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# THE ALKYLATION OF SOME RUTHENIUM(II) COMPLEXES OF AMBIDENT HETEROCYCLIC LIGANDS

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## Summary

The reactions of the complexes [Ru(diene)$L_2$] (HL = heterocyclic thiol) with methyl iodide have been investigated. The products are the iodide-bridged dimers [{(diene)LRu($\mu$-I)}$_2$] and the *S*-alkylated derivative LMe. No thioether complexes could be isolated from these reactions.

Although it is well-established that the reactivity of heterocyclic ligands may be modified by coordination to a transition metal [1,2,3], there have been few studies of the behaviour of substituted heterocycles. We have recently become interested in complexes of 2(1*H*)-pyridinethione (**1**) and 2(1*H*)-pyrimidinethione (**2**), compounds which can act as monodentate N or S donors, and also as bidentate bridging or chelating ligands [4,5,6]. We considered that this ambident behaviour might also be reflected in the reactions of such complexes with electrophiles, and we report herein a study of the alkylation of the complexes [Ru(diene)$L_2$] with methyl iodide.

The complexes [Ru(diene)$L_2$] (diene = 1,5-cyclooctadiene, cod; or bicyclo-[2.2.1]hepta-1,4-diene, nbd; HL = 2(1*H*)-pyridinethione or 2(1*H*)-pyrimidinethione) were prepared as yellow needles by the reaction of [{Ru(diene)$Cl_2$}$_n$] [7] with excess HL in dmf in the presence of anhydrous sodium carbonate [8]. Satisfactory elemental analyses and electron-impact mass spectra were obtained for each of the four compounds. As reported previously [8], the product obtained in each case consisted exclusively of only one of the possible isomers of [Ru(diene)$L_2$], and a TLC examination of the mother liquors failed to reveal the presence of any other isomers. The $^1$H NMR spectra of these complexes were recorded in a variety of solvents ($CDCl_3$, $CD_2Cl_2$ or $CD_3OD$) and at a variety of magnetic fields (80, 90, 250 and 400 MHz), and in each case a single set of resonances due to the protons on the heterocyclic ring were obtained. This is consistent only with the molecular $C_2$ symmetry in the complexes **3** or **4**. The crystal structure of the complex [$(Ph_3P)_2$Ru(2-pyS)$_2$] has been reported [9], and the molecule shown to possess a

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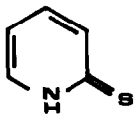

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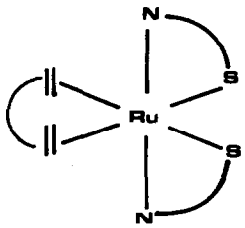

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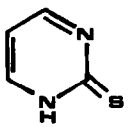

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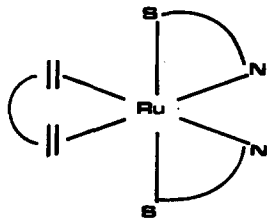

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highly distorted octahedral geometry in which the sulphur atoms are mutually *trans*, i.e. of type **4**.

Figure 1 shows the 250 MHz spectrum of the complex [Ru(nbd)(2-pyS)$_2$], and clearly demonstrates the non-equivalence of the olefinic protons arising from the molecular $C_2$ symmetry. The protons of the bicyclo[2.2.1]hepta-1,4-diene analyse as an $(ABCM)_2$ set, with the two protons of the bridgehead $CH_2$ group appearing equivalent. The spectrum of the cycloocta-1,5-diene complexes is considerably more complex, and the 250 MHz spectrum of diene resonances in [Ru(cod)(2-pyS)$_2$] is shown in Fig. 2.

A molecular model of [Ru(nbd)(2-pyS)$_2$] constructed using the Ru–S and Ru–N distances from ref. 9, and an idealised Ru–olefin distance of 2.1 Å indicated that a structure of type **3** would exhibit a severe steric interaction between H(6) of the pyridine and an olefinic proton (closest approach < 2.0 Å). This in itself suggests that structure **4**, in which there are no such close contacts, might be favoured, and we considered that structure **3** was less likely.

