Mixed Tetranuclear Rhenium–Ruthenium Compounds formed by Carbon–Sulphur Bond Cleavage in Reactions of $[Re_2(pyS)_2(CO)_6]$ (pyS = pyridine-2-thionate) with $[Ru_3(CO)_{12}]$. Crystal Structures of $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ and $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$†

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The dinuclear compound $[Re_2(pyS)_2(CO)_6]$ (pyS = pyridine-2-thionate) reacts with $[Ru_3(CO)_{12}]$ to give a series of compounds containing $ReRu_3$, Re_2Ru_2, and Re_3Ru groups and which are formally built up by the combination of $Re(pyS)(CO)_3$ and $Ru(CO)_x$ (x = 2, 3 or 4) units. The compound $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ is formed by C–S bond cleavage and exists as two non-interconverting but inseparable isomers in solution. A single crystal selected from the crystallised mixture was found by X-ray structure determination to contain just one pure diastereomer as a mixture of enantiomers. The four metal atoms are linked by a μ_4-S ligand and a disordered 2-pyridyl ligand bridges two $Ru(CO)_3$ groups. The isomers in solution result from the interchange of $Re(CO)_4$ and $Ru(CO)_4$ units. Two non-interconvertible isomers of the compound $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$ were separated and each structurally characterised. Their structures are extremely similar (except that one has CH_2Cl_2 molecules in the crystal) differing only in the orientation of the 2-pyridyl bridges. Full crystallographic characterisation depended upon the correct positioning of C and N atoms. The compound $[Re_3Ru(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(pyS)_2(CO)_{11}]$ also forms separable non-interconverting isomers. One contains two doubly bridging pyS ligands and the other one doubly and one triply bridging pyS ligand. Therefore isomerism in these compounds has three separate origins.

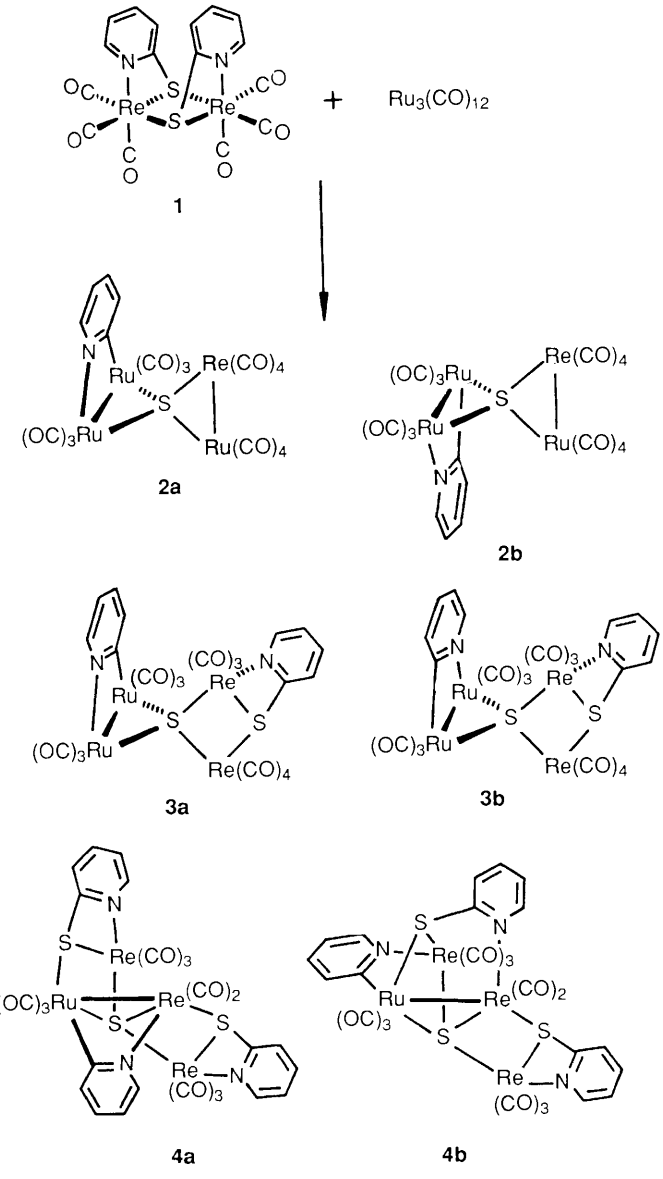
The compound $[Re_2(CO)_{10}]$ reacts with pyridine-2-thione (pySH) in refluxing xylene to give a good yield of the dinuclear compound $[Re_2(pyS)_2(CO)_6]$ **1** in which the pyS ligands bridge as five-electron donors as illustrated in Scheme 1.[1] The pyridine rings are on the same side of the Re_2S_2 ring. Compound **1** is cleaved by various monodentate ligands L to give $[Re(pyS)(CO)_3L]$ containing pyS as a chelating ligand. Solutions containing a mixture of **1** and the analogous 6-methylpyridine-2-thionato (mpyS) complex reach an equilibrium over several days at room temperature involving the mixed-ligand compound $[Re_2(pyS)(mpyS)(CO)_6]$. These three species may be separated by TLC but a solution of the mixed-ligand compound regenerates the three-component mixture over days at room temperature. We believe that this scrambling process occurs *via* the 16-electron mononuclear species $[Re(pyS)(CO)_3]$ or the corresponding 18-electron species with a co-ordinated solvent ligand.[1] We considered that these transient monomers might be presursors to heterometallic compounds and treated **1** with $[Ru_3(CO)_{12}]$ with the idea of generating $[ReRu(pyS)(CO)_x]$ (x = 7 or 8). Instead we obtained a series of tetranuclear mixed-metal compounds each containing μ_4-sulphido and μ-2-pyridyl ligands formed by cleavage of a C–S bond of a pyS ligand. These compounds are the subject of this paper. A communication of some of this work has appeared.[2]

Results and Discussion

Syntheses.—Equimolar amounts of dimer **1** and $[Ru_3(CO)_{12}]$ were heated to reflux in xylene for 30 min to give a mixture which was separated by successive TLC treatment into five components: yellow crystals of $[ReRu_3S(C_5H_4N)(CO)_{14}]$ **2**, $[Re_2Ru_2S(C_5H_4N)(pyS)(CO)_{13}]$ as isomers **3a** and **3b**, obtained separately as lemon-yellow crystals and $[Re_3RuS(C_5H_4N)(pyS)_2(CO)_{11}]$ also as separated isomers **4a** and **4b**, each as orange crystals. These samples were characterised by elemental analysis, IR and ^1H NMR spectra and single-crystal X-ray diffraction. The X-ray structures of **4a** and **4b** were reported in a communication;[2] our results are summarised in Scheme 1.

