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Synthesis, characterisation and reactivity of siloxyl-substituted derivatives of $[Ru_3(CO)_{12}]$. Crystal structure of *trans*-$[Ru_2(CO)_8\{Si(OSiMe_3)_3\}_2]$ †

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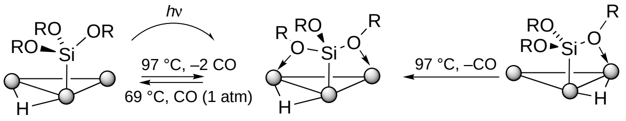
Thermal reactions of the bulky siloxysilanes $HSi(OSiMe_3)_3$ and $HSiMe(OSiMe_3)_2$ with $[Ru_3(CO)_{12}]$ led to the formation of siloxyl-substituted triruthenium clusters. Formal replacement of one or more CO ligands from $[Ru_3(CO)_{12}]$ *via* oxidative addition generates $[Ru_3H(CO)_{11}\{\eta^1\text{-}Si(OSiMe_3)_3\}]$ **1**, $[Ru_3H_2(CO)_{10}\{\eta^1\text{-}Si(OSiMe_3)_3\}_2]$ **3**, $[Ru_3H(CO)_{11}\{\eta^1\text{-}SiMe(OSiMe_3)_2\}]$ **4** and $[Ru_3H_2(CO)_{10}\{\eta^1\text{-}SiMe(OSiMe_3)_2\}_2]$ **6**. Also formed are $[Ru_3H(CO)_{10}\{\eta^2\text{-}Si(OSiMe_3)_3\}]$ **2** and $[Ru_3H(CO)_{10}\{\eta^2\text{-}SiMe(OSiMe_3)_2\}]$ **5** in which a second CO molecule has been displaced from clusters **1** and **4** respectively, resulting in the formation of a dative SiO→Ru interaction. The siloxyl-substituted compounds are thermodynamically unstable and decompose to dinuclear species, $[Ru_2(CO)_8\{Si(OR)_3\}_2]$, and $[Ru_4H_4(CO)_{12}]$ within several hours. Alternatively the dinuclear complexes can be synthesized cleanly and selectively by the photochemical reaction of $[Ru_3(CO)_{12}]$ with the appropriate silane and *trans*-$[Ru_2(CO)_8\{Si(OSiMe_3)_3\}_2]$ **7** has been characterised by X-ray crystallography at 193 K. The structure is strongly disordered.

In reactions with transition-metal centres silanes often behave in a similar fashion to molecular hydrogen, readily undergoing oxidative addition.[1] However, the chemistry of the alkoxysilyl derivatives is made more complicated and more interesting by the possibility of additional dative O→M donor interactions. Four-membered $\overline{M{-}Si{-}O{-}M}'$ ring systems where silicon forms a σ bond to one metal and interacts with a second metal atom *via* a dative O→M′ bond were first established in 1989[2a] and are now quite well known.[2] The nature of the dative interaction may be kinetically labile and is strongly dependent upon the substituents at both the silicon atom and the metal atom, M′. The unusual nature of such interactions, together with their possible relevance to catalysis[2c] and surface phenomena,[3a] particularly in the case of siloxyl ligands such as $Si(OSiMe_3)_3$,[3] has prompted an exploration into the interactions between metal carbonyl clusters and alkoxysilyl ligands. The preparation of trialkoxysilyl-substituted osmium species from labilised clusters, $[Os_3(CO)_{12-x}(NCMe)_x]$, $x = 1$ or 2,[4,5] and $[\{Os_3(CO)_{10}(NCMe)\}_2(\mu\text{-dppe})]$ $(dppe = Ph_2PCH_2CH_2PPh_2)$,[6] has been reported. The $Si(OR)_3$ (R = Me or Et) unit has been observed to act as a one-, three- or five-electron donor in this environment and sequential interconversions between these bonding modes have been effected (Scheme 1).[4,5]



Scheme 1 1 atm = 101 325 Pa

Here we describe our efforts to synthesize siloxyl-substituted ruthenium clusters from $[Ru_3(CO)_{12}]$ using thermal and photochemical means. Reagents of the type $HSi(OR)_3$, $HSiR(OR)_2$ and $HSiR_2(OR)$ were investigated to assess the effects that alterations in both steric and electronic properties of the silane would have upon the derivatives synthesized.

