DALTON
FULL PAPER

Syntheses of new ruthenium clusters containing sulfur, ynyl and diynyl ligands. Crystal structures of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$, $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ and $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$

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Received 10th April 2001, Accepted 18th June 2001
First published as an Advance Article on the web 6th August 2001

Reaction of $Ru_3(CO)_{12}$ and $S(C{\equiv}CSiMe_3)_2$ in toluene gave $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **1**. The thermolysis of **1** provokes the rupture of the $S\text{–}C_{sp}$ bond of the $SC{\equiv}CSiMe_3$ ligand and C–C coupling reactions between two acetylide groups affording the clusters $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **2**, $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **3**, $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ **4** and $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **5**. All compounds have been characterized by IR and NMR techniques as well as FAB^+ mass spectrometry. Crystal structures of **1**, **4**, and **5** have been determined by X-ray diffraction methods. The pathways of the thermolysis of **1** to give **2**–**5** have been investigated.

Introduction

The synthesis of transition metal compounds with bridging polycarbon ligands containing unsaturated C–C bonds has recently received a great deal of attention due to the possibility that these new materials might exhibit interesting electrical and optical properties.[1]

Carty and co-workers[2] have shown that facile rupture of the $P\text{–}C_{sp}$ bonds of tertiary alkynyl phosphines in the presence of metal carbonyls affords ready access to binuclear and cluster compounds containing phosphido ($\mu\text{-}PR_2$) and terminal, edge or face bound alkynyl groups. More recently binuclear iron and ruthenium complexes such as $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)$[2f] and $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)$[2d,e] have been utilised as precursors for higher nuclearity clusters bearing polyynyl ligands formed *via* head to head or head to tail coupling of the alkynyl groups.

On the other hand, the study of reactions that involve cleavage or formation of C–S bonds is an interesting subject both from the point of view of hydrodesulfurisation processes as well as the syntheses of organic products.[3] In addition, the propensity of sulfur ligands to bridge metal centers and help maintain the structural integrity of metal cluster compounds is well known.

However, despite the fact that the PPh_2 group is isoelectronic with the SR fragment, cluster chemistry with ligands containing S–C (alkyne) bonds remains almost unexplored. Jeannin and co-workers[4] have reported reactions between the thioalkyne $C_2H_5SC{\equiv}CR$ (R = alkyl or aryl group) and iron or ruthenium carbonyls generating several complexes with C_2H_5S and $C{\equiv}CR$ ligands *via* cleavage of the $S\text{–}C_{sp}$ bond in all cases.

In this paper we report the synthesis of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **1**, as the sole compound in high yield, from the reaction of $Ru_3(CO)_{12}$ and $S(C{\equiv}CSiMe_3)_2$, indicating that only one of the two $S\text{–}C_{sp}$ bonds in the precursor was cleaved. The pyrolysis of **1** afforded the new compounds $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **2**, $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **3**, $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ **4** and $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)\text{-}C(C{\equiv}CSiMe_3)]$ **5**, by rupture of the remaining $S\text{–}C_{sp}$ bond and C–C coupling reactions. These studies confirm that thioalkyne ligands are potentially versatile sources of polynuclear complexes stabilised by bridging sulfur ligands and bearing multifunctional alkynyl and polyalkynyl fragments.

