Novel Hexanuclear Ruthenium Clusters with Unusual Metal Framework Geometries: 'Boat' and 'Sofa' Configurations of the Ru_6 Core†

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The thermal reaction of $[Ru_3(CO)_{12}]$ with the thioureas $SC(NHR)_2$ (R = Et or Ph) in tetrahydrofuran at 130 °C has been studied. With the ethyl substituent, the hexanuclear cluster $[Ru_6(CO)_{14}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}\eta^2\text{-}EtNCSNHEt)(\mu_3\text{-}\eta^2\text{-}EtNCNHEt)]$ has been isolated and structurally characterized: the molecule presents an unusual Ru_6 framework analogous to the boat conformation of cyclohexane. With the phenyl substituent, another hexanuclear cluster $[Ru_6(CO)_{16}(\mu\text{-}H)(\mu_5\text{-}S)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$ has been isolated, the molecular structure of which reveals a previously unreported Ru_6 metal core reminiscent of the sofa conformation of cyclohexane.

The reaction of thioureas $SC(NHR)_2$ with triruthenium dodecacarbonyl leads to a multitude of new and unique cluster complexes.[1–7] Trinuclear complexes of the type $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}RNCSNRH)]$ were obtained from the reaction of $[Ru_3(CO)_{12}]$ with thiourea (R = H) and its dimethyl and diphenyl derivatives (R = Me or Ph).[1] In the case of diethylthiourea, in addition to the analogous trinuclear cluster $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}EtNCSNHEt)]$ the tetranuclear clusters $[Ru_4(CO)_{8-n}(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NRH)\}_n]$ (n = 1 or 2, R = Et) were isolated.[2] With diisopropylthiourea the sole products were tetranuclear clusters of the same type (R = Pr^i).[2] In the reaction of $[Ru_3(CO)_{12}]$ with di-*tert*-butylthiourea two complexes $[Ru_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}S)(\eta^2\text{-}CH_2CMe_2NHCNHBu^t)]$ and $[Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}SRu(CO)_3(\eta^2\text{-}CH_2CMe_2NHCNHBu^t)\}]$ were isolated, in which not only C–S bond breaking of the thiourea is observed but also C–H activation of one of the Bu^t groups.[3] Thus the nature of the thiourea substituents R has a strong influence on the type of cluster formed. In the following we report the formation of hexanuclear ruthenium clusters exhibiting unusual metal framework geometries from reactions of $[Ru_3(CO)_{12}]$ and thioureas.

Results and Discussion

The thermal reaction of $[Ru_3(CO)_{12}]$ with *N,N'*-diethylthiourea in tetrahydrofuran at 130 °C yields a complex mixture from which the new hexanuclear cluster $[Ru_6(CO)_{14}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}\eta^2\text{-}EtNCSNHEt)(\mu_3\text{-}\eta^2\text{-}EtNCNHEt)]$ **1** can be isolated, along with known tetranuclear clusters $[Ru_4(CO)_{8-n}(\mu\text{-}CO)_3(\mu_4\text{-}S)\{C(NEtH)\}_n]$ (n = 1 or 2).[2] The analogous reaction of $[Ru_3(CO)_{12}]$ with *N,N'*-diphenylthiourea yields the hexanuclear cluster $[Ru_6(CO)_{16}(\mu\text{-}H)(\mu_5\text{-}S)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$ **2**.

In both cases it is supposed that the reaction proceeds through the intermediacy of the corresponding trinuclear clusters $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}RNCSNR)$ (R = Et **3** or Ph **4**) (Scheme 1). Thus compound **4**, available from $[Ru_3(CO)_{12}]$ and $(PhNH)_2CS$ (thf, 66 °C),[2] is indeed converted into **2** upon heating of a thf solution in a pressure Schlenk tube at 130 °C.

The trinuclear clusters **3** and **4**, resulting from a hydrogen transfer from the thiourea onto the metal core and the fixation of the residual thioureato fragment on the metal core, presumably undergo a condensation reaction with elimination of H_2 and CO, producing a hexanuclear boat cluster. In this structure a sulfur atom was cleaved from the thioureato backbone and has taken a tetrapodal position over the base of the boat framework, leaving behind a $\mu_3\text{-}\eta^2$-diaminocarbene ligand. Further elimination of a carbodiimide fragment converts the boat structure into the sofa structure in which the sulfur atom co-ordinates to a fifth ruthenium atom and thus functions as a μ_5 ligand. The corresponding hexanuclear compounds have been isolated for R = Et (**1**, boat configuration) and R = Ph (**2** sofa configuration). The eliminated $(PhN)_2C$, however, has not been detected in the reaction mixture.

Compound **1** is obtained in the form of black crystals, soluble only in polar solvents like CH_2Cl_2, acetone and thf giving deep green solutions. Its infrared spectrum in CH_2Cl_2 shows in addition to absorptions due to terminal carbonyls, also those of bridging carbonyls. In the ^1H NMR spectrum are found the well resolved resonances of the ethyl groups and a broad signal due to the NH proton; no signals are observed in the hydride region. Contrary to **1**, compound **2** is obtained as red crystals soluble in non-polar solvents resulting in red solutions. The infrared spectrum shows absorptions due only to terminal carbonyl groups. In the ^1H NMR spectrum a hydride signal at δ −22.1, in addition to the expected signals of the thioureato ligand is observed.

The structures of compounds **1** and **2** were determined through single-crystal X-ray structure analysis (Table 1). As a result of these investigations, the Schakal plot[8] of **1** is displayed in Fig. 1 and that of **2** in Fig. 2. The atomic coordinates and important bond lengths and angles for **1** and **2** are given in Tables 2 and 3 and 4 and 5, respectively.

The metal framework of compound **1** consists of six ruthenium atoms. Four of these atoms form an approximately planar trapezoid (planar to within ±0.03 Å). The distances Ru(1)–Ru(5) and Ru(2)–Ru(4) are unusually long [3.231(3) and 3.081(3) Å]; Ru(1)–Ru(2) [2.917(3) Å] and Ru(4)–Ru(5) [2.930(3) Å] are also longer than those found in $[Ru_3(CO)_{12}]$.[9] The two edges Ru(1)–Ru(5) and Ru(2)–Ru(4) are bridged by two additional ruthenium atoms Ru(3) and Ru(6); the average distance of Ru(3) and Ru(6) to the basal ruthenium atom they bridge is 2.763(2) Å. Atoms Ru(3) and Ru(6) do not lie in the plane of the trapezoid, but are bent out of it to one side. The distance of Ru(3) to the plane is 0.743(4) Å and that of Ru(6) is 0.835(4) Å. The metal framework can be described as analogous to the boat conformation of cyclohexane.

