Bis(allyl) Ruthenium(IV) Complexes. Part 1. Synthesis of Complexes containing Four-membered Ruthenium Heterocycles. Crystal Structure of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(SNC_7H_4S\text{-}2)Cl]$†

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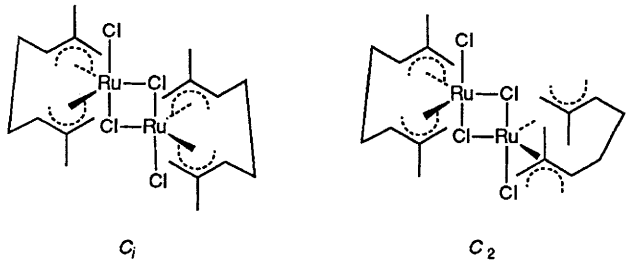
The dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** ($C_{10}H_{16}$ = 2,7-dimethyloctadienediyl) reacts with benzothiazole-2-thiol and pyridine-2-thiol to give, as initial products, $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(SNC_7H_4SH\text{-}2)Cl_2]$ **2** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4SH\text{-}2)Cl_2]$ **4** respectively. Intramolecular loss of HCl from complexes **2** and **4** leads to the formation of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(SNC_7H_4S\text{-}2)Cl]$ **3** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4S\text{-}2)Cl]$ **5** respectively. Complex **1** reacts with sodium dithiocarbamate to form $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(S_2CNEt_2)Cl]$ **6** directly. Complexes **3** and **5** react with MeCN in the presence of silver salts to form $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(SNC_7H_4S\text{-}2)(NCMe)][BF_4]$ **7** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4S\text{-}2)(NCMe)][PF_6]$ **8** respectively. The X-ray structure of **3** [space group $P2_1$ (no. 4), a = 11.627(3), b = 17.961(4), c = 8.206(3) Å, β = 90.21(2)°, Z = 4] is reported.

An exciting and challenging area of research deals with the chemistry of organometallic compounds in high formal oxidation states, and the possible application of such systems to homogeneous catalysis.[1,2] Our interest has been focused on the synthesis and co-ordination chemistry of new ruthenium complexes in the +4 oxidation state.

Although the dimeric chloro-bridged bis(allyl) complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** has been known for many years,[3] its chemistry has not been developed to any great extent. Its reaction with neutral monodentate ligands, to form monomeric complexes of the type $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ [L = CO, pyridine, phosphines, $P(OMe)_3$ or Bu^tNC], has been reported.[3–5] The X-ray structure of **1** reported by Colombo and Allegra[6] shows that the complex has overall C_i molecular symmetry, while the respective 2,7-dimethyloctadienediyl groups have local C_2 symmetry (Fig. 1). The co-ordination about the ruthenium represents a trigonal bipyramid with the chiral octadienediyl groups of the two subunits occupying equatorial sites. As is evidenced from the X-ray structure of the monomeric adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(PF_3)Cl_2]$,[7] the geometry about the ruthenium remains trigonal bipyramidal, with the chloro ligands occupying the axial sites, after cleavage of the parent dimer. Recently Cox and Roulet[8] have shown by ^1H NMR studies that **1** exists as two diastereoisomers. One isomer has C_i symmetry (X-ray structure of **1**),[6] while they propose the second isomer to have C_2 symmetry (Fig. 1). In non-co-ordinating solvents these isomers interconvert by means of chloride-bridge rupture and monomer formation, not by an intramolecular process involving the octadienediyl ligands.[8] In the same paper it is also established that when **1** is dissolved in co-ordinating solvents the dimer is cleaved and exists as the equatorially solvated monomer in the case of pyridine and S-bound dimethyl sulphoxide (dmso), while the less strongly co-ordinating MeCN and O-bound dimethylformamide (dmf) solvents co-ordinate at either the axial or equatorial sites of the monomer, and in solution the latter two isomeric forms exist in equilibrium.



C_i C_2

Fig. 1 Schematic representation of the C_i and C_2 isomers of complex **1**

In this paper the reaction of complex **1** with bidentate ligands is investigated. With benzothiazole-2-thiol (SNC_7H_4SH-2) and pyridine-2-thiol (NC_5H_4SH-2) an interesting two-step reaction sequence is involved which finally results in the formation of neutral monomeric complexes of the type $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(N\text{–}S)Cl]$ (N–S = SNC_7H_4S-2, **3**; or NC_5H_4S-2, **5**), while reaction with $[S_2CNEt_2]^-$ leads directly to this type of complex. We also report the preparation of the cationic complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(N\text{–}S)(NCMe)][X]$ (N–S = SNC_7H_4S-2, X = BF_4^- **7**; N–S = NC_5H_4S-2, X = PF_6^- **8**), formed from **3** and **5** respectively. X-Ray structure analysis of complex **3** shows that it is monomeric, and reveals a strained four-membered ruthenium heterocycle containing a localized C=N double bond.

Results and Discussion

Although experimental detail concerning the preparation of the dimeric starting material $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** is vague in the original report,[3] we have found that the preparation is readily achieved by heating a mixture of isoprene (large excess) and $RuCl_3 \cdot xH_2O$ in absolute EtOH in a sealed vessel at 65–70 °C for 3 d. Complex **1** is obtained, typically in 65–70% yield, as a purple crystalline solid and was used without further purification. No apparent difference in the yield was found when the reaction is carried out in either the presence or absence of air.

