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Ruthenium(II) Complexes of Modified 1,10-Phenanthrolines. 1. Synthesis and Properties of Complexes Containing Dipyridophenazines and a Dicyanomethylene-Substituted 1,10-Phenanthroline[1]

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Complexes of ruthenium(II) with the polypyridyl ligands dipyrido[3,2-*a*:2′,3′-*c*]phenazine, the 9-phenyldipyrido[3,2-*a*:2′,3′-*c*]phenazinium cation, 4,7-dichloro-1,10-phenanthroline, and 4,7-bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline (BDCMP) have been prepared and their UV/visible absorption and emission characteristics determined. Electrochemical, infrared, and NMR results have also been obtained for several of the complexes. The results of these studies indicate the existence of a weakly coupled bichromophoric system for the two dipyridophenazine complexes, with almost independent Ru^{II}(bpy)$_3$- and phenazine-like chromophore units. In the case of the BDCMP complexes, a substantially modified Ru^{II}(phen)$_3$ π-electron system is indicated with evidence of both strong σ-donor and π-acceptor character for the coordinated BDCMP ligand.

Introduction

The photophysical and photochemical properties of the tris(2,2′-bipyridine)ruthenium(II) ion (Ru(bpy)$_3^{2+}$) and related Ru(diimine)$_3^{2+}$ complexes have been the subject of much attention in recent years. In addition to the considerable interest in the unusual excited-state properties exhibited by these complexes,[3] their potential use as photosensitizers in the photochemical and photoelectrochemical conversion of solar energy continues to stimulate much of this activity.[4]

Despite many favorable characteristics, including the existence of a relatively long-lived (600 ns) and energetic metal dπ to ligand π^* charge-transfer (MLCT) excited state with the ability to serve as both an electron-transfer reductant and oxidant, the use of the Ru(bpy)$_3^{2+}$ ion in this context has several drawbacks. Among these is the poor matching of the Ru(bpy)$_3^{2+}$ absorption spectrum with the solar emission spectrum, owing to the relatively high energy of the MLCT transition.[3-5]

In the course of the ca. 24 years of research on the excited-state properties of this system,[6] a variety of substituted 2,2′-bipyridine and 1,10-phenanthroline (phen) systems as well as other α,α'-diimine systems have been investigated as alternative ligands for Ru(II). Among the strategies that have been employed for the development of longer wavelength absorbing Ru(diimine)$_3^{2+}$ complexes, the extension of the π-electronic system of the α,α'-diimine ligand both through the addition of nitro,[7] phenyl,[8] benzo,[9] and other[5,10] groups to the ligand framework and through the construction of new polypyridine systems with multiple α,α'-diimine coordination sites[11] has been explored.

We describe here the synthesis and study of some new additions to this family of Ru(II)–polypyridine complexes involving two novel ligand systems formally derived from 1,10-phenanthroline. In these ligands the phen electronic π system has been modified, in one case, by coupling to a phenazine dye chromophore and, in the other, by substitution of dicyanomethylene groups in the 4,7-positions (Figure 1).

Experimental Section

Absorption spectra were recorded on a Perkin-Elmer 575 spectrometer. Emission spectra were run on a Perkin-Elmer Model MPF-44A fluorimeter equipped with a xenon lamp and a Perkin-Elmer spectral correction unit calibrated against rhodamine B up to 700 nm. Luminescence lifetimes were measured on a home-built apparatus.[12] A Molectron DL 200 nitrogen laser provided excitation pulses of ~10 ns at 440 nm with output energy of 100–300 μJ. Irradiation was perpendicular to the path of the detector, which consisted of a Spex $^1/_4$-m monochromator equipped with a 1P28 photomultiplier. The signal was recorded by a Biomation 6500 transient recorder interfaced to a Hewlett-Packard 9825A calculator equipped with a HP 9872A graphics plotter. This system enabled signal averaging and data analysis to be performed digitally.

Cyclic voltammetry was performed as previously described.[13] The working electrode and counterelectrode were platinum wires, and the reference electrode was a silver wire. Concentrations of substances studied were in the range 10^{-3}–10^{-4} M with 0.1 M tetrabutylammonium tetrafluoroborate supporting electrolyte in acetonitrile. When measurements on the sample were completed, ferrocene was added, and further scans were run for voltage calibration. Variation of ΔE_p and i_a/i_c with sweep rate were consistent with reversible or

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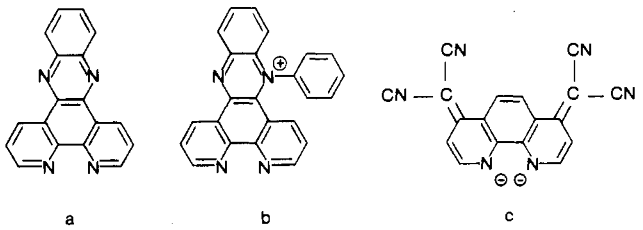

Figure 1. Molecular structures: (a) dipyrido[3,2-*a*:2′,3′-*c*]phenazine (DP); (b) the 9-phenyldipyrido[3,2-*a*:2′,3′-*c*]phenazinium cation (9-PDP); (c) the dianion of 4,7-bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline (BDCMP).

quasi-reversible features and comparable with the values found for the known reversible ferrocene/ferrocenium couple unless otherwise noted. Controlled-potential electrolysis was performed in the same cell but with the center compartment used for a silver–silver bromide reference electrode. For electrolysis, the working electrode and counterelectrode were platinum foil and the electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate. The counterelectrode solution was also 0.1 M in benzophenone. Electrolysis was carried out with a Princeton Applied Research Model 173 unit. Prior to their use in electrochemistry experiments, all complexes and ligands were dried at 110 °C under vacuum.

NMR spectra were recorded on a Varian FT80 spectrometer. Elemental analyses were performed in the General Electric Microanalytical Laboratory and by Galbraith Laboratories, Knoxville, TN.

Materials. 4,7-Dichloro-1,10-phenanthroline (Cl_2phen),[14] 4,7-bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline (BDCMP),[13] and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (DP)[15] were prepared as previously described. Dichlorobis(1,10-phenanthroline)ruthenium(II) was synthesized by using the procedure for dichlorobis(2,2′-bipyridine)ruthenium(II).[16]

The 9-phenyldipyrido[3,2-*a*:2′,3′-*c*]phenazinium ion, $C_{24}H_{15}N_4^+$ (9-PDP), was obtained as the olive green $ZnCl_3^-$ salt by a method similar to that used for the 9-phenyldipyrido[2,3-*a*:3′,2′-*c*]phenazinium ion[17] with a yield of 75% on a 5–10-mmol scale. The 1,10-phenanthroline-5,6-dione used in this preparation was obtained from G. F. Smith Chemical Co. Anal. Calcd for $C_{24}H_{15}N_4ZnCl_3$: C, 54.3; H, 2.9; N, 10.6. Found: C 53.8; H, 3.1; N, 10.4.

Other chemicals and solvents were obtained and/or purified as in earlier work.[13] Syntheses of ruthenium complexes were routinely conducted under a nitrogen atmosphere but worked up in air.

