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Note

Synthesis and structural characterization of ruthenium and osmium carbonyl clusters containing 4,6-dimethylpyrimidine-2-thione

Yat-Kun Au, Kung-Kai Cheung, Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong

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Abstract

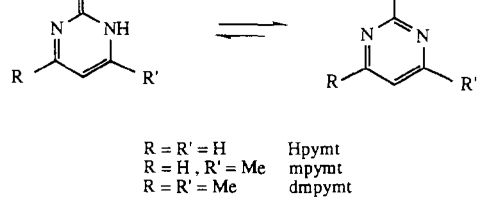
$Os_3(CO)_{10}(MeCN)_2$ reacts with 4,6-dimethylpyrimidine-2-thione (dmpymt) in CH_2Cl_2 at room temperature to give $Os_3(CO)_{10}(\mu$-H)(μ-dmpymt) (**1**) and $Os_3(CO)_{10}(\mu$-H)(μ-SH) (**2**). The corresponding reaction of $Ru_3(CO)_{10}(MeCN)_2$ with dmpymt gives $Ru_3(CO)_9(\mu$-H)(μ_3-η^2-dmpymt) (**3**), $Ru_3(CO)_{10}(\mu$-H)(μ-dmpymt) (**4**) and $Ru_3(CO)_{10}(\mu$-dmpymt$)_2$ (**5**). Cluster **4** is thermally unstable and converts to **3** readily on standing. Clusters **1**, **2**, **3** and **5** are fully characterized by IR, ^{1}H NMR, MS and X-ray crystallography. Crystals of **1** are orthorhombic, space group *Pnma* with unit-cell dimensions $a = 14.932(2)$, $b = 16.290(2)$, $c = 18.649(2)$ Å. Crystals of **2** are triclinic, space group $P\bar{1}$, $Z = 4$, with unit-cell dimensions $a = 9.163(1)$, $b = 14.123(3)$, $c = 14.305(2)$ Å, $\alpha = 70.31(1)$, $\beta = 89.32(1)$, $\gamma = 76.60(1)°$. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.793(1)$, $b = 15.558(1)$, $c = 17.259(1)$ Å, $\beta = 93.79(1)°$. Complex **5** is monoclinic, space group *C2/c*, with $a = 17.972(7)$, $b = 12.988(6)$, $c = 13.516(4)$ Å, $\beta = 111.57(3)°$.

Keywords: Crystal structures; Ruthenium complexes; Osmium complexes; Carbonyl complexes; S,N-ligand complexes; Cluster complexes

1. Introduction

Studies of the reactivity of S or N containing molecules towards metal clusters have attracted much attention. In these reactions, the metal clusters catalyzed the C–X bond cleavage (X = S, N) reactions leading to hydrodesulfurization [1–4] and hydrodenitrogenation [5]. Recent work by Adams et al. on the reactions of small strained-ring heterocycles such as thiisane [6], thietane [7–10] and azetidine [11] with trinuclear metal clusters have demonstrated the facile ring opening reaction for the heterocycles when they are coordinated to metal cluster complexes. Reactions of other aromatic heterocycles and their substituted derivatives including thiophene [12], selenophene [13], furan [13] and phosphabenzene [14] with transition metal clusters have also been reported recently.

Our interest in the reactivity of pyrimidine-2-thione (Hpymt) towards metal carbonyl clusters stemmed from its high coordination potential towards multimetal centres. It has been shown that pyridine-2-thione ligands can act as a seven-electron donor by bridging four metal atoms [15]. Similar to pyridine-2-thione, Hpymt exists in tautomeric equilibrium (–N=C–SH ⇌ NH–C=S) with the thione form dominating in its solid state, Fig. 1. Coordination compounds containing pyrimidine-2-thione are known for many p-block [16] and d-block metals [17–21]. Pyrimidine-2-thione is capable of coordinating as (i) a monodentate ligand via the S atom (type A) [20], (ii) a bridging bidentate ligand via



R = R' = H Hpymt
R = H, R' = Me mpymt
R = R' = Me dmpymt

Fig. 1. Tautomerization of pyrimidine-2-thione type ligands.

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* Corresponding author. Fax: (852) 8571586.

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Table 1
Spectroscopic data for the clusters **1**, **2**, **3**, **4** and **5**

Cluster	IR, ν(CO) (cm^{-1})	^{1}H NMR, δ	FAB–MS (m/z)
1	[a] 2115(w), 2076(s) 2068(m), 2028(s) 2015(m), 1999(w) 1990(m)	[c] 6.79(s, 1H, aryl H) 2.42(s, 6H, $-CH_3$) −17.39(s, 1H, OsH)	997(M^+) (996) [e]
2	[a] 2108(w), 2084(vw) 2068(s), 2059(s) 2022(s), 2017(m) 2004(m), 1988(w) 1986(w)	[c] 2.25(br, 1H, SH) −14.25(s, 1H, OsH)	891(M^+) (890)
3	[a] 2084(m), 2057(s) 2032(vs), 2006(m) 1996(m), 1970(w) 1961(w)	[c] 6.96(s, 1H, aryl H) 2.76(s, 3H, $-CH_3$) 2.38(s, 3H, $-CH_3$) −13.28(s, 1H, RuH)	672($M-CO$)$^+$ (698)
4	[b] 2104(w), 2067(s) 2058(m), 2020(s) 1991(w)	[c] 6.83(s, 1H, aryl H) 2.39(s, 6H, $-CH_3$) −15.39(s, 1H, RuH)	723(M^+) (723)
5	[b] 2101(w), 2068(m) 2054(s), 2015(m) 1998(w), 1977(vw) 1970(m)	[d] 6.87(s, 1H, aryl H) 6.49(s, 1H, aryl H) 2.39(m, 6H, $-CH_3$) 2.25(m, 6H, $-CH_3$)	864(M^+) (864)

M^+ = parent molecular ion based on ^{192}Os and ^{101}Ru. s = strong, m = medium, w = weak, br = broad, vw = very weak, s = singlet, m = multiplet.