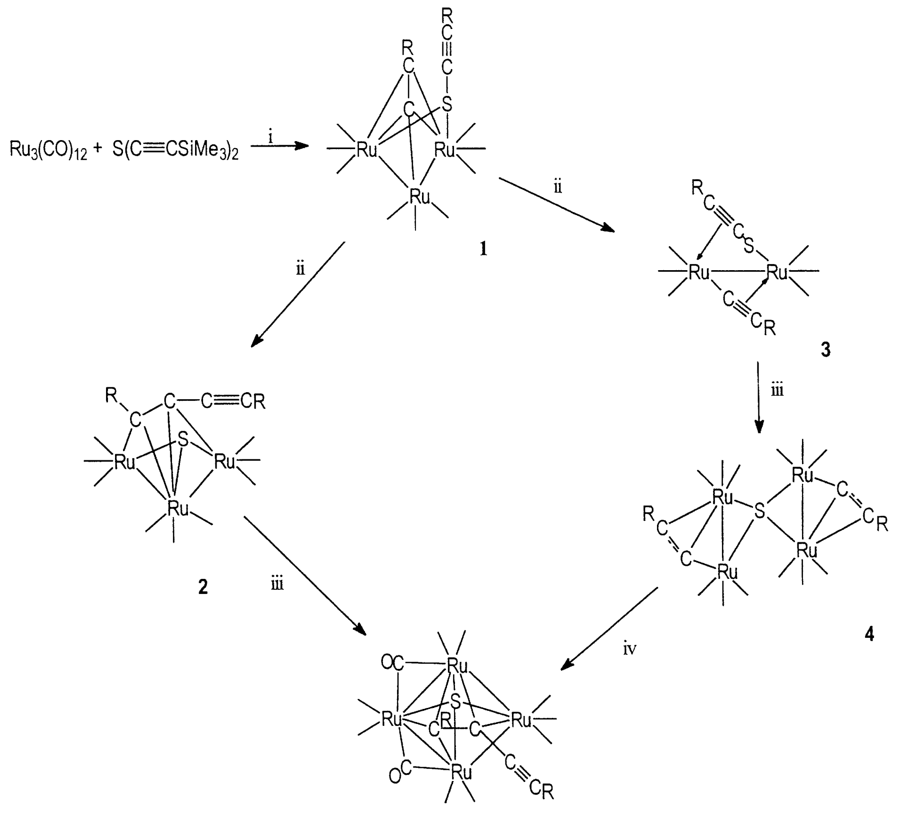
Results and discussion

Transition metal complexes with $RC{\equiv}CS^-$ ligands are scarce.[5] Weigand and Robl[5a,b] have prepared alkyne thiolate mononuclear complexes of Ru^{II} and Pt^{II} and we have recently reported[5c] the synthesis of complexes $[(RC_5H_4)(R'C_5H_4)Ti(SC{\equiv}CSiMe_3)_2]$ ($R = R' = SiMe_3$; $R = SiMe_3$, $R' = PPh_2$) which can serve as metalloligands to generate titanium–platinum dinuclear compounds. In addition, Jeannin *et al.*[4] have described the syntheses of some iron and ruthenium clusters using alkyl alkynyl sulfide ligands by preferential rupture of the $S\text{–}C_{sp}$ bonds over $S\text{–}C_{sp^3}$ bonds in all cases.

With the above results in mind, we decided to explore the strategy of using thioether ligands containing two identical alkyne groups in order to attempt to cleave both $S\text{–}C_{sp}$ bonds to generate metallosulfur clusters with discrete or coupled alkynyl groups.

The reaction between $Ru_3(CO)_{12}$ and excess of the freshly prepared ligand $S(C{\equiv}CSiMe_3)_2$ in toluene at 65 °C afforded the new compound $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}$

DOI: 10.1039/b103202j



R = SiMe$_3$; i = 65 °C, toluene; ii = 115 °C, xylene; iii = 115 °C, Ru$_3$(CO)$_{12}$; iv = 115 °C, -CO

Scheme 1

CSiMe$_3$)] **1** in high yield (71%) together with traces of another unidentified compound. The use of $Ru_3(CO)_{10}(CNMe)_2$ as starting material also gave complex **1** but in lower yield.

In the ^1H NMR spectrum of **1** the resonances of the SiMe$_3$ groups appear as singlets at 0.59 and 0.19 ppm indicating their inequivalence. The carbonyl stretching frequencies observed in the IR spectrum assigned to terminal CO ligands show a pattern similar to those observed for compounds $[Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CR)]$[8] and $[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)]$.[4a] The presence of all of these groups was also confirmed by their characteristic ^{13}C NMR resonances which appear in the expected range. A positive FAB$^+$ mass spectrum gave the molecular ion $[M + H]^+$ at *m*/*z* 783 together with several peaks due to CO loss.

