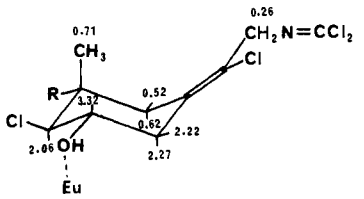
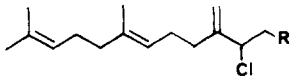
Chart I. Eu(fod)$_3$-Induced Shifts ($\Delta\delta$) of Selected Protons in the ^{1}H NMR Spectrum of **1**



The remaining stereochemical assignments were made by analysis of Eu(fod)$_3$-induced shifts (Chart I) in the ^{1}H NMR spectrum of **1.** Using established procedures,[13] the induced shifts of the ring protons were used to calculate an average location for the europium atom. Europium–proton distances calculated from induced shifts for the C-13 methyl group and the C-15 methylene group indicated an axial methyl group and a 3(14)-*Z* tetrasubstituted olefin. The carbon skeleton **11** is a new sesquiterpene skeleton for which we suggest the name axinyssane.[14]

A second carbonimidic dichloride **12,** $C_{16}H_{24}NCl_3$,[15] was isolated as a minor product (0.2% dry weight). The infrared

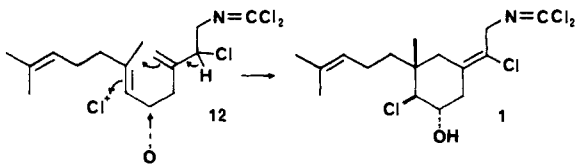


12 R = -N=CCl$_2$
13 R = -N$^+$≡C$^-$
14 R = -NHCHO

(1645 cm^{-1}) spectrum indicated the presence of a carbonimidic dichloride functionality. The ^{1}H NMR spectrum of **12** contained three methyl signals at δ 1.61, 1.62, and 1.68, exocyclic methylene proton signals at 5.08 and 5.22, two overlapping olefinic signals at 5.12 and 5.16, and two mutually coupled signals at 3.40 (d, 2 H, J = 7 Hz) and 4.64 (t, 1 H, J = 7 Hz). Using reaction conditions outlined above, the carbonimidic dichloride **12** could be reduced to an unstable isonitrile **13,**[16] which was hydrolyzed to a formamide **14.** In the ^{1}H NMR spectrum[17] of the formamide **14,** coupling between the -NH proton at δ 5.88 and the methylene protons at 3.46 and 3.91 allowed assignment of the formamide at C-1 and chlorine at C-2. The ^{13}C NMR spectrum of **12**[15] contained signals at chemical shifts predicted for a trans linear isoprenoid chain. The ^{1}H NMR and mass spectra support this assignment.

Since *P. pitys* is capable of chlorination reactions, we propose that the carbonimidic dichlorides may result from enzymatic chlorination of the corresponding isonitriles, which have not been detected. The axinyssane skeleton can result from a "chloronium ion" initiated cyclization of the minor carbonimidic dichloride or an equivalent molecule (Scheme I). Although we have not yet found a biological function for the carbonimidic dichlorides **1** and **12,** the corresponding isonitriles **3** and **13** inhibit the growth of *Staphylococcus aureus.*

Scheme I. Possible Biosynthesis of Axinyssane Skeleton



Acknowledgments. We wish to thank Dr. Bill Stewart for the collection of *P. pitys,* which was identified by Ms. Linda Jones. Antimicrobial screening was performed by Mrs. Marilynne Tseng. NMR spectra were obtained at the UCSD NMR Facility, supported by the National Institutes of Health (RR-708). This research was supported by grants from the National Institutes of Health (AI-11969) and the National Science Foundation (PCM-02539).

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(5) ^{13}C NMR δ ($CDCl_3$) 132.9 (s), 132.0 (s), 127.1 (s), 124.3 (s), 123.6 (d), 74.8 (d), 70.8 (d), 57.4 (t), 40.9 (t), 40.7 (s), 40.0 (t), 38.4 (t), 25.7 (q), 21.7 (t), 19.4 (q), 17.7 (q).

