Geometrical Isomerism in 2-Hydroxypyridinate and Pyridine-2-thiolate Complexes derived from the Ruthenium(IV) Bis(allyl) Dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$†

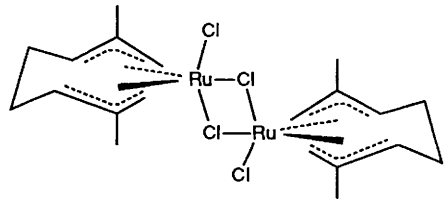
Jonathan W. Steed and Derek A. Tocher*
Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, UK

Reaction of the ruthenium(IV) chloro-bridged dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ with a range of 2-hydroxypyridinate and pyridine-2-thiolate ligands (HL = 2-hydroxypyridine, 6-chloro-2-hydroxypyridine, 2-hydroxy-6-methylpyridine, 2-hydroxy-4-methylquinoline, 8-hydroxyquinoline, pyrrolidin-2-one, quinoline-2-thiol and 6-methylpyridine-2-thiol) gives the neutral, chelate compounds $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(L)]$ each of which exists as both axial and equatorial geometric isomers. These isomers occur in varying ratios and may be distinguished by their characteristic ^1H NMR spectra. The X-ray crystal structures of eq-$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_6H_3(O)Cl\text{-}6\}]$ and of eq-$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)]$ are reported.

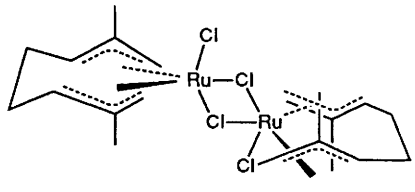
Recent interest[1–6] has focused strongly on the chemistry of the hitherto neglected ruthenium(IV) bis(allyl) chloro-bridged dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **1**[7,8] especially in connection with ligands related to pyridine-2-thiol,[5] which are of considerable interest in their own right.[9,10] Previously we have investigated the reactions of the closely related ruthenium(II) arene complexes $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$[11] with a range of ligands related to 2-hydroxypyridine[12] and with a wide range of carboxylates (arene = C_6H_6, *p*-$MeC_6H_4CHMe_2$, $C_6H_3Me_3$-1,3,5, $C_6H_2Me_4$-1,2,4,5 or C_6Me_6).[13] Cotton and co-workers[14] have also characterised the complex $[Ru(p\text{-}MeC_6H_4CHMe_2)Cl(NC_5H_4O)]$. Toerien and van Rooyen[5] recently demonstrated that the reaction of **1** with benzothiazole-2-thiol ($N_2C_7H_5SH$) and pyridine-2-thiol (NC_5H_4SH) proceeds *via* a two-step process initially involving bridge cleavage to give a neutral complex exhibiting equatorial co-ordination of the pyridyl nitrogen atom. Subsequent refluxing of these complexes in solutions containing $Na_2[CO_3]$ brings about the intramolecular loss of HCl and gives complexes containing $N_2C_7H_5S$ and NC_5H_4S as anionic chelates.

2-Hydroxypyridine has been shown[12] to co-ordinate initially through the pyridone oxygen atom in ruthenium(II) arene systems, at room temperature, to give complexes such as $[Ru(\eta^6\text{-}C_6H_6)Cl_2(OC_5H_4NH)]$ **2**. Subsequent deprotonation on refluxing forms the chelate complex $[Ru(\eta^6\text{-}C_6H_6)Cl(NC_5H_4O)]$ **3**, which is related to those described by Toerien and van Rooyen[5] for the ruthenium(IV) system. These workers[5] also attempted the reaction of **1** with 2-hydroxypyridine but were unable to identify the products formed. As an extension to our previous work we now report the reactions of **1** with a range of ligands related to 2-hydroxypyridine and pyridine-2-thiol.

The geometry about the ruthenium ion in complex **1** is loosely described as trigonal bipyramidal[5] with chloride ligands occupying the axial sites and one equatorial position, while the bis(allyl) ligand is in the remaining two equatorial sites. Complex **1** has been shown to exist as two diastereoisomers, of C_i and C_2 symmetry,[3] which arise as a consequence of the chirality of the '$C_{10}H_{16}Ru$' unit. This phenomenon is readily observed in the ^1H NMR spectrum which displays eight lines corresponding to the terminal allyl protons and four resonances attributable to the methyl substituents. Mononuclear species derived from **1**, while existing as two enantiomers, display



C_i isomer



C_2 isomer

1

signals corresponding to only a single diastereoisomer (four terminal allyl and two methyl resonances) if the two halves of the bis(allyl) ligand are inequivalent (*e.g.* as a consequence of inequivalent axial sites of the trigonal bipyramid[3,5,15]) or, in the more symmetrical equatorially substituted compounds $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ (L = pyridine, PPh_3, PF_3, CO, Bu^{t}CN, *etc.*),[16] two terminal allyl and a single methyl resonance.

Results and Discussion

In our previous study we showed that the chelate complex $[Ru(\eta^6\text{-}C_6H_6)Cl(O_2CCF_3)]$ was a useful synthetic precursor to **3** and related products. This synthetic route is not available in the case of the bis(allyl)ruthenium(IV) system, however, since the reaction of **1** with trifluoroacetic acid or silver trifluoroacetate gives the relatively inert aqua complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(OH_2)]$.[17] Fortunately, we find that direct interaction of **1** with 2-hydroxypyridine in CH_2Cl_2 at room temperature gives a good yield (*ca.* 70%) of an orange-red complex **4**. The infrared spectrum showed no bands attributable to ν(OH) or to ν(NH) but did display a band at 1596 cm^{-1} (*cf.* 1585 cm^{-1} for Tl[NC_5H_4O] and 1635 cm^{-1} for the free ligand[18]) which is tentatively attributed to ν_{asym}(OCN) of the co-ordinated hydroxypyridinate anion. The assignment

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

of ν_{sym}(OCN) at lower wavenumber is ambiguous due to the presence of bands arising from the pyridyl ring. A weak band is also observed at 317 cm^{-1} corresponding to ν(RuCl). The ^1H NMR spectrum shows the characteristic four-line pattern (Table 1) for the terminal allyl protons of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand (δ 5.05, 4.24, 4.07 and 3.00) and two relatively widely separated signals for the methyl substituents (δ 2.38 and 2.24) indicative of inequivalent axial sites on the trigonal-bipyramidal ruthenium atom. A fast atom bombardment (FAB) mass spectrum displayed a strong molecular ion peak at m/z = 367 (based on ^{102}Ru and ^{35}Cl) with the expected isotope distribution pattern. Fragmentation peaks associated with loss of a single chloride ligand and loss of both chloride and hydroxypyridinate ligands were also observed, and a peak at m/z = 136 is due to the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand. These observations, in conjunction with microanalytical data, lead us to formulate **4** as a chelate complex [Ru(η³:η³-$C_{10}H_{16}$)Cl(NC_5H_4O)], which is structurally related to **3** and to the complexes prepared by Toerien and van Rooyen.[5] It was also noted that the ^1H NMR spectrum of crude **4** produced in this way showed small traces of a second compound with only two terminal allyl resonances (δ 4.90 and 4.04) and a broad peak at δ 10.40. We were unable to isolate this second product but tentatively suggest it to be an analogue of the ruthenium(II) monodentate pyridone adduct [Ru(η⁶-C_6H_6)Cl_2(OC_5H_4NH)], for which the amine proton is observed at δ 11.56. The ready formation of chelate complexes such as **4** markedly contrasts with studies on the pyridine-2-thiolate analogues,[5] and is attributed to the greater acidity of the hydroxyl proton.