The side of the trapezoid facing Ru(3) and Ru(6) is capped

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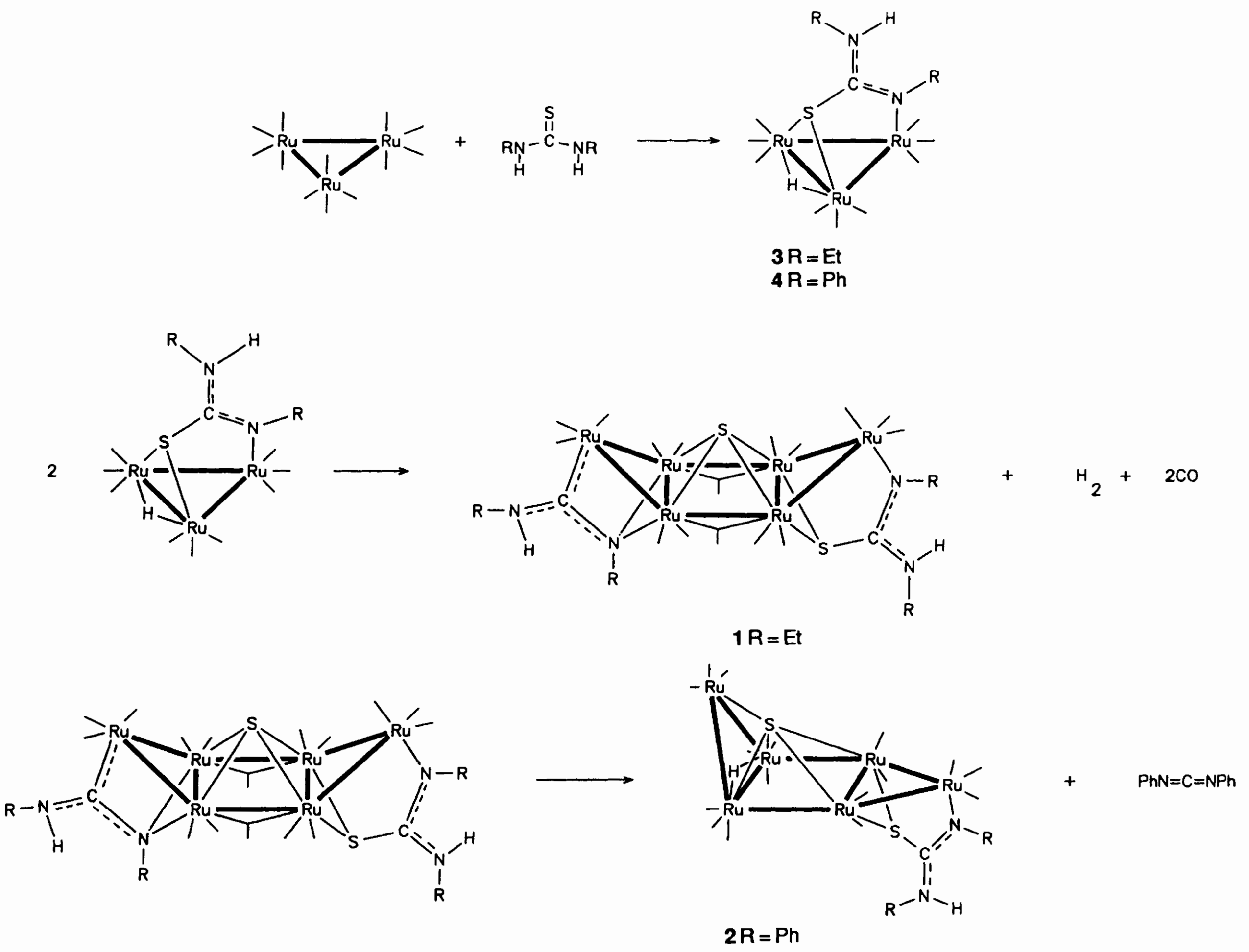
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1

Table 1 Data for crystal-structure analyses[a]

	1	2
Molecular formula	$C_{26}H_{22}N_4O_{16}Ru_6S_2$	$C_{29}H_{12}N_2O_{16}Ru_6S_2$
M	1317.0	1314.96
Crystal dimensions/mm	0.49 × 0.11 × 0.11	0.57 × 0.53 × 0.38
Crystal colour, shape	Black block	Red block
Crystal system	Monoclinic	Monoclinic
a/Å	9.331(2)	9.2712(4)
b/Å	20.617(7)	20.7267(18)
c/Å	20.563(4)	20.4375(10)
β/°	94.94(2)	92.561(4)
U/Å^3	3941.2(18)	3923.4(4)
D_c/g cm^{-3}	2.22	2.226
μ(Mo-Kα)/mm^{-1}	2.37	2.38
F(000)	2520	2496
No. of unique data	5938	6878
No. of observed data used [$F_o > 3.5\sigma(F_o)$]	3542	5746
Instrumental error factor k[b]	0.0023	0.003
$R(R')$[c]	0.11 (0.136)	0.034 (0.057)
Final electron-density difference features (maximum, minimum)/e Å^{-3}	5.18, −4.90	0.62, −1.66

[a] Details in common: data collected on a Stoe-Siemens AED 2 four-circle diffractometer; graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å; space group $P2_1/n$; Z = 4; 293 K; scan mode ω–2θ; maximum 2θ = 50°. [b] Refinement was by full-matrix least squares with a weighting scheme of the form $w^{-1} = \sigma^2(F_o) + k(F_o^2)$. [c] $R = \Sigma(F_o - F_c)/F_o$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

by a μ_4-sulfur ligand. The distances of this sulfur atom to Ru(1) and Ru(5) [mean 2.433(5) Å] are significantly shorter than those to Ru(2) and Ru(4) [mean 2.520(5) Å].

