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Coordination of Polythiaether Macrocycles to Metal Cluster Complexes. 1. Synthesis and Structural Characterization of $Ru_5(CO)_{13}(\mu\text{-}\eta^1\text{-}12S3)(\mu_5\text{-}C)$ and $Ru_5(CO)_{11}(\mu\text{-}\eta^3\text{-}12S3)(\mu_5\text{-}C)$, 12S3 = 1,5,9-Trithiacyclododecane

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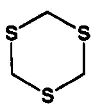
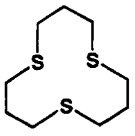
The reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**, with 1,5,9-trithiacyclododecane (12S3) in hexane solvent at reflux has yielded the new cluster complex $Ru_5(CO)_{13}(\mu\text{-}\eta^1\text{-}12S3)(\mu_5\text{-}C)$, **2**, in 86% yield. When **1** and 12S3 were heated to reflux in octane solvent the new complex $Ru_5(CO)_{11}(\mu\text{-}\eta^3\text{-}12S3)(\mu_5\text{-}C)$, **3**, was formed in 75% yield. Compound **2** and be converted to **3** in 80% yield at 125 °C. Compounds **2** and **3** were both characterized by single crystal X-ray diffraction analyses. Both compounds contain a square pyramidal cluster of five ruthenium atoms with a μ_5-carbido ligand. In **2** the 12S3 ligand bridges one edge of the square base of the $Ru_5(\mu_5\text{-}C)$ cluster by using only one of its sulfur atoms. The other two sulfur atoms are uncoordinated. In the transformation of **2** to **3**, two CO ligands were eliminated and the two uncoordinated sulfur atoms became coordinated to one of the sulfur-bridged ruthenium atoms. Crystal data for **2**: space group = $P2_1/n$, a = 14.335(3) Å, b = 15.188(3) Å, c = 15.439(3) Å, β = 91.83(2)°, Z = 4, 2249 reflections, R = 0.034. For **3**·CH_2Cl_2: space group = $P2_12_12_1$, a = 14.213(4) Å, b = 17.431(4) Å, c = 13.713(4) Å, Z = 4, 2797 reflections, R = 0.036.

Introduction

Polythiaether macrocycles have recently attracted attention because of their ability to serve as ligands for the transition elements.[1] To date, however, there have been very few examples of the coordination of polythiaether macrocycles to metal carbonyl cluster complexes.[2,3] Most studies have involved the small six membered heterocycle 1,3,5-trithiane, 6S3, which has been shown



6S3



12S3

to favor coordination to triangular faces in metal cluster complexes (e.g. $Ir_4(CO)_9(6S3)$,[3a] $Rh_4(CO)_9(6S3)$,[3b] and $Ru_3(CO)_9(6S3)$[3c,d]) with one sulfur atom attached to each of the three metal atoms.

We have recently discovered that the macrocycle 1,5,9-trithiacyclododecane (12S3) can be prepared catalytically by the cyclooligomerization of thietane using trirhenium clusters.[4] Accordingly, we have proceeded to investigate some of the coordination behavior of 12S3 to metal cluster complexes. In this report is described the results of some of our recent studies of the complexation of 12S3 to the carbide containing cluster $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**.[5]

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM-500 FT-NMR spectrometer. $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**, was prepared by the previously reported procedure.[5] 1,5,9-trithiacyclododecane, 12S3, was prepared by our recently discovered procedure for the catalytic cyclooligomerization of thietane.[4b] Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $Ru_5(CO)_{13}(\mu\text{-}\eta^1\text{-}12S3)(\mu_5\text{-}C)$, 2. A 25-mg amount of **1** (0.027 mmol) and a 7.3-mg amount of 12S3 (0.033 mmol) were dissolved in 50 mL of hexane. The resulting solution was refluxed for 5 h in the presence of a slow purge with nitrogen and then filtered hot under nitrogen. Any solid which remained in the reaction flask at this time was dissolved in CH_2Cl_2 and also filtered. The volume was reduced to

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approximately 30 mL and the solution was allowed to stand for 12 h. During this time 25.7 mg of dark brown precipitate formed and was collected. It was identified as $Ru_5(CO)_{13}(\mu\text{-}\eta^1\text{-}12S3)(\mu_5\text{-}C)$, **2**, yield 86%. Analytical and spectral data for **2**. IR ν_{CO} (cm^{-1}) in CH_2Cl_2: 2081 (m), 2046 (s), 2029 (m), 2016 (vs). ^1H NMR (δ in $CDCl_3$): 3.68 (m, 2H), 3.25 (m, 2H), 2.95 (q, 4H), 2.75 (m, 2H), 2.60 (m, 4H), 2.32 (m, 2H), 1.89 (q, 2H). Anal. Calcd (found) for **2**: C, 25.02 (24.87); H, 1.64 (1.57).

