Tetranuclear Ruthenium Clusters containing a Pseudo-octahedral Ru_4S_2 Framework and Diaminocarbene Ligands†

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The tetranuclear ruthenium clusters $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHR)_2\}_2]$ **1** (R = Pr^i) and **3** (R = Et) and $[Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHR)_2\}]$ **2** (R = Pr^i) and **4** (R = Et) were obtained from the thermal reaction of $[Ru_3(CO)_{12}]$ with thioureas $SC(NHR)_2$ (R = Pr^i or Et). In the case of diethylthiourea, a trinuclear cluster $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}NEtCSNHEt)]$ **5** was isolated in addition to **3** and **4**. The single-crystal X-ray structure analyses of **1** and **2** reveal a pseudo-octahedral Ru_4S_2 skeleton with three μ-carbonyl bridges in the Ru_4 plane; **1** has two terminal diaminocarbene ligands and six terminal carbonyls, whereas there is only one terminal diaminocarbene ligand but seven terminal carbonyls in **2**.

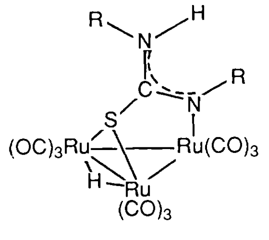
The reactivity of thiourea and its *N,N'*-dialkyl-substituted derivatives towards dodecacarbonyltriruthenium varies remarkably depending on the substituents. Thiourea itself and its dimethyl derivative react at room temperature with N–H activation to give trinuclear clusters $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}NRCSNHR)]$ **A** (R = H or Me).[1] The analogous reaction with di-*tert*-butylthiourea, however, yields the clusters $[Ru_3(\mu\text{-}H)(CO)_8(\mu_3\text{-}S)(CH_2CMe_2NHCNHBu^t)]$ **B** and $[Ru_3(\mu\text{-}H)(CO)_9\{\mu_3\text{-}S\text{-}Ru(CO)_3(CH_2CMe_2NHCNHBu^t)\}]$ **C** in which the C=S bond of the thiourea has been cleaved; the sulphido atom and the carbene ligand are both co-ordinated to the cluster.[2] In this paper we report on the reactions of $[Ru_3(CO)_{12}]$ with diisopropyl- and diethyl-thiourea.

Results

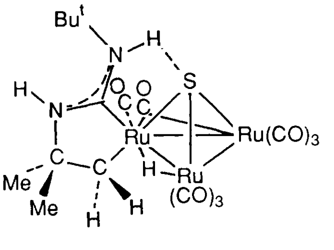
The tetranuclear clusters $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHPr^i)_2\}_2]$ **1** and $[Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHPr^i)_2\}]$ **2** were obtained from the reaction of $[Ru_3(CO)_{12}]$ with diisopropylthiourea in tetrahydrofuran (thf) (Scheme 1). They were isolated as dark red crystals by thin-layer chromatography and slow evaporation of their dichloromethane solutions. The analogous reaction with diethylthiourea yields the complexes $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHEt)_2\}_2]$ **3** and $[Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHEt)_2\}]$ **4** as red-brown solids. In addition to **3** and **4**, the trinuclear cluster $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}NEtCSNHEt)]$ **5** was isolated as an orange crystalline material.

The infrared spectra of the clusters **1**–**4** show, in addition to the absorptions of terminal carbonyls, bands characteristic of bridging carbonyl ligands. The ^1H NMR spectra show only broad signals for the aliphatic and NH protons between δ 5.7 and 0.8, suggesting a strongly hindered rotation of the alkyl groups about the C–C and C–N axes (Table 1). The IR spectrum of **5** reveals the ν(CO) absorption pattern typical for the $Ru_3(CO)_9$ moiety, analogous to $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}NPhCSNHPh)]$.[1] In the ^1H NMR spectrum **5** gives rise to the characteristic resonance of the NEtCSNHEt ligand as well as to a signal of the μ-hydride at δ −13.18.

The molecular structures of compounds **1** and **2** were determined by single-crystal X-ray structure analysis; they are illustrated in Figs. 1–3. Fractional atomic coordinates of **1** are given in Table 2, important bond lengths and angles in Table 3.



A R = H or Me



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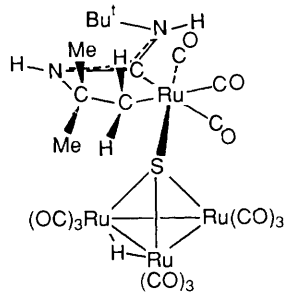