[a] Recorded in n-hexane.

[b] Recorded in CH_2Cl_2.

[c] Recorded in CD_2Cl_2 at 298 K.

[d] Recorded in $CDCl_3$ at 298 K.

[e] Calculated value in parentheses.

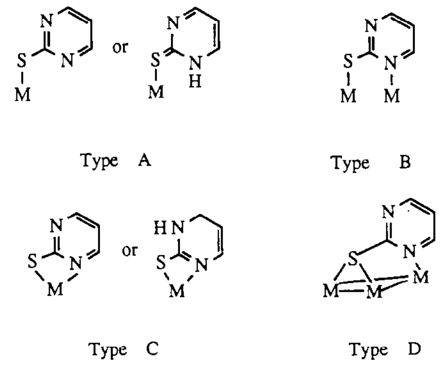

Fig. 2. Some coordination modes of the Hpymt ligand.

S and one of the N atoms (type B) [19], (iii) a chelating ligand via S and N (type C) [17] and (iv) a bidentate ligand bridging three metal centres (type D) [22] (Fig. 2).

2. Experimental

2.1. General

All operations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were purified, distilled from the appropriate drying agents and stored under nitrogen prior to use. Products were separated by thin layer chromatography (TLC) on silica gel (type 60) GF_{254} Merck 7730. IR spectra were recorded on a BIO-RAD FTS-7 IR spectrometer in CH_2Cl_2 or n-hexane. ^{1}H NMR spectra were recorded in CD_2Cl_2 or $CDCl_3$ on a JEOL GSX 270 FT-NMR spectrometer. Mass spectra were recorded on a Finnigan MAT 95 with fast atom bombardment technique. Spectroscopic data for the clusters **1**–**5** are given in Table 1.

2.2. Syntheses

The compounds $Os_3(CO)_{10}(MeCN)_2$ and $Ru_3(CO)_{10}(MeCN)_2$ were prepared according to a published procedure [23]. 4,6-Dimethylpyrimidine-2-thione was prepared by treating thiourea with acetylacetone in ethanol [24] and was recrystallized from a methanol/ethanol (1/1) mixture. $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ were used as received (Aldrich).

2.2.1. Synthesis of clusters $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}dmpymt)]$ (1) and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SH)]$ (2)

A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (100 mg, 0.107 mmol) in CH_2Cl_2 (20 cm^3) was stirred with an excess

Table 2
Crystal data for clusters **1**, **2**, **3** and **5**

	1	**2**	**3**	**5**
Formula	$C_{16}H_8N_2O_{10}SOs_3$	$C_{10}H_2O_{10}SOs_3$	$C_{15}H_8N_2O_9SRu_3$	$C_{22}H_{14}N_4O_{10}S_2Ru_3$
Formula weight	990.91	884.78	695.51	861.70
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	*Pnma*	$P\bar{1}$	$P2_1/c$	*C2/c*
a (Å)	14.932(2)	9.163(1)	7.793(1)	17.972(7)
b (Å)	16.290(2)	14.123(3)	15.558(1)	12.988(6)
c (Å)	18.649(2)	14.305(2)	17.259(1)	13.516(4)
α (°)	90.0	70.31(1)	90.0	90.0
β (°)	90.0	89.32(1)	93.79(1)	111.57(3)
γ (°)	90.0	76.60(1)	90.0	90.0
U (Å^3)	4536.0	1691.1	2087.6	2933.7
Z	8	4	4	4
D_{calc} (g cm^{-3})	2.903	3.476	2.214	1.952
μ (Mo Kα) (cm^{-1})	169.3	226.8	21.5	16.9
Temperature (°C)	293	293	293	293
$F(000)$	3536	1464	1328	1672
Data collection range, 2θ (°)	2–45	2–50	2–46	2–45
Unique reflections	3347	5922	3028	2005
Observed reflections with $I > 3\sigma(I)$	2301	5172	2264	1361
Transmission factors	0.647–0.999	0.495–0.999	0.931–0.999	0.839–0.999
R [a]	0.035	0.054	0.028	0.071
R_w [b]	0.047	0.070	0.036	0.086
No. of parameters, P	313	333	271	131
Weighting scheme [c], p	0.06	0.055	0.03	0.07
Goodness-of-fit, S [d]	1.194	2.028	1.289	1.911
Largest shift/e.s.d. final cycle	0.01	0.07	0.01	0.05

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
[c] Weighting scheme: $4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$.
[d] $S = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

of 4,6-dimethylpyrimidine-2-thione (15.1 mg, 0.1 mmol) at room temperature. The solution immediately changed from light yellow to yellow and the solvent was removed under vacuum after 30 min of stirring. The residue was then redissolved in CH_2Cl_2 (2 cm^3) and separated by TLC using an n-hexane/CH_2Cl_2 solvent mixture (80/20 vol./vol.). Two yellow products were obtained. The first yellow product ($R_f \sim 0.8$) $[Os_3(CO)_{10}(\mu\text{-dmpymt})]$ (**1**) in 43% yield was recrystallized from a CH_2Cl_2/n-hexane mixture at −10 °C as yellow crystals. The second yellow product ($R_f \sim 0.4$) $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SH})]$ (**2**) in 50% yield was recrystallized from a CH_2Cl_2/n-hexane mixture at −10 °C as orange crystals.

