Journal of Organometallic Chemistry, 311 (1986) 207–215
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CHEMISTRY OF CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM COMPLEXES

II *. NOVEL MONONUCLEAR CYCLOPENTADIENYLRUTHENIUM COMPLEXES CONTAINING AROMATIC AMINE LIGANDS. A FACILE SYNTHETIC ROUTE

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(Received March 3rd, 1986)

Summary

The reaction of $[(\eta\text{-}C_5H_4R)Ru(\eta\text{-}C_8H_{12})Cl]$ (R = H, Me; C_8H_{12} = cycloocta-1,5-diene) with bidentate amine ligands has been used to prepare a series of novel cyclopentadienylruthenium(II) diamine complexes, $[(\eta\text{-}C_5H_4R)Ru(diamine)Cl]$ (R = H, Me; diamine = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine). These complexes have been completely characterized by microanalysis, ^1H and ^{13}C NMR spectroscopy, $^1H/^{13}C$ heteronuclear shift correlation spectroscopy, and visible spectroscopy.

Introduction

Amine complexes form one of the cornerstones of the coordination chemistry of ruthenium, for instance featuring as photosensitizers, in water-splitting chemistry, and as mixed-valence species of the Creutz–Taube type [1]. There are, however, surprisingly few organometallic complexes of ruthenium containing amine ligands, and, in particular, there have been no reported syntheses of neutral cyclopentadienylruthenium(II) complexes containing phenanthroline and bipyridine ligands [2,3]. Cationic complexes of the type $[(\eta\text{-}C_5H_5)Ru(diamine)(PPh_3)]^+$ (diamine = ethylenediamine, propylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, biimidazole, bibenzimidazole, 2,2′-pyridyl-benzimidazole) [4] and $[(\eta^5\text{-}C_9H_7)Ru(di-$

* For Part I see ref. 7.

0022-328X/86/$03.50

amine)(PPh_3)]$^+$ (diamine = ethylenediamine, propylenediamine, 2,2′-bipyridine, biimidazole, 1,10-phenanthroline) [5] are, however, known, confirming the expectation that there should be no inherent reason why cyclopentadienylruthenium(II) bipyridine and phenanthroline complexes should not be stable.

We described previously the synthesis and remarkable reactivity of the cyclopentadienylruthenium(II) complex [(η-C_5H_5)Ru(η-C_8H_{12})Cl] (C_8H_{12} = cycloocta-1,5-diene) [6,7]. We noted that the cyclooctadiene ligand undergoes facile displacement in the presence of a wide range of donor ligands including other diolefins, phosphines and isonitriles [6,7]. These observations contrast directly with the more traditional routes to half-sandwich complexes of the type [(η-C_5H_5)RuL_2X] which have, by and large, been based on two synthetic precursors, [(η-C_5H_5)Ru$(CO)_2$Cl] and [(η-C_5H_5)Ru$(PPh_3)_2$Cl] [2]. Thus most of the problems associated with the use of the latter synthons (e.g. forcing thermal reaction conditions, ligand competition and the resulting low yields of products) are not encountered in the [(η-C_5H_5)Ru(η-C_8H_{12})Cl] system, and the cyclooctadiene ligand is rapidly and cleanly displaced even by aromatic amine ligands [6]. This observation has led us to briefly explore this as a synthetic route to a range of novel, neutral cyclopentadienylruthenium(II) amine complexes, compounds which we expected might provide a new platform for the chemistry of the {(η-C_5R_5)RuL_2} unit complementary to that of the complexes [(η-C_5H_5)Ru$(PR_3)_2$Cl] [2]. We report here on the synthesis and characterization of a representative series of complexes [(η-C_5H_4R)Ru(diamine)Cl] (R = H, Me; diamine = 1,10-phenanthroline, 2,2′-bipyridine and substituted derivatives thereof), the first examples of neutral cyclopentadienylruthenium(II) diamine complexes.

Results and discussion

Treatment of the labile cyclooctadiene complexes [(η-C_5H_4R)Ru(η-C_8H_{12})Cl] (R = H, Me; C_8H_{12} = cycloocta-1,5-diene) with an equimolar amount of a diamine ligand in acetone at room temperature results in rapid displacement of the cyclooctadiene ligand and the formation of the new, neutral amine complexes [(η-C_5H_4R)Ru(diamine)Cl] (**1–18**, Table 1) in essentially quantitative yield as determined by visible spectroscopy (see below).