Ru(phen)$_2$(Cl$_2$phen)X$_2$ (X = AsF$_6^-$, Cl$^-$). Ru(phen)$_2$Cl$_2$·2H$_2$O (2.20 g, 4.00 mmol) and Cl_2phen (1.03 g, 4.14 mmol) were refluxed in 400 mL of ethanol for 24 h, cooled, and filtered. Addition of 2.6 g (11.4 mmol) of $KAsF_6$ in 75 mL of 1:1 ethanol/water, cooling to 0 °C, filtration, and drying gave 2.99 g (69%) of red-brown solid. Two additional crops totalling 1.05 g (24%) were obtained by reduction of the volume of the mother liquor. Purification of the first solid was effected by dissolution in 50 mL of acetone, filtration, and slow addition of the filtrate to ~300 mL of ether; yield 2.97 g of light orange powder. Anal. Calcd for $C_{36}H_{22}N_6Cl_2As_2F_{12}Ru$: C, 39.7; H, 2.0; N, 7.7; Cl, 6.5; As, 13.8; F, 21.0. Found: C, 39.5; H, 2.0; N, 7.7; Cl, 6.7; As, 13.6; F, 20.9. For later synthetic purposes the AsF_6^- was replaced by Cl^-. The AsF_6^- salt was dissolved in a minimum amount of acetone, and a solution of $(n\text{-}C_4H_9)_4NCl$ in acetone was added dropwise unitl precipitation was complete. Recovery was about 95% of the theoretical yield.

Ru(Cl$_2$phen)$_3$X$_2$ (X = AsF$_6^-$, Cl$^-$). Commercial hydrated ruthenium trichloride (146 mg, 0.55 mmol of Ru) and Cl_2phen (0.50 g, 2.00 mmol) were refluxed in 75 mL of 95% ethanol for 4 days during which a red-brown solid was deposited. This solid was removed by filtration, washed with ethanol, and dried (171 mg). The combined filtrates were treated with $KAsF_6$ as described for Ru(phen)$_2$(Cl$_2$phen)(AsF$_6$)$_2$ to give 374 mg of red-orange Ru(Cl$_2$phen)$_3$(AsF$_6$)$_2$. This was taken up in acetone and, after filtration, was precipitated with water to give 340 mg (0.28 mmol, 56%) of red-orange powder. Anal. Calcd for $C_{36}H_{18}N_6Cl_6As_2F_{12}Ru$: C, 35.3; H, 1.5; N, 6.9; Cl, 17.4. Found: C, 35.5; H, 1.7; N, 6.8; Cl, 16.7. Conversion to the Cl^- salt was accomplished as described for Ru(phen)$_2$(Cl$_2$phen)Cl$_2$.

The solid that precipitated during the synthesis was too insoluble for further purification. Analyses on two separate preparations fit the formulation Ru(Cl$_2$phen)$_2$Cl$_3$·2H$_2$O. Anal. Calcd for $C_{24}H_{16}N_4O_2Cl_7Ru$: C, 38.9; H, 2.2; N, 7.6; Cl, 33.5. Found: C, 39.2, 39.0; H, 2.0, 2.0; N, 7.5, 7.2; Cl, 33.2, 33.0.

Ru(phen)$_2$(9-PDP)(ClO$_4$)$_3$·H$_2$O. A mixture of 317 mg (0.60 mmol) of (9-PDP)ZnCl$_3$, 330 mg (0.60 mmol) of Cl$_2$Ru(phen)$_2$·2H$_2$O, and 150 mL of 2:1 ethanol/water was refluxed for 2 days. The solvent was removed under reduced pressure, the solid dissolved in 50 mL of H_2O, and the solution filtered. Slow addition of 0.84 g of $NaClO_4$·H_2O in 10 mL of H_2O gave a red-brown precipitate that was collected and washed with H_2O. The product was taken into acetone, precipitated with ether, and dried at 40 °C under vacuum; yield 407 mg (0.36 mmol, 60%) of yellow-brown powder. Anal. Calcd for $C_{48}H_{33}N_8O_{13}Cl_3Ru$: C, 50.7; H, 2.9; N, 9.9; Cl, 9.4. Found: C, 50.5; H, 3.1; N, 10.4; Cl, 9.2.

Initial emission studies of this product indicated two emission bands in the range 600–630 nm. Efforts to purify this material by recrystallization did not noticeably alter either the emission or absorption spectra. Further purifications of a very small sample sufficient for qualitative emission and absorption spectroscopy was achieved by means of high-pressure liquid chromatography.[18]

Analytical and preparative liquid chromatography was carried out on a Waters Associates Model ALC 244 liquid chromatograph fitted with a Du Pont Zorbax ODS column and a HP 1040A spectrophotometric detector. The mobile phase was methanol/water modified with 2 g of tetrabutylammonium chloride/L and 50 mg of phosphoric acid/L. The gradient was linear from 50 to 100% methanol in 30 min at 1.5 mL/min. A 20-μL sample of the product from the above preparation in methanol (2 mg/mL) gave at least three peaks under these conditions, the largest of which (at detector settings of 200–550 nm) showed a visible/UV spectrum that was apparently unchanged from that of the starting material. This fraction was collected from two consecutive injections of 20-μL samples and used for qualitative absorption and emission measurements. Whereas no apparent change was noted in the absorption spectrum, the emission spectrum now showed only one emission band at 600 nm, suggesting that a small amount of an unknown impurity was responsible for the more complex emission spectrum observed initially.

Ru(DP)$_3$X$_2$ (X = AsF$_6^-$, ClO$_4^-$). Hydrated ruthenium trichloride (143 mg, 0.55 mmol of Ru) and DP (708 mg, 2.50 mmol) were refluxed in 100 mL of ethanol for 3 days. The solid left after removal of solvent was Soxhlet extracted overnight with benzene to remove unreacted DP. The remaining solid was then extracted with ethanol until fresh extract was no longer orange. Slow addition of 0.5 g of $KAsF_6$ in ethanol/water to the orange extract solution precipitated the product, which was collected, washed with H_2O, and dried. This material (137 mg) was taken up in ~20 mL of acetone and the resultant mixture was filtered and reprecipitated with ~25 mL of H_2O to give 118 mg (0.089 mmol, 16%) of bright orange-red solid. Anal. Calcd for $C_{54}H_{30}N_{12}As_2F_{12}Ru$: C, 48.9; H, 2.3; N, 12.7. Found: C, 49.3; H, 2.1; N, 12.5. The ClO_4^- salt was obtained by first converting to the Cl^- salt as for Ru(phen)$_2$(Cl$_2$phen)Cl$_2$, dissolution in ethanol, and addition of aqueous $NaClO_4$ to precipitate Ru(DP)$_3$(ClO$_4$)$_2$·3H$_2$O. Anal. Calcd for $C_{54}H_{36}N_{12}O_{11}Cl_2Ru$: C, 54.0; H, 3.0; N, 14.0; Cl, 5.9. Found: C, 54.3; H, 3.1; N, 14.2; Cl, 5.9.