Preparation of $Ru_5(CO)_{11}(\mu\text{-}\eta^3\text{-}12S3)(\mu_5\text{-}C)$, 3. A 25.0-mg amount of **1** (0.027 mmol) and 7.3 mg of 12S3 (0.033 mmol) were dissolved in 50 mL of octane and then heated to reflux for 4 h. After cooling to room temperature, a brown precipitate formed. The solid was washed with 3 × 10-mL portions of hexanes, dissolved with 30 mL of CH_2Cl_2, and filtered under nitrogen. The solvent volume was reduced to approximately 10 mL, 20 mL of hexane was added, and the solution was placed in a freezer at −14 °C. After 12 h, 21.3 mg of $Ru_5(CO)_{11}(\mu\text{-}\eta^3\text{-}12S3)(\mu_5\text{-}C)$, **3**, precipitated and was collected (yield 75%). Spectral data for **3** follow. IR (ν_{CO}, cm^{-1} in CH_2Cl_2): 2055 (s), 2016 (vs), 1990 (vs), 1972 (m, sh), 1939 (m), 1915 (sh). ^1H NMR (δ in CD_2Cl_2): 4.03 (ddd, 1H), 3.91 (ddd, 1H), 3.59 (ddd, 1H), 3.50 (ddd, 1H), 3.01 (m, 2H), 2.93−2.61 (m, 8H), 2.47 (t, 1H), 2.39 (m, 1H), 2.02 (m, 1H), 1.85 (m, 1H). A spectrum taken in acetone-d_6 solvent showed an additional resonance, a singlet at 5.63 ppm, indicative of the presence of 1 equiv of CH_2Cl_2 that had cocrystallized with each unit of the complex. This was further confirmed by a single crystal X-ray diffraction analysis. Anal. Calcd (found) for **3**·CH_2Cl_2: C, 23.32 (23.45); H, 1.78 (1.71).

Conversion of 2 to 3. A 20.0-mg amount of **2** was dissolved in 5 mL of CH_2Cl_2. A 30-mL portion of octane was added and the solution was heated to reflux under a nitrogen purge for 3 h. The reaction mixture was allowed to cool, and a brown precipitate formed. The supernatant liquid was removed via syringe; the brown precipitate was washed with 3 × 10-mL portions of hexanes and then dried under vacuum. A 15.1-mg sample of **3** (80% yield) was collected.

Crystallographic Analysis. Crystals of **2** suitable for diffraction analysis were grown by dissolving **2** in a hot hexane solvent and allowing the solution to cool to room temperature over a period of 12 h. Crystals of **3** suitable for diffraction analysis were grown from a CH_2Cl_2/hexanes 2/1 mixture at −14 °C. The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cells of the crystals were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Tables 1−7. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN motif structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Lorentz/polarization (Lp) and absorption corrections (empirical based on ψ scans) were applied to the data for each structure. Full matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2+(0.02I_{net})^2]^{1/2}Lp$.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established on the basis of the patterns of systematic absences observed during the collection of the intensity data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the 12S3 ligand were calculated by assuming idealized tetrahedral geometries at the carbon atoms and C−H distances of 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined.

Table 1. Crystallographic Data for Compounds 2 and 3

	2	3
empirical formula	$Ru_5S_3O_{13}C_{23}H_{18}$	$Ru_5S_3O_{11}C_{21}H_{18}\cdot CH_2Cl_2$
formula weight	1103.92	1132.83
crystal system	monoclinic	orthorhombic
lattice parameters		
a (Å)	14.335(3)	14.213(4)
b (Å)	15.188(3)	17.431(4)
c (Å)	15.439(3)	13.713(4)
α (deg)	90.0	90.0
β (deg)	91.83(2)	90.0
γ (deg)	90.0	90.0
V (Å^3)	3360(1)	3397(1)
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 15)
Z value	4	4
D_{calc}, g/cm^3	2.18	2.21
μ(Mo Kα), cm^{-1}	23.92	25.18
temp (°C)	20	20
$2\theta_{max}$ (deg)	41.0	41.0
no. obsd; total; $I > 3\sigma(I)$	3548; 2249	3736; 2797
no. of variables	397	383
residuals:[a] R, R_w	0.034; 0.029	0.036; 0.034
goodness of fit indicator (GOF)[b]	1.59	1.33
max shift in final cycle	0.01	0.09
largest peak in final diff map, e$^-$/Å^3	0.85	0.54
abs corr, max/min	empirical, 1.0/0.88	empirical, 1.0/0.92

[a] $R = \sum_{hkl}(||F_o| - |F_c||/\sum_{hkl}|F_o|$, $R_w = [\sum_{hkl}w(|F_o| - |F_c|^2)/\sum_{hkl}F_o^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$. [b] GOF = $[\sum_{hkl}(|F_o| - |F_c|/\sigma(F_o)]/(n_{data} - n_{vari})$.