A hexane solution of **1** kept at −20 °C over 24 h, gave suitable crystals for a single crystal X-ray diffraction study, confirming the structure which will be discussed in the following section. Compound **1** crystallises in a chiral space group $P2_12_12_1$ and the reported X-ray data correspond to only one of the possible enantiomers. Studies of the optical activity of **1** confirmed the presence of a racemic mixture.

Taking into account our experience in C–C coupling reactions between acetylide fragments to generate longer chain polycarbon ligands, compound **1** was heated in xylene at 115 °C for 45 min affording complexes **2**–**5** after column chromatography on silica gel (Scheme 1). The new compounds have been characterized by IR, NMR spectroscopy and FAB$^+$ mass spectrometry. Complementary X-ray diffraction studies have been carried out on **4** and **5**.

Compound $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **2** was obtained in only small amounts (5% yield) as a pale yellow oil from the first band from the column chromatography together with $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **3** (1% yield). In order to separate pure samples of both complexes a long 30 cm column was required. The IR spectrum of **2** in the carbonyl region is similar to those reported for $[Ru_3(CO)_9(\mu_3\text{-}NOMe)(\mu_3\text{-}\eta^2\text{-}RC_2Ph)]$[6] and $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)]$.[7] In addition, a band that appears at 2127 cm^{-1} was assigned to $\nu(C{\equiv}C)$. The ^1H and ^{13}C NMR resonances revealed the presence of CO and the organic groups in the molecule. The FAB$^+$ mass spectrum exhibited peaks indicating the sequential loss of nine CO ligands. The presence of sulfur in the molecule was inferred from the analytical data, although good C, H analyses could not be obtained, presumably due to the oily nature of the compound. All attempts at crystallization were unsuccessful. However all of the spectroscopic data including the presence of $\nu(C{\equiv}C)$ for a free acetylene suggest that **2** is an open triangular cluster with the sulfur atom and $C(SiMe_3)$-$C(C{\equiv}CSiMe_3)$ ligands bridging the three metals.

The FAB$^+$ mass spectrum of the compound $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **3** revealed a molecular ion at *m*/*z* 596 as well as the sequential loss of six carbonyls. Two different SiMe$_3$ groups (0.20 and 0.52 ppm) with similar chemical shifts to those shown in complex **1** (0.19 and 0.59 ppm) are present in the ^1H NMR spectrum. Additionally the ν(CO) pattern in the IR spectrum closely resembles those observed in $[Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}CR)]$[8] and $[Fe_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CC_6H_5)(\mu\text{-}\eta^2\text{-}C{\equiv}CC_6H_5)]$.[4b] The spectroscopic data obtained for **3** are in good agreement with a dinuclear framework formed by two Ru(CO)$_3$ fragments bridged by alkynethiolate and acetylide ligands. The tetranuclear compound $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ **4** is formed in low yield *via* **3** from C–S bond activation and cleavage at the μ-η^3-alkynethio group with metal fragment addition. The ^1H NMR spectrum exhibited only one signal at 0.30 ppm for the SiMe$_3$ group indicating the equivalence of both groups. In the FAB$^+$ mass spectrum peaks were observed for the molecular ion and loss of twelve carbonyl ligands. The ν(CO) IR frequencies exhibited a pattern analogous to that observed for compound $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CC_6H_5)_2]$.[4b] The characterization of **4** based on spectroscopic data has been confirmed by a single crystal X-ray structure determination. The framework of this complex consists of two

Ru–Ru units joined through a sulfur atom which has a distorted tetrahedral configuration. To the best of our knowledge, the iron analogue $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CC_6H_5)_2]$ prepared by reaction of $[Fe_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CC_6H_5)(\mu\text{-}\eta^2\text{-}C{\equiv}CC_6H_5)]$ with $Fe_2(CO)_9$, is the only other example reported to have a similar structure.