Unlike its ruthenium(II) arene analogues, **4** might be expected to exist as two geometrical isomers (**4a**, **4b**) distinguishable by ^1H NMR spectroscopy, as a consequence of the stereochemical inequivalence of the axial and equatorial sites of the trigonal-bipyramidal ruthenium atom. However, both [Ru(η³:η³-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)] and [Ru(η³:η³-$C_{10}H_{16}$)Cl(NC_5H_4S)][5] are reported to exist solely as equatorial isomers (type **a**), with the pyridyl nitrogen atom occupying the equatorial site of the trigonal-bipyramidal ruthenium atom. The ^1H NMR spectrum of **4** (obtained from a sample synthesised by direct interaction of **1** with the non-deprotonated 2-hydroxypyridine ligand) is interpreted in terms of a single isomer, possessing a set of resonances qualitatively similar, in the allyl region, to those exhibited by [Ru(η³:η³-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)] and [Ru(η³:η³-$C_{10}H_{16}$)Cl(NC_5H_4S)].[5]

It might be supposed that, analogously to the ruthenium(II) arene system,[12] 2-hydroxypyridine would react with compound **1** in a two-step process, co-ordinating initially *via* the pyridone oxygen atom at the equatorial site of the '$C_{10}H_{16}RuCl_2$' unit (as observed in all previous cases of monodentate co-ordination to the $C_{10}H_{16}RuCl_2$ unit[3,4,6,16] and suggested by the ^1H NMR spectrum of the trace product described above). Subsequent deprotonation of such an adduct would then be expected to give a complex possessing a pyridyl ring occupying an axial site, a geometry at variance with that observed crystallographically for [Ru(η³:η³-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)].[5] However, at some stage in the reaction a rearrangement must take place such that the relatively unhindered pyridone oxygen atom of the 2-hydroxypyridinate ligand preferentially occupies the more hindered axial site. This proposal is consistent with the isomerisation of **1** in MeCN solution,[3] where the predominant species is observed to be a monomeric, bridge-cleaved complex with a chloride ligand in the equatorial position and the acetonitrile axially located.

Indirect evidence for an intramolecular rearrangement of a pyridone intermediate in the formation of compound **4** comes from reaction of sodium 2-hydroxypyridinate with **1**. Again the major product (95%, evaluated by integration of the ^1H NMR spectrum) consists of the isomer **4a**, however smaller quantities of a geometric isomer **4b** are also observed. The ^1H NMR data of **4b** are in Table 1. This reaction, which uses the performed anionic ligand, presumably increases the rate of the chelation step such that there is insufficient time for the equatorial–axial rearrangement to occur and hence a significant quantity of the less-stable axial isomer is observed.

In an attempt to confirm the formulation of **4a** and **4b** and synthesise further compounds displaying both axial and equatorial pyridyl fragments, we investigated the reaction of **1** with 6-chloro-2-hydroxypyridine, 2-hydroxy-4-methylquinoline and 2-hydroxy-6-methylpyridine. These ligands contain bulky *ortho* substituents which might be expected to interact unfavourably with the remaining axial chloride ligand in complexes of type **a** and thus may display less preference for the equatorial form. Reaction with the neutral pyridinols was found to be slow at room temperature and significantly more efficient conversions were obtained through use of the sodium salts of the ligands or addition of anhydrous sodium carbonate to the reaction mixtures. In this way compounds of formula [Ru(η³:η³-$C_{10}H_{16}$)Cl{NC_5H_3(O)Cl-6}] **5**, [Ru(η³:η³-$C_{10}H_{16}$)Cl{NC_9H_5(O)Me-4}] **6** and [Ru(η³:η³-$C_{10}H_{16}$)Cl{NC_5H_3(O)Me-6}] **7** were obtained (C,H,N analysis) in good yields. Like **4**, complexes **5**–**7** display no bands attributable to ν(OH) or ν(NH) in their infrared spectra but possess peaks at 1589 (**5**), 1550 (**6**) and 1558 cm^{-1} (**7**) tentatively assigned to ν_{asym}(OCN) as well as peaks arising as a consequence of pyridyl C=C modes[17] (see Experimental section) and bands due to ν(RuCl). The ^1H NMR spectra of these materials proved complex, each possessing two sets of signals, present in a ratio of approximately 3:1 in the case of **5**, 6:1 for **6** and 3:2 for **7**. The spectrum of **5**, for example, displays four singlets for the major product due to terminal allyl protons (δ 5.25, 4.36, 4.27 and 4.96) and two methyl resonances (δ 2.32 and 2.16) and similarly the minor product **5b** displays resonances at δ 4.95, 4.66, 4.56 and 3.73 (terminal allyl) and 2.49 and 2.37 (methyl). These spectra could conceivably be attributed to pairs of diastereoisomers of **5**–**7** if the compounds were dimeric, since binuclear compounds containing two 'η³:η³-$C_{10}H_{16}$Ru' units have been shown to display a total of eight terminal allyl resonances and four methyl signals.[3,18-20] However, electron-impact mass spectra exhibit strong molecular ion peaks at m/z 401 (**5**), 431 (**6**) and 381 (**7**) with isotope distribution patterns consistent with the presence of a single ruthenium atom in each case, implying the formation of mononuclear complexes. The mononuclear nature of **5** was confirmed by a single-crystal X-ray structure determination (see below). Fractional crystallisation of **5** from an acetone solution gave red-brown crystals of a single isomer which was shown to be the major isomer **5a**, by low-temperature dissolution of the crystalline material and simultaneous recording of its ^1H NMR spectrum (193 K). The structure determination (Fig. 1) showed **5a** to be a mononuclear chelate compound, with the nitrogen atom equatorial, closely related to the equatorial structure assigned to **4a**, and observed crystallographically in the case of [Ru(η³:η³-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)].[5] Complex **5b** is therefore assigned a similar structure with the pyridyl nitrogen atom axial. By analogy, similar isomeric structures are assigned to **6a**, **6b** and **7a**, **7b**. The major products are assigned the structures with the nitrogen atoms equatorially co-ordinated, allowing the bulky pyridyl fragments to avoid the axial sites which are sterically crowded by the methyl groups of the bis(allyl), 2,7-dimethylocta-2,6-diene-1,8-diyl ligand.