Compound **3** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was established on the basis of the patterns of systematic absences observed during the collection of the intensity data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the 12S3 ligand were calculated by assuming idealized tetrahedral geometries at the carbon atoms and using C−H = 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined. The thermal parameters of three of the carbon atoms, C(7), C(8), and C(9), were found to be a little larger and more anisotropic than normal, and it is suspected that there may be some disorder in the positions of these three atoms, but a suitable disorder model could not be refined. A molecule of CH_2Cl_2 from the crystallization solvent was found cocrystallized with the complex in the final stages of the analysis. This was included in the analysis and was satisfactorily refined. A test for enantiomorph was made by inverting the coordinates of all atoms and refining again, but this did not produce an improvement in the R-factors and the original set of positional parameters was thus retained.

Results and Discussion

When the reaction of 12S3 with $Ru_5(CO)_{15}(\mu_5\text{-}C)$ was performed in hexane solvent at reflux for 4 h, the new compound, $Ru_5(CO)_{13}(\mu\text{-}\eta^1\text{-}12S3)(\mu_5\text{-}C)$, **2**, was obtained in 86% yield. Compound **2** was characterized by a combination of IR, ^1H NMR, and single crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. The molecule contains a square pyramidal $Ru_5(\mu_5\text{-}C)$ cluster that is analogous to that of its parent, $Ru_5(CO)_{15}(\mu_5\text{-}C)$,

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(6) (a) *International Tables for X-ray Crystallography*; Vol. IV, Kynoch Press: Birmingham, England, 1975; Table 2.2B, pp 99−101. (b) *Ibid.*, Table 2.3.1, pp 149−150.

Table 2. Positional Parameters and *B*(eq) Values (Å^2) for 2

atom	*x*	*y*	*z*	*B*(eq)
Ru(1)	0.39784(7)	0.32267(7)	0.54973(6)	3.36(5)
Ru(2)	0.21077(7)	0.26499(7)	0.52332(6)	3.70(6)
Ru(3)	0.21672(7)	0.20101(7)	0.70261(7)	3.96(6)
Ru(4)	0.40221(7)	0.26713(7)	0.71605(6)	3.37(5)
Ru(5)	0.34578(7)	0.14520(7)	0.58359(7)	3.84(5)
S(1)	0.5268(2)	0.3164(2)	0.6415(2)	3.7(2)
S(2)	0.7842(3)	0.5137(3)	0.6972(3)	7.1(3)
O(11)	0.4650(7)	0.3254(8)	0.3657(6)	8.1(7)
O(12)	0.3747(7)	0.5188(7)	0.5448(7)	7.0(6)
O(21)	0.1147(7)	0.4429(7)	0.5278(7)	6.4(6)
O(22)	0.2566(7)	0.2712(6)	0.3335(6)	6.7(6)
O(23)	0.0360(7)	0.1579(7)	0.4766(7)	7.7(7)
O(31)	0.1306(8)	0.3371(9)	0.8163(7)	9.6(8)
O(32)	0.0408(7)	0.0942(7)	0.6731(7)	7.5(7)
O(33)	0.2776(8)	0.078(1)	0.8473(9)	12(1)
O(41)	0.4838(8)	0.1539(8)	0.8637(7)	8.4(7)
O(42)	0.3565(9)	0.4211(7)	0.8304(8)	8.9(8)
O(51)	0.488(1)	0.1149(8)	0.4455(9)	12(1)
O(52)	0.442(1)	0.0203(8)	0.7088(9)	12(1)
O(53)	0.2111(8)	0.0119(7)	0.5074(7)	7.5(7)
C(1)	0.2987(8)	0.2706(8)	0.6262(8)	4.1(6)
C(2)	0.5804(8)	0.4202(8)	0.6719(8)	4.5(7)
C(3)	0.632(1)	0.420(1)	0.7589(8)	5.1(8)
C(4)	0.694(1)	0.502(1)	0.7715(9)	5.7(8)
C(5)	0.860(1)	0.427(1)	0.729(1)	7(1)
C(6)	0.926(1)	0.404(1)	0.658(1)	8(1)
C(7)	0.882(1)	0.355(1)	0.580(1)	6.4(9)
C(8)	0.766(1)	0.2213(9)	0.5288(9)	5.8(8)
C(9)	0.6732(9)	0.271(1)	0.5357(8)	5.2(8)
C(10)	0.6261(8)	0.2475(8)	0.6198(8)	4.6(7)
C(11)	0.440(1)	0.325(1)	0.435(1)	5.6(8)
C(12)	0.381(1)	0.444(1)	0.5458(8)	4.6(8)
C(21)	0.150(1)	0.373(1)	0.5259(8)	4.6(8)
C(22)	0.240(1)	0.2690(8)	0.406(1)	4.7(7)
C(23)	0.100(1)	0.198(1)	0.498(1)	5.3(8)
C(31)	0.161(1)	0.284(1)	0.772(1)	6(1)
C(32)	0.107(1)	0.1364(9)	0.680(1)	5.2(8)
C(33)	0.254(1)	0.127(1)	0.793(1)	8(1)
C(41)	0.453(1)	0.198(1)	0.8104(9)	5.0(8)
C(42)	0.379(1)	0.363(1)	0.790(1)	5.2(8)
C(51)	0.431(1)	0.134(1)	0.498(1)	7(1)
C(52)	0.405(1)	0.071(1)	0.661(1)	7(1)
C(53)	0.259(1)	0.065(1)	0.536(1)	6(1)