The ^1H NMR spectrum of complex **1** in $CDCl_3$ (Table 1), following room-temperature dissolution, is in agreement with that found by Cox and Roulet.[8] The presence of eight

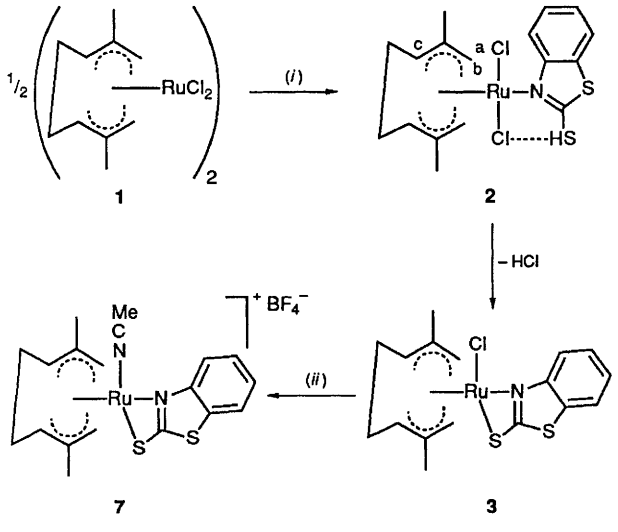
† Benzothiazole-2-thiolato-κ^2N,S'-chloro[(1,2,3,6,7,8-η)-2,7-dimethylocta-2,6-diene-1,8-diyl]ruthenium.

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

Table 1 Proton NMR data for complexes **1**–**8**[a]

Complex	Octadienediyl[b] H_a	H_b	H_c	CH_2	Me	Others[c]
1[d]	6.09(s), 5.72(s), 5.40(s), 5.22(s), 5.07(s), 4.87(s), 4.74(s), 4.49(s)		4.73(m) 4.65(m) 4.49(m) 4.45(m)	2.7–2.4(m)	2.47(s) 2.38(s) 2.28(s) 2.24(s)	
2	4.92 (s, 2 H)	4.27 (s, 2 H)	5.16 (m, 2 H)	3.19 (m, 2 H) 2.50 (m, 2 H)	2.32 (s, 6 H)	13.59 (br s, 1 H, SH), 7.52 [d, 1 H, $J(H^4-H^5)$ 7.74, H^4], 7.32 (m, 3 H, H^{5-7})
3	4.96 (s, 1 H) 4.42 (s, 1 H)	4.34 (s, 1 H) 3.18 (s, 1 H)	4.55 (m, 1 H) 4.00 (m, 1 H)	2.7–2.4 (m, 4 H)	2.49 (s, 3 H) 2.36 (s, 3 H)	8.61 [dd, 1 H, $J(H^4-H^5)$ 7.6, $J(H^4-H^6)$ 1.1, H^4], 7.67 [dd, 1 H, $J(H^7-H^6)$ 7.8, $J(H^7-H^5)$ 1.1, H^7], 7.33 [td, 1 H, $J(H^6-H^7) = J(H^6-H^5)$ 7.8, $J(H^6-H^4)$ 1.1, H^6], 7.24 [td, 1 H, $J(H^5-H^4) = J(H^5-H^6)$ 7.6, $J(H^5-H^7)$ 1.1, H^5]
4	4.79 (s, 2 H)	4.16 (s, 2 H)	5.09 (m, 2 H)	3.19 (m, 2 H) 2.49 (m, 2 H)	2.28 (s, 6 H)	13.99 (br s, 1 H, SH), 7.77 [br d, 1 H, $J(H^6-H^5)$ 8.45, H^6], 7.47 (m, 1 H, H^4), 7.31 (m, 1 H, H^5), 6.78 (m, 1 H, H^3)
5	4.51 (s, 1 H) 4.07 (s, 1 H)	3.89 (s, 1 H) 3.07 (s, 1 H)	4.42 (m, 1 H) 3.74 (m, 1 H)	2.7–2.4 (m, 4 H)	2.47 (s, 3 H) 2.30 (s, 3 H)	8.80 [br d, 1 H, $J(H^6-H^5)$ 5.19, H^6], 7.39 (m, 1 H, H^4), 6.78 (m, 1 H, H^5), 6.63 [d, 1 H, $J(H^3-H^4)$ 8.21, H^3]
6	4.49 (s, 1 H) 3.71 (s, 1 H)	3.66 (s, 1 H) 2.46 (s, 1 H)	4.20 (m, 1 H) 3.09 (m, 1 H)	2.7–2.4 (m, 4 H)	2.40 (s, 3 H) 2.10 (s, 3 H)	3.8–3.6 (m, 2 H, N-CH_2), 3.47 [qd, 2 H, J(geminal) 2.23, $J(CH_2-CH_3)$ 7.16, N-CH_2], 1.21 [t, 3 H, $J(CH_3-CH_2)$ 7.16, Me], 1.11 [t, 3 H, $J(CH_3-CH_2)$ 7.16, Me]
7	4.78 (s, 1 H) 4.18 (s, 1 H)	4.10 (s, 1 H) 3.38 (s, 1 H)	5.13 [t, 1 H, $J(H_c-CH_2)$ 6.88], 4.64 [t, 1 H, $J(H_c-CH_2)$ 6.89]	3.2–2.9 (m, 4 H)	2.55 (s, 3 H) 2.48 (s, 3 H)	7.75 [dd, 1 H, $J(H^4-H^5)$ 7.65, $J(H^4-H^6)$ 1.36, H^4], 7.47 [dd, 1 H, $J(H^7-H^6)$ 7.35, $J(H^7-H^5)$ 1.46, H^7], 7.34 (m, 2 H, H^5 and H^6), 2.70 (s, 3 H, MeCN)
8[e]	4.78 (s, 1 H) 4.08 (s, 1 H)	3.89 (s, 1 H) 3.23 (s, 1 H)	4.75 (m, 1 H) 4.38 (m, 1 H)	3.0–2.8 (m, 4 H)	2.61 (s, 3 H) 2.51 (s, 3 H)	8.51 [d, 1 H, $J(H^6-H^5)$ 5.70, H^6], 7.73 (m, 1 H, H^4), 7.13 (m, 1 H, H^5), 6.94 [d, 1 H, $J(H^3-H^4)$ 8.96, H^3], 2.69 (s, 3 H, MeCN)

[a] All spectra recorded at 303 K in $CDCl_3$ unless otherwise indicated. Chemical shift (δ) in ppm. [b] Numbering shown in Scheme 1. [c] Numbering according to systematic numbering of non-hydrogen skeleton of thiol. Given as: chemical shift (δ) in ppm, multiplicity, relative intensity, J/Hz, assignment. [d] Resonances not specifically assigned to different diastereoisomers; see text. [e] Recorded in [$^2H_6$]acetone.