C

The molecular structure of **1** shows a square-planar arrangement of the four ruthenium atoms. Three carbonyls, located in the plane of the square, bridge three of the four edges, giving rise to a shortening of the corresponding Ru–Ru distances [2.7183(7)–2.7559(9) Å], as compared with the non-bridged edge [Ru(3)–Ru(4) 2.8636(8) Å]. Both sides of the ruthenium framework are symmetricaly capped by μ_4-sulfur atoms. The Ru–S bonds involving Ru(1) and Ru(2) [2.5282(15)–2.5662(15) Å] are about 11 pm longer than those involving Ru(3) and Ru(4) [2.4349(15)–2.4565(16) Å], reflecting the higher electron density at Ru(1) and Ru(2), caused by two di(isopropylamino)carbene ligands. Surprisingly, both carbene ligands are oriented towards the same side of the framework. Moreover, the torsion angles S(2)–Ru(1)–C(1)–N(1) [−1.8(3)°] and S(2)–Ru(2)–C(8)–N(3) [−2.4(3)°] indicate the carbene ligands to be bonded in a symmetrical fashion with respect to the Ru_4S_2 framework. As shown in Fig. 1, the structure is almost symmetrical with respect to a mirror plane defined by atoms S(1), S(2) and C(16); only the HNPr^i groups at N(1) and N(3) are twisted with respect to this

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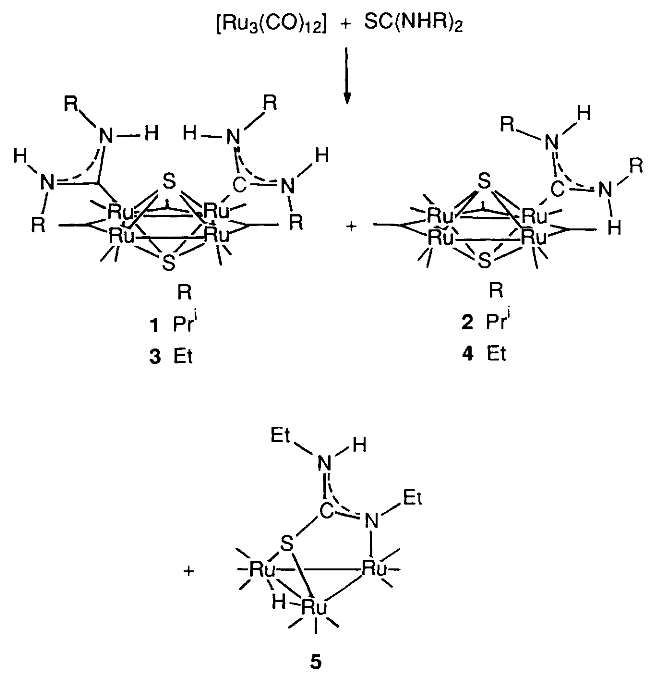
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical[a] and spectroscopic data for compounds **1**–**5**

						Analysis (%)		
Compound	Yield (%)	ν_{CO}[b]/cm^{-1}	ν_{NH}[c]/cm^{-1}	ν_{CN}[c]/cm^{-1}	$^1H(\delta)$[d]	C	H	N
1	22	2072vw, 2039m, 2006s, 1985m, 1971vs, 1960m (sh), 1940w, 1851m, 1834m, 1813m	3362, 3348	1548, 1509	5.57 (br, 1 H, NH), 5.39 (br, 1 H, NH), 5.15 (br, 1 H, NH), 4.81 (br, 2 H, CH + NH), 3.73 (br, 1 H, CH), 3.40 (br, 2 H, 2 CH), 1.33 (br, 12 H, 4 Me), 1.06 (br, 6 H, 2 Me), 0.86 (br, 6 H, 2 Me)	28.1 (28.3)	3.2 (3.3)	5.4 (5.7)
2	24	2073m, 2034vs, 2026vs, 1998s, 1989s, 1977s, 1952vw, 1864m, 1852w, 1829m	3383, 3343	1555, 1506	5.56 (br, 1 H, NH), 4.45 (br, 2 H, NH + CH), 3.49 (br, 1 H, CH), 1.41 (br, 6 H, 2 Me), 1.24 (br, 3 H, Me), 1.04 (br, 3 H, Me)	23.9 (23.3)	1.9 (1.8)	3.5 (3.2)
3	4	2076vw, 2040m, 2034w (sh), 2007vs, 1986s, 1972vs, 1950m, 1852m, 1836m, 1814m	3428, 3370	1554, 1506	5.71 (br, 2 H, 2 NH), 4.54 (br, 2 H, 2 NH), 3.94 (br, 4 H, 2 CH_2), 3.02 (br, 4 H, 2 CH_2), 1.41–0.86 (m, 12 H, 4 Me)	25.1 (24.8)	2.6 (2.6)	5.9 (6.1)
4	7	2074w, 2046vw, 2033vs, 2028vs (sh), 1997s (sh), 1990s, 1977m, 1952vw, 1865w, 1847vw, 1829w	3453, 3378	1549, 1493	5.66 (br, 1 H, NH), 5.15 (br, 1 H, NH), 3.99 (br, 2 H, CH_2), 2.95 (br, 2 H, CH_2), 1.47–0.87 (m, 6 H, 2 Me)	21.2 (21.2)	1.3 (1.4)	3.4 (3.3)
5	12	2082w, 2052w, 2031vs, 2004vs, 1992s	3427	1596	4.52 (s, br, 1 H, NH), 3.53 (d, q, J = 6.9, 2 H, CH_2), 3.22 (q, J = 7.3, 3 H, Me), 1.21 (t, J = 6.9, 3 H, Me), 1.05 (t, J = 7.3, 3 H, Me), −13.18 (s, 1 H, Ru_2H)	24.5 (24.5)	1.8 (1.8)	4.1 (4.1)

[a] Calculated values are given in parentheses. [b] Measured in cyclohexane. [c] In KBr. [d] Chemical shifts (δ), coupling constants in Hz, measurements at ambient temperatures in $CDCl_3$.