Experimental

General

All reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from the usual drying agents prior to use. Separations were carried out by thin-layer chromatography in air with Kieselgel 60-PF-254 (Merck). Photolysis experiments were carried out in an irradiation vessel using a water-cooled high-pressure mercury lamp (180 W, TQ 150 Heraeus). The starting material $[Ru_3(CO)_{12}]$ was prepared according to the literature;[7] $HSi(OSiMe_3)_3$, $HSiMe(OSiMe_3)_2$ and $HSiMe_2(OEt)$ from United Chemical Technologies and $HBF_4{\cdot}Et_2O$ from Aldrich were used as received. The NMR spectra were recorded on a Bruker 300 or AM 400 spectrometer; ^1H shifts are reported with respect to δ 0 for $SiMe_4$. Infrared spectra were obtained using a Bruker IFS66, a Perkin-Elmer 398 or a FT 1710 spectrophotometer; FAB (fast atom bombardment) mass spectra were resolved using Kratos instruments with 3-nitrobenzyl alcohol as matrix and laser desorption mass spectra obtained using a LaserTec (time of flight, TOF) instrument and dithranol (anthracene-1,8,9-triol) as matrix. Only very accurate elemental analyses would be useful in characterising the compounds considering the very similar calculated elemental values for **1** and **2**, **4** and **5**. Unfortunately the samples are very sensitive and after analysis were always seen to be contaminated with $[Ru_4H_4(CO)_{12}]$ casting doubt on the accuracy of the obtained elemental percentages. Approximate product yields are given in the text but not reported in the Experimental section due to the reactivity of the products with the silica. Thus, although the relative proportions of clusters displaying high-field signals could be assessed from ^1H NMR spectra of crude reaction mixtures, the yields of isolated clusters following TLC separation were affected by subsequent reactions occurring on the silica surface.

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† Dedicated to Professor A. Müller (University of Bielefeld, Germany) on the occasion of his 60th birthday, with our best wishes.

Reaction of $[Ru_3(CO)_{12}]$ with $HSi(OSiMe_3)_3$ or $HSiMe(OSiMe_3)_2$

In a typical reaction, $[Ru_3(CO)_{12}]$ (126 mg, 0.2 mmol) was suspended in hexane (100 cm^3) and heated to reflux to produce an orange solution. The siloxysilane, $HSi(OSiMe_3)_3$ (0.4 cm^3, 1.1 mmol) or $HSiMe(OSiMe_3)_2$ (0.4 cm^3, 1.2 mmol), was added and the reflux continued for about 1 h until all the starting cluster had been consumed. The purple solution was concentrated and the products separated by chromatography using hexane as eluent.

Reaction with $HSi(OSiMe_3)_3$ yielded three major products in order of elution; yellow $[Ru_3H(CO)_{10}\{\eta^2\text{-}Si(OSiMe_3)_3\}]$ **2**, yellow $[Ru_3H_2(CO)_{10}\{Si(OSiMe_3)_3\}_2]$ **3** and purple $[Ru_3H(CO)_{11}\{\eta^1\text{-}Si(OSiMe_3)_3\}]$ **1**. Reaction with $HSiMe(OSiMe_3)_2$ yielded three major products in order of elution; yellow $[Ru_3H(CO)_{10}\{\eta^2\text{-}SiMe(OSiMe_3)_2\}]$ **5**, yellow $[Ru_3H_2(CO)_{10}\{SiMe(OSiMe_3)_2\}_2]$ **6** and purple $[Ru_3H(CO)_{11}\{\eta^1\text{-}SiMe(OSiMe_3)_2\}]$ **4**.

Photochemical reaction of $[Ru_3(CO)_{12}]$ with $HSi(OSiMe_3)_3$ or $HSiMe(OSiMe_3)_2$

The compound $[Ru_3(CO)_{12}]$ (32 mg, 0.05 mmol) was dissolved in hexane (100 cm^3) and $HSi(OSiMe_3)_3$ (0.4 cm^3, 1.1 mmol) or $HSiMe(OSiMe_3)_2$ (0.4 cm^3, 1.2 mmol) added. The yellow solution was irradiated at room temperature for 4 h and then the solvent removed to leave a brown-purple residue. The products were characterised by ^1H NMR spectroscopy as **1** (5), **2** (80) and **3** (10%).

Synthesis of *trans*-$[Ru_2(CO)_8\{Si(OSiMe_3)_3\}_2]$ 7

If the same photochemical reaction described above is carried out at 40 °C, then compound **7** is formed in more than 90% yield and the remaining material is $[Ru_4H_4(CO)_{12}]$. Alternatively, lower yields of **7** can be obtained by addition of $HBF_4{\cdot}Et_2O$ (3 drops) to a hexane solution of **1**, **2** and **3** prepared from $[Ru_3(CO)_{12}]$ (0.05 mmol) as described above. The solution was stirred at room temperature for 18 h and, after filtering through silica, TLC separation using cyclohexane as eluent yielded yellow *trans*-$[Ru_2(CO)_8\{Si(OSiMe_3)_3\}_2]$ **7** (≈40% yield), purple **1** (≈ 40% yield) and $[Ru_4H_4(CO)_{12}]$ (≈ 20% yield).

