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A CYCLOMETALLATED ANALOGUE OF TRIS(2,2′-BIPYRIDINE)RUTHENIUM(II)

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Summary

A cyclometallated analogue of the well-known tris(2,2′-bipyridine)ruthenium(II) cation has been prepared from 2-phenylpyridine. The bis(2,2′-bipyridine)(2-phenylpyridine-*C*,*N*)ruthenium(II) cation is readily prepared from $[Ru(bipy)_2Cl_2]$ * and 2-phenylpyridine in the presence of silver(I); the spectroscopic and electrochemical properties of this species are compared with those of $[Ru(bipy)_3]^{2+}$.

Introduction

Derivatives of tris(2,2′-bipyridine)ruthenium(II) and tris(1,10-phenanthroline)ruthenium(II) have excited considerable interest in recent years; the photophysical, spectroscopic and electrochemical properties have been the subject of particular scrutiny in view of their extensive utilisation in solar energy conversion systems [1]. Our interests in the chemistry of coordinated heterocyclic ligands [2] led us to investigate the cyclometallated bonding modes exhibited by 2-phenylpyridine, 2,2′-bipyridine, 2,4′-bipyridine and 2,2′ : 6′,2″-terpyridine and related compounds [3]. We are prompted to describe our studies on ruthenium(II) systems following the recent description of the preparation and two-dimensional ^1H NMR spectra of the bis (2,2′-bipyridine)(2-(4-nitrophenyl)pyridine-*C*,*N*)ruthenium(II) cation [4].

Results and discussion

The reaction of $[Ru(bipy)_2Cl_2]$, $[Ru(bipy)_2(CO)_2][PF_6]_2$ or $[Ru(bipy)_2(CO)Cl][PF_6]$ with 2-phenylpyridine (HL) in the presence or absence of sodium hydrogen carbonate or trimethylamine *N*-oxide in a variety of solvents led only to the recovery of unreacted starting materials, or the 'expected' coordination complexes, $[Ru(bipy)_2(HL)_2]^{2+}$. The desired cyclometallated species, $[Ru(bipy)_2L]^+$, was ob-

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* bipy = 2,2′-bipyridine.

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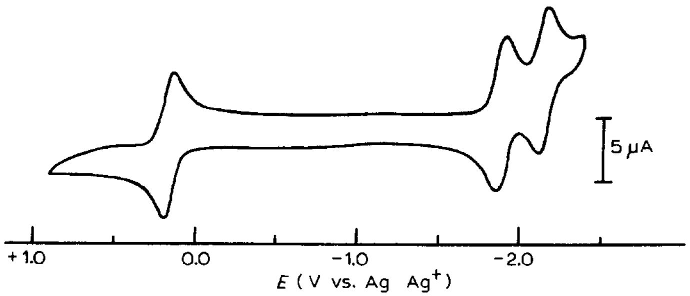

Fig. 1. Cyclic voltammogram of $[Ru(bipy)_2(L)][PF_6]$. Acetonitrile solution, tetra-n-butylammonium tetrafluoroborate supporting electrolyte, reference Ag/Ag^+, 298 K.

tained by the reaction of stoichiometric amounts of $[Ru(bipy)_2Cl_2]$ and phenylpyridine in dichloromethane in the presence of silver(I) tetrafluoroborate. Under these conditions stoichiometric amounts of silver(I) are required, and precipitates of silver(I) chloride form during the course of the reaction. The product of the reaction may be isolated as the deep red hexafluorophosphate salt, $[Ru(bipy)_2L][PF_6]$.

The complex is soluble in polar organic solvents (methanol, acetonitrile, acetone etc.,) to give intensely coloured red-purple solutions. Methanolic solutions of the hexafluorophosphate salt exhibited absorption maxima at 365, 402, 486 and 543 nm. This represents a shift to lower energy of all the absorptions with respect to $[Ru(bipy)_3]^{2+}$, and the spectrum is obviously more complex. In view of the continuing disagreements regarding the assignment of the electronic transitions in the $[Ru(bipy)_3]^{2+}$ cation, we have made no attempt at a full analysis of the electronic spectrum of the complex.

The infra-red spectrum of the compound is considerably more complex than that of the corresponding tris(2,2′-bipyridine)ruthenium(II) salt. Strong bands are observed at 1599, 1572, 1470, 1459, 1442, 1417, 758, 739 and 730 cm^{-1}. There is no band which may be unambiguously assigned to the ruthenium–carbon stretch, which is, however, expected to be weak.