The triangular Ru(2)–Ru(3)–Ru(4) substructure in compound **1** on the side facing away from the sulfur is bridged by the μ_3-η^2-bound diethylthioureato ligand. As in the trinuclear cluster **3**, the sulfur atom of the thioureato ligand is bridging and the nitrogen atom is co-ordinated terminally. The distances Ru(2)–

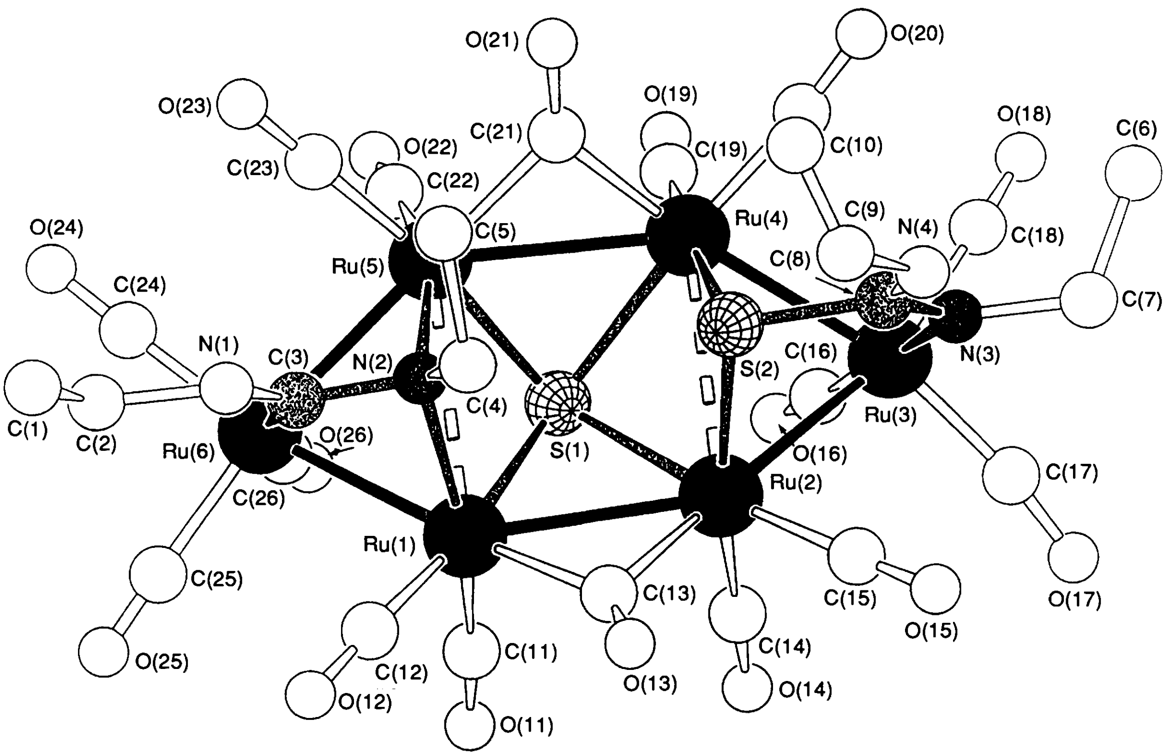


Fig. 1 SCHAKAL plot of compound **1**

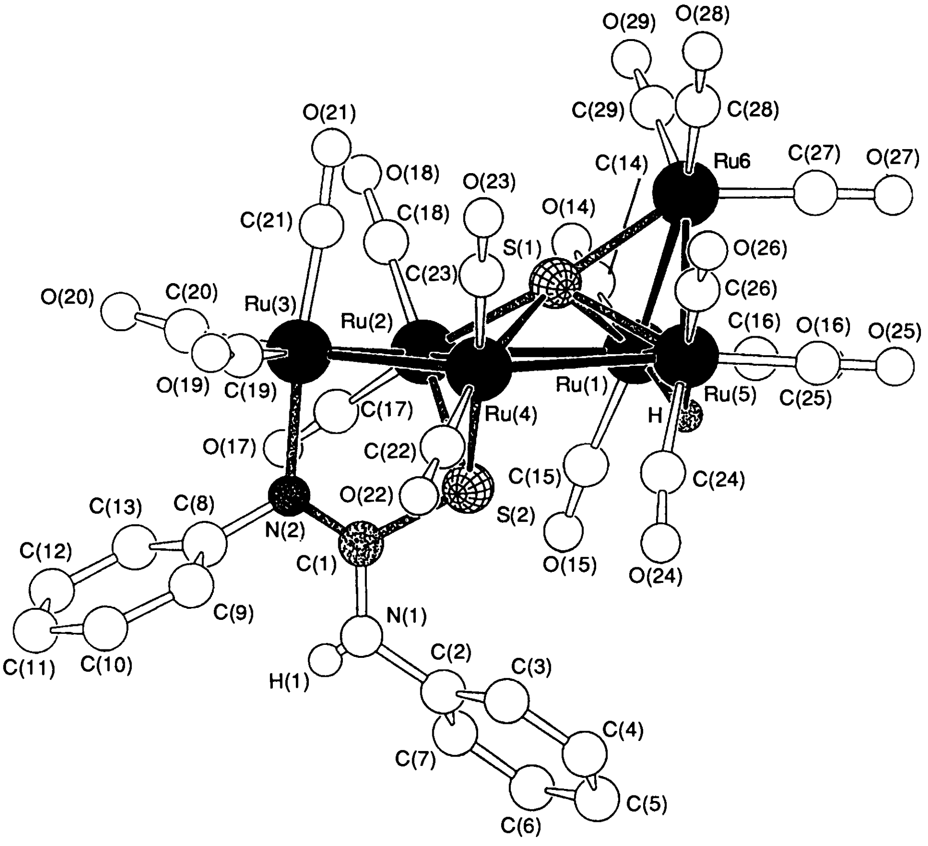


Fig. 2 SCHAKAL plot of compound **2**

S and Ru(4)–S [mean 2.424(5) Å] like Ru(3)–N(3) [2.145(24) Å] are similar to those found in **3**. The *cis* orientation of the N(4)-bound ethyl residue is probably the result of the repulsive action of the N(3)-bound ethyl group.