Synthesis of *trans*-$[Ru_2(CO)_8\{SiMe_2(OEt)\}_2]$ 8

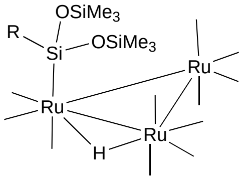
The compound $[Ru_3(CO)_{12}]$ (32 mg, 0.05 mmol) was dissolved in hexane (80 cm^3) and $HSiMe_2(OEt)$ (0.2 cm^3, 1.5 mmol) added. The solution was irradiated at 25 °C for 2 h to yield a yellow solution of **8** in quantitative yield (as observed by IR spectroscopy). Note that removal of the solvent *in vacuo* causes decomposition and yields of **8** are approximately halved if purification *via* TLC is carried out.

Thermal reaction of $[Ru_3(CO)_{12}]$ with $HSiMe_2(OEt)$

The compound $[Ru_3(CO)_{12}]$ (639 mg, 0.1 mmol) was dissolved in hexane (150 cm^3) with heating and $HSiMe_2(OEt)$ (0.4 cm^3, 2.9 mmol) added. The yellow solution was heated at reflux for 1.5 h. After concentration of the solution and TLC separation, using CH_2Cl_2–hexane (1 : 1) as eluent, compound **8** was isolated (≈30% yield) with a blue, unstable compound: 300 MHz ^1H NMR ($CDCl_3$, 298 K) δ 3.62 (2 H, q, OCH_2), 1.18 (3 H, t, OCH_2CH_3), 0.73 (6 H, s, CH_3) and -16.18 (s, Ru–H–Ru). Further data could not be obtained due to the unstable nature of the product.

Crystallography

Crystals of compound **7** were grown from pentane solutions at 278 K. A crystal was immersed in highly viscous perfluoropolyether to exclude oxygen and prevent solvent loss. It was then mounted on a glass fibre and plunged in a cold (193 K) nitrogen stream.



1 R = OSiMe3
4 R = Me

Crystal data and data collection. Compound **7**, $C_{26}H_{54}O_{14}Ru_2Si_8$, $M = 1017.55$, yellow prism, crystal dimensions 0.45 × 0.3 × 0.25 mm, cubic, $a = 17.324(2)$ Å (by least-squares refinement on 25 reflections with $8 < \theta < 18°$ measured at positive and negative θ values), $U = 5199.29$ Å^3, $F(000) = 2088$, $T = 193$ K, space group $Pa\bar{3}$ (no. 205), $Z = 4$, $D_c = 1.300$ Mg m^{-3}; Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation, graphite-monochromated ($\lambda = 0.710\,73$ Å), $\mu = 0.81$ mm^{-1}, no absorption correction. Data collection by ω scans up to $\theta = 24°$, $-h$, $+k$, $+l$; three standard reflections measured every 2 h showed no significant decay; 4078 reflections, 1340 unique ($R_{int} = 0.058$), all used for the refinement, 650 observed [$I > 2\sigma(I)$]. The data set shows unusually rapid decay of mean intensities with increasing diffraction angle.

Structure solution and refinement. The structure was solved by the Patterson method and subsequent Fourier-difference syntheses[8] and refined by full-matrix least squares on the F^2 data using the SHELXL 93 program.[9] The CO ligands at Ru showed strong disorder with a ring-like electron-density distribution. Their positions were approximated by four C and four O split-atom positions which are multiplied by the three-fold axis parallel to the Ru–Ru axis to a total of 12 CO positions. Refinement of the occupation factors led to a Ru : CO ratio of 4.5 : 1, but a change to the idealised value of 4 : 1 gave no significant increase of R values. Thus the occupation factors for the 1 : 4 stoichiometry have been fixed. For all non-H atoms including the disordered CO groups anisotropic thermal parameters could be refined. All hydrogen positions were calculated and isotropic thermal parameters fixed at 1.2 times the U_{eq} values of the corresponding C atoms. Using a weighting scheme $w^{-1} = \sigma^2(F^2) + (0.88P)^2 + 0.78P$ where $P = (2F_c + F_o)/3$ final $wR_2 = 0.162$ (for all data), $R = 0.048$ (for the observed data) and a goodness of fit = 1.04 were obtained; maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 0.45$ e Å^{-3}. All heavier atoms, even the Ru, show unusually high anisotropic thermal parameters, about four times higher than usual. This behaviour was confirmed by an independent measurement of a second crystal on a different diffractometer (P4, Siemens), which gave almost the same results.

CCDC reference number 186/750.