Table 3. Intramolecular Distances for Compound 2[a]

atoms	distance	atoms	distance
Ru(1)−Ru(2)	2.838(2)	Ru−C(av)	1.85(2)
Ru(1)−Ru(4)	2.702(1)	S(1)−C(2)	1.81(1)
Ru(1)−Ru(5)	2.846(2)	S(1)−C(10)	1.81(1)
Ru(1)−S(1)	2.294(3)	S(2)−C(4)	1.77(1)
Ru(1)−C(1)	2.04(1)	S(2)−C(5)	1.77(2)
Ru(2)−Ru(3)	2.932(2)	S(3)−C(7)	1.79(1)
Ru(2)−Ru(5)	2.804(2)	S(3)−C(8)	1.77(1)
Ru(2)−C(1)	2.00(1)	O−C(av)	1.15(2)
Ru(3)−Ru(4)	2.844(2)	C(2)−C(3)	1.52(2)
Ru(3)−Ru(5)	2.791(2)	C(3)−C(4)	1.53(2)
Ru(3)−C(1)	2.00(1)	C(5)−C(6)	1.52(2)
Ru(4)−Ru(5)	2.853(2)	C(6)−C(7)	1.52(2)
Ru(4)−S(1)	2.282(3)	C(8)−C(9)	1.54(2)
Ru(4)−C(1)	2.00(1)	C(9)−C(10)	1.52(2)
Ru(5)−C(1)	2.14(1)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 4. Intramolecular Bond Angles for 2[a]

atoms	angle	atoms	angle
Ru(2)−Ru(1)−Ru(4)	91.91(5)	Ru(1)−Ru(5)−Ru(3)	90.83(4)
Ru(2)−Ru(1)−Ru(5)	59.11(4)	Ru(1)−Ru(5)−Ru(4)	56.60(4)
Ru(2)−Ru(1)−S(1)	144.6(1)	Ru(2)−Ru(5)−Ru(3)	63.22(4)
Ru(4)−Ru(1)−Ru(5)	61.83(4)	Ru(2)−Ru(5)−Ru(4)	89.51(4)
Ru(4)−Ru(1)−S(1)	53.60(8)	Ru(3)−Ru(5)−Ru(4)	60.49(4)
Ru(5)−Ru(1)−S(1)	93.1(1)	Ru(1)−S(1)−Ru(4)	72.4(1)
S(1)−Ru(1)−C(11)	107.8(4)	Ru(1)−S(1)−C(2)	116.8(4)
S(1)−Ru(1)−C(12)	99.5(4)	Ru(1)−S(1)−C(10)	122.3(4)
Ru(1)−Ru(2)−Ru(3)	88.16(4)	Ru(4)−S(1)−C(2)	119.2(4)
Ru(1)−Ru(2)−Ru(5)	60.58(4)	Ru(4)−S(1)−C(10)	122.5(4)
Ru(3)−Ru(2)−Ru(5)	58.18(4)	C(2)−S(1)−C(10)	102.8(6)
Ru(2)−Ru(3)−Ru(4)	87.18(4)	C(4)−S(2)−C(5)	101.8(7)
Ru(2)−Ru(3)−Ru(5)	58.60(4)	C(7)−S(3)−C(8)	100.2(7)
Ru(4)−Ru(3)−Ru(5)	60.83(4)	S(1)−C(2)−C(3)	115(1)
Ru(1)−Ru(4)−Ru(3)	92.73(5)	C(2)−C(3)−C(4)	112(1)
Ru(1)−Ru(4)−Ru(5)	61.57(4)	S(2)−C(4)−C(3)	115(1)
Ru(1)−Ru(4)−S(1)	54.03(8)	S(2)−C(5)−C(6)	111(1)
Ru(3)−Ru(4)−Ru(5)	58.67(4)	C(5)−C(6)−C(7)	115(1)
Ru(3)−Ru(4)−S(1)	145.5(1)	S(3)−C(7)−C(6)	110(1)
Ru(5)−Ru(4)−S(1)	93.19(9)	S(3)−C(8)−C(9)	115(1)
S(1)−Ru(4)−C(1)	102.5(4)	C(8)−C(9)−C(10)	111(1)
S(1)−Ru(4)−C(41)	106.2(4)	S(1)−C(10)−C(9)	113(1)
S(1)−Ru(4)−C(42)	102.2(4)	Ru−C−O(av)	177(2)
Ru(1)−Ru(5)−Ru(2)	60.30(4)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table 5. Positional Parameters and *B*(eq) Values (Å^2) for $Ru_5(CO)_{11}(\mu\text{-}\eta^3\text{-}12S3)(\mu_5\text{-}C)$, 3