Ru(phen)$_2$(BDCMP)·2H$_2$O. Method A. A 128-mg sample of NaH (56.9%, 3.03 mmol) was washed with petroleum ether to remove the mineral oil. After addition of 10 mL of Me_2SO to the dry NaH, 278 mg (4.21 mmol) of malononitrile was added in small portions. Finally, 411 mg (0.53 mmol) of Ru(phen)$_2$(Cl$_2$phen)Cl$_2$ and another 10 mL of Me_2SO were added. The mixture was heated at 90–95 °C for 18 h and cooled to ambient temperature, ~1 mL of H_2O added, and the Me_2SO removed under reduced pressure. The residue was mixed vigorously with 100 mL of H_2O and dried to give 380 mg (0.49 mmol, 93%) of Ru(phen)$_2$(BDCMP)·2H$_2$O. Anal. Calcd for $C_{42}H_{26}N_{10}O_2Ru$: C, 62.8; H, 3.3; N, 17.4; Cl, 0. Found: C, 62.9; H, 3.2; N, 17.4; Cl, 0.5.

Method B. A mixture of 275 mg (0.50 mmol) of Ru(phen)$_2$Cl$_2$·2H$_2$O and 272 mg (0.265 mmol) of (Et$_4$N)$_3$Na(BDCMP)$_2$[13] in 60 mL of absolute ethanol was refluxed for 3 days

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during which a red solid was deposited. After cooling, the solid was collected by filtration, washed with ethanol, and dried to give 371 mg (0.46 mmol, 92%) of product. Anal. Calcd for $C_{42}H_{26}N_{10}O_2Ru$: C, 62.8; H, 3.3; N, 17.4; Cl, 0. Found: C, 61.1; H, 3.2; N, 17.4; Cl, 0.5.

The products obtained from methods A and B were found to give identical ^1H NMR, infrared, and visible–ultraviolet absorption spectra.

$[(C_6H_5)_3PCH_3]_4[Ru(BDCMP)_3]\cdot 4H_4O$. The synthesis paralleled that of method A for $Ru(phen)_2(BDCMP)\cdot 2H_2O$ using 0.20 mmol of $Ru(Cl_2phen)_3Cl_2$, 6.00 mmol of NaH, and 8.26 mmol of $H_2C(CN)_2$ in 50 mL of Me_2SO. Heating at 95 °C for 7 days resulted in a color change from red to red-violet. The solid left after quenching with 0.5 mL of water followed by Me_2SO removal was dissolved in water and 1.0 mmol of $[(C_6H_5)_3PCH_3]Cl$ in water added dropwise. Filtration, washing with water, and vacuum drying at 110 °C gave 293 mg (0.13 mmol, 66% yield) of a deep red-violet solid. Anal. Calcd for $C_{130}H_{98}N_{18}O_4P_4Ru$: C 70.9; H, 4.5; N, 11.4; P, 5.6. Found: C, 71.0; H, 4.5; N, 11.5; P, 5.7.

Results

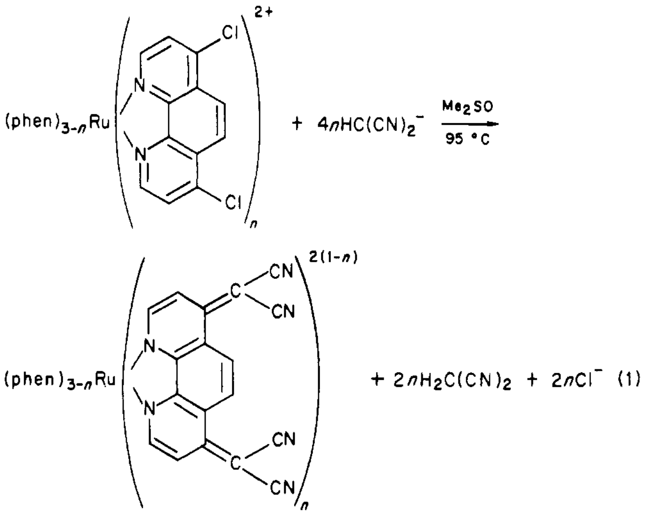
Syntheses. The various organic ligands used in this work have all been described previously except for the 9-phenyldipyrido[3,2-*a*:2′,3′-*c*]phenazinium ion [9-PDP] (Figure 1b). This species was prepared in good yield as the olive green "$ZnCl_3^-$" salt starting from 1,10-phenanthroline-5,6-dione using a procedure analogous to that described for the preparation of the isomeric 9-phenyldipyrido[2,3-*a*:3′,2′-*c*]phenazinium ion.[17] The parent compound, dipyrido[3,2-*a*:2′,3′-*c*]phenazine [DP] (Figure 1a), has been employed previously as a ligand in complexes with both ruthenium(II)[19] and copper(II).[15]

These dipyridophenazine ligands were used to obtain the corresponding $Ru(phen)_{3-n}(L)_n^{m+}$ (L = 9-PDP, $n = 1$, $m = 3$; L = DP, $n = 3$, $m = 2$) complexes starting from $Ru(phen)_2Cl_2$ and $RuCl_3$ by established procedures. Attempts to prepare the tris complex of the cationic 9-PDP ligand in this manner proved unsuccessful.

The inability to obtain $Ru(9\text{-}PDP)_3^{5+}$ from $RuCl_3$ and 9-PDP may relate to a reduced σ-donor ability for the positively charged 9-PDP ligand. As an alternative route to a tris cationic ligand complex we attempted to methylate the neutral DP ligands in $Ru(DP)_3^{2+}$ at one of the nitrogen atoms by a procedure previously used to alkylate 4,4′-bipyridine coordinated at one end of ruthenium(II).[20] No evidence for reaction with either $(CH_3)_2SO_2$ or CH_3I was noted by absorption spectroscopy.

In an earlier publication we reported the synthesis of the compound 4,7-bis(dicyanomethylidene)-1,4,7-tetrahydro-1,10-phenanthroline (BDCMP) as its disodium salt using 4,7-dichloro-1,10-phenanthroline (Cl_2phen) and excess $NaHC(CN)_2$.[13] This ligand, in the form of its more soluble tetraethylammonium sodium salt, $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$, was used successfully to prepare the uncharged BDCMP–ruthenium(II) complex $Ru(phen)_2(BDCMP)$ by displacement of Cl^- from $Ru(phen)_2Cl_2$. However, attempts to obtain the $Ru(BDCMP)_3^{4-}$ complex from the dianionic ligand and $RuCl_3$ were unsuccessful.

It was subsequently found that both the mono and tris BDCMP complexes of ruthenium(II) could be prepared from the corresponding Cl_2phen complexes by reaction of the coordinated Cl_2phen ligands with $HC(CN)_2^-$ in a manner analogous to that employed for the free ligand (eq 1).



Elemental analysis and spectroscopic data indicate complete replacement of all Cl atoms to give the corresponding $Ru(phen)_{3-n}(BDCMP)_n^{2(1-n)}$ complexes in good yield. The neutral $Ru(phen)_2(BDCMP)$ derivative obtained in this manner is indistinguishable from the product of the ligand-displacement reaction on the basis of infrared, ^1H NMR, absorption spectral, and elemental analysis data. The tetraanionic $Ru(BDCMP)_3^{4-}$ species was isolated and characterized as the $(C_6H_5)_3PCH_3^+$ salt, after unsuccessful attempts to obtain a crystalline tetraethylammonium derivative.