Characterisation of Mixed-metal Products.—$[ReRu_3S(C_5H_4N)(CO)_{14}]$ **2**. This yellow crystalline compound appeared to be homogeneous but the observation of 15 IR absorptions around 2000 cm^{-1} for cyclohexane solutions indicated that more than one isomer was present or that the compound was more complex than as formulated above. The ^1H NMR spectrum showed four multiplets (Fig. 1 and Table 1). Generally spectra of this ligand system are easily analysed since four well separated multiplets are usually observed, the most easily assigned feature being the H^6 signal at highest δ value. This resonance normally appears as a fairly narrow doublet [$J(H^5H^6)$ = *ca.* 5.5 Hz] with further small couplings to the H^4 and H^3 protons. We have analysed the four multiplets observed for compound **2** and interpret these as the result of two approximately equally intense sets of overlapping 2-pyridyl resonances. For example the H^6 signal appeared as two doublets of multiplets giving the appearance of a triplet with further fine coupling. Careful chromatography, collecting the upper and lower extremes of the yellow band separately, gave no evidence for even a partial separation, so that before

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1

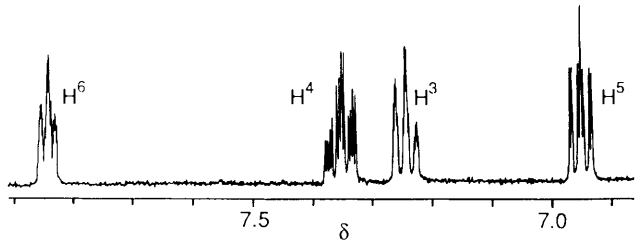


Fig. 1 The ^1H NMR spectrum of $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ **2** (400 MHz, CD_2Cl_2, 20 °C) showing the overlapping multiplets for the two isomers which is clearly so for H^6 and H^4 but not for H^3 and H^5

the X-ray structure had been determined we believed incorrectly that the molecular formula was double that given above with the molecule containing two different 2-pyridyl ligands.

A single-crystal X-ray structure of compound **2** was determined for a crystal selected from those grown by slow evaporation of a dichloromethane–hexane solution. The molecular structure shown in Fig. 2 is electron-precise and the μ_4-S atom links the two metal–metal bonded dinuclear units, $Ru_2(C_5H_4N)(CO)_6$ and $ReRu(CO)_8$. Bond lengths and angles

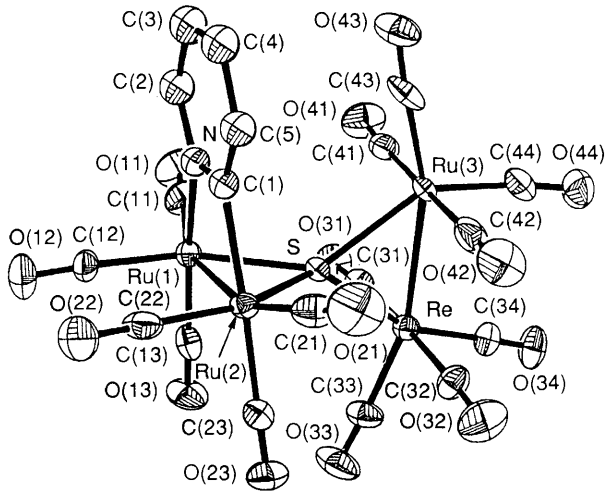


Fig. 2 Molecular structure of $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ **2**

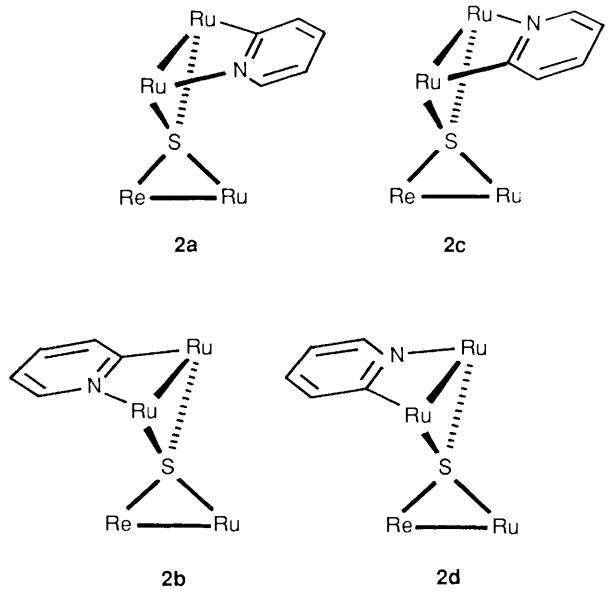


Fig. 3 Predicted isomers of $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ **2**. The crystal selected for X-ray structure determination (Fig. 2) contained a disordered arrangement of the enantiomers **2a** and **2c**. The other isomers **2b** and **2d** are believed to be present in the bulk sample of **2**

are in Table 2. There are two obvious potential sources of disorder: the orientation of the 2-pyridyl ligand and the arrangements of the $Ru(CO)_4$ and $Re(CO)_4$ groups. We refined the structure with the Ru(3) and Re atoms in the positions shown in Fig. 2 but also with these atoms reversed. Further we allowed the fractional populations of Ru and Re in the two sites to refine. The only satisfactory refinement was one with close to 1.00 fractional populations of Ru and Re atoms in the sites shown in Fig. 2. We did, however, establish that there is orientational disorder for the 2-pyridyl ligand so that the best refinement was with a fractional population of 0.36 for N(1) and C(1) as in Fig. 2 together with a 0.64 population of the reverse orientation of these atoms, labelled as C(1a) and N(1a) when reversed. Molecule **2** is chiral and the observed disorder corresponds to a disordered distribution of enantiomers through the crystal. Clearly these isomers cannot account for the overlapping ^1H NMR signals seen in Fig. 1.

