

Rhodium Complexes of the Binucleating Ligands Pyridine-2-thiolate and Benzothiazole-2-thiolate. Crystal Structures of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ and $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{tfbb})\}_2]\cdot\text{Me}_2\text{CO}$ (tfbb = tetrafluorobenzobarrelene)[†]

Miguel A. Ciriano, Fernando Viguri, Jesus J. Perez-Torrente, Fernando J. Lahoz, and Luis A. Oro *

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain

Antonio Tiripicchio * and Marisa Tiripicchio-Camellini

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffattometrica del C.N.R., Vialle dell Scienze, 43100 Parma, Italy

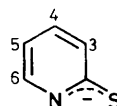
The binuclear complexes $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{diolefin})\}_2]$ [$\text{SC}_5\text{H}_4\text{N}$ = pyridine-2-thiolate, diolefin = cyclo-octa-1,5-diene (cod) (**1**), norborna-2,5-diene (nbd) (**2**), or tetrafluorobenzobarrelene (tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene) (tfbb) (**3**)] are prepared by reaction of $\text{LiSC}_5\text{H}_4\text{N}$ with the appropriate complex $[\{\text{Rh}(\mu\text{-Cl})(\text{diolefin})\}_2]$ and show fluxional behaviour in solution associated with the bridging ligands. The related compounds $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{diolefin})\}_2]$ [$\text{C}_7\text{H}_4\text{NS}_2$ = benzothiazole-2-thiolate, diolefin = cod (**5**), nbd (**6**), or tfbb (**7**)] are prepared by a similar route. Carbonylation reactions of (**1**) and (**5**) give the tetracarbonyl complexes $[\{\text{Rh}(\mu\text{-L})(\text{CO})_2\}_2]$ [L = $\text{SC}_5\text{H}_4\text{N}$ (**4**) or $\text{C}_7\text{H}_4\text{NS}_2$ (**8**) respectively]. Triphenylphosphine replaces carbon monoxide stepwise in compound (**4**) yielding the mono- (**10**) and di-substituted (**11**) complexes whilst the disubstituted complex $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})(\text{PPh}_3)\}_2]$ (**9**) is obtained from compound (**8**). Methyl iodide adds to complexes (**4**) and (**10**) affording respectively the diacetyl complexes $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}(\text{CO})\}_2]$ (**12**) and $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}_2(\text{CO})(\text{PPh}_3)\}_2]$ (**13**). The molecular structures of (**3**) and (**4**) have been determined by X-ray analyses. Crystals of (**3**) are triclinic, space group $P\bar{1}$, with $a = 13.772(7)$, $b = 14.184(8)$, $c = 9.738(4)$ Å, $\alpha = 108.99(2)$, $\beta = 75.65(3)$, $\gamma = 106.04(3)^\circ$, and $Z = 2$. Crystals of (**4**) are orthorhombic, space group $P2_12_12$ (no. 18), with $a = 14.637(6)$, $b = 6.734(4)$, $c = 8.852(5)$ Å, and $Z = 2$. Both complexes are binuclear with two pyridine-2-thiolate groups acting as bridges. In (**4**) both ligands, having a head-to-tail disposition, bridge the metal centres through the N and S atoms whereas in (**3**) one of the pyridine-2-thiolate ligands bridges through the S atom only. The square-planar environments of the Rh atoms are completed by two tfbb ligands [(**3**)] or four CO groups [(**4**)], with metal-metal separations of 3.028(2) and 2.941(2) Å respectively.

Complexes with bidentate ligands having soft and hard donor atoms have received considerable attention in stoichiometric and catalytic reactions, particularly those in which an arm of the chelate is a tertiary phosphine and the other a readily replaceable site.¹ In addition, designed binucleating ligands offer the possibility to form homo- or hetero-binuclear complexes² in which both metals are electronically different; 2-(diphenylphosphino)pyridine is one of the most studied examples.³

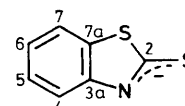
We have reported that ligands having an N-C-X (X = N or O) structural disposition of the donor atoms similar to 2-(diphenylphosphino)pyridine act as binucleating species and hold the metal atoms in close proximity in the complexes $[\text{Rh}_2(\mu\text{-napy})_2(\text{nbd})_2][\text{ClO}_4]_2$,^{4a} $[\{\text{Rh}(\mu\text{-L})(\text{nbd})\}_2]$,^{4b} $[\text{Rh}_3(\mu\text{-Onapy})_2(\text{CO})_2(\text{cod})_2][\text{ClO}_4]_4$,^{4c} and $[\text{Rh}_4(\mu\text{-Opy})_4(\mu\text{-CO})_2(\text{CO})_4]$ ^{4d} (nbd = norborna-2,5-diene, napy = 1,8-naphthyridine, HL = 1H-pyrrolo[2,3-b]pyridine, Onapy = 1,8-naph-

thyridin-2-onate, cod = cyclo-octa-1,5-diene, and Opy = 2-pyridonate) with the neutral complexes being the most resistant to bridge splitting reactions. Following these studies we began to explore in 1984 the preparation and reactivity of complexes⁵ with the ligand pyridine-2-thiolate ($\text{SC}_5\text{H}_4\text{N}^-$), which has a similar N-C-S structural group to that mentioned above and should combine the properties of pyrazolate⁶ and thiolate⁷ complexes that have given rise to an extensive chemistry.

Two papers dealing with the co-ordination chemistry of heterocyclic thione donors⁸ and of pyridine-2-thiolate⁹ have appeared recently. Indeed $[\text{Pt}_2(\mu\text{-SC}_5\text{H}_4\text{N})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{-NH}_2)_2]\text{Cl}_2\cdot 3\text{H}_2\text{O}$,¹⁰ $[\text{Rh}_2(\mu\text{-SC}_5\text{H}_4\text{N})_2\text{Cl}_2(\text{SC}_5\text{H}_4\text{NH})_2(\text{CO})_2]\cdot 2\text{CHCl}_3$,¹¹ and $[\text{Pd}_2(\mu\text{-SC}_5\text{H}_4\text{N})_4]$ ¹² are the only well



Pyridine-2-thiolate



Benzothiazole-2-thiolate

[†] Di- μ -(pyridine-2-thiolato-S,N)-bis[dicarbonylrhodium(I)] and μ -(pyridine-2-thiolato-S)- μ -(pyridine-2-thiolato-S,N)-bis[tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene- $\text{C}^{2,3,5,6}(\text{Rh})$]rhodium(I)]-acetone (1/1) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii-xx.

established binuclear complexes with pyridine-2-thiolate bridges; other platinum(III) binuclear complexes with the