atom	*x*	*y*	*z*	*B*(eq)
Ru(1)	0.37503(9)	0.23741(7)	0.32572(9)	4.02(7)
Ru(2)	0.2038(1)	0.31443(7)	0.3608(1)	4.55(7)
Ru(3)	0.10348(8)	0.19745(7)	0.2536(1)	3.62(6)
Ru(4)	0.28609(8)	0.12212(7)	0.23313(8)	3.07(6)
Ru(5)	0.2521(1)	0.27842(7)	0.1671(1)	4.22(6)
S(1)	0.4402(2)	0.1338(2)	0.2449(3)	4.4(2)
S(2)	0.2672(3)	0.0183(2)	0.3354(3)	3.5(2)
S(3)	0.2818(3)	0.0497(2)	0.0872(3)	4.4(2)
O(11)	0.507(1)	0.3738(8)	0.326(1)	9(1)
O(12)	0.4102(8)	0.2125(7)	0.5389(8)	6.6(7)
O(21)	0.330(1)	0.4502(9)	0.409(2)	14(1)
O(22)	0.028(1)	0.4168(8)	0.345(1)	9(1)
O(23)	0.156(1)	0.258(1)	0.565(1)	11(1)
O(31)	−0.063(1)	0.300(1)	0.191(1)	11(1)
O(32)	0.009(1)	0.1137(7)	0.423(1)	7.7(8)
O(33)	0.0589(8)	0.0775(8)	0.099(1)	7.1(8)
O(51)	0.441(1)	0.345(1)	0.099(1)	12(1)
O(52)	0.139(1)	0.4218(9)	0.129(1)	11(1)
O(53)	0.205(1)	0.2065(8)	−0.0282(9)	8.9(9)
C(1)	0.237(1)	0.2118(8)	0.297(1)	3.9(7)
C(2)	0.509(1)	0.0650(9)	0.317(1)	4.7(9)
C(3)	0.455(1)	0.0304(8)	0.400(1)	4.1(8)
C(4)	0.378(1)	−0.0291(8)	0.367(1)	4.5(8)
C(5)	0.211(1)	−0.0663(8)	0.281(1)	4.8(9)
C(6)	0.239(2)	−0.085(1)	0.182(2)	9(1)
C(7)	0.250(3)	−0.049(1)	0.103(1)	12(2)
C(8)	0.399(2)	0.039(2)	0.045(2)	17(3)
C(9)	0.458(3)	0.100(2)	0.056(2)	14(3)
C(10)	0.509(1)	0.137(1)	0.133(1)	6(1)
C(11)	0.459(1)	0.320(1)	0.324(1)	5(1)
C(12)	0.397(1)	0.217(1)	0.457(1)	4.6(9)
C(21)	0.284(2)	0.398(1)	0.390(1)	8(1)
C(22)	0.091(1)	0.3774(9)	0.347(1)	5(1)
C(23)	0.176(1)	0.284(1)	0.491(1)	6(1)
C(31)	−0.002(1)	0.264(1)	0.213(1)	5(1)
C(32)	0.045(1)	0.148(1)	0.359(1)	5(1)
C(33)	0.081(1)	0.122(1)	0.157(1)	5(1)
C(51)	0.371(1)	0.325(1)	0.130(1)	8(1)
C(52)	0.180(2)	0.367(1)	0.149(1)	8(1)
C(53)	0.221(1)	0.2300(9)	0.046(1)	5(1)