Appropriate selection of the counterion imparted good solubility of the cationic complexes in a variety of solvents. The neutral complex $Ru(phen)_2(BDCMP)$ has good solubility only in Me_2SO and DMF and is only slightly soluble in most other polar organic solvents. This complex is insoluble in water but dissolves readily in concentrated solutions of strong acids such as HCl or H_2SO_4. Dilution with water reprecipitates the original complex. These solutions in strong acid show no apparent changes on long standing, and absorption spectra run several days after the initial solution preparation were identical with that originally obtained. On the other hand, significant changes in both band positions and intensities were observed in acetonitrile solutions that were prepared in air and allowed to stand for extended periods. The data reported in this paper for the $Ru(phen)_2(BDCMP)$ complex in acetonitrile were obtained on solutions prepared in an inert atmosphere in a glovebox, under which conditions the solutions appear to be indefinitely stable.

On the basis of the absorption and emission spectral data obtained in concentrated HCl solution, a likely explanation for the observed solubility of the $Ru(phen)_2(BDCMP)$ complex in strong acids is the reversible protonation of the dicyanomethylene groups of the coordinated BDCMP ligand (eq 2).[21,22] Analogous protonation equilibria have been observed

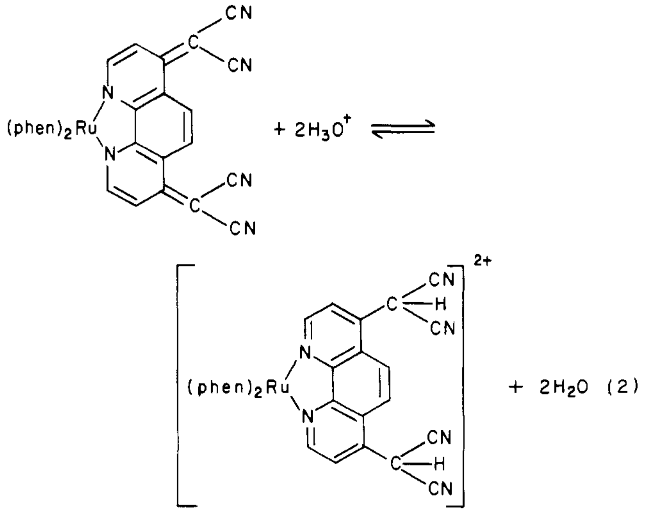


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Table I. NMR Spectra of Selected Ligands and Their Ruthenium(II) Complexes

		chem shift,[a] δ			
		non-phen ligand			
compd	solvent	2,9-H	3,8-H	5,6-H	other signals
Cl_2phen	*c*	9.10 d	7.70 d	8.27 s	
Ru(Cl_2phen)$_3^{2+}$	*d*	8.15 d	7.94 d	8.62 s	
Ru(phen)$_2$(Cl_2phen)$^{2+}$	*e*	8.2–8.7 m	7.92 d	8.38 s	phen: 8.2–8.7 m (2,9-H), 7.6–7.9 m (3,8-H), 8.7–8.9 m (4,7-H), 8.38 s (5,6-H)
BDCMP[b]	*d*	8.31 d	6.93 d	8.47 s	
Ru(phen)$_2$(BDCMP)	*d*	6.75 d	7.07 d	8.66 s	phen: 8.0–8.3 m (2,9-H), 7.6–8.0 m (3,8-H), 8.5–8.8 m (4,7-H), 8.32 s (5,6-H)
Ru(BDCMP)$_3$[$CH_3P(C_6H_5)_3$]$_4$	*d*	6.76 d	7.24 d	8.63 s	7.75 (C_6H_5, J_{P-H} ~ 6 Hz), 3.15 d (CH_3, J_{P-H} ~ 11 Hz)

[a] Relative to internal tetramethylsilane; s = singlet, d = doublet, m = multiplet. [b] From [$(C_2H_5)_4N$]$_3$Na(BDCMP)$_2$ as in ref 13. [c] Chloroform-*d*. [d] Dimethyl-d_6 sulfoxide. [e] Acetone-d_6.

Table II. Absorption and Emission Data for Ligands and Complexes[a]

	absorption		emission		
	λ_{max}, nm (log ε (M^{-1} cm^{-1}))		λ_{max}, nm		
species	<340 nm	>340 nm	uncor	cor	lifetime,[b] μs
Ru(phen)$_3^{2+}$	262 (5.10)[c]	446 (4.30)[c]	593[d,e]	605, 625[d,e]	0.92[d,e]
Ru(bpy)$_3^{2+}$		423 sh (4.08), 452 (4.11)[f]	607[d,e]	613, 627[d,e]	0.60[d,e]
DP[g]	214 (4.39), 241 (4.53), 270 (4.81), 295 (4.34)	342 (3.92), 350 (3.97) 359 (4.11), 367 (4.05), 378 (4.16)	453, 490, 533	544	<0.01
Ru(DP)$_3^{2+}$	220 (5.25), 280 (5.64), 317 (4.62)	343 sh (4.54), 353 sh (4.60), 361 (4.62), 369 (4.63), 433 sh (4.33), 455 (4.35)	602	615	0.73
(9-PDP)$ZnCl_3$[e]	208 (4.54), 277 (4.56), 301 (4.44), 313 (4.38)	408 (4.32)	542	604	<0.01
Ru(phen)$_2$(9-PDP)$^{3+}$	223 (5.31), 264 (5.38)	398 (4.41), ~440 sh (4.28)	600		0.53
Cl_2phen	235 (4.56), 266 (4.58), 302 (3.92), 330 (2.83)	344 (2.36)	352, 368, 387, 407 w		<0.01
Ru(phen)$_2$(Cl_2phen)$^{2+}$	225 (4.87), 264 (5.07)	438 (4.26)	627	644	2.2
Ru(bpy)$_2$(Cl_2bpy)$^{2+}$		448 (4.10)[h]		645[h]	0.42[h]
Ru(Cl_2bpy)$_3^{2+}$		462 (4.23)[h]		632[h]	0.48[h]
Ru(Cl_2phen)$_3^{2+}$	213 (5.29), 266 (5.41), 305 (4.23), 318 sh (3.89)	440 (4.35), 457 (4.35)	612	628	2.5
BDCMP^{2-}[i]	213 (4.61), 250 (4.34), 273 (4.35)	391 (4.51), 411 (4.57)	610		<0.01
Ru(phen)$_2$(BDCMP)	222 (4.99), 264 (4.95)	463 (4.64)	610	622	1.4
Ru(phen)$_2$($BDCMPH_2$)$^{2+}$[j]	226 (4.90), 264 (4.92)	434 (4.16), 465 sh (4.03)	632		
Ru(BDCMP)$_3^{4-}$	222 (5.26), 258 (4.82), 267 (4.78), 275 (4.75)	381 (4.80), 502 (4.70),	683	>700	1.4

[a] In acetonitrile solution at room temperature, except as noted. [b] ±15%. [c] Staniewicz, R. J.; Sympson, R. F.; Hendricker, D. G. *Inorg. Chem.* 1977, *16*, 2166. [d] Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* 1976, *98*, 6536. [e] In water. [f] Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* 1980, *63*, 1675. [g] In ethanol. [h] Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Isr. J. Chem.* 1982, *27*, 87. [i] As [$(C_2H_5)_4N$]$_3$Na(BDCMP)$_2$. [j] In 12 M HCl.

for other dicyanomethylene derivative in strong acid media.[23] This would effectively result in the conversion of the neutral complex to a cationic species with probable greater solubility in aqueous media.