Conversion of cluster **4** to **5** occurred rapidly on heating the former to 115 °C in xylene. The ^1H NMR spectrum of **5** exhibited two singlets at 0.13 and 0.03 ppm due to the presence of two distinct $SiMe_3$ groups. A FAB^+ mass spectrum gave a parent ion at *m*/*z* 938 followed by peaks corresponding to the loss of 11 CO groups. The infrared spectrum in the *ν*(CO) region was similar to that of the related molecule $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)]$ prepared by Adams *et al.*[7] *via* the reaction of $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}HC_2Ph)]$ with $Ru(CO)_5$. The molecular structure of **5** has been confirmed by a full X-ray diffraction study.

We have also carried out some experiments in order to clarify the pathways of the thermolysis reaction (Scheme 1).

We suggest that the formation of $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **5** as the main product of the thermolysis of **1** may follow two independent pathways. Initially when a sample of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **1** is heated at 115 °C it generates compounds $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **2** and $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **3**. The S–C bond activation in the alkynethiolate ligand followed by C–C coupling between the two alkynyl groups present in compound **1** leads to **2**. Finally, a sample of the trinuclear cluster **2** which possesses a free $-C{\equiv}CR$ ligand heated with an excess of $Ru_3(CO)_{12}$ is fully converted into complex **5.**

On the other hand, the loss of an $Ru(CO)_3$ unit from **1** affords **3** which undergoes an analogous S–C bond cleavage on reaction with $Ru_3(CO)_{12}$ to afford **4**. Loss of CO from **4** on heating leads clearly to **5**. The **3** → **4** → **5** conversion is rapid. Indeed when a sample of compound **3** or **4** was heated at the same temperature both complexes were quickly converted into **5**. The tetranuclear cluster **5** is thermally stable and does not revert to **2** or **4** either on heating alone or under CO.

Crystal and molecular structures of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ 1, $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ 4 and $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ 5

Selected bond distances and angles for complexes **1**, **4** and **5** are collected in Table 1. Compound **1** crystallizes in space group $P2_12_12_1$ and final refinement revealed the presence of only one enantiomer on the basis of the Flack parameter.[9] This molecule has 50 valence electrons and adopts the expected open triangular framework. The Ru–Ru bond distances [2.8397(5) and 2.8204(5) Å] are similar to those exhibited by $[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)]$ [R = CH_3, 2.843(1) and 2.847(1) Å; R = Ph, 2.8391(8) and 2.8524(8) Å],[4a] $[Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]$[8a] and $[Ru_3(CO)_9(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)]$.[10] In addition the Ru–S distances [2.4353(7) and 2.4337(7) Å] are comparable to the values of 2.424(2) and 2.4116(2) Å reported for $[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)]$.[4a] The $SC{\equiv}C^tBu$ and $C{\equiv}C^tBu$ fragments behave as three and five electron donors respectively in this molecule. The alkynethiolate ligand bridges the two ruthenium atoms of the open edge of the Ru_3 triangle. The molecular structure of **1** is illustrated in Fig. 1.

The compound $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ **4** (Fig. 2), shows two crystallographically independent molecules in the asymmetric unit. Discussion will therefore be limited to only one of these molecules.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**, **4** and **5**