1.[5] The 12S3 ligand is coordinated to the cluster through only one of its sulfur atoms. However, it is bonded to two of the metal atoms in the square base in a bridging mode by using both of its lone pairs of electrons. The sulfur atom is displaced only 0.30 Å from the least-squares plane defined by the four basal metal atoms. The coordination of the sulfur atom produces a substantial shortening on the bridged metal−metal bond, Ru(1)−Ru(4) = 2.702(1) Å. In **1**, the average Ru−Ru bond distance among the atoms of the square base is 2.86(2) Å. The Ru(1)−Ru(2) and Ru(3)−Ru(4) distances in **2** are similar to those found in **1**, 2.838(2) and 2.844(2) Å, but the Ru(2)−Ru(3) distance at 2.932(2) Å is significantly longer.[5] The Ru−Ru distances between

Table 6. Intramolecular Distances for 3[a]

atoms	distance	atoms	distance
Ru(1)–Ru(2)	2.821(2)	Ru(4)–S(2)	2.304(4)
Ru(1)–Ru(4)	2.692(2)	Ru(4)–S(3)	2.367(4)
Ru(1)–Ru(5)	2.879(2)	Ru(4)–C(1)	1.92(1)
Ru(1)–S(1)	2.312(4)	Ru(5)–C(1)	2.13(1)
Ru(1)–C(1)	2.06(1)	Ru(5)–C(51)	1.94(2)
Ru(1)–C(11)	1.87(2)	Ru(5)–C(52)	1.86(2)
Ru(1)–C(12)	1.86(2)	Ru(5)–C(53)	1.92(2)
Ru(2)–Ru(3)	2.890(2)	S(1)–C(2)	1.83(1)
Ru(2)–Ru(5)	2.814(2)	S(1)–C(10)	1.83(2)
Ru(2)–C(1)	2.05(1)	S(2)–C(4)	1.83(1)
Ru(2)–C(21)	1.89(2)	S(2)–C(5)	1.83(1)
Ru(2)–C(22)	1.96(2)	S(3)–C(7)	1.79(2)
Ru(2)–C(23)	1.91(2)	S(3)–C(8)	1.77(3)
Ru(3)–Ru(4)	2.922(2)	O–C(av)	1.15(2)
Ru(3)–Ru(5)	2.804(2)	C(2)–C(3)	1.50(2)
Ru(3)–C(1)	2.00(1)	C(3)–C(4)	1.58(2)
Ru(3)–C(31)	1.97(2)	C(5)–C(6)	1.44(2)
Ru(3)–C(32)	1.88(2)	C(6)–C(7)	1.26(2)
Ru(3)–C(33)	1.88(2)	C(8)–C(9)	1.36(4)
Ru(4)–Ru(5)	2.911(2)	C(9)–C(10)	1.44(3)
Ru(4)–S(1)	2.205(4)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 7. Intramolecular Bond Angles for 3[a]

atoms	angle	atoms	angle
Ru(2)–Ru(1)–Ru(4)	91.75(5)	Ru(3)–Ru(4)–S(2)	101.0(1)
Ru(2)–Ru(1)–Ru(5)	59.15(5)	Ru(3)–Ru(4)–S(3)	107.3(1)
Ru(2)–Ru(1)–S(1)	143.0(1)	Ru(5)–Ru(4)–S(1)	95.8(1)
Ru(4)–Ru(1)–Ru(5)	62.89(5)	Ru(5)–Ru(4)–S(2)	154.8(1)
Ru(4)–Ru(1)–S(1)	51.6(1)	Ru(5)–Ru(4)–S(3)	103.4(1)
Ru(5)–Ru(1)–S(1)	94.3(1)	S(1)–Ru(4)–S(2)	98.2(1)
Ru(1)–Ru(2)–Ru(3)	90.18(5)	S(1)–Ru(4)–S(3)	97.9(2)
Ru(1)–Ru(2)–Ru(5)	61.47(4)	S(2)–Ru(4)–S(3)	95.3(1)
Ru(3)–Ru(2)–Ru(5)	58.87(5)	Ru(1)–Ru(5)–Ru(2)	59.38(5)
Ru(2)–Ru(3)–Ru(4)	85.85(5)	Ru(1)–Ru(5)–Ru(3)	90.74(5)
Ru(2)–Ru(3)–Ru(5)	59.21(5)	Ru(1)–Ru(5)–Ru(4)	55.41(4)
Ru(4)–Ru(3)–Ru(5)	61.07(4)	Ru(2)–Ru(5)–Ru(3)	61.92(5)
Ru(1)–Ru(4)–Ru(3)	92.08(5)	Ru(2)–Ru(5)–Ru(4)	87.47(5)
Ru(1)–Ru(4)–Ru(5)	61.70(5)	Ru(3)–Ru(5)–Ru(4)	61.47(4)
Ru(1)–Ru(4)–S(1)	55.3(1)	Ru(1)–S(1)–Ru(4)	73.1(1)
Ru(1)–Ru(4)–S(2)	110.7(1)	C(2)–S(1)–C(10)	100.8(7)
Ru(1)–Ru(4)–S(3)	144.0(1)	C(4)–S(2)–C(5)	96.0(7)
Ru(3)–Ru(4)–Ru(5)	57.45(4)	C(7)–S(3)–C(8)	100(2)
Ru(3)–Ru(4)–S(1)	146.5(1)	Ru–C–O(av)	174(2)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