The second triangular substructure composed of Ru(1), Ru(5) and Ru(6) in compound **1** is bridged, on the side opposite to atom S(1) by a μ_3-η^2-bound *N*,*N*′-diethyldiaminocarbene ligand. The N atom bridges Ru(1) and Ru(5) [mean 2.26(2) Å] while the carbene carbon atom is bound exclusively to Ru(6) [Ru(6)–C(3), 2.10(2) Å]. In the sp^2-hybridized diaminocarbene

Table 2 Atomic parameters of compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.0521(2)	0.8899(1)	0.1450(1)	O(13)	0.211(2)	0.893(1)	0.022(1)
Ru(2)	0.0875(2)	0.7695(1)	0.0736(1)	C(14)	0.236(3)	0.740(2)	0.133(2)
Ru(3)	−0.0122(3)	0.6436(1)	0.0592(1)	O(14)	0.336(3)	0.726(2)	0.166(1)
Ru(4)	−0.2274(2)	0.7293(1)	0.0851(1)	C(15)	0.197(3)	0.741(2)	0.003(2)
Ru(5)	−0.2817(2)	0.8516(1)	0.1523(1)	O(15)	0.254(2)	0.729(1)	−0.038(1)
Ru(6)	−0.1286(3)	0.9374(1)	0.2338(1)	C(16)	0.031(5)	0.634(1)	0.152(2)
S(1)	−0.0617(7)	0.7875(3)	0.1687(3)	O(16)	0.050(3)	0.626(1)	0.205(1)
S(2)	−0.1228(7)	0.7837(3)	−0.0035(3)	C(17)	0.166(3)	0.604(2)	0.047(1)
C(1)	−0.20(2)	1.140(7)	0.146(6)	O(17)	0.288(3)	0.583(2)	0.044(2)
C(1a)	−0.33(1)	1.127(6)	0.145(6)	C(18)	−0.129(4)	0.565(2)	0.054(2)
C(2)	−0.231(5)	1.085(2)	0.163(2)	O(18)	−0.197(3)	0.522(1)	0.060(2)
N(1)	−0.206(3)	1.034(1)	0.119(1)	C(19)	−0.294(3)	0.679(2)	0.152(2)
C(3)	−0.172(3)	0.973(1)	0.139(1)	O(19)	−0.325(3)	0.646(1)	0.192(1)
N(2)	−0.155(2)	0.924(1)	0.096(1)	C(20)	−0.337(4)	0.677(2)	0.026(1)
C(4)	−0.177(3)	0.939(1)	0.025(1)	O(20)	−0.410(3)	0.646(1)	−0.009(1)
C(5)	−0.339(3)	0.947(2)	−0.002(2)	C(21)	−0.399(3)	0.797(2)	0.079(1)
C(6)	−0.176(5)	0.575(2)	−0.111(2)	O(21)	−0.509(2)	0.802(1)	0.049(1)
C(7)	−0.042(4)	0.614(2)	−0.094(2)	C(22)	−0.360(3)	0.807(2)	0.223(2)
N(3)	−0.058(3)	0.666(1)	−0.042(1)	O(22)	−0.398(3)	0.785(2)	0.267(1)
C(8)	−0.105(3)	0.722(2)	−0.061(1)	C(23)	−0.443(3)	0.907(2)	0.150(1)
N(4)	−0.139(4)	0.737(2)	−0.125(1)	O(23)	−0.536(3)	0.943(2)	0.147(1)
C(9)	−0.186(6)	0.802(2)	−0.151(2)	C(24)	−0.288(4)	0.969(2)	0.273(1)
C(10)	−0.339(5)	0.813(3)	−0.153(3)	O(24)	−0.383(3)	0.989(2)	0.297(1)
C(11)	0.197(3)	0.869(2)	0.205(2)	C(25)	0.003(3)	1.003(1)	0.270(1)
O(11)	0.295(2)	0.854(1)	0.246(1)	O(25)	0.074(4)	1.039(2)	0.292(2)
C(12)	0.122(3)	0.973(1)	0.140(1)	C(26)	−0.079(4)	0.877(2)	0.303(2)
O(12)	0.177(3)	1.024(1)	0.141(1)	O(26)	−0.048(4)	0.834(2)	0.341(2)
C(13)	0.155(3)	0.868(1)	0.060(1)				