2.2.2. Synthesis of clusters $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-dmpymt})]$ (3), $[Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-dmpymt})]$ (4) and $[Ru_3(CO)_{10}(\mu\text{-dmpymt})_2]$ (5)

To a CH_2Cl_2 (15 cm^3) solution of freshly prepared $[Ru_3(CO)_{11}(MeCN)_2]$ (106 mg, 0.160 mmol) was added 4,6-dimethylpyrimidine-2-thione (23 mg, 0.165 mmol) at room temperature. The colour of the reaction mixture changed to orange immediately. After stirring for 30 min, the solution was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (2 cm^3) and separated by TLC using an n-hexane/CH_2Cl_2 solvent mixture (90/10 vol./vol.) $[Ru_3(CO)_{12}]$ in 21% yield, an orange product $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-dmpymt})]$ (**3**) in 33% yield, a pale yellow product $[Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-dmpymt})]$ (**4**) in 25% yield and a pale yellow product $[Ru_3(CO)_{10}(\mu\text{-dmpymt})_2]$ (**5**) in 7% yield were obtained.

2.3. Crystal and molecular structure determination

Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2/n-hexane mixture of the complex at −10 °C. X-ray data were collected at room temperature in the ω–2θ scan mode on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects. Absorption corrections by the ψ-scan mode [25] were also applied. Crystal data, data collection and structure solution parameters are summarized in Table 2. All structures were solved by a combination of direct methods (MULTAN), the Patterson method and difference Fourier techniques using the SDP package [26]. Final coordinates for the non-hydrogen atoms are listed in Tables 3–6 for clusters **1**, **2**, **3** and **5**, respectively.

Hydrogen atoms on the organic ligand were generated in their idealized position (C–H, 0.95 Å) while the hydride atoms on the metal clusters were estimated by potential energy calculations [27].

Table 3
Positional parameters and their e.s.d.s for cluster **1**

Atom	*x*	*y*	*z*
Os1	0.97452(4)	0.16163(3)	0.32181(3)
Os2	0.15858(4)	0.16213(3)	0.80638(3)
Os3	1.08838(6)	0.250	0.41659(4)
Os4	0.06011(5)	0.250	0.70054(4)
S1	1.0405(3)	0.250	0.2330(3)
S2	0.0772(3)	0.250	0.8856(3)
O11	0.8300(7)	0.0842(7)	0.2254(6)
O12	1.1200(7)	0.0331(6)	0.2993(7)
O13	0.9028(9)	0.0697(8)	0.4508(6)
O21	0.0113(8)	0.0335(7)	0.8182(7)
O22	0.2579(9)	0.0762(8)	0.6850(6)
O23	0.2837(7)	0.0833(9)	0.9147(6)
O31	0.920(1)	0.250	0.5132(8)
O32	1.238(1)	0.250	0.3050(9)
O33	1.1715(9)	0.3926(8)	0.4961(7)
O41	−0.105(1)	0.250	0.799(1)
O42	0.234(1)	0.250	0.6139(8)
O43	−0.008(1)	0.1021(8)	0.6183(7)
N1	0.9620(8)	0.1762(8)	0.1244(6)
N2	0.1399(7)	0.3226(8)	1.0032(7)
C1	0.976(1)	0.250	0.150(1)
C2	0.9200(9)	0.175(1)	0.0607(8)
C3	0.901(2)	0.250	0.025(1)
C4	0.903(1)	0.094(1)	0.025(1)
C5	0.128(1)	0.250	0.971(1)
C6	0.1730(9)	0.323(1)	1.0689(6)
C7	0.195(1)	0.250	1.102(1)
C8	0.186(1)	0.405(1)	1.1026(9)
C11	0.884(1)	0.1147(8)	0.2587(8)
C12	1.0639(9)	0.0790(9)	0.3097(7)
C13	0.928(1)	0.106(1)	0.4025(9)
C21	0.067(1)	0.0795(9)	0.8136(7)
C22	0.222(1)	0.1090(9)	0.7313(7)
C23	0.236(1)	0.114(1)	0.8776(8)
C31	0.979(1)	0.250	0.477(1)
C32	1.181(2)	0.250	0.345(1)
C33	1.139(1)	0.3411(9)	0.464(1)
C41	−0.043(2)	0.250	0.761(2)
C42	0.171(1)	0.250	0.647(1)
C43	0.017(1)	0.1569(9)	0.6490(8)

