Ruthenium Complexes with Diazadienes. Part II* Syntheses and N.m.r. Spectroscopic Characterization of $[Ru(bipy)_2(diazadiene)]^{2+}$ Complexes

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Summary

Thermal substitution of chloride in $Ru(bipy)_2Cl_2 \cdot 2H_2O$ with diazadienes (dad) R′N=CR–CR=NR′ yields the mixed $[(bipy)_2Ru(dad)]^{2+}$ complexes, which are analogous to the $[Ru(bipy)_3]^{2+}$ cation. Full n.m.r. assignments are given for several complexes; conformational rigidity is displayed by dad-attached phenyl groups in one of them. The u.v. spectra, which show dad-dependent first c.t.-absorption bands, are compared to that of $[Ru(bipy)_3]^{2+}$.

Introduction

Tris(bipyridyl)ruthenium(II) has been investigated with special reference to the problem of solar energy conversion[1]. Together with some cocatalysts, $[Ru(bipy)_3]^{2+}$ has been shown to split water to yield hydrogen and oxygen during irradiation[2]. One attempt aimed to apply complexes of bipyridyls with nonpolar substituents in thin layer[1] or micella systems[3].

From our work with 1,4-diaza-1,3-dienes (dad) R′N=CR–CR=NR′ [4], which show a coordination chemistry similar to bipyridyl[5], we knew that the synthesis of compounds with controlled solubility properties should be much easier. Dads are obtained by simple condensation of 1,2-dicarbonyl compounds with primary amines[6].

Although dads show better acceptor properties than bipy or phen[5] we anticipated that the electronic behaviour of a tris-(bipy)chelate and a corresponding bis(bipy)dad complex should be very similar.

Results and Discussion

Preparation

The well known $Ru(bipy)_2Cl_2 \cdot 2H_2O$[7] exchanges the two chloro ligands when treated with nucleophiles[8] in a slow thermal process. Reactions of this starting material with dad ligands, L1–L8, which are listed together with the complexes, C1–C8, in Table 1, show differences when heated in boiling ethanol, depending upon the steric requirements of the entering ligand. While ligands, L1, L3, L4, L6 and L8 derived from glyoxal and aromatic or aliphatic amines $R'NH_2$ give the desired cations (Equation 1), biacetylbis(i-propylimine) or glyoxalbis(t-butylimine) did not react and biacetylbis(phenylimine) gave a product which probably contains a monocoordinate ligand. L7 on the other hand reacted properly, but from the n.m.r. (*vide infra*) a considerable steric bulk is obvious. After the substitution, which can be monitored by the change from red-violet to brown-yellow, the cations are precipitated as PF_6^--salts.

$$Ru(bipy)_2Cl_2 + \underset{L1–L8}{dad} \xrightarrow[2.\ +NH_4PF_6,\ -NH_4Cl]{1.\ EtOH,\ 80°} \underset{C1–C8}{[Ru(bipy)_2(dad)](PF_6)_2} \quad (1)$$

In general, the complexes are insoluble in nonpolar solvents like hexane, chloroform and tetrahydrofuran, poorly soluble in dichloromethane, ethanol and water, soluble in acetone, acetonitrile and DMF. Dilute solutions of C1 decompose after several days contact with air.

N.m.r. data

From Equation (1), and the analytical results, it is clear that the complex cations must be chiral tris(chelates) with two bipy and one dad ligand. According to Figure 1 the two halves of one bipyridyl must be nonequivalent (ring A *trans* to dad-N, ring B *trans* to bipy-N) and prochiral substituents on dad should split. Thus rather complex n.m.r. spectra are to be expected (Tables).

All spectra except the high temperature n.m.r. of C7 were measured in acetone-d_6 and chemical shifts are in ppm relative to TMS. 360 MHz as well as 270 MHz spectra show the predicted number of 8 signal groups for the bipy moiety; a complete assignment is given in Figure 1. The assignment was performed by comparison with $[Ru(bipy)_3]^{2+}$ [9], $[Ru(bipy)_2$-