Table 3 Important bond lengths (Å) and angles (°) of compound **1**

Ru(1)–Ru(2)	2.917(3)	Ru(5)–N(2)	2.30(2)	Ru(2)–S(2)	2.432(7)	N(2)–C(4)	1.48(3)
Ru(1)–Ru(5)	3.231(3)	Ru(6)–C(3)	2.10(2)	Ru(3)–Ru(4)	2.760(3)	C(4)–C(5)	1.57(4)
Ru(1)–Ru(6)	2.768(3)	S(2)–C(8)	1.76(3)	Ru(3)–N(3)	2.15(2)	C(6)–C(7)	1.51(5)
Ru(1)–S(1)	2.431(7)	C(1)–C(2)	1.2(2)	Ru(4)–Ru(5)	2.930(3)	C(7)–N(3)	1.51(4)
Ru(1)–N(2)	2.22(2)	C(1a)–C(2)	1.3(1)	Ru(4)–S(1)	2.515(7)	N(3)–C(8)	1.29(4)
Ru(2)–Ru(3)	2.764(3)	C(2)–N(1)	1.42(5)	Ru(4)–S(2)	2.416(7)	C(8)–N(4)	1.36(4)
Ru(2)–Ru(4)	3.081(3)	N(1)–C(3)	1.34(4)	Ru(5)–Ru(6)	2.758(3)	N(4)–C(9)	1.48(5)
Ru(2)–S(1)	2.524(7)	C(3)–N(2)	1.36(3)	Ru(5)–S(1)	2.434(7)	C(9)–C(10)	1.45(7)
Ru(2)–Ru(1)–Ru(5)	87.94(8)	Ru(4)–Ru(5)–N(2)	101.9(5)	Ru(2)–Ru(3)–Ru(4)	67.80(8)	Ru(6)–C(3)–N(2)	109(2)
Ru(2)–Ru(1)–Ru(6)	137.3(1)	Ru(6)–Ru(5)–S(1)	82.9(2)	Ru(2)–Ru(3)–N(3)	86.7(6)	N(1)–C(3)–N(2)	122(2)
Ru(2)–Ru(1)–S(1)	55.4(2)	Ru(6)–Ru(5)–N(2)	67.8(5)	Ru(4)–Ru(3)–N(3)	88.1(6)	Ru(1)–N(2)–Ru(5)	91.3(8)
Ru(2)–Ru(1)–N(2)	100.0(5)	S(1)–Ru(5)–N(2)	87.6(6)	Ru(2)–Ru(4)–Ru(3)	56.16(8)	Ru(1)–N(2)–C(3)	95(2)
Ru(5)–Ru(1)–Ru(6)	54.07(8)	Ru(1)–Ru(6)–Ru(5)	71.58(8)	Ru(2)–Ru(4)–Ru(5)	90.61(8)	Ru(1)–N(2)–C(4)	124(2)
Ru(5)–Ru(1)–S(1)	48.4(2)	Ru(1)–Ru(6)–C(3)	65.7(7)	Ru(2)–Ru(4)–S(1)	52.4(2)	Ru(5)–N(2)–C(3)	94(2)
Ru(5)–Ru(1)–N(2)	45.3(5)	Ru(5)–Ru(6)–C(3)	67.3(7)	Ru(2)–Ru(4)–S(2)	50.8(2)	Ru(5)–N(2)–C(4)	127(2)
Ru(6)–Ru(1)–S(1)	82.8(2)	Ru(1)–S(1)–Ru(2)	72.1(2)	Ru(3)–Ru(4)–Ru(5)	142.9(1)	C(3)–N(2)–C(4)	118(2)
Ru(6)–Ru(1)–N(2)	68.6(5)	Ru(1)–S(1)–Ru(4)	122.0(3)	Ru(3)–Ru(4)–S(1)	91.3(2)	N(2)–C(4)–C(5)	115(2)
S(1)–Ru(1)–N(2)	89.5(6)	Ru(1)–S(1)–Ru(5)	83.3(2)	Ru(3)–Ru(4)–S(2)	78.7(2)	C(6)–C(7)–N(3)	114(3)
Ru(1)–Ru(2)–Ru(3)	143.2(1)	Ru(2)–S(1)–Ru(4)	75.4(2)	Ru(5)–Ru(4)–S(1)	52.4(2)	Ru(3)–N(3)–C(7)	121(2)
Ru(1)–Ru(2)–Ru(4)	92.29(8)	Ru(2)–S(1)–Ru(5)	119.1(3)	Ru(5)–Ru(4)–S(2)	93.2(2)	Ru(3)–N(3)–C(8)	121(2)
Ru(1)–Ru(2)–S(1)	52.5(2)	Ru(4)–S(1)–Ru(5)	72.6(2)	S(1)–Ru(4)–S(2)	91.7(2)	C(7)–N(3)–C(8)	118(3)
Ru(1)–Ru(2)–S(2)	96.1(2)	Ru(2)–S(2)–Ru(4)	78.9(2)	Ru(1)–Ru(5)–Ru(4)	89.07(8)	S(2)–C(8)–N(3)	120(2)
Ru(3)–Ru(2)–Ru(4)	56.04(8)	Ru(2)–S(2)–C(8)	104(1)	Ru(1)–Ru(5)–Ru(6)	54.35(7)	S(2)–C(8)–N(4)	117(3)
Ru(3)–Ru(2)–S(1)	91.0(2)	Ru(4)–S(2)–C(8)	104(1)	Ru(1)–Ru(5)–S(1)	48.3(2)	N(3)–C(8)–N(4)	122(3)
Ru(3)–Ru(2)–S(2)	78.3(2)	C(1)–C(2)–N(1)	116(7)	Ru(1)–Ru(5)–N(2)	43.4(5)	C(8)–N(4)–C(9)	126(3)
Ru(4)–Ru(2)–S(1)	52.2(2)	C(1a)–C(2)–N(1)	117(6)	Ru(4)–Ru(5)–Ru(6)	137.5(1)	N(4)–C(9)–C(10)	115(4)
Ru(4)–Ru(2)–S(2)	50.3(2)	C(2)–N(1)–C(3)	123(3)	Ru(4)–Ru(5)–S(1)	55.0(2)		
S(1)–Ru(2)–S(2)	91.1(2)	Ru(6)–C(3)–N(1)	129(2)				

system the bond length of the Ru-bound N(2) to the carbene atom C(3) [1.34(4) Å] is as long as that of the uncomplexed N(1) to C(3) [1.36(3) Å]. As with the diethylthioureato ligand, the N(1)-bound ethyl group adopts a *cis* conformation. The C(1) atom of this ethyl group is disordered in the crystal; two atomic positions with occupancies 0.6[C(1)] and 0.4[C(1a)] could be identified. In Fig. 1 the position of C(1) is represented as midway between these two positions.

The co-ordination sphere of compound **1** is completed with 16 carbonyls. Both Ru(3) and Ru(6) are bound to three terminal carbonyls, while two terminal CO groups are bound to each of the remaining ruthenium atoms. The edges Ru(1)–Ru(2) and Ru(4)–Ru(5) are bridged by two μ-carbonyl ligands. The hydrogen atoms of the ethyl groups could not be localized because of the poor crystal quality. High electron density was found exclusively in the neighbourhood of the ruthenium atoms. The ligands donate a total of 46 electrons to the metal framework. For a boat-type cluster with eight metal–metal