Neutral cyclopentadienylruthenium(II) complexes of the type [(η-C_5H_5)RuL_2X] (L = donor ligand, X = halide) are generally synthesized by the treatment of a suitable synthetic precursor with a cyclopentadienylating agent (as typified by the preparation of [(η-C_5H_5)Ru$(PPh_3)_2$Cl] [2]), or more commonly by ligand exchange in such preformed systems as encountered for instance in the preparation of [(η-C_5H_5)Ru$(PR_3)_2$Cl] [2] and [(η-C_5H_5)Ru$(CNR)_2$Cl] [8]. However, as illustrated by [(η-C_5H_5)Ru$(PPh_3)_2$Cl] which undergoes rapid loss of one of the bulky triphenylphosphine ligands and facile ionization by chloride loss in solution [2], the competitive formation of cationic complexes of the type [(η-C_5H_5)RuL_3]$^+$ can restrict the range of neutral [(η-C_5H_5)RuL_2Cl] complexes synthesizable by this procedure. In line with this, the complexes [(η-C_5H_5)Ru$(PPh_3)_2$Cl] and [(η^5-C_9H_7)-Ru$(PPh_3)_2$Cl] have both been found to react with diamines to give cationic products of the type [(η-C_5H_5)Ru(diamine)(PPh_3)]$^+$ [4] and [(η^5-C_9H_7)Ru(diamine)(PPh_3)]$^+$ [5]. It is unlikely that these reactions proceed via the intermediacy of neutral species of the type [(η-C_5H_5)Ru(diamine)Cl], but rather through well-known cationic, solvolysed intermediates of the form [(η-C_5H_5)Ru$(PPh_3)_2$(solvent)]$^+$ [2], substitut-

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR THE NEW CYCLOPENTADIENYLRUTHENIUM(II) 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDINE COMPLEXES [a,b]

Complex	Colour	Yield (%)	Analysis (Found (calcd.) (%))			
			C	H	N	Cl
[(η-C_5H_5)(Ru(phen)Cl] (**1**)	red/brown	90.0	53.59 (53.48)	3.48 (3.43)	7.45 (7.34)	9.12 (9.29)
[(η-C_5H_5)Ru(2,9-Me_2-phen)Cl] (**2**)	red/brown	85.4	55.79 (55.67)	4.05 (4.18)	6.53 (6.83)	8.54 (8.65)
[(η-C_5H_5)Ru(4,7-Me_2-phen)Cl] (**3**)	purple/brown	87.8	55.08 (55.67)	4.07 (4.18)	6.84 (6.83)	8.65 (8.65)
[(η-C_5H_5)Ru(5,6-Me_2-phen)Cl] (**4**)	red/brown	90.2	55.35 (55.67)	4.10 (4.18)	6.80 (6.83)	8.49 (8.65)
[(η-C_5H_5)Ru(3,4,7,8-Me_4-phen)Cl] (**5**)	red/brown	90.0	57.24 (57.60)	4.95 (4.83)	6.44 (6.40)	8.74 (8.10)
[(η-C_5H_5)Ru(4,7-Ph_2-phen)Cl] (**6**)	purple/brown	76.4	65.67 (65.23)	3.80 (3.96)	5.19 (5.25)	6.69 (6.64)
[(η-C_5H_5)Ru(5-NO_2-phen)Cl] (**7**)	purple	84.4	47.57 (47.84)	2.68 (2.83)	9.98 (9.84)	7.79 (8.31)
[(η-C_5H_4Me)Ru(phen)Cl] (**8**)	purple	81.1	54.43 (54.61)	3.42 (3.82)	7.27 (7.07)	9.19 (8.96)
[(ν-C_5H_4Me)Ru(2,9-Me_2-phen)Cl] (**9**)	red/brown	80.4	56.77 (56.66)	4.56 (4.51)	6.91 (6.61)	7.37 (8.36)
[(η-C_5H_4Me)Ru(4,7-Me_2-phen)Cl] (**10**)	red/brown	89.8	56.37 (56.66)	4.59 (4.51)	6.71 (6.61)	8.49 (8.36)
[(η-C_5H_4Me)Ru(5,6-Me_2-phen)Cl] (**11**)	red/brown	89.6	56.35 (56.66)	4.80 (4.51)	6.64 (6.61)	8.43 (8.36)
[(η-C_5H_4Me)Ru(3,4,7,8-Me_4phen)Cl] (**12**)	red/purple	82.0	56.20 (58.46)	4.98 (5.13)	6.25 (6.20)	7.89 (7.84)
[(η-C_5H_4Me)Ru(4,7-Ph_2-phen)Cl] (**13**)	red/purple	78.5	65.39 (65.74)	4.12 (4.32)	5.32 (5.11)	6.29 (6.46)
[(η-C_5H_4Me)Ru(5-NO_2-phen)Cl] (**14**)	purple	83.7	48.52 (48.81)	3.19 (3.19)	9.17 (9.48)	8.06 (8.00)
[(η-C_5H_5)Ru(bipy)Cl] (**15**)	red/brown	84.2	50.14 (50.35)	3.65 (3.66)	7.92 (7.83)	9.99 (9.91)
[(η-C_5H_5)Ru(4,4′-Me_2-bipy)Cl] (**16**)	red/brown	82.9	52.84 (52.92)	4.57 (4.44)	6.98 (7.26)	9.01 (9.19)
[(η-C_5H_4Me)Ru(bipy)Cl] (**17**)	red/brown	78.2	51.23 (51.67)	4.06 (4.07)	6.88 (7.53)	9.74 (9.53)
[(η-C_5H_4Me)Ru(4,4′-Me_2-bipy)Cl] (**18**)	deep red	82.5	53.19 (54.06)	4.88 (4.79)	6.90 (7.00)	9.02 (8.87)