Four isomers of the compound might be envisaged: **2a**–**2d** (Fig. 3). Isomers **2a** and **2c** are enantiomers and these are diastereomerically related to the other enantiomeric pair, **2b** and **2d**. The crystal examined contains a disordered arrangement of **2a** and **2c**, but to account for the ^1H NMR spectrum we

Table 1 Selected spectroscopic data

Compound	ν(CO)/cm^{-1}	^{1}H NMR *
1 $[Re_2(pyS)_2(CO)_6]$	2039s, 2023vs, 1947m, 1933s, 1917vs	7.97 (ddd, H^6), 7.32 (ddd, H^4), 7.03 (ddd, H^5), 6.50 (ddd, H^3)
2a, **2b** $[ReRu_3S(C_5H_4N)(CO)_{14}]$	2110w, 2079s, 2075m, 2064s, 2050vs, 2041w, 2033m, 2015m, 2004s, 2000m, 1993w, 1977m, 1971m, 1947m, 1942m	7.85 (ddd, H^6), 7.83 (ddd, H^6), 7.36 (ddd, H^4), 7.33 (ddd, H^4), 7.24 (ddd, H^3, H^3), 6.95 (ddd, H^5, H^5)
3a $[Re_2Ru_2S(C_5H_4N)(pyS)(CO)_{13}]$	2102m, 2075s, 2045vs, 2027s, 2010s, 2006s, 2002s, 1994s, 1986m, 1971m, 1954s, 1950s, 1930s, 1921s, 1915m	8.54 (ddd, H^{6y}), 7.91 (ddd, H^{4y}), 7.76 (ddd, H^{6x}), 7.55 (ddd, H^{5y}), 7.21 (ddd, H^{3y}), 7.11 (ddd, H^{4x}), 6.97 (ddd, H^{3x}), 6.72 (ddd, H^{5x})
3b $[Re_2Ru_2S(C_5H_4N)(pyS)(CO)_{13}]$	2102m, 2075s, 2045vs, 2027s, 2011s, 2007s, 1990s, 1982m, 1973w, 1953s, 1932s, 1921s, 1915w	8.47 (ddd, H^{6y}), 7.94 (ddd, H^{4y}), 7.58 (ddd, H^{6x}), 7.51 (ddd, H^{5y}), 7.23 (ddd, H^{3y}), 7.19 (ddd, H^{3x}), 7.06 (ddd, H^{4x}), 6.74 (ddd, H^{5x})
4a $[Re_3RuS(C_5H_4N)(pyS)_2(CO)_{11}]$	2146w, 2046vs, 2037w, 2030w, 2021s, 2001s, 1958s, 1918s, 1891m	8.90 (m, H^6), 8.24 (m, H^6), 7.96–7.86 (m, H^4, H^6), 7.66–7.56 (m, H^3, H^4), 7.52–7.44 (m, H^4, H^5), 7.26 (ddd, H^3), 7.18–7.12 (m, H^5, H^3), 7.06 (ddd, H^5)
4b $[Re_3RuS(C_5H_4N)(pyS)_2(CO)_{11}]$	2062m, 2030s, 2018(sh), 2015vs, 2020m, 1957m, 1934s, 1929m, 1913s, 1904m, 1890w	8.88 (m, H^6, H^6), 8.50 (ddd, H^6), 7.80 (ddd, H^3), 7.74–7.66 (m, H^3), 7.66–7.50 (m, H^4, H^4), 7.40 (ddd, H^4), 7.34 (ddd, H^4), 7.16 (ddd, H^3), 7.11 (ddd, H^5), 6.68 (ddd, H^5)

* The superscripts x and y refer to the 2-pyridyl and pyS groups respectively.

Table 2 Selected bond lengths (Å) and angles (°) for the compound $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ **2**

Ru(1)–Ru(2)	2.719(1)	Ru(1)–C(11)	1.94(1)
Re–Ru(3)	2.894(1)	Ru(1)–C(12)	1.88(1)
Ru(1)–S	2.393(3)	Ru(1)–C(13)	1.95(1)
Ru(2)–S	2.380(2)	Ru(2)–C(21)	1.91(1)
Ru(3)–S	2.417(3)	Ru(2)–C(22)	1.90(1)
Re–S	2.414(2)	Ru(2)–C(23)	1.96(1)
Ru(2)–C(1)	2.100(9)	Ru(3)–C(41)	1.96(1)
Ru(1)–N(1)	2.10(1)	Ru(3)–C(42)	1.96(1)
C(1)–N(1)	1.32(1)	Ru(3)–C(43)	1.95(1)
N(1)–C(2)	1.38(2)	Ru(3)–C(44)	1.88(1)
C(2)–C(3)	1.42(2)	Re–C(31)	2.00(1)
C(3)–C(4)	1.36(2)	Re–C(32)	1.96(1)
C(4)–C(5)	1.42(2)	Re–C(33)	1.92(1)
C(1)–C(5)	1.36(2)	Re–C(34)	1.91(1)
Ru(1)–S–Ru(2)	69.6(1)	S–Ru(1)–N(1)	83.1(3)
Ru(1)–S–Ru(3)	134.8(1)	S–Ru(2)–C(1)	82.5(2)
Ru(1)–S–Re	128.8(1)	Ru(2)–C(1)–N(1)	109.5(7)
Ru(2)–S–Ru(3)	127.5(1)	Ru(1)–N(1)–C(1)	109.4(7)
Ru(2)–S–Re	133.7(1)	Ru(1)–Ru(2)–C(1)	70.5(2)
Ru(3)–S–Re	73.6(1)	Ru(2)–Ru(1)–N(1)	70.6(3)
Ru(1)–Ru(2)–S	55.2(1)	C(1)–Ru(2)–C(21)	93.6(5)
Ru(2)–Ru(1)–S	55.1(1)	C(1)–Ru(2)–C(22)	90.2(5)
Re–Ru(3)–S	53.2(1)	N(1)–Ru(1)–C(11)	96.5(5)
Ru(3)–Re–S	53.3(1)	N(1)–Ru(1)–C(12)	91.0(5)

believe that the solution contains all four isomers in close to equal population. Crystallisation has led to the diastereomerically but not enantiomerically pure crystal that was chosen for study. We have no evidence that the separated isomers interconvert at room temperature. Isomers resulting from the orientation of 2-pyridyl ligands have been seen previously. We separated head-to-head from head-to-tail isomers of the 2-pyridyl complex $[Os_2(\mu\text{-}C_5H_4N)_2(CO)_6]$[3] and the X-ray structures of the corresponding compounds from 4-methylpyridine have been determined.[4] More recently isomeric clusters $[Ru_5H(C)(C_5H_4N)(CO)_{14}]$ containing different orientations of this ligand have been separated and structurally characterised.[5] Enantiomers of $[Os_3H(\mu\text{-}C_5H_4N)(CO)_{10}]$ differ only in the 2-pyridyl orientation and these have been resolved.[6] There is apparently a very large barrier to the reorientation of μ-2-pyridyl bridges in all observed cases.