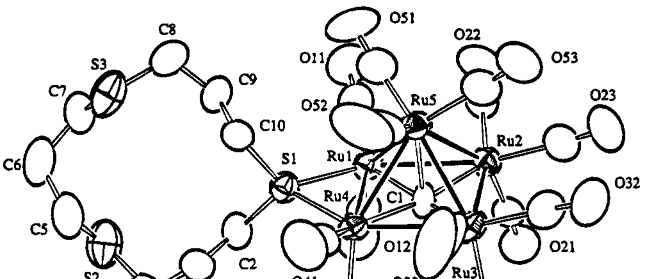


Figure 1. An ORTEP diagram of $Ru_5(CO)_{11}(12S3)(\mu_5\text{-}C)$, **2**, showing 40% probability thermal ellipsoids.

the apical atom Ru(5) and the sulfur bridged metal atoms are significantly longer, Ru(1)–Ru(5) = 2.846(2) Å and Ru(4)–Ru(5) = 2.853(2) Å, than the two other apical–basal Ru–Ru distances, Ru(2)–Ru(5) = 2.804(2) Å and Ru(3)–Ru(5) = 2.791(2) Å, but the average of the four, 2.824 Å, is quite close to the average value found in **1**, 2.83(2) Å. When phosphines are substituted for the CO ligands in **1**, the substitution also occurs exclusively at the basal ruthenium atoms but in contrast to that in **2**, it occurs at the sites that lie approximately perpendicular to the basal plane. The effect of phosphine substitution is to increase the length of the associated Ru–Ru distances.[5] The carbido ligand in **2** is displaced 0.15(1) Å from the Ru_4 basal plane in the direction away from that of the apical metal atom Ru(5). A similar displacement, 0.11(2) Å, was observed for the carbido ligand in **1**. The 12S3 ligand displays a conformation that is similar to that found for the free molecule[7] and in the complex $Os_4(CO)_{13}(\mu\text{-}\eta^1\text{-}12S3)$, **4**,[2] where the 12S3 ligand is coordinated to the two wingtip metal atoms of an Os_4 butterfly tetrahedron through one of its sulfur atoms. The sulfur–carbon distances involving the coordinated sulfur atom seem to be normal for C–S single bonds, ranging from 1.77(1) to 1.81(1) Å.

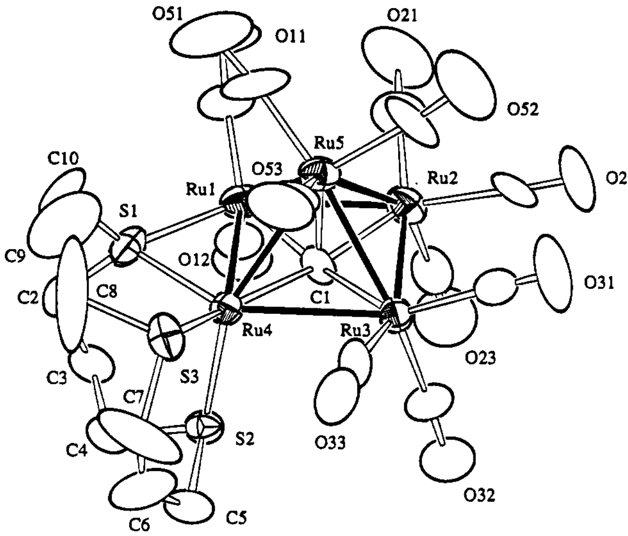
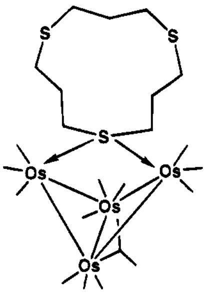


Figure 2. An ORTEP diagram of $Ru_5(CO)_{11}(12S3)(\mu_5\text{-}C)$, **3**, showing 40% probability thermal ellipsoids.