Table 1. Analytical and physical data for the binuclear complexes

Compound	Colour	Yield (%)	Analysis (%) ^a			<i>M</i> ^b
			C	H	N	
(1) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{cod})\}_2$]	Yellow	95	48.9 (48.60)	5.1 (5.00)	4.1 (4.35)	629 (644)
(2) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{nbd})\}_2$]	Red	40	47.1 (47.20)	4.1 (3.95)	4.6 (4.60)	638 (610)
(3) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{tfbb})\}_2$] $\cdot\text{Me}_2\text{CO}$	Orange	80	47.4 (47.45)	2.8 (3.00)	2.8 (3.00)	901 (936)
(4) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2$]	Green-purple	73	31.0 (31.25)	1.6 (1.50)	5.1 (5.20)	<i>c</i>
(5) [$\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{cod})\}_2$]	Yellow	90	47.5 (47.65)	4.3 (4.25)	3.7 (3.70)	732 (754)
(6) [$\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{nbd})\}_2$]	Red	90	47.1 (46.55)	3.9 (3.35)	3.9 (3.85)	780 (722)
(7) [$\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{tfbb})\}_2$]	Orange	95	46.8 (46.05)	2.8 (2.05)	2.7 (2.80)	1 021 (990)
(8) [$\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})_2\}_2$]	Dark red	90	33.0 (33.25)	1.3 (1.25)	4.6 (4.30)	671 (650)
(9) [$\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})(\text{PPh}_3)\}_2$]	Orange	87	55.9 (55.80)	3.5 (3.40)	2.6 (2.50)	1 054 (1 118)
(10) [$\text{Rh}_2(\mu\text{-SC}_5\text{H}_4\text{N})_2(\text{CO})_3(\text{PPh}_3)$]	Orange	70	48.2 (48.20)	2.9 (3.00)	3.6 (3.65)	<i>c</i>
(11) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)\}_2$]	Orange	72	57.3 (57.25)	4.3 (3.80)	2.5 (2.80)	<i>c</i>
(12) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\}_2(\text{CO})_2$]	Brown	84	23.5 (23.35)	1.5 (1.70)	3.5 (3.40)	823 (822)
(13) [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\}_2(\text{CO})(\text{PPh}_3)$] $\cdot 0.5\text{C}_7\text{H}_8$	Orange	60	40.0 (39.65)	3.1 (3.00)	2.7 (2.50)	900 (1 102)

^a Calculated values are given in parentheses. ^b In CHCl_3 . ^c Decomposes in solution.**Table 2.** Hydrogen-1 and carbon-13 n.m.r. data for the binuclear complexes *

Compound	¹ H (δ)	¹³ C (δ)
(1)	($[\text{C}_6\text{H}_6]$ acetone, 20 °C) 7.75 (d, 2 H, H ⁶), 7.24 (m, 2 H, H ⁴ or H ⁵), 6.95 (m, 2 H, H ³), 6.71 (m, 2 H, H ⁴ or H ⁵), 4.31 (m, 8 H, =CH, cod), 2.43 (m, 8 H, CH ₂ , cod), 1.84 (m, 8 H, CH ₂ , cod)	(CDCl ₃ , 20 °C) 170.7 (CS), 149.0, 134.7, 128.8, 118.1 (C ³ , C ⁴ , C ⁵ , C ⁶), 80.3 [d, <i>J</i> (Rh–C) 12, =CH, cod], 31.2 (CH ₂ , cod)
(2)	(CDCl ₃ , 20 °C) 8.26 (d, 2 H, H ⁶), 7.07 (m, 4 H, H ⁴ , H ³), 6.67 (m, 2 H, H ⁵), 4.09 (m, 8 H, =CH, nbd), 3.85 (m, 4 H, CH, nbd), 1.34 (m, 4 H, CH ₂ , nbd)	
(3)	(CDCl ₃ , 20 °C) 8.25 (d, 2 H, H ⁶), 7.19 (m, 4 H, H ⁴ , H ³), 6.80 (m, 2 H, H ⁵), 5.65 (m, 4 H, CH, tfbb), 3.96 (m, 8 H, =CH, tfbb), 2.16 (s, 3 H, acetone)	
(4)	(CDCl ₃ , 20 °C) 8.20 (d, 2 H, H ⁶), 7.25 (m, 2 H, H ⁴ or H ³), 7.07 (m, 2 H, H ³ or H ⁴), 6.67 (m, 2 H, H ⁵)	(CDCl ₃ , –50 °C) 187.5 [d, <i>J</i> (Rh–C) 67, CO], 183.4 [d, <i>J</i> (Rh–C) 68, CO], 173.0 (CS), 152.5, 135.1, 129.2, 118.6 (C ³ , C ⁴ , C ⁵ , C ⁶)
(5)	(CDCl ₃ , –60 °C) 8.73 (d, 2 H, H ⁴), 7.40 (dd of d, 2 H, H ⁵ or H ⁶), 7.13 (m, 4 H, H ⁷ and H ⁶ or H ⁵), 5.02 (m, 2 H, =CH, cod), 4.40 (m, 2 H, =CH, cod), 4.31 (m, 2 H, =CH, cod), 3.82 (m, 2 H, =CH, cod), 2.8–2.3 (m, 8 H, CH ₂ , cod), 2.1–1.7 (m, 8 H, CH ₂ , cod)	(CDCl ₃ , –50 °C) 180.0 (CS), 151.3, 134.8 (C ^{3a} , C ^{7a}), 125.9, 123.8, 120.2, 119.8 (C ⁴ , C ⁵ , C ⁶ , C ⁷), 81.8 [d, <i>J</i> (Rh–C) 13, =CH, cod], 80.6 [d, 2 C, <i>J</i> (Rh–C) 13, =CH, cod], 78.6 [d, <i>J</i> (Rh–C) 12, =CH, cod], 31.7, 31.5, 31.3, 30.6 (CH ₂ , cod)
(6)	(CDCl ₃ , 20 °C) 8.71 (d, 2 H, H ⁴), 7.40 (dd of d, 2 H, H ⁵ or H ⁶), 7.32 (ad, 2 H, H ⁷), 7.12 (dd of d, 2 H, H ⁵ or H ⁶), 4.34 (m, 8 H, =CH, nbd), 4.03 (m, 4 H, CH, nbd), 1.44 (s, 4 H, CH ₂ , nbd)	
(7)	(CDCl ₃ , 20 °C) 8.36 (m, 2 H, H ⁴), 7.43 (d, 2 H, H ⁷), 7.40 (dd of d, 2 H, H ⁵ or H ⁶), 7.19 (dd of d, 2 H, H ⁵ or H ⁶), 5.7 (m, 4 H, CH, tfbb), 4.1 (m, 8 H, =CH, tfbb)	
(8)	(CDCl ₃ , 20 °C) 8.33 (d of m, 2 H, H ⁴), 7.39 (dd of d, 2 H, H ⁵ or H ⁶), 7.34 (d of m, 2 H, H ⁷), 7.22 (dd of d, 2 H, H ⁵ or H ⁶)	(CDCl ₃ , 20 °C) 185.7 [d, <i>J</i> (Rh–C) 66.1, CO], 182.8 (CS), 181.7 [d, <i>J</i> (Rh–C) 69, CO], 151.1, 133.5 (C ^{3a} , C ^{7a}), 125.9, 124.4, 120.4, 119.3 (C ⁴ , C ⁵ , C ⁶ , C ⁷)
(9)	(CDCl ₃ , 20 °C) 8.2 (d, 2 H, H ⁴), 7.7 (m, 12 H, PPh ₃), 7.2 (m, 20 H, PPh ₃ and C ₇ H ₄ NS ₂), 6.8 (m, 4 H, C ₇ H ₄ NS ₂)	
(12)	(CDCl ₃ , 20 °C) 8.53 (d, 2 H, H ⁶), 7.51 (t of d, 2 H, H ³), 7.03 (d, 2 H, H ³), 6.99 (m, 2 H, H ⁴), 3.06 (s, 6 H, Me)	(CDCl ₃ , 20 °C) 214.4 [d, <i>J</i> (Rh–C) 21, COMe], 183.8 [d, <i>J</i> (Rh–C) 65.0, CO], 163.1 (CS), 148.4, 139.0, 132.2, 122.5 (C ³ , C ⁴ , C ⁵ , C ⁶), 46.4 (CH ₃ CO)
(13)	(CDCl ₃ , 20 °C) 8.49 (d, 1 H, H ⁶), 7.8–7.0 (m, 20 H, toluene, SC ₅ H ₄ N and PPh ₃), 6.80 (m, 1 H), 6.61 (m, 2 H), 6.40 (m, 1 H), 3.30 (s, 3 H, Me), 3.08 (s, 3 H, Me), 2.36 (s, 1.5 H, toluene)	(CDCl ₃ , 20 °C) 227.7 [dd, ¹ <i>J</i> (Rh–C) 25, ² <i>J</i> (P–C) 5, COMe], 219.2 [d, <i>J</i> (Rh–C) 21, COMe], 184.4 [d, <i>J</i> (Rh–C) 64, CO], 169.1, 164.0 (CS), 148.5, 147.6, 137.9, 136.3, 131.5, 130.5, 121.7, 120.9 (SC ₅ H ₄ N), 134.7 (d, PPh ₃), 131.0 (d, C _{ipso}), 130.4 (s, PPh ₃), 127.8 (d, PPh ₃), 129.0, 128.2, 125.3 (toluene), 46.9, 44.2 (CH ₃ CO), 21.4 (Me, toluene)