Infrared Spectra. The only compounds with notably useful infrared features are the BDCMP complexes that show two strong, well-defined absorptions characteristic of the $=C(CN)_2$ group.[22] These occur at 2146 and 2180 cm^{-1} in Ru(phen)$_2$(BDCMP) and at 2135 and 2165 cm^{-1} in Ru(BDCMP)$_3^{4-}$ and are comparable in frequency and relative intensity to those in the Na^+ and Li^+ complexes.[13]

^{1}H NMR Spectra. Assignment of NMR features was made only for the Cl_2phen and BDCMP ligands and their complexes. These are presented in Table I. In each case, the 2,9- and 3,8-protons appear as clear doublets (*J* = 5–6 Hz) and the 5,6-protons as a singlet. This pattern of ^{1}H NMR peaks is typical of 4,7-substituted 1,10-phenanthrolines, and the assignment of the resonances for the free ligands and their complexes follows that made in previous ^{1}H NMR studies of such systems.[24] The large upfield shift of the doublets assigned to the 2,9-hydrogens of the ligands on coordination is a well-known phenomenon and presumably reflects the increased shielding of these protons in the complexes due to their close proximity to the metal ion. The 3,8- and 5,6-proton resonances on the 4,7-substituted 1,10-phenanthroline are generally much less affected by coordination and often show a slight downfield shift.

Other Data. Further characterization of the complexes by their absorption and emission spectra and by their electrochemical properties is given in Tables II and III, respectively. Emission lifetimes for the uncomplexed ligands are less than the 0.01-μs limit of the measuring system. Although in the cyclic voltammograms the separation between the cathodic

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Table III. Cyclic Voltammetry Potentials for Complexes and Selected Ligands in Acetonitrile Solutions of 0.1 M Tetrabutylammonium Tetrafluoroborate[a]

	$E_{1/2}$, V (ΔE_p)	
species	oxidn	redn
$Ru(phen)_3^{2+}$[b]	1.40	−1.41, −1.54, −1.84
$Ru(bpy)_3^{2+}$[b]	1.35	−1.33, −1.52, −1.76
$Ru(DP)_3^{2+}$	1.37 (50)	−1.00 (~80),[c] −1.08 (~80)[c]
DP	*d*	−1.29 (30)
$Ru(phen)_2(9\text{-}PDP)^{3+}$	0.09 (60), 1.36 (80)	−0.50 (100), −1.42 (~130), −1.63 (~150)
9-PDP	0.07 (130)	*e*
$Ru(phen)_2(Cl_2phen)^{2+}$	1.29 (75)	−1.22 (E_{pc}, irrev), −1.52 (E_{pc}, irrev)
$Ru(bpy)_2(Cl_2bpy)^{2+}$[f]	1.39 (69)	−1.05 (64), −1.40 (70), −1.65 (E_{pc}, irrev)
$Ru(Cl_2phen)_3^{2+}$	1.37 (55)	−1.16 (E_{pc}, irrev)
$Ru(Cl_2bpy)_3^{2+}$[f]	1.52 (68)	−0.97 (63), −1.12 (66), −1.39 (E_{pc}, irrev)
BDCMP[g]	0.47 (E_{pa}, irrev), 0.66 (E_{pa}, irrev)	*d*
$Ru(phen)_2(BDCMP)$	0.55 (70), 0.86 (80), 1.43 (90)	−1.52 (100), −1.74 (80)
$Ru(BDCMP)_3^{4-}$	*h*	*h*

[a] Values (vs. SCE) were obtained by taking the average of the anodic and cathodic peak potentials (±0.01 V) except as indicated using ferrocene as an internal standard with $E_{1/2}$(oxidn) = +0.35 V vs. SCE. Separation between anodic (E_{pa}) and cathodic (E_{pc}) peak potentials in mV (ΔE_p) are indicated in parentheses. Values cited are for a scan rate of 100 mV/s. [b] Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* 1973, *95*, 6582. [c] Reduction peaks are strongly overlapped; values less certain. [d] No redox processes observed within the limits of the anodic (cathodic) scan [+1.7 V (−2.3 V) vs. SCE]. [e] Not determined. [f] Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* 1980, *63*, 1675. The values reported in this paper are referenced to the normal hydrogen electrode with $E_{1/2}$ for the $Ru(bpy)_3^{2+}$ oxidation taken as 1.26 V. The values given in the table have been converted to *E* vs. SCE by adding 0.09 V, such that $E_{1/2}$(oxidn) for $Ru(bpy)_3^{2+}$ is 1.35 V vs. SCE.[b] [g] Ackermann, M. N.; Interrante, L. V. *J. Org. Chem.* 1982, *47*, , 1994. [h] No reproducible features observed.

and anodic peaks is somewhat larger than that expected theoretically for a reversible one-electron-transfer process ($\Delta E_p = 59/n$ mV, where n = number of electrons transferred), similar values were obtained for the internal reference standard ferrocene, which is known to be reversible.[25] Moreover, judging from previous observations, ΔE_p values in this range appear to be the norm rather than the exception in cyclic voltammetric measurements carried out in nonaqueous media.[11]

Only $Ru(BDCMP)_3^{4-}$ failed to give any reproducible features on either oxidation or reduction. For the other complexes all of the features appeared to be reversible or quasi-reversible except for the reduction of the two Cl_2phen complexes. The voltammogram for $Ru(phen)_2(BDCMP)$, which exhibits five well-defined redox features, is shown in Figure 2.

Discussion

The ruthenium(II) complexes described in this paper are appropriately viewed as derivatives of the parent tris(1,10-phenanthroline)ruthenium(II) complex $Ru(phen)_3^{2+}$, whose photophysical and photochemical properties, along with those of the closely related $Ru(bpy)_3^{2+}$, have been much studied.[3] This complex exhibits strong absorption in the visible region, which has been attributed to M $dt_{2g} \rightarrow$ L π^* transitions. However, unlike its $Ru(bpy)_3^{2+}$ relative, where combinations of only the antisymmetric (ψ) π^* ligand orbital are believed to be energetically accessible, transitions to states that involve both the symmetric (χ) and antisymmetric π^* orbitals are anticipated for $Ru(phen)_3^{2+}$, rendering detailed assignment of the various visible transitions quite difficult.[3,26]

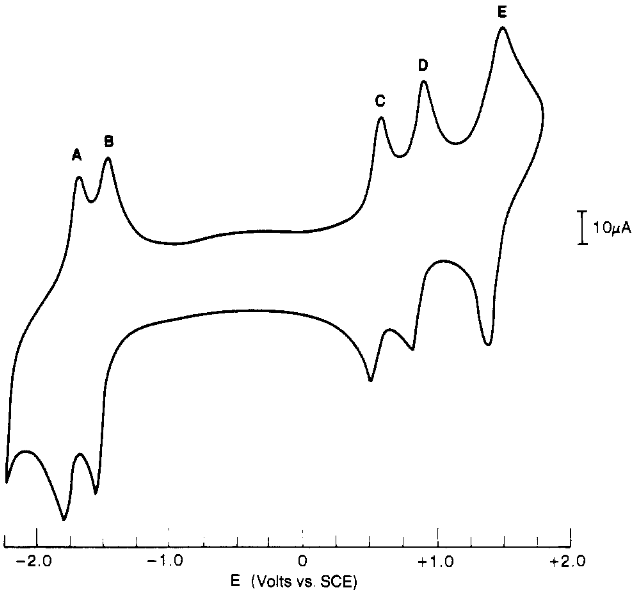

Figure 2. Cyclic voltammogram of ≃0.5 mM $Ru(phen)_2(BDCMP)$ in CH_3CN with 0.1 M $(n\text{-}Bu)_4NBF_4$ at a Pt electrode.