$[Re_2Ru_2S(C_5H_4N)(pyS)(CO)_{13}]$ **3**. Before separation of the isomers, the ^{1}H NMR spectrum of this compound showed four sets of 2-pyridyl resonances in the ratio 2:3:2:3. TLC allowed the separation into isomers **3a** and **3b**, each of which contained two non-equivalent pyridyl rings. The separated isomers showed no tendency to interconvert at room temperature. We could not discriminate unequivocally between a μ-2-pyridyl and a pyS ligand from NMR spectra so that the proper characterisation of **3a** and **3b** depended upon X-ray structure determinations.

The molecular structures of compounds **3a** (molecule A of the two independent molecules A and B in the unit cell) and **3b**·0.5CH_2Cl_2 in their crystals are shown in Figs. 4 and 5 respectively. Bond lengths and angles are in Table 3. Superficially, *i.e.* ignoring the orientations of the 2-pyridyl bridges, these molecular structures appear to be completely identical and bond lengths and angles are not significantly different in the two compounds. The only difference between the isomers is the 2-pyridyl ligand orientations and to establish this we needed to examine carefully the refinement of the carbon and nitrogen atoms bonded to ruthenium. Reversing these atoms in each isomer gave unsatisfactory thermal parameters for them and attempts to refine the populations of nitrogen and carbon atoms at these sites gave populations in each isomer consistent with the arrangements in Figs. 4 and 5. This was not surprising since crystals were obtained from diastereomerically pure samples which do not interconvert and any disorder involving 2-pyridyl orientational disorder would have required the presence of the different diastereomers.

In considering the possible isomers of **3**, there are four possible sites of attachment of the N atom associated with the μ-pyS ligand if the $Re(CO)_3$ group is to remain *facial*. The N atom could be attached at either side of either Re atom. The two observed isomers correspond with two of the four possibilities but we have not found any evidence for the others.

Isomers **3a** and **3b** contain only one metal–metal bond each and are electron-precise. Their formation could be easily rationalised by the addition of a CO to **1** to give $[Re_2(pyS)_2(CO)_7]$ in which the pyS ligands are three and five-electron donors respectively. The three-electron donor could be bridged through the S atom and oxidative addition of this to an $Ru_2(CO)_6$ unit would give **3a** and **3b**. This may not be the actual mechanism since the formation of the other products requires the fragmentation of **1** so there is no reason to believe that this does not occur generally. The formal addition of one $Ru_2(CO)_6$ unit to a pyS ligand of $[Re_2(pyS)_2(CO)_7]$ to give **3a** and **3b** could be envisaged as being followed by a similar addition of another $Ru_2(CO)_6$ unit to the remaining pyS bridge to give the hypothetical compound $[Re_2Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{20}]$. We have no evidence for this as a product and the reactions of

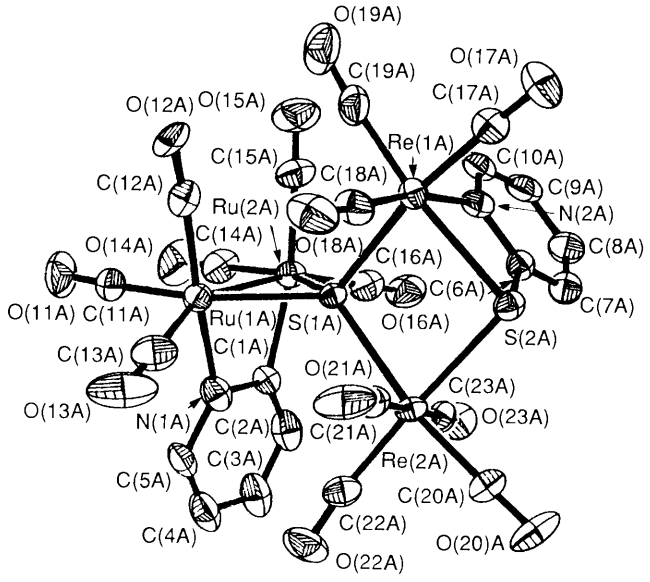


Fig. 4 Molecular structure of $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(pyS)(CO)_{13}]$ **3a** showing one of the two independent molecules in the unit cell

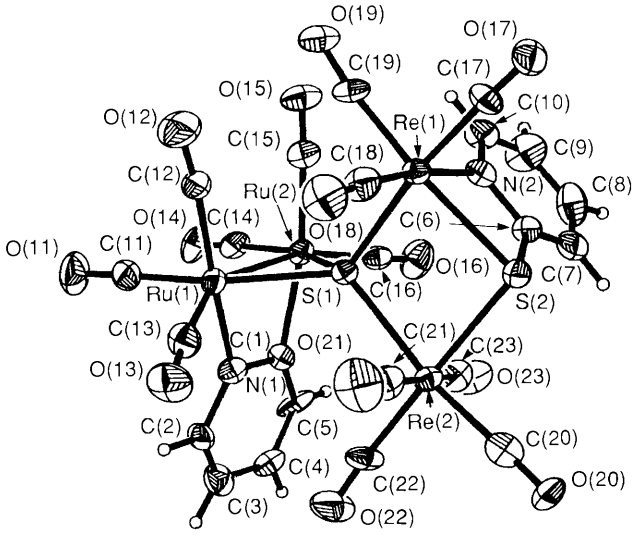


Fig. 5 Molecular structure of $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(pyS)(CO)_{13}]$ **3b**

3a or **3b** with $[Ru_3(CO)_{12}]$ gave no new products that we could identify.

$[Re_3Ru(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(pyS)_2(CO)_{11}]$ **4**. Two isomers of this product, **4a** and **4b**, were isolated and their X-ray structures have been reported in a communication.[1] The ^1H NMR spectrum of each (Table 1) shows three non-equivalent 2-pyridyl rings consistent with their X-ray structures. The co-ordination geometries of the μ_4-S atoms in **2**, **3a** and **3b** are only distorted from tetrahedral geometries as a result of short M–M distances. There are two small and four large M–S–M angles at each μ_4–S atom. On the other hand there is very severe distortion at the sulphido atoms in **4a** and **4b** as indicated in Scheme 1. The main difference between the isomers **4a** and **4b** is that **4a** has two doubly bridging five-electron donating pyS bridges of the sort found in the starting material $[Re_2(pyS)_2(CO)_6]$ whereas **4b** has one pyS bridge of this kind and a five-electron donating triply bridging pyS ligand. The electron counts are the same for the two molecules and the co-ordination spheres of the metal atoms are very similar in the two isomers. There is no evidence for the conversion of one isomer into the other.