We have also investigated the electrochemical properties of the cyclometallated complex, and the cyclic voltammogram obtained for an acetonitrile solution ($[^nBu_4N][BF_4]$ supporting electrolyte, potential vs. Ag/Ag^+) is shown in Fig. 1. It is evident that there is a reversible oxidation at +0.17 V (+0.47 V vs. NHE) and two reversible reductions at −1.90 V (−1.60 V vs. NHE) and −2.16 V (−1.86 V vs. NHE). It is immediately obvious that the redox properties of the cyclometallated compound are markedly different from those of tris(2,2′-bipyridine)ruthenium(II). The oxidation to the ruthenium(III) state is considerably more facile, +0.47 compared to +1.354 V vs. NHE. This may be due to a difference in the overall charge on the electrogenerated species (+2 as opposed to +3), or to the differing electronic effects of the cyclometallated ligand. The reductions are also shifted to a more negative potential, the corresponding reductions in $[Ru(bipy)_3]^{2+}$ occurring at −1.332 and −1.517 V vs. NHE respectively.

Electrochemical preparation of the ruthenium(III) complex at a platinum OTTLE * electrode led to the formation of a purple solution. The absorption

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* Optically Transparent Thin Layer Electrode.

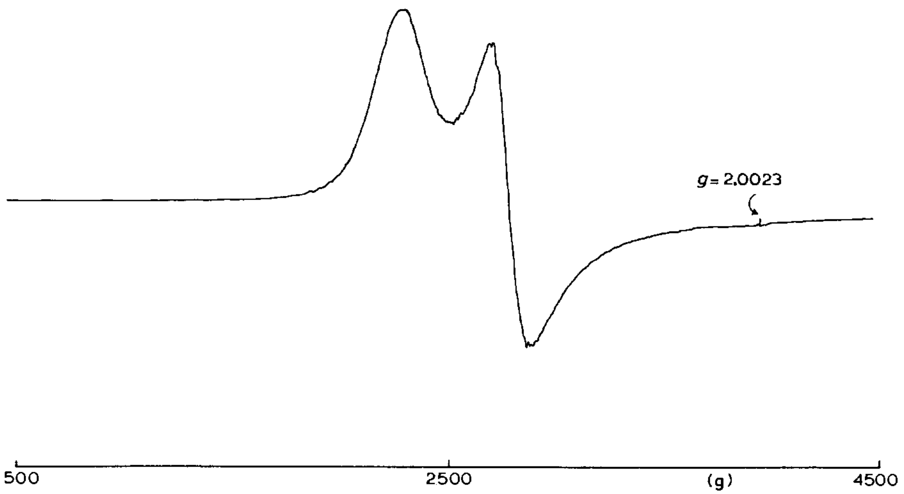

Fig. 2. EPR spectrum of $[Ru(bipy)_2(L)]^{3+}$. Acetonitrile glass, X-band 9.091 GHz; 77 K.

maxima at 486 and 543 nm diminished in intensity, whilst a maximum at 730 nm developed; associated with this change, was an isosbestic point at 630 nm. The ruthenium(III) complex was paramagnetic, and exhibited a well resolved EPR spectrum, as shown in Fig. 2. The solution also exhibited a broad, contact shifted ^{1}H NMR spectrum, fully in accord with the proposed structure.

The ^{1}H NMR spectrum of the cyclometallated ruthenium(II) complex will now be discussed in some detail, since it exhibits a number of interesting features, and provides unequivocal support for the proposed structure. The ^{1}H NMR spectrum of the complex (10 mg in 0.5 cm^3 of DMSO-d_6, 250 MHz, 293 K) is shown in Fig. 3, together with the numbering scheme adopted. It was assumed that the cyclometallated complex possessed a geometry similar to that of the tris(2,2′-bipyridine)ruthenium(II) complex. The symmetry of the cyclometallated complex is, however, lower, and every proton in the molecule is chemically and magnetically inequivalent. The most obvious features in the spectrum are a set of four overlapping doublets in the δ 8.0–8.76 region. Each of these integrates as one proton, and the coupling constants are all in the region 7.9–8.2 Hz. Slightly further upfield is an overlapping doublet (J 8.1 Hz) and triplet of doublets (J 7.8, 1.5 Hz). The high field region of the spectrum exhibits a doublet of triplets at δ 7.04 (J 6.0, 1.1 Hz), a pair of overlapping doublets of triplets at δ 6.85 and 6.78 (J 7.1, 1.4 Hz) and a doublet of doublets at δ 6.33 (J 7.2, 1.1 Hz). Decoupling experiments established the δ 6.33 resonance to be part of an AHMX system, with components at δ 6.33, 6.78, 6.85 and 7.9. The 3-bond *ortho* couplings are all in the region of 7.5–8.5 Hz, which precludes assignment as a pyridine ring, where $J_{5,6}$ 5–6 Hz. This is thus the unique cyclometallated ring (C). The upfield shift of the δ 6.33 resonance suggests that it should be assigned to the proton adjacent to the Ru–C bond, H(9); this assignment was confirmed by the detection of a large negative nuclear Overhauser effect (NOE) from H(13) (δ 8.68) to H(12). The downfield shift of H(12) is due to Van der Waals deshielding, as is also seen in H(3,3′) of 2,2′-bipyridine complexes.