In previous studies of derivatives of $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$, electrochemical data have been used, along with other information, in rationalizing the observed changes in absorption and emission spectra.[3-11] In particular, the potential for the first reduction of the metal complex has been taken as indicative of the relative energy of the first ligand π^* orbital whereas the first oxidation has been used as a measure of the metal dt_{2g} orbital energy, on the assumption that the following processes occur on reduction and oxidation, respectively:

$$[M^{II}L_3]^{2+} + e^- \rightarrow [M^{II}L_2(L^-)]^+$$

$$[M^{II}L_3]^{2+} \rightarrow [M^{III}L_3]^{3+} + e^-$$

Considerable independent evidence for the production of a "ligand-localized" MLCT excited state on optical excitation of $Ru(bpy)_3^{2+}$ and related $Ru(diimine)_3^{2+}$ complexes has been obtained in the last few years, and for several mixed-ligand systems virtually independent MLCT transitions involving the different ligands in the complex have been identified.[3]

In this context, ruthenium(II) complexes of ligands that are more easily reducible than phen generally exhibit MLCT transitions at lower energy than the corresponding $Ru(phen)_3^{2+}$ complex, as long as the $Ru(L)_3^{2+/3+}$ redox potential is approximately the same. Among the factors that are believed to lead to lower π^* orbital energies is the degree of delocalization of the π-electron system. Substituents that effectively extend the π system such as benzo groups in the 5,6;5′,6′-position and nitro groups in the 4,4′-positions of bpy have been among the most effective in lowering the energy of the MLCT transitions.[7,9]

The phen derivatives chosen for this study all have substituents that would be expected to appreciably modify the phen electronic π system. The DP and 9-PDP ligands effectively combine the bpy ligand structure with the known organic chromogen, phenazine, which is attached at the bpy 2,3,3′,2′-position. The 9-PDP derivative, in particular, is a close relative to the brown-yellow organic dye Flavinduline O[17] and has its own intense visible absorption and emission

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(25) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

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(Table II). The compound BDCMP, on the other hand, has the strongly electron-accepting dicyanomethylene groups attached to the phen ring system in the 4,7-positions, in direct conjugation with the two pyridyl ring nitrogens. This ligand also absorbs extensively in the visible region and emits out at 610 nm (Table II). On coordination to ruthenium(II) these ligands give complexes that exhibit both close similarities and distinct differences with respect to the parent $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$ systems.

DP and 9-PDP Complexes. In certain respects, the spectral and electrochemical properties of the ruthenium(II) complexes of these dipyridophenazines closely resemble those of $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$. In particular, both the absorption and emission spectra of the $Ru(DP)_3^{2+}$ complex in the visible region correspond closely in appearance and band positions to that of $Ru(bpy)_3^{2+}$. Significant differences appear only below ca. 400 nm where strong absorption bands quite similar in shape, intensity, and energy to those of the free DP ligand occur.

Even for 9-PDP, whose absorption extends appreciably further into the visible region, the absorption spectrum can be viewed as basically an additive combination of the spectra of $Ru(bpy)_3^{2+}$ and the slightly perturbed 9-PDP ligand. Thus, in addition to the strong bands in the UV region attributable to internal π to π^* transitions of the coordinated 9-PDP and phen ligands, an intense, fairly narrow, visible absorption band is observed for the $Ru(phen)_2(9\text{-PDP})^{3+}$ complex at 398 nm, superimposed on the broad MLCT transitions of the $Ru(phen)_2$("bpy") core. This 398-nm band is quite similar in appearance and intensity to the visible absorption band of 9-PDP at 408 nm and is ascribed to that same, presumably $\pi \rightarrow \pi^*$, intraligand transition.

The emission spectra of these two complexes are closely similar to one another and to that of the $Ru(bpy)_3^{2+}$ complex, consisting of a single, broad band near 600 nm. The lifetime of this emission is also essentially the same in the three cases and is consistent with expectations for a $MLCT^3$ excited state centered on the bpy portion of the complexes.

The cyclic voltammetry data obtained for these two complexes (Table III) show apparently reversible oxidations at about the same potential (~1.4 V vs. SCE) as is observed for $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$, presumably due to the analogous $RuL_3^{2+/3+}$ redox process. In addition, the $Ru(phen)_2(9\text{-PDP})^{3+}$ complex shows another reversible oxidation at $E_{1/2} = +0.09$ V vs. SCE that probably arises from oxidation of the coordinated 9-PDP ligand, as is suggested by the cyclic voltammetry results obtained for its chlorozincate salt (Table III). Both the DP- and 9-PDP–ruthenium(II) complexes show reduction waves at potentials considerably less negative than those of $Ru(phen)_3^{2+}$, suggesting that the first ligand π^* level in these complexes lies at lower energy than that in $Ru(phen)_3^{2+}$.

Judging from prior work on other $Ru(diimine)_3$ complexes, this redox data would lead one to anticipate an appreciable red shift in the MLCT absorption for these complexes. The absence of such a shift in the absorption spectra is believed to be a consequence of the bichromophoric character of these complexes where, to the first approximation, the optical transitions and redox processes are effectively localized within the "separate" $Ru(phen)_2$("bpy") and phenazine π systems and are little perturbed by the connection of these units through the 3,3′-positions of the "bpy" ligand.

Cl_2phen Complexes. Included in the list of spectral and redox data are the results obtained for the ruthenium(II) complexes of 4,7-dichloro-1,10-phenanthroline. Although these complexes were prepared as precursors to the BDCMP complexes, their spectral and redox properties exhibit several features of significant independent interest. These particular complexes have apparently not been previously reported, although the analogous $Ru(bpy)_{3-n}(L)_n^{2+}$ (n = 1, 3) complexes, where L = 4,4′-dichloro-2,2′-bipyridine (Cl_2bpy) have been examined recently as potential photosensitizers for the water-splitting reaction.[5]

As was noted in the case of the $Ru(Cl_2bpy)_3^{2+}$ complex, the substitution of the 4,7-hydrogen atoms in phen by the more electronegative chlorine atoms does produce a small red shift in the relevant MLCT absorption and emission bands for $Ru(Cl_2phen)_3^{2+}$ (Table II). A lowering of the energy of the π^* orbital of the Cl-substituted ligands relative to bpy and phen is also suggested by the less negative reduction potentials observed for the corresponding ruthenium(II) complexes (Table III). The absorption spectra of the mixed-ligand complexes, $Ru(bpy)_2(Cl_2bpy)^{2+}$ and $Ru(phen)_2(Cl_2phen)^{2+}$, both show a slight blue shift while the emission bands are red shifted.