Good evidence for the equatorial nature of compounds **4a**–**7a** comes from their ^1H NMR spectra which, in common with those of [Ru(η³:η³-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)] and [Ru(η³:η³-$C_{10}H_{16}$)Cl(NC_5H_4S)],[5] have the two central resonances, due to the terminal allyl protons, occurring at very similar chemical shifts. The pattern differs markedly from that observed for **4b**–**7b** and [Ru(η³:η³-$C_{10}H_{16}$)Cl(L–L)][BF_4][15] (L–L = 2,2′-bipyridyl or 1,10-phenanthroline) where one of these resonances is shifted significantly upfield relative to the other three, possibly as a consequence of ring-current effects of the aromatic moiety. Another observation which may serve to distinguish between the two possible isomers is the differences in the resonances assigned to the internal allyl protons. In the case of **4a**–**7a** these

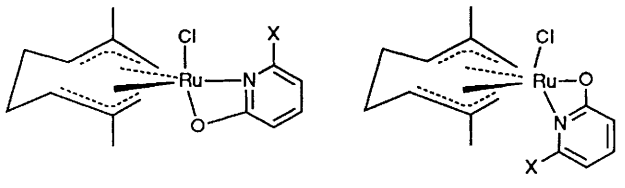
Table 1 Proton NMR data for new complexes[a]

Compound	δ				
	Terminal allyl	Internal allyl	Ethylenic	Me	Ligand
4a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4O)]$ (N equatorial)	5.05 (s, 1 H) 4.24 (s, 1 H) 4.07 (s, 1 H) 3.00 (s, 1 H)	4.19 (m, 1 H) 3.46 (m, 1 H)	2.78 (m, 4 H)	2.38 (s, 3 H) 2.24 (s, 3 H)	8.30 (d, 1 H, ^3J = 5.4) 7.48 (t, 1 H, ^3J = 8.6) 6.66 (t, 1 H, ^3J = 6.0) 5.94 (d, 1 H, ^3J = 8.6)
4b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4O)]$ (O equatorial)	5.24 (s, 1 H) 4.69 (s, 1 H) 4.36 (s, 1 H) 3.24 (s, 1 H)	4.40 (m, 1 H) 3.31 (m, 1 H)	2.78 (m, 4 H)	2.42 (s, 3 H) 2.12 (s, 3 H)	7.43 (t, 1 H)[b] 7.08 (d, 1 H, ^3J = 5.9) 6.32 (t, 1 H, ^3J = 6.1) 6.16 (d, 1 H, ^3J = 8.7)
5a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}]$ (N equatorial)	5.25 (s, 1 H) 4.36 (s, 1 H) 4.27 (s, 1 H) 2.96 (s, 1 H)	4.32 (m, 1 H) 3.59 (m, 1 H)	2.69 (m, 4 H)	2.32 (s, 3 H) 2.16 (s, 3 H)	7.48 (dd, 1 H, ^3J = 8.4, 7.6) 6.62 (d, 1 H, ^3J = 7.6) 5.92 (d, 1 H, ^3J = 8.4)
5b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}]$ (O equatorial)	4.95 (s, 1 H) 4.66 (s, 1 H) 4.56 (s, 1 H) 3.73 (s, 1 H)	4.81 (m, 1 H) 4.56 (t, 1 H, ^3J = 5.4)	2.69 (m, 4 H)	2.49 (s, 3 H) 2.37 (s, 3 H)	7.45 (dd, 1 H, ^3J = 7.6, 8.6) 6.35 (d, ^3J = 7.6) 6.08 (d, ^3J = 8.6)
6a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_9H_5(O)Me\text{-}4\}]$ (N equatorial)	5.31 (s, 1 H) 4.43 (s, 1 H) 4.36 (s, 1 H) 2.97 (s, 1 H)	4.43 (m, 1 H) 3.64 (m, 1 H)	2.76 (m, 4 H)	2.39 (s, 3 H) 2.21 (s, 3 H)	8.49 (d, 1 H, ^3J = 8.4) 7.76 (d, 1 H, ^3J = 8.2) 7.54 (t, 1 H, ^3J = 7.0) 7.28 (t, 1 H, ^3J = 7.0) 6.01 (s, 1 H) 2.54 (s, 3 H, CH_3)
6b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_9H_5(O)Me\text{-}4\}]$ (O equatorial)	5.15 (s, 1 H) 4.80 (s, 1 H) 4.56 (s, 1 H) 3.53 (s, 1 H)	4.62 (t, 1 H, ^3J = 5.6) 4.39 (m, 1 H)	2.65 (m, 4 H)	2.45 (s, 3 H) 2.30 (s, 3 H)	7.73 (d, 1 H, ^3J = 8.2) 7.39 (t, 1 H, ^3J = 7.0) 7.18 (t, 1 H, ^3J = 7.6) 6.88 (d, 1 H, ^3J = 8.4) 6.32 (s, 1 H) 2.52 (s, 3 H, CH_3)
7a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Me\text{-}6\}]$ (N equatorial)	5.21 (s, 1 H) 4.31 (s, 1 H) 4.30 (s, 1 H) 2.91 (s, 1 H)	4.37 (m, 1 H) 3.56 (m, 1 H)	2.73 (m, 4 H)	2.36 (s, 3 H) 2.17 (s, 3 H)	7.28 (dd, 1 H, ^3J = 8.4, 7.6) 6.33 (d, 1 H, ^3J = 7.6) 5.71 (d, 1 H, ^3J = 8.4)
7b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Me\text{-}6\}]$ (O equatorial)	5.10 (s, 1 H) 4.77 (s, 1 H) 4.51 (s, 1 H) 3.70 (s, 1 H)	4.61 (t, 1 H, ^3J = 6.2) 4.14 (m, 1 H)	2.59 (m, 4 H)	2.33 (s, 3 H) 2.11 (s, 3 H)	7.28 (m, 1 H) 6.07 (virtual t, 2 H)
8a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6O)]$ (N equatorial)	4.34 (s, 1 H) 3.98 (s, 1 H) 3.87 (s, 1 H) 2.70 (s, 1 H)	4.95 (AXX′, 1 H, ^3J = 6.2) 4.37 (AXX′, 1 H, ^3J = 5.6)	3.22 (m, 2 H) 2.72 (m, 1 H) 2.64 (m, 1 H)	2.41 (s, 3 H) 2.08 (s, 3 H)	9.28 (dd, 1 H, ^3J = 4.9, ^4J = 1.3) 8.13 (dd, 1 H, ^3J = 8.4, ^4J = 1.2) 7.39 (dd, 1 H, ^3J = 5.0, 5.0) 7.24 (t, 1 H, ^3J = 7.9) 6.85 (d, 1 H, ^3J = 7.9) 6.67 (d, 1 H, ^3J = 8.0)

Table 1 (*continued*)

