also serves to inhibit photodecomposition and to enhance the excited-state lifetime in CH_2Cl_2, although the effects are not as pronounced as for phenyl substitution. An advantage of methyl substitution is that it does not significantly perturb the excited-state energy.

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Registry No. $[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2}$, 14323-06-9; $[\mathrm{Ru(bpy)_2(phen)}]\mathrm{Cl_2}$, 60828-36-6; $[\mathrm{Ru(phen)_2(bpy)}]\mathrm{Cl_2}$, 60828-37-7; $[\mathrm{Ru(phen)_3}]\mathrm{Cl_2}$, 23570-43-6; $[\mathrm{Ru(bpy)_2(Me_2bpy)}]\mathrm{Cl_2}$, 77461-13-3; $[\mathrm{Ru(Me_2bpy)_2(bpy)}]\mathrm{Cl_2}$, 119998-53-7; $[\mathrm{Ru(phen)_2(Me_2bpy)}]\mathrm{Cl_2}$, 119998-54-8; $[\mathrm{Ru(bpy)_2(Ph_2bpy)}]\mathrm{Cl_2}$, 77494-67-8; $[\mathrm{Ru(Ph_2bpy)_2(bpy)}]\mathrm{Cl_2}$, 119998-55-9; $[\mathrm{Ru(Ph_2bpy)_3}]\mathrm{Cl_2}$, 31790-57-5; $[\mathrm{Ru(phen)_2(Ph_2bpy)}]\mathrm{Cl_2}$, 119998-56-0; $[\mathrm{Ru(bpy)_2(Me\text{-}phen)}]\mathrm{Cl_2}$, 119998-57-1; $[\mathrm{Ru(phen)_2(Me\text{-}phen)}]\mathrm{Cl_2}$, 119998-58-2; bpy, 366-18-7; phen, 66-71-7; $\mathrm{Me_2bpy}$, 1134-35-6; $\mathrm{Ph_2bpy}$, 6153-92-0.

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Preparation, Photochemistry, and Electronic Structures of Coumarin Laser Dye Complexes of Cyclopentadienylruthenium(II)

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The syntheses and characterization of six new compounds that contain the $CpRu^+$ ($Cp = \eta^5\text{-}C_5H_5$) moiety bound to a substituted coumarin laser dye are reported. The complexes prepared are of the general form $[CpRu(\eta^6\text{-laser dye})]PF_6$, where laser dye = coumarin-1 (7-(diethylamino)-4-methylcoumarin), coumarin-2 (4,6-dimethyl-7-(ethylamino)coumarin), coumarin-6 (3-(2-benzothiazolyl)-7-(diethylamino)coumarin), coumarin-311 (7-(dimethylamino)-4-methylcoumarin), coumarin-334 (10-acetyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one), or coumarin-338 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid 1,1-dimethylethyl ester). The structures of all of the new complexes except the complex of coumarin-6 were determined by ^1H and ^{13}C NMR spectroscopy and contain the $CpRu^+$ group bound to the benzenoid moiety of the coumarin system. The $CpRu^+$ group binds to the benzothiazole group of the coumarin-6 compound. Photolysis of the complexes in CH_3CN solutions results in the formation of $CpRu(CH_3CN)_3^+$ and the free dye. The complexes of the dyes other than coumarin-6 exhibit low-lying MLCT bands and are not emissive. The coumarin-6 complex retains the low-lying intramolecular charge-transfer band present in the free dye and emits in fluid solution at room temperature with $\lambda_{max} = 532$ nm and $\Phi = 0.11 \pm 0.02$. The laser dye centered emission band of the complex is red-shifted 25 nm with respect to the free coumarin-6 emission.

Introduction

For the past several years, our group has investigated the arene photosubstitution reactions of $[CpM(arene)]^+$ complexes (M = Ru, Fe; Cp = η^5-cyclopentadienyl, arene = η^6-arene). The photochemical release of the arene from the metal in these complexes occurs via nucleophilic attack of the medium on the distorted a^3E_1 ligand field excited state in an associative or associative-interchange mechanism.[1,2] Kinetic data for related thermal arene displacement reactions of $CpRu(anthracene)PF_6$[3] are consistent with two possible mechanisms.[4] Differentiation of these mechanisms depends on the kinetic properties of a proposed "slipped ring" η^4-arene complex reaction intermediate. At the time of these original studies, a spectroscopic probe sensitive to $\eta^6 \rightarrow \eta^4$ coordination changes was not available. Recently, we became interested in the possibility that either the UV–vis spectral bands or the emissive properties of a strongly absorbing arene might serve as the sensitive probe. To this end we have synthesized $CpRu^+$ complexes of substituted coumarin laser dyes, which appeared ideal for these studies. These new laser dye complexes exhibit strong electronic transitions that respond to arene coordination changes in both absorption and emission spectroscopic experiments.

Experimental Section

Dichloromethane and acetonitrile were of spectroscopic grade and were used without further purification. Laser dyes were obtained from the Eastman Kodak Co. All other reagents were reagent grade and were used as received. Room-temperature UV–vis spectra of the compounds were obtained (acetonitrile solution) with a Cary 17D spectrometer. Emission and excitation profiles were recorded on a Spex F112X spectrofluorometer. NMR spectra were obtained on an IBM Bruker 200-MHz spectrometer (^1H) and an IBM Bruker 300-MHz spectrometer (^{13}C). IR spectra were obtained (dichloromethane solution) for the compounds with a Perkin-Elmer 1710 FT spectrophotometer.