(6) ^{1}H NMR δ ($CDCl_3$) 0.92 (s, 3 H), 1.63 (s, 3 H), 1.70 (s, 3 H), 1.97 (dd, 1 H, J = 13, 11 Hz), 2.15 (d, 1 H, J = 14 Hz), 2.41 (dd, 1 H, J = 14, 3 Hz), 2.59 (s, 1 H, -OH), 3.44 (m, 1 H, J = 13, 5, 3 Hz), 3.78 (m, 1 H, J = 11, 10, 5 Hz), 3.82 (d, 1 H, J = 10 Hz), 4.25 (d, 1 H, J = 15 Hz), 4.31 (d, 1 H, J = 15 Hz), 5.09 (t, 1 H, J = 6 Hz).

(7) ^{1}H NMR δ ($CDCl_3$) 0.88 (s, 3 H), 1.62 (s, 3 H), 1.69 (s, 3 H), 1.91 (dd, 1 H, J = 13, 11 Hz), 2.09 d, 1 H, J = 14 Hz), 2.57 (s, 1 H, -OH), 2.70 (dd, 1 H, J = 14, 3 Hz), 3.41 (m, 1 H, J = 13, 5, 3 Hz), 3.73 (m, 1 H, J = 11, 10, 5 Hz), 3.82 (d, 1 H, J = 10 Hz), 4.21 (d, 2 H, J = 6 Hz), 5.09 (t, 1 H, J = 6 Hz), 8.18 (s, 1 H).

(8) ^{1}H NMR δ ($CDCl_3$) 0.87 (s, 3 H), 1.62 (s, 3 H), 1.69 (s, 3 H), 1.91 (dd, 1 H, J = 12, 11 Hz), 2.11 (d, 1 H, J = 14 Hz), 2.70 (dd, 1 H, J = 14, 3 Hz), 3.40 (m, 1 H, J = 12, 5, 3 Hz), 3.68 (s, 3 H), 3.76 (m, 1 H, J = 11, 10, 5 Hz), 3.81 (d, 1 H, J = 10 Hz), 3.97 (dd, 1 H, J = 15, 6 Hz), 4.14 (dd, 1 H, J = 15, 6 Hz), 5.08 (t, 1 H, J = 6 Hz).

(9) ^{1}H NMR δ ($CDCl_3$) 0.89 (s, 3 H), 1.62 (s, 3 H), 1.70 (s, 3 H), 1.98 (t, 1 H, J = 11 Hz), 2.10 (d, 1 H, J = 14 Hz), 2.52 (dd, 1 H, J = 14, 3 Hz), 2.65 (s, 1 H, -OH), 3.49 (m, 1 H, J = 11, 5, 3 Hz), 3.77 (m, 1 H, J = 11, 10, 5 Hz), 3.83 (d, 1 H, J = 10 Hz), 4.36 (s, 2 H), 5.10 (br t, 1 H, J = 6 Hz).

(10) IR ($CHCl_3$) 1665 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.87 (d, 6 H, J = 6 Hz), 1.11 (s, 3 H), 2.36 (d, 1 H, J = 16 Hz), 2.53 (d, 1 H, J = 16 Hz), 4.65 (dd, 1 H, J = 3.5, 1.5 Hz), 5.99 (dd, 1 H, J = 10, 1.5 Hz), 6.82 (dd, 1 H, J = 10, 3.5 Hz).

(11) ^{1}H NMR δ ($CDCl_3$), 0.93 (s, 3 H), 1.63 (s, 3 H), 1.70 (s, 3 H), 2.10 (s, 3 H), 2.72 (dd, 1 H, J = 14, 2 Hz), 3.38 (m, 1 H, J = 13, 5, 2 Hz), 3.69 (s, 3 H), 3.89 (d, 1 H, J = 10 Hz), 3.97 (dd, 1 H, J = 15, 6 Hz), 4.14 (dd, 1 H, J = 15, 6 Hz), 5.01 (m, 1 H, J = 11, 10, 5 Hz), 5.09 (t, 1 H, J = 6 Hz).

(12) IR ($CHCl_3$) 1690 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.00 (s, 3 H), 1.10 (t, 3 H, J = 7 Hz), 1.59 (s, 3 H), 1.67 (s, 3 H), 1.9–2.3 (m, 8 H), 5.06 (t, 1 H, J = 6 Hz), 5.88 (s, 1 H).

(13) In this example, the simplified formula $\Delta\delta = -k/r^3$ was employed (A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.,* **73,** 553 (1973)): C-13 methyl group, r_{calcd} = 7.4, r_{ax} = 7.3, r_{eq} = 8.6; C-15 methylene group, r_{calcd} = 9.9, r_Z = 9.7, r_E = 7.4 Å. (Subscripts refer to the alternative geometrical arrangements.)