A structure of type **3** would be expected to show strong NOE effects from H(6) of the pyridine to *one* of the olefinic protons. Attempts to observe such NOE effects from H(6) to the olefinic protons, and from each of the olefinic protons to the pyridine, were unsuccessful at 90, 250 or 400 MHz, although, in each case, the expected effects at $J$ coupled protons were observed. Although the non-observance of an NOE is not rigid proof of the structure, we consider it to be circumstantial evidence for the formulation of the complexes as type **4**.

We expected that treatment of [Ru(diene)L$_2$] with methyl iodide would lead to *S*-alkylation and the formation of thioether complexes of the type [Ru(diene)(LMe)$_2$] or [Ru(LMe)$_2$I$_2$] [10]. The reaction of [Ru(nbd)(2-pyS)$_2$] with excess methyl iodide in refluxing methanol resulted in the precipitation of an orange-red microcrystalline

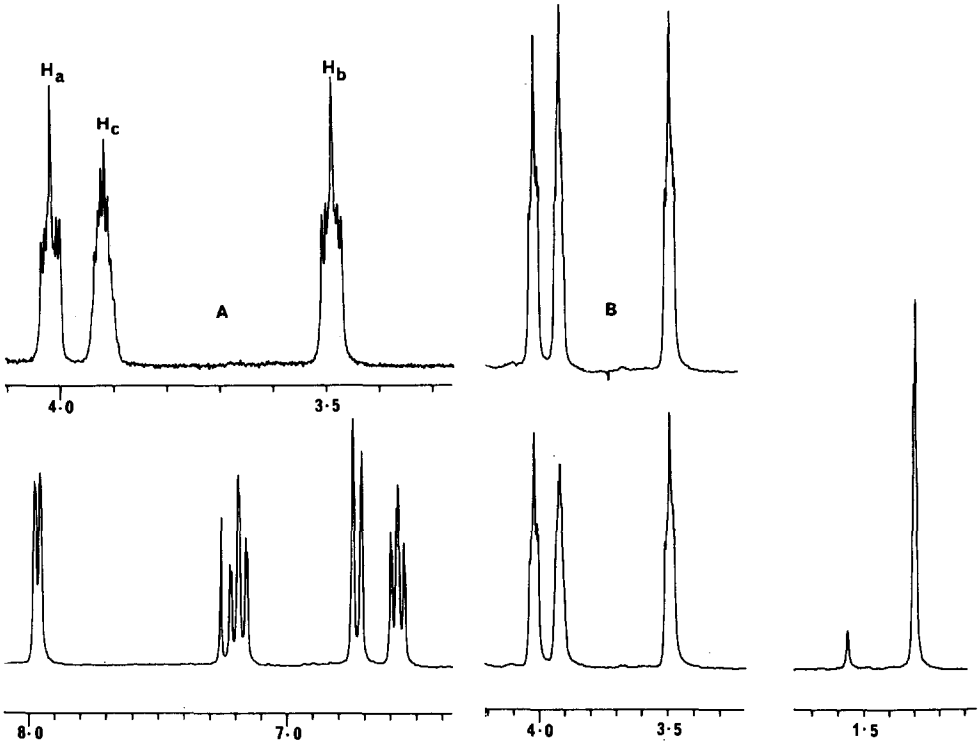



Fig. 1. 250 MHz $^1$H NMR spectrum of [Ru(nbd)(2-pyS)$_2$]; $CDCl_3$ solution, 28 transients, 90° pulse. Inset A. Expansion of the resonances of the olefinic protons ($H_a$ and $H_b$) and the bridge methine group ($H_c$); Gaussian multiplied, LB = −0.31 Hz, GB = 0.5. Inset B. Effect of irradiation at $\delta$ 1.31 ppm, confirming the assignment of $H_c$.

solid. Elemental analysis of this complex suggested an empirical formula of [Ru(nbd)(2-pyS)I], but the mass spectrum showed a parent ion for the dimeric species [$Ru_2$(nbd)$_2$(2-pyS)$_2I_2$]. The 250 MHz $^1$H NMR spectrum of a $CDCl_3$ solution of this complex is shown in Fig. 3, and clearly shows only one set of resonances for the heterocyclic ligand. Most importantly, the olefinic protons appear as four triplets, and the bridgehead methylene group as an AB quartet. Assuming the complex to be a bisiodo bridged dimer, this is only consistent with a structure possessing a $C_2$ axis passing through the two iodine atoms, or one with a $C_2$ axis passing through the centre of, and perpendicular to, the $Ru_2I_2$ plane. On the basis of the $^1$H NMR spectra it is not possible to distinguish between structures **5** to **8**, although **6** or **8** appear to be the most likely if the starting material is of type **4**.