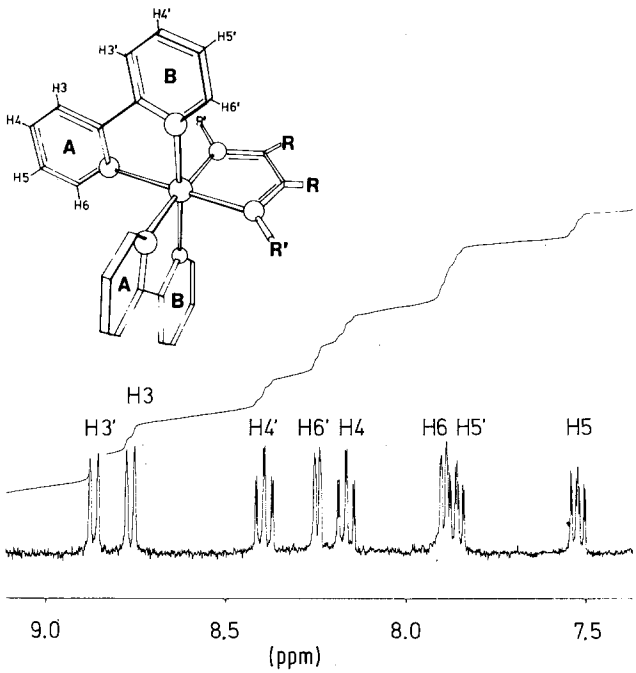

Figure 1. Numbering scheme and 360-MHz n.m.r. spectrum of the bipy moiety in $[Ru(bipy)_2(dad)]^{2+}$ (this *e.g.*: C3 in acetone-d_6).

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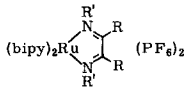
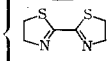
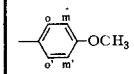
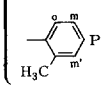
Table 1. Chemical shift values for the dad part of the $[Ru(bipy)_2(dad)]^{2+}$ complexes



	R	R'				
C1	–H	$-CH_2-CH_2-CH_2-CH_3$	H(α) 3.94	H(β) 0.85	H(γ)1.09	H(δ) 0.47t
	8.93s	α β γ δ	H(α′) 3.82			
C2	$-CH_3$	$-CH_2-CH_2-CH_2-CH_3$	H(α) 3.86[a]	H(β) 1.17	H(γ) 0.86	H(δ) 0.43t
	2.72s	α β γ δ	H(α) 3.89	H(β′) 0.69		
C3	–H		H(α) 3.9 (sept)[b]	H(β) 1.31(d)[b]		
	9.10s			H(β′) 0.84(d)		
C4	–H		H(α) 3.31[c]	H(β)–H(δ) 1.70–0.59[d]		
	9.02s					
C5			H(α) 3.73	H(β) 4.11		
			H(α′) 3.88	H(β′) 4.44		
C6	–H		H(o), H(o′) 6.73	H(m), H(m′) 6.60		H(p-OCH_3) 3.68s
	9.07s					
C7	$-CH_3$		H(o), H(o′) 6.34[e]	H(m), H(m′) 6.60		H(p-OCH_3) 3.61s
+130°	2.67s					
C7	$-CH_3$		H(o) 7.06	H(m), H(m′) 6.56		H(p-OCH_3) 3.72s
–70°	2.58s		H(o′) 5.60			
C8	–H		H(o)–H(m′) 7.12, 7.06, 6.88			H(o-CH_3) 1.56s
	9.24s					

[a] $J_{\alpha\alpha} = 12$ Hz, $J_{\alpha\beta} = J_{\alpha'\beta'} = 5$ Hz, $J_{\alpha'\beta} = J_{\alpha\beta'} = 12$ Hz; [b] $J_{\alpha\beta} = J_{\alpha\beta'} = 7$ Hz; [c] $J_{\alpha\beta} = 3$ Hz, $J_{\alpha\beta'} = 12$ Hz; [d] not resolved; [e] broad band; [f] signals with no special index appear as resolved multiplets.

Table 2. δ- and J-values for the bipy part of C3

H(3)	H(3′)	H(4)	H(4′)	H(5)	H(5′)	H(6)	H(6′)
8.76	8.86	8.17	8.39	7.52	7.85	7.90	8.25 (ppm)

$J_{3,4}$ 8.1; $J_{4,5}$ 7.6; $J_{5,6}$ 5.6; $J_{3,5}$ 1.3; $J_{4,6}$ 1.5;
$J_{3',4'}$ 8.2; $J_{4',5'}$ 7.6; $J_{5',6'}$ 5.4; $J_{3',5'}$ 1.3; $J_{4',6'}$ 1.5 (Hz).

$(en)]^{2+}$ [9], *N,N′*-dimethylene bridged $[bipy\text{-}N,N'\text{-}C_2H_4]^{2+}$ [10] and bipy[11] itself. The δ- and J-values of C3 are listed in Table 2.

