165. Fixation of 1,3,5-Trithiane to a Trinuclear Ruthenium Framework: Synthesis, Structure, and Fluxionality of $[Ru_3(CO)_6(\mu_2\text{-}CO)_3\{\mu_3\text{-}(\eta^3\text{-}C_3S_3H_6)\}]$

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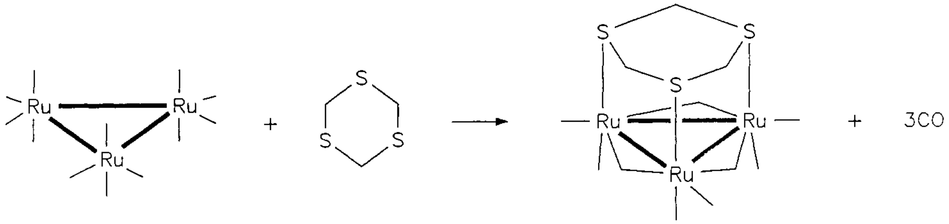
The reaction of dodecacarbonyltriruthenium with 1,3,5-trithiacyclohexane (1,3,5-trithiane) in refluxing THF yields $[Ru_3(CO)_6(\mu_2\text{-}CO)_3\{\mu_3\text{-}(\eta^3\text{-}C_3S_3H_6)\}]$ (**1**) in which the three S-atoms of the cyclic ligand coordinate to the three Ru-atoms of the metal core. X-Ray diffraction reveals a nearly perfect C_{3v} symmetry for the molecule. The variable-temperature ^{13}C-NMR spectra show the carbonyl ligands to be fluxional in solution.

Introduction. – Cyclic thioethers have been shown previously to serve as multidentate ligands in coordinating to transition metals. *Cooper* and coworkers studied reactions of 1,4,7-trithiacyclononane (1,4,7-trithionane) and 1,5,9-trithiacyclododecane with Ru^{II} salts to form mononuclear homoleptic complexes [1], while *Schröder* and coworkers used the nine-membered thioether in reactions with Ir salts [2]. In both cases, the structural integrity of the thioether was preserved while bonding facially to the metal atom. *Hill et al.* have reported the coordination of cyclic thioethers to neutral Ru^{II} compounds to give mononuclear complexes containing facially bound thiane ligands [3]. The coordination of 1,3,5-trithiacyclohexane in cluster chemistry has been pioneered by *Evans* using tetranuclear Rh complexes [4] and by *Roulet* using tetranuclear Ir complexes [5]. Ruthenium clusters have been reacted with 1,4,7-trithiacyclononane and 1,5,9-trithiacyclododecane by *J. Lewis et al.* recently; a series of tri-, tetra-, penta-, and hexanuclear clusters have been isolated and characterized from this reaction [6]. In this paper, we report the reaction of $Ru_3(CO)_{12}$ with 1,3,5-trithiacyclohexane to give the new trinuclear cluster $[Ru_3(CO)_6(\mu_2\text{-}CO)_3\{\mu_3\text{-}(\eta^3\text{-}C_3S_3H_6)\}]$ (**1**).

Synthesis and Crystallographic Studies of 1. – Reflux of an equimolar solution of 1,3,5-trithiane and dodecacarbonyltriruthenium in THF followed by chromatography yielded **1** as a yellow solid (71 %, *Scheme*). Slow evaporation of a THF solution resulted

Scheme



in yellow crystals of **1**. Compound **1** was soluble only in very polar solvents such as THF or acetone. IR Spectra of the title compound showed four terminal C=O absorptions along with a predominant absorption in the bridging C=O region. Two *doublets* of equal intensity were observed in the ^1H-NMR spectrum and can be attributed to the CH_2 protons of the trithiane ligand.

The molecular structure of **1** was determined by single-crystal X-ray structural analysis and is presented in *Fig. 1*. Selected bond distances and angles are given in *Tables 1* and *2*, respectively.