Table 4 Atomic parameters of compound **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru(1)	0.702 91(4)	0.202 92(2)	0.358 33(2)
Ru(2)	0.609 41(4)	0.136 39(2)	0.223 28(2)
Ru(3)	0.686 72(4)	0.055 00(2)	0.126 80(2)
Ru(4)	0.899 19(4)	0.081 62(2)	0.219 42(2)
Ru(5)	0.983 33(4)	0.138 94(2)	0.354 92(2)
Ru(6)	0.761 12(4)	0.089 68(2)	0.427 51(2)
S(1)	0.755 3(1)	0.098 12(6)	0.314 59(6)
S(2)	0.826 1(1)	0.189 44(6)	0.189 02(6)
N(1)	0.857 3(7)	0.240 0(3)	0.071 8(3)
N(2)	0.751 5(5)	0.138 0(2)	0.072 6(2)
C(1)	0.809 7(6)	0.187 4(3)	0.102 0(2)
C(2)	0.934 2(7)	0.293 3(3)	0.103 5(3)
C(3)	0.074 4(8)	0.284 3(4)	0.126 9(4)
C(4)	1.144(1)	0.335 5(5)	0.157 4(5)
C(5)	1.079(1)	0.394 2(4)	0.162 4(4)
C(6)	0.938(2)	0.401 7(4)	0.138 7(5)
C(7)	0.866(1)	0.351 0(4)	0.109 4(4)
C(8)	0.740 4(8)	0.139 2(3)	0.002 4(3)
C(9)	0.860 3(8)	0.124 9(4)	−0.033 4(3)
C(10)	0.842(1)	0.123 5(5)	−0.101 9(4)
C(11)	0.711(1)	0.135 6(5)	−0.133 5(4)
C(12)	0.594(1)	0.151 0(4)	−0.096 6(4)
C(13)	0.609 0(8)	0.151 8(4)	−0.029 6(3)
C(14)	0.502 2(6)	0.195 4(3)	0.373 3(3)
C(15)	0.677 8(8)	0.273 0(3)	0.296 2(3)
C(16)	0.728 4(7)	0.253 7(3)	0.435 6(3)
C(17)	0.490 3(7)	0.179 3(3)	0.162 3(3)
C(18)	0.450 9(6)	0.088 2(3)	0.247 8(3)
C(19)	0.792 5(7)	−0.002 3(4)	0.071 8(3)
C(20)	0.507 3(7)	0.045 9(3)	0.078 3(3)
C(21)	0.641 2(7)	−0.013 6(3)	0.182 5(3)
C(22)	1.033 5(7)	0.080 5(3)	0.155 8(3)
C(23)	0.948 5(8)	−0.003 1(3)	0.240 5(3)
C(24)	1.108 1(6)	0.175 8(3)	0.291 4(3)
C(25)	1.079 9(6)	0.172 8(3)	0.431 5(3)
C(26)	1.088 7(6)	0.061 0(3)	0.367 6(3)
C(27)	0.828 2(7)	0.126 3(3)	0.508 2(3)
C(28)	0.833 4(6)	0.007 2(3)	0.450 2(3)
C(29)	0.567 5(6)	0.073 3(3)	0.453 1(3)
O(14)	0.385 2(5)	0.193 8(3)	0.384 7(3)
O(15)	0.659 0(9)	0.318 3(3)	0.265 1(3)
O(16)	0.741 1(7)	0.284 9(3)	0.480 5(3)
O(17)	0.418 1(6)	0.206 0(3)	0.124 8(3)
O(18)	0.354 7(5)	0.058 8(3)	0.261 3(3)
O(19)	0.854 5(6)	−0.037 4(3)	0.043 9(3)
O(20)	0.398 1(5)	0.036 7(3)	0.052 2(3)
O(21)	0.610 2(7)	−0.056 1(3)	0.214 1(3)
O(22)	1.115 1(6)	0.080 6(3)	0.115 3(3)
O(23)	0.983 1(8)	−0.055 4(2)	0.252 5(4)
O(24)	1.191 5(5)	0.200 3(3)	0.260 2(2)
O(25)	1.134 2(5)	0.193 1(3)	0.476 7(2)
O(26)	1.154 6(5)	0.015 4(2)	0.376 7(2)
O(27)	0.875 9(6)	0.148 1(3)	0.555 0(2)
O(28)	0.876 1(6)	−0.044 2(2)	0.462 5(3)
O(29)	0.452 9(5)	0.064 5(3)	0.466 3(3)

bonds, however, only 44 electrons are required. As a result the bonds between the atoms Ru(1), Ru(2), Ru(3) and Ru(4) are elongated. The bridging carbonyl groups seem to be more effective than the sulfur atom of the thioureato ligand in keeping the metal framework together. Even weaker is the stabilizing effect of the bridging nitrogen atom of the diaminocarbene ligand, accounting for the bond length of 3.231(3) Å. The elongation of the distances Ru(1)–Ru(5) and Ru(2)–Ru(4) observed in **1** can be interpreted as a bond order of 0.5, which in turn satisfies the effective atomic number rule for **1**.

Another example of a boat-like cluster, $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu\text{-}OH)_2]$, has been reported recently by Adams *et al.*[10] The basic structure of this cluster is similar to that of **1**, and the overall electron count also gives 46 electrons. Two metal–metal bonds, corresponding to Ru(1)–Ru(5) and Ru(2)–Ru(4) in **1**, are significantly longer than the others. According to the authors, both surplus electrons are supposed to occupy an antibonding orbital in the middle of the cluster and thus cause a weakening of the corresponding metal–metal bond. This interpretation could also be applied to **1**.

The metal framework of compound **2** consists of a unique arrangement of six metal atoms which can be considered analogous to the sofa conformer of cyclohexane. The base of the hexanuclear skeleton forms an approximately planar array of five ruthenium atoms [Ru(1), Ru(2), Ru(3), Ru(4) and Ru(5)], arranged in an envelope-like fashion with Ru(4) occupying the flap position and showing the most significant deviation from the plane of the remaining atoms [0.1071(5) Å]. The Ru(1)–Ru(5) edge is bridged by a sixth ruthenium atom [Ru(6)] arranged at an angle of approximately 90° with respect to the plane of the other ruthenium atoms. A five-co-ordinate sulfur bridges four in-plane ruthenium atoms [Ru(1), Ru(2), Ru(4) and Ru(5)] and the out-of-plane ruthenium atom [Ru(6)]. This sulfur forms a plane with ruthenium atoms 2, 4 and 6 and itself shows the maximum deviation from that plane of 0.0459(12) Å. The opposing side of the cluster base contains a μ_3-η^2-diphenylthioureato ligand in which the sulfur spans Ru(2) and Ru(4) and the nitrogen atom is bound in a terminal fashion to Ru(3). A bridging hydride is found between Ru(1) and Ru(5). Each ruthenium co-ordination sphere is completed with terminal carbonyl groups, two in the case of the metal atoms Ru(2) and Ru(4) and three for Ru(1), Ru(3), Ru(5) and Ru(6). The molecule possesses an approximate mirror plane passing through Ru(6), S(1), S(2), C(1), N(2) and Ru(3), and distortion to that symmetry is due to a slight twisting of the molecule probably resulting from the unusual co-ordination of the sulfido ligand.

In compound **2** the metal–metal bond distances span a wide range, whereas the metal–sulfur bond distances display a variable but more limited range. The longest metal–metal bonds are found between Ru(1) and Ru(2) [3.1713(6) Å] and Ru(4) and Ru(5) [3.0817(5) Å]. Somewhat shorter, though almost identical metal–metal bond lengths are found opposite to the longest Ru–Ru bonds [Ru(2)–Ru(4) 2.9208(5) Å, Ru(1)–Ru(5) 2.9221(5) Å]; the slightly longer of these contains the bridging hydride. Shorter but relatively consistent bonds are found to the apical Ru(6) and the bridging Ru(3) (average Ru–Ru 2.7522 Å). Among the two types of sulfur atoms, metal–sulfur bond distances vary from 2.3136(12) [Ru(6)–S(1)] to 2.4312(12) Å [Ru(4)–S(1)]. Surprisingly both the long and the short metal–sulfur bonds are associated with the five-co-ordinate sulfur suggesting a unique co-ordination mode for this atom.