	1	**4**	**5**
Ru1–Ru2	2.8397(5)	2.7140(6)	2.7591(3)
Ru2–Ru3	2.8204(5)		
Ru2–Ru4			2.8541(4)
Ru1–Ru3			2.7762(4)
Ru3–Ru4		2.7190(7)	2.7410(3)
Ru1–S	2.4353(7)	2.3750(13)	2.4752(6)
Ru2–S		2.3730(12)	2.3904(6)
Ru4–S		2.3818(14)	2.5128(7)
Ru3–S	2.4337(7)	2.3735(13)	2.4167(6)
Ru1–C1	2.245(2)	2.008(6)	2.3202(2)
Ru1–C2	2.353(2)		2.300(2)
Ru2–C1	1.947(2)	2.277(5)	
Ru2–C2		2.411(6)	2.188(2)
Ru3–C1	2.242(2)		2.242(2)
Ru3–C2	2.360(2)		
Ru4–C1			2.301(2)
Ru4–C2			2.342(2)
Ru3–C4		2.008(5)	
Ru4–C4		2.287(5)	
Ru4–C3		2.411(5)	
C1–C2	1.289(3)	1.257(8)	1.424(3)
C2–C3			1.438(3)
C3–C4	1.201(4)	1.247(8)	1.203(4)
S–C3	1.700(2)		
Si–C4	1.841(3)		
C1–C2–C3			122.2(2)
C4–C3–C2			172.0(3)
Ru1–Ru2–Ru3	72.637(16)		
Ru1–Ru2–Ru4			79.779(7)
Ru1–Ru3–Ru4			81.472(9)
Ru2–Ru4–Ru3			95.050(9)
Ru2–Ru1–Ru3			96.431(8)
Ru1–S–Ru2		69.73	
Ru2–S–Ru3		133.18(69)	
Ru3–S–Ru1	87.02	131.74(6)	
Ru2–S–Ru4		135.41(6)	
Ru3–S–Ru4		69.75(4)	
Ru1–S–Ru4		128.78(6)	
C4–C3–S	175.7		
Ru1–S–C3	106.26		
Ru3–S–C3	107.97		
C3–C4–Si	178.3(2)		

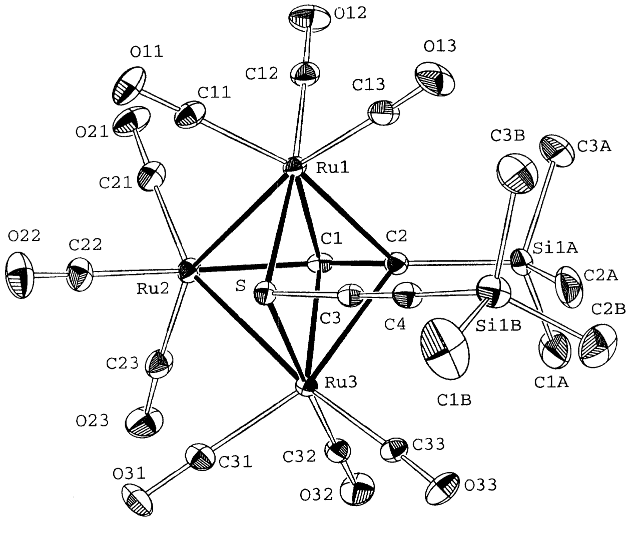


Fig. 1 Molecular structure of compound **1**.

The molecular structure of **4** is quite unusual and the related tetrairon cluster $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}C{\equiv}CC_6H_5)_2]$[4b] is the only other example of this type reported to date. The molecule can be viewed as two almost identical $Ru_2(CO)_6(\mu\text{-}C{\equiv}CSiMe_3)$ fragments (see Table 1) linked by a sulfur atom coordinated in tetrahedral fashion to four Ru atoms and acting as a six electron donor, contributing all of its valence electrons to the cluster. Ru–Ru bonds are almost equal in length and the angles formed with the sulfur atom are essentially identical. The two distances within the acetylide group C3–C4 [1.247(8) Å] and

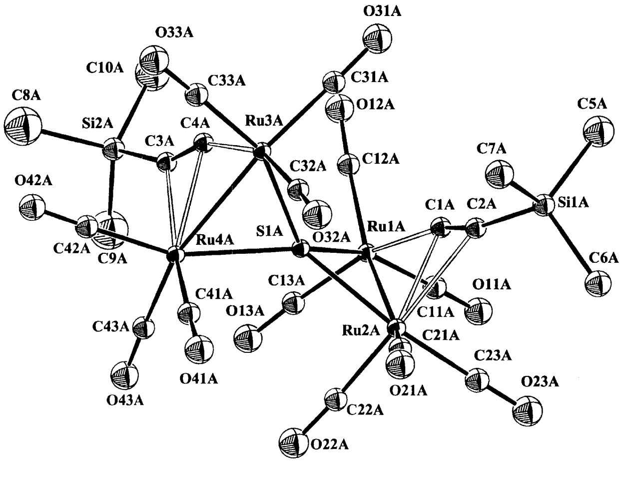


Fig. 2 Molecular structure of compound **4**.