(14) The full name of **1** becomes (1*R**,5*S**,6*S**)-6,14-dichloro-5-hydroxy-9,3(14)-(*Z*)-axinyssadien-15-yl carbonimidic dichloride.

(15) IR (film) 1645 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.61 (s, 3 H), 1.62 (s, 3 H), 1.68 (s, 3 H), 1.9–2.2 (m, 8 H), 3.40 (d, 2 H, J = 7 Hz), 4.64 (t, 1 H, J = 7 Hz), 5.08 (br s, 1 H), 5.12 (br t, 1 H), 5.16 (br t, 1 H), 5.22 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$) 145.9 (s), 136.0 (s), 131.3 (s), 124.3 (d), 123.3 (d), 114.4 (t), 62.4 (d), 59.5 (t), 39.6 (t), 31.7 (t), 26.7 (t), 26.2 (t), 25.7 (q), 17.7 (q), 16.1 (q) (N=CCl_2 signal not observed).

(16) IR ($CHCl_3$) 2130 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.61 (s, 3 H), 1.62 (s, 3 H), 1.68 (s, 3 H), 3.76 (d, 2 H, J = 7 Hz), 4.53 (t, 1 H, J = 7 Hz), 5 08 (m, 2 H), 5.16 (br s, 1 H), 5.27 (br s, 1 H).

(17) IR ($CHCl_3$) 3140, 1680 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.60 (s, 3 H), 1.62 (s, 3 H), 1.68 (s, 3 H), 2.0–2.2 (m, 8 H), 3.46 (m, 1 H, J = 14, 9, 5 Hz), 3.91 (m, 1 H, J = 14, 7, 5 Hz), 4.49 (dd, 1 H, J = 9, 5 Hz), 5.08 (br s, 1 H), 5.12 (m, 2 H), 5.22 (br s, 1 H), 5.88 (br, 1 H, -NH), 8.21 (br s, 1 H).

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Mixed Ammine–Olefin Complexes of Ruthenium(II)

Sir:

The known olefin complexes of ruthenium are largely confined to examples where the formal oxidation state at ruthenium is relatively low and strong π-acid ligands such as CO

or $P(C_6H_5)_3$ are also present.[1] In its complexes, Ru(II) has the spin-paired d^6 electron configuration and even ammine and pyridine complexes can have chemical properties which are more commonly associated with organometallic complexes.[2] In some ways, the ammine and pyridine complexes of Ru(II) represent a conceptual link between organometallic chemistry and the chemistry of classical coordination compounds. We find that their reactivity extends to olefin binding and that the resulting olefin complexes can have high chemical stabilities in solution.

In acetone solution a reaction occurs between $AgClO_4$ and *cis*-$Ru(bpy)_2Cl_2$ (bpy is 2,2′-bipyridine) to give an intermediate which in turn reacts rapidly with an excess of 2,5-norbornadiene (C_7H_8):

$$cis\text{-}(bpy)_2RuCl_2 + 2Ag^+ \xrightarrow{S} cis\text{-}[Ru(bpy)_2S_2]^{2+} + 2AgCl \quad (1)$$

$$[cis\text{-}Ru(bpy)_2S_2]^{2+} + C_7H_8 \rightarrow Ru(bpy)_2(C_7H_8)^{2+} + 2S \quad (2)$$

(S is solvent)

The expected cis geometry of the norbornadiene product, isolated as the PF_6^- salt,[3] is supported by the 60-Mhz ^1H NMR spectrum in CD_3CN which contains a series of multiplets assignable to the bpy ligands[4] from τ 1.23 to 1.90 and multiplets assignable to the bound diolefin at τ 3.61, 4.87, 5.91, and 8.44. The highest field resonance is a triplet assignable to the bridgehead protons arising from exclusive geminate coupling. Integration yielded an 8(bpy):1:1:1:1 pattern consistent with the C_2 symmetry of a cis complex.

