepted that phosphites are better $\pi$-acceptor ligands than phosphines.[29] However, a consistent argument based only on $\sigma$-bonding can be put forward to explain differences such as in metal–phosphorus bond lengths.[30]

**The Series $(Cl_3Si)[Os(CO)_4]_n(SiCl_3)$ ($n$ = 1–3).** Some spectroscopic data for this interesting series of molecules and for $Os_3(CO)_{12}(SiMeCl_2)_2$ are given in Table VIII. The $^{13}C$ NMR spectrum of the trinuclear derivatives indicate the linear $SiOs_3Si$ chain is maintained in solution. The carbonyl signals in an approximate 2:1 ratio may be unambiguously assigned to the carbonyl ligands of the terminal and central osmium atoms, respectively.

In contrast to the case of molecules such as $Mn_2(CO)_{10}$,[31] the equatorial carbonyl groups on the ruthenium atoms in $[Ru(CO)_4(SnMe_3)]_2$ are eclipsed.[32] If $[Os(CO)_4(SiCl_3)]_2$ has the same arrangement, then all three molecules in the series $(Cl_3Si)[Os(CO)_4]_n(SiCl_3)$ have $D_{4h}$ symmetry if the threefold symmetry of the $SiCl_3$ group is ignored. For such a symmetry one, two, and three infrared-active CO stretches are predicted respectively for the first, second, and third member of the series. The nature of the $A_{2u}$ mode for $[Os(CO)_4(SiCl_3)]_2$ is depicted in **5**. The corresponding mode for $Os_3(CO)_{12}(SiCl_3)_2$ is similar (it involves only the carbonyls on the terminal osmium atoms); there is, of course, no counterpart for the mononuclear derivative. From a consideration of the infrared spectra of the three molecules, the $A_{2u}$ mode for $[Os(CO)_4]_{2,3}(SiCl_3)_2$ may confidently be assigned to the highest energy absorption in each case. It is expected to be of weak intensity because of the low dipole moment change associated with the vibration. Similarly, from a comparison of the spectra it is probable that the band at 2053 cm⁻¹ in the spectrum of $Os_3(CO)_{12}(SiCl_3)_2$ is due to the $E_u$ mode which mainly involves the carbonyls of the terminal osmium atoms (which are directly bonded to the $SiCl_3$ ligands) and the band at 1991 cm⁻¹ to the $E_u$ mode which mainly involves the carbonyls of the central osmium atom. (The spectrum is shown in Figure 3.)



**5**

Table VIII. Spectroscopic and Melting Point Data for $(Cl_3Si)[Os(CO)_4]_n(SiCl_3)$ ($n$ = 1–3) and $Os_3(CO)_{12}(SiMeCl_2)_2$

| compd | mp, °C | $\nu$(CO), cm⁻¹ [a] | $^{13}C$ NMR, ppm[b] |
|---|---|---|---|
| *trans*-$Os(CO)_4(SiCl_3)_2$[c] | 182 | 2081 vs | 170.3[d] |
| $[Os(CO)_4(SiCl_3)]_2$[e] | 148–151 | 2093 w, 2053 vs | 178.2 |
| $Os_3(CO)_{12}(SiCl_3)_2$ | >185 dec | 2114 w, 2050 vs, 1991 m | 186.8, 177.9[f] |
| $Os_3(CO)_{12}(SiMeCl_2)_2$ | >177 dec | 2106 w, 2038 s, 1986 m | 188.2, 180.3,[f] 29.7[g] |

[a] Hexane solution. [b] $CDCl_3$ solution (except where noted); values are quoted downfield from $Me_4Si$. [c] Reference 13. [d] Toluene-$d_8$ solution; Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407. [e] Reference 9. [f] In approximate ratio of 1:2; high-field signal assigned to carbonyl groups on terminal osmium atoms. [g] Si–$CH_3$, $^1H$ NMR: δ 1.46.