There is the potential of adding a $Ru_2(CO)_6$ unit to the compounds **4a** and **4b** at each remaining pyS ligand to give more extended cages of the type $[Re_3Ru_3(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(pyS)(CO)_{18}]$ and $[Re_3Ru_5(\mu_4\text{-}S)_3(C_5H_4N)_3(CO)_{25}]$. We have no evidence for such species from the original synthesis but it is possible that they could be made by treating **4a** or **4b** with $[Ru_3(CO)_{12}]$. These compounds would have chains of three or four M_2 units linked by μ_4-S ligands. We are attempting to synthesise these compounds at present.

A very minor product from the reaction of **1** with $[Ru_3(CO)_{12}]$ is the compound $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$. This could only be characterised by obtaining a crystal suitable for determining an X-ray structure which will be reported later with some other related ruthenium compounds formed in other ways. This is the only evidence we have for the transfer of pyS ligands between Re and Ru atoms in this chemistry since all the

Table 3 Selected bond lengths (Å) and angles (°) for the isomers **3a** and **3b** of the compound $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$

	3a		**3b**	
	Molecule A	Molecule B		
Ru(1)–Ru(2)	2.706(1)	2.701(1)	2.715(2)	
Ru(1)–S(1)	2.412(2)	2.409(2)	2.417(4)	
Ru(2)–S(1)	2.416(2)	2.419(2)	2.412(5)	
Re(1)–S(1)	2.543(2)	2.553(2)	2.532(4)	
Re(2)–S(1)	2.541(2)	2.545(2)	2.527(4)	
Re(1)–S(2)	2.533(2)	2.547(2)	2.542(4)	
Re(2)–S(2)	2.514(2)	2.508(2)	2.512(4)	
Ru(1)–N(1)	2.114(8)	2.124(9)		
Ru(1)–C(1)			2.07(1)	
Ru(2)–N(1)			2.11(1)	
Ru(2)–C(1)	2.076(8)	2.102(9)		
Re(1)–N(2)	2.181(7)	2.170(6)	2.19(2)	
N(1)–C(1)	1.35(1)	1.33(1)	1.36(2)	
C(1)–C(2)	1.38(1)	1.39(1)	1.41(2)	
C(2)–C(3)	1.41(2)	1.43(2)	1.33(3)	
C(3)–C(4)	1.37(2)	1.37(2)	1.40(3)	
C(4)–C(5)	1.41(2)	1.39(2)	1.33(3)	
C(5)–N(1)	1.38(1)	1.39(1)	1.37(2)	
S(2)–C(6)	1.768(9)	1.762(8)	1.76(2)	
N(2)–C(6)	1.35(1)	1.35(1)	1.36(2)	
C(6)–C(7)	1.38(1)	1.39(1)	1.38(3)	
C(7)–C(8)	1.41(2)	1.39(1)	1.39(4)	
C(8)–C(9)	1.40(2)	1.38(1)	1.37(4)	
C(9)–C(10)	1.39(2)	1.40(1)	1.40(3)	
C(10)–N(2)	1.36(1)	1.35(1)	1.31(3)	
Averages				All molecules
M–CO	1.927	1.928	1.932	1.929
Re–CO	1.936	1.938	1.940	1.938
Ru–CO	1.915	1.916	1.922	1.918
M–CO *trans* to S	1.902	1.907	1.907	1.905
M–CO *trans* to CO	1.997	2.000	1.995	1.997
Ru(1)–S(1)–Ru(2)	68.18(6)	68.05(6)	68.4(1)	
Ru(1)–S(1)–Re(1)	124.91(8)	123.23(8)	124.8(2)	
Ru(1)–S(1)–Re(2)	122.37(8)	124.42(8)	122.8(2)	
Ru(2)–S(1)–Re(1)	120.99(8)	123.14(8)	121.2(2)	
Ru(2)–S(1)–Re(2)	125.63(8)	123.09(8)	124.4(2)	
Re(1)–S(1)–Re(2)	96.52(7)	96.56(6)	96.8(2)	
Re(1)–S(2)–Re(2)	97.46(7)	97.70(7)	96.9(2)	
Ru(1)–Ru(2)–S(1)	55.83(5)	55.79(5)	55.9(1)	
Ru(2)–Ru(1)–S(1)	55.99(5)	56.15(5)	55.7(1)	
S(1)–Re(1)–S(2)	79.62(7)	79.23(7)	80.1(1)	
S(1)–Re(2)–S(2)	80.00(7)	80.12(7)	80.8(1)	
S(1)–Ru(1)–N(1)	84.9(2)	84.7(2)		
S(1)–Ru(2)–C(1)	83.6(2)	84.0(2)		
S(1)–Ru(1)–C(1)			87.0(5)	
S(1)–Ru(2)–N(1)			84.6(4)	
S(1)–Re(1)–N(2)	83.3(2)	85.5(2)	84.9(4)	
S(2)–Re(1)–N(2)	65.5(2)	65.1(2)	65.9(4)	
Re(1)–S(2)–C(6)	80.3(3)	80.0(3)	79.5(5)	

Table 4 Crystal data and parameters related to the structure determination and refinement for compounds **2**, **3a** and **3b**

	2	**3a**	**3b**
Formula	$C_{19}H_4NO_{14}ReRu_3S$	$C_{23}H_8N_2O_{13}Re_2Ru_2S_2$	$C_{23.5}H_9ClN_2O_{13}Re_2Ru_2S_2$
M	991.709	1158.99	1201.46
Colour	Orange	Light yellow	Yellow
Size/mm	0.20 × 0.25 × 0.30	0.35 × 0.23 × 0.20	0.20 × 0.18 × 0.10
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a/Å	9.507(2)	15.623(3)	10.470(2)
b/Å	16.440(3)	18.738(2)	18.805(3)
c/Å	17.440(2)	10.635(2)	17.064(5)
α/°	90	84.23(1)	90
β/°	93.82(2)	89.07(1)	107.07(2)
γ/°	90	87.48(1)	90
U/Å^3	2720(1)	3094(1)	3211(1)
Z	4	4	4
D_c/g cm^{-3}	2.42	2.49	2.40
μ(Mo-Kα)/cm^{-1}	62.4	90.4	88.0
F(000)	1840	2136	2220
Diffractometer	Nicolet R3v/m	Enraf-Nonius CAD4	Nicolet R3v/m
No. orientation reflection, 2θ range/°	29, 13–27	23, 10–36	30, 6–24
T/°C	20	25	20
Unique data	5119	10 884	5620
Structure solution	Direct methods	Patterson	Direct methods
Reflections used in structure refinement	4123	8807	3742
No. parameters	322	793	410
R	0.0473	0.0295	0.0559
R'	0.0464	0.0310	0.0504
Weight w in weighting scheme	$1/[\sigma^2(F_o) + 0.000\,329F_o^2]$	$4F_o^2/[\sigma(F_o)^2]^2$	$1/[\sigma^2(F_o) + 0.0005F_o^2]$
Max. shift/e.s.d. in final least-squares refinement	0.001	0.05	0.011
Max. height in final Fourier/e Å^{-3}	2.1	1.2	1.1