* Chemical shifts (δ) in p.p.m., coupling constants in Hz, d = doublet, t = triplet, m = multiplet, a = apparent. For proton and carbon numbering see p. 25.

related ligand pyrimidine-2-thiolate have been described recently¹³ although the anionic ligand acts generally as a chelate in spite of its small bite.^{8,14}

Herein we report in full the preparation, structure, and some reactions of binuclear complexes with bridging pyridine-2-thiolate (SC₅H₄N) and the related benzothiazole-2-thiolate (C₇H₄NS₂). Part of this work has been the subject of preliminary communications.^{15,16}

Results and Discussion

The slightly acidic proton of pyridine-2-thiol (p*K*_a 9.97)⁸ can be conveniently abstracted by *n*-butyl-lithium in anhydrous diethyl ether to give a white suspension of lithium pyridine-2-thiolate. These suspensions react readily with the complexes [$\{\text{Rh}(\mu\text{-Cl})(\text{diolfin})\}_2$] at room temperature affording the orange or red compounds [$\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{diolfin})\}_2$] [diolfin = cod (1), nbd (2), or tetrafluorobenzobarrelene (tetra-

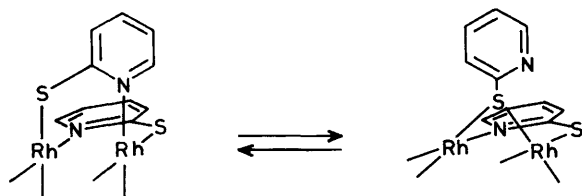
fluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tfbb) (3)] and lithium chloride. Complexes (1) and (3) are isolated as air-stable microcrystalline solids in high yield by crystallization of the reaction mixture in acetone. Complex (3) crystallizes with one molecule of acetone (Table 1) whilst complex (2) gives green cationic rhodium species in acetone solutions containing lithium chloride and is isolated in moderate yield. Complex (2) can be alternatively prepared by reaction of $[\text{Rh}(\text{acac})(\text{nbd})]$ (acac = acetylacetonate) with pyridine-2-thiol in dichloromethane.

The presence of the deprotonated ligand in complexes (1)—(3) is inferred from the absence of both $\nu(\text{NH})$ in the i.r. spectra and a low-field resonance in the ^1H n.m.r. spectra.* Molecular weight measurements in chloroform confirm their binuclear nature.

Carbon monoxide easily replaces the diolefin in complexes (1)—(3) to give the dichroic purple-green complex $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ (4). The pattern and relative intensity of the more intense $\nu(\text{CO})$ bands of (4) (at 2 080vs, 2 055s, 2 015vs, 1 980w cm^{-1}) resembles closely those of the compounds $[\{\text{Rh}(\text{Onapy})(\text{CO})_2\}_2]$ ¹⁷ and $[\{\text{Rh}(\mu\text{-RNNR})(\text{CO})_2\}_2]$ ($\text{R} = p\text{-tolyl}$),¹⁸ which have an approximately face-to-face disposition of the *cis*-dicarbonylrhodium environments. On the contrary, the thiolato or chloro-bridged¹⁹ complexes $[\{\text{Rh}(\mu\text{-X})(\text{CO})_2\}_2]$ ($\text{X} = \text{Cl}$ or SR , $\text{R} = \text{alkyl}$ or aryl), in which the hinge angle is very open, show a different pattern of $\nu(\text{CO})$ bands suggesting that both pyridine-2-thiolato ligands in (4) do not bridge in a thiolato mode. Shoulders on the strong bands are observed in the solution i.r. spectrum (at 2 050 and 2 000 cm^{-1}). Frequently, a higher number of $\nu(\text{CO})$ bands than expected has been reported¹⁹ for carbonylthiolato complexes and explained in terms of the fluxionality generally shown by this type of compound.

N.m.r. studies on (4) are useful to analyze the more complex results of compounds (1)—(3). Its ^1H n.m.r. spectrum does not change in the range -50 to 20°C . Nevertheless, the fluxional behaviour of (4) is detected by its $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum which, in the stopped-exchange region at -50°C (see Table 2), shows two doublet resonances arising from two sets of equivalent carbonyl groups in accordance with both the structure found in the solid-state by *X*-ray diffraction studies (see below) and the head-to-head isomer. On warming, the four carbonyl groups became equivalent giving rise to a doublet resonance at δ 185 p.p.m. [$^1J(\text{Rh}-\text{C})$ 67 Hz]. Such a change is due to a process which causes the carbonyl scrambling without dissociation of the carbonyl groups since the coupling constant is retained above coalescence.

Fluxionality of complexes containing sulphur ligands is a well documented phenomenon associated with low-energy inversion barriers around the co-ordinated sulphur.²⁰ Nevertheless, dissociation of the $\text{N}-\text{Rh}$ bond assisted by formation of a thiolate bridge would give rise to the interconversion of the co-ordination modes of the pyridine-2-thiolato ligands, represented below, and would also produce carbonyl scrambling. This is



also a plausible explanation for the variable-temperature ^1H n.m.r. spectrum of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{tfbb})\}_2]$ (3) (see Figure 1) which, in the stopped-exchange region, shows one resonance for each proton of the molecule in accordance with a rigid structure lacking an element of symmetry; the spectroscopic data are in

accordance with the structure found in the solid state by *X*-ray diffraction methods (see below). Complexes (1) and (2) show time-averaged resonances in their ^1H n.m.r. spectra at room temperature but, on cooling, several rigid species are detected in solution† accounting for the easy interconversion of binuclear structures bridged by pyridine-2-thiolato ligands.