[a] phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine. [b] None of the compounds **1**–**18** melt below 280 °C.

ing first the weakly coordinated solvent molecule, followed by rapid chelate closure and displacement of the triphenylphosphine ligand to give the product.

It is thus a notable feature of the chemistry of the complexes [(η-C_5H_4R)Ru(η-C_8H_{12})Cl] that only the neutral diamine complexes [(η-C_5H_4R)Ru(diamine)Cl] are obtained under the experimental conditions described here. Preliminary kinetic studies of this system [9] have revealed that the formation of the reaction products in acetone does not proceed via initial chloride labilization (i.e. via a cationic intermediate), and that the rate-determining step is the cleavage of the first ruthenium–olefin bond [9]. These results are testimony to the high lability of the

cyclooctadiene ligand in $[(\eta\text{-}C_5H_4R)Ru(\eta\text{-}C_8H_{12})Cl]$ and the unusual nature of this complex as a synthetic precursor to cyclopentadienylruthenium chemistry.

The new cyclopentadienylruthenium(II) complexes **1–18** are all obtained as high-melting red-brown to purple coloured crystalline solids. The compounds are all air-stable in the solid state although in solution there is some evidence of decomposition occurring over a period of several hours in air. Rapid reactions with water [9] however, make it imperative that all solvents are thoroughly dried before use in the reactions or for the purification of these compounds. The solubility of **1–18** in organic solvents varies significantly with the nature of the amine ligand substituents; compounds of 2,9-Me_2-1,10-phenanthroline are by far the most soluble in acetone at room temperature while others, especially those of 5-NO_2-1,10-phenanthroline and 5,6-Me_2-1,10-phenanthroline are only sparingly so.

The insolubility of certain of **1–18** coupled with their sensitivity to moisture, gives rise to a certain amount of difficulty in recrystallizing these compounds. In our hands, we have found the materials produced in the reactions to be of sufficient purity for most synthetic purposes, while with a little care, and presupposing stringent purification of all reagents and solvents, analytically pure compounds can also be obtained in this manner (Table 1). None of **1–18** melt below 280°C, although varying degrees of thermal decomposition occur on heating the solids in air.

The complete assignment of the ^1H NMR spectra for the series of compounds **1–18** is unambiguous (Table 2), whereas the ^{13}C NMR signals may only be assigned to a varying degree (Table 3). An atom labelling scheme is illustrated in Figs. 1 and 2.