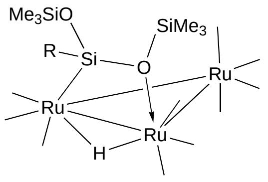
Results and Discussion

Several siloxyl-substituted triruthenium clusters can be isolated from the thermal reaction of $[Ru_3(CO)_{12}]$ with the bulky siloxysilanes $HSi(OSiMe_3)_3$ and $HSiMe(OSiMe_3)_2$. Loss of one CO ligand from the cluster followed by oxidative addition of a H–Si bond generates the purple compounds $[Ru_3H(CO)_{11}\{\eta^1\text{-}Si(OSiMe_3)_3\}]$ **1** and $[Ru_3H(CO)_{11}\{\eta^1\text{-}SiMe(OSiMe_3)_2\}]$ **4**, respectively. The ^1H NMR spectrum of each compound displays a high-field resonance, at δ -16.02 for compound **1** and -16.13 for **4**, typical of a bridging hydrogen atom bound to ruthenium. A single signal assignable to the $SiMe_3$ units is apparent in both cases indicating that the barrier to rotation about the Ru–Si bond is low. In addition the IR spectra of compounds **1** and **4** display a similar pattern of CO stretches indicating that the number and arrangement of CO ligands are cognate in both species. The proposed molecular formula of **4** is confirmed by mass spectrometry whilst the highest observed molecular ion peak for compound **1** corresponds to $M^+ - CO$.

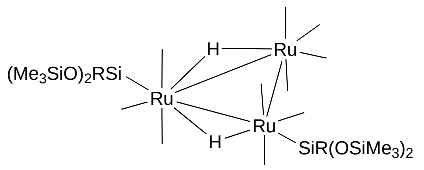
Table 1 Analytical and spectroscopic data for compounds **1**–**8**

Complex[a]	Spectroscopic data[b]
1 $[Ru_3H(CO)_{11}\{\eta^1\text{-}Si(OSiMe_3)_3\}]$	IR: 2083w, 2068w, 2042vs, 2025w, 2014w
Mass: *m/z* 879 ($M^+ - CO$) (Calc. for $^1H_{28}{}^{12}C_{20}{}^{16}O_{14}{}^{101}Ru_3{}^{28}Si_4$ 907)	^{1}H: 0.16 (s, $SiMe_3$), −16.02 (s, Ru–H–Ru)
2 $[Ru_3H(CO)_{10}\{\eta^2\text{-}Si(OSiMe_3)_3\}]$	IR: 2088w, 2051s, 2044m (sh), 2025vs, 1976w
Mass: *m/z* 878 (M^+) (Calc. for $^1H_{28}{}^{12}C_{19}{}^{16}O_{13}{}^{101}Ru_3{}^{28}Si_4$ 879)	^{1}H: 0.18 (s, $SiMe_3$), −14.41 (s, Ru–H–Ru)
3 $[Ru_3H_2(CO)_{10}\{\eta^1\text{-}Si(OSiMe_3)_3\}_2]$	IR: 2089m, 2059m, 2043vs, 2027m
Mass: *m/z* 1036 ($M^+ - 5CO$) (Calc. for $^1H_{56}{}^{12}C_{28}{}^{16}O_{16}{}^{101}Ru_3{}^{28}Si_8$ 1175)	^{1}H: 0.18 (s, $SiMe_3)_3$, −14.94 (d, J_{HH} 1.5, Ru–H–Ru), −16.50 (d, J_{HH} 1.5, Ru–H–Ru)
4 $[Ru_3H(CO)_{11}\{\eta^1\text{-}SiMe(OSiMe_3)_2\}]$	IR: 2084w, 2060m, 2040vs, 2025m, 2017w, 1985w
Mass: *m/z* 831 (M^+) (Calc. for $^1H_{22}{}^{12}C_{18}{}^{16}O_{13}{}^{101}Ru_3{}^{28}Si_3$ 833)	^{1}H: 0.48 (3 H, s, SiMe), 0.15 (18 H, s, $SiMe_3$), −16.13 (s, Ru–H–Ru)
5 $[Ru_3H(CO)_{10}\{\eta^2\text{-}SiMe(OSiMe_3)_2\}]$	IR: 2085w, 2055s, 2041m (sh), 2023m (br)
Mass: *m/z* 777 ($M^+ - CO$) (Calc. for $^1H_{22}{}^{12}C_{17}{}^{16}O_{12}{}^{101}Ru_3\ {}^{28}Si_3$ 805)	^{1}H: 0.60 (3 H, s, SiMe), 0.16 (18 H, s, $OSiMe_3$), −14.42 (s, Ru–H–Ru)
6 $[Ru_3H_2(CO)_{10}\{SiMe(OSiMe_3)_2\}_2]$	IR: 2088w, 2059m, 2042vs, 2029m
Mass: *m/z* 1025 (M^+) (Calc. for $^1H_{44}{}^{12}C_{24}{}^{16}O_{14}{}^{101}Ru_3{}^{28}Si_6$ 1027)	^{1}H: 0.53 (6 H, s, SiMe), 0.18 (36 H, s, $OSiMe_3$), −15.03 (d, J_{HH} 1.5, Ru–H–Ru), −16.50 (d, J_{HH} 1.5, Ru–H–Ru)
7 *trans*-$[Ru_2(CO)_8\{Si(OSiMe_3)_3\}_2]$	IR: 2050m, 2025vs
Mass: *m/z* 1018 (M^+) (Calc. for $^1H_{54}{}^{12}C_{26}{}^{16}O_{14}{}^{101}Ru_2{}^{28}Si_8$ 1016)	^{1}H: 0.18 (s, $SiMe_3$)
8 *trans*-$[Ru_2(CO)_8\{SiMe_2(OEt)\}_2]$	IR: 2040m, 2018vs
Mass: *m/z* 633 (M^+) (Calc. for $^1H_{22}{}^{12}C_{16}{}^{16}O_{10}{}^{101}Ru_2{}^{28}Si_2$ 632)	^{1}H: 3.75 (4 H, q, J_{HH} 7, OCH_2), 1.25 (6 H, t, J_{HH} 7, OCH_2CH_3), 0.72 (12 H, s, CH_3)