In order to avoid the interconversion of isomers and to provide structurally similar systems, but having modified electronic environments, the complexes with the bulky benzothiazole-2-thiolato ligand $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{diolefin})\}_2]$ [diolefin = cod (5), nbd (6), or tfbb (7)] were prepared. The synthetic methods are similar to those described above for (1)—(3) although deprotonation of 2-mercaptobenzothiazole ($\text{p}K_a$ 6.9)⁸ can be alternatively accomplished by KOH in methanol to give (5)—(7) in high yield. Complexes (5)—(7) are air-stable crystalline solids whose molecular weights in solution correspond to binuclear species and resonances due to NH or SH are not detected in their ^1H n.m.r. spectra as should be expected for the anionic ligand.

^1H N.m.r. spectra of (5)—(7) (Table 2) show time-averaged signals at around room temperature. Interestingly, all of them display one apparent doublet due to the H^4 proton of the aromatic ring shifted to low field. The shifting should arise from proximity effects associated with the binucleating co-ordination mode through the nitrogen and sulphur of benzothiazole-2-thiolate.

Rotation of the diolefin in complex (5) freezes on cooling yielding one single rigid species in solution whose ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra are consistent with both the rigid head-to-tail and head-to-head structures. On the other hand, complexes (6) and (7) exist as several rigid structures at low temperature.

Carbon monoxide reacts with complex (5) readily at atmospheric pressure giving the tetracarbonyl complex $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})_2\}_2]$ (8) [$\nu(\text{CO})$: 2 085vs, 2 065s, 2 023vs, and 1 990w cm^{-1} in CH_2Cl_2]. Complex (8) is apparently rigid up to room temperature, in contrast with (4), and exists in solution as the head-to-tail and head-to-head isomers in relative proportions 15:1 (determined by ^1H n.m.r.).

Triphenylphosphine easily replaces two carbonyl groups in complex (8) to give the orange crystalline compound $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})(\text{PPh}_3)\}_2]$ (9) [$\nu(\text{CO})$: 1 990s and 1 981s cm^{-1} in hexane]. Its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum [δ 42.2 p.p.m., d, $^1J(\text{Rh}-\text{P})$ 162 Hz, CDCl_3 , 20°C] reveals that one rigid single isomer having equivalent phosphine ligands is formed in solution. The phosphine ligands should be *trans* to the sulphur atoms since the coupling constant is similar to that found for the thiolate-bridged rhodium phosphine complexes.²²

Substitution of carbonyl groups by PPh_3 in complex (4) can be carried out stepwise. Addition of PPh_3 to (4) in a 1:1 molar ratio gives a red-orange air-sensitive solution of $[\text{Rh}_2(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_3(\text{PPh}_3)]$ (10) [$\nu(\text{CO})$: 2 060s, 1 995vs, and 1 980vs cm^{-1} in CH_2Cl_2]. Its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum displays a broad doublet [δ 40.4 p.p.m., $^1J(\text{Rh}-\text{P})$ 154 Hz, $^{2J}\text{H}_6$ acetone, 20°C] which becomes sharp at low temperature [δ 40.4 p.p.m., $^1J(\text{Rh}-\text{P})$ 162 Hz, -60°C]. On the other hand, complex (10) rearranges slowly in solution giving the tetracarbonyl complex (4) and the disubstitution product $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)\}_2]$ (11), which are detected by i.r. spectroscopy and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. respectively. In fact, crystals of complex (4) suitable for *X*-ray diffraction methods were grown from a solution of (10) in acetone cooled in a freezer for three weeks. A further addition of one mole of PPh_3 to (10) produces evolution

* A weak and a broad $\nu(\text{NH})$ band at 3 150 and 2 850 cm^{-1} respectively and a resonance at δ 14.1 p.p.m. are observed in the i.r. and ^1H n.m.r. spectra of pyridine-2-thiol under the same conditions.

† Complex (1) has the head-to-tail structure in the solid state.²¹

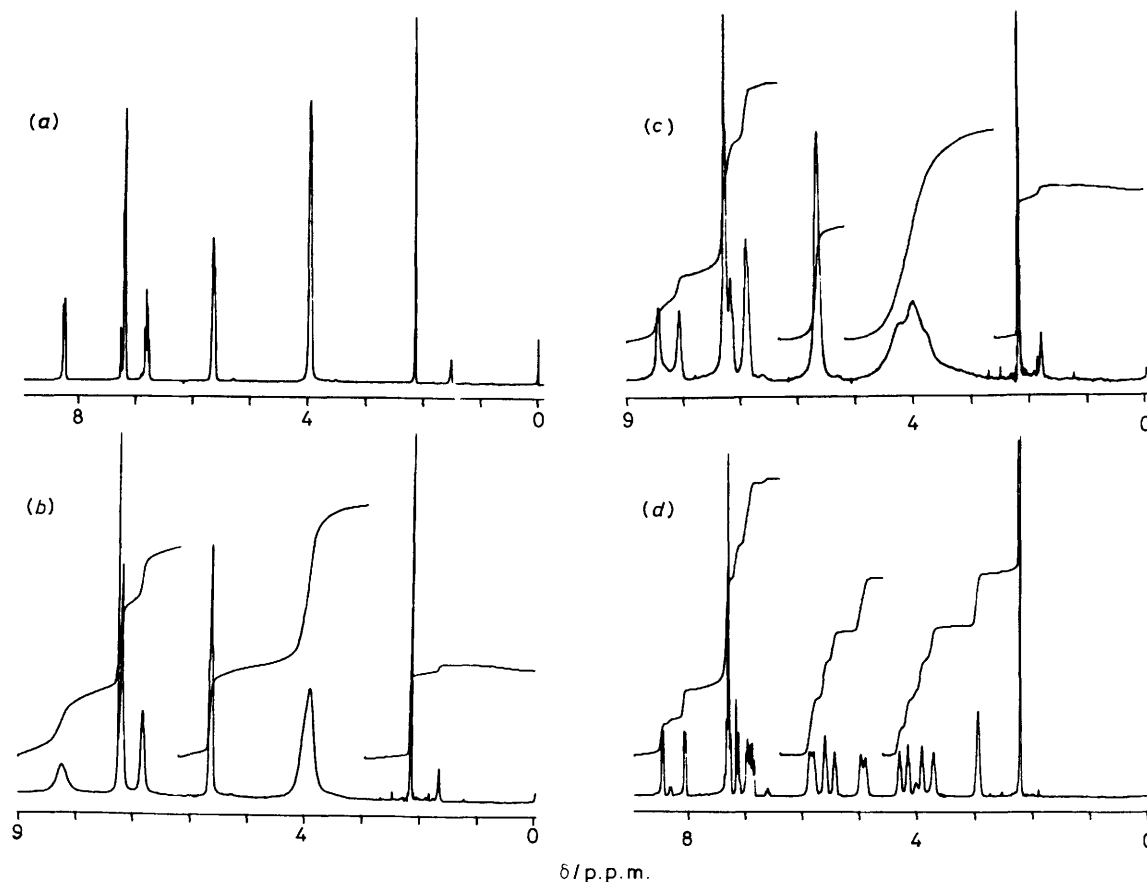


Figure 1. ^1H N.m.r. spectrum of complex (3) at: (a) 50, (b) 5, (c) -15 , and (d) -60°C in CDCl_3

of carbon monoxide and formation of the disubstituted complex (11) [$\nu(\text{CO})$: 1990(sh), 1985s, and 1970m cm^{-1} in cyclohexane] which is isolated as an air-sensitive crystalline solid. Complex (11) is fluxional and exhibits in its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum a sharp doublet at low temperature [δ 42.1 p.p.m., $^1J(\text{Rh-P})$ 162 Hz, $[\text{C}_6\text{H}_6]$ acetone, -60°C]. The spectroscopic properties of the rigid structure of (11) closely resemble those of the related complex (9) and both should have the same structure.