The assignment of the ^1H NMR spectra is simplified by comparisons which may be made in a series of related compounds and by the use of coupling constants. The use of $^1H/^{13}C$ heteronuclear shift correlation spectra aids in the assignment of ^{13}C NMR spectra from already assigned ^1H spectra. This is illustrated by two examples, a 1,10-phenanthroline derivative (complex **2**, Fig. 3) and a 2,2′-bipyridine derivative (complex **16**, Fig. 4). Considering the phenanthroline complexes, the A position shows a signal both in the ^1H and ^{13}C spectrum that is characterized by a low field shift. When a proton occupies the A position its chemical shift is generally 1.5 ppm lower field than the next signal (usually H_C). When H_A is replaced by Me_A the methyl protons resonate ± 0.6 ppm low field of the methyl signals observed for other positions. In the ^{13}C spectra C_A is found usually ± 6 ppm low field of the next signal (one of the ring shared phenanthroline carbon atoms) this separation being exaggerated in complexes **2** and **9**, when the A position is methyl substituted, to ± 15 ppm. There is a surprisingly large difference in the $^1H/^1H$ coupling constants

(Continued on p. 214)

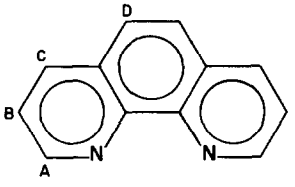

Fig. 1. Atom numbering scheme for the 1,10-phenanthroline ligands.

TABLE 2

^{1}H NMR DATA FOR THE NEW CYCLOPENTADIENYLRUTHENIUM(II) 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDINE COMPLEXES [a]

Complex	
1 [b]	9.69 (dd, 2H, H_A), 8.27 (dd, 2H, H_C), 7.90 (s, 2H, H_D) 7.71 (dd, 2H, H_B), 4.32 (s, 5H, C_5H_5)
2 [c]	8.08 (d, 2H, H_C), 7.74 (s, 2H, H_D), 7.63 (d, 2H, H_B), 4.12 (s, 5H, C_5H_5), 3.45 (s, 6H, Me_A)
3 [d]	9.75 (d, 2H, H_A), 8.05 (s, 2H, H_D), 7.53 (d, 2H, H_B), 4.26 (s, 5H, C_5H_5), 2.84 (s, 6H, Me_C)
4 [e]	9.85 (dd, 2H, H_A), 8.40 (dd, 2H, H_C), 7.68 (dd, 2H, H_B), 4.31 (s, 5H, C_5H_5), 2.71 (s, 6H, Me_D)
5 [f]	9.68 (s, 2H, H_A), 8.03 (s, 2H, H_D), 4.25 (s, 5H, C_5H_5), 2.71 (s, 6H, Me), 2.60 (s, 6H, Me)
6 [g]	10.05 (dd, 1H, H_A), 10.02 (dd, 1H, $H_{A'}$), 9.00 (dd, 1H, $H_{C'}$), 8.84 (s, 1H, H_D), 8.43 (dd, 1H, H_C), 7.85 (dd, 1H, $H_{B'}$), 7.81 (dd, 1H, H_B), 4.40 (s, 5H, C_5H_5)
7 [h]	9.97 (d, 2H, H_A), 7.96 (s, 2H, H_D), 7.67 (d, 2H, H_B), 7.57 (m, 10H, Ph), 4.38 (s, 5H, C_5H_5)
8 [i,j]	9.84 (dd, 2H, H_A), 8.23 (dd, 2H, H_C), 7.84 (s, 2H, H_D), 7.68 (dd, 2H, H_B), 4.23 (m, 2H, C_5H_4Me), 4.03 (m, 2H, C_5M_4Me), 1.79 (s, 3H, Me′)
9 [i,k]	8.06 (d, 2H, H_C), 7.72 (s, 2H, H_D), 7.62 (d, 2H, H_B), 3.95 (m, 2H, C_5H_4Me), 3.85 (m, 2H, C_5H_4Me), 3.44 (s, 6H, Me_A), 1.74 (s, 3H, Me′)
10 [i,l]	9.70 (d, 2H, H_A), 8.04 (s, 2H, H_D), 7.54 (d, 2H, H_C), 4.17 (m, 2H, C_5H_4Me), 3.96 (m, 2H, C_5H_4Me), 2.83 (s, 6H, Me_C), 1.77 (s, 3H, Me′)
11 [i,m]	9.81 (dd, 2H, H_A), 8.40 (dd, 2H, H_C), 7.69 (dd, 2H, H_B), 4.21 (m, 2H, C_5H_4Me), 4.01 (m, 2H, C_5H_4Me), 2.72 (s, 6H, Me_D), 1.79 (s, 3H, Me′)
12 [f,i]	9.63 (s, 2H, H_A), 8.02 (s, 2H, H_D), 4.15 (m, 2H, C_5H_4Me), 3.95 (m, 2H, C_5H_4Me), 2.70 (s, 6H, Me), 2.60 (s, 6H, Me), 1.78 (s, 3H, Me′)
13 [i,n]	9.99 (dd, 1H, H_D), 9.96 (dd, 1H, $H_{A'}$), 8.97 (dd, 1H, H_C), 8.82 (s, 1H, $H_{D'}$), 8.41 (dd, 1H, $H_{C'}$), 7.85 (dd, 1H, H_B), 7.79 (dd, 1H, $H_{B'}$), 4.29 (m, 2H, C_5H_4Me), 4.10 (m, 2H, C_5H_4Me), 1.80 (s, 3H, Me′)
14 [i,o]	9.92 (d, 2H, H_A), 7.96 (s, 2H, H_D), 7.68 (d, 2H, H_B), 7.60 (m, 10H, Ph), 4.30 (m, 2H, C_5H_4Me), 4.09 (m, 2H, C_5H_4Me), 1.85 (s, 3H, Me′)
15 [p]	9.64 (dd, 2H, H_A), 8.03 (dd, 2H, H_D), 7.78 (m, 2H, H_C), 7.34 (m, 2H, H_B), 4.24 (s, 5H, C_5H_5)
16 [q]	9.42 (dd, 2H, H_A), 7.83 (d, 2H, H_D), 7.14 (dd, 2H, H_B), 4.17 (s, 5H, C_5H_5), 2.46 (s, 6H, Me_C)
17 [i,r]	9.55 (dd, 2H, H_A), 8.00 (dd, 2H, H_D), 7.68 (m, 2H, H_C), 7.31 (m, 2H, H_B), 4.13 (m, 2H, C_5H_4Me), 3.91 (m, 2H, C_5H_4Me), 1.79 (s, 3H, Me′)
18 [i,s]	9.38 (dd, 2H, H_A), 7.83 (d, 2H, H_D), 7.14 (dd, 2H, H_B), 4.08 (m, 2H, C_5H_4Me), 3.84 (m, 2H, C_5H_4Me), 2.44 (s, 6H, Me_C), 1.75 (s, 3H, Me′)