[a] Mass spectra data given as: *m/z* (assignment); fast atom bombardment or TOF. [b] IR data (cm^{-1}) determined in hexane solution, unless otherwise stated; NMR data ($CDCl_3$, 298 K), unless otherwise stated, given as chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment].



2 R = OSiMe$_3$
5 R = Me



3 R = OSiMe$_3$
6 R = Me

The close resemblence of the spectroscopic data (Table 1) of these two clusters provides strong evidence that they possess analogous structures.

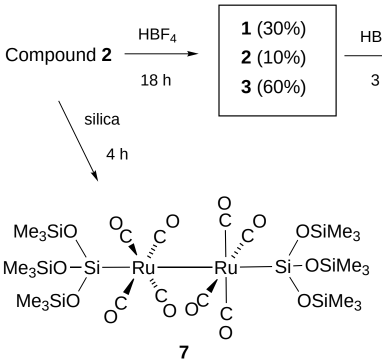
A drawing is shown for the proposed molecular structure of compounds **1** and **4** although we are unable to determine the orientation of the silicon ligand. Their purple colour is unusual and of note. The closely related species $[Os_3H(CO)_{10}(NCMe)\{\eta^1\text{-}Si(OEt)_3\}]$ has been reported by Adams *et al.*[4,5] and structurally characterised by X-ray diffraction: the alkoxysilyl ligand occupies an equatorial site and there is a hydrogen atom bridging an Os–Os bond.

Also formed in the same reactions are the clusters $[Ru_3H(CO)_{10}\{\eta^2\text{-}Si(OSiMe_3)_3\}]$ **2** and $[Ru_3H(CO)_{10}\{\eta^2\text{-}SiMe(OSiMe_3)_2\}]$ **5** which are formally related to compounds **1** and **4** by replacement of a CO ligand with a Si–O→Ru interaction. These two compounds exhibit similar spectroscopic properties (Table 1) and IR data indicate that the structure and compositions of both species are closely related. A high-field resonance, at δ −14.41 (**2**) and −14.42 (**5**) is observed in the ^{1}H NMR spectrum of each compound which is characteristic of a hydrogen atom bridging a Ru–Ru bond. Mass spectrometric data for compound **2** are consistent with the presence of only ten CO ligands per molecule.

To ensure that the cluster attains a saturated electron count of 48 we propose that the $Si(OSiMe_3)_3$ or $SiMe(OSiMe_3)_2$ ligand provides a further two electrons *via* a Si–O→Ru interaction in addition to the one electron provided by the Ru–Si σ bond. Although in both cases only a single low-field resonance, assignable to the $OSiMe_3$ moieties, is observed at room temperature this type of η^2-bonding interaction has previously been reported for the bimetallic complex $[(OC)_3Fe\{\mu\text{-}Si(OSiMe_3)_2(\overline{OSiMe_3)\}(\mu\text{-dppm})P}dCl]$ (dppm = $Ph_2PCH_2PPh_2$).[3b,c] Its crystal structure revealed the presence of a four-membered Si–Fe–Pd–O ring although low-temperature ^{1}H NMR spectroscopy (243 K) exhibited a single resonance attributable to the $SiMe_3$ groups. Thus the fact that both clusters **2** and **5** exhibit a single ^{1}H NMR spectroscopic resonance due to the $OSiMe_3$ units does not contradict their proposed formulae. The alkoxysilyl-substituted osmium cluster $[Os_3H(CO)_{10}\{\eta^2\text{-}Si(OMe)_3\}]$, related to **2** and **5**, was synthesized from $[Os_3(CO)_{10}(NCMe)_2]$.[5] The reaction proceeded in a stepwise fashion: displacement of the first MeCN ligand resulted in the formation of $[Os_3H(CO)_{10}(NCMe)\{\eta^1\text{-}Si(OMe)_3\}]$ and the second MeCN molecule may be displaced by refluxing the compound for a short time to yield $[Os_3H(CO)_{10}\{\eta^2\text{-}Si(OMe)_3\}]$.