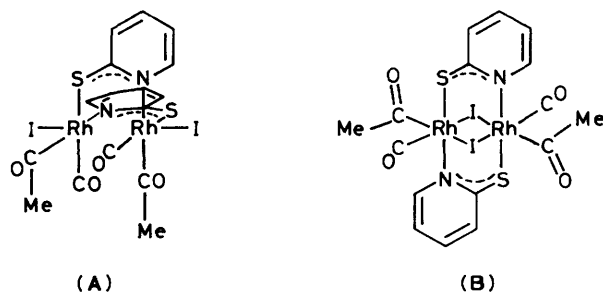
Methyl iodide reacts readily at room temperature with complex (4) giving a brown solution from which the binuclear diacyl complex $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}(\text{CO})\}_2]$ (12) is isolated in high yield as a microcrystalline solid. The i.r. spectrum of (12) shows one sharp terminal $\nu(\text{CO})$ band at 2075 cm^{-1} for both carbonyl groups and a broad band for the acetyl groups at 1710 cm^{-1} . Confirmation of the presence of equivalent acetyl groups in (12) comes from its ^1H , $^{13}\text{C}\{-^1\text{H}\}$, and ^{13}C attached proton test n.m.r. spectra (see Table 2). Structures (A) and (B) below fit with the spectroscopic data although (A), in

which the rhodium atoms are five-co-ordinated, is in accordance with the well known large *trans* influence of the acyl group.²³

Interestingly, one single and symmetrical isomer is formed mainly in this reaction, which should take place stepwise, *i.e.* the addition of methyl iodide takes place on one of the metal centres followed by *cis* insertion of the carbonyl group into the Rh-Me bond. This process then occurs on the other metal centre. Attempts to isolate the monoacetyl complex by reacting equimolecular amounts of complex (4) and methyl iodide were not successful since the reaction is very slow under these conditions, giving a mixture of compounds as observed by ^1H n.m.r.

Similarly, complex (10) reacts with an excess of methyl iodide in toluene to give a separable mixture of complexes (12) and $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}_2(\text{CO})(\text{PPh}_3)\}_2]$ (13). The latter is a minor product from this reaction in accordance with the above observed decomposition of the starting material. Complex (13) is isolated as a single isomer as shown by its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum (δ 33.8 p.p.m., d, $^1J(\text{Rh-P})$ 132 Hz, CDCl_3) which displays $\nu(\text{CO})$ bands at 2060 cm^{-1} for the terminal carbonyl group, and 1710 and 1675 cm^{-1} for the acetyl groups. Each rhodium atom bears an acetyl group. Thus, the carbon bonded to rhodium of one of the acetyl groups gives rise to a doublet of doublets by coupling with the rhodium and phosphorus nuclei of the triphenylphosphine in *cis* position; the other acetyl ligand does not show coupling with the phosphorus nucleus and hence is bonded to the rhodium atom that bears the terminal carbonyl group. Obviously, the molecule is asymmetric and several structures can be proposed to account for the spectroscopic data.

Addition of methyl iodide to the related binuclear compound $[\{\text{Rh}(\mu\text{-SBu}^t)(\text{CO})(\text{PMe}_2\text{Ph})\}_2]$ takes place only on one



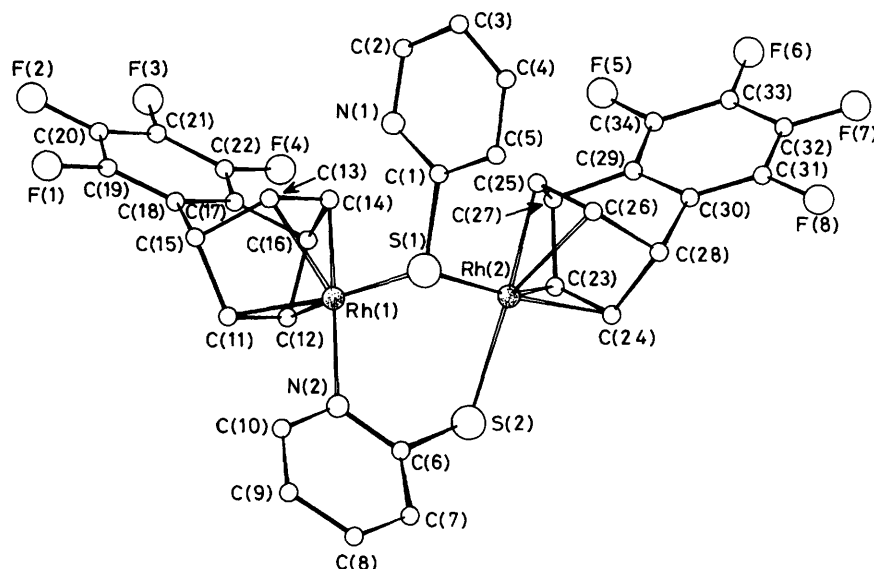


Figure 2. View of the molecular structure of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{tfbb})\}_2]$ (3) with the atomic numbering scheme

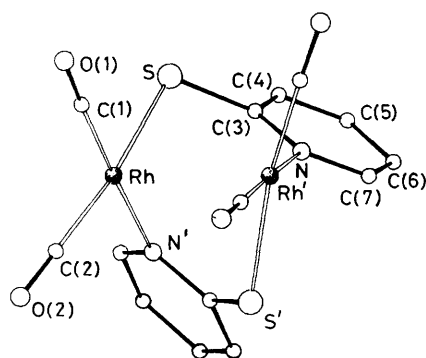


Figure 3. View of the molecular structure of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ (4) with the atomic numbering scheme

Table 3. Selected bond distances (Å) and angles (°) for $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{tfbb})\}_2]$ (3) with e.s.d.s in parentheses*