Compound	δ				
	Terminal allyl	Internal allyl	Ethylenic	Me	Ligand
8b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6O)]$ (O equatorial)	4.87 (s, 1 H) 4.58 (s, 1 H) 4.02 (s, 1 H) 3.09 (s, 1 H)	5.13 (m, 1 H) 4.15 (m, 1 H)	3.22 (m, 2 H) 2.72 (m, 1 H) 2.64 (m, 1 H)	2.54 (s, 3 H) 1.71 (s, 3 H)	7.99 (d, 1 H, ^3J = 8.4) 7.78 (d, 1 H, ^3J = 4.9) 7.36 (t, 1 H, ^3J = 7.9) 7.12 (dd, 1 H, ^3J = 5.0, 5.0) 6.83 (d, 1 H, ^3J = 7.9) 6.67 (d, 1 H, ^3J = 8.0)
9a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_4H_6O)]$ (N equatorial)	5.14 (s, 1 H) 4.25 (s, 1 H) 4.16 (s, 1 H) 2.81 (s, 1 H)	4.06 (m, 1 H) 3.29 (m, 1 H)	2.70 (m, 4 H)	2.29 (s, 3 H) 2.18 (s, 3 H)	3.83 (m, 2 H) 3.38 (t, 4 H, ^3J = 7.0)
9b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_4H_6O)]$ (O equatorial)	5.22 (s, 1 H) 4.63 (s, 1 H) 4.51 (s, 1 H)[d] 3.15 (s, 1 H)[d]	4.32 (m, 1 H) 3.72 (m, 1 H)	2.47 (m, 4 H)	2.36 (s, 3 H) 2.27 (s, 3 H)	3.83 (m, 2 H) 3.38 (t, 4 H, ^3J = 7.0)
10 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NC_9H_6SH)]$	4.85 (s, 2 H) 4.17 (s, 2 H)[d]	5.16 (m, 2 H)	3.24 (m, 2 H) 2.54 (m, 2 H)	2.33 (s, 6 H)	13.96 (s, 1 H, SH) 7.65 (m, 3 H) 7.58 (t, 1 H, ^3J = 7.8) 7.43 (d, 1 H, ^3J = 7.9) 7.38 (t, 1 H, ^3J = 8.1)
11 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\{NC_5H_3(SH)Me\text{-}6\}]$	4.80 (s, 2 H) 4.16 (s, 2 H)[d]	5.09 (m, 2 H)	3.20 (m, 2 H) 2.52 (m, 2 H)	2.29 (s, 6 H)	13.81 (s, 1 H, SH) 7.59 (d, 1 H, ^3J = 8.7) 7.25 (t, 1 H, ^3J = 8.5) 6.56 (d, 1 H, ^3J = 7.0) 2.35 (s, 3 H, CH_3)
12a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)]$ (N equatorial)	5.00 (s, 1 H) 4.57 (s, 1 H) 4.19 (s, 1 H) 3.14 (s, 1 H)	4.88 (m, 1 H) 4.06 (m, 1 H)	2.68 (m, 1 H) 2.49 (m, 3 H)	2.53 (s, 3 H) 2.36 (s, 3 H)	9.35 (d, 1 H, ^3J = 8.6) 7.70 (d, 1 H, ^3J = 8.7) 7.58 (d, 1 H, ^3J = 7.0) 7.56 (t, 1 H, ^3J = 8.7) 7.33 (t, 1 H, ^3J = 8.0) 6.63 (d, 1 H, ^3J = 8.6)
12b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)]$ (S equatorial)	4.95 (s, 1 H) 4.49 (s, 1 H) 4.31 (s, 1 H) 3.45 (s, 1 H)	4.63 (m, 1 H) 4.43 (m, 1 H)	2.68 (m, 1 H) 2.49 (s, 3 H)	2.46 (s, 3 H) 2.05 (s, 3 H)	7.70 (d, 1 H)[b] 7.56 (m, 2 H) 7.50 (t, 1 H, ^3J = 6.9) 7.30 (d, 1 H, ^3J = 8.7) 6.71 (d, 1 H, ^3J = 8.8)
13a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(S)Me\text{-}6\}]$ (N equatorial)	4.91 (s, 1 H) 4.45 (s, 1 H) 4.15 (s, 1 H) 3.10 (s, 1 H)	4.79 (m, 1 H) 3.96 (m, 1 H)	2.36 (m, 4 H)	2.64 (s, 3 H) 2.31 (s, 3 H)	7.20 (t, 1 H, ^3J = 7.8) 6.49 (d, 1 H, ^3J = 7.6) 6.43 (d, 1 H, ^3J = 8.2) 2.48 (s, 3 H, CH_3)
13b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(S)Me\text{-}6\}]$ (S equatorial)	5.02 (s, 1 H) 4.88 (s, 1 H) 4.65 (s, 1 H) 3.88 (s, 1 H)	5.02 (t, 1 H, ^3J = 3.9) 4.66 (m, 1 H)	2.72 (m, 2 H) 2.58 (m, 2 H)	2.79 (s, 3 H) 2.48 (s, 3 H)	7.79 (t, 1 H, ^3J = 7.9) 7.25 (m, 2 H) 2.48 (s, 3 H, CH_3)

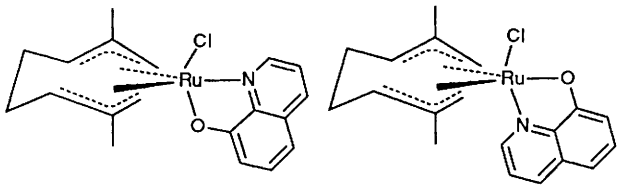
[a] In $CDCl_3$, s = singlet, d = doublet, J(H–H) in Hz, t = triplet, m = multiplet. [b] Coupling constant unmeasurable due to overlapping signals of major isomers [c] Solvent $(CD_3)_2CO$. [d] Singlets noticeably broader than those arising from other terminal allyl protons on the same molecule.



X = H(4), Cl(5), Me(7)

Equatorial isomer (type **a**) Axial isomer (type **b**)

4a **4b**
5a **5b**
7a **7b**



8a **8b**

occur as two broad, poorly resolved, singlet-like resonances at δ *ca.* 4.3 and 3.5. Conversely, the spectra of **4b**–**7b** display the corresponding resonances as much sharper signals at δ *ca.* 4.7 and 4.2 4.5, one occurring as a virtual triplet and the other as a well resolved five-line multiplet.

To confirm these observations the reaction of compound **1** with 8-hydroxyquinoline (NC_9H_6OH) was examined, Both isomers resulting from this reaction might be expected to possess an aromatic ring in the axial site and so display ^1H NMR spectra typical of type **b** compounds. Two products were indeed obtained, $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6O)]$ **8a**, **8b** although, presumably due to the relatively unhindered nature of the ligand, the isomer ratio was in excess of 20:1 (in retrospect an unsurprising result given the observation of only a single isomer of **4** arising from reaction with the neutral ligand). The mononuclear nature of these materials was confirmed by a FAB mass spectrum. The ^1H NMR spectra of both materials displayed the expected four-line patterns for the terminal allyl protons [δ 4.34, 3.98, 3.87 and 2.70 (major isomer **8a**); 4.87, 4.58, 4.02 and 3.09 (minor isomer **8b**)] which are qualitatively similar to those of type **b** complexes. The signals attributed to the internal allyl protons occurred as sharp resonances strongly resembling those observed for the cationic bipyridine and phenanthroline complexes.[15] Logically, and by analogy with **4a**, **4b**, the major product will be of the N-equatorial, O-axial type. Evidence for this comes from the consistent upfield shift of the signals due to the allyl protons of the major isomer relative to the minor one, presumably as a consequence of the closer proximity of the aromatic ring to the bis(allyl) ligand when the pyridyl fragment occupies the axial site.

Reaction of compound **1** with α-pyrrolidinone, HNC_4H_6O, also gives rise to an axial and an equatorial isomer, related to **5**–**7**, namely $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_4H_6O)]$ **9a**, **9b**. The solid-state infrared spectrum of **9** displays strong, broad peaks at 1540 and 1407 cm^{-1} (signals due to individual isomers not resolved) corresponding to the antisymmetric and symmetric ν(OCN) modes [in this particular case the assignment may be made with confidence due to the absence of pyridyl ν(C=C) bands]. The ^1H NMR data are in Table 1. The major product (present in a ratio of approximately 5:2) displays a pattern of four terminal allyl proton resonances characteristic of an equatorial isomer. The relatively abundant minor isomer exhibits a spectrum similar to those of complexes of type **b**, although in the absence of an aromatic ring the distinction is less obvious. Clearly isomerism in **9** is unlikely to be a consequence of unfavourable steric interactions between the chloride ligand and bulky *ortho* ring substituents which are absent in this case. The formation of substantial quantities of the axial isomer is rather attributed to the stereochemical non-rigidity of the saturated five-membered ring of the hydroxypyrrolidinate ligand which allows the relief of otherwise unfavourable steric interactions between the co-ordinated ligands.