Table 4
Positional parameters and their e.s.d.s for cluster **2**

Atom	*x*	*y*	*z*
Os1	0.28279(7)	−0.17318(4)	−0.02070(4)
Os2	0.00411(7)	−0.18919(5)	−0.09170(4)
Os3	0.13973(7)	−0.32513(4)	0.09664(5)
Os4	−0.17837(6)	−0.24327(4)	0.49919(4)
Os5	−0.43949(6)	−0.24732(4)	0.60769(4)
Os6	−0.44538(6)	−0.25553(4)	0.41334(4)
S1	0.2483(5)	−0.2343(3)	−0.1586(3)
S2	−0.2111(5)	−0.3881(3)	0.6444(3)
O11	0.407(2)	0.007(1)	−0.1481(9)
O12	0.287(2)	−0.1027(8)	0.1545(8)
O13	0.591(2)	−0.320(1)	0.046(1)
O21	−0.281(1)	−0.1201(9)	−0.0011(9)
O22	−0.121(2)	−0.031(1)	−0.295(1)
O23	−0.103(2)	−0.371(1)	−0.108(1)
O31	0.379(2)	−0.4121(9)	0.267(1)
O32	−0.090(2)	−0.455(1)	0.175(1)
O33	0.309(2)	−0.471(1)	−0.008(1)
O34	−0.032(2)	−0.160(1)	0.1784(9)
O41	−0.006(1)	−0.3807(9)	0.3902(9)
O42	−0.169(2)	−0.0525(9)	0.3245(9)
O43	0.078(2)	−0.210(1)	0.611(1)
O51	−0.393(2)	−0.211(1)	0.8024(8)
O52	−0.648(2)	−0.391(1)	0.672(1)
O53	−0.702(2)	−0.0622(9)	0.541(1)
O61	−0.339(2)	−0.258(1)	0.2125(9)
O62	−0.334(2)	−0.4937(9)	0.501(1)
O63	−0.777(1)	−0.254(1)	0.386(1)
O64	−0.526(1)	−0.0172(8)	0.3448(9)
C11	0.358(2)	−0.057(1)	−0.106(1)
C12	0.289(2)	−0.130(1)	0.088(1)
C13	0.476(2)	−0.264(1)	0.025(1)
C21	−0.176(2)	−0.145(1)	−0.032(1)
C22	−0.070(2)	−0.088(1)	−0.221(1)
C23	−0.064(2)	−0.303(1)	−0.102(1)
C31	0.285(2)	−0.383(1)	0.208(1)
C32	−0.001(2)	−0.407(1)	0.146(1)
C33	0.246(2)	−0.416(1)	0.030(1)
C34	0.034(2)	−0.221(1)	0.148(1)
C41	−0.068(2)	−0.331(1)	0.432(1)
C42	−0.175(2)	−0.125(1)	0.391(1)
C43	−0.015(2)	−0.225(1)	0.572(1)
C51	−0.409(2)	−0.225(1)	0.732(1)
C52	−0.573(2)	−0.339(1)	0.649(1)
C53	−0.598(2)	−0.130(1)	0.565(1)
C61	−0.376(2)	−0.260(1)	0.287(1)
C62	−0.374(2)	−0.406(1)	0.470(1)
C63	−0.651(2)	−0.258(1)	0.399(1)
C64	−0.494(2)	−0.105(1)	0.370(1)

3. Results and discussion

Treatment of $Os_3(CO)_{10}(MeCN)_2$ with a stoichiometric amount of 4,6-dimethylpyrimidine-2-thione (dmpymt) at room temperature in CH_2Cl_2 affords two yellow cluster complexes $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-dmpymt})]$ (**1**) and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SH)]$ (**2**) in moderate yield. The molecular formulae of **1** and **2** were initially established from their FAB mass spectra and ^1H NMR spectra. Single crystal X-ray analysis was undertaken to establish their molecular structures. **1** crystallizes in the orthorhombic system with two crystallographic independent half molecules in the asymmetric unit. Both molecules are bisected by crystallographic mirror planes with Os(3), S(1), C(1), C(3), C(31), O(31), C(32), O(32) of molecule **1** and Os(4), S(2), C(5), C(7), C(41), O(41), C(42), O(42) of molecule **2** on the mirror planes. The molecular structure of **1** is shown in Fig. 3 and some selected bond parameters are listed in Table 7. The dmpymt ligand is found to bridge one Os–Os edge via its exocyclic sulfur atom. The Os–S distance (2.405(4) Å) is similar to those found in other sulfur bridged triosmium clusters, e.g. 2.413(3) Å in $[Os_3(CO)_{10}(\mu\text{-}$