Scheme 1

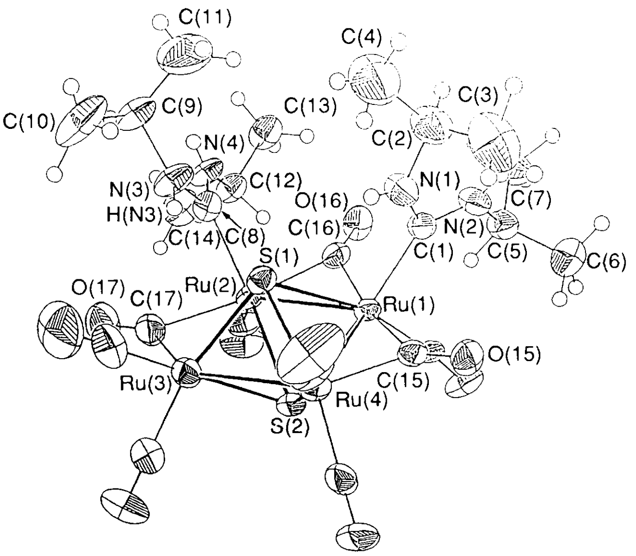


Fig. 1 Molecular structure of compound **1** (ORTEP plot,[3] thermal ellipsoids, 50% probability)

mirror plane, presumably because of steric reasons. This steric hindrance, in addition to the orientation of carbonyl ligand C(16)–O(16), prevents the carbene ligands from free rotation, thus explaining the poor resolution of the proton NMR spectrum. Atoms Ru(1) and Ru(2) co-ordinate one, Ru(3) and Ru(4) two terminal carbonyls, respectively.

The molecular structure of compound **2** (Tables 4 and 5) is very similar to that of **1**, showing the same Ru_4S_2 core and the same arrangement of the bridging carbonyl ligands. However, **2** contains only one di(isopropylamino)carbene ligand and therefore one more terminal carbonyl than **1**. The bond distances of the carbonyl-bridged metal atoms Ru(1)–Ru(2) [2.7481(4) Å], Ru(1)–Ru(4) [2.7419(4) Å] and Ru(2)–Ru(3) [2.7520(4) Å] are not significantly shorter than the non-bridged metal–metal distance Ru(3)–Ru(4) [2.8260(4) Å]. The higher electronic density at Ru(1), caused by the carbene ligand, is distributed over the whole ruthenium framework, and this is reflected in the unsymmetrical carbonyl bridges. The Ru–S bond lengths indicate the transmission of electron density from Ru(1) [2.5599(9), 2.5688(8) Å] *via* Ru(2) [2.5000(9), 2.4925(9) Å] to Ru(3) [2.4519(9), 2.4568(9) Å]. However Ru(4), also directly bonded to Ru(1), shows the same [2.4518(9), 2.4513(9) Å] bond lengths to sulfur as does Ru(3). As for **1**, the poor resolution of the ^1H NMR spectrum of **2** can be accounted for by the presence of the carbonyl bridges which hinder the rotation of the carbene ligand.

Although $[Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHR)_2\}]$ **2** (R =

Table 2 Fractional atomic coordinates for compound **1** with estimated standard deviations (e.s.d.s) in the last digit printed