The bipy alters only slightly with changing dad. H3 and H3′ moves upfield with aromatic dads, while H6′ moves downfield with such ligands. The assignment of ring A and ring B to the unprimed and primed set of protons is most easily done by comparison with $[Ru(bipy)_3]^{2+}$ [9] which contains 6 equivalent pyridyl rings of the environment A (overall anisotropic shift influence). The shielding influence of the dad on H6′ is striking if one compares its δ-values (8.23–8.96 in C1–C8) with 10.2 in $Ru(bipy)_2Cl_2$ and 9.30 in $[Ru(bipy)_2(en)]^{2+}$ [9].

Table 1 lists the chemical shifts for the dad moiety in complexes C1–C8. C1–C5 contain prochiral groups in the N-substituent, but proper resolution of diastereotopic protons could only be achieved in C1–C3. The *n*-butyl group shows the CH_2 inequivalence not only for $CH_2(\alpha)$ but also for $CH_2(\beta)$; for the biacetyl complex C2 the separation $\Delta\delta[H(\beta)–H(\beta')]$ is even greater than $\Delta\delta[H(\alpha)–H(\alpha')]$ which indicates a restricted rotation and special conformation along the $=N–C_\alpha–C_\beta$ chain. The $^2J_{H_\alpha–H_{\beta,\beta'}}$ coupling in the cyclohexyl derivate C4 (3 and 12 Hz) indicates the axial position of H_α.

A very interesting difference is displayed in the spectra of C6 and C7. While the aromatic protons of the *p*-methoxyphenyl substituent in the glyoxal-derived complex, C6, behave quite normally, there are four broad signals for two *ortho*- and two *meta*-protons in the room temperature scan of C7. Figure 2 shows the bipy and aromatic protons part of C7 at three different temperatures. The –70 °C spectrum reveals two signals of equal intensity at 5.60 and 7.06 ppm for two different *ortho*-protons which collapse to one signal at 6.34 ppm, but are still broad at +130 °C. During temperature variation, the A and B sets of the bipy moiety are not interchanged. This proves that there is no fast bond-breaking or other intramolecular isomerisation (racemisation) process[12], although there is evidence for very low barrier intramolecular ligand rearrangement induced by dad in dad $M(CO)_4$ compounds[13].

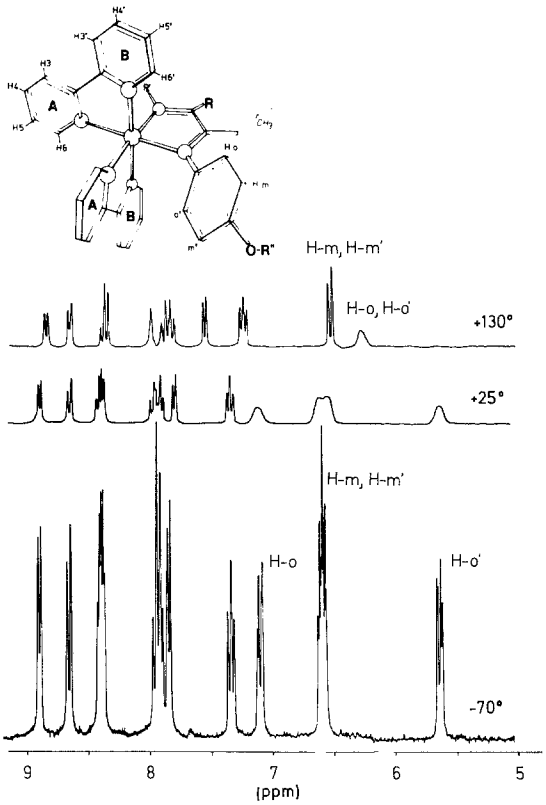


Figure 2. Temperature dependent 270-MHz n.m.r. spectrum of the bipy and aromatic proton moieties of C7.

The change in the *ortho*- and *meta*-proton resonances must be due to the severely hindered phenyl ring rotation around the =N–C bond, a phenomenon which has been observed with such ligands of the biacetyl series in $[Fe(dad)_3]^{2+}$ [14] and in *cis*-$Ru(dad)_2Cl_2$[15]. From these results we anticipate that there is hindered rotation in C8, too, but this cannot be derived from the n.m.r. results. The high field shift of the *ortho*-methyl group (0.84 ppm) compared to the free ligand indicates a position of this group in the shielding region of the pyridyl ring B (*ortho'*-position, Figure 2).