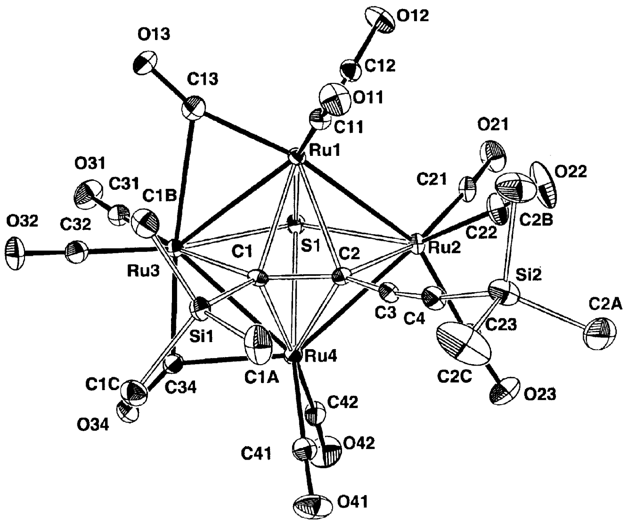


Fig. 3 Molecular structure of compound **5**.

C1–C2 [1.257(8) Å] are shorter than that observed in compound **1** for the μ-C≡CR ligand [1.289(3) Å] and larger than in μ-SC≡CR [1.201(4) Å] in agreement with the different coordination modes and electron donor characteristics.

The compound $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)\text{-}C(C{\equiv}CSiMe_3)]$ **5** is structurally similar to the compounds $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)]$[7] and $[Ru_4(CO)_9(\mu\text{-}CO)\text{-}(PPh_3)(\mu_4\text{-}NOMe)(\mu_4\text{-}\eta^2\text{-}HC_2Ph)]$.[6] A pictorial representation of **5** is given in Fig. 3. The four ruthenium atoms form a distorted parallelogram with three short [Ru1–Ru2 2.7591(3), Ru1–Ru3 2.7762(4) and Ru3–Ru4 2.7410(3) Å] ruthenium–ruthenium bonds and one Ru2–Ru4 [2.8541 (4) Å] slightly longer but still within the normal range for Ru–Ru distances in electron precise clusters.[2a] This arrangement of four Ru–Ru bonds is consistent with an electron count of 64 electrons achieved when the sulfur atom contributes four electrons and the alkyne six electrons to the cluster. However as with other sulfido[7] and phosphinidene (μ_4-PR) clusters[8b,c] of this type, the entire Ru_4SC_2 skeleton of **5** resembles a pentagonal bipyramid with the base consisting of Ru2, Ru3, S1, C1 and C2 and with Ru1 and Ru4 as the apical vertices of the bipyramid. According to the Wade–Mingos Polyhedral Skeletal Electron Pair (PSEP) rules the vertex atoms in the pentagonal bipyramidal framework of **5** contribute eight skeletal electron pairs [three $Ru(CO)_3$ fragments ($6e^-$), $Ru(CO)_2$ ($0e^-$), S ($4e^-$) 2CR ($6e^-$)], appropriate for a *closo* seven vertex polyhedron, as observed. The cluster also has two bridging CO groups bridging shorter Ru1–Ru3, Ru3–Ru4 bonds, again a common feature of other members of this class. The Ru–S distances to the μ_4-S ligand (av. 2.4485 Å) are longer than in **4** (av. 2.3758 Å) where the sulfur atom is essentially encapsulated within a tetrahedron of ruthenium atoms and functions as a six electron donor.

Experimental

General procedures

All experiments were carried out under an atmosphere of argon using Schlenk techniques.[11] Solvents were dried by known procedures and distilled before use.[12] The starting material $S(C{\equiv}CSiMe_3)_2$ was prepared as described in the literature.[13] All other reagents were used as obtained commercially. Microanalyses were determined with a Perkin-Elmer 2400 microanalyser. Infrared spectra (solution and KBr) were recorded on a Perkin-Elmer 1600 FT spectrophotometer. NMR spectra were measured on a Bruker AMX-300 instrument with chemical shifts reported in ppm relative to external standards ($SiMe_3$ for ^1H and ^{13}C), and mass spectra (FAB^+) on a VG Autospec spectrometer.