Atom	*x*	*y*	*z*
Ru(1)	0.410 72(4)	0.024 71(4)	0.196 962(21)
Ru(2)	0.248 68(4)	0.284 39(4)	0.191 339(22)
Ru(3)	0.048 91(4)	0.216 00(4)	0.285 22(3)
Ru(4)	0.222 76(4)	−0.056 85(4)	0.292 168(24)
S(1)	0.300 59(13)	0.122 12(12)	0.319 46(7)
S(2)	0.146 29(13)	0.106 00(13)	0.173 41(8)
C(1)	0.618 2(5)	−0.041 6(5)	0.236 1(3)
C(2)	0.763 3(7)	−0.100 5(8)	0.359 9(4)
C(3)	0.817 1(12)	−0.249 7(11)	0.378 2(6)
C(4)	0.738 4(14)	−0.036 5(20)	0.433 2(7)
C(5)	0.755 2(6)	−0.069 7(6)	0.111 3(3)
C(6)	0.800 5(9)	−0.206 4(8)	0.088 4(5)
C(7)	0.862 8(8)	−0.002 4(10)	0.086 0(5)
C(8)	0.326 0(5)	0.417 4(5)	0.234 2(3)
C(9)	0.363 1(7)	0.487 7(6)	0.361 6(3)
C(10)	0.276 0(17)	0.485 2(12)	0.434 8(6)
C(11)	0.521 9(12)	0.437 4(12)	0.372 0(7)
C(12)	0.389 6(6)	0.544 8(6)	0.111 8(3)
C(13)	0.538 5(8)	0.551 1(8)	0.095 9(4)
C(14)	0.274 2(9)	0.672 4(7)	0.083 3(5)
C(15)	0.412 7(5)	−0.163 0(5)	0.251 4(3)
C(16)	0.447 7(5)	0.200 5(5)	0.147 0(3)
C(17)	0.048 7(6)	0.398 2(6)	0.234 5(4)
C(18)	0.442 1(5)	−0.046 4(5)	0.105 7(3)
C(19)	0.187 8(6)	0.386 3(5)	0.094 3(3)
C(20)	−0.009 6(7)	0.268 3(7)	0.382 9(4)
C(21)	−0.137 5(7)	0.236 7(7)	0.259 2(4)
C(22)	0.127 0(6)	−0.167 4(6)	0.268 3(4)
C(23)	0.254 0(9)	−0.146 6(6)	0.394 2(4)
N(1)	0.634 4(6)	−0.052 1(6)	0.312 7(3)
N(2)	0.738 4(5)	−0.078 3(5)	0.195 9(3)
N(3)	0.318 2(6)	0.411 5(5)	0.311 0(3)
N(4)	0.376 6(6)	0.505 7(4)	0.195 9(3)
O(15)	0.485 5(4)	−0.273 5(4)	0.255 6(3)
O(16)	0.535 6(4)	0.230 2(4)	0.111 74(24)
O(17)	−0.021 0(5)	0.509 0(4)	0.230 2(3)
O(18)	0.447 7(5)	−0.093 0(4)	0.050 12(22)
O(19)	0.148 1(6)	0.441 7(5)	0.034 4(3)
O(20)	−0.045 8(7)	0.300 3(8)	0.441 4(4)
O(21)	−0.250 2(6)	0.249 4(7)	0.243 5(4)
O(22)	0.069 2(5)	−0.235 2(5)	0.252 5(3)
O(23)	0.276 7(9)	−0.199 8(6)	0.456 9(3)

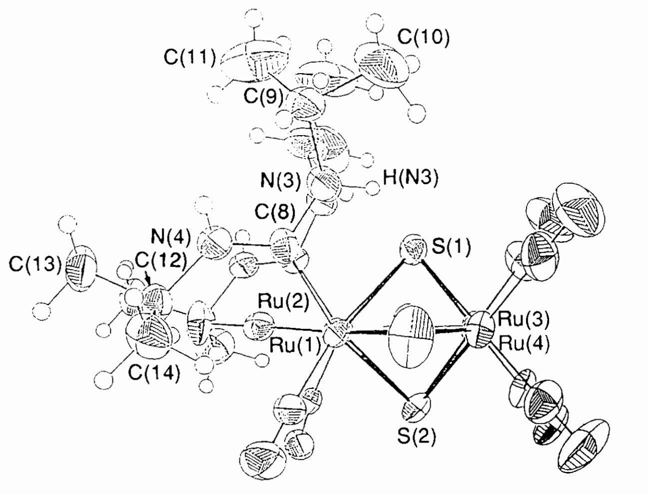


Fig. 2 Side view of compound **1** (ORTEP plot,[3] thermal ellipsoids, 50% probability)

Pr^i) and **4** (R = Et) may formally be derived from the diaminocarbene-substituted clusters $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHR)_2\}_2]$ **1** (R = Pr^i) and **3** (R = Et) by replacement of a carbene by a carbonyl ligand, all attempts to transform the former into the latter type cluster by carbon monoxide substitution failed. The thermolysis of **5** gives only decomposition products, suggesting that the formation of **3** and **4** does not proceed through the intermediacy of **5**.

Discussion

The thermally induced reactions of $[Ru_3(CO)_{12}]$ with di-isopropyl- and diethyl-thiourea lead to the formation of the tetranuclear clusters **1**–**4** which contain a square-planar skeleton of four metal atoms, two μ_4-bridging sulfido ligands on the opposite sides of the metal framework, as well as three bridging carbonyl ligands. The cluster framework is isoelectronic to that of the carbene-free cluster $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2]$ **6** and its disubstituted derivative $[Ru_4(CO)_7(\mu\text{-}CO)_2(\mu_4\text{-}S)_2(PMe_2Ph)_2]$ **7** reported by Adams *et al.*[4] However, while in **7** the two phosphine ligands are co-ordinated in a transoid fashion to two ruthenium atoms diagonal with respect to the Ru_4 square, the two diaminocarbene ligands in **1** and **3** are attached to vicinal ruthenium atoms of the Ru_4 square and arranged in a cisoid fashion in spite of considerable steric hindrance. While the phenyl(dimethylamino)carbene-substituted cluster $[Ru_4(CO)_8(\mu_4\text{-}S)_2\{C(Ph)NMe_2\}]$, synthesised from **6** and $[W(CO)_5\{C(Ph)NMe_2\}]$,[5] was found to contain two carbonyl bridges and a semibridging carbonyl, the X-ray structure analysis of **2** reveals three bridging carbonyl ligands. This indicates that the $C(NHPr^i)_2$ ligand is a stronger σ donor or weaker π acceptor than the $C(Ph)NMe_2$ ligand.