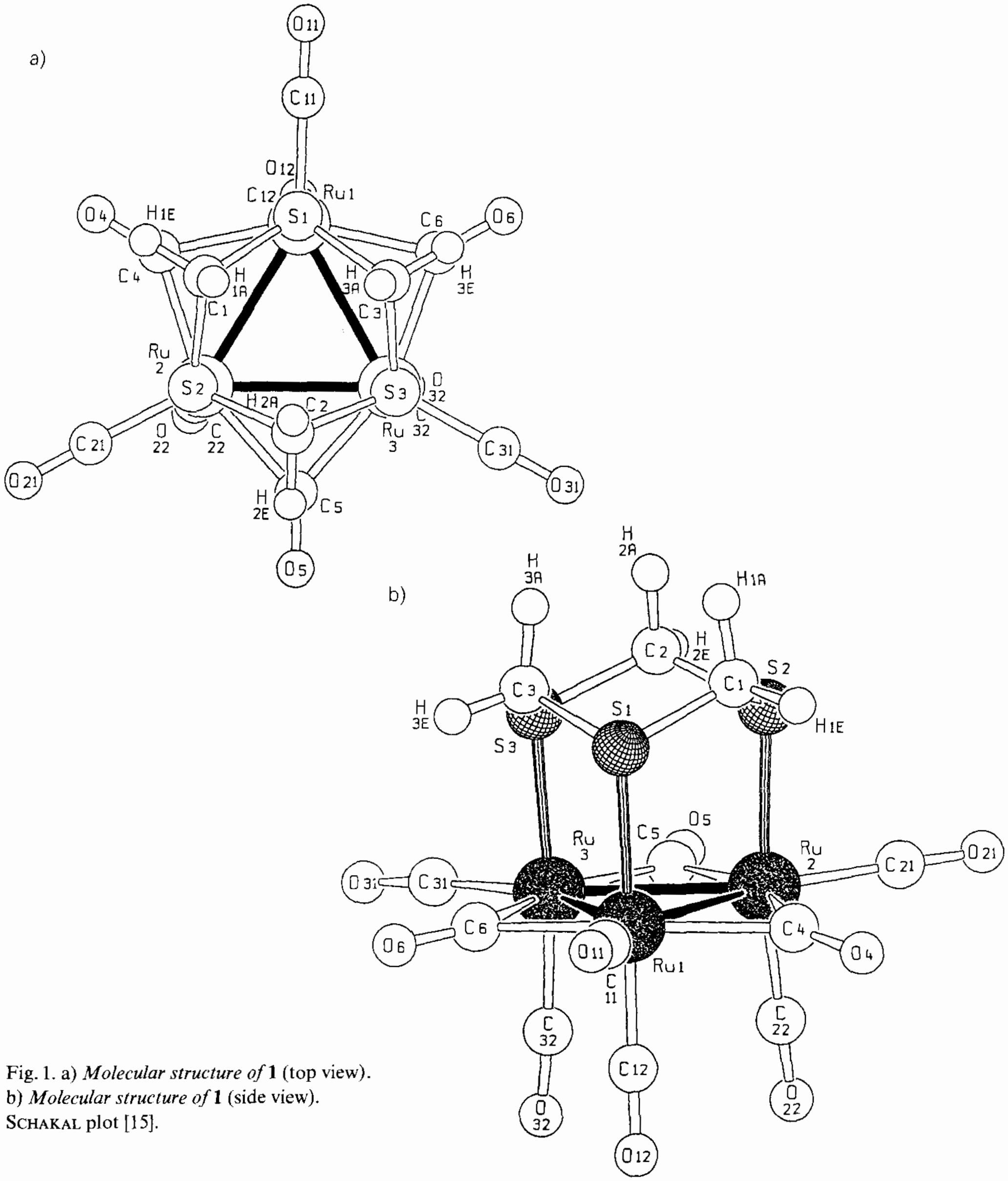


Fig. 1. a) *Molecular structure of* **1** (top view).
b) *Molecular structure of* **1** (side view).
SCHAKAL plot [15].

Table 1. *Selected Bond Lengths* [Å] *of* **1**

Ru(1)–Ru(2)	2.8687(8)	Ru(2)–S(2)	2.4276(18)	Ru(3)–C(31)	1.894(10)
Ru(1)–Ru(3)	2.8378(9)	Ru(2)–C(4)	2.150(8)	Ru(3)–C(32)	1.882(7)
Ru(1)–S(1)	2.4315(17)	Ru(2)–C(5)	2.143(9)	S(1)–C(1)	1.798(7)
Ru(1)–C(4)	2.155(8)	Ru(2)–C(21)	1.887(8)	S(1)–C(3)	1.805(7)
Ru(1)–C(6)	2.124(8)	Ru(2)–C(22)	1.865(8)	S(2)–C(1)	1.823(7)
Ru(1)–C(11)	1.911(8)	Ru(3)–S(3)	2.4248(18)	S(2)–C(2)	1.788(9)
Ru(1)–C(12)	1.884(8)	Ru(3)–C(5)	2.117(8)	S(3)–C(2)	1.798(9)
Ru(2)–Ru(3)	2.8306(13)	Ru(3)–C(6)	2.158(8)	S(3)–C(3)	1.809(7)