A third type of triruthenium cluster $[Ru_3H_2(CO)_{10}\{SiR(OSiMe_3)_2\}_2]$, R = OSiMe$_3$ **3** or Me **6**, may be isolated from the thermal reaction of $[Ru_3(CO)_{12}]$ with $HSi(OSiMe_3)_3$ or $HSiMe(OSiMe_3)_2$, respectively. As expected the two species display a similar pattern of carbonyl absorptions in their IR spectra and the ^{1}H NMR spectrum of each cluster exhibits two hydride resonances split by a small ^{1}H–^{1}H nuclear coupling of 1.5 Hz; δ −14.94 (d) and −16.50 (d) for **3** and −15.03 (d) and −16.50 (d) for **6**. The proposed formulae are confirmed by mass spectrometry although the highest molecular ion peak observed for compounds **3** and **6** is $M^+ - 5CO$ and M^+, respectively (Table 1). A closely related compound, $[Os_3H_2(CO)_{10}(SiPh_3)_2]$, has been reported with very similar spectroscopic data; ^{1}H NMR (high-field region) δ −16.48 (d) and −16.70 (d), J_{HH} = 1.4 Hz. In accord with these observations a structure containing two equatorial η^1-alkoxysilyl ligands is proposed for compounds **3** and **6**.[10]

A ^{1}H NMR spectrum taken of the reaction mixture of either $HSi(OSiMe_3)_3$ or $HSiMe(OSiMe_3)_2$ with $[Ru_3(CO)_{12}]$ prior to TLC separation indicates that the major product (>75%) is the yellow μ-η^2-SiO isomer, either **2** or **5**, depending on the silane employed. However after TLC separation each reaction yields three clusters in approximately equal quantities. This suggests that chemical or equilibrating reactions occur on the silica. Thus we explored the reaction of cluster **2** with $HBF_4\cdot Et_2O$ in an attempt to mimic the acidic conditions experienced by the compounds on silica.[11] A few drops of $HBF_4\cdot Et_2O$ were added



Scheme 2

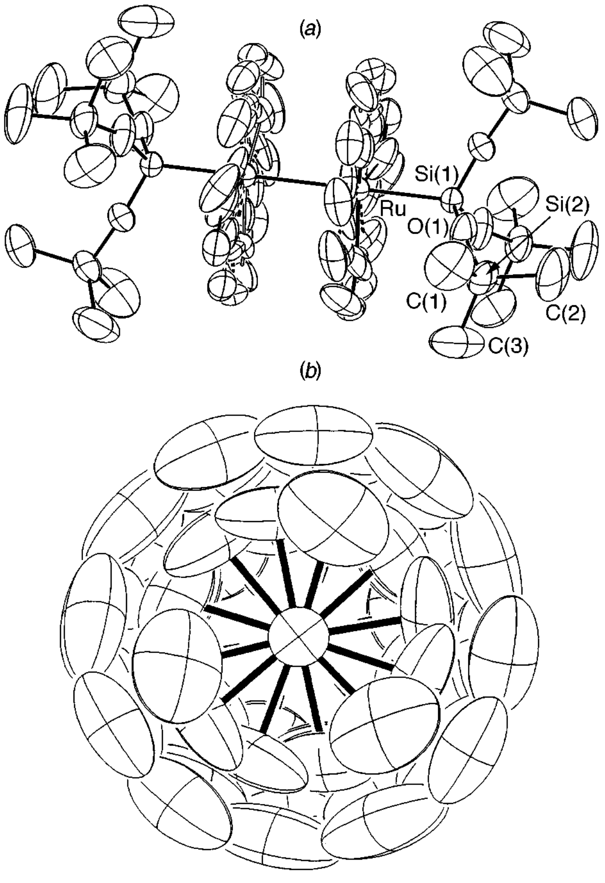


Fig. 1 (*a*) Diagram of the structure of complex **7** with $C3_i$ symmetry in the crystal showing 20% probability thermal ellipsoids. (*b*) Disordered Ru(CO)$_4$ co-ordination. Projection along the Ru–Ru axis, showing 50% probability thermal ellipsoids; Si(OSiMe$_3$)$_3$ ligands omitted

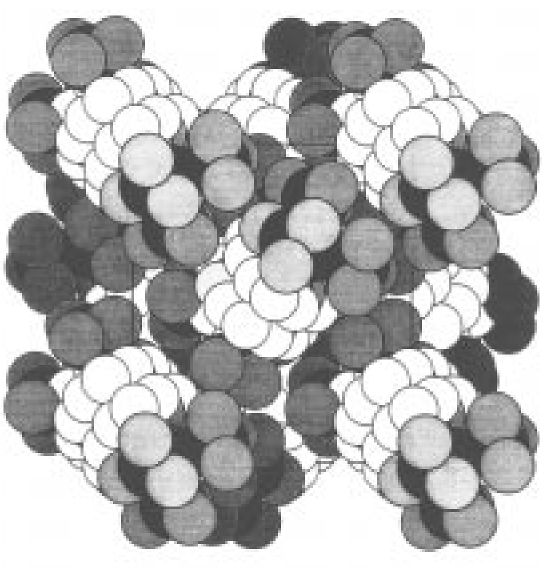


Fig. 2 Packing diagram for a unit cell of complex **7** (hydrogen atoms omitted). van der Waals radii; O white, C grey, Si black