Rh(1)···Rh(2)	3.028(2)	Rh(2)–S(1)	2.339(2)
Rh(1)–S(1)	2.349(2)	Rh(2)–S(2)	2.320(2)
Rh(1)–N(2)	2.112(6)	Rh(2)–C(23)	2.126(6)
Rh(1)–C(11)	2.122(8)	Rh(2)–C(24)	2.122(6)
Rh(1)–C(12)	2.128(8)	Rh(2)–C(25)	2.122(6)
Rh(1)–C(13)	2.082(8)	Rh(2)–C(26)	2.123(6)
Rh(1)–C(14)	2.117(8)		
S(1)–C(1)	1.782(6)	S(2)–C(6)	1.742(6)
C(1)–N(1)	1.323(11)	C(6)–N(2)	1.341(11)
N(1)–C(2)	1.332(9)	N(2)–C(10)	1.342(8)
C(2)–C(3)	1.372(13)	C(9)–C(10)	1.345(12)
C(3)–C(4)	1.369(15)	C(8)–C(9)	1.349(16)
C(4)–C(5)	1.363(10)	C(7)–C(8)	1.359(11)
C(1)–C(5)	1.384(11)	C(6)–C(7)	1.373(12)
C(11)–C(12)	1.366(9)	C(23)–C(24)	1.379(12)
C(13)–C(14)	1.381(8)	C(25)–C(26)	1.390(12)
C(11)–C(15)	1.488(11)	C(23)–C(27)	1.532(10)
C(13)–C(15)	1.539(10)	C(25)–C(27)	1.525(8)
C(12)–C(16)	1.514(9)	C(24)–C(28)	1.528(9)
C(14)–C(16)	1.523(9)	C(26)–C(28)	1.519(9)
S(1)–Rh(1)–N(2)	81.5(2)	S(1)–Rh(2)–S(2)	94.8(1)
S(1)–Rh(1)–M(1)	176.5(3)	S(1)–Rh(2)–M(3)	170.5(2)
S(1)–Rh(1)–M(2)	106.5(3)	S(1)–Rh(2)–M(4)	100.5(2)
N(2)–Rh(1)–M(1)	102.0(3)	S(2)–Rh(2)–M(3)	94.5(2)
N(2)–Rh(1)–M(2)	163.8(3)	S(2)–Rh(2)–M(4)	164.5(2)
M(1)–Rh(1)–M(2)	70.3(3)	M(3)–Rh(2)–M(4)	70.3(3)
Rh(1)–S(1)–Rh(2)	80.5(1)	Rh(1)–N(2)–C(6)	119.1(5)
Rh(1)–S(1)–C(1)	117.0(2)	Rh(2)–S(2)–C(6)	113.1(3)
Rh(2)–S(1)–C(1)	105.5(2)	S(2)–C(6)–N(2)	116.9(5)
S(1)–C(1)–N(1)	117.6(5)	N(2)–C(6)–C(7)	123.5(6)
S(1)–C(1)–C(5)	119.4(5)	S(2)–C(6)–C(7)	119.6(7)
N(1)–C(1)–C(5)	123.0(6)	C(6)–N(2)–C(10)	118.3(6)
C(1)–N(1)–C(2)	116.7(7)	N(2)–C(10)–C(9)	123.7(8)
N(1)–C(2)–C(3)	124.3(7)	C(8)–C(9)–C(10)	118.1(8)
C(2)–C(3)–C(4)	117.9(8)	C(7)–C(8)–C(9)	119.6(8)
C(3)–C(4)–C(5)	119.2(8)	C(6)–C(7)–C(8)	120.6(8)
C(1)–C(5)–C(4)	118.9(7)		

* M(1), M(2), M(3), and M(4) are the midpoints of the olefinic bonds C(11)–C(12), C(13)–C(14), C(23)–C(24), and C(25)–C(26) respectively.

of the metal centres giving²⁴ the complex $[(\text{PhMe}_2\text{P})(\text{MeCO})\text{IrRh}(\mu\text{-SBu}^t)_2\text{Rh}(\text{CO})(\text{PMe}_2\text{Ph})]$; a further addition of methyl iodide on the second metal centre occurs only under forcing conditions. The smooth double oxidative-addition of MeI to complex (4) shows the enhanced reactivity of the complexes with pyridine-2-thiolate *versus* the analogous alkanethiolate complexes towards this type of reaction.

In contrast, the analogous iridium complex $[\{\text{Ir}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ undergoes a transannular oxidative-addition reaction with methyl iodide to give the di-iridium compound $[\text{Ir}_2(\mu\text{-SC}_5\text{H}_4\text{N})_2(\text{Me})\text{I}(\text{CO})_4]$ ²⁵ highlighting the difference in reactivity of similar systems of rhodium and iridium notably by the higher tendency of iridium to form metal–metal bonds.

X-Ray Crystal Structures of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{tfbb})\}_2]\cdot\text{Me}_2\text{CO}$ (3) and $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ (4).—Both structures consist of binuclear Rh molecules with two bridging pyridine-2-thiolate ligands and ancillary ligands. The structures are depicted in Figures 2 and 3; selected bond distances and angles are given in Tables 3 and 4.

In (4), having a crystallographically imposed C_2 symmetry, both pyridine-2-thiolate ligands bridge the metal centres through the S and N atoms, whereas in (3) one of the ligands symmetrically bridges the Rh atoms through the S atom only. The Rh–S and Rh–N bond distances involving the *N,S*-bridging ligands are 2.320(2) and 2.112(6) Å in (3) and 2.364(2) and

Table 4. Selected bond distances (Å) and angles (°) for complex $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ (**4**) with e.s.d.s in parentheses*

Rh...Rh'	2.941(2)	S-C(3)	1.738(8)
Rh-S	2.364(2)	N-C(3)	1.350(10)
Rh-N'	2.118(6)	N-C(7)	1.352(11)
Rh-C(1)	1.859(8)	C(3)-C(4)	1.408(11)
Rh-C(2)	1.871(9)	C(4)-C(5)	1.365(13)
C(1)-O(1)	1.125(10)	C(5)-C(6)	1.375(14)
C(2)-O(2)	1.128(11)	C(6)-C(7)	1.365(12)
S-Rh-N'	89.9(2)	Rh-S-C(3)	105.6(2)
S-Rh-C(1)	87.4(2)	Rh'-N-C(3)	120.9(5)
S-Rh-C(2)	171.3(3)	S-C(3)-N	120.8(5)
N'-Rh-C(1)	177.3(3)	S-C(3)-C(4)	120.0(6)
N'-Rh-C(2)	90.0(3)	N-C(3)-C(4)	119.1(7)
C(1)-Rh-C(2)	92.7(4)	C(3)-C(4)-C(5)	120.0(8)
Rh-C(1)-O(1)	178.2(7)	C(4)-C(5)-C(6)	120.3(8)
Rh-C(2)-O(2)	178.1(8)	C(5)-C(6)-C(7)	118.0(8)
		N-C(7)-C(6)	123.0(8)

* Primed atoms are related to the unprimed ones by a two-fold axis (symmetry equivalent position $1 - x, -y, z$).

2.118(6) Å in (**4**). The slightly distorted square-planar co-ordination around the Rh atoms, which in (**3**) involves two S atoms around Rh(2) and one S and one N atoms around Rh(1) is completed in (**3**) by two tfbb molecules interacting in a conventional η^2 -fashion through the olefinic bonds [Rh(1)-M(1) 2.012(8), Rh(1)-M(2) 1.983(8), Rh(2)-M(3) 2.009(6), and Rh(2)-M(4) 2.006(6) Å; M(1), M(2), M(3), and M(4) are the midpoints of the C(11)-C(12), C(13)-C(14), C(23)-C(24), and C(25)-C(26) bonds] and in (**4**) by terminal carbonyl groups.

Noteworthy is the very different reciprocal disposition of the Rh co-ordination planes in (**3**) and (**4**), as the dihedral angle between them is 81.2(1)° in the former and 18.9(2)° in the latter. In both complexes the pyridine-2-thiolate ligands bridge two *cis* positions of the square-planar environments of the Rh atoms. The rhodium-rhodium separations, 3.028(2) in (**3**) and 2.941(2) Å in (**4**), are indicative of the presence of a weak metal-metal interaction.