Preparation of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ 1

$Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) and $S(C{\equiv}CSiMe_3)_2$ (0.32 g, 1.41 mmol) in toluene (30 cm^3) were heated at 65 °C for 3 h. The solvent was removed *in vacuo* and the resulting residue was chromatographed on silica gel. Elution with n-hexane yielded a yellow band which afforded $Ru_3(CO)_{12}$ in trace amounts. A second, yellow band gave $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **1** (0.26 g, 71%). Crystals suitable for X-ray study were obtained from hexane at −20 °C. (Found: C, 28.8; H, 2.6%; M^+ 782. $C_{19}H_{18}O_9Ru_3SSi_2$ requires: C, 29.2; H, 2.3%; M^+ 782); ν_{max}/cm^{-1} (CO) 2092 w, 2073 s, 2051 s, 2017 s, 1986 w (hexane); δ_H ($CDCl_3$) 0.59 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$); δ_C ($CDCl_3$) 198.0 (Ru–CO), 190.3 (Ru–CO), 189.3 (Ru–CO), 165.6 (S–*C*≡C), 105.4 and 50.5 (C≡C), 82.7 (S–C≡*C*), 1.1 ($SiMe_3$) and −0.2 ($SiMe_3$); *m*/*z* 783 ($[M + H]^+$), 755 ($[M + H]^+ - CO$), 727 ($[M + H]^+ - 2CO$), 699 ($[M + H]^+ - 3CO$), 671 ($[M + H]^+ - 4CO$), 643 ($[M + H]^+ - 5CO$), 615 ($[M + H]^+ - 6CO$), 587 ($[M + H]^+ - 7CO$), 559 ($[M + H]^+ - 8CO$), 531 ($[M + H]^+ - 9CO$).

Thermolysis of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$

A xylene (20 cm^3) solution of $[Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SC{\equiv}CSiMe_3)\text{-}(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ (0.2 g, 0.26 mmol) was heated at 115 °C for 45 min, then the solvent was removed under vacuum. Column chromatography on silica gel, using n-hexane as eluent, yielded a pale yellow band of $[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}C(SiMe_3)\text{-}C(C{\equiv}CSiMe_3)]$ **2** (5%) followed by $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ **3** (1%). A third band afforded $[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ **4** as yellow crystals (1%) and finally an orange band gave $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ **5** (55%).

$[Ru_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ 2

Pale yellow oil. ν_{max}/cm^{-1} (C≡C) 2127 w, (CO) 2086 m, 2057 vs, 2018 s, 2010 s, 1998 m (hexane); δ_H ($CDCl_3$) 0.24 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$); δ_C ($CDCl_3$) 195.4 (Ru–CO), 140.5 (C_{diyne}), 119.8 (C_{diyne}), 106.6 (C_{diyne}), 77.0 (C_{diyne}), −0.5 ($SiMe_3$), −1.5 ($SiMe_3$); *m*/*z* 697 ($M^+ - CSiMe_3$), 669–445 ($M^+ - n$CO) (*n* = 1–9).

$[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SC{\equiv}CSiMe_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)]$ 3

Pale yellow oil. ν_{max}/cm^{-1} (CO) 2077 m, 2052 vs, 2012 m, 1999 s, 1983 w (hexane); δ_H ($CDCl_3$) 0.20 (s, 9H, $SiMe_3$), 0.52 (s, 9H, $SiMe_3$); *m*/*z* 596 (M^+), 568 ($M^+ - 1CO$), 540 ($M^+ - 2CO$), 512 ($M^+ - 3CO$), 484 ($M^+ - 4CO$), 456 ($M^+ - 5CO$), 428 ($M^+ - 6CO$).