For each determination: Mo-Kα radiation (λ = 0.710 73 Å), graphite monochromator, scan mode ω–2θ, rejection criterion $F_o \leqslant 3\sigma(F_o)$, 2$\theta$ collection range 5–50°, Lorentz-polarisation, empirical absorption corrections (ψ-scan method).

other products have one pyS (cleaved in some cases) per Re atom.

Experimental

The compound $[Re_2(pyS)_2(CO)_6]$ **1** was synthesised as we have described earlier[1] and $[Ru_3(CO)_{12}]$ was used as supplied by Aldrich Chemical Co.

Reaction of $[Re_2(pyS)_2(CO)_6]$ **1** *with* $[Ru_3(CO)_{12}]$.—A solution of $[Ru_3(CO)_{12}]$ (0.220 g, 0.313 mmol) and $[Re_2(pyS)_2(CO)_6]$ (0.238 g, 0.313 mmol) in *m*-xylene (50 cm^3) was heated under reflux under nitrogen for 30 min. The solvent was removed under reduced pressure and the deep yellow solid residue separated by TLC [SiO_2, light petroleum (b.p. < 40 °C)–dichloromethane (7:3 v/v)] to give several broad bands which were collected in three fractions corresponding to the major concentrations of material on the plates. These three bands yielded $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ (0.100 g, 32%) as yellow crystals from slow evaporation of a dichloromethane–hexane solution (Found: C, 23.55; H, 0.45; N, 1.3; S, 2.95. $C_{19}H_4NO_{14}ReRu_3S$ requires C, 23.0; H, 0.4; N, 1.4; S, 3.25%), $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$ (0.114 g, 31%) as lemon-yellow crystals from a dichloromethane–methanol mixture (Found: C, 23.65; H, 0.75; N, 2.15; S, 5.55. $C_{23}H_8N_2O_{13}Re_2Ru_2S_2$ requires C, 23.85; H, 0.7; N, 2.4; S, 5.55%) and $[Re_3Ru(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(pyS)_2(CO)_{11}]$ (0.070 g, 18%) as orange crystals. Yields varied with small changes of conditions, for example yields of 10, 36 and 11% were obtained for the three bands by only minor changes in conditions.

Separation of Isomers.—(*a*) $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$. All attempts to separate the isomers **2a** and **2b** by careful TLC were unsuccessful, although rechromatography separated a pure mixture of **2a** and **2b** from very small amounts of other materials. A trace quantity of a compound characterised as $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ was obtained and its characterisation and X-ray structure will be reported elsewhere.

(*b*) $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$. The band containing this material was rechromatographed by TLC [SiO_2, light petroleum (b.p. 30–40 °C)–dichloromethane–toluene (15:2:1 v/v/v)]. The slowly moving material separated into two bands giving pure compounds **3a** and **3b**. Crystals of each were obtained by adding a layer of methanol to a dichloromethane solution and allowing slow diffusion to occur.

(*c*) $[Re_3Ru(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(pyS)_2(CO)_{11}]$. This mixture was readily separated into two bands by TLC as in the original work-up. This gave isomer **4a** (50%) as orange crystals from a dichloromethane solution (Found: C, 23.2; H, 1.0; N, 2.95. $C_{26}H_{12}N_3O_{11}Re_3RuS_3$ requires C, 24.05; H, 1.0; N, 3.25%) and **4b** (50%) as orange crystals from a dichloromethane–methanol mixture.

Several other minor products were obtained from the reaction but none in sufficient quantity to allow characterisation.

X-Ray Structure Determination for Compounds **2**, **3a** *and* **3b**.—The crystal structures of compounds **4a** and **4b** were reported previously.[2] Crystals were obtained from a mixture of **2a** and **2b** by slow evaporation of a dichloromethane–hexane mixture. We selected a good crystal of **2** (0.20 × 0.25 × 0.30 mm) for structure determination but could not be sure which of the two components of the ^{1}H NMR spectrum should be assigned to this species. Crystals of the isomers **3a** and **3b** were obtained separately by methanol diffusion into a dichloromethane solution of each; respective crystal sizes 0.35 × 0.23 × 0.20 and 0.20 × 0.18 × 0.10 mm. Crystal data, details of the intensity data collections, structure solutions, and refinements are given in Table 4. Crystal and instrument stabilities were checked by using two or three reflections measured periodically throughout the data collections; minimal decay was observed but the full data sets were corrected for this.

Table 5 Fractional atomic coordinates ($\times 10^4$) for the compound $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	2267(1)	8548(1)	4808(1)	O(22)	5310(12)	4838(6)	3359(7)
Ru(1)	3286(1)	7148(1)	2819(1)	C(22)	4592(14)	5307(7)	3611(8)
Ru(2)	3406(1)	6099(1)	4027(1)	O(23)	5825(11)	6908(6)	4992(5)
Ru(3)	−212(1)	7612(1)	4319(1)	C(23)	4967(13)	6610(7)	4639(7)
S	2180(3)	7362(1)	3989(1)	O(31)	1985(11)	9642(5)	3350(5)
C(1)	1753(10)	5760(5)	3232(5)	C(31)	2037(13)	9248(6)	3872(7)
N(1A)	1753(10)	5760(5)	3232(5)	O(32)	2863(14)	7501(6)	6277(6)
C(1A)	1711(11)	6262(5)	2640(5)	C(32)	2615(15)	7877(7)	5729(7)
N(1)	1711(11)	6262(5)	2640(5)	O(33)	5331(11)	9114(7)	4944(7)
C(2)	717(15)	6171(8)	2029(7)	C(33)	4191(14)	8911(7)	4916(8)
C(3)	−293(16)	5532(8)	2035(8)	O(34)	1223(11)	9962(5)	5757(5)
C(4)	−259(15)	5030(8)	2656(7)	C(34)	1596(14)	9426(7)	5401(6)
C(5)	805(14)	5142(7)	3260(7)	O(41)	−860(13)	8724(7)	2924(6)
O(11)	2048(15)	8361(6)	1627(6)	C(41)	−573(13)	8341(7)	3438(8)
C(11)	2501(16)	7919(8)	2066(7)	O(42)	277(13)	6478(6)	5716(6)
O(12)	5283(12)	6209(7)	1876(6)	C(42)	121(14)	6891(9)	5209(8)
C(12)	4502(14)	6560(8)	2213(7)	O(43)	−2315(11)	6420(6)	3480(7)
O(13)	5790(10)	8232(6)	3363(6)	C(43)	−1489(13)	6831(8)	3794(8)
C(13)	4856(14)	7851(7)	3167(7)	O(44)	−1889(12)	8622(7)	5386(6)
O(21)	2300(14)	5010(7)	5272(6)	C(44)	−1327(14)	8241(8)	4946(8)
C(21)	2732(15)	5451(7)	4831(7)				