Table 2 Selected bond lengths (Å) and angles (°) for complex **7**

Ru–Ru	2.909(1)	Si(2)–O(1)	1.611(6)
Ru–Si(1)	2.402(2)	Si(2)–C(1)	1.854(2)
Ru–C (CO)	1.85(12)–1.94(10)	Si(2)–C(2)	1.759(14)
Si(1)–O(1)	1.531(6)	Si(2)–C(3)	1.783(9)
O(1)–Si(1)–Ru	113.0(3)	Si(1)–O(1)–Si(2)	164.4(6)
O(1)–Si(2)–C(1)	108.1(6)	C(2)–Si(2)–C(1)	113.8(8)
O(1)–Si(2)–C(2)	107.8(6)	C(3)–Si(2)–C(1)	100.0(7)
O(1)–Si(2)–C(3)	112.3(5)	C(2)–Si(2)–C(3)	114.7(7)
O(1)–Si(1)–O(1′)	105.7(3)		

to a hexane solution of cluster **2** and after 18 h the solution was found to contain a mixture of **1** (≈30), **2** (≈10) and **3** (≈60%). Longer exposure to acidic conditions (3 d) resulted in the formation of *trans*-[Ru$_2$(CO)$_8${Si(OSiMe$_3$)$_3$}$_2$] **7** (≈10%) and [Ru$_4$H$_4$(CO)$_{12}$] (≈ 90%). In contrast addition of silica to a hexane solution of **2** did not produce similar results but a quantitative conversion into **7** after 4 h (Scheme 2).

Compound **7** may be synthesized in virtually quantitative yield *via* the photochemical reaction of HSi(OSiMe$_3$)$_3$ with [Ru$_3$(CO)$_{12}$] at 40 °C and has been characterised by IR and ^{1}H NMR spectroscopy, mass spectrometry (Table 1) and single-crystal X-ray diffraction. The crystal structure is affected by severe disorder effects (see Experimental section), in the region of the CO ligands. A thermal ellipsoid plot is shown in Fig. 1(*a*). Selected bond distances and angles are given in Table 2. The dinuclear molecules of **7** are centrosymmetric, the linear Si–Ru–Ru–Si array is oriented along the three-fold axis (molecular $C3_i$ symmetry) and the Si(OMe$_3$)$_3$ groups adopt a staggered arrangement. The Ru–Si bonds and unique Ru–Ru bond display typical single-bond distances, 2.402(2) and 2.909(1) Å, respectively. Each Ru atom is co-ordinated by four CO ligands which are highly disordered and show large anisotropic displacement parameters despite a low data collection temperature (193 K). From the X-ray experiment alone it is impossible to distinguish between a strong static disorder or high dynamic mobility. The refined split atom model with 12 nearly equidistant CO positions around each Ru atom is consistent with free rotation [Fig. 1(*b*)] and therefore a discussion of the co-ordination geometry around Ru is not warranted. Within the Si(OSiMe$_3$)$_3$ moiety the interior Si–O bonds are slightly shorter than the peripheral ones; Si(1)–O(1) 1.531(6) and Si(2)–O(1) 1.611(6) Å. The dumb-bell-like shape of compound **7** causes it to stack in a criss-cross fashion in the solid state (Fig. 2) forming a variant of the cubic close packed (c.c.p.) arrangement. The unusually high anisotropic displacement parameters of all atoms suggest a certain additional mobility of the molecules within the lattice. Apparently, the structure approaches the case of plastic crystals.

Analogous silyl-substituted dinuclear ruthenium compounds, *trans*-[Ru$_2$(CO)$_8$(SiR$_3$)$_2$], have been previously reported, formed in the reaction of [Ru$_3$(CO)$_{12}$] with HSiR$_3$, R = Me, Et or Pr,[12] and assumed, by analysis of their IR spectra, to possess the structure displayed by **7**. No evidence for trinuclear species was seen although admittedly, harsher reaction conditions (pyrolysis at 85 °C in hexane for 114 h) were employed. In an attempt to assess the factors, electronic *versus* steric, determining the formation of tri- or di-ruthenium compounds we investigated the thermal reaction of [Ru$_3$(CO)$_{12}$] with HSiMe$_2$(OEt). Several products formed in this reaction but only one stable species, [Ru$_2$(CO)$_8${SiMe$_2$(OEt)}$_2$] **8**, could be isolated and characterised by IR, ^{1}H NMR and mass spectroscopic methods. All data indicate that **8** adopts the same structure confirmed for complex **7**. Exploring the analogous photochemical reaction we found that at low temperature (273 K) the irradiation products were identical to those obtained in the thermal reaction whilst irradiation at higher temperatures (313 K) resulted in the selective formation of **8** (>90% yield).