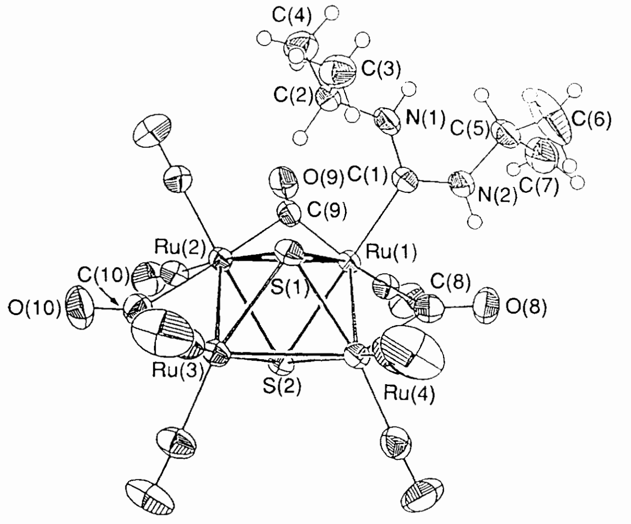


Fig. 3 Molecular structure of compound **2** (ORTEP plot,[3] thermal ellipsoids, 50% probability)

The number of transition-metal clusters containing carbene ligands is still rather limited.[5–8] To our knowledge, **1** and **3** are the first examples of tetranuclear ruthenium clusters containing two carbene ligands.

Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. The solvents were dried over drying agents and distilled under nitrogen prior to use. Infrared spectra were recorded on a Perkin-Elmer 1720 X spectrometer and ^1H NMR spectra on a Bruker WP 200 instrument using the residual proton signal of the deuteriated solvent as the internal standard. Elemental analyses were performed at the microanalytical

Table 3 Important bond lengths (Å) and angles (°) of compound **1** with e.s.d.s in parentheses

Ru(1)–Ru(2)	2.7183(7)	C(1)–N(1)	1.330(7)
Ru(1)–Ru(4)	2.7379(9)	C(1)–N(2)	1.340(7)
Ru(1)–S(1)	2.5662(15)	C(2)–C(3)	1.506(14)
Ru(1)–S(2)	2.5282(15)	C(2)–C(4)	1.516(13)
Ru(1)–C(1)	2.068(5)	C(2)–N(1)	1.456(8)
Ru(1)–C(15)	2.098(5)	C(5)–C(6)	1.506(9)
Ru(1)–C(16)	2.110(5)	C(5)–C(7)	1.513(9)
Ru(2)–Ru(3)	2.7559(9)	C(5)–N(2)	1.465(7)
Ru(2)–S(1)	2.5631(15)	C(8)–N(3)	1.326(7)
Ru(2)–S(2)	2.5411(13)	C(8)–N(4)	1.311(7)
Ru(2)–C(8)	2.094(5)	C(9)–C(10)	1.515(11)
Ru(2)–C(16)	2.067(5)	C(9)–C(11)	1.510(13)
Ru(2)–C(17)	2.144(6)	C(9)–N(3)	1.473(7)
Ru(3)–Ru(4)	2.8636(8)	C(12)–C(13)	1.532(9)
Ru(3)–S(1)	2.4441(15)	C(12)–C(14)	1.499(9)
Ru(3)–S(2)	2.4349(15)	C(12)–N(4)	1.471(7)
Ru(3)–C(17)	2.031(6)	C(15)–O(15)	1.165(6)
Ru(4)–S(1)	2.4384(13)	C(16)–O(16)	1.160(6)
Ru(4)–S(2)	2.4565(16)	C(17)–O(17)	1.159(7)
Ru(4)–C(15)	2.028(5)		