[a] Positions recorded in ppm downfield of TMS, spectra collected at 500.13 MHz using CD_2Cl_2 solutions (303 K). [b] J_{AB} 5.1, J_{BC} 8.0, J_{AC} 1.1 Hz. [c] J_{BC} 8.2 Hz. [d] J_{AB} 5.1 Hz. [e] J_{AB} 5.1, J_{BC} 8.3, J_{AC} 1.2 Hz. [f] Unambiguous assignment of signals due to Me_B and Me_C was not possible. [g] J_{AB} 5.2, $J_{A'B'}$ 5.2, J_{BC} 8.0, $J_{B'C'}$ 8.6, J_{AC} 1.1, $J_{A'C'}$ 1.2 Hz. [h] J_{AB} 5.3 Hz. [i] The label Me′ for complexes **8–14**, **17** and **18** refers to the methyl group on the cyclopentadienyl ring. [j] J_{AB} 5.1, J_{BC} 8.1, J_{AC} 1.1 Hz. [k] J_{BC} 8.2 Hz. [l] J_{AB} 5.3 Hz. [m] J_{AB} 5.1, J_{BC} 8.3, J_{AC} 1.1 Hz. [n] J_{AB} 5.3, $J_{A'B'}$ 5.1, J_{BC} 8.0, $J_{B'C'}$ 8.5, J_{AC} 1.2, $J_{A'C'}$ 1.1 Hz. [o] J_{AB} 5.4 Hz. [p] J_{AB} 5.3, J_{BC} 7.6, J_{CD} 8.1, J_{AC} 1.3, J_{BD} 1.0 Hz. [q] J_{AB} 5.7, J_{BD} 0.9 Hz. [r] J_{AB} 5.3, J_{BC} 7.5, J_{CD} 8.0, J_{AC} 1.2, J_{BD} 0.6 Hz. [s] J_{AB} 5.6, J_{BD} 0.8 Hz.