The lengths of the Ru–Ru bonds in compound **2** spanned by the thioureato ligand are significantly different from the same bonds in **4**.[1] However the bridging sulfur of the thioureato ligand retains metal–sulfur bond lengths comparable to **4** as well as the double-bond character between C(1) and N(2). As in the case of **1**, unusually long bond lengths are encountered among those metal atoms comprising the base of the cluster **2** [3.1713(6) Å]. Bond lengths of this magnitude have been reported previously for ruthenium clusters containing sulfur ligands.[11] In considering ruthenium–sulfur bond distances one observes a range of some 12 pm. The shortest of these bonds can be rationalized in part through electron-counting procedures. Donation of all six valence electrons on S(1) is necessary to satisfy the effective atomic number rule and specifically two of these valence electrons must go to Ru(6) thus resulting in an

Table 5 Important bond lengths (Å) and angles (°) of compound **2**

Ru(1)–Ru(2)	3.1713(6)	Ru(4)–S(1)	2.431(1)
Ru(1)–Ru(5)	2.9221(5)	Ru(4)–S(2)	2.409(1)
Ru(1)–Ru(6)	2.7807(6)	Ru(5)–Ru(6)	2.7858(5)
Ru(1)–S(1)	2.407(1)	Ru(5)–S(1)	2.389(1)
Ru(2)–Ru(3)	2.7156(6)	Ru(6)–S(1)	2.314(1)
Ru(2)–Ru(4)	2.9208(5)	S(2)–C(1)	1.779(5)
Ru(2)–S(1)	2.391(1)	N(1)–C(1)	1.336(8)
Ru(2)–S(2)	2.421(1)	N(1)–C(2)	1.451(9)
Ru(3)–Ru(4)	2.7268(6)	N(2)–C(1)	1.295(7)
Ru(3)–N(2)	2.146(5)	N(2)–C(8)	1.433(7)
Ru(4)–Ru(5)	3.0817(5)		
Ru(2)–Ru(1)–Ru(5)	89.47(2)	Ru(1)–Ru(5)–Ru(4)	90.38(2)
Ru(2)–Ru(1)–Ru(6)	96.59(2)	Ru(1)–Ru(5)–Ru(6)	58.25(1)
Ru(2)–Ru(1)–S(1)	48.41(3)	Ru(1)–Ru(5)–S(1)	52.74(3)
Ru(5)–Ru(1)–Ru(6)	58.42(1)	Ru(4)–Ru(5)–Ru(6)	100.00(2)
Ru(5)–Ru(1)–S(1)	52.18(3)	Ru(4)–Ru(5)–S(1)	50.86(3)
Ru(6)–Ru(1)–S(1)	52.35(3)	Ru(6)–Ru(5)–S(1)	52.41(3)
Ru(1)–Ru(2)–Ru(3)	146.24(2)	Ru(1)–Ru(6)–Ru(5)	63.33(1)
Ru(1)–Ru(2)–Ru(4)	88.66(2)	Ru(1)–Ru(6)–S(1)	55.48(3)
Ru(1)–Ru(2)–S(1)	48.84(3)	Ru(5)–Ru(6)–S(1)	54.94(3)
Ru(1)–Ru(2)–S(2)	81.72(3)	Ru(1)–S(1)–Ru(2)	82.75(4)
Ru(3)–Ru(2)–Ru(4)	57.73(1)	Ru(1)–S(1)–Ru(4)	123.45(5)
Ru(3)–Ru(2)–S(1)	101.67(3)	Ru(1)–S(1)–Ru(5)	75.08(4)
Ru(3)–Ru(2)–S(2)	79.79(3)	Ru(1)–S(1)–Ru(6)	72.17(4)
Ru(4)–Ru(2)–S(1)	53.35(3)	Ru(2)–S(1)–Ru(4)	74.56(4)
Ru(4)–Ru(2)–S(2)	52.59(3)	Ru(2)–S(1)–Ru(5)	127.80(5)
S(1)–Ru(2)–S(2)	85.89(4)	Ru(2)–S(1)–Ru(6)	142.29(5)
Ru(2)–Ru(3)–Ru(4)	64.92(1)	Ru(4)–S(1)–Ru(5)	79.48(4)
Ru(2)–Ru(3)–N(2)	88.1(1)	Ru(4)–S(1)–Ru(6)	143.00(5)
Ru(4)–Ru(3)–N(2)	89.2(1)	Ru(5)–S(1)–Ru(6)	72.65(4)
Ru(2)–Ru(4)–Ru(3)	57.36(1)	Ru(2)–S(2)–Ru(4)	74.42(4)
Ru(2)–Ru(4)–Ru(5)	91.27(1)	Ru(2)–S(2)–C(1)	104.1(2)
Ru(2)–Ru(4)–S(1)	52.09(3)	Ru(4)–S(2)–C(1)	104.3(2)
Ru(2)–Ru(4)–S(2)	52.99(3)	C(1)–N(1)–C(2)	125.5(5)
Ru(3)–Ru(4)–Ru(5)	147.99(2)	Ru(3)–N(2)–C(1)	121.1(4)
Ru(3)–Ru(4)–S(1)	100.30(3)	Ru(3)–N(2)–C(8)	121.5(4)
Ru(3)–Ru(4)–S(2)	79.78(3)	C(1)–N(2)–C(8)	117.3(5)
Ru(5)–Ru(4)–S(1)	49.66(3)	S(2)–C(1)–N(1)	115.3(4)
Ru(5)–Ru(4)–S(2)	86.04(3)	S(2)–C(1)–N(2)	119.9(4)
S(1)–Ru(4)–S(2)	85.29(4)	N(1)–C(1)–N(2)	124.8(5)

increased bond order and corresponding decreased bond length. Finding all the noticeably short Ru–S bonds to the five-co-ordinate sulfur lends further support to full electron donation by S(1). Through electron donation sulfur may subsequently decrease the bond order of the adjacent metal–metal bonds and thus contribute to their lengthening. Bridging hydride atoms have also been shown to increase metal–metal bond lengths[12] and this effect must also be considered. Furthermore, given such a framework geometry, the five-co-ordinate sulfur atom in bonding to Ru(6) is forced to accept a position only 1.0968(12) Å above the plane of the five basal ruthenium atoms. Such an exceptionally close approach by S(1) could contribute further to lengthening the metal–metal bonds of the rectangular base.[13] Examples of five-co-ordinate sulfur in metal cluster complexes do exist. In the early seventies the structure of a mineral known as argentian pentlandite was published which displayed sulfur in a square-pyramidal co-ordination.[14] More recently Adams *et al.*[15] have identified several complexes in which a sulfur ligand bridges four ruthenium or osmium atoms and also co-ordinates a molybdenum atom in a fifth axial position. Further examples involve either six-co-ordinate sulfur[16] or encapsulation of the chalocogen by multiple metal atoms.[13,17] We believe compound **2** to be a unique example of μ_5-sulfur spanning five mutually bonded ruthenium atoms. The atypical co-ordination of S(1) is further exemplified by the diverse bond lengths and geometry exhibited throughout its co-ordination sphere.