Scheme 1. (*i*) SNC_7H_4SH-2; (*ii*) MeCN, $AgBF_4$

distinct resonances for the terminal allyl protons (H_a and H_b), four resonances for the internal allyl protons (H_c), and four resonances for the methyl protons supports the proposed[8] existence of two diastereoisomeric forms of **1** which, in non-co-ordinating solvents, are present in an approximate 1:1 ratio.

Treatment of complex **1** with the multifunctional ligand SNC_7H_4SH-2 in CH_2Cl_2 at room temperature rapidly leads to quantitative cleavage of the dimer to give $[Ru(\eta^3:\eta^3-C_{10}H_{16})(SNC_7H_4SH\text{-}2)Cl_2]$ **2** as an intermediate product which is of sufficient stability to be isolated (Scheme 1). Since the benzothiazole can exist as either the thiol or thione tautomer,[9,10] monodentate co-ordination to a metal centre can take place through either the N or the thione S atom. Examples of both modes of co-ordination for SNC_7H_4SH-2, and other related sulphur- and nitrogen-containing heterocyclic thione (thiol) ligands, have been reported.[11] Evidence for either S- or N-co-ordination for this class of ligand has been based largely on differences in the infrared spectra of the free and complexed ligands. In the present case, the reported[12,13] assignment of ν(C=N) and ν(C–N=S) bands in the region 1600–1400 cm^{-1} should be treated with caution since this corresponds to the region where ν(C=C) bands due to the 1,2-disubstituted benzene moiety appear.[14,15a] However, the ν(C=N) and ν(C–S) bands at lower energy are more instructive in this regard. In the infrared spectrum of complex **2**, recorded in the solid state (KBr), both the ν(C=N) band at 1251 cm^{-1} and the ν(C–S) band at 676 cm^{-1} show a positive shift relative to the free ligand (in KBr), where the respective bands occur at 1245 and 665 cm^{-1}. This shift corresponds to that reported[16] for the related N-co-ordinated 4,5-dihydrothiazole-2-thiol ligand, and thus suggests N-co-ordination in **2**. It should be noted that neither solution (CH_2Cl_2) nor solid state (KBr) infrared spectra of **2** show absorption bands assignable to either N–H or S–H[15b] bond stretching.

The ^{13}C NMR spectrum (Table 2) of complex **2** shows that the C^2 carbon atom of the co-ordinated benzothiazole ligand resonates at lower field (δ 192.2) compared with the corre-

Table 2 Selected ^{13}C-{^1H} NMR data[a]

Complex	Octadienediyl C_a	C_b	C_c	CH_2	Me	Others[b]
2	73.6	127.3	99.0	36.9	21.0	192.2 (C^2), 140.0 (C^{3a}), 128.6 (C^{7a}), 127.4 (C^5), 124.9 (C^6), 121.0 (C^4), 113.2 (C^7)
3[c]	77.8 76.1	121.0 114.9	96.4 86.3	34.6 31.3	20.2 18.9	179.6 (C^2), 152.8 (C^{3a}), 130.6 (C^{7a}), 126.3 (C^5), 123.8 (C^6), 120.9 (C^4), 120.4 (C^7)
4	72.6	126.0	99.0	36.9	20.9	178.0 (C^2), 135.8 (C^6), 135.6 (C^4), 132.5 (C^5), 115.9 (C^3)
5	76.8 76.4	118.4 112.8	94.2 87.8	34.6 31.1	19.7 18.8	207.1 (C^2), 148.5 (C^6), 135.9 (C^4), 124.9 (C^5), 116.1 (C^3)
6[c]	73.4 75.8	113.8 108.1	97.9 88.5	34.7 31.1	18.7 18.4	204.5 (quaternary), 42.9 (CH_2), 42.4 (CH_2), 12.3 (Me), 12.2 (Me)

[a] All spectra recorded at 303 K in $CDCl_3$. Chemical shift (δ) in ppm. [b] Numbered according to systematic numbering for thiol. [c] Assigned with the aid of two-dimensional ^1H–^{13}C HETCOR spectra.

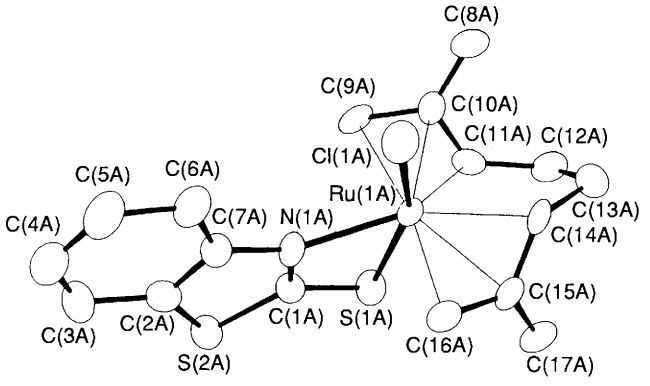


Fig. 2 Molecular structure of complex **3** with all hydrogen atoms omitted

sponding carbon atom in the free ligand which resonates at δ 190.9 in $CDCl_3$. By contrast, it is reported[17] that co-ordination of 1,3-imidazolidine-2-thione to copper(I) *via* the thione S atom is accompanied by a high-field shift of the C^2 thione carbon atom relative to the free ligand. This strongly suggests that the benzothiazole ligand in complex **2** is not co-ordinated through the thione S atom, but rather through the N donor atom.