The chloride bridged polymer, $(C_7H_8RuCl_2)_x$,[5] as a suspension in acetone, underwent a rapid reaction with a stoichiometric amount of 2,2′-bipyridine to give the yellow crystalline material $(Ru(bpy)(C_7H_8)Cl_2)$.[3] The ^1H NMR spectrum in $CDCl_3$ consists of multiplet bpy resonances between τ 1.82 and 2.63 and three resonances attributable to the diolefin ligand (τ 4.99, triplet; 5.94, multiplet; 8.39, triplet). Integration gave the ratio 4(bpy):2:1:1. The diolefin region of the ^1H NMR spectrum closely resembles that of $(C_7H_8)Mo(CO)_4$,[6] consistent with at least C_{2v} symmetry, and the ^1H NMR data suggest that the product is *trans*-$[Ru(bpy)(C_7H_8)Cl_2]$.

Both bpy complexes are remarkably stable when compared to many known olefin complexes. They remain unchanged in nonaqueous solvents in the presence of air for several days. In refluxing nonaqueous solvents (ethanol for $[Ru(bpy)_2C_7H_8]^{2+}$ and DMF for $Ru(bpy)(C_7H_8)Cl_2$) an excess of 2,2′-bipyridine converts both of them into the well-known $Ru(bpy)_3^{2+}$ ion.

We have also been able to prepare a series of alkene (cyclohexene, norbornene) and alkyne (acetylene, 1-octyne, 1-hexyne, 3-hexyne) complexes of pentaammine-ruthenium(II) by reactions between the hydrocarbons and the salt $[Ru(NH_3)_5H_2O](PF_6)_2$[7] in acetone (e.g.,

$$Ru(NH_3)_5S^{2+} + C_2H_5C{\equiv}CC_2H_5 \rightarrow Ru(NH_3)_5(3\text{-hexyne})^{2+} + S \quad (3)$$

where S is water or acetone). In all cases the complexes were isolated as PF_6^- or $S_2O_6^{2-}$ salts and satisfactory elemental analyses were obtained.[3] The complexes are well behaved in the solid state but are air sensitive in solution by reactions which are currently under investigation. In the ^1H NMR spectrum of the 3-hexyne complex in CD_3CN–acetonitrile there are two resonances attributable to the ammine protons at τ 6.60 (broad, area 3) and at 7.60 (broad, area 12). For the bound alkyne, the methyl protons appear at τ 7.90 (triplet, area 6) and the methylene protons at 8.40 (quartet, area 4). Apparently the proximity of the methylene protons to the metal–alkyne linkage results in a shielding effect that positions them upfield relative to the insulated methyl protons.

Table I. Reduction Potential and Spectral Data

Complex	λ_{max}, nm (ϵ)[a]	$E_{1/2}$, V (Ru(III) → Ru(II))[b]
$Ru(bpy)_3^{2+}$	454 (13 800)	1.29
cis-$Ru(bpy)_2(C_7H_8)^{2+}$	421 (6780)	1.70[c]
cis-$Ru(bpy)_2Cl_2$	553[d] (9100)	0.32[d]
trans-$Ru(bpy)(C_7H_8)Cl_2$	390 (1460)	1.04[e]
$Ru(NH_3)_5py^{2+}$	407 (7700)[f]	0.38[f]
$Ru(NH_3)_5(3\text{-hexyne})^{2+}$	300 (~800)[g]	0.54[h]

[a] λ_{max} in acetonitrile for the lowest energy absorption band only. ϵ is the molar extinction coefficient in M^{-1} cm^{-1}. [b] In 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$–acetonitrile at 22 ± 2 °C vs. the saturated sodium chloride calomel electrode. Determined by cyclic voltammetry at a scan rate of 200 mV. $\Delta E_p = E_{p,a} - E_{p,c}$ values were in the range 70 to 80 mV. [c] $E_{p,a}$; irreversible Ru(II) → Ru(III) oxidation even at scan rates as high as 20 V/s. [d] J. N. Braddock and T. J. Meyer, *Inorg. Chem.*, **12**, 723 (1973). [e] n = 1.0 where n is the electrochemical stoichiometry determined by coulometry. [f] Reference 7a. [g] Additional absorption bands appear at λ_{max} 260 nm (ϵ ~1270) and at 210 (~3500). The free ligand absorbs at λ_{max} 214 nm. [h] ΔE_p = 100 mV.