Experimental

All operations were carried out under nitrogen using standard Schlenk techniques. Solvents were purified, distilled from the appropriate drying agents and stored under nitrogen prior to use. Preparative thin-layer chromatography was performed on plates coated with Al_2O_3. Infrared spectra were recorded on a Perkin Elmer FT IR 1720 spectrophotometer using cyclohexane solutions or KBr pellets, ^1H NMR spectra on a Bruker WM 400 instrument. Elemental analyses were performed by Mikroelementaranalytisches Laboratorium der Eidgenössischen Technischen Hochschule Zürich.

The compound $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$ was prepared according to a published procedure.[1] Other reagents were purchased from Fluka and used as received.

$[Ru_6(CO)_{14}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}\eta^2\text{-}EtNCSNHEt)(\mu_3\text{-}\eta^2\text{-}EtNCNHEt)]$ **1**.—A solution of $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and $SC(NHEt)_2$ (73 mg, 0.55 mmol) in thf (20 cm^3) was prepared in a pressure Schlenk tube (125 cm^3). The tube was placed in a preheated 130 °C oil-bath and the solution stirred for 35 min. After evaporation of the solvent the residue was dissolved in dichloromethane (5 cm^3) and separated by thin-layer chromatography [cyclohexane–dichloromethane (1:1)]. Besides the tetranuclear clusters $[Ru_4(CO)_{8-n}(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NEtH)\}_n]$ (n = 1 or 2),[2] compound **1** was extracted with dichloromethane from a green band and dried *in vacuo*. Yield 2 mg (trace). Spectroscopic data for **1**: IR (dichloromethane) ν(CO) 2079m, 2051s, 2034vs, 2003m, 1991m, 1977m, 1854w and 1831w; (KBr) ν(NH) 3426w, 3371w, ν(CN) 1588m cm^{-1}; ^1H NMR (C_2D_6O, 298 K): δ 3.92 (m, 4 H, 2CH$_2$), 3.63 (s br, 2 H, NH), 3.52 (q, 2 H, CH$_2$, J = 7.2), 3.45 (q, 2 H, CH$_2$, J = 7.0), 1.44 (t, 3 H, CH$_3$, J = 7.2), 1.40 (t, 3 H, CH$_3$, J = 7.3), 1.23 (t, 3 H, CH$_3$, J = 7.1), and 1.16 (t, 3 H, CH$_3$, J = 7.0 Hz).

$[Ru_6(CO)_{16}(\mu\text{-}H)(\mu_5\text{-}S)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$ **2**.—*Direct synthesis.* A solution of $[Ru_3(CO)_{12}]$ (50 mg, 0.078 mmol) and $(PhNH)_2CS$ (19 mg, 0.083 mmol) in thf (25 cm^3) was prepared in a pressure Schlenk tube (125 cm^3). The tube was placed in a preheated 130 °C oil-bath and allowed to stir for 35 min. Following evaporation of the solvent, the residue was dissolved in dichloromethane (2–3 cm^3) and the products separated by preparative TLC [cyclohexane–dichloromethane (75:25)] yielding compound **2** as the major product (20 mg, 0.015 mmol, 39%).

Thermolysis of **4**. A solution of compound **4** (34 mg, 0.04 mmol) in thf (20 cm^3) was prepared in a pressure Schlenk tube (125 cm^3). The tube was placed in a preheated 130 °C oil-bath and the solution stirred for 35 min. Following evaporation of the solvent, the residue was dissolved in dichloromethane and the products separated by preparative TLC [cyclohexane–dichloromethane (60:40)]. Elution of the solvent mixture allowed the separation of **2** as the major product and three additional products in yields ranging from 2 to 9%. The fast-moving band contained the previously reported compound $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)]$.[18] The band immediately following contained **2** (13.3 mg, 0.010 mmol, 46%). The remaining two bands contained in order of elution, a blue compound (1.7 mg) and a green compound (9.6 mg). Compound **2** was recrystallized from dichloromethane. Spectroscopic data for **2**: IR (cyclohexane) ν(CO) 2092w, 2070s, 2061s, 2046m, 2023m, 2012s and 1949m; (KBr) ν(NH) 3374, ν(CN) 1565 cm^{-1}; ^1H NMR (C_2D_6O, 298 K) δ 9.16 (s), 7.35 (m), −22.10 (s) (Found: C, 26.95; H, 0.80; N, 1.90. Calc. for $C_{29}H_{12}N_2O_{16}Ru_6S_2$: C, 26.5; H, 0.9; N, 2.1%).

Crystal Structure Determination and Refinement.—The crystal data and experimental parameters for compounds **1** and **2** are given in Table 1. Crystals of **1** were grown from acetone, and those of **2** from dichloromethane. The data for **1** were corrected for absorption using SHELX 76[19] [transmission factors 0.815 (maximum) and 0.765 (minimum)]. The structures were solved by direct methods (SHELX);[20] all further calculations were carried out using the NRCVAX system.[21] Difference maps revealed the positions of the non-hydrogen atoms which were refined anisotropically.

Due to the poor quality of the crystal of compound **1** the atoms C(1), C(1a), C(3), N(2), C(15), C(17), C(22), C(24) and C(25) could only be refined isotropically. For C(1) two positions have been found and refined with the occupancy factors 0.6 [C(1)] and 0.4 [C(1a)]; in Fig. 1 the position of C(1) is drawn midway between both determined positions. For compound **2** all hydrogen atoms of the phenyl groups were placed in calculated positions. The hydride position was located in the final difference map.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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