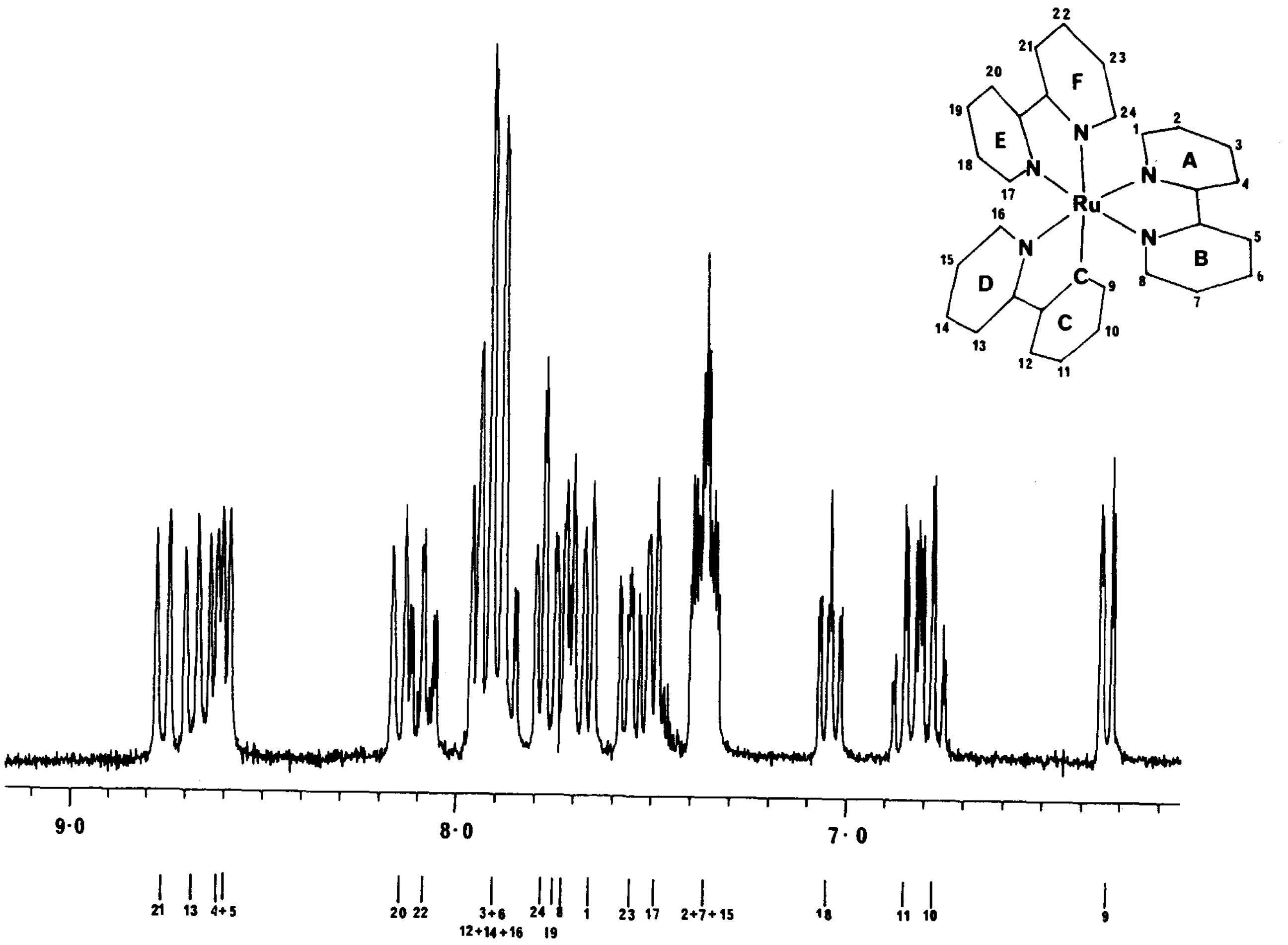

Fig. 3. ^1H NMR spectrum of $[Ru(bipy)_2(L)][PF_6]$. 10 mg in 0.5 cm^3 DMSO-d_6, 250 MHz, 80 transients, 90° pulse, 1 s relaxation delay, Gaussian multiplied, 293 K.