The coordination of the alkynes is reflected in the shift to lower wavenumbers of the C≡C stretching vibration. In 1-hexyne the shift is from 2120 cm^{-1} in the free ligand to 1920 cm^{-1} in the ruthenium complex. For 1-octyne, the shift is from 2120 to 1920 cm^{-1}; for 3-hexyne, it is 2118 to 1995 cm^{-1}. This change in stretching frequency of the acetylenic bond of ~200 cm^{-1} is comparable with that found in weakly bound Pt^{II}–alkyne complexes.[8]

Of primary interest to us are the effects of the hydrocarbon ligands on the metal site and, ultimately, the effect of the metal on the chemical properties of the ligands. A considerable amount is known concerning the effects of ligands on the spectral and redox properties of Ru(II) in both the ammine and bpy series of complexes.[2,7a,9-15] Spectral and reduction potential data for selected complexes reported here are given in Table I. Data for related complexes are included for comparison.

From the data in Table I, it seems apparent that bound alkenes and alkynes can have a dramatic effect on the electronic properties at Ru(II). Bipyridine complexes of Ru(II) have characteristic, low energy π^*(bpy) ← dπ(Ru) CT absorption bands[16] which vary systematically in energy with the π-accepting or -donating properties of the remaining two ligands. Because of the CT transitions, the bpy groups act as "spectator" ligands[13,14] for the Ru(II)–hydrocarbon interaction.[13,14] The marked increase in the CT λ_{max} for the norbornadiene complexes compared with those of their bpy analogues (Table I) suggests that there is far greater stabilization of the dπ levels and that back-bonding is more extensive to norbornadiene than to bpy. This conclusion is supported by the reduction potential data. For the three comparisons made in Table I, the Ru(III)/Ru(II) potentials are significantly higher for the hydrocarbons than for pyridines as ligands most likely because of an enhanced stabilization of Ru(II) by back-bonding.[2]

Acknowledgments are made to the Materials Research Center of The University of North Carolina under Grant DAHC15-73-G9 with the National Science Foundation and to the Army Research Office Durham under Grant DAAG29-76-G-0135 for support of this research. We would also like to thank David Harris of The University of North Carolina for the ^1H NMR data.

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(3) Satisfactory elemental analyses were obtained in all cases. Examples follow. Calcd for *trans*-$[Ru(bpy)(C_7H_8)Cl_2]$: C, 48.34; H, 3.84; N, 6.36. Found: C, 48.57; H, 3.53; N, 6.64. Calcd for $[Ru(bpy)_2(C_7H_8)](ClO_4)_2$: C, 45.21; H, 3.05; N, 7.81. Found: C, 45.17; H, 3.40; N, 7.87. Calcd for $[Ru(NH_3)_5C_2H_5C{\equiv}CC_2H_5](PF_6)_2$: C, 12.9; H, 4.5; N, 12.5. Found: C, 12.7; H, 4.5; N, 12.6. Calcd also for $[Ru(NH_3)_5C_2H_2]S_2O_6{\cdot}\frac{1}{2}H_2O$: C, 6.30; N, 18.36; H, 4.76; S, 16.81; H_2O, 2.36; Ru, 26.5. Found: C, 6.53; N, 18.47; H, 4.13; S, 16.74; H_2O; 2.12; Ru, 27.01.
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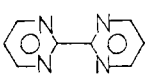
Ruthenium(II)–Bipyrimidine Complexes. Spectroscopic and Electrochemical Properties of a Novel Series of Compounds

Sir:

In our search for well-defined oligonuclear metal complexes we investigated the system ruthenium(II)–2,2′-bipyrimidine[1] (abbreviated as bipym). The four ligating sites of this molecule



are expected to lead to ligand bridged compounds of various complexity and various degrees of electronic interaction between the metallic centers. Related mononuclear ruthenium complexes have recently received considerable attention as systems capable of photodecomposing water.[2-5] This communication reports the syntheses and some spectroscopic and electrochemical properties of a series of novel Ru(II)bipym complexes.