The reaction of [Ru(cod)(2-pyS)$_2$] with methyl iodide in methanol proceeded in a similar manner, to give a red-brown precipitate of the complex [{Ru(cod)(2-pyS)($\mu$-I)}$_2$], which had analytical, mass spectral and $^1$H NMR properties fully in accord with this formulation, and consistent with those of the corresponding nbd complex. Red or orange solids were also obtained from the reaction of the 2-pyrimidinethiolate complexes with methyl iodide, and these showed $^1$H NMR spectra very similar to those of the pyridinethiolate complexes.

In the case of the 2-pyridinethiolate products, the $^1$H NMR spectrum of the

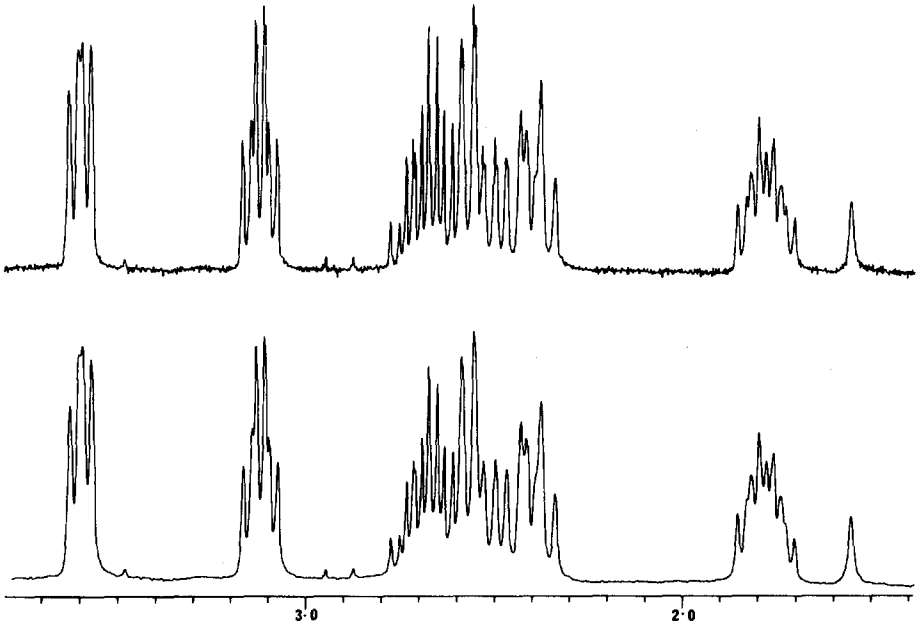



Fig. 2. 250 MHz $^1$H NMR spectrum of [Ru(cod)(2-pyS)$_2$]; $CDCl_3$ solution, 32 transients, 90° pulse. Upper trace. Gaussian multiplied, LB = −0.31 Hz, GB = 0.5.

product exhibited a set of low intensity peaks (marked* in Fig. 3), due to a second isomer of [$Ru_2$(diene)$_2L_2I_2$], with the same overall symmetry. This second isomer could not be separated by recrystallisation, although it could be detected by TLC.