Ru(2)–Ru(1)–Ru(4)	91.93(3)	Ru(1)–Ru(4)–S(1)	59.10(3)
Ru(2)–Ru(1)–S(1)	57.94(4)	Ru(1)–Ru(4)–S(2)	57.95(4)
Ru(2)–Ru(1)–S(2)	57.80(3)	Ru(1)–Ru(4)–C(15)	49.53(14)
Ru(2)–Ru(1)–C(1)	120.30(14)	Ru(3)–Ru(4)–S(1)	54.18(4)
Ru(2)–Ru(1)–C(16)	48.72(14)	Ru(3)–Ru(4)–S(2)	53.82(4)
Ru(4)–Ru(1)–S(1)	54.62(3)	S(1)–Ru(4)–S(2)	78.23(5)
Ru(4)–Ru(1)–S(2)	55.44(4)	Ru(1)–S(1)–Ru(2)	64.00(4)
Ru(4)–Ru(1)–C(1)	116.57(14)	Ru(1)–S(1)–Ru(3)	102.49(5)
Ru(4)–Ru(1)–C(15)	47.35(13)	Ru(1)–S(1)–Ru(4)	66.28(4)
S(1)–Ru(1)–S(2)	74.63(5)	Ru(2)–S(1)–Ru(3)	66.74(4)
S(1)–Ru(1)–C(1)	96.17(14)	Ru(2)–S(1)–Ru(4)	103.28(5)
S(2)–Ru(1)–C(1)	170.21(14)	Ru(3)–S(1)–Ru(4)	71.82(4)
Ru(1)–Ru(2)–Ru(3)	91.10(3)	Ru(1)–S(2)–Ru(2)	64.85(3)
Ru(1)–Ru(2)–S(1)	58.05(4)	Ru(1)–S(2)–Ru(3)	103.87(5)
Ru(1)–Ru(2)–S(2)	57.34(4)	Ru(1)–S(2)–Ru(4)	66.62(4)
Ru(1)–Ru(2)–C(8)	120.80(14)	Ru(2)–S(2)–Ru(3)	67.22(4)
Ru(1)–Ru(2)–C(16)	50.09(13)	Ru(2)–S(2)–Ru(4)	103.41(5)
Ru(3)–Ru(2)–S(1)	54.56(3)	Ru(3)–S(2)–Ru(4)	71.66(4)
Ru(3)–Ru(2)–S(2)	54.55(4)	Ru(1)–C(1)–N(1)	115.1(4)
Ru(3)–Ru(2)–C(8)	113.66(14)	Ru(1)–C(1)–N(2)	129.5(4)
Ru(3)–Ru(2)–C(17)	46.95(16)	N(1)–C(1)–N(2)	115.4(5)
S(1)–Ru(2)–S(2)	74.46(4)	Ru(2)–C(8)–N(3)	113.9(3)
S(1)–Ru(2)–C(8)	93.07(14)	Ru(2)–C(8)–N(4)	129.2(4)
S(2)–Ru(2)–C(8)	166.34(14)	N(3)–C(8)–N(4)	117.0(5)
Ru(2)–Ru(3)–Ru(4)	88.52(3)	Ru(1)–C(15)–Ru(4)	83.12(19)
Ru(2)–Ru(3)–S(1)	58.70(4)	Ru(1)–C(15)–O(15)	138.6(4)
Ru(2)–Ru(3)–S(2)	58.23(3)	Ru(4)–C(15)–O(15)	138.3(4)
Ru(2)–Ru(3)–C(17)	50.49(16)	Ru(1)–C(16)–Ru(2)	81.19(18)
Ru(4)–Ru(3)–S(1)	54.00(3)	Ru(1)–C(16)–O(16)	137.9(4)
Ru(4)–Ru(3)–S(2)	54.52(4)	Ru(2)–C(16)–O(16)	140.9(4)
S(1)–Ru(3)–S(2)	78.54(5)	Ru(2)–C(17)–Ru(3)	82.56(21)
Ru(1)–Ru(4)–Ru(3)	88.45(3)	Ru(2)–C(17)–O(17)	137.5(5)
		Ru(3)–C(17)–O(17)	140.0(5)

laboratories of the Rheinisch–Westfälische Technische Hochschule Aachen (Germany) and the Eidgenössische Technische Hochschule Zürich (Switzerland).

Reaction of $[Ru_3(CO)_{12}]$ *with* $SC(NHPr^i)_2$.—A solution of $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and $SC(NHPr^i)_2$ (80 mg, 0.5 mmol) in thf (30 cm^3) was refluxed for 8 h. After evaporation of the solvent the residue was dissolved in CH_2Cl_2 (5 cm^3) and separated by preparative TLC (Al_2O_3; CH_2Cl_2–cyclohexane, 1 : 1). The products $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHPr^i)_2\}_2]$ **1** and $[Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHPr^i)_2\}]$ **2**, were extracted with CH_2Cl_2 from the first and the second band, respectively, and crystallized from dichloromethane.

Table 4 Fractional atomic coordinates for compound **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru(1)	−0.106 65(3)	0.320 497(22)	0.176 086(21)
Ru(2)	0.171 74(3)	0.400 423(24)	0.326 262(21)
Ru(3)	0.124 54(3)	0.257 356(25)	0.459 504(22)
Ru(4)	−0.162 52(3)	0.176 738(24)	0.305 370(23)
S(1)	0.088 68(10)	0.188 53(7)	0.264 03(7)
S(2)	−0.072 51(10)	0.381 52(7)	0.381 49(7)
C(1)	−0.130 2(4)	0.257 8(3)	0.0101 1(3)
C(2)	0.152 0(4)	0.222 1(3)	0.020 9(3)
C(3)	0.193 8(6)	0.096 3(4)	0.007 0(5)
C(4)	0.248 4(6)	0.295 3(5)	−0.024 7(4)
C(5)	−0.307 4(5)	0.224 8(4)	−0.180 3(3)
C(6)	−0.335 2(12)	0.093 4(6)	−0.221 1(6)
C(7)	−0.448 8(6)	0.286 7(6)	−0.222 1(4)
C(8)	−0.286 9(4)	0.185 7(3)	0.156 8(3)
C(9)	0.050 3(4)	0.444 0(3)	0.172 9(3)
C(10)	0.305 3(5)	0.369 8(4)	0.488 4(3)
C(11)	−0.262 0(4)	0.420 1(3)	0.139 7(3)
C(12)	0.358 0(4)	0.389 3(3)	0.283 4(3)
C(13)	0.220 2(5)	0.562 4(4)	0.382 5(3)
C(14)	0.240 6(6)	0.130 9(4)	0.494 3(3)
C(15)	0.106 4(5)	0.299 1(4)	0.602 4(3)
C(16)	−0.169 0(6)	0.015 5(4)	0.288 2(3)
C(17)	−0.338 6(5)	0.176 4(3)	0.359 9(3)
N(1)	−0.013 2(4)	0.225 4(3)	−0.032 7(3)
N(2)	−0.266 7(4)	0.254 6(3)	−0.060 6(3)
O(8)	−0.398 7(3)	0.145 8(3)	0.089 03(24)
O(9)	0.077 9(3)	0.512 27(24)	0.127 26(21)
O(10)	0.420 4(4)	0.410 9(3)	0.548 8(3)
O(11)	−0.357 2(4)	0.480 5(3)	0.117 2(3)
O(12)	0.468 0(4)	0.378 2(3)	0.256 5(3)
O(13)	0.249 7(4)	0.658 7(3)	0.411 6(3)
O(14)	0.310 1(5)	0.054 9(3)	0.513 0(3)
O(15)	0.099 9(4)	0.325 0(3)	0.689 62(24)
O(16)	−0.169 6(6)	−0.082 5(3)	0.278 4(3)
O(17)	−0.447 9(4)	0.174 4(3)	0.389 3(3)