In addition to the infrared and ^{13}C NMR evidence, we propose that initial co-ordination of the benzothiazole to complex **1** proceeds *via* the N rather than the thione S atom, and equatorially rather than axially since (*i*) the ^1H NMR spectrum of **2** shows single resonances for the methyl, terminal allyl, and internal allyl protons which is in agreement with that what is found for simple adducts of **1** containing equatorially co-ordinated monodentate ligands[3,4,8] (also X-ray structure of PF_3 adduct),[7] (*ii*) complex **3** has (X-ray structure, see below) the N donor atom occupying an equatorial site and the thiolate S atom an axial site (co-ordination through the S atom of the thione tautomer would require a rearrangement, at least from equatorial to axial co-ordination, of the benzothiazole ligand which is not observed in the NMR spectrum during the conversion of **2** into **3**) and (*iii*) the presence of a very acidic proton in **2** (δ 13.6) suggests that, on co-ordination, the thiol proton is activated and is probably closely associated (*e.g.* hydrogen bonded) with an axially co-ordinated chloride ligand

Table 3 Selected bond lengths (Å) for compound **3**

Cl(1A)–Ru(1A)	2.423(3)	Cl(1B)–Ru(1B)	2.406(3)
S(1A)–Ru(1A)	2.421(3)	S(1B)–Ru(1B)	2.428(3)
C(1A)–N(1A)	1.335(14)	C(1B)–N(1B)	1.291(13)
C(7A)–N(1A)	1.382(13)	C(7B)–N(1B)	1.385(14)
C(8A)–C(10A)	1.52(2)	C(8B)–C(10B)	1.48(2)
C(9A)–Ru(1A)	2.247(10)	C(9B)–Ru(1B)	2.207(11)
C(10A)–Ru(1A)	2.236(12)	C(10B)–Ru(1B)	2.184(12)
C(11A)–Ru(1A)	2.269(11)	C(11B)–Ru(1B)	2.191(11)
C(15A)–C(16A)	1.42(2)	C(15B)–C(16B)	1.37(2)
C(15A)–C(17A)	1.55(2)	C(15B)–C(17B)	1.56(2)
C(16A)–Ru(1A)	2.206(10)	C(16B)–Ru(1B)	2.277(11)
S(1A)–C(1A)	1.718(11)	S(1B)–C(1B)	1.718(11)
C(1A)–S(2A)	1.734(11)	C(1B)–S(2B)	1.748(11)
S(2A)–C(2A)	1.748(11)	S(2B)–C(2B)	1.701(11)
N(1A)–Ru(1A)	2.147(9)	N(1B)–Ru(1B)	2.215(9)
C(9A)–C(10A)	1.39(2)	C(9B)–C(10B)	1.42(2)
C(10A)–C(11A)	1.449(14)	C(10B)–C(11B)	1.394(14)
C(14A)–C(15A)	1.44(2)	C(14B)–C(15B)	1.42(2)
C(14A)–Ru(1A)	2.253(10)	C(14B)–Ru(1B)	2.214(10)
C(15A)–Ru(1A)	2.238(10)	C(15B)–Ru(1B)	2.221(10)

[this might explain the absence of ν(N–H) or ν(S–H) bands in the IR spectrum of **2**].

In solution, intramolecular interaction between an axially co-ordinated chloride ion and the, now activated, thiol proton in complex **2** eventually leads to the slow release of HCl, followed by ring closure, to form [Ru(η^3:η^3-$C_{10}H_{16}$)(SNC_7H_4S-2)Cl] **3** (Scheme 1). This slow conversion in solution, over a period of hours at room temperature, is observed in the ^1H NMR spectrum of **2** by the growth of peaks due to the formation of **3**. The rate of conversion can be increased by boiling a solution of complex **2** in CH_2Cl_2, $CHCl_3$ or acetone. The HCl released is readily detected in the vapours of these solvents using moistened universal pH indicator paper. However, complete conversion is more readily achieved, within minutes, by boiling an ethanolic solution of **2** in the presence of a slight excess of Na_2CO_3.

The formation of a monomeric complex containing a strained four-membered heterocyclic ring system, instead of a dimeric compound with bridging benzothiazole ligands,[18] can be ascribed to the rate of co-ordination (step 1) of the ligand to **1** which far exceeds the rate of dehydrohalogenation (step 2). Thus rupture of the chloro-bridges in the parent complex **1**, to form the monomeric complex **2**, precludes dimer formation.

It is important to note that, since the parent dimers (both the C_i and proposed C_2 isomers of **1**) contain chiral subunits as a result of the conformations of the octadienediyl groups, and since the conformation of the octadienediyl group remains fixed once co-ordinated to the ruthenium, cleavage of **1** by an incoming ligand would result in the formation of chiral monomeric products. Furthermore, these different enantiomers of the monomeric complexes would give rise to identical NMR spectra, and this is clearly seen by the reduction in the number of octadienediyl proton resonances in going from the parent dimer to the substituted monomeric adducts **2**–**8**.