Reactions with Pyridine-2-thiols.—Sterically hindered ligands such as 6-chloro-2-hydroxypyridine, 2-hydroxy-4-methylquinoline and 2-hydroxy-6-methylpyridine are often observed to bridge across two metal centres[21] rather than form strained four-membered chelate rings. Nevertheless we have described above how the reaction of compound **1** with these ligands leads to the formation of mononuclear complexes **5**–**7**. We reasoned though that reaction of **1** with ligands containing larger donor atoms such as sulfur, as well as a sterically hindering *ortho* substituent, might lead to the formation of bridged, binuclear complexes. It should be noted however that pyridine-2-thiol has already been observed to form a mononuclear compound on reaction with **1**,[5] this mode of co-ordination being attributed to the slowness of the deprotonation step relative to the rate of co-ordination of the ligand in a monodentate fashion *via* the pyridyl nitrogen atom.[5]

We have now investigated the reaction of the more hindered pyridinethiols, quinoline-2-thiol and 6-methylpyridine-2-thiol and of their sodium salts with compound **1** in an attempt to prepare binuclear species. The reactions involving the free ligands gave only mononuclear bridge-cleaved species $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NC_9H_6SH)]$ **10** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NC_5H_3MeSH)]$ **11** in which the ligands are probably co-ordinated in a monodentate fashion *via* the pyridyl nitrogen atom, by analogy with $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(N_2C_7H_5S)]$ and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4S)]$.[5] The infrared spectra (Nujol) of both of these complexes display several strong bands in the region 1600–1400 cm^{-1} corresponding to ν(C=C) and ν(C=N) ring modes, and ν(RuCl) bands are observed at 316, 289 and 317, 297 cm^{-1} for **10** and **11** respectively. No bands unambiguously assignable to ν(SH) or ν(NH) were seen, as was the case in Toerien and van Rooyen's study.[5] Reaction of **1** with the preformed sodium salt of quinoline-2-thiol led to a species displaying a ^1H NMR spectrum containing a four-line pattern for the terminal allyl protons (δ 5.00, 4.57, 4.19 and 3.14), which was difficult unambiguously to assign to either axial or equatorial co-ordination but consistent with the chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)]$ **12a**. The internal allyl resonances, which consist of two narrow multiplets, occurring at δ 4.88 and 4.06, imply equatorial co-ordination. The solid-state infrared spectrum of **12a** (KBr disc) displays similar bands to **10** at 1608, 1589, 1498 and 1421 cm^{-1}. In addition, two bands of medium intensity are observed at 1545 and 1448 cm^{-1} and are tentatively assigned to ν(S–C=N). The Nujol spectrum displays ν(RuCl) 303 cm^{-1} and the FAB mass spectrum exhibits a strong molecular ion peak at *m/z* 433 along with fragmentation peaks consistent with the proposed structure. A quantity of a second isomer **12b** was also observed (**12a**:**12b** 5:1). A single-crystal X-ray structure determination (Fig. 2) revealed a complex possessing an equatorial structure, very similar to that of **5a** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(N_2C_7H_5S)]$.[5] Low-temperature dissolution of the crystalline sample and simultaneous recording of its ^1H NMR spectrum showed this structure to represent **12a**, the form strongly predominant in solution.

The relationship between the mode of ligand co-ordination and the ^1H NMR spectral pattern is less well defined for the pyridinethiolate complexes than it was for hydroxypyridinates, especially in terms of the positions of the terminal allyl resonances {the anomaly is, to some extent, shared by the pyridine-2-thiolate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4S)]$[5]} to the extent that it is not possible unambiguously to assign structure for a given isomer in isolation.

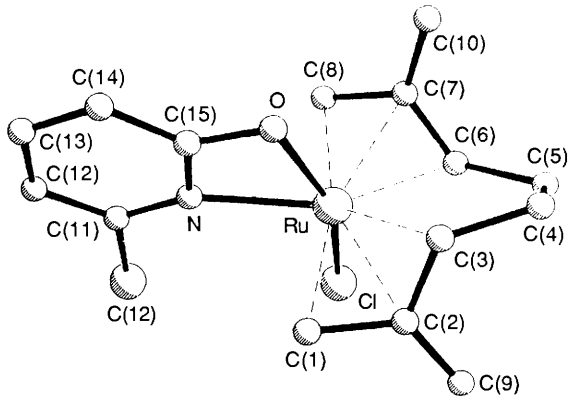


Fig. 1 Molecular structure of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}]$ **5a** showing the atom numbering scheme adopted

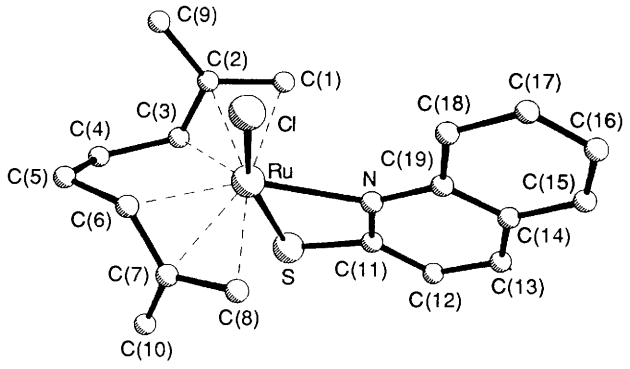


Fig. 2 Molecular structure of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)]$ **12a** showing the atom numbering scheme adopted

Table 2 Fractional atomic coordinates ($\times 10^4$) for $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}]$ **5a**

Atom	*x*	*y*	*z*
Ru	1896(1)	3798	5763(1)
Cl(1)	2024(3)	5845(2)	5592(2)
Cl(2)	−1071(6)	5917(4)	7002(2)
N	88(6)	3826(12)	6687(4)
O	1224(11)	2211(7)	6259(4)
C(1)	−608(10)	3783(15)	5139(4)
C(2)	800(10)	3695(12)	4615(4)
C(3)	1904(12)	2728(8)	4757(6)
C(4)	3572(15)	2528(12)	4347(5)
C(5)	4938(12)	3403(10)	4566(6)
C(6)	4596(10)	3930(12)	5312(5)
C(7)	4638(13)	3283(10)	5981(6)
C(8)	3977(10)	3926(14)	6596(4)
C(9)	1113(14)	4573(11)	4045(6)
C(10)	5103(19)	2038(12)	6050(7)
C(11)	−924(13)	4446(12)	7145(6)
C(12)	−1843(13)	3941(25)	7705(6)
C(13)	−1728(18)	2740(19)	7782(7)
C(14)	−710(18)	2108(13)	7319(6)
C(15)	202(17)	2650(11)	6744(6)

A comparison of the spectra of two isomers of the same compound may however provide a worthwhile indication as to the likely geometry.

Reaction of compound **1** with the sodium salt of 6-methylpyridine-2-thiol also led to mononuclear species (FAB mass spectrum, molecular ion *m/z* 397), $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(S)Me\text{-}6\}]$ (**13a**, **13b**; ratio 1:3), directly analogous to **7a**, **7b**.

Isomer Ratios.—If a model invoking two sets of competing steric interactions (*i*) between axial ligand fragments and dimethyloctadienediyl methyl substituents and (*ii*) between *ortho*-pyridyl substituents and axial chloride ligands is assumed it becomes possible to rationalise the preferences in isomer ratio. The unsubstituted 2-hydroxypyridinate and pyridine-2-thiolate[5] ligands display uniquely equatorial pyridyl coordination (type **a**). When bulky ring substituents are introduced *ortho* to the pyridyl nitrogen atom (*e.g.* complexes **5**–**7**) the interactions of these substituents with the axial chloride ligands destabilise the type **a** form relative to **b** and thus two isomers are observed. The axial (type **b**) form would thus be expected to become more predominant as the size of the ring substituent increases. This argument is qualitatively compatible with the observed isomer ratios for complexes **4**–**7**.