Table 2. *Selected Bond Angles* [°] *of* **1**

Ru(2)–Ru(1)–Ru(3)	59.47(3)	S(2)–Ru(2)–C(4)	93.44(21)	Ru(3)–S(3)–C(3)	108.86(23)
Ru(2)–Ru(1)–S(1)	92.02(4)	S(2)–Ru(2)–C(5)	91.45(20)	C(2)–S(3)–C(3)	98.0(3)
Ru(2)–Ru(1)–C(4)	48.13(21)	C(4)–Ru(2)–C(5)	155.6(3)	S(1)–C(1)–S(2)	114.1(4)
Ru(2)–Ru(1)–C(6)	108.47(22)	Ru(1)–Ru(3)–Ru(2)	60.807(24)	S(2)–C(2)–S(3)	117.1(4)
Ru(3)–Ru(1)–S(1)	92.51(4)	Ru(1)–Ru(3)–S(3)	92.58(5)	S(1)–C(3)–S(3)	115.3(4)
Ru(3)–Ru(1)–C(4)	107.42(21)	Ru(1)–Ru(3)–C(5)	109.56(24)	Ru(1)–C(4)–Ru(2)	83.6(3)
Ru(3)–Ru(1)–C(6)	49.01(22)	Ru(1)–Ru(3)–C(6)	47.99(22)	Ru(1)–C(4)–O(4)	137.5(6)
S(1)–Ru(1)–C(4)	94.15(21)	S(3)–Ru(3)–C(5)	89.56(20)	Ru(3)–C(5)–O(5)	138.8(8)
S(1)–Ru(1)–C(6)	92.12(21)	S(3)–Ru(3)–C(6)	92.12(21)	Ru(2)–C(4)–O(4)	137.9(7)
C(4)–Ru(1)–C(6)	155.9(3)	C(5)–Ru(3)–C(6)	157.5(3)	Ru(2)–C(5)–Ru(3)	83.3(3)
Ru(1)–Ru(2)–Ru(3)	59.720(19)	Ru(1)–S(1)–C(1)	110.6(3)	Ru(2)–C(5)–O(5)	137.8(7)
Ru(1)–Ru(2)–S(2)	92.00(5)	Ru(1)–S(1)–C(3)	108.71(23)	Ru(1)–C(6)–Ru(3)	83.0(3)
Ru(1)–Ru(2)–C(4)	48.28(22)	C(1)–S(1)–C(3)	100.9(3)	Ru(1)–C(6)–O(6)	138.8(7)
Ru(1)–Ru(2)–C(5)	107.68(22)	Ru(2)–S(2)–C(1)	110.74(25)	Ru(3)–C(6)–O(6)	137.9(7)
Ru(3)–Ru(2)–S(2)	93.30(5)	Ru(2)–S(2)–C(2)	109.02(25)	Ru(2)–Ru(3)–S(3)	92.10(6)
Ru(3)–Ru(2)–C(4)	107.82(22)	C(1)–S(2)–C(2)	98.0(3)	Ru(2)–Ru(3)–C(5)	48.75(24)
Ru(3)–Ru(2)–C(5)	47.96(22)	Ru(3)–S(3)–C(2)	110.50(24)	Ru(2)–Ru(3)–C(6)	108.79(22)

The metal framework of **1** is a triangular array of three Ru-atoms. To each Ru-atom is bonded two terminal CO groups, one of which takes an axial position and the other an equatorial position. Metal–metal bonds are further spanned by μ_2-CO ligands. In a plane above and parallel to the plane of the Ru triangle lie the three S-atoms of a tripodal 1,3,5-trithiane ligand. Each S-atom is σ-bonded to the Ru-atom beneath it. The CH$_2$ groups of the trithiane ligand occupy regular positions above the plane of the S-atoms. H-Atoms were placed at calculated axial and equatorial positions. Overall, the trithiane ligand assumes a chair-like conformation.