The ^1H NMR spectrum of [Ru(η^3:η^3-$C_{10}H_{16}$)-(SNC_7H_4SH-2)Cl_2] **2** recorded at 303 K shows single resonances for the respective octadienediyl protons, implying that the two halves of the ligand are in equivalent environments. This indicates that in solution at 303 K there is free rotation of the benzothiazole ligand about the Ru–N bond in **2**. By contrast, once ring closure occurs to form complex **3** the molecule is locked in a given conformation and the two halves of the octadienediyl ligand experience different environments. This results in the doubling of the respective octadienediyl proton resonances, with the exception of the aliphatic methylene resonances which are less well resolved than in **2**. The fact that the two halves of the octadienediyl ligand in **3** are in different environments is further illustrated by the ^{13}C-{^1H} NMR spectrum in which each carbon atom in the octadienediyl

Table 4 Selected bond angles (°) for compound **3**

C(1A)–S(1A)–Ru(1A)	79.4(4)	C(1B)–S(1B)–Ru(1B)	79.5(4)
S(1A)–C(1A)–N(1A)	113.6(8)	S(1B)–C(1B)–N(1B)	116.1(8)
C(1A)–N(1A)–Ru(1A)	99.0(6)	C(1B)–N(1B)–Ru(1B)	97.5(7)
C(14A)–C(15A)–C(17A)	122.5(10)	C(14B)–C(15B)–C(17B)	120.8(10)
Cl(1A)–Ru(1A)–S(1A)	156.4(1)	Cl(1B)–Ru(1B)–S(1B)	155.5(1)
S(1A)–Ru(1A)–N(1A)	68.0(3)	S(1B)–Ru(1B)–N(1B)	66.8(2)
Cl(1A)–Ru(1A)–C(10A)	86.7(3)	Cl(1B)–Ru(1B)–C(10B)	87.3(3)
N(1A)–Ru(1A)–C(10A)	119.9(3)	N(1B)–Ru(1B)–C(10B)	120.0(3)
S(1A)–Ru(1A)–C(15A)	87.7(3)	S(1B)–Ru(1B)–C(15B)	87.5(3)
S(2A)–C(1A)–N(1A)	116.2(8)	S(2B)–C(1B)–N(1B)	114.1(8)
C(7A)–N(1A)–Ru(1A)	151.0(7)	C(7B)–N(1B)–Ru(1B)	147.7(7)
C(14A)–C(15A)–C(16A)	114.6(10)	C(14B)–C(15B)–C(16B)	115.2(10)
C(16A)–C(15A)–C(17A)	122.7(10)	C(16B)–C(15B)–C(17B)	123.9(11)
Cl(1A)–Ru(1A)–N(1A)	88.6(3)	Cl(1B)–Ru(1B)–N(1B)	88.9(2)
S(1A)–Ru(1A)–C(10A)	106.5(3)	S(1B)–Ru(1B)–C(10B)	107.2(3)
Cl(1A)–Ru(1A)–C(15A)	102.6(3)	Cl(1B)–Ru(1B)–C(15B)	101.8(3)
N(1A)–Ru(1A)–C(15A)	119.1(4)	N(1B)–Ru(1B)–C(15B)	117.7(4)
C(10A)–Ru(1A)–C(15A)	120.3(4)	C(10B)–Ru(1B)–C(15B)	121.6(4)

Table 5 Fractional coordinates ($\times 10^4$) for compound **3**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cl(1A)	6 944(2)	−66(2)	4 320(3)	Cl(1B)	8 068(2)	3 911(2)	−671(3)
S(1A)	2 961(2)	486(2)	4 578(3)	S(1B)	12 039(2)	3 365(2)	−408(3)
C(1A)	3 662(9)	1 020(6)	3 156(12)	C(1B)	11 322(9)	2 822(6)	−1 804(12)
S(2A)	3 155(3)	1 743(2)	1 952(3)	S(2B)	11 836(3)	2 105(2)	−3 044(4)
C(2A)	4 551(9)	1 828(6)	1 190(13)	C(2B)	10 486(9)	2 021(6)	−3 831(12)
C(3A)	4 921(11)	2 305(6)	−109(14)	C(3B)	10 055(12)	1 551(6)	−5 055(14)
C(4A)	6 045(11)	2 268(7)	−512(15)	C(4B)	8 953(10)	1 564(7)	−5 517(14)
C(5A)	6 804(10)	1 768(7)	180(14)	C(5B)	8 204(12)	2 083(8)	−4 817(15)
C(6A)	6 443(10)	1 270(7)	1 370(13)	C(6B)	8 577(10)	2 565(7)	−3 634(13)
C(7A)	5 277(9)	1 313(6)	1 859(12)	C(7B)	9 693(10)	2 525(6)	−3 152(13)
N(1A)	4 784(8)	873(5)	3 049(10)	N(1B)	10 244(8)	2 967(5)	−2 006(10)
C(8A)	5 848(11)	−1 697(7)	4 253(14)	C(8B)	9 207(9)	5 558(7)	−722(14)
C(9A)	4 678(10)	−750(6)	2 659(12)	C(9B)	10 302(11)	4 581(6)	−2 328(13)
C(10A)	4 816(9)	−1 190(7)	4 041(11)	C(10B)	10 174(9)	5 029(7)	−916(12)
C(11A)	3 926(9)	−1 079(6)	5 248(12)	C(11B)	11 040(8)	4 908(6)	232(11)
C(12A)	3 983(11)	−1 407(6)	6 902(14)	C(12B)	11 023(10)	5 256(6)	1 933(14)
C(13A)	5 016(9)	−1 141(7)	7 922(13)	C(13B)	9 996(10)	4 956(7)	2 924(11)
C(14A)	5 476(11)	−383(7)	7 314(11)	C(14B)	9 535(9)	4 211(6)	2 293(11)
C(15A)	4 824(10)	294(6)	7 478(12)	C(15B)	10 168(11)	3 537(7)	2 447(12)
C(16A)	5 259(10)	907(6)	6 571(12)	C(16B)	9 708(11)	2 936(6)	1 642(12)
C(17A)	3 681(10)	330(7)	8 429(12)	C(17B)	11 327(10)	3 515(7)	3 405(12)
Ru(1A)	4 895(1)	0	4 830(1)	Ru(1B)	10 106(1)	3 863(1)	−163(1)

ligand gives rise to a separate resonance. By comparison, like carbons in complex **2** give rise to a single resonance.