TABLE 1

^{1}H NMR CHEMICAL SHIFTS FOR CYCLOMETALLATED RUTHENIUM(II) COMPLEXES

Proton	δ (ppm)	δ(4-nitrophenyl) [4]
1	7.66/7.70	7.61/7.64
2	7.40	7.40
3	7.95	7.96/7.98
4	8.62/8.60	8.65/8.67
5	8.60/8.62	8.67/8.65
6	7.95	7.98/7.96
7	7.40	7.40
8	7.70/7.66	7.64/6.61
9	6.33	6.67
10	6.78	7.59
11	6.85	–
12	7.90	8.66
13	8.68	8.71
14	7.90	7.96
15	7.40	7.36
16	7.90	7.79
17	7.50	7.59
18	7.04	7.17
19	7.74	7.84
20	8.15	8.48
21	8.76	8.79
22	8.08	8.13
23	7.55	7.58
24	7.80	7.75

The doublet of triplets at δ 7.04 was shown to be part of a second AHMX system, δ 7.04, 7.5, 7.74 and 8.15. The coupling constant of the δ 7.5 doublet to the doublet of triplets at δ 7.04 of 5.6 Hz means that these two resonances may be assigned to H(6) and H(5) respectively of a pyridine ring. The unique upfield shifts of these two resonances makes it possible to assign this AHMX system to ring **E**, which is directly above the metallated phenyl ring.

Similar decoupling experiments established four more AHMX systems. Two of these systems exhibited very similar chemical shifts for all of the protons, and these may thus be assigned to the **A** and **B** rings, which are both *trans* to pyridine, and in very similar environments. Assignment of the resonances between these two rings was not completed; attempted NOE experiments gave ambiguous results. The assignment of rings **D** and **F** was on the basis of the NOE between H(13) of ring **D** and H(12) of ring **C**.

The complete assignments are shown in Fig. 3, and are tabulated in Table 1. Table 1 also contains the assignments reported for the 4-nitrophenyl derivative [4]. It is obvious that the assignments for the **A**, **B**, **D**, **E** and **F** rings correlate very well indeed. The origin of the upfield shift ($\Delta\delta$ 0.33) of H(20) of ring **E** is not clear, but this ring is in a unique position over the cyclometallated ring **C**. The upfield shift of all of the protons on ring **C** with respect to the 4-nitrophenyl analogue is fully consistent with the replacement of a nitro group by hydrogen.

The upfield shift of the proton adjacent to the site of metallation is now recognised as a common feature of compounds of this type. It has previously been observed in the complexes [Ir(bipy)$_2$(bipy-*C*,*N*)]$^{n+}$ [5] and [Pd(2,4'-bipy-*C*,*N*)L]$^{n+}$ [6]. It is also worthy of note that protons in this environment exhibit unusual relaxation properties. Thus, the resonance due to H(9) in the cyclometallated complex is broadened considerably ($w_{\frac{1}{2}}$ 100 Hz) at 400 MHz. We are investigating this phenomenon further.

Experimental

2-Phenylpyridine was used as supplied by the Aldrich Chemical Company without further purification. Ruthenium trichloride trihydrate was obtained from Johnson Matthey. The bis(2,2'-bipyridine)ruthenium(II) complexes were all prepared by the literature methods [1]. ^{1}H NMR spectra were recorded on a Bruker WM 250 spectrophotometer at 293 K. Electronic spectra were recorded on a Pye Unicam PU 8800 spectrophotometer.

[Ru(bipy)$_2$(L)][PF$_6$]

2-Phenylpyridine (2.0 cm^3, excess) and [Ru(bipy)$_2$Cl$_2$] (0.380 g, 0.785 mmol) were dissolved in dichloromethane (25 cm^3) and the solution heated to reflux. Silver(I) tetrafluoroborate (0.310 g, 1.570 mmol) was added, and the solution maintained at reflux for 30 min. After this period, the reaction mixture was filtered through Celite to remove the suspension of silver chloride, and the filtrate treated with methanolic ammonium hexafluorophosphate solution. The solvent was removed in vacuo and the dark coloured residue recrystallised from methanol (10 cm^3) to yield the title complex as a dark red microcrystalline solid (0.250 g, 45%) (Found: C, 52.0; H, 3.3; N, 9.7. $C_{31}H_{24}N_5F_6PRu$ calcd.: C, 52.2; H, 3.4; N, 9.8%).

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