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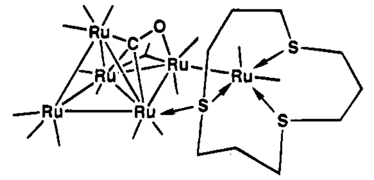

5

When a solution of 12S3 and $Ru_5(CO)_{15}(\mu_5\text{-}C)$ in octane solvent was heated to reflux for 4 h, the compound $Ru_5(CO)_{11}(\mu\text{-}\eta^3\text{-}12S3)(\mu_5\text{-}C)$, **3**, was formed in 75% yield. Compound **3** was also characterized by a single crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 2. This molecule also contains a square pyramidal $Ru_5(\mu_5\text{-}C)$ cluster analogous to that in **1** and **2**, but in this molecule the 12S3 ligand has a $\mu\text{-}\eta^3$ tridentate coordination. All three sulfur atoms are coordinated to the

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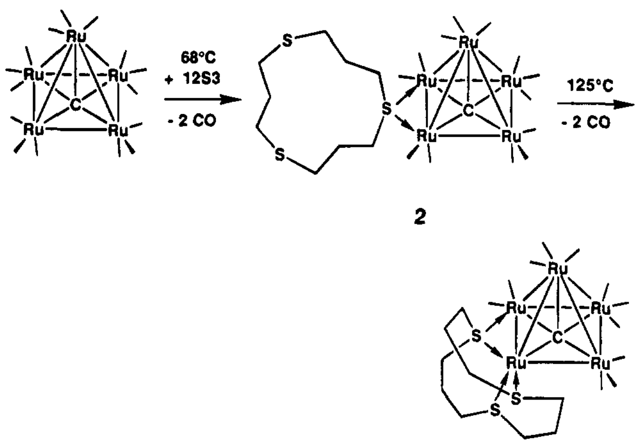
(7) Rawle, S. C.; Admans, G. A.; Cooper, S. R. *J. Chem. Soc., Dalton Trans.* **1988**, 93.

ruthenium atom Ru(4) in the basal plane. However, the sulfur atom S(1) also uses its second lone pair of electrons to coordinate to one of the neighboring ruthenium atoms Ru(1) and thus forms a bridging interaction similar to that found in **2**. As found in **2** the sulfur-bridged metal–metal bond Ru(1)–Ru(4) is significantly shorter than all of the others, 2.692(2) Å. Otherwise, the metal–metal bonds to Ru(4) are the longest in the molecule, Ru(3)–Ru(4) = 2.922(2) Å and Ru(4)–Ru(5) = 2.911(2) Å. The carbido ligand in **2** is displaced 0.10(1) Å from the Ru_4 basal plane in the direction away from that of the apical metal atom Ru(5). The observation of highly anisotropic thermal parameters of three of the carbon atoms, C(7), C(8), and C(9), in the macrocycle suggests the presence of some minor disorder in the positions of these atoms which may have adversely affected the values of the bond distances between them.

A similarly coordinated 12S3 ligand was found in the complex $Ru_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}\eta^3\text{-}12S3)$, **5**, that was obtained from the reaction of 12S3 with $Ru_3(CO)_{12}$ in refluxing THF.[2] The 12S3 ligand in **3** serves as an eight-electron donor. The cluster has a total of 74 valence electrons and obeys the conventional electron-counting rules.[8]

Compound **2** appears to be an intermediate in the formation of **3**. When a solution of **2** in octane solvent was heated to reflux, it was decarbonylated and converted to **3** in 80% yield; see Scheme 1.

Scheme 1



Our studies further demonstrate that 12S3 can be an effective ligand in polynuclear metal carbonyl complexes.[2] It was observed that the 12S3 ligand exhibits a distinct preference to coordinate all of its sulfur atoms to one metal atom in a cluster when it is fully coordinated. Thus, the differences between 6S3 and 12S3 are similar to those between bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane, where the former exhibits preference to bridge pairs of metal atoms and the latter exhibits a preference to chelate to a single metal atom.[9] Unlike phosphines, however, the potential for the sulfur atoms to exhibit bridging coordination is also displayed and indicated through the isolation of the intermediate complex **2** in the formation of **3**, this appears to play an important role in the introduction of the ligand into complexation to the cluster in this square pyrmidal cluster complex.

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Supplementary Material Available: Tables of crystal data, final atomic positional parameters, selected bond distances and angles, and anisotropic thermal parameters for **2** and **3** (11 pages). Ordering information is given on any current masthead page.

OM9405145

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(8) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F.; Kaesz, H. D.; Adams, R. D., Eds.; VCH Publishers: New York, 1990, Chapter 2.

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