All the pyridine-2-thiolate ligands are perfectly planar. The S...N bite of these ligands does not seem to be influenced by their different co-ordination behaviour [2.636(6) and 2.666(7) Å in the *N,S*- and *S*-bridging ligands respectively of (**3**) and 2.692(7) Å in the *N,S*-bridging ligand in (**4**)].

The Rh-S, Rh-N, and C-S distances in (**3**) and (**4**) are comparable with those involving the pyridine-2-thiolate ligands found in $[\text{Rh}_2(\mu\text{-SC}_5\text{H}_4\text{N})_2\text{Cl}_2(\text{SC}_5\text{H}_4\text{NH})_2(\text{CO})_2]$ ¹¹ [2.339(2), 2.123(4), and 1.732(6) Å respectively], even if the Rh atoms are in different oxidation states and environments. It is noteworthy that in this complex both pyridine-2-thiolate and pyridine-2-thiol ligands are present; the protonated ligands co-ordinate to Rh atoms through the S atom only with a longer Rh-S bond distance [2.427(3) Å].

Experimental

All reactions were carried out under a nitrogen atmosphere at room temperature using Schlenk techniques. Solvents were dried and distilled under nitrogen immediately prior to use. The starting materials $[\{\text{Rh}(\mu\text{-Cl})(\text{diolfin})\}_2]$ (diolfin = cod,²⁶ nbd,²⁷ or tfbb²⁸) were prepared according to reported methods.

¹H, ¹³C, and ³¹P n.m.r. spectra were recorded on a Varian XL-200 spectrometer operating at 200.057, 50.309, and 80.984 MHz respectively; chemical shifts are reported relative to tetramethylsilane and phosphoric acid as external references. I.r. spectra (4 000–200 cm⁻¹) were recorded on a Perkin-Elmer

783 spectrometer using Nujol mulls between polyethylene sheets or in solution in NaCl cells. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Molecular weights were determined with a Knauer osmometer using chloroform solutions.

Preparation of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{diolfin})\}_2]$ (1**)–(**3**).**—A white suspension of lithium pyridine-2-thiolate (0.2 mmol) was prepared by addition of *n*-butyl-lithium (1.43 cm³, 1.40 mol dm⁻³ in hexane, 0.2 mmol) to a suspension of pyridine-2-thiol (22 mg, 0.2 mmol) in diethyl ether (10 cm³). The appropriate solid compound $[\{\text{Rh}(\mu\text{-Cl})(\text{diolfin})\}_2]$ (0.1 mmol) was added to the above suspension and reacted for 30 min. The solvents were pumped off and the residue [**1**] or [**3**] washed with acetone–water (2:1) (5 cm³), filtered off, and washed with acetone–water (2:1). To isolate complex (**2**), the residue was extracted with hexane (30 cm³). Evaporation of the extract to 3 cm³ and cooling overnight in a freezer rendered (**2**) as a microcrystalline solid.

Preparation of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2\}_2]$ (4**).**—Dry carbon monoxide was bubbled through a solution of complex (**1**) in dichloromethane (3 cm³) for 5 min. Hexane (10 cm³) was then added and the bubbling continued for a further 15 min to give a microcrystalline solid which was washed with cold hexane (3 cm³). Complex (**4**) is air-sensitive in solution.

Preparation of $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{diolfin})\}_2]$ (5**)–(**7**).**—To a solution of lithium benzothiazole-2-thiolate (0.2 mmol) in diethyl ether (10 cm³) (prepared as described above for lithium pyridine-2-thiolate but starting from 2-mercaptobenzothiazole) the appropriate solid compound $[\{\text{Rh}(\mu\text{-Cl})(\text{diolfin})\}_2]$ (0.1 mmol) was added. The mixture was reacted for 15 min and the solvents then pumped off. The residue was washed with acetone–water (4:1) (5 cm³) to give the compounds as microcrystalline solids which were separated by filtration and washed with acetone–water (4:1).

Preparation of $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})_2\}_2]$ (8**).**—Solid 2-mercaptobenzothiazole (17 mg, 0.1 mmol) was added to a suspension of $[\text{Rh}(\text{acac})(\text{CO})_2]$ (26 mg, 0.1 mmol) in methanol (10 cm³) to give a red solution after 15 min. Evaporation of the solution under vacuum to 2 cm³ rendered the complex as a microcrystalline solid; the crystallization was completed by addition of water (0.5 cm³) and then the solid was filtered off and washed with methanol–water (5:1).

Preparation of $[\{\text{Rh}(\mu\text{-C}_7\text{H}_4\text{NS}_2)(\text{CO})(\text{PPh}_3)\}_2]$ (9**).**—Carbon monoxide was bubbled through a solution of complex (**5**) (72 mg, 0.2 mmol) in dichloromethane (10 cm³) for 15 min. Solid triphenylphosphine (52 mg, 0.2 mmol) was then added to give an orange solution with evolution of carbon monoxide. Evaporation of this solution to 1 cm³ and addition of hexane (5 cm³) gave the complex as a crystalline solid which was filtered off, washed with cold hexane (5 cm³), and vacuum dried.

Preparation of $[\text{Rh}_2(\mu\text{-SC}_5\text{H}_4\text{N})_2(\text{CO})_3(\text{PPh}_3)]$ (10**) and $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)\}_2]$ (**11**).**—Carbon monoxide was bubbled through a solution of complex (**1**) (64 mg, 0.1 mmol) in acetone (3 cm³) for 10 min. Addition of a solution of triphenylphosphine (26 mg, 0.1 mmol) in acetone (3 cm³) at –20 °C under an atmosphere of carbon monoxide gave a red-orange solution from which orange air-sensitive crystals of compound (**10**) were obtained by cooling to –78 °C. The solid was washed with cold diethyl ether (2 cm³) and dried under vacuum. Complex (**11**) was obtained in a similar way by adding the stoichiometric amount of triphenylphosphine and working at room temperature.

Table 5. Final atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex (3)