Table 5
Positional parameters and their e.s.d.s for cluster 3

Atom	*x*	*y*	*z*
Ru1	0.27480(6)	0.22504(3)	0.22113(3)
Ru2	0.00115(5)	0.26258(3)	0.11595(3)
Ru3	0.26573(6)	0.38152(3)	0.13362(3)
S	0.4241(2)	0.2549(1)	0.10719(8)
O11	0.1979(6)	0.0411(3)	0.1735(3)
O12	0.6055(7)	0.1985(5)	0.3257(4)
O13	0.0426(7)	0.2122(3)	0.3547(3)
O21	−0.1539(6)	0.3562(3)	0.2458(3)
O22	−0.2288(6)	0.1135(3)	0.1577(3)
O23	−0.2371(7)	0.3631(3)	0.0009(3)
O31	0.0441(7)	0.5243(3)	0.1929(3)
O32	0.5883(7)	0.4929(4)	0.1587(4)
O33	0.1749(8)	0.4309(4)	−0.0322(3)
N1	0.4178(6)	0.1546(3)	−0.0129(3)
N2	0.1405(5)	0.1922(3)	0.0274(2)
C1	0.3145(7)	0.1949(4)	0.0315(3)
C2	0.3456(7)	0.1043(4)	−0.0699(3)
C3	0.1697(7)	0.0978(4)	−0.0788(3)
C4	0.0668(7)	0.1425(4)	−0.0298(3)
C5	−0.1226(7)	0.1359(5)	−0.0433(4)
C6	0.4647(8)	0.0575(5)	−0.1197(4)
C11	0.2266(7)	0.1095(4)	0.1935(3)
C12	0.4865(9)	0.2113(5)	0.2870(4)
C13	0.1291(9)	0.2185(4)	0.3042(4)
C21	−0.0889(8)	0.3219(4)	0.1971(4)
C22	−0.1411(7)	0.1661(4)	0.1384(4)
C23	−0.1461(8)	0.3237(4)	0.0406(4)
C31	0.1265(9)	0.4700(4)	0.1705(4)
C32	0.4742(8)	0.4498(4)	0.1517(4)
C33	0.2086(9)	0.4130(4)	0.0302(4)

Table 6
Positional parameters and their e.s.d.s for cluster 5

Atom	*x*	*y*	*z*
Ru1	0.000	0.0639(1)	0.250
Ru2	0.09634(6)	0.24415(9)	0.26708(8)
S1	0.0224(2)	0.3046(3)	0.3749(2)
O11	−0.1333(8)	−0.092(1)	0.230(1)
O12	0.0530(7)	0.082(1)	0.4921(9)
O21	0.2220(7)	0.139(1)	0.454(1)
O22	0.2115(6)	0.4246(9)	0.2937(9)
O23	0.1542(7)	0.138(1)	0.1103(8)
N1	0.0990(6)	0.4803(9)	0.4249(7)
N2	−0.0425(6)	0.4920(9)	0.3509(7)
C1	0.0267(7)	0.442(1)	0.381(1)
C2	0.1030(8)	0.585(1)	0.436(1)
C3	0.0358(8)	0.643(1)	0.405(1)
C4	−0.0383(7)	0.596(1)	0.363(1)
C5	−0.1155(9)	0.653(1)	0.332(1)
C6	0.186(1)	0.628(2)	0.487(1)
C11	−0.085(1)	−0.033(2)	0.238(1)
C12	0.0331(9)	0.076(1)	0.402(1)
C21	0.1741(9)	0.176(1)	0.385(1)
C22	0.1637(8)	0.365(1)	0.282(1)
C23	0.1334(9)	0.176(1)	0.168(1)

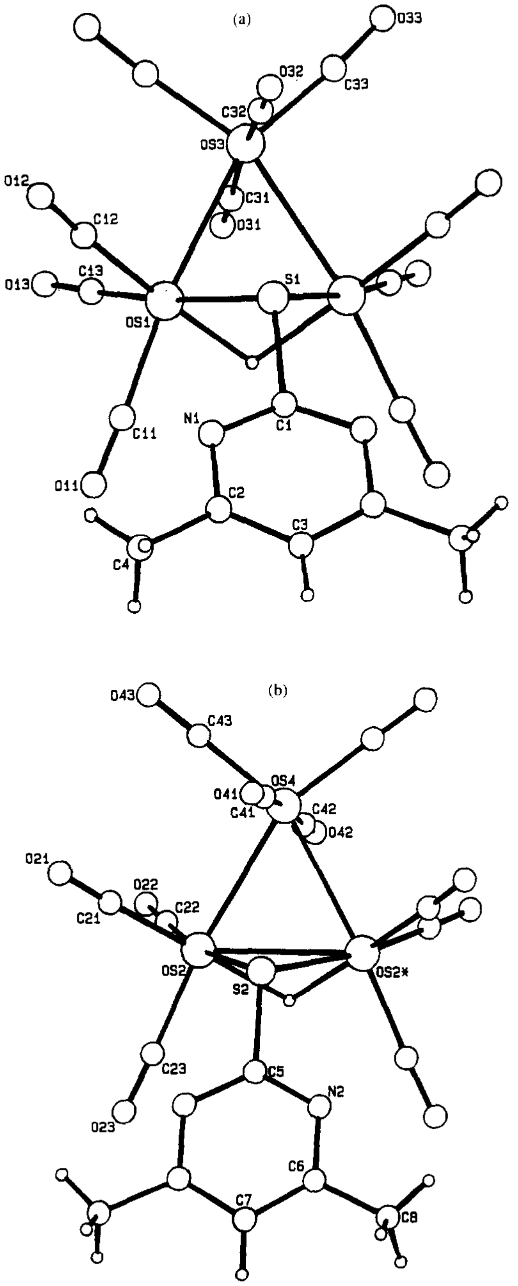

Fig. 3. Perspective view of cluster **1**: (a) molecule 1, (b) molecule 2; the hydride position was obtained from potential energy calculations.