Compounds **1**–**6** are formally generated by loss of one or two CO ligands from $[Ru_3(CO)_{12}]$ followed by oxidative addition of a H–Si bond to the unsaturated Ru_3 framework. However, alternatively the cluster may fragment into $\{Ru(CO)_4\}$ units which react with siloxysilanes to produce reactive mononuclear species capable of recombining to form di- or tri-nuclear compounds. Any remarks concerning the mechanism of these reactions based upon our observations can only be speculative.

The siloxysilyl-substituted triruthenium species are stable for large silyl groups, $Si(OSiMe_3)_3$ and $SiMe(OSiMe_3)_2$, allowing derivatives to be isolated and characterised. Gradual decomposition of the silyl-substituted Ru_3 clusters proceeds to synthesize Ru_2 complexes with the general formula $[Ru_2(CO)_8\{SiR(OR')_2\}_2]$ and this process can be enhanced by acid or silica. However, in reactions using smaller silanes such as $HSiMe_2(OEt)$, the trinuclear species, if produced, is short-lived and only dinuclear complexes have been isolated. Thus the size and electronegativity of the silyl moiety clearly has a drastic effect on the ease with which decomposition to the dinuclear species occurs. Large silane ligands and siloxy-substituents at the silicon centre help to stabilise trinuclear species of which the stability follows the trend $Si(OSiMe_3)_3 \approx SiMe(OSiMe_3)_2 \gg SiMe_2(OEt) > SiR_3$, R = Me, Et, Pr or Ph.

Conclusion

The reactions of siloxysilanes with $[Ru_3(CO)_{12}]$ are strongly dependent upon the steric and electronic properties of the silyl ligand. The use of bulky silanes such as $HSi(OSiMe_3)_3$ and $HSiMe(OSiMe_3)_2$ has made it possible to isolate siloxysilyl-substituted triruthenium clusters. In the presence of acid or silica these trinuclear species undergo further transformations and decomposition into the dinuclear complexes $[Ru_2(CO)_8\{SiR(OR')_2\}_2]$. In contrast, only analogous dinuclear species can be isolated from the reaction of $[Ru_3(CO)_{12}]$ with smaller silanes $HSiMe_2(OEt)$, $HSiR_3$ (R = Me, Et, Pr or Ph). Therefore in general siloxysilyl-substituted Ru_3 clusters exhibit greater stability, with respect to dinuclear species, when the siloxyl moiety is large and when the Si atom is substituted by OR rather than R groups.

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References

1 B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1982, **25**, 1.

2 (*a*) P. Braunstein, M. Knorr, A. Tiripicchio and M. Tiripicchio Camellini, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1361; (*b*) P. Braunstein, T. Faure, M. Knorr, F. Balegroune and D. Grandjean, *J. Organomet. Chem.*, 1993, **462**, 271; (*c*) P. Braunstein, M. Knorr and T. Stährfeldt, *J. Chem. Soc., Chem. Commun.*, 1994, 1913; (*d*) P. Braunstein and M. Knorr, *J. Organomet. Chem.*, 1995, **500**, 21; (*e*) P. Braunstein and M. Knorr in *Metal–Ligand Interactions, Structure and Reactivity*, NATO ASI Series, eds. N. Russo and D. R. Salahub, Kluwer, Dordrecht, 1996, vol. 474, p. 49.

3 (*a*) P. Braunstein, *New J. Chem.*, 1994, **18**, 51; (*b*) M. Knorr and P. Braunstein, *Bull. Soc. Chim. Fr.*, 1992, **129**, 663; (*c*) M. Knorr, P. Braunstein, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 1995, **14**, 4910.

4 R. D. Adams, J. E. Cortopassi and M. P. Pompeo, *Inorg. Chem.*, 1991, **30**, 2960.

5 R. D. Adams, J. E. Cortopassi and M. P. Pompeo, *Inorg.Chem.*, 1992, **31**, 2563.

6 B. F. G. Johnson, J. Lewis, M. Monari, D. Braga, F. Grepioni and C. Gradella, *J. Chem. Soc., Dalton Trans.*, 1990, 2863.

7 M. I. Bruce, C. M. Jensen and N. L. Jones, *Inorg. Synth.*, 1990, **28**, 216.

8 G. M. Sheldrick, SHELXTL PLUS, Release 4.2, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.

9 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.

10 A. C. Willis, F. W. B. Einstein, R. M. Ramadan and R. K. Pomeroy, *Organometallics*, 1983, **2**, 935.

11 R. Bender and P. Braunstein, *J. Chem. Soc., Chem. Commun.*, 1983, 334.

12 S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 1969, 2559.

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