In the case of **13a**, **13b** the isomer ratio was observed to be 1:3, *i.e.* for **13** it is the N_{axial} (type **b**) form which predominates. Evidence for this comes from the allyl region of the ^1H NMR spectra of **7** and **13**. The terminal allyl signals for the *major* isomer in the spectrum of **13** display a grouping characteristic of

Table 3 Fractional atomic coordinates ($\times 10^4$) for $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)]$ **12a**

Atom	*x*	*y*	*z*
Ru	2539(1)	842(1)	2926(1)
S	1601(2)	1212(2)	4190(1)
Cl	3717(2)	−113(2)	1950(1)
N	2364(5)	−601(4)	3765(4)
C(1)	619(7)	211(6)	1946(5)
C(2)	936(7)	1167(6)	1551(5)
C(3)	1014(6)	2061(6)	2170(5)
C(4)	1517(8)	3168(6)	2016(6)
C(5)	2973(8)	3144(6)	2016(5)
C(6)	3727(7)	2185(5)	2593(5)
C(7)	4069(6)	2102(6)	3618(5)
C(8)	4567(7)	1101(6)	4000(6)
C(9)	1208(9)	1233(7)	580(5)
C(10)	3841(8)	2997(6)	4239(6)
C(11)	1892(6)	−144(6)	4435(4)
C(12)	1653(8)	−696(6)	5195(5)
C(13)	1894(8)	−1765(7)	5265(5)
C(14)	2342(7)	−2304(6)	4565(6)
C(15)	2555(9)	−3421(7)	4580(7)
C(16)	2954(10)	−3910(7)	3892(8)
C(17)	3155(8)	−3325(7)	3136(7)
C(18)	2959(8)	−2217(6)	3092(6)
C(19)	2561(7)	−1715(5)	3801(5)

Table 4 Selected bond lengths (Å) and angles (°) for compound **5a**

Ru–Cl(1)	2.381(3)	Ru–C(1)	2.219(8)
Ru–O	2.099(8)	Ru–C(2)	2.239(8)
Ru–N	2.166(6)	Ru–C(3)	2.195(10)
O–C(15)	1.278(14)	Ru–C(6)	2.222(8)
N–C(15)	1.361(18)	Ru–C(7)	2.211(10)
Cl(2)–C(11)	1.718(15)	Ru–C(8)	2.193(8)
Cl(1)–Ru–N	96.4(4)	Ru–O–C(15)	95.6(7)
Cl(1)–Ru–O	158.1(2)	Ru–N–C(15)	90.2(7)
N–Ru–O	61.9(4)	N–C(15)–O	112.4(10)

Table 5 Selected bond lengths (Å) and angles (°) for compound **12a**

Ru–Cl	2.461(2)	Ru–C(1)	2.209(6)
Ru–S	2.386(2)	Ru–C(2)	2.206(6)
Ru–N	2.221(5)	Ru–C(3)	2.229(6)
S–C(11)	1.741(7)	Ru–C(6)	2.231(7)
N–C(11)	1.351(9)	Ru–C(7)	2.245(6)
		Ru–C(8)	2.225(7)
Cl–Ru–N	93.7(2)	Ru–S–C(11)	83.2(3)
Cl–Ru–S	160.0(1)	Ru–N–C(11)	99.5(4)
N–Ru–S	67.0(2)	N–C(11)–S	110.2(5)

an axial isomer with three signals between δ 4.5 and 5 and the other one shifted upfield to δ 3.88 (*cf.* **7b**, δ 5.10, 4.77, 4.51 and 3.70). The signals for the minor isomer are much more evenly distributed (δ 4.91, 4.45, 4.15 and 3.10; *cf.* **7a**, 5.21, 4.31, 4.30 and 2.91). Turning to the internal allyl proton resonances, **4a**, **5a** and **7a** (equatorial isomers) display poorly resolved, singlet-like multiplets (δ 4.19 and 3.46, **4**: 4.32 and 3.59 ppm, **5a**; 4.37 and 3.56, **7a**) as does the *minor* product in the case of **13** (δ 4.79 and 3.96), although the actual values are shifted downfield by 0.5 ppm (an observation consistent with most of the other signals on moving to the sulfur donor atom of the pyridinethiolate ligand). In contrast the corresponding signals for **5b** and **7b** occur as a sharp triplet and sharp, five-line multiplet pair (δ 4.81 and 4.56, **5b**; 4.61 and 4.14, **7b**) as do the corresponding resonances for the major isomer in the case of **13**, again with an overall downfield chemical shift (δ 5.02 and 4.66).

Complete proof of these deductions on the identity of **13a**, **13b** must await a single-crystal X-ray structure determination and concomitant low-temperature NMR experiment, but the evidence would seem to point towards a consistent relationship between equatorial:axial isomer ratio and the relative magnitudes of the various steric interactions.

X-Ray Structure Determinations.—The crystal structures of compounds **5a** and **12a** are shown in Figs. 1 and 2, and fractional atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3, and, 4 and 5. The details of the structure solutions and refinement are in the Experimental section. As observed in previous structures containing the '(η^3:η^3-$C_{10}H_{16}$)Ru' unit[2,4–6,8,19] the geometry about the ruthenium ions in both **5a** and **12a** is conveniently described as a distorted trigonal bipyramid, although a pentagonal-bipyramidal description can also be justified in this type of bis(allyl)-ruthenium(IV) system.[22] The 2,7-dimethylocta-2,6-diene-1,8-diyl ligand shows the usual local C_2 symmetry and there is no significant variation in the Ru–C distances. The ruthenium chloride distances in **5a** and **12a** are 2.381(3) and 2.461(2) Å respectively. The former is similar to that observed for $Ru-Cl_{terminal}$ (2.386 Å) in the parent chloro-bridged dimer[8] but rather shorter than the norm for other (η^3:η^3-$C_{10}H_{16}$)Ru systems (2.40–2.42 Å).[4–6] It is similar to that observed in [Ru(η^6-C_6H_6)Cl{NC_5H_3(O)Me-6}][12] [2.392(2) Å]. The longer Ru–Cl bond in **12a** may be attributed to the *trans* effect of the sulfur donor atom. The ruthenium–oxygen distance is rather short in **5a** [2.099(8) when compared to 2.120(5)[12] and 2.153(6) Å[14] in related ruthenium(II) arene systems] whereas the ruthenium–nitrogen distance is somewhat longer [2.166(6) as against 2.091(5)[12] and 2.084(7) Å].[14] In general the structure of **5a** is closely related to that of [Ru(η^6-C_6H_6)Cl{NC_5H_3(O)Me-6}][12] with one important difference. In the latter structure the *ortho*-methyl group possesses apparently little stereochemical consequence and resides on the opposite side of the molecule to the chloride ligand. The more sterically demanding nature of the bis(allyl) ligand in **5a** causes the chloride ligand and the *o*-chloride ring substituent to lie virtually eclipsed with one another (the pyridyl ring is inclined at 6.2° to the plane containing the chlorine, nitrogen and oxygen atoms), the chlorine–chlorine non-bonded distance being 3.48(1) Å. As a result the Ru–N–C(11) angle is opened up to 149(1)°, compared to 143.4(5)° in the case of **3**[12] and 124(1)° when the 2-hydroxy-6-methylpyridinate ion is in the less sterically demanding bridging mode,[21] and is indicative of significant strain in the complex. Steric strain in the complex is also apparent in the very large Cl(1)–Ru–N angle 96.4(4)°. In undistorted structures this angle averages *ca.* 85°[1,4] and indeed the Cl–Ru–S angle in [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-SCN)}$_2$][20] is only 80.3(1)°. Values of 88.6(3)° in [Ru(η^3:η^3-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)][5] and 90.3(1)° in [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl$_2$}$_2$(μ-dppm)] [dppm = bis(diphenylphosphino)methane][6] have been found.