SC(H)MeCH$_2$C(H)Me(I))(μ-H)] [28]. The plane defined by Os(1), Os(1′) and S(1) (Os(2), Os(2′) and S(2)) is almost perpendicular to the osmium triangle (dihedral angle 105.3° (103.8°)). The pyrimidine ring is essentially planar with a maximum deviation from the mean plane of 0.02 Å. The bridging hydride, as evident from ^{1}H NMR, cannot be determined by X-ray analysis. However, potential energy calculations suggest it bridges the Os(1)–Os(1′) edge. Cluster complex **2** has been synthesized by another method [29] and was characterized by spectroscopic techniques. The X-ray analysis of **2** showed that it crystallized in the triclinic system with two crystallographically indepen-

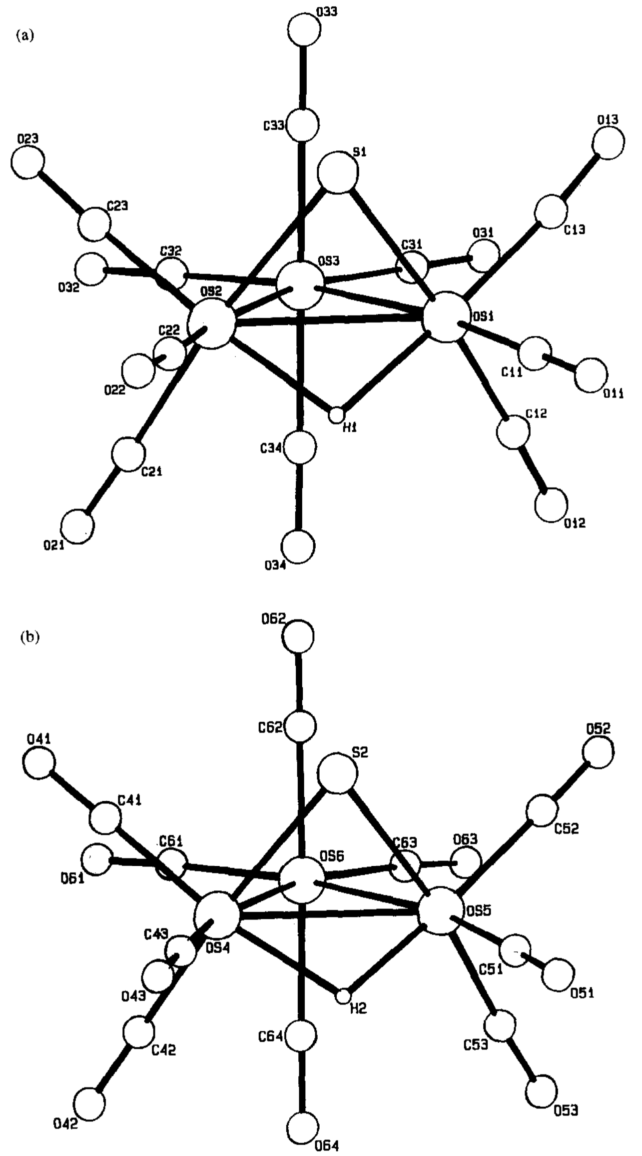

Fig. 4. Perspective view of cluster **2**: (a) molecule 1, (b) molecule 2; the hydride position was obtained from potential energy calculations.

dent but structurally very similar molecules in the asymmetric unit. The molecular structure of both are shown in Fig. 4 and some selected bond parameters are presented in Table 8. The Os(1)–Os(2) is doubly bridged by a thiol group and a hydride ligand although none of the hydrogen atoms position can be directly located by X-ray analysis. However, good evidence was obtained from ^{1}H NMR, IR and potential energy calculations (on the hydride). The Os–S bond distances (2.452(2) Å) are significantly longer than those in cluster **1**. An idealized C_s symmetry is present in both complexes **1** and **2**. Isolation of **2** in moderate yield from the reaction suggested the dmpymt ligand might undergo C–S bond cleavage upon coordination to the cluster framework under mild conditions. However, **1** cannot convert to **2** under either thermal or photochemical conditions. Therefore, **1** may not be an intermediate for the formation of **2** and we are unable to establish the fate of the eliminated moiety if dmpymt underwent C–S bond cleavage.

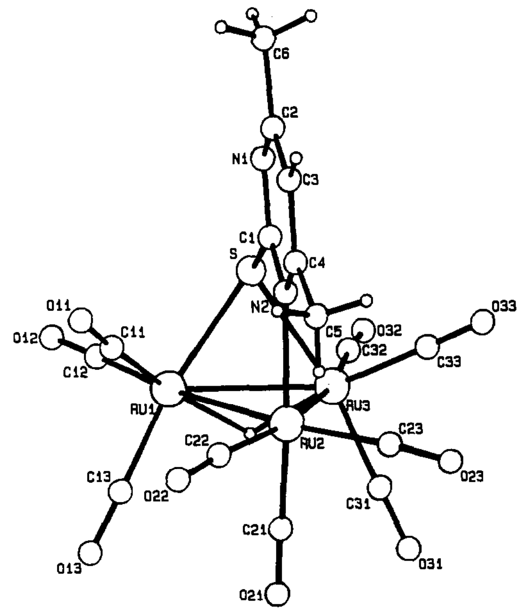

Fig. 5. Perspective view of cluster **3**; the hydride position was obtained from potential energy calculations.