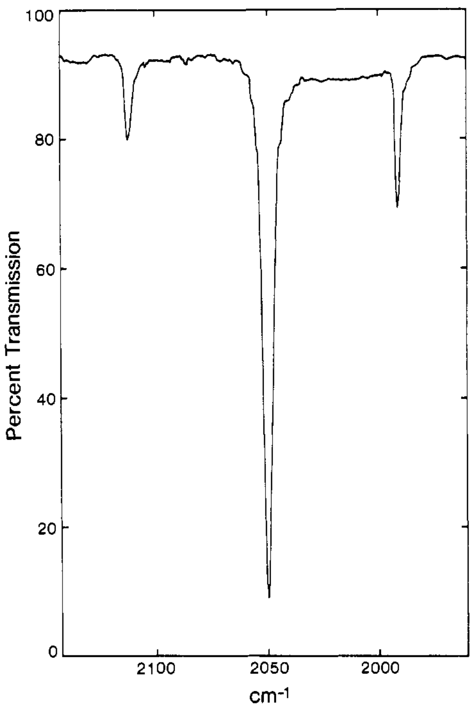


**Figure 3.** Carbonyl stretching region of the infrared spectrum of $Os_3(CO)_{12}(SiCl_3)_2$ in hexane solution.

As mentioned in the discussion on the crystallographic results, it appears that, in $Os_3(CO)_{12}(SiCl_3)_2$, the trans influence of the one osmium atom causes a lengthening of the bond between the other two. This may indicate that the osmium–osmium bonds in $Os_3(CO)_{12}(SiCl_3)_2$ are weaker than that in $Os_2(CO)_8(SiCl_3)_2$. Superficially, however, the two compounds appeared of comparable stability. That this is the case raises the intriguing possibility that higher members of the series might be stable if routes to their synthesis could be found.

**Crystal Structure of $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$.** An ORTEP view of $Os_3H_3(CO)_9(SiCl_3)_3$ is shown in Figure 4; bond lengths and angles are reported in Table VI. (The preparation of this compound has been described previously: it is the major product when $Os_3(CO)_{12}$ and $Cl_3SiH$ are reacted in hexane at 140 °C in an evacuated flask.[8])

The molecule $Os_3(\mu\text{-}H)_3(CO)_9(SiMeCl_2)_3$ was found to have $D_{3h}$ symmetry with the methyl substituent of the silicon ligand in the plane of the osmium atoms. There were two conformers

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(26) Probably because of different steric interactions, angles of the same type about the group 4 element are significantly different. For this reason, the range of the angle in question is quoted rather than the mean.

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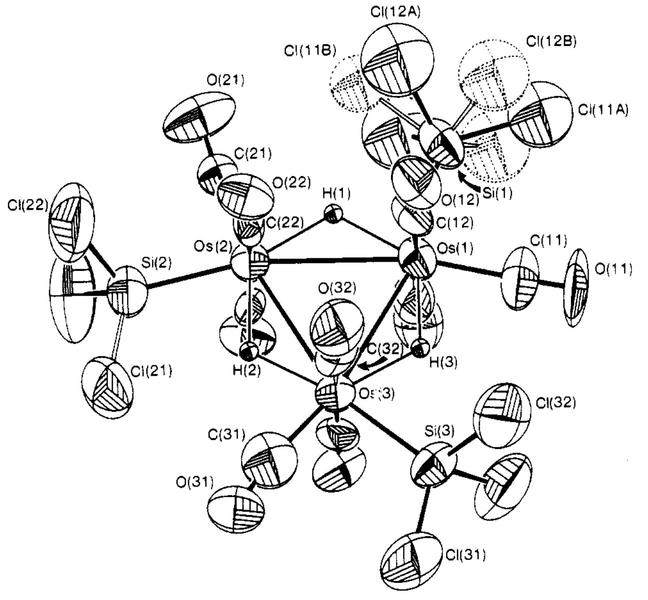

**Figure 4.** Projection of the $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$ molecule, showing the atom-labeling scheme. Both sets of disordered chlorine atoms about Si(1) are shown. Hydrogen atoms are drawn as small spheres at their calculated positions.

present in the same crystal: in one, each methyl group was on the side of the OsHOs bridge, and in the other, each was on the side of the in-plane carbonyl.[8] It is interesting that in the present structure, within an individual molecule, the corresponding in-plane chlorine substituent of one silicon ligand is on the side of the OsHOs bond and in a second it is on the side of the in-plane carbonyl, while in the third, it is disordered between the two positions.

The Os–$SiCl_3$ distances measured in the two structural determinations reported here are not significantly different: 2.377 (3) Å in $Os_3(CO)_{12}(SiCl_3)_2$ and a mean value of 2.383 Å in $Os_3H_3(CO)_9(SiCl_3)_3$. These lengths are slightly shorter than the Os–Si bond lengths in $Os_3H_3(CO)_9(SiMeCl_2)_3$ (mean value 2.410 Å) although the difference is barely significant. This, as discussed previously, may indicate more double-bond character in the Os–$SiCl_3$ linkage.