The steric strain in this complex is a significant contributory factor in the observation of appreciable quantities of the axial isomer **5b**, where no strong chlorine–chlorine interactions would be apparent. However, resulting steric interactions between the bis(allyl) ligand and the chloride substituent in **5b** mean that **5a** is still the predominant isomer observed.

For compound **12a** the Ru–S distance [2.386(2) Å] is significantly shorter than the equivalent distances in [Ru(η^3:η^3-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)][5] [2.425(4) Å] and in [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-SCN)}$_2$][19] [2.490(4) Å] (where the sulfur atom occupies the equatorial site). In the former case a geometrical factor may be involved since the sulfur atom in **12a** is attached to a six-membered ring, as opposed to a five-membered one in the $N_2C_7H_5S$ complex. This is also reflected in the angle Cl–Ru–S which is opened out to 160.0(1)° compared to 156.4(1)° in [Ru(η^3:η^3-$C_{10}H_{16}$)Cl($N_2C_7H_5S$)].[5] The ruthenium–nitrogen distance, 2.221(5) Å, is remarkably long when compared to the bond lengths noted above (2.09–2.16 Å) and probably, like the long Ru–Cl distance, is a reflection of the better donor properties of the sulfur atom and also perhaps its greater bulk.

Conclusion

In spite of the use of preformed salts of ligands expected to bring about bridged, binuclear complexation, only mononuclear species have been observed. It has been shown that ligands related to 2-hydroxypyridine show two distinct chelate co-ordination geometries when bound to the 'η^3:η^3-$C_{10}H_{16}Ru^{IV}$' moiety. These isomers may be distinguished from one another by analysis of the allyl regions of their ^{1}H NMR spectra. By variation of the substitution of the *ortho* site of the ligand and the donor atoms it is possible selectively to synthesise a predominance of either co-ordination geometry.

Experimental

Instrumental.—The IR spectra were recorded on a PE983 grating spectrometer between 4000 and 200 cm^{-1} as either KBr disks or Nujol mulls on CsI plates, NMR spectra on a Varian VXR400 spectrometer. Microanalyses were carried out by the departmental service at University College London. Mass spectra were run by the University of London Intercollegiate Research Service (ULIRS) at the School of Pharmacy. All manipulations were carried out under nitrogen with degassed solvents using conventional Schlenk-line techniques, although no significant air sensitivity of the products was noted.

Starting Materials.—The compound [{Ru(η^3:η^3-$C_{10}H_{16}$)-Cl(μ-Cl)}$_2$] was prepared by published literature methods[3,5,7] by prolonged heating of ruthenium trichloride in ethanol in the presence of a large excess of isoprene. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by dissolution in water and boiling to dryness. Sodium salts were prepared from reaction of sodium metal with the relevant ligand in dry tetrahydrofuran (thf), or in the neat ligand. All other reagents and materials were obtained from the usual commercial sources, with the exception of 6-methylpyridine-2-thiol which was synthesised by the literature method.[23,24]

Preparations.—[Ru(η^3:η^3-$C_{10}H_{16}$)Cl(NC_5H_4O)] **4**. The compound [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.0970 g, 0.157 mmol) was dissolved in dichloromethane (5 cm^3) and 2-hydroxypyridine (0.1018 g, 1.070 mmol) added. After stirring for 5 h the reaction mixture was evaporated to *ca.* $\frac{1}{4}$ volume and the solution diluted with hexane (5 cm^3). The product separated on standing at *ca.* 250 K for 1 h and was filtered off and washed with hexane. Yield: 0.0844 g, 0.230 mmol, 73% (Found: C, 49.70; H, 5.70; Cl, 10.80; N, 4.50. Calc. for $C_{15}H_{20}ClNORu$: C, 49.10; H, 5.50; Cl, 9.70; N, 3.80%). Infrared: ν_{asym}(OCN) 1596, ν(RuCl) 317 cm^{-1}. The product may also be prepared more cleanly, in comparable yield, by suspension of **1** in acetone (5 cm^3) and