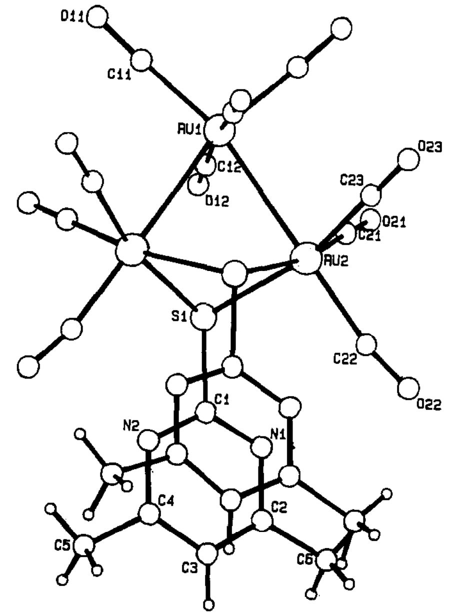

Fig. 6. Perspective view of cluster **5**.

The corresponding reaction of Ru$_3$(CO)$_{10}$(MeCN)$_2$ with dmpymt at room temperature gives very different products. Three major products [Ru$_3$(CO)$_9$(μ-H)(μ_3-η^2-dmpymt)] (**3**), [Ru$_3$(CO)$_{10}$(μ-H)(μ-dmpymt)] (**4**) and [Ru$_3$(CO)$_{10}$(μ-dmpymt)$_2$] (**5**) can be isolated and fully characterized. An X-ray structure analysis of **3** revealed that the molecule consists of a triruthenium metal core with three terminal CO ligands coordinated to each metal centre. The dmpymt ligand is bonded to the Ru$_3$

Table 7
Selected bond lengths (Å) and bond angles (°) for cluster **1**

Molecule 1		Molecule 2	
Os(1)–Os(3)	2.8437(9)	Os(2)–Os(4)	2.8473(9)
Os(1)–Os(1′)	2.879(1)	Os(2)–Os(2′)	2.863(1)
Os(1)–S(1)	2.405(4)	Os(2)–S(2)	2.389(4)
S(1)–C(1)	1.83(2)	S(2)–C(5)	1.76(2)
N(1)–C(1)	1.31(2)	N(2)–C(5)	1.34(2)
N(1)–C(2)	1.34(2)	N(2)–C(6)	1.32(2)
C(2)–C(3)	1.42(2)	C(6)–C(7)	1.38(2)
C(2)–C(4)	1.49(3)	C(6)–C(8)	1.49(2)
Os(1)–H(1)	1.874	Os(2)–H(2)	1.875
Os(1)–Os(3)–Os(1′)	60.8(1)	Os(2)–Os(4)–Os(2′)	60.4(1)
Os(3)–Os(1)–S(1)	83.1(2)	Os(4)–Os(2)–S(2)	82.2(2)
Os(1)–S(1)–C(1)	111.5(5)	Os(2)–S(2)–C(5)	109.9(5)
C(1)–N(1)–C(2)	114(1)	C(5)–N(2)–C(6)	119(1)
S(1)–C(1)–N(1)	113(1)	S(2)–C(5)–N(2)	117.6(9)
N(1)–C(2)–C(3)	119(2)	N(2)–C(6)–C(7)	120(1)
Os(1)–H(1)–Os(1′)	100.4	Os(2)–H(2)–Os(2′)	99.6
Os–C–O (av.)	176.3	Os–C–O (av.)	177.5

Table 8
Selected bond lengths (Å) and bond angles (°) for cluster **2**

Molecule 1		Molecule 2	
Os(1)–Os(2)	2.844(1)	Os(4)–Os(5)	2.8376(8)
Os(1)–Os(3)	2.8225(9)	Os(4)–Os(6)	2.8168(9)
Os(2)–Os(3)	2.8246(8)	Os(5)–Os(6)	2.8230(9)
Os(1)–S(1)	2.455(6)	Os(4)–S(2)	2.448(4)
Os(2)–S(1)	2.456(4)	Os(5)–S(2)	2.450(4)
Os(1)–C(11)	1.95(2)	Os(4)–C(41)	1.93(2)
Os(1)–C(12)	1.85(2)	Os(4)–C(42)	1.87(1)
Os(1)–C(13)	1.90(2)	Os(4)–C(43)	1.94(2)
Os(2)–C(21)	1.92(2)	Os(5)–C(51)	1.94(2)
Os(2)–C(22)	1.92(1)	Os(5)–C(52)	1.92(2)
Os(2)–C(23)	1.90(3)	Os(5)–C(53)	1.86(1)
Os(3)–C(31)	1.91(2)	Os(6)–C(61)	1.92(2)
Os(3)–C(32)	1.90(2)	Os(6)–C(62)	1.95(1)
Os(3)–C(33)	1.94(3)	Os(6)–C(63)	1.91(2)
Os(3)–C(34)	1.92(2)	Os(6)–C(64)	1.94(1)
Os(1)–H(1)	1.89	Os(4)–H(2)	1.92
Os(2)–H(1)	1.88	Os(5)–H(2)	1.79
Os(2)–Os(1)–Os(3)	59.80(2)	Os(5)–Os(4)–Os(6)	59.90(2)
Os(1)–Os(2)–Os(3)	59.73(2)	Os(4)–Os(5)–Os(6)	59.68(2)
Os(1)–Os(3)–Os(2)	60.48(2)	Os(4)–Os(6)–Os(5)	60.41(2)
Os(2)–Os(1)–S(1)	54.6(2)	Os(5)–Os(4)–S(2)	54.63(9)
Os(3)–Os(1)–S(1)	87.2(2)	Os(6)–Os(4)–S(2)	86.9(2)
Os(1)–Os(2)–S(1)	54.7(1)	Os(4)–Os(5)–S(2)	54.57(9)
Os(3)–Os(2)–S(1)	87.16(9)	Os(6)–Os(5)–S(2)	86.7(2)
Os(1)–S(1)–Os(2)	70.8(1)	Os(4)–S(2)–Os(5)	70.80(9)
Os(1)–H(1)–Os(2)	98.1	Os(4)–H(2)–Os(5)	99.8
Os–C–O (av.)	177.1	Os–C–O (av.)	177.6