Table 2 Crystal and refinement details for complexes **1**, **4** and **5**

	1	**4**	**5**
Formula	$C_{19}H_{18}O_9SSi_2Ru_3$	$C_{22}H_{18}O_{12}SSi_2Ru_4$	$C_{21}H_{18}O_{11}SSi_2Ru_4$
M	781.78	966.88	938.87
T/K	180(2)	180(2)	160(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2/c$
a/Å	9.5045(12)	9.8445(9)	17.1122(19)
b/Å	16.499(2)	12.8209(12)	9.9572(9)
c/Å	18.014(2)	27.638(3)	17.7322(18)
α/°		99.767(12)	
β/°		95.019(11)	101.522(12)
γ/°		97.193(11)	
V/Å^3	2824.8(6)	3389.6(6)	2960.5(5)
Z	4	4	4
D_c/mg m^{-3}	1.838	1.895	2.106
F(000)	1520	1864	1808
Crystal size/mm	0.40 × 0.40 × 0.20	0.50 × 0.10 × 0.07	0.35 × 0.10 × 0.07
μ/mm^{-1}	1.783	1.931	2.20
2θ range/°	3.3–52.1	3.3–52.1	3.3–52.1
Reflections measured	27385	25238	22878
Independent reflections	5417	9214	5608
R	0.0169	0.0464	0.0246
R_w	0.0426	0.1021	0.0502
Goodness of fit	1.080	1.009	1.015

$[Ru_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ 4

Crystals suitable for X-ray study were obtained from hexane at −20 °C. ν_{max}/cm^{-1} (CO) 2097 vw, 2081 m, 2063 vs, 2049 w, 2024 m, 2015 s (hexane); δ_H ($CDCl_3$) 0.30 (s, 18H, $SiMe_3$); m/z 966 (M^+), 910–630 ($M^+ - n$CO) (n = 2–12).

$[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}C(SiMe_3)C(C{\equiv}CSiMe_3)]$ 5

Crystals suitable for X-ray study were obtained from hexane at −20 °C. (55% yield). (Found: C, 26.6; H, 2.1%; M^+ 938. $C_{21}H_{18}O_{11}Ru_4SSi_2$ requires: C, 26.9; H, 1.9%; M^+ 938); ν_{max}/cm^{-1} (CO) 2090 w, 2062 m, 2055 (sh), 2040 vs, 2024 w, 2014 w, 1994 m, 1861 w (hexane); δ_H ($CDCl_3$) 0.13 (s, 9H, $SiMe_3$), 0.03 (s, 9H, $SiMe_3$); m/z 938 (M^+), 910–630 ($M^+ - n$CO) (n = 1–11).

Crystal structure determinations for compounds 1, 4, and 5

Intensity data were collected at low temperature on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device diffractometer and using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Crystal data and structure refinement parameters are listed in Table 2. For intensity measurement the final unit cell parameters were obtained by means of a least-squares refinement of a set of 5000 well measured reflections, and crystal decay was monitored in the course of data collection by measuring 200 reflections per image. No significant fluctuations of intensities were observed during data collection. Numerical corrections for absorption were applied to the data by indexation of the crystal faces,[14] the latter being optimized by using the program X-SHAPE.[15]

Structures were solved by direct methods using SIR92[16] and refined by least-squares procedures on a F^2 with the aid of SHELXL97.[17] Included in the package is WinGX32,[18] and refinements were performed by minimizing the function: $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are respectively the observed and calculated structure factors. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[19] All hydrogen atoms were located in difference Fourier maps but introduced in the process of refinement with a riding model, and their isotropic thermal parameters fixed at values 20% higher than the carbons atoms to which they are connected. For all of the structures all non-hydrogens atoms were anisotropically refined. In the last cycles of refinement weighting schemes were applied where weights were calculated from the following formula: $w = 1/[\sigma^2 F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

The graphical interface employed during calculations was XPMA[20] and the drawings of molecules were made using the program ZORTEP[20] with 50% probability displacement ellipsoids for non-hydrogen atoms.

CCDC reference numbers 162095–162097.

See http://www.rsc.org/suppdata/dt/b1/b103202j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (Spain) (Project PB-97–0020) for financial support.

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