TABLE 3

^{13}C NMR DATA FOR THE NEW CYCLOPENTADIENYLRUTHENIUM(II) 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDINE COMPLEXES [a,b]

Complex	
1	154.7 (C_A), 148.0, 135.4 (C_{bridge}), 133.8 (C_C), 127.2 (C_D), 124.6 (C_B), 69.3 (C_5H_5)
2	162.9 (C_A), 147.6 (C_{bridge}), 133.2 (C_C), 126.8 (C_{bridge}), 124.7 (C_D), 123.9 (C_B), 67.3 (C_5H_5), 28.5 (Me_A)
3	154.3 (C_A), 147.8 (C_{bridge}), 143.7 (C_C), 129.7 (C_{bridge}), 125.5 (C_D), 123.3 (C_B), 68.6 (C_5H_5), 18.7 (Me_C)
4	153.5 (C_A), 147.1 (C_{bridge}), 130.9 [c] (C_D), 130.7 [c] (C_{bridge}), 130.5 (C_C), 69.2 (C_5H_5), 15.1 (Me_D)
5	155.4 (C_A), 146.6 (C_{bridge}), 141.3 (C_C), 132.9 [c] (C_B), 128.5 [c] (C_{bridge}), 122.9 (C_D), 68.2 (C_5H_5), 17.9 [d] (Me_C), 14.5 [d] (Me_B)
6	154.4 (C_A), 148.6 (C_C), 146.6, 137.1 (C_{bridge}), 130.1, 129.3, 129.2, 128.3 (C_{Ph}), 125.2 [c] (C_D), 125.0 [c] (C_B), 69.2 (C_5H_5)
7 [e]	157.7, 156.0 (C_A, $C_{A'}$), 135.3, 130.8 (C_C,$C_{C'}$), 127.1, 126.6 (C_D, $C_{D'}$), 125.8, 125.7 (C_B,$C_{B'}$), 70.5 (C_5H_5)
8 [f]	154.3 (C_A), 148.0 (C_{bridge}), 133.5 (C_C), 130.2 (C_{bridge}), 127.1 (C_D), 124.6 (C_B), 89.4 [g], 71.0, 65.0 (C_5H_4Me), 13.0 (Me')
9 [f]	163.7 (C_A), 148.6 (C_{bridge}), 134.0 (C_C), 127.8 (C_{bridge}), 125.7 (C_D), 124.9 (C_B), 85.6 [g], 67.7, 67.5 (C_5H_4Me), 29.5 (Me_A), 12.6 (Me')
10 [f]	153.9 (C_A), 147.8 (C_{bridge}), 143.3 (C_C), 129.6 (C_{bridge}), 125.5 (C_D), 123.3 (C_B), 88.6 [g], 70.4, 64.4 (C_5H_4Me), 18.6 (Me_C), 13.0 (Me')
11 [f]	153.2 (C_A), 147.2, 131.0 [c] (C_{bridge}), 130.7 [c] (C_D), 130.3 (C_C), 124.2 (C_B), 89.5 [g], 71.2, 65.2 (C_5H_4Me), 15.2 (Me_D), 12.9 (Me')
12 [f]	155.1 (C_A), 146.6 (C_{bridge}), 141.1 (C_C), 133.0 [c] (C_B), 128.4 [c] (C_{bridge}), 123.0 (C_D), 88.4 [g], 70.3, 64.0 (C_5H_4Me), 17.9 [d] (Me_C), 14.5 [d] (Me_B), 13.0 (Me')
13 [f]	153.0 (C_A), 147.5 (C_{bridge}), 145.2 (C_C), 136.1 (C_{bridge}), 127.9, 127.8, 127.1, 125.9 (C_{Ph}), 124.1 [c] (C_D), 124.0 [c] (C_B), 88.9 [g], 70.5, 64.5 (C_5H_4Me), 12.1 (Me')
14 [e,f]	156.4, 154.7 (C_A,$C_{A'}$), 134.1, 129.4 (C_C,$C_{C'}$), 126.1, 125.7 (C_D,$C_{D'}$), 125.0, 124.8 (C_B,$C_{B'}$), 90.3 [g], 71.3, 65.1 (C_5H_4Me), 12.1 (Me')
15	156.4 (C_{bridge}), 155.4 (C_A), 134.9 (C_C), 125.1 (C_B), 122.1 (C_D), 69.9 (C_5H_5)
16	155.9 (C_{bridge}), 154.7 (C_A), 147.0 (C_C), 126.2 (C_B), 122.8 (C_D), 68.9 (C_5H_5), 21.3 (Me_C)
17 [f]	156.0 (C_{bridge}), 154.9 (C_A), 134.5 (C_C), 124.9 (C_B), 122.0 (C_D), 89.9 [g], 71.4, 65.4 (C_5H_4Me), 12.8 (Me')
18 [f]	155.8 (C_{bridge}), 154.3 (C_A), 146.5 (C_C), 126.1 (C_B), 122.6 (C_D), 88.7 [g], 70.5, 64.6 (C_5H_4Me), 21.2 (Me_C), 12.9 (Me')