Electronic spectra

The electronic absorption spectra of C2, C5, C6 and C7 are depicted in Figure 3. One obvious feature is a band at 283 nm with almost identical intensity (ε = *ca.* 50.000 $l \cdot mol^{-1} \cdot cm^{-1}$) which shows up in $[Ru(bipy)_3]^{2+}$ at the same wavelength, but with *ca.* 3/2 times the intensity, and can thus be assigned to the same intra-ligand $\pi \rightarrow \pi^*$ transition of coordinated bipy[16]. The main differences occur in the visible part of the spectrum and can be attributed to the dad influence. Compared to $Ru(bipy)_2Cl_2$ or $Ru(dad)_2Cl_2$[17] the increased ligand field strength of six N-donors shifts the c.t.-transition(s) to shorter wavelengths. If one assumes ligand-ligand interactions to be small compared to ligand-metal interactions, one might expect the absorption spectrum of the $Ru(bipy)_2$ moiety to be similar to that of $[Ru(bipy)_2(en)]^{2+}$ [18], plus a typical Ru(dad) charge-transfer absorption. If the dad is not very different in acceptor character from bipy, the overall spectrum should be similar to $[Ru(bipy)_3]^{2+}$.

The first c.t.-absorption bands of the complexes C are compared to those of $(dad)Mo(CO)_4$ complexes[4] in Table 3.

The data indicate that the N-alkyl substituted dad ligands give rise to spectra similar to $[Ru(bipy)_3]^{2+}$. From the molybdenum compounds, it is clear that these ligands are only slightly better acceptors than bipy. This changes with N-aromatic ligands in both series. The bis(thiazolinyl) ligand is outstanding in both series, and we were able to show that the polarographic reduction potential of L5 is almost as low as that of L6[19].

First experiments with a long chain alkyl N-substituent of dad resulted in a complex with very different solubility and an abnormal behaviour in the n.m.r. and u.v. (very broad bands). With the introduction of dad the charge-transfer absorption can be influenced in a predictable manner, but the fluorescence measurements at room temperature performed so far on C2, C3, C6 and C7 did not show the strong luminescence typical for $[Ru(bipy)_3]^{2+}$ under the same conditions.

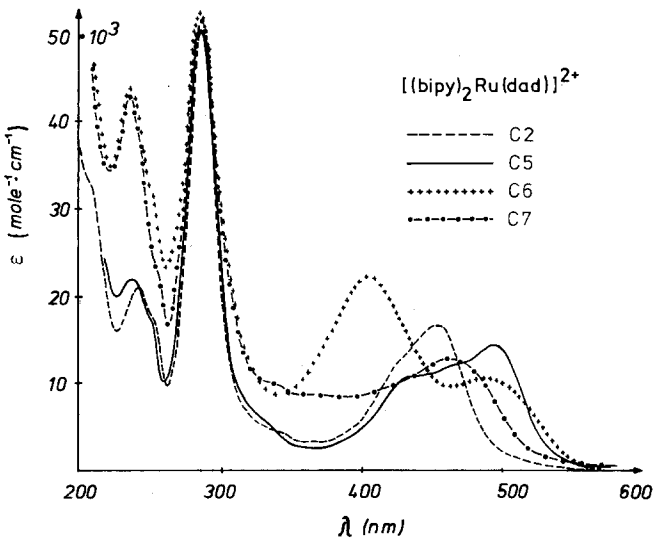


Figure 3. Electronic absorption spectra of some $[Ru(bipy)_2(dad)]^{2+}$ complexes in MeCN.

Table 3. First c.t. absorption bands of complexes $[Ru(bipy)_2(dad)]^{2+}$ (MeCN) and the corresponding molybdenum complexes $(dad)Mo(CO)_4(C_6H_2)$.

	$[Ru(bipy)_2(dad)]^{2+}$	$(dad)Mo(CO)_4$
	λ (nm)	λ (nm)
C1	452	532
C2	453	521
C3	450	537
C4	452	539
C5	495	560
C6	492	606
C7	463	551
C8	492	574
$[Ru(bipy)_3]^{2+}$	450	495

Experimental

$RuCl_3 \cdot 3H_2O$ (Ru 37.65%) (DEGUSSA, Hanau, Germany) was used without further purification. Solvents were purified according to standard procedures, and all reactions were carried out under N_2 to prevent eventual oxidative or hydrolytic decomposition. Ligands were obtained from the condensation of aqueous glyoxal of biacetyl with the appropriate primary amine, following literature procedures[6].

Bis(bipyridyl)dichlororuthenium(II), $Ru(bipy)_2Cl_2 \cdot 2H_2O$, was prepared according to Whitten *et al.*[77].