addition of sodium 2-hydroxypyridinate. The reaction mixture was stirred for 5 h during which time it changed from pink to orange and the starting material was taken up into solution. The mixture was filtered over Celite and evaporated to an oil. This oil was dissolved in diethyl ether (1 cm^3) and layered with hexane (1 cm^3) from which the product separated as orange crystals after 12 h.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}$] **5**. The compound [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2$] (0.0728 g, 0.118 mmol) was suspended in acetone (5 cm^3) and sodium 6-chloro-2-hydroxypyridinate (0.0366 g, 0.242 mmol) added. The reaction mixture was stirred for 36 h during which time it changed from pink to orange and the starting material was taken up into solution. The mixture was filtered over Celite and evaporated to an oil. This oil was dissolved in diethyl ether (1 cm^3) and layered with hexane (1 cm^3) from which the product separated as deep red crystals after 12 h. Yield: 0.0452 g, 0.113 mmol, 48% (Found: C, 44.85; H, 4.50; N, 3.35. Calc. for $C_{15}H_{19}Cl_2NORu$: C, 44.90; H, 4.75; N, 3.50%). Infrared: 1589, 1437; ν(RuCl) 312 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_9H_5(O)Me\text{-}4\}$] **6**. Following a procedure analogous to that described for **5** using sodium 2-hydroxy-4-methylquinolinate an orange-yellow powder was isolated. Yield: 0.104 g, 0.241 mmol, 67% (Found: C, 56.15; H, 6.15; N, 2.85. Calc. for $C_{20}H_{24}ClNORu$: C, 55.75; H, 5.60; N, 3.25%). Infrared: 1657, 1600, 1550, 1507, 1465, 1446, 1416, 1403; ν(RuCl) 310 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Me\text{-}6\}$] **7**. The compound [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2$] (0.0920 g, 0.149 mmol) was dissolved in dichloromethane (5 cm^3) and 2-hydroxy-6-methylpyridine (0.0325 g, 0.298 mmol) added. The mixture was stirred with $Na_2[CO_3]$ (0.05 g, excess) for 24 h during which time an orange colouration was observed to form. The reaction mixture was filtered over Celite and the filtrate evaporated to an orange oil. The product was obtained as orange crystals by recrystallisation from diethyl ether. Yield: 0.0831 g, 0.218 mmol, 73% (Found: C, 50.30; H, 5.80; N, 3.55. Calc. for $C_{14}H_{22}ClNORu$: C, 50.45; H, 5.80; N, 3.70%). Infrared: 1558, 1464; ν(RuCl) 322 cm^{-1}. The complex was also synthesised in similar yield by use of the sodium salt of the ligand in a similar way to that outlined for **4**.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6O)$] **8**. The compound [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2$] (0.0744 g, 0.121 mmol) was suspended in acetone (5 cm^3) and 8-hydroxyquinoline (0.0361 g, 0.249 mmol) added. The reaction mixture was stirred for 2 h in the presence of $Na_2[CO_3]$ (0.05 g, excess) during which time it changed from pink to orange and the starting material was taken up into solution. The mixture was filtered over Celite and evaporated to an oil which was recrystallised from diethyl ether to give an orange product. Yield: 0.0750 g, 0.180 mmol, 74% (Found: C, 54.40; H, 5.65; N, 3.40. Calc. for $C_{19}H_{22}ClNORu$: C, 54.75; H, 5.30; N, 3.35%). Infrared: 1591, 1562, 1493; ν(RuCl) 318 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_4H_6O)$] **9**. The compound [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2$] (0.1185 g, 0.192 mmol) was dissolved in dichloromethane (5 cm^3) and α-pyrrolidinone (0.05 cm^3, 0.6 mmol) added. The mixture was stirred with $Na_2[CO_3]$ (0.05 g, excess) for 24 h during which time a dark colouration was observed. The reaction mixture was filtered over Celite and the filtrate evaporated to an oil. The product was obtained as yellow crystals by recrystallisation from diethyl ether. Yield: 0.0280 g, 0.078 mmol, 20% (Found: C, 45.85; H, 6.50; N, 4.00. Calc. for $C_{14}H_{22}ClNORu$: C, 47.10; H, 6.20; N, 3.95%). Infrared: ν(OCN) 1540, 1407; ν(RuCl) 313 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NC_9H_6SH)$] **10**. The compound [$\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2$] (0.1064 g, 0.173 mmol) was suspended in acetone (5 cm^3) and quinoline-2-thiol (0.0557 g, 0.345 mmol) added. The reaction mixture was stirred for 3 h during which time it changed from pink to orange and the starting material was taken up into solution. The mixture was filtered and evaporated to *ca.* $\frac{1}{4}$ volume. Diethyl ether (4 cm^3) was added and the product obtained as an orange precipitate. Yield: 0.0870 g, 0.185 mmol, 53% (Found: C, 48.60; H, 4.75; N, 2.90. Calc. for $C_{19}H_{23}Cl_2NRuS$: C, 48.60; H, 4.95; N, 3.00%). Infrared: 1617, 1585; ν(RuCl) 289, 316 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\{NC_5H_3(SH)Me\text{-}6\}$] **11**. Following a procedure analogous to that outlined for compound **10** above using 6-methylpyridine-2-thiol over a period of 24 h an orange-brown product was obtained. Yield: 0.0817 g, 0.205 mmol, 88% (Found: C, 43.35; H, 5.05; N, 2.60. Calc. for $C_{16}H_{23}Cl_2NRuS$: C, 44.30; H, 5.35; N, 3.25%). Infrared: 1612, 1589; ν(RuCl) 297, 317 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)$] **12**. Following a procedure analogous to that described for compound **5** using sodium quinoline-2-thiolate an orange-brown powder was isolated. Yield: 0.050 g, 0.115 mmol, 46% (Found: C, 52.10; H, 5.15; N, 3.20. Calc. for $C_{19}H_{22}ClNRuS$: C, 52.70; H, 5.10; N, 3.25%). Infrared: ν(C=C) 1608, 1589, 1498, 1421; ν(S–C=N) 1545, 1448; ν(RuCl) 303 cm^{-1}.

[$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(S)Me\text{-}6\}$] **13**. Following a procedure analogous to that described for compound **5** using sodium 6-methylpyridine-2-thiolate an orange-brown powder was isolated. Yield: 0.045 g, 0.124 mmol, 66% (Found: C, 48.50; H, 6.10; N, 2.95. Calc. for $C_{16}H_{22}ClNRuS$: C, 48.40; H, 5.60; N, 3.50%). Infrared: 1597, 1583, 1545; ν(RuCl) 303 cm^{-1}.

X-Ray Crystal Structure Determinations.—(*i*) [$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}$] **5a**. *Crystal data.* $C_{15}H_{19}Cl_2NORu$, M = 401.32, orthorhombic, space group $Pc2_1n$, a = 7.636(3), b = 11.519(3), c = 18.054(8) Å, U = 1588 $Å^3$ (by least-squares refinement of diffractometer angles for 32 automatically centred reflections in the range $14 \leqslant 2\theta \leqslant 24°$, λ = 0.710 73 Å), $F(000)$ = 808, D_c = 1.68 g cm^{-3}, μ(Mo-Kα) = 13.0 cm^{-1}, Z = 4. Orange block, 0.35 × 0.20 × 0.20 mm.

Data collection and processing. Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. The ω–2θ technique was used to collect a data set ($+h,+k,+l$) consisting of 1715 reflections in the range $5 \leqslant 2\theta \leqslant 50°$. Of the 1455 unique data 1302 were observed to have $I \geqslant 1.5\sigma(I)$ and used in structure solution and refinement. Three standard reflections monitored throughout the data collection showed no appreciable change in intensity. The data were corrected for Lorentz and polarisation effects and for absorption, from additional azimuthal scan data (maximum, minimum transmission 0.903, 0.818).

Structure solution and refinement. The structure was solved by conventional direct methods and Fourier difference techniques. Refinement was attempted in the orthorhombic space groups $Pcmn$ and $Pc2_1n$ and proceeded most smoothly in the latter, the asymmetric unit being observed to contain one complete molecule. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions with a common isotropic thermal parameter [r(CH) 0.96 Å, U_{iso} 0.08 $Å^2$]. Full-matrix least-squares refinement gave R = 0.0386, R' = 0.0439 in the final cycle from 180 parameters. A weighting scheme $w^{-1} = \sigma^2(F) + 0.003\,058F^2$ was applied and the maximum shift/e.s.d. in the final cycle was 0.03. The largest residual peak was 0.51 e $Å^{-3}$. No short intermolecular contacts were observed.

(*ii*) [$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_9H_6S)$] **12a**. *Crystal data.* $C_{19}H_{22}ClNRuS$, M = 433.0, monoclinic, space group $P2_1/c$, a = 10.434(3), b = 12.518(2), c = 14.561(4) Å, β = 108.30(2)°, U = 1805.6 $Å^3$ (by least-squares refinement of diffractometer angles for 29 reflections in the range $13 \leqslant 2\theta \leqslant 28°$, λ = 0.710 73 Å), $F(000)$ = 880, D_c = 1.59 g cm^{-3}, μ(Mo-Kα) = 11.1 cm^{-1}, Z = 4. Orange block, 0.50 × 0.40 × 0.25 mm.

Data collection and refinement. As described above. A total of 3491 reflections were collected ($+h,+k,\pm l$). Of the 3148 unique data 2314 were observed [$I \geqslant 3\sigma(I)$] and employed in structure solution and refinement. An absorption correction was applied (maximum, minimum transmission 0.955, 0.725).

Structure analysis and refinement. Direct methods followed by alternating cycles of least-squares refinement and Fourier-

difference analysis. Non-hydrogen atoms anisotropic. Hydrogen atoms were placed in idealised positions, r(CH) 0.96 Å, and a common isotropic thermal parameter, U_{iso}, refined to 0.090(6) Å^2. Full-matrix least-squares refinement gave $R = 0.0435$, $R' = 0.0503$ in the final cycle from 209 parameters. A weighting scheme of $w^{-1} = \sigma^2(F) + 0.003\,564F^2$ was applied and the maximum shift/e.s.d. in the final cycle was 0.06. The largest residual peak was 0.90 e Å^{-3} associated with the ruthenium atom.

All calculations were carried out using the SHELXTL PLUS[25] program package on a MicroVax II computer.

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

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