Two sides of the Ru triangle are slightly shorter than the third (Ru(1)–Ru(3), 2.8378(9) Å; Ru(2)–Ru(3), 2.8306(13) Å *vs.* Ru(2)–Ru(3), 2.8687(8) Å). These metal–metal distances are little changed from those in [Ru$_3$(CO)$_{12}$] [7] in spite of the presence of the μ_2-CO ligands. All μ_2-CO groups are nearly symmetric with respect to the metal–metal bonds over which they extend and can be considered bridging CO ligands [8]. The Ru triangle and the bridging CO groups occupy a plane in which atom C(4) shows the maximum deviation from that plane of 0.153(9)°. Calculated distances between Ru- and S-atoms again display only slight variations (mean Ru–S distance = 2.4280(10) Å) and are generally longer than those found in the hexanuclear Ru species of *Lewis* [4]. Within the tripodal ligand C–S bonds are uniform and contribute little to distortions in the symmetry of the molecule. The dihedral angle between the plane formed by the three S-atoms and that formed by the metal base is calculated at 0.14(6) Å. A nearly perfect C_3 axis extends through the center of the molecule and contains three vertical mirror planes. The somewhat analogous structures involving tetrahedral metal frameworks in which the trithiane molecule is bonded to the triangular metal base (M = Rh [4]; M = Ir [5]), show similar trends in terms of metal–metal, metal–S, and S–C bonds. A species of C_{3v} symmetry occurs as one isomer for the Ir cluster [5].

^{13}C-NMR Study of 1 in Solution. – Variable-temperature ^{13}C-NMR spectra of **1** in (D$_8$)THF indicate that, at 183 K, the predominant species present is that determined crystallographically. Specifically, at 183 K three well-defined resonances are found in the CO region; the signal at 263.1 ppm is attributed to the bridging carbonyls, the two signals at 199.3 and 197.6 ppm are assigned to the axial and the equatorial carbonyls, respectively, in accordance with arguments put forward by *Aime et al.* [9]. Spectra obtained at higher temperatures show a decrease in the intensity of the bridging and equatorial CO signals, until they ultimately fall below the noise level. At room temperature, one signal in