The two-dimensional ^1H–^{13}C heteronuclear correlation (HETCOR) NMR spectrum of complex **3** reveals that the proton resonances at δ 4.96 (H_a) and 3.18 (H_b) arise from terminal allylic protons which are bonded to the same carbon atom (C_a at δ 76.1). Similarly, the proton resonances at δ 4.42 (H_a) and 4.34 (H_b) arise from the second set of terminal allylic protons of the octadienediyl ligand which are in turn bonded to the second C_a carbon atom which gives rise to a resonance at δ 77.8. Owing to the symmetry of the octadienediyl ligand, no further unambiguous assignments showing proton association could be made from the HETCOR spectrum. Excluding the CH_2 groups (which give rise to a broad multiplet in the ^1H NMR spectrum) the remaining proton–carbon correlations of the octadienediyl group in **3** are listed in δ(ppm) with the ^{13}C resonances given in parentheses: 4.55, H_c (96.4, C_c); 4.00, H_c (86.3, C_c); 2.49, Me (18.9); and 2.36, Me (20.2).

Diffraction-quality crystals of [Ru(η^3:η^3-$C_{10}H_{16}$)(SNC$_7$H$_4$S-2)Cl] **3** were obtained by recrystallisation from CH_2Cl_2–Et_2O mixtures. The crystal-structure determination reveals the existence of two independent molecules in the asymmetric unit. However, these molecules are structurally almost identical, and for clarity only one is shown in Fig. 2. The two independent molecules are labelled A and B respectively. Selected bond lengths and angles are presented in Tables 3 and 4, fractional coordinates in Table 5.

The structure of complex **3** shows that only one of two possible enantiomers is present. The geometry about the ruthenium atom is a distorted trigonal bipyramid. The benzothiazole ligand is co-ordinated edge-on to the ruthenium through the N atom, which resides in an equatorial position along with the allyl groups, and the thiolate S atom which is *trans* to the chloride ligand in an axial position. The arrangement of the octadienediyl group, which has local C_2 symmetry, is similar to that found in the crystal structures of the dimeric complex **1**[6] and its PF_3 adduct.[7]

A striking feature is the small S(1)–Ru–N(1) bond angle of 67.4(3)° (average) which deviates significantly from the ideal 90°, and is indicative of the strain in the four-membered heterocycle. This ring strain is also reflected in the C(1)–N(1)–Ru angle of 98.3(7)° (average), and the C(1)–S(1)–Ru angle of 79.5(4)° (average). The average C(1)–N bond length of 1.313(14) Å shows the existence of a localised C=N double bond with little or no delocalisation involving atom S(1). This value agrees favourably with the average value of 1.324(14) Å, for a C=N double bond, obtained in a crystallographic data base search for molecules containing a benzothiazole structural unit.[19] The

coplanarity of the chloride ligand and the benzothiazole-2-thiolate group is indicated by the Cl(1)–Ru–N(1)–C(1) torsion angle of 4(1)° (average).

The reaction of complex **1** with NC_5H_4SH-2 also involves a two-step sequence, and is in all respects analogous to that found with SNC_7H_4SH-2 (Scheme 1). The initial product formed involves monodentate co-ordination of the NC_5H_4SH-2 *via* either the S atom of the thione tautomer or the N atom of the thiol tautomer to give $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4SH\text{-}2)Cl_2]$ **4**. Although it has been reported[11,20] that monodentate co-ordination of NC_5H_4SH-2 usually proceeds *via* the thione S atom, it is not certain which mode of co-ordination is adopted in complex **4** since the infrared spectrum (KBr) shows no ν(N–H), ν(C=S) or ν(S–H)[15b] absorptions. As with complex **2**, the lack of ν(N–H) or ν(S–H) hands could be due to intramolecular hydrogen bonding involving one of the axially co-ordinated chloride ligands.

Inspection of the ^1H NMR spectrum of complex **4** reveals that the methyl, terminal allyl, and internal allyl protons of the octadienediyl group give rise to single resonances, confirming that the NC_5H_4SH-2 occupies an equatorial position. By contrast, axial co-ordination would give rise to two sets of resonances for the respective octadienediyl protons; see for example the ^1H NMR data for the MeCN and dmf solvates of complex **1** in ref. 8.

The ^1H NMR spectrum of complex **4** shows a resonance at δ 13.99 due to the activated thiol proton. In similar fashion to **2**, loss of HCl in solution is accompanied by ring closure to form $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4S\text{-}2)Cl]$ **5**. Comparison of the ^1H and $^{13}C\text{-}\{^1H\}$ data for **4** and **5** shows that in solution at 303 K there is free rotation about the Ru–L (L = N or S donor atom of NC_5H_4SH-2) bond in **4**, while complex **5** shows the characteristic doubling of the octadienediyl resonances confirming the presence of an N–S chelate ring.

A preliminary investigation of the reaction of complex **1** with 2-aminopyridine, under the same conditions used before suggests a similar reaction sequence leading to the formation of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4NH\text{-}2)Cl]$. From the ^1H NMR spectrum of the crude product, recorded in $CDCl_3$, the doubled-up octadienediyl resonances are identified at δ 4.65 and 4.40 (2 H_a), 3.91 and 3.53 (2 H_b), 4.20 and 4.19 (2 H_c), 2.8–2.4 (aliphatic CH_2, 4 H), and 2.40 and 2.30 (2 Me) which is similar to what is found for complexes **3** and **5**. The co-ordinated NC_5H_4NH-2 shows resonances at δ 8.47, 7.67, 7.11 and 6.88 due to the four aromatic protons, and 8.67(br) due to the N–H group. Reaction of **1** with 2-hydroxypyridine, however, leads to a mixture of products which could not be identified.