Treatment of the mother liquors from the reactions of the 2-pyS complexes, with

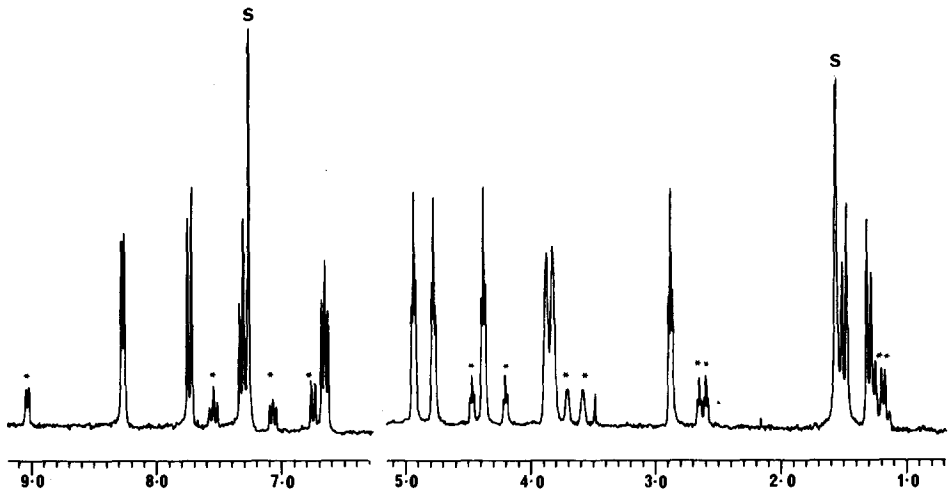
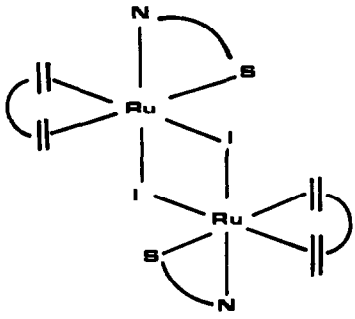



Fig. 3. 250 MHz $^1$H NMR spectrum of [(Ru(nbd)(2-pyS)($\mu$-I))$_2$]; $CDCl_3$, 80 transients, 90° pulse. Peaks marked S are due to a solvent impurity, and those marked* to an unidentified isomer of the product.

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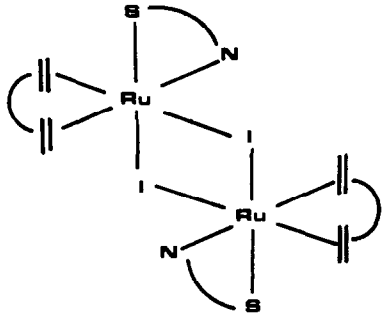


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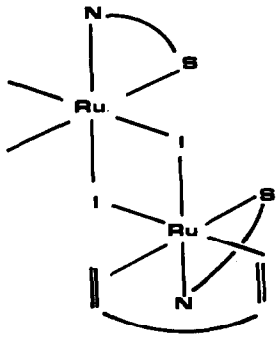


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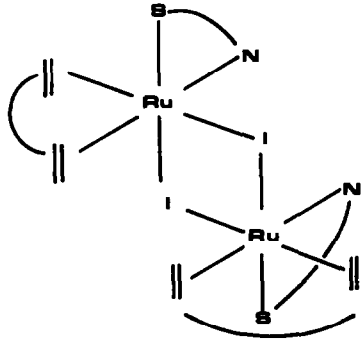


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a few drops of hydriodic acid, followed by concentration in vacuo, led to the crystallisation of the hydriodide of 2-methylthiopyridine. The product was identified as the *S*-methylated derivative, rather than the *N*-methiodide of 2-mercaptopyridine, by its $^1$H NMR, spectrum, which exhibited an *S*-methyl resonance at $\delta$2.46 ppm. The ABCD pattern of the heterocyclic ring was assigned on the basis of NOE difference spectroscopy. Irradiation at $\delta$ 2.46 ppm led to a large NOE at the doublet at $\delta$ 7.71 ppm, which is accordingly assigned to H(3). The remaining protons were assigned on the basis of decoupling experiments.

We had hoped to be able to prepare a number of related complexes $[RuL_2(2\text{-pyS})_2]$ by the displacement of the diene from $[Ru(diene)(2\text{-pyS})_2]$. However, the complexes were recovered unchanged after heating to reflux with methanolic solutions of 2,2′-bipyridine or dppe, stirring with cyclohexene or ethylene for prolonged periods, or treatment with 2 atmospheres of hydrogen in the presence of platinum black.