[a] Positions recorded in ppm downfield of TMS, spectra collected at 125.76 MHz using CD_2Cl_2 solutions (303 K). [b] The signals due to the bridge-head carbon atoms in complexes **1–14** could not be unambiguously assigned and are labelled only as C_{bridge}. [c] Assignment may be reversed. [d] Methyl signal assignment may be reversed. [e] Bridge-head signals were too weak to be observed with reasonable collection time. [f] The label Me' for complexes **8–14**, **17** and **18** refers to the methyl group on the cyclopentadienyl ring. [g] ^{13}C signal due to the methylated cyclopentadienyl ring carbon atom.

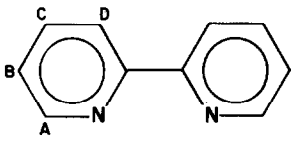

Fig. 2. Atom numbering scheme for the 2,2′-bipyridine ligands.

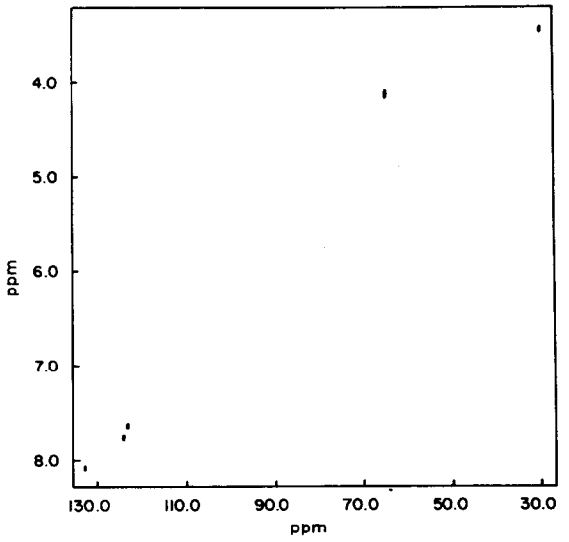

Fig. 3. $^{1}H/^{13}C$ Heteronuclear shift correlation spectrum for complex **2**.

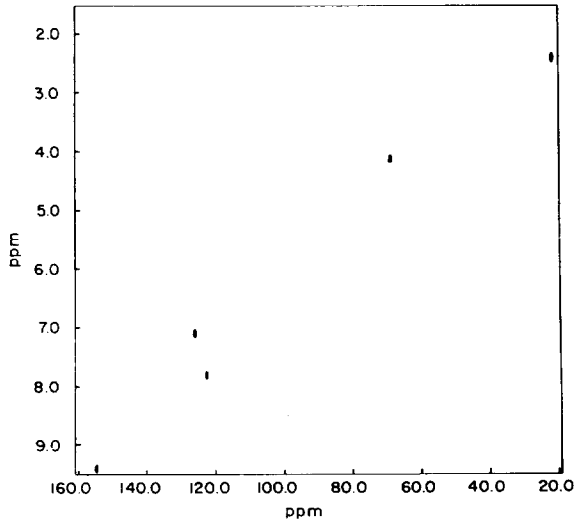

Fig. 4. $^{1}H/^{13}C$ Heteronuclear shift correlation spectrum for complex **16**.