General procedure

A suspension of $Ru(bipy)_2Cl_2 \cdot 2H_2O$ (*ca.* 0.5 mmol) and the appropriate diazadiene (*ca.* 0.7 mmol) in abs. EtOH (50 cm^3) were boiled under reflux for several hours until all starting material had dissolved and the solution had changed from red-violet to brown-yellow. On addition of NH_4PF_6 (*ca.* 1.5 fold excess in *ca.* 10 cm^3 EtOH) the product precipitated. It was filtered off, washed with EtOH and hexane and dried *in vacuo*. Further purification is possible by precipitation from Me_2CO : hexane.

Glyoxalbis(n-butylimine)bis(bipyridyl)ruthenium(II)-hexafluorophosphate (C1)

1 h reflux, the yellow product was precipitated from Me_2CO: hexane. Yield: 42%. (Found: C, 40.9; H, 4.2; N, 9.6. $C_{30}H_{36}N_6RuP_2F_{12}$ calcd.: C, 41,3; H, 4,2; N, 9.6%.) M.p., 210 °C (dec.).

Biacetylbis(n-butylimine)bis(bipyridyl)ruthenium(II)-hexafluorophosphate (C2)

2 h reflux; after thoroughly washing with EtOH the red crystalline product needed no further purification. Yield: 72%. (Found: C, 42.4; H, 4.5; N, 9.3. $C_{32}H_{40}N_6RuP_2F_{12}$ calcd.: C, 42.7; H, 4.5; N, 9.3%.)

Glyoxalbis(i-propylimine)bis(bipyridyl)ruthenium(II)-hexafluorophosphate (C3)

5 h reflux; the dried product was washed with $CHCl_3$ until no violet colour occurred. Yield: 47%. (Found: C, 39.4; H, 3.8; N, 9.8. $C_{28}H_{32}N_6RuP_2F_{12}$ calcd.: C, 39.9; H, 3.8; N, 10.0%.)

Glyoxalbis(cyclohexylimine)bis(bipyridyl)ruthenium(II)-hexafluorophosphate (C4)

3 h reflux; the yellow product was precipitated from Me_2CO : hexane. Yield: 59%. (Found: C, 44.1; H, 4.4; N, 8.9. $C_{34}H_{40}N_6RuP_2F_{12}$ calcd.: C, 44.2; H, 4.4; N, 9.1%.) M.p., 253 °C (dec.).

(Bisthiazolinyl)bis(bipyridyl)ruthenium(II)-hexafluorophosphate (C5)

2 h reflux; Yield: 93%. (Found: C, 35.4; H, 3.0; N, 9.3. $C_{26}H_{24}N_6RuP_2F_{12}S_2$ calcd.: C, 35.7; H, 2.8; N, 9.6%.)

Glyoxalbis(p-methoxyphenylimine)bis(bipyridyl)-ruthenium(II)hexafluorophosphate (C6)

3 h reflux; after repeated precipitation from Me_2CO/hexane dark brown crystals were obtained. Yield: 69%. (Found: C, 43.9; H, 3.3; N, 8.6. $C_{36}H_{32}N_6RuP_2F_{12}O_2$ calcd.: C, 44.5; H, 3.3; N, 8.65%.) M.p., 178 °C (dec.).

Biacetylbis(p-methoxyphenylimine)bis(bipyridyl)-ruthenium(II)hexafluorophosphate (C7)

2 h reflux; the precipitate was washed with EtOH, and then 1 : 1 EtOH/hexane until no red-violet colour occurred, then with hexane and dried *in vacuo*. Yield: 38%. (Found: C, 45.3; H, 3.6; N, 8.3. $C_{38}H_{36}N_6RuP_2F_{12}O_2$ calcd.: C, 45.65; H, 3.6; N 8.4%.) M.p., 258 °C (dec.).

Glyoxalbis(o-methylphenylimine)bis(bipyridyl)ruthenium(II)-hexafluorophosphate (C8)

After 8 days reflux, only part of the starting complex had reacted with the diazadiene. The reaction solution was filtered into a flask containing a solution of NH_4PF_6 in EtOH. The product precipitated and was filtered off and washed with EtOH, until no red-violet colour occurred, and then with hexane. After drying *in vacuo* a fine, red powder was obtained. Yield: 38%. (Found: C, 45.5; H, 3.4; N, 8.8. $C_{36}H_{32}N_6RuP_2F_{12}$ calcd.: C, 46.0; H, 3.4; N, 8.9%.) M.p., 227 °C (dec.).

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