The ion $Ru(bipym)_3^{2+}$ (I) was prepared by refluxing commercial $RuCl_3{\cdot}xH_2O$ (130 mg) with a fivefold excess of bipym in 30 mL of ethanol–water (2:1) for 30 h. The resulting hot solution was filtered and diluted with 50 mL of ethanol. Upon cooling the chloride salt was obtained in 90% yield as an orange microcrystalline solid. The same procedure using $Ru(bipy)_2Cl_2$[6] (bipy is 2,2′-bipyridine) in aqueous solution gave the mixed complex $Ru(bipy)_2bipym^{2+}$ (II) which was isolated as the orange PF_6 salt. If a Ru:bipym ratio of 2:1 was used, the green binuclear complex $[(bipy)_2RubipymRu(bipy)_2]^{4+}$ (III) could be isolated in 88% yield. Refluxing an aqueous solution of $Ru(bipym)_3^{2+}$ with a slight excess of $Ru(bipy)_2Cl_2$ gave a dark green solution from which the tetranuclear complex $[[(bipy)_2Rubipym]_3Ru]^{8+}$ (IV) could be precipitated with saturated NH_4PF_6 solution. Ion-exchange chromatography showed no additional components. Elution of the complex was possible only with 12 M HCl demonstrating thus the high positive charge. Analytical data are summarized in Table I. The ligand bipym was prepared according to the method given in ref 1 and purchased from Lancaster Synthesis, LTD, Lancaster, England.

Table II. Charge-Transfer Absorption and Emission Spectra of Ruthenium(II)–Bipyrimidine Complexes

Complex	Absorption,[a] λ_{max} (nm)	$10^{-4}\,\epsilon$	Emission
I	452, 412, 331	0.74, 0.76, 1.48	644,[c] 616,[d] 674,[d] 740[b,d]
$Ru(bipy)_3^{2+}$ [e]	452, 423[b]	1.46	613,[c] 627[c]
II	475,[b] 415, 398[b]	1.13	~680,[c] 667,[d] 720,[d] 800[b,d]
III	606, 560,[b] 408	0.76, 3.13	769,[d] 850[d]
IV	613, 580,[b] 408	1.74, 4.94	

[a] Aqueous solution; ϵ is given only for band maxima. [b] Shoulder. [c] Aqueous solution, 25 °C, corrected. [d] Solid compound, 15 ± 4 K. [e] Reference 4.

Important spectroscopic data of the new compounds are given in Table II. The striking similarity in the charge-transfer absorption spectra of $Ru(bipy)_3^{2+}$ and $Ru(bipym)_3^{2+}$ is duplicated in the band position of the emission spectra. The quantum yield for I is 0.09 (2) (20 °C, aqueous solution) compared with 0.042 (2) for $Ru(bipy)_3^{2+}$ under the same conditions.[7] The emission intensity of I does not change in the pH range 4.5–8. At lower pH it rapidly decreases. No emission is observed below pH 1 indicating a slightly enhanced basicity of the excited state, pK_a of $Ru(bipym)_3^{2+}$ being approximately −1 as determined from a spectrophotometric titration. In remarkable contrast to other polypyridine complexes having emission lifetimes between 0.33 and 4.68 μs (25 °C),[4] the luminescence of I is not quenched by dioxygen. This observation is attributed to the significantly shorter lifetime of the excited state of I. In aqueous solution the emission lifetime of $Ru(bipym)_3^{2+}$ varies smoothly from 0.096 (2) μs at 1.5 °C to 0.064 (2) μs at 30 °C, whereas for a solid sample it increases from 0.11 (1) μs at 278 K to 7.25 (5) μs at 7.6 K. Low temperature luminescence spectra of I, II, and III as solids (Figures 1 and 2) exhibit the ~1.3 kK progression as typically observed in the emission of related ruthenium compounds.[8] No luminescence could be detected up to 900 nm for the tetranuclear complex IV.

Cyclic voltammetry in aqueous solution of the bipym com-

Table I. Analytical Data for the Ruthenium–Bipyrimidine Complexes. Experimental Values in Parentheses

Complex	Ru	C	H	N	F or Cl
$[Ru(bipym)_3]Cl_2{\cdot}4H_2O$ (I)	14.1 (14.4)	40.1 (40.1)	3.6 (3.3)	23.4 (23.4)	9.9 (9.9)
$[Ru(bipy)_2bipym](PF_6)_2$ (II)	11.7 (12.1)	39.0 (38.8)	2.6 (2.6)	13.0 (13.0)	26.5 (26.6)
$[(bipy)_2RubipymRu(bipy)_2](PF_6)_4{\cdot}H_2O$ (III)	12.8 (13.6)	36.4 (36.4)	2.5 (2.5)	10.6 (10.7)	28.8 (29.0)
$[[(bipy)_2Rubipym]_3Ru](PF_6)_8{\cdot}2H_2O$ (IV)	13.4 (13.4)	33.5 (33.8)	2.3 (2.5)	11.2 (11.1)	