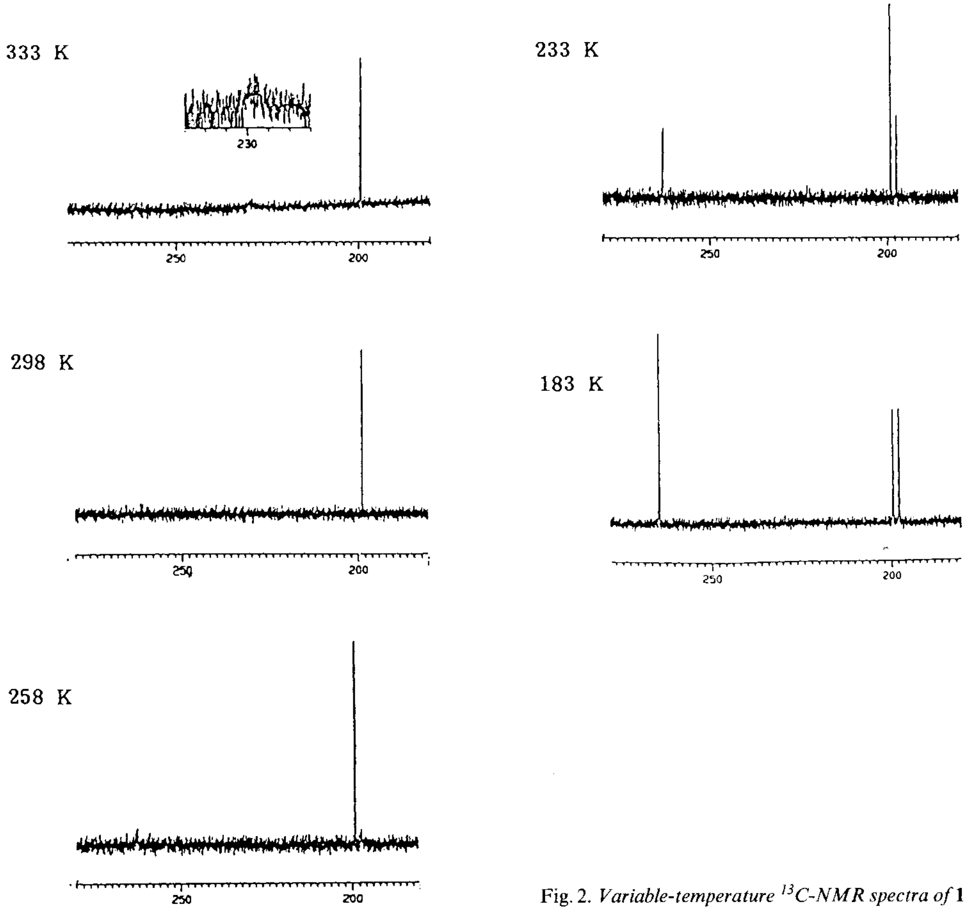


Fig. 2. *Variable-temperature ^{13}C-NMR spectra of* **1**

the CO region is found at 198.94 ppm corresponding to axial carbonyls, while the averaged signal (229.3 ppm) resulting from coalescence of the bridging and equatorial peaks becomes apparent only at 333 K and above. This behavior is illustrated in *Fig. 2*. These results imply that bridging and equatorial CO ligands in **1** take part in a 'merry-go-round' process similar to that postulated as one possible mechanism for CO exchange in $[Ru_3(CO)_{12}]$ [10] [11], while the axial CO ligands remain static over the temperature range studied. For the Ir counterpart, $[Ir_4(CO)_9(C_3S_3H_6)]$, a similar CO exchange process was observed among equatorial and axial CO groups: the isolation and X-ray characterization of two isomers, one with bridging and one with only terminal equatorial CO ligands, confirmed the NMR interpretation [5].

Experimental Part

1. *General.* $[Ru_3(CO)_{12}]$ was prepared according to a standard procedure [12]. 1,3,5-Trithiane was purchased from *Fluka* and used as received. All operations were carried out under N_2 using standard *Schlenk* techniques. Solvents were purified, distilled from the appropriate drying agents, and stored under N_2. Prep. TLC was performed on plates coated with Al_2O_3. IR Spectra: *Perkin Elmer FT IR 1720* spectrophotometer. ^1H- and ^{13}C-NMR Spectra: *Bruker WM 400* in (D_8)THF at normal atmospheric pressure: δ in ppm, J in Hz. Elemental analysis was performed by Mikroelementaranalytisches Laboratorium der Eidgenössischen Technischen Hochschule, Zürich.

2. *Nonacarbonyl{μ_3-[η^3-(1,3,5-trithiane)]}triruthenium* (**1**). A soln. of $[Ru_3(CO)_{12}]$ (64.3 mg, 0.101 mmol) and 1,3,5-trithiane (14.7 mg, 0.106 mmol) in THF (25 ml) was refluxed in a 125-ml *Schlenk* tube for 3 h. The resulting yellow soln. was allowed to cool to r.t. and the volume of THF reduced to 5 ml. To the THF soln. was then added 25 ml of CH_2Cl_2 producing a finely divided yellow precipitate. The solid was isolated, dissolved in 2 ml THF, and chromatographed on Al_2O_3 TLC plates. Elution with CH_2Cl_2/THF 1:3, gave **1** (49.6 mg, 71.1%) and some unreacted $[Ru_3(CO)_{12}]$. Isolation of **1** required rinsing the Al_2O_3 with alternating portions of THF and MeOH. Yellow crystals of **1** were obtained by slow evaporation of a THF soln. The filtrate from the original separation contained no products in any significant concentration.

Data of **1**: IR (THF, 298 K): 2052*m*, 2004*s*, 1972*w*, 1950*m*, 1810*s*. ^1H-NMR ((D_8)THF, 298 K): 4.16 (*d*, 3 H); 2.38 (*d*, 3 H). ^{13}C-NMR ((D_8)THF, 233 K): 263.07; 199.26; 197.59. Anal. calc. for $C_{12}H_6O_9Ru_3S_3 \cdot 0.15\ C_4H_8O$ (704.32): C 21.49, H 1.03; found: C 21.53, H 1.06.

3. *Crystal-Structure Determination.* Data for the crystal structure analysis were collected on a *Stoe-Siemans AED 2* four-circle diffractometer at r.t. using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and with ω/Θ scan mode. Maximum value $(\sin\Theta)/\lambda$ was 0.5946. $C_{12}H_6O_9Ru_3S_3$ (693.56): yellow, rectangular crystal with dimensions 0.42 × 0.34 × 0.30 mm, orthorhombic ($Pna2_1$) with $a = 12.7535(4)$, $b = 12.7835(4)$, $c = 11.2755(6)$ Å, $V = 1838.29(13)$ Å^3, $Z = 4$, $D_c = 2.484$ g/cm^3, $F(000) = 1320$, $\mu = 27.6$ cm^{-1}. From a total of 1711 reflections, 1622 (with $I > 2.5\ \sigma$) were used in refinement of 243 parameters to yield residual $R = 0.024$ and $R_w = 0.035$. All atoms except H-atoms were treated anisotropically. H-Atoms were added in calculated positions and held fixed. The structure was solved by direct methods (SHELXS [13]); all further calculations were carried out using the NRCVAX system [14].

Supplementary Material. Complete lists of bond lengths and angles, observed and calculated structure factors, crystal data, fractional atomic coordinates, and anisotropic thermal parameters have been deposited at the *Cambridge Crystallographic Data Center* and are available upon request.

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