The osmium–osmium vectors (mean 3.129 Å) found in $Os_3H_3(CO)_9(SiCl_3)_3$ are virtually identical with those found in one conformer of $Os_3H_3(CO)_9(SiMeCl_2)_3$ (3.125 (2) Å); the other conformer had slightly longer Os–Os bonds (3.155 (2) Å). As previously stated, these are among the longest distances determined for such bonds.[8] We are continuing the investigation of silanes with various osmium clusters.

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**Registry No.** A, 84750-97-0; B, 79329-41-2; $Os_3(CO)_{12}(SiMeCl_2)_2$, 84750-98-1; $Os_3(CO)_{12}$, 15696-40-9; Os, 7440-04-2.

**Supplementary Material Available:** Listings of anisotropic thermal parameters and observed and calculated structure factors for A and B (24 pages). Ordering information is given on any current masthead page.

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# Crystal Structures of $V^{IV}$, $V^{V}$, and $V^{IV}V^{V}$ Complexes of the (*S*)-[[1-(2-Pyridyl)ethyl]imino]diacetate Ion. Comparison of the Molecular Structure of the Binuclear Mixed-Valence $V^{IV}V^{V}$ Complex with Those of Constituent $V^{IV}$ and $V^{V}$ Complexes

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The crystal structures of $[VO(S\text{-peida})(H_2O)]\cdot 2H_2O$ (**1**), $Na[V_2O_3(S\text{-peida})_2]\cdot NaClO_4\cdot H_2O$ (**2**), and $Li[VO_2(S\text{-peida})]\cdot 2CH_3OH$ (**3**) have been determined by single-crystal X-ray diffraction ($S$-peida$^{2-}$, (*S*)-[[1-(2-pyridyl)ethyl]imino]diacetate). Every vanadium atom in **1**–**3** has an octahedral coordination with a donor atom disposition similar to the others: the axial sites are occupied by $O^{2-}$ and N (tertiary), and there are two O (OOC), one N (pyridine), and one L ($L = H_2O$ in **1**; $L = O^{2-}$ in **2** and **3**) in the equatorial sites. The two coordination octahedra in the mixed-valence binuclear $[V_2O_3(S\text{-peida})_2]^-$ are linked together by sharing the equatorial $O^{2-}$ ($O_b$) ligand. The $O{=}V_A{-}O_b{-}V_B{=}O$ segment in the dimer has an approximate trans-planar structure ($V{-}O_b{-}V = 179.5\ (3)°$; the torsion angle between the two V=O bonds is 164.3 (2)°). The $V_A{-}O_b$ bond (1.875 (4) Å) differs significantly from the $V_B{-}O_b$ bond (1.763 (4) Å) in length, and furthermore, the volumes of the coordination octahedra around $V_A$ and $V_B$ are close to those of **1** ($V^{IV}$) and **3** ($V^{V}$), respectively: i.e., $V_A$ and $V_B$ are inequivalent. These structural features indicate that the mixed-valence dimer should be classified as a class II ion; however, the reflectance spectrum of **2** in the 9000–20 000-cm$^{-1}$ region resembles that of $(NH_4)_3[V_2O_3(nta)_2]\cdot 3H_2O$, in which the anion is known to be a class III ion ($nta^{3-}$ = nitrilotriacetate). Crystal data: **1**, space group $P2_1$, $a = 7.707\ (3)$ Å, $b = 11.608\ (3)$ Å, $c = 8.802\ (6)$ Å, $\beta = 91.84\ (3)°$, $Z = 2$; **2**, space group $P2_1$, $a = 12.680\ (5)$ Å, $b = 15.273\ (6)$ Å, $c = 7.856\ (3)$ Å, $\beta = 98.25\ (6)°$, $Z = 2$; **3**, space group $P2_12_12_1$, $a = 19.387\ (2)$ Å, $b = 10.259\ (1)$ Å, $c = 8.645\ (1)$ Å, $Z = 4$. The structures were refined by least squares to $R = 0.041$, 0.040, and 0.034 for **1**, **2**, and **3**, respectively, with 2013, 2971, and 1871 reflections $[F_o^2 > 3\sigma(F_o^2)]$.

## Introduction

Coordination chemistry of early transition metals has been drawing increasing attention of chemists, but available structural data are much more limited as compared with those of the other transition elements. During the kinetic study of oxovanadium(IV) complexes we have found the new mixed-valence complex $[V_2O_3(nta)_2]^{3-}$ ($nta^{3-}$ = nitrilotriacetate), in which the two V atoms are linked linearly with the oxide.[2] We

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