The reaction of complex **1** with sodium dithiocarbamate in CH_2Cl_2–EtOH mixtures is slower than with the neutral ligands studied due mainly to the lower solubility of the $[S_2CNEt_2]^-$ in CH_2Cl_2. The reaction is envisaged to involve dimer cleavage followed immediately by ring closure and loss of NaCl to form $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(S_2CNEt_2)Cl]$ **6** as the sole product. In similar fashion to **3** and **5** the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **6** show doubling of the octadienediyl resonances due to the fixed conformation of the Ru–S–C–S ring system. The two ethyl groups of the ligand are in different environments and show separate sets of resonances in the NMR spectrum, indicative of the restricted rotation about the $^-S_2C\text{–}NEt_2$ bond.[21]

From two-dimensional $^1H\text{–}^1H$ correlation spectroscopy (COSY) and $^1H\text{–}^{13}C$ HETCOR NMR spectroscopy for complex **6** it is possible to distinguish those protons (excepting the aliphatic CH_2 protons which give rise to a broad multiplet) and carbon atoms which form part of one half of the octadienediyl ligand. The proton resonances, and the resonances of the respective carbon atoms (given in parentheses), in the two halves of the octadienediyl ligand are listed in δ(ppm): 4.49, H_a and 2.46, H_b (73.4, C_a); 3.09, H_c (88.5, C_c); 2.40, Me (18.7); 3.71, H_a and 3.66, H_b (75.8, C_a); 4.20, H_c (97.9, C_c); and 2.10, Me (18.4).

Inspection of the chemical shifts of the octadienediyl proton resonances for the neutral complexes **2**–**6** reveals a consistent downfield shift in the order **6** < **5** < **4** ≤ **3** ≈ **2**. This suggests that the electron-donating ability of the ligands decrease in the order, $[S_2CNEt_2]^-$ > NC_5H_4S-2 > NC_5H_4NH-2 > N-bound NC_5H_4SH-2 ≥ SNC_7H_4S-2 ≈ N-bound SNC_7H_4-SH-2. Although similar changes in the ^{13}C chemical shifts of the octadienediyl ligands in these complexes occur, these changes are less consistent than are found with the proton spectra. Notable, however, is that both the ^1H and ^{13}C chemical shifts of the Me and especially the CH_2 groups, neither of which is directly involved in bonding to the ruthenium, are least affected by changes in the co-ordination sphere of the ruthenium.

The chloride ligands in complexes **3** and **5** are readily abstracted by $AgBF_4$ and $AgPF_6$ in MeCN (Scheme 1) to form the yellow cationic complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(SNC_7H_4S\text{-}2)(NCMe)][BF_4]$ **7** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(NC_5H_4S\text{-}2)(NCMe)][PF_6]$ **8** respectively. These salts are stable to air in both the solid and in solution.

Proton NMR spectra of complexes **7** and **8** are similar to those found for the respective precursors **3** and **5**, with additional resonances at δ 2.70 and 2.69, respectively, assigned to the co-ordinated MeCN ligands. Because of the low solubilities of **7** and **8**, infrared spectra were recorded as KBr pellets. The co-ordinated MeCN gives rise to ν(C≡N) absorptions at 2322 and 2295 **7** and 2321 and 2293 cm^{-1} **8**. The presence of two absorptions at slightly different energy, and of equal intensity, for the respective compounds can be ascribed to environmental effects in the crystal lattice.[22]

Experimental

Materials.—Commercial $RuCl_3 \cdot xH_2O$ was purchased from Fluka and Strem Chemicals. All reagents and solvents used were commercially available and used without further purification. Owing to the stability of the ruthenium complexes studied, all reactions and manipulations were carried out in the presence of air.

Characterisation.—Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded at 303 K using a Bruker AC 300 spectrometer operating at 300.13 and 75.47 MHz for the respective nuclei. Spectra were referenced relative to $SiMe_4$ (δ 0 ppm) using the residual signal from the deuteriated solvents. Standard Bruker software was used to obtain the two-dimensional spectra, and use was made of the ASPECT 3000 computer to process the raw data. Infrared spectra were recorded as KBr pellets using a Bomen M-100 FTIR spectrometer. Elemental analyses were carried out by the Division of Energy Technology, Council for Scientific and Industrial Research, South Africa. Melting points were determined using a Gallenkamp apparatus and are uncorrected.

Crystallography.—Crystal data for complex **3**. $C_{17}H_{20}ClNRuS_2$, M = 438.99, dark orange cubic crystal with dimensions 0.31 × 0.31 × 0.38 mm, monoclinic, space group $P2_1$ (no. 4), a = 11.627(3), b = 17.961(4), c = 8.206(3) Å, β = 90.21(2)° (by least-squares refinement of the setting of 25 accurately measured reflections in the range 16 ≤ θ ≤ 17°), U = 1713.6 Å^3, Z = 4, D_c = 1.72 g cm^{-3}, $F(000)$ = 888, μ(Mo-Kα) = 11.9 cm^{-1}.

Data collection and processing. Diffraction intensities were measured with graphite-monochromatized Mo-Kα radiation (λ = 0.7107 Å) on a CAD4 diffractometer in the ω–2θ mode with 3 ≤ θ ≤ 30° (h 0–16, k 0–25, l −11 to 11), ω = 1.15 + 0.35 tan θ, variable scan rate 5.49° s^{-1}, maximum scan time 60 s per reflection. A total of 4786 reflections were measured, of which 3927 unique reflections with $I > 2\sigma(I)$ were considered observed and used in the analysis. A semiempirical method for the absorption correction (maximum and minimum correction factors 0.999 and 0.973) was applied.[23]

Structure analysis and refinement. The structure was solved by usual Patterson and Fourier methods, and all non-hydrogen atoms were refined anisotropically using a block-diagonal least-

squares method (SHELX 76).[24] The hydrogen atoms were placed in calculated positions with a common isotropic thermal parameter that refined to $U_{iso} = 0.084(8)$ Å. Convergence was reached at $R' = 0.044$ [weights $\sigma^{-2}(F)$] and $R = 0.051$ for 411 variables. Atomic scattering factors were taken from ref. 25. Final atomic coordinates for the non-hydrogen atoms are given in Table 5.