The $Ru^{2+/3+}$ potential in the Cl_2phen complexes is little altered with respect to $Ru(phen)_3^{2+}$, suggesting a comparable dπ-orbital energy, whereas in the case of $Ru(Cl_2bpy)_3^{2+}$ a substantial shift in this potential, relative to that of $Ru(bpy)_3^{2+}$, to more positive values was observed. Another notable difference that appears in the data obtained for the Cl_2phen complexes relative to that of the Cl_2bpy system is in the results of the excited-state lifetime measurements (Table II). A fivefold increase in the lifetimes of the excited states for the Cl_2phen complexes with respect to that for the Cl_2bpy derivatives is observed. Indeed, these complexes exhibit the longest lifetimes of the new complexes reported here and are among the longest of any of the known $Ru(diimine)_3^{2+}$ complexes. It has been noted previously that phenyl substitution in the 4,7-position of phen also results in a substantial increase in emission lifetime whereas substitution of phenyl in the same positions of bpy had little or no effect.[8]

In the case of the two Cl_2phen complexes studied here it was noted that the cyclic voltammetry behavior is reversible only if the $Ru^{2+/3+}$ couple is scanned and reversible if ligand reduction is included. In the latter case successive scans lead to large current enhancements; the $Ru^{2+/3+}$ couple remains well-defined, but the other features are degraded. These changes in the cyclic voltammograms are accompanied by the deposition of a brown film on the working electrode. When this electrode is transferred to fresh electrolyte after a period of scanning, the observed $Ru^{2+/3}$ wave persists, suggesting that an electroactive and presumably polymeric film of the complex is formed on the electrode as a result of electroreduction. We propose that ligand reduction in this case leads to loss of Cl^- from Cl_2phen, leaving a radical at the 4- or 7-position. These radicals then couple to produce a polymer in which Ru(II) is imbedded. As the polymer layer grows on the electrode, the current is enhanced due to the greater number of Ru(II) sites present.

Previous studies of polypyridyl complexes of ruthenium(II) containing conjugated olefinic groups have evidenced a similar process on electrochemical reduction.[27] Here, the reduction of the complex presumably initiates a free-radical, anionic olefin polymerization process that leads to stable, electroactive polymer films containing imbedded $Ru(diimine)_3$ groups. Recently a related oxidative electropolymerization process has been reported for Ru(II) complexes of amino-substituted 1,10-phenanthroline and pyridines.[28]

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(28) Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1283.

Preliminary efforts to examine the possible utility of the $Ru(phen)_{3-n}(Cl_2phen)_n^{2+}$-derived electroactive films as electrocatalysts for the electrochemical oxidation of organic substrates have been frustrated by the apparently irreproducible nature of the reductive polymerization process in this case.[29]

BDCMP Complexes. The reaction of the coordinated Cl_2phen igand in the $Ru(phen)_{1-x}(Cl_2phen)_x^{2+}$ complexes with excess $HC(CN)_2^-$ was found to be a highly efficient way of producing the corresponding BDCMP complexes of Ru(II) and, in fact, the only effective way of obtaining the $Ru(BDCMP)_3^{4-}$ complex. In the process of this conversion of Cl_2phen to BDCMP, the phenanthroline ring system undergoes considerable modification in which the heterocyclic nitrogen atoms acquire substantial negative charge (Figure 1c). Indeed, a substantial increase in the σ-donor ability of this ligand relative to that of phen is apparent in its strong affinity for alkali-metal ions and the proton.[13]

Moreover, both physical property studies[13] and the results of a recent structure determination[30] show that protonation occurs at the nitrogen atoms of the free ligand, rather than at the dicyanomethylene groups, indicating that the negative charge resides primarily at these positions. On the other hand the strongly electron-accepting dicyanomethylene groups in direct conjugation with these nitrogen atoms should be quite effective in withdrawing some of the charge from these positions in the free ligand and in complexes of this ligand with metal atoms having filled dπ orbitals. Thus, both strong σ-donor and π-acceptor character is anticipated for this ligand when it is used in conjuction with a metal ion such as Ru^{2+}.

Another notable feature of this ligand is its unusual redox behavior. Unlike 1,10-phenanthroline, which does not undergo oxidation in the electrochemically accessible potential range, the mixed Et_4N^+/Na^+ salt of the BDCMP ligand exhibits two one-electron-oxidation waves at 0.47 and 0.66 V vs. SCE, corresponding to the conversion of the dianion to the monoanionic and neutral species, for which a fully conjugated π-electron structure can be written. In the free ligand this oxidation is irreversible on the CV time scale, indicating a low stability for the oxidized forms when not coordinated to a transition-metal ion. The results obtained in the electrochemical study of the $Ru(phen)_2(BDCMP)$ complex suggest that the stability of these oxidized forms is considerably enhanced on coordination of the BDCMP ligand to Ru(II). Moreover, significant changes in the redox potentials are observed for both the coordinated BDCMP and phen ligands, indicating an appreciable redistribution of charge within the Ru(II) complex.

As is shown in Figure 2, five, apparently reversible, redox processes are observed in the CV scan between −2.2 and +1.8 V vs. SCE, at least two of which can be reasonably associated with the coordinated BDCMP ligand. The oxidation peaks at +0.58 and +0.90 V vs. SCE correspond to the two irreversible oxidation waves observed for the free ligand appropriately shifted to more positive potentials due to charge donation from the BDCMP ligand to the $Ru(phen)_2$ unit. In this case, however, these redox processes are apparently reversible, at least on the CV time scale, as reduction peaks of comparable intensity are observed in reverse scan at +0.51 and +0.82 V vs. SCE. The third oxidation process at $E_{1/2}$ = 1.43 V vs. SCE occurs at close to the same potential as the single oxidation process in $Ru(phen)_3^{2+}$ (1.40 V vs. SCE) and, by analogy, is attributed to the $Ru^{2+/3+}$ couple. The occurrence of this process at the essentially the same potential as for $Ru(phen)_3^{2+}$ is remarkable in view of the increased negative charge in the $Ru(phen)_2(BDCMP)$ complex and suggests that the BDCMP ligand is an effective π acceptor as well as a good σ donor.

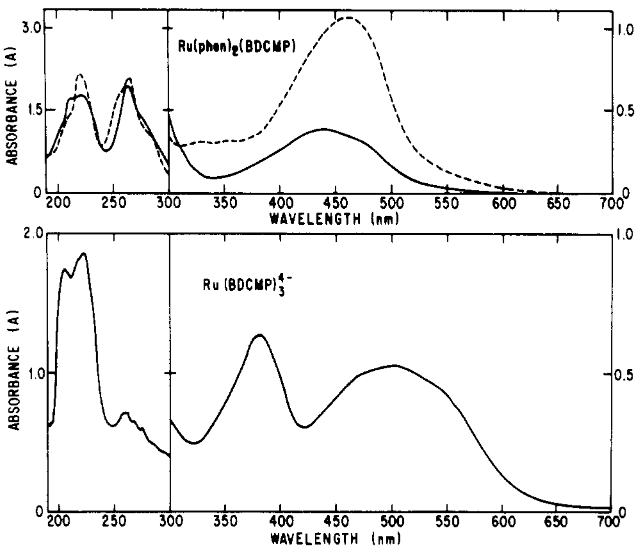

Figure 3. UV–vis absorption spectra of Ru–BDCMP complexes $Ru(phen)_2(BDCMP)$ (2.4×10^{-5} M) in CH_3CN (---) and 12 M HCl (—) and $[(C_6H_5)_3PCH_3]_4Ru(BDCMP)_3$ (9.8×10^{-6} M) in CH_3CN.