Table 6 Fractional atomic coordinates for the compound $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$ **3a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1A)	0.226 59(2)	0.000 03(2)	0.428 06(3)	Re(1B)	0.743 79(2)	0.494 59(2)	0.507 83(3)
Re(2A)	0.409 97(2)	0.106 39(2)	0.279 85(3)	Re(2B)	0.614 67(2)	0.346 43(2)	0.394 19(3)
Ru(1A)	0.222 00(5)	0.049 13(4)	0.015 41(7)	Ru(1B)	0.763 47(5)	0.471 33(4)	0.103 87(7)
Ru(2A)	0.152 08(4)	0.161 77(4)	0.127 28(7)	Ru(2B)	0.869 56(4)	0.370 34(4)	0.225 26(7)
S(1A)	0.258 8(1)	0.077 2(1)	0.223 7(2)	S(1B)	0.741 4(1)	0.420 9(1)	0.318 7(2)
S(2A)	0.351 4(1)	0.068 1(1)	0.496 6(2)	S(2B)	0.657 2(1)	0.389 2(1)	0.599 3(2)
O(11A)	0.114 5(6)	0.067 5(5)	−0.221 4(7)	O(11B)	0.867 8(6)	0.489 1(5)	−0.139 0(7)
O(12A)	0.112 2(7)	−0.075 4(5)	0.110(1)	O(12B)	0.838 2(6)	0.608 5(4)	0.178 8(8)
O(13A)	0.366 5(7)	−0.043 2(6)	−0.088(1)	O(13B)	0.590 4(6)	0.541 9(6)	0.020(1)
O(14A)	0.040 9(6)	0.215 0(5)	−0.095 2(8)	O(14B)	0.998 4(5)	0.363 2(5)	0.011 3(8)
O(15A)	−0.001 8(5)	0.087 6(6)	0.252(1)	O(15B)	0.986 3(5)	0.470 0(4)	0.343 7(8)
O(16A)	0.135 5(6)	0.296 5(4)	0.269 1(8)	O(16B)	0.936 2(5)	0.237 0(4)	0.391 4(9)
O(17A)	0.214 0(6)	−0.079 7(4)	0.692 9(7)	O(17B)	0.709 1(6)	0.571 3(4)	0.745 2(7)
O(18A)	0.309 2(6)	−0.131 8(4)	0.316 6(8)	O(18B)	0.620 0(5)	0.606 1(4)	0.368 9(8)
O(19A)	0.053 0(5)	−0.059 4(5)	0.382 4(9)	O(19B)	0.887 8(4)	0.597 3(3)	0.449 7(8)
O(20A)	0.582 2(5)	0.128 5(5)	0.399 5(9)	O(20B)	0.478 2(5)	0.258 1(4)	0.538 6(7)
O(21A)	0.471 7(5)	−0.051 5(4)	0.246 4(9)	O(21B)	0.492 7(5)	0.481 8(5)	0.344 3(9)
O(22A)	0.501 0(5)	0.150 5(5)	0.027 5(8)	O(22B)	0.535 1(5)	0.297 9(5)	0.157 3(7)
O(23A)	0.349 6(5)	0.266 6(4)	0.292 7(8)	O(23B)	0.744 9(4)	0.214 1(3)	0.423 6(7)
N(1A)	0.285 7(5)	0.143 4(5)	−0.048 6(7)	N(1B)	0.732 0(5)	0.368 3(5)	0.056 2(7)
N(2A)	0.190 8(5)	0.103 2(4)	0.496 5(7)	N(2B)	0.819 1(4)	0.404 5(3)	0.599 0(6)
C(1A)	0.254 5(6)	0.198 1(4)	0.015 4(8)	C(1B)	0.782 6(5)	0.318 8(4)	0.119 9(8)
C(2A)	0.286 5(8)	0.266 0(6)	−0.008(1)	C(2B)	0.776 9(8)	0.246 8(6)	0.103(1)
C(3A)	0.350 6(9)	0.277 3(7)	−0.101(1)	C(3B)	0.715 2(8)	0.229 3(7)	0.014(1)
C(4A)	0.381 5(7)	0.222 2(7)	−0.167(1)	C(4B)	0.664 3(8)	0.280 9(7)	−0.051(1)
C(5A)	0.348 0(7)	0.153 5(6)	−0.142 0(9)	C(5B)	0.673 6(7)	0.352 9(7)	−0.033 9(9)
C(6A)	0.266 4(5)	0.130 6(5)	0.522 3(8)	C(6B)	0.761 7(5)	0.354 1(4)	0.633 2(7)
C(7A)	0.270 8(7)	0.196 7(5)	0.567 9(9)	C(7B)	0.786 8(6)	0.286 3(5)	0.689 6(8)
C(8A)	0.194 1(8)	0.236 2(6)	0.588(1)	C(8B)	0.873 1(7)	0.272 9(5)	0.716 6(9)
C(9A)	0.116 7(7)	0.206 6(6)	0.560(1)	C(9B)	0.931 8(6)	0.325 2(5)	0.686 9(9)
C(10A)	0.115 4(6)	0.139 9(6)	0.513 1(9)	C(10B)	0.902 6(5)	0.390 7(5)	0.624 6(8)
C(11A)	0.156 4(7)	0.060 9(6)	−0.133 7(9)	C(11B)	0.827 8(7)	0.483 1(6)	−0.049 4(9)
C(12A)	0.153 2(7)	−0.028 6(6)	0.080(1)	C(12B)	0.809 8(6)	0.557 3(5)	0.155 9(9)
C(13A)	0.314 2(8)	−0.011 6(6)	−0.043(1)	C(13B)	0.654 2(7)	0.515 5(6)	0.051(1)
C(14A)	0.081 4(7)	0.196 4(6)	−0.010(1)	C(14B)	0.950 0(7)	0.365 1(6)	0.091(1)
C(15A)	0.056 0(7)	0.114 4(6)	0.209(1)	C(15B)	0.941 8(5)	0.432 8(5)	0.302 4(9)
C(16A)	0.143 9(7)	0.245 5(6)	0.221(1)	C(16B)	0.908 9(6)	0.285 8(5)	0.332(1)
C(17A)	0.217 2(7)	−0.049 9(5)	0.592(1)	C(17B)	0.724 9(6)	0.542 3(5)	0.656 9(9)
C(18A)	0.280 9(6)	−0.082 7(5)	0.361(1)	C(18B)	0.665 3(6)	0.563 4(5)	0.421 6(9)
C(19A)	0.118 6(7)	−0.035 5(6)	0.395(1)	C(19B)	0.833 6(6)	0.557 6(4)	0.465 9(9)
C(20A)	0.518 2(6)	0.120 8(5)	0.353(1)	C(20B)	0.528 0(6)	0.292 0(5)	0.484 4(9)
C(21A)	0.447 3(6)	0.004 1(5)	0.262 7(9)	C(21B)	0.536 9(5)	0.433 4(6)	0.366(1)
C(22A)	0.462 5(6)	0.133 4(5)	0.119(1)	C(22B)	0.569 3(6)	0.316 4(6)	0.241(1)
C(23A)	0.371 1(6)	0.208 5(5)	0.289 2(9)	C(23B)	0.696 5(6)	0.260 4(5)	0.413 8(9)