Reaction of $[Ru_3(CO)_{12}]$ *with* $SC(NHEt)_2$.—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 refluxed for 1 h. After evaporation of the solvent the residue was dissolved in CH_2Cl_2 (5 cm^3) and separated by preparative TLC (Al_2O_3; CH_2Cl_2–cyclohexane, 1 : 1). The products $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}NEtCSNHEt)]$ **5**, $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHEt)_2\}_2]$ **3** and $[Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHEt)_2\}]$ **4** were extracted with CH_2Cl_2 from the first, the second and the third band, respectively, and obtained by evaporation of the solvent.

X-Ray Structure Determinations.—The crystals were prepared as described in the Experimental section and sealed in Lindemann glass capillaries.

Crystal data for compound **1**. $C_{23}H_{32}N_4O_9Ru_4S_2$, *M* 977.0, triclinic, space group $P\bar{1}$, $a = 10.048(3)$, $b = 10.883(2)$, $c = 17.384(5)$ Å, $\alpha = 80.97(2)$, $\beta = 87.57(2)$, $\gamma = 70.14(1)°$, $U = 1765.6$ Å^3 (from 26 reflections with $27 \leqslant 2\theta \leqslant 34°$, $\lambda = 0.710\,73$ Å), $Z = 2$, $D_c = 1.846$ g cm^{-3}, $F(000) = 956$. Pale orange rod, which darkened during data collection. Crystal dimensions 0.42 × 0.19 × 0.08 mm, μ(Mo-Kα) = 18.2 cm^{-1}.

Data collection and processing. Stoe-Siemens AED 2 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å, $2\theta_{max} = 50°$), ω–2θ mode. No correction was made for absorption. 4404 Unique reflections were measured giving 4293 with $I > 2.5\sigma(I)$. Weights based on counting statistics were used, the weight modifier *k* in kF_o^2 being 0.0015.

Structure analysis and refinement. The structure was solved by direct methods (SHELXS[9]) and refined using the NRCVAX system.[10] Although some of the hydrogen atoms could be located from the difference maps, they were all introduced in ideal positions (C–H 1.08 Å) and refined isotropically. Refinement converged with agreement factors of $R = 0.036$ and $R' = 0.048$. The final difference map exhibited electron-density

Table 5 Important bond lengths (Å) and angles (°) of compound **2** with e.s.d.s in parentheses

Ru(1)–Ru(2)	2.7481(4)	Ru(3)–C(10)	1.978(4)
Ru(1)–Ru(4)	2.7419(4)	Ru(4)–S(1)	2.4518(9)
Ru(1)–S(1)	2.5599(9)	Ru(4)–S(2)	2.4513(9)
Ru(1)–S(2)	2.5688(8)	Ru(4)–C(8)	1.993(4)
Ru(1)–C(1)	2.099(3)	C(1)–N(1)	1.339(5)
Ru(1)–C(8)	2.172(4)	C(1)–N(2)	1.318(5)
Ru(1)–C(9)	2.016(3)	C(2)–C(3)	1.523(6)
Ru(2)–Ru(3)	2.7520(4)	C(2)–C(4)	1.511(6)
Ru(2)–S(1)	2.5000(9)	C(2)–N(1)	1.465(5)
Ru(2)–S(2)	2.4925(9)	C(5)–C(6)	1.526(8)
Ru(2)–C(9)	2.179(3)	C(5)–C(7)	1.504(6)
Ru(2)–C(10)	2.245(4)	C(5)–N(2)	1.476(5)
Ru(3)–Ru(4)	2.8260(4)	C(8)–O(8)	1.164(5)
Ru(3)–S(1)	2.4519(9)	C(9)–O(9)	1.151(4)
Ru(3)–S(2)	2.4568(9)	C(10)–O(10)	1.149(5)