core via the exocyclic sulfur atom and one of the nitrogen atoms on the heterocycle, see Fig. 5. Thus the dmpymt ligand acts as a face capping, five-electron donor to the cluster. A similar bonding mode has been observed in [Cu$_6$(dmpymt)$_6$] [29]. The Ru–Ru distance (2.8631(6) Å) doubly bridged by the sulfur atom and the hydride ligand is, as expected, significantly longer than the other two Ru–Ru distances (2.7698(6), 2.7720(6) Å) (Table 9). The observed molecular structure is fully consistent with the spectroscopic data obtained in solution.

Cluster complex **4** (Ru analog of **1**) undergoes CO displacement to give **3** on standing in solution even at low temperature (−10 °C). This conversion is essentially

Table 9
Selected bond lengths (Å) and bond angles (°) for cluster **3**

Ru(1)–Ru(2)	2.7698(6)	N(1)–C(1)	1.308(7)
Ru(1)–Ru(3)	2.8631(6)	N(1)–C(2)	1.350(7)
Ru(2)–Ru(3)	2.7720(6)	N(2)–C(1)	1.354(7)
Ru(1)–S	2.396(2)	N(2)–C(4)	1.352(7)
Ru(2)–N(2)	2.221(4)	C(2)–C(3)	1.373(8)
Ru(3)–S	2.384(2)	C(3)–C(4)	1.390(8)
S–C(1)	1.779(5)	C(2)–C(6)	1.496(9)
Ru(2)–Ru(1)–Ru(3)	58.93(2)	C(1)–N(1)–C(2)	117.5(5)
Ru(2)–Ru(1)–S	79.39(4)	Ru(2)–N(2)–C(1)	118.9(3)
Ru(3)–Ru(1)–S	53.02(4)	C(1)–N(2)–C(4)	115.5(4)
Ru(1)–Ru(2)–Ru(3)	62.21(2)	S–C(1)–N(1)	113.4(4)
Ru(1)–Ru(3)–Ru(2)	58.85(2)	S–C(1)–N(2)	119.1(4)
Ru(1)–Ru(3)–S	53.39(4)	N(1)–C(1)–N(2)	127.5(5)
Ru(2)–Ru(3)–S	79.53(4)	N(1)–C(2)–C(3)	119.4(5)
Ru(1)–S–Ru(3)	73.59(5)	C(2)–C(3)–C(4)	120.4(5)
Ru(1)–S–C(1)	105.5(2)	N(2)–C(4)–C(3)	119.8(5)
Ru(3)–S–C(1)	110.2(2)	Ru–C–O (av.)	176.5

Table 10
Selected bond lengths (Å) and bond angles (°) for cluster **5**

Ru(1)–Ru(2)	2.871(2)	N(2)–C(1)	1.33(2)
Ru(2)–S(1)	2.434(4)	N(2)–C(4)	1.36(2)
S(1)–C(1)	1.78(1)	C(2)–C(3)	1.36(2)
N(1)–C(1)	1.31(1)	C(3)–C(4)	1.38(2)
N(1)–C(2)	1.37(2)	C(4)–C(5)	1.49(2)
C(2)–C(6)	1.50(2)	S(1)---S(1′)	3.171(6)
Ru(1)–Ru(2)–S(1)	82.27(9)	N(1)–C(2)–C(3)	122(1)
Ru(1)–Ru(2)–C(21)	85.7(5)	C(2)–C(3)–C(4)	120(1)
Ru(2)–S(1)–C(1)	109.1(5)	N(2)–C(4)–C(3)	119(1)
C(1)–N(1)–C(2)	116(2)	N(1)–C(2)–C(6)	115(1)
C(1)–N(2)–C(4)	117(2)	C(3)–C(2)–C(6)	123(1)
S(1)–C(1)–N(1)	114.9(9)	N(2)–C(4)–C(5)	117(1)
S(1)–C(1)–N(2)	117.3(9)	C(3)–C(4)–C(5)	124(1)
N(1)–C(1)–N(2)	127(1)	Ru–C–O (av.)	176.4

quantitative and irreversible as indicated by ^{1}H NMR and IR spectroscopies. Due to the thermal instability of **4**, no structure analysis can be performed. However, the molecular structure of **4** is expected to be similar to **1** based on IR, ^{1}H NMR and mass spectroscopic results (see Table 1).

An X-ray structure analysis of **5** showed that it consists of a triruthenium metal core with ten terminal CO coordinated to the metal core. Two dmpymt ligands bridge the same Ru–Ru edge via their exocyclic S atoms. The molecule structure is shown in Fig. 6 and some important bond parameters are presented in Table 10. Molecule **5** possesses a C_{2v} idealized symmetry and lies on the crystallographic two-fold axis so that half of the molecule is independent. The doubly bridged Ru–Ru distance is 3.321(1) Å and is regarded as non-bonding. This is expected as the cluster contains 50 cluster valence electrons. The S(1)–S(1′) distance is 3.171(6) Å.

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