TABLE 4

VISIBLE SPECTRAL DATA FOR THE NEW CYCLOPENTADIENYLRUTHENIUM(II) 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDINE COMPLEXES

Complex	λ_{max} (nm) [a]	ϵ ($\times 10^3$) [a]
1	486	6.1
2	467	5.2
3	482	6.8
4	484	6.6
5	469	6.5
6	498	10.2
7	520	4.1
8	495	5.1
9	493	4.7
10	488	5.8
11	491	5.7
12	473	4.9
13	507	9.2
14	522	5.6
15 [b]	363 (503)	5.8 (4.8)
16 [b]	358 (517)	2.4 (1.8)
17 [b]	365 (509)	4.8 (3.8)
18 [b]	363 (505)	5.4 (3.9)

[a] Visible spectra recorded in CH_2Cl_2 at 298 K. [b] A second less intense peak is also observed, its λ_{max} and ϵ values being recorded in parentheses.

for adjacent protons around the ring, the average values for J_{AB} and J_{BC} being 5.2 and 8.2 Hz respectively.

The similarity of the bipyridine complexes to the phenanthroline systems makes the NMR spectral assignment of complexes **15–18** relatively straightforward. Position A (Fig. 2) suffers from a similar low field shift, and the use of coupling constants allows the unambiguous assignment of all the signals in the ^1H NMR spectra of these complexes. A single $^1H/^{13}C$ heteronuclear shift correlation spectrum (Fig. 4) and comparisons allows the assignment of the ^{13}C spectra of these complexes. A similar variation in the adjacent atom $^1H/^1H$ coupling constants is observed with average values of J_{AB}, J_{BC} and J_{CD} being 5.5, 7.5 and 8.0 Hz respectively.

The visible spectra of **1–18** are quite characteristic with charge transfer bands having the typically high extinction coefficients (Table 4). The bipyridine complexes **15–18** have two absorption bands in the visible region, the most intense centred at about 510 nm; these have extinction coefficients of about 5×10^3 and 4×10^3 respectively. Only one charge transfer band is observed in the visible spectra of the phenanthroline complexes **1–14**, appearing between 467 and 522 nm with extinction coefficients in the range 4.1×10^3 to 10.2×10^3. It is possible that a second charge transfer bond is shifted into the UV.

Conclusion

The reaction of $[(\eta\text{-}C_5H_4R)Ru(\eta\text{-}C_8H_{12})Cl]$ (R = H, Me; C_8H_{12} = cycloocta-1,5-diene) with bidentate amine ligands has been used to prepare a series of novel

cyclopentadienylruthenium(II) diamine complexes [(η-C_5H_4R)Ru(diamine)Cl]. One of the main reasons for our interest in complexes of this type was the anticipation that they may provide new centres for the chemistry of the {(η-C_5H_5)RuL_2} unit complementary to those of the complexes [(η-C_5H_5)Ru(PR_3)$_2$Cl]. Preliminary results have served to lend support to this expectation, but being intimately related to kinetic studies presently being carried out on the reactivity of the complexes [(η-C_5H_5)Ru(diamine)X], will be discussed elsewhere.

Experimental

All reactions were carried out using Schlenk-type techniques and under an inert atmosphere. Product work-up was in air. The complex [(η-C_5H_5)Ru(η-C_8H_{12})Cl] was prepared by the published procedure [6,7], and [(η-C_5H_4Me)Ru(η-C_8H_{12})Cl] by an analogous method. The ligands were all used as purchased (1,10-phenanthroline, 2,2′-bipyridine, Merck; 5-nitro-1,10-phenanthroline, Koch-Light Laboratories Ltd; all others G. Frederick Smith Chemical Company). All solvents were routinely dried [10] and were distilled under an inert atmosphere before use. Visible spectra were recorded using a Cary 210 spectrophotometer with a thermostatted (25°C) cell compartment. ^1H, ^{13}C and $^1H/^{13}C$ heteronuclear shift correlation spectra were recorded at 303 K using a Bruker WM500 (500 MHz) spectrometer. Microanalyses were performed by the microanalytical section of the Analytical Division, NCRL.

General synthetic procedure

A solution of [(η-C_5H_4R)Ru(η-C_8H_{12})Cl] (1.0 mmol) in freshly distilled acetone (25 ml) was treated with a solution of ligand (1.05 mmol in 5 ml acetone). The mixture was stirred at 25°C overnight. Filtration in air, followed by washing of the solid with ether and pentane, gave the required product as a purple or red crystalline solid. In the case of compounds containing the 2,9-Me_2-1,10-phenanthroline ligand, the volume of reaction solution was first reduced by half under vacuum before the filtration.

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