We are at present investigating the scope of this novel reaction, and are seeking other examples of reactions in which the chemical modification of a coordinated ligand results in ligand loss from the complex. Reactions of this type are of interest in the preparation of metal-free macrocycles via template reactions, and we have already shown that a mismatch of macrocycle donor properties with the template ion does indeed lead to metal-free species [11].

## Experimental

All preparations were conducted under dry nitrogen using dried degassed solvents. $[(Ru(diene)Cl_2)_n]$ [7] and $[Ru(diene)(2\text{-}pyS)_2]$ [8] were prepared by published methods.

*Bis(2-pyrimidinethiolato-NS)(cycloocta-1,5-diene)ruthenium(II)*

$[(Ru(cod)Cl_2)_n]$ (0.27 g, 1 mmol), anhydrous $Na_2CO_3$ (1.0 g, excess) and 2(1*H*)-pyrimidinethione (0.45 g, 4 mmol) were heated to reflux in dmf (5 ml) for 10 min to give an orange-brown solution. This was filtered hot, and the filtrate treated with methanol (25 ml) and cooled, to give yellow needles of the title complex (0.26 g, 60%) (Found: C, 44.38; H, 4.30; N, 12.94; MS 432. $C_{16}H_{18}N_4RuS_2$ calcd.: C, 44.54; H, 4.17; N, 12.98%.

Bis(2-pyrimidinethiolato-NS)(bicyclo[2.2.1]hepta-1,4-diene)ruthenium(II) was prepared analogously in 65% yield (Found: C, 43.46; H, 3.27; N, 13.38; MS 416. $C_{15}H_{14}N_4RuS_2$ calcd.: C, 43.37; H, 3.37; N, 13.49%.

*$[\{Ru(cod)(2\text{-}pyS)(\mu\text{-}I)\}_2]$.* $[Ru(cod)(2\text{-}pyS)_2]$ (0.43 g, 1 mmol) was dissolved in methanol (25 ml) and excess methyl iodide (1 ml) added. The solution was heated to reflux for 2 h, after which period a red solid had been precipitated. The solution was cooled and the product collected by filtration (0.40 g, 89%) (Found: 34.65; H, 3.40; N, 3.19; MS 894. $C_{26}H_{34}I_2N_2Ru_2S_2$ calcd.: C, 34.97; H, 3.58; N, 3.14%. The mother liquor was treated with two drops of concentrated hydriodic acid and concentrated to half the volume, when crystals of 2-methylthiopyridinium iodide were obtained. (Found: C, 28.26; H, 3.16; N, 5.49. $C_6H_8NSI$ calcd.: C, 28.45; H, 3.16; N, 5.54%. $\delta$ (dmso-$d_6$): 2.46, s, *S*-Me, 3H; 8.73, dd, H(6), 1H; 8.10, td, H(4), 1H; 7.71, d, H(3), 1H; 7.51 ppm, t, H(5), 1H).

$[\{Ru(nbd)(2\text{-}pyS)(\mu\text{-}I)\}_2]$ (Found: C, 33.60; H, 2.90; N, 3.28; MS 862. $C_{24}H_{24}I_2N_2Ru_2S_2$ calcd.: C, 33.48; H, 2.79; N, 3.26%) and the other complexes were prepared in a similar manner.

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## References

1 R.D. Gillard, Coord. Chem. Rev., 16 (1975) 67.
2 E.C. Constable, Polyhedron, 2 (1983) 551.
3 E.C. Constable and K.R. Seddon, J. Chem. Soc., Chem. Commun., (1982) 34
4 I.P. Evans and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1974) 946.
5 C.K. Brown, D. Georgiu and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1973) 929.
6 J. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc. A, (1970) 2765.
7 M.A. Bennett and G. Wilkinson, Chem. Ind., (1959) 1516; E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 3178.
8 P. Powell, J. Organomet. Chem., 65 (1974) 89.
9 S.R. Fletcher and A.C. Skapski, J. Chem. Soc., Dalton Trans., (1972) 635.
10 E.C. Constable and J. Lewis, unpublished results.
11 E.C. Constable, M.J. Liptrot, J. Lewis, P.R. Raithby and M. Schroder, Polyhedron, (1983) in press.