On the cathodic side of the cyclic voltammogram, two additional redox processes are observed that are attributed to the successive one-electron reduction of the two coordinated phen ligands. These processes occur at more negative potentials than the first two reductions in $Ru(phen)_3^{2+}$, indicating a net transfer of charge from BDCMP to these phen ligands.

Despite these indications of a redistribution of charge in this complex and a somewhat higher phen π*-orbital energy, the absorption and emission spectra are not markedly different from that of $Ru(phen)_3^{2+}$, with visible absorption and emission band maxima actually at slightly lower energies. The lifetime observed for the excited-state species is about 50% higher than that reported for $Ru(phen)_3^{2+}$, at 1.4 μs.

The $Ru(phen)_2(BDCMP)$ complex is insoluble in water but dissolves readily in strong acids such as 12 M HCl from which it can be recovered without change by dilution with water. This reversible solution of the complex in strong acid is accompanied by changes in visible absorption and emission as well as in the ^1H and ^{13}C NMR spectra,[31] which are consistent with expectations for the formation of a bis(dicyanomethyl)-substituted 1,10-phenanthroline complex (eq 2). In particular, the ^{13}C NMR spectrum in 12 M HCl shows a peak of the appropriate intensity in the aliphatic carbon region at 37.6 ppm (referenced to Me_4Si at 0 ppm), which is shown to be a methine carbon (CH) by off-resonance decoupling. A peak of similar intensity also appears in this region (37.2 ppm) in the spectrum of the unprotonated complex in Me_2SO-d_6; however, this peak is not split by H coupling in the off-resonance decoupling experiment.[31] We suggest that these peaks arise from the same dicyanomethyl (or dicyanomethylene) carbon atoms that are abnormally shielded[32] in the case of the unprotonated complex due to resonance interaction with the negatively charged imide nitrogens and the ruthenium(II) dπ orbitals. The absorption and emission spectra of this complex in strong acid media differ significantly, particularly in terms of the band intensities, from that obtained in acetonitrile solution (Figure 3). These spectra do resemble closely those of the $Ru(phen)_2(Cl_2phen)^{2+}$ complex, indicating a rough equivalence between the −Cl and $-CH(CN)_2$ substitutents in

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terms of their inductive effect on the phen π-electron system.

The visible absorption and emission spectra of the tris complex, $Ru(BDCMP)_3^{4-}$, are the most red shifted compared to the other complexes in this study. Two well-separated absorption bands are observed for this complex (Table II; Figure 3), one of which (381 nm) is relatively narrow and resembles closely in shape, intensity, and energy the main visible absorption band of the free ligand at ~400 nm. On the basis of prior studies of dicyanomethylene-substituted organic dye systems,[33] this band can be reasonably attributed to a basically ligand-centered transition, in which negative charge is transferred from the nitrogen atoms to the dicyanomethylene groups.

The extremely broad absorption band at lower energies (502 nm) has no obvious counterpart in the spectrum of the free ligand and probably rises from MLCT; however, the complex shape and broad character of this band suggest that it is comprised of several transitions, the precise nature of which is impossible to determine on the basis of the data currently available. The relatively long lifetime of the corresponding emission at >700 nm is, at least, consistent with expectations for a MLCT excited state for this system.

Efforts to determine the redox properties of this complex were frustrated by the totally irreproducible character of the cyclic voltammograms obtained. Both oxidation and reduction features were observed in the several potential scans made, but their occurrence and position depended on the range of potentials scanned and no reversible or even reproducible features could be characterized even after repetitive cycling within the same potential limits. In addition to an apparent instability toward electrochemical oxidation or reduction, this complex also exhibits an unusual sensitivity toward oxygen under certain conditions. Solutions of this complex in acetonitrile, when maintained in an inert atmosphere, can be exposed to room light without apparent change; moreover, they also seem to be unaffected by exposure to air or oxygen if room light is excluded. On the other hand, exposure to both air and light produces an irreversible change in the color of these solutions from red-violet to orange-red, and in the absorption spectrum the broad band at 502 nm is replaced by an absorption at around 460 nm. Similar changes were observed in other solvents, including water, acetone, ethanol, and dichloromethane. Attempts to reverse this reaction by removal of the oxygen or the addition of a reducing agent (thiosulfate) did not prove successful. Further studies of this photoreaction with oxygen, including the identification of the photoproducts, were not attempted.

In the absence of oxygen, this complex is indefinitely stable in both aqueous and nonaqueous solution and can be recovered from these solutions on addition of a nonsolvent or evaporation. It absorbs more strongly in the visible region than the $Ru(bpy)_3^{2+}$ system (Table III) and has an energetic excited state whose lifetime is even longer than that of $Ru(bpy)_3^{2+}$. As such, it is a worthy subject for further investigation of photochemical electron-transfer processes as well as for possible use in photochemical energy conversion processes that do not require exposure to oxygen.

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Registry No. $(9\text{-PDP})ZnCl_3$, 92543-36-7; $Ru(phen)_2(Cl_2phen)(AsF_6)_2$, 92543-38-9; $Ru(phen)_2(Cl_2phen)Cl_2$, 92543-39-0; $Ru(phen)_2Cl_2$, 85718-09-8; $Ru(Cl_2phen)_3(AsF_6)_2$, 92543-41-4; $Ru(Cl_2phen)_3Cl_2$, 23757-38-2; $Ru(phen)_2(9\text{-PDP})(ClO_4)_3$, 92575-07-0; $Ru(DP)_3(AsF_6)_2$, 92543-43-6; $Ru(DP)_3(ClO_4)_2$, 92543-44-7; $Ru(phen)_2(BDCMP)$, 92543-45-8; $[(C_6H_5)_3PCH_3]_4[Ru(BDCMP)_3]$, 92575-09-2; $[Ru(phen)_2(BDCMPH_2)]^{2+}$, 92543-46-9; malononitrile, 109-77-3.

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Interaction of Complexes of Composition $MnLX_2$ (L = Tertiary Phosphine) with Dioxygen

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The complexes $MnBr_2PMe_3$, $MnBr_2PEt_3$, and $MnBr_2PPhMe_2$ have been prepared as films on infrared windows under completely anhydrous conditions with care being taken to eliminate all free phosphine. These films have been exposed to dioxygenation/evacuation cycles in a specially designed infrared cell with infrared spectra being monitored under carefully controlled conditions. This work has indicated that such complexes do exist in solid-state films and do interact with dioxygen. However, the extent of the reversibility of the interaction with dioxygen is markedly dependent upon the nature of the tertiary phosphine ligand employed. All of the solid-state complexes studied in this work exhibit an irreversible decay channel in the presence of dioxygen to a phosphine oxide complex decomposition product at ambient temperature.

Introduction

There exists a lively controversy at the present time concerning the existence of complexes of composition $MnLX_2$ (L = tertiary phosphine, X = anion) and their interaction with dioxygen. McAuliffe and co-workers first reported the preparation and characterization of a broad series of the manganese(II) complexes and suggested that the complexes mimicked myoglobin in their behavior with dioxygen.[1] Green

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