Table 7 Fractional atomic coordinates ($\times 10^4$) for the compound $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]\cdot 0.5CH_2Cl_2$ **3b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	−5462(1)	−352(1)	−7853(1)	O(13)	−4212(15)	−3061(8)	−6245(9)
Re(2)	−2977(1)	−602(1)	−5757(1)	C(14)	−606(20)	−1792(11)	−8350(10)
Ru(1)	−3111(1)	−2320(1)	−7479(1)	O(14)	57(14)	−2160(7)	−8599(8)
Ru(2)	−1676(1)	−1243(1)	−7863(1)	C(15)	−2843(18)	−1012(10)	−8928(11)
S(1)	−3390(4)	−1080(2)	−7195(2)	O(15)	−3453(15)	−910(9)	−9577(9)
N(1)	−561(13)	−1683(7)	−6733(8)	C(16)	−652(18)	−357(11)	−7738(10)
C(1)	−1255(16)	−2260(9)	−6612(10)	O(16)	−81(17)	132(9)	−7692(10)
C(2)	−569(18)	−2715(9)	−5971(11)	C(17)	−6978(18)	276(10)	−8235(12)
C(3)	674(21)	−2593(11)	−5506(13)	O(17)	−7827(13)	654(7)	−8444(9)
C(4)	1358(20)	−1988(11)	−5639(12)	C(18)	−6646(19)	−1050(11)	−7602(12)
C(5)	725(16)	−1568(13)	−6256(11)	O(18)	−7250(15)	−1485(8)	−7420(9)
S(2)	−4518(4)	349(2)	−6536(3)	C(19)	−5955(16)	−736(10)	−8928(11)
N(2)	−4055(14)	484(8)	−7939(9)	O(19)	−6309(13)	−907(8)	−9598(8)
C(6)	−3700(16)	767(9)	−7173(10)	C(20)	−2878(16)	−134(11)	−4751(13)
C(7)	−2792(19)	1316(11)	−6992(13)	O(20)	−2835(14)	121(7)	−4142(8)
C(8)	−2293(22)	1592(11)	−7602(17)	C(21)	−4515(20)	−1184(11)	−5645(11)
C(9)	−2669(24)	1272(14)	−8358(16)	O(21)	−5353(17)	−1530(9)	−5595(11)
C(10)	−3613(20)	725(10)	−8529(12)	C(22)	−1848(21)	−1323(12)	−5122(11)
C(11)	−2399(23)	−3094(11)	−7931(12)	O(22)	−1144(20)	−1705(10)	−4713(10)
O(11)	−1987(18)	−3578(8)	−8172(10)	C(23)	−1384(16)	−97(10)	−5889(11)
C(12)	−4739(20)	−2329(10)	−8410(12)	O(23)	−472(13)	173(8)	−5930(8)
O(12)	−5649(17)	−2399(9)	−8942(10)	Cl	−321(9)	4331(4)	4600(5)
C(13)	−3837(18)	−2804(10)	−6733(13)	C(30)	−806(44)	4841(21)	5337(21)

Lorentz and polarisation corrections and absorption corrections based on scans were made in each case.

The structure of compound **2** was solved by direct methods[7] and the non-H atoms were refined anisotropically except for those of the 2-pyridyl ring. The model that refined best involved 322 parameters and has disorder between the C(1)N(1) orientation for the 2-pyridyl bridge shown in Fig. 2 with a population of 0.36 and the reverse C(1a)N(1a) orientation with a population of 0.64.

The structure of compound **3a** was solved by Patterson heavy-atom methods[8] which revealed the eight metal atoms of the two independent molecules A and B in the unit cell. All the non-H atoms were refined anisotropically employing a model with 793 parameters. Anomalous dispersion effects were included in F_c and $\Delta f'$ and $\Delta f''$ and scattering factors were obtained from standard sources.[9]

The structure of compound **3b**·$0.5CH_2Cl_2$ was solved by direct methods[7] and all non-H atoms, except those of the CH_2Cl_2 molecules, were refined anisotropically and H atoms for the 2-pyridyl ligands were included in the model in idealised positions with C–H distances fixed at 0.96 Å and U_{iso} at 0.08 Å^2. The CH_2Cl_2 molecule refined best with site occupancy of 0.5 which resulted in the stoichiometry **3b**·$0.5CH_2Cl_2$. In both **3a** and **3b**·$0.5CH_2Cl_2$ the orientations of the 2-pyridyl rings were established by monitoring the thermal parameters of the Ru-bonded carbon and nitrogen atoms when these were interchanged.

All calculations were performed on Microvax II computers using SDP/VAX[10] for **3a** and SHELXTL PLUS for **2** and **3b**.[7] Final atomic coordinates are given in Tables 5–7.

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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