Ru(2)–Ru(1)–Ru(4)	89.533(11)	Ru(1)–Ru(4)–S(2)	58.974(21)
Ru(2)–Ru(1)–S(1)	56.064(21)	Ru(1)–Ru(4)–C(8)	51.70(11)
Ru(2)–Ru(1)–S(2)	55.788(20)	Ru(3)–Ru(4)–S(1)	54.812(21)
Ru(2)–Ru(1)–C(1)	123.90(10)	Ru(3)–Ru(4)–S(2)	54.935(21)
Ru(2)–Ru(1)–C(9)	51.68(10)	S(1)–Ru(4)–S(2)	77.86(3)
Ru(4)–Ru(1)–S(1)	54.959(21)	Ru(1)–S(1)–Ru(2)	65.778(22)
Ru(4)–Ru(1)–S(2)	54.861(20)	Ru(1)–S(1)–Ru(3)	104.35(3)
Ru(4)–Ru(1)–C(1)	121.31(10)	Ru(1)–S(1)–Ru(4)	66.298(23)
Ru(4)–Ru(1)–C(8)	46.07(10)	Ru(2)–S(1)–Ru(3)	67.516(24)
S(1)–Ru(1)–S(2)	73.84(3)	Ru(2)–S(1)–Ru(4)	102.66(3)
S(1)–Ru(1)–C(1)	102.25(9)	Ru(3)–S(1)–Ru(4)	70.38(3)
S(2)–Ru(1)–C(1)	175.60(10)	Ru(1)–S(2)–Ru(2)	65.751(22)
Ru(1)–Ru(2)–Ru(3)	92.087(11)	Ru(1)–S(2)–Ru(3)	103.95(3)
Ru(1)–Ru(2)–S(1)	58.158(21)	Ru(1)–S(2)–Ru(4)	66.164(22)
Ru(1)–Ru(2)–S(2)	58.460(20)	Ru(2)–S(2)–Ru(3)	67.562(23)
Ru(1)–Ru(2)–C(9)	46.56(9)	Ru(2)–S(2)–Ru(4)	102.89(3)
Ru(3)–Ru(2)–S(1)	55.409(21)	Ru(3)–S(2)–Ru(4)	70.310(24)
Ru(3)–Ru(2)–S(2)	55.601(21)	Ru(1)–C(1)–N(1)	124.77(25)
Ru(3)–Ru(2)–C(10)	45.23(10)	Ru(1)–C(1)–N(2)	119.8(3)
S(1)–Ru(2)–S(2)	76.21(3)	N(1)–C(1)–N(2)	115.3(3)
Ru(2)–Ru(3)–Ru(4)	87.742(11)	Ru(1)–C(8)–Ru(4)	82.24(14)
Ru(2)–Ru(3)–S(1)	57.075(22)	Ru(1)–C(8)–O(8)	135.2(3)
Ru(2)–Ru(3)–S(2)	56.837(21)	Ru(4)–C(8)–O(8)	142.6(3)
Ru(2)–Ru(3)–C(10)	53.68(11)	Ru(1)–C(9)–Ru(2)	81.76(13)
Ru(4)–Ru(3)–S(1)	54.806(22)	Ru(1)–C(9)–O(9)	145.6(3)
Ru(4)–Ru(3)–S(2)	54.755(21)	Ru(2)–C(9)–O(9)	132.5(3)
S(1)–Ru(3)–S(2)	77.75(3)	Ru(2)–C(10)–Ru(3)	80.09(14)
Ru(1)–Ru(4)–Ru(3)	90.635(11)	Ru(2)–C(10)–O(10)	132.9(3)
Ru(1)–Ru(4)–S(1)	58.743(21)	Ru(3)–C(10)–O(10)	146.0(3)

maxima and minima of 1.12 e Å^{-3}, near a ruthenium atom, and -1.15 e Å^{-3}, respectively.

Crystal data for compound **2**. $C_{17}H_{16}N_2O_{10}Ru_4S_2$, *M* 876.7, triclinic, space group $P\bar{1}$, $a = 8.944(1)$, $b = 11.782(1)$, $c = 13.058(1)$ Å, $\alpha = 101.50(1)$, $\beta = 105.17(1)$, $\gamma = 91.08(1)°$, $U = 1297.7$ Å^3 (24 reflections, $30 \leqslant 2\theta \leqslant 39°$, $\lambda = 0.710\,73$ Å), $Z = 2$, $D_c = 2.244$ g cm^{-3}, $F(000) = 1116$. Crystal form: red block, with dimensions 0.49 × 0.30 × 0.23 mm, μ(Mo-Kα) = 25.1 cm^{-1}.

Data collection and processing. As for compound **1**. 4572 Unique reflections were measured giving 4082 with $I > 2.5\sigma(I)$. Weights based on counting statistics were used, the weight modifier k in kF_o^2 being 0.003.

Structure analysis and refinement. As for compound **1**. Refinement converged with agreement factors of $R = 0.026$ and $R' = 0.046$. The final difference map exhibited electron-density maxima and minima of 0.76 e Å^{-3}, near a ruthenium atom, and -1.08 e Å^{-3}, respectively.

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

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