Atom	x	y	z	Atom	x	y	z
Rh(1)	2 787(1)	4 537(1)	6 665(1)	C(14)	2 364(5)	3 064(5)	6 996(7)
Rh(2)	1 385(1)	3 846(1)	4 409(1)	C(15)	3 649(5)	4 067(5)	8 536(8)
S(1)	1 230(1)	4 962(1)	6 787(2)	C(16)	3 339(5)	2 712(5)	6 101(8)
S(2)	2 911(1)	4 827(1)	3 510(2)	C(17)	3 790(5)	2 351(5)	7 066(8)
F(1)	4 504(4)	3 545(4)	10 644(5)	C(18)	3 940(5)	3 089(6)	8 379(8)
F(2)	4 854(5)	1 683(4)	10 101(7)	C(19)	4 325(6)	2 856(6)	9 355(8)
F(3)	4 528(5)	260(4)	7 558(7)	C(20)	4 509(7)	1 905(6)	9 100(10)
F(4)	3 859(4)	682(3)	5 534(5)	C(21)	4 349(7)	1 185(6)	7 811(10)
F(5)	262(4)	-534(3)	2 779(5)	C(22)	3 995(6)	1 411(5)	6 794(8)
F(6)	-1 188(4)	-1 567(3)	1 122(5)	C(23)	1 584(6)	2 468(5)	2 754(7)
F(7)	-2 181(3)	-556(3)	214(5)	C(24)	1 077(5)	2 981(4)	2 272(7)
F(8)	-1 724(3)	1 506(3)	941(5)	C(25)	336(5)	2 526(4)	4 855(7)
N(1)	239(4)	3 764(5)	8 538(6)	C(26)	-163(5)	3 050(5)	4 362(7)
N(2)	3 386(4)	5 931(4)	6 106(6)	C(27)	849(5)	1 744(5)	3 615(7)
C(1)	114(5)	4 357(4)	7 819(6)	C(28)	-90(5)	2 713(4)	2 698(7)
C(2)	-601(6)	3 339(6)	9 333(8)	C(29)	57(5)	1 037(5)	2 686(7)
C(3)	-1 570(6)	3 462(6)	9 420(8)	C(30)	-463(5)	1 557(5)	2 210(7)
C(4)	-1 680(6)	4 074(6)	8 658(9)	C(31)	-1 201(5)	1 031(5)	1 415(7)
C(5)	-833(5)	4 529(5)	7 848(8)	C(32)	-1 454(5)	-23(5)	1 032(7)
C(6)	3 300(5)	5 980(5)	4 790(8)	C(33)	-964(5)	-544(5)	1 507(7)
C(7)	3 530(6)	6 912(6)	4 508(11)	C(34)	-205(5)	-1(5)	2 336(8)
C(8)	3 858(7)	7 782(6)	5 541(11)	O(1)*	3 396(12)	8 376(12)	2 470(16)
C(9)	3 976(7)	7 726(6)	6 845(10)	O(2)*	1 942(13)	10 350(13)	4 721(20)
C(10)	3 739(5)	6 801(5)	7 086(9)	C(351)*	2 870(14)	8 986(14)	2 852(20)
C(11)	4 149(5)	4 452(5)	7 224(8)	C(352)*	2 328(18)	9 759(19)	3 682(28)
C(12)	3 996(5)	3 729(5)	5 924(8)	C(36)	3 013(10)	9 926(10)	2 255(15)
C(13)	2 530(5)	3 803(5)	8 299(7)	C(37)	2 161(11)	8 866(11)	3 989(16)

* O(1) and C(351) have site occupancy factor 0.6, O(2) and C(352) 0.4.

Table 6. Final atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex (4)

Atom	x	y	z
Rh	10 328(1)	2 064(1)	1 767(1)
S	8 867(1)	2 346(3)	2 885(2)
O(1)	9 422(5)	2 970(13)	-1 172(7)
O(2)	12 217(4)	2 400(12)	482(8)
N	9 103(4)	-1 385(10)	3 906(7)
C(1)	9 775(5)	2 648(13)	-70(9)
C(2)	11 503(6)	2 250(16)	947(9)
C(3)	8 814(4)	470(11)	4 231(8)
C(4)	8 429(6)	855(14)	5 659(10)
C(5)	8 356(6)	-637(15)	6 696(9)
C(6)	8 668(6)	-2 511(14)	6 360(10)
C(7)	9 030(5)	-2 829(13)	4 960(9)

Reactions with Methyl Iodide.—Preparation of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}(\text{CO})\}_2]$ (12). Carbon monoxide was bubbled through a suspension of complex (1) (100 mg, 0.16 mmol) in toluene (5 cm³) for 10 min to give a solution of complex (4) which was treated with methyl iodide (0.2 cm³, 3.2 mmol) for 2 h to give a brown solution. Concentration of the solution to 1 cm³ under vacuum and addition of hexane (10 cm³) gave the compound as a microcrystalline solid.

Preparation of $[\{\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}\}_2(\text{CO})(\text{PPh}_3)]$ (13). To a solution of complex (4) (0.1 mmol) in toluene (5 cm³), prepared as above, was added triphenylphosphine (0.26 g, 0.1 mmol) and then methyl iodide (0.2 cm³, 3.2 mmol). The mixture was reacted overnight to give an orange crystalline solid which was separated by filtration and washed with hexane.

Crystal Structure Determinations of Complexes (3) and (4).—**Crystal data for (3).** $\text{C}_{34}\text{H}_{20}\text{F}_8\text{N}_2\text{Rh}_2\text{S}_2\cdot(\text{CH}_3)_2\text{CO}$. $M = 936.54$, triclinic, space group $P\bar{1}$, $a = 13.772(7)$, $b = 14.184(8)$, $c = 9.738(4)$ Å, $\alpha = 108.99(2)$, $\beta = 75.65(3)$, $\gamma = 106.04(3)^\circ$,

$U = 1 702(1)$ Å³ (by least-squares refinement of the 2 θ values in the range 20–30° of 30 accurately measured reflections), $Z = 2$, $\lambda = 0.710 69$ Å, $D_c = 1.827$ g cm⁻³, $F(000) = 928$, and $\mu(\text{Mo-K}\alpha) = 11.5$ cm⁻¹; crystal dimensions, $0.20 \times 0.27 \times 0.30$ mm. No absorption correction was applied.

Crystal data for (4). $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4\text{Rh}_2\text{S}_2$, $M = 538.16$, orthorhombic, space group $P2_12_12$ (no. 18), $a = 14.637(6)$, $b = 6.734(4)$, $c = 8.852(5)$ Å, $U = 872.5(8)$ Å³ (by least-squares refinement of the 2 θ values in the range 20–34° of 25 accurately measured reflections), $Z = 2$, $\lambda = 0.710 69$ Å, $D_c = 2.048$ g cm⁻³, $F(000) = 520$, and $\mu(\text{Mo-K}\alpha) = 21.12$ cm⁻¹; crystal dimensions, $0.25 \times 0.30 \times 0.35$ mm. A semiempirical method for the absorption correction (maximum and minimum transmission factors 1.245 and 1.000) was applied.²⁹

Data collection and processing. (3), Siemens AED diffractometer, $\theta/2\theta$ mode, niobium-filtered Mo- K_α radiation; all reflections with θ in the range 3–25° were measured. Of 5 637 independent reflections, 3 861 having $I > 2\sigma(I)$ were considered observed and used in the analysis. (4), Phillips PW-1100 diffractometer, $\omega/2\theta$ mode, graphite monochromated Mo- K_α radiation; all reflections with θ in the range 3–30° were measured. Of 1 507 independent reflections, 1 193 having $I > 3\sigma(I)$ were considered observed and used in the analysis.

Structure solution and refinement. Patterson and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms excepting those of the acetone molecule of (3). This solvent molecule was found to be disordered and distributed in two positions with unequal occupancy factors. All hydrogen atoms for both complexes (3) and (4) were localized in Fourier difference maps and refined isotropically. Final R and R' values were 0.037 and 0.051 for (3) and 0.030 and 0.046 for (4). The SHELX system of computer programs was used.³⁰ Atomic scattering factors, corrected for anomalous dispersion of Rh and S, were taken from ref. 31. All calculations were performed on the CYBER 76 and CRAY X-MP/12 computers of the Centro di

Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 5 for (3) and Table 6 for (4).

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

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