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

Preparations.—[{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] **1**. The compound $RuCl_3 \cdot xH_2O$ (2.0 g) was dissolved in absolute ethanol (30 cm^3) and the solution transferred to a Schlenk tube (150 cm^3) fitted with a single Teflon (ROTAFLO) tap. Isoprene (90 cm^3) was added to the ethanol solution and the tap tightly shut. The sealed Schlenk tube was immersed in an oil-bath at 65–70 °C for 3 d. Complex **1** precipitated from the dark red solution as purple crystals which were collected on a sintered glass frit, washed consecutively with ethanol, methanol and diethyl ether, and dried under vacuum. Yield: 1.45 g (*ca.* 62%), m.p. 198–208 °C (decomp.).

[Ru(η^3:η^3-$C_{10}H_{16}$)(SNC_7H_4SH-2)Cl_2] **2**. To compound **1** (154 mg, 0.25 mmol) dissolved in dichloromethane (15 cm^3) was added benzothiazole-2-thiol (84 mg, 0.50 mmol). The solution immediately turned from purple to orange-red. After stirring for 3 h at room temperature the dichloromethane was removed *in vacuo* and complex **2** was obtained quantitatively as a dry reddish solid. The ^{1}H NMR spectrum in $CDCl_3$ showed only the presence of **2**, which was used without further purification. Melting points were found to be variable, and dependent on the rate of heating as a result of conversion into **3**; see Discussion.

[Ru(η^3:η^3-$C_{10}H_{16}$)(NC_5H_4SH-2)Cl_2] **4**. Using the above procedure, the dimer **1** (154 mg, 0.25 mmol) was treated with pyridine-2-thiol (56 mg, 0.50 mmol). The solid orange-red product **4** was obtained in quantitative yield (according to ^{1}H NMR spectroscopy) and used without further purification. As with **2**, melting points were variable due to conversion into **5**; see Discussion.

[Ru(η^3:η^3-$C_{10}H_{16}$)(SNC_7H_4S-2)Cl] **3**. Compound **2** (240 mg, 0.50 mmol) in ethanol (20 cm^3) was heated till the reddish mixture boiled. Sodium carbonate (79 mg, 0.75 mmol) was added and the mixture boiled for 3–4 min. During this time the solution turned orange. The warm solution was filtered through paper, and the ethanol removed *in vacuo*. The orange-brown residue was extracted with dichloromethane and filtered through a short column of Celite filter aid. Recrystallisation from warm ethanol or dichloromethane–diethyl ether mixtures gave dark orange crystals of complex **3**. Yield: 200 mg (91%), m.p. 220–225 °C (decomp.) (Found: C, 47.10; H, 4.65; N, 3.20. $C_{17}H_{20}ClNRuS_2$ requires C, 46.50; H, 4.60; N, 3.20%).

[Ru(η^3:η^3-$C_{10}H_{16}$)(NC_5H_4S-2)Cl] **5**. Using the above procedure, compound **4** (210 mg, 0.50 mmol) was heated in ethanol (20 cm^3) in the presence of Na_2CO_3 (79 mg, 0.75 mmol). Recrystallisation from warm ethanol gave yellow needle-like crystals of complex **5**. Yield: 178 mg (93%), m.p. 171–172 °C (decomp.) (Found: C, 47.80; H, 5.35; N, 3.70. $C_{15}H_{20}ClNRuS$ requires C, 47.05; H, 5.25; N, 3.65%).

[Ru(η^3:η^3-$C_{10}H_{16}$)(S_2CNEt_2)Cl] **6**.—To compound **1** (154 mg, 0.25 mmol) dissolved in dichloromethane (15 cm^3) was added sodium diethyldithiocarbamate (113 mg, 0.50 mmol). After adding a small amount of ethanol (2 cm^3) to aid dissolution of the salt, the mixture was stirred at room temperature overnight. The yellow solution was filtered through Celite filter aid, and the solvents removed *in vacuo*. The residue was extracted with dichloromethane and filtered through Celite filter aid. Recrystallisation from chloroform gave yellow crystals of complex **6**. Yield: 181 mg (86%), m.p. 162–164 °C (Found: C, 43.20; H, 6.35; N, 3.40. $C_{15}H_{26}ClNRuS_2$ requires C, 42.80; H, 6.20; N, 3.35%).

[Ru(η^3:η^3-$C_{10}H_{16}$)(SNC_7H_4S-2)(NCMe)][BF_4] **7**. Compound **3** (439 mg, 1.0 mmol) was dissolved in acetonitrile (20 cm^3), and the resulting dark yellow solution was treated with silver tetrafluoroborate (195 mg, 1.0 mmol). Silver chloride immediately began to precipitate and the solution turned pale yellow. The mixture was shaded from light and stirred at room temperature for 5 h. After filtration through Celite filter aid, the acetonitrile was removed *in vacuo* and the solid extracted with dichloromethane. Filtration through Celite, followed by slow evaporation of the dichloromethane, gave yellow crystals of complex **7**. Yield: 462 mg (87%), m.p. 215–219 °C (decomp.) (Found: C, 42.30; H, 4.25; N, 5.20. $C_{19}H_{23}BF_4N_2RuS_2$ requires C, 42.95; H, 4.35; N, 5.25%).

[Ru(η^3:η^3-$C_{10}H_{16}$)(NC_5H_4S-2)(NCMe)][PF_6] **8**. Using the above procedure, compound **5** (383 mg, 1.0 mmol) in acetonitrile (20 cm^3) was treated with silver hexafluorophosphate (253 mg, 1.0 mmol) at room temperature. Recrystallisation from dichloromethane gave yellow crystals of complex **8**. Yield: 467 mg (88%), m.p. 165–170 °C (decomp.) (Found: C, 38.50; H, 4.30; N, 5.30. $C_{17}H_{23}F_6N_2PRuS$ requires C, 38.25; H, 4.35; N, 5.25%).

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