Synthesis of $[CpRu(laser\ dye)]PF_6$ Compounds. The starting materials $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[CpRu(CH_3CN)_3]PF_6$ were prepared by literature procedures.[5,6]

$[CpRu(coum\text{-}1)]PF_6$. To a degassed flask containing 100.0 mg (0.230 mmol) of $[CpRu(CH_3CN)_3]PF_6$ and 53.3 mg (0.230 mmol) of the laser dye coumarin-1 (7-(diethylamino)-4-methylcoumarin) was added 25 mL of N_2-degassed 1,2-dichloroethane. The solution immediately assumed an intense golden brown hue. The solution was bubbled with N_2 for another 5 min and then was stirred for 2 h. The solvent was removed by rotary evaporation to yield a dark yellow residue, which was redissolved in acetone and adsorbed on a short diatomaceous earth column. The column was allowed to equilibrate for 1 h and then was eluted with pentane to remove excess coumarin-1. The washed product was stripped off the column with acetone and then sent through a short alumina column. Evaporation of the eluate followed by recrystallization from acetone–ether yielded 59.0 mg (0.109 mmol) of light yellow $[CpRu(coum\text{-}1)]PF_6$ (47% yield). ^1H NMR (methylene-d_2 chloride): δ 6.47 (d, aryl H (bound ring), 1 H, $J = 6.6$ Hz), 6.33 (s, aryl H (bound ring), 1 H), 6.13 (s, aryl H_3 (unbound ring), 1 H), 5.72 (d, aryl H (bound ring), 1 H, $J = 6.6$ Hz), 5.10 (s, Cp, 5 H), 3.37 (q, ethyl CH_2, 4 H, $J = 7.18$ Hz), 2.46 (s, aryl CH_3, 3 H), 1.23 (t, ethyl CH_3, 6 H, $J = 7.20$ Hz). Anal. Calcd for $C_{19}H_{22}NO_2RuPF_6$: C, 42.07; H, 4.09; N, 2.58. Found: C, 42.15; H, 4.03; N, 2.70. IR data (cm^{-1}): 1765 s, 1631 m, 1569 s, 1513 w.

$[CpRu(coum\text{-}2)]PF_6$. The coumarin-2 complex was prepared by the same method used to obtain $[CpRu(coum\text{-}1)]PF_6$, except coumarin-2

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* To whom correspondence should be addressed.

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(3) Where hapticity is not explicitly noted, maximum hapticity is assumed. Thus, molecules formulated as $CpRu(arene)^+$ shall refer to $CpRu(\eta^6\text{-arene})^+$ complexes.

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(50.0 mg (0.230 mmol); 4,6-dimethyl-7-(ethylamino)coumarin) was used instead of coumarin-1. This procedure yielded 58.0 mg (0.109 mmol) of light yellow [CpRu(coum-2)]PF_6 (48% yield). ^1H NMR (methylene-d_2 chloride): δ 6.37 (s, aryl H (bound ring), 1 H), 6.31 (s, H_3 (unbound ring), 1 H), 6.24 (s, aryl H (bound ring), 1 H), 5.08 (s, Cp, 5 H), 3.35 (q, ethyl CH_2, 2 H), 2.45 (s, CH_3, 3 H), 2.27 (s, CH_3, 3 H), 1.33 (t, ethyl CH_3, 3 H). Anal. Calcd for $C_{18}H_{20}NO_2RuPF_6$: C, 40.91; H, 3.82; N, 2.65. Found: C, 41.04; H, 4.04; N, 2.76. IR data (cm^{-1}): 1759 s, 1710 w, 1631 m, 1565 s, 1535 m.

[CpRu(coum-311)]PF_6. A solution of 46.8 mg (0.230 mmol) of coumarin-311 (7-(dimethylamino)-4-methylcoumarin) in 15 mL of 1,2-dichloroethane was bubbled with N_2 for 20 min. When 99.9 mg (0.230 mmol) of [CpRu($CH_3CN)_3$]PF_6 was then added under positive N_2 pressure, an immediate color change from pink to intense golden brown occurred. The solution was bubbled with N_2 for another 5 min and then stirred for 2 h. The reaction mixture was worked up in the manner outlined above to yield 57.2 mg (0.111 mmol) of light yellow [CpRu(coum-311)]PF_6 (48% yield). ^1H NMR (acetonitrile-d_3): δ 6.34 (m, $H_{5,6,8}$ (bound ring), 3 H), 5.64 (d, H_3 (unbound ring), 1 H, J = 4.34 Hz), 5.18 (s, Cp, 5 H), 2.91 (s, amino CH_3, 6 H) 2.40 (s, aryl CH_3, 3 H). Anal. Calcd for $C_{17}H_{18}NO_2RuPF_6$: C, 39.69; H, 3.53; N, 2.72. Found: C, 40.00; H, 3.73; N, 2.91. IR data (cm^{-1}): 1773 m, 1754 s, 1710 w, 1631 m, 1573 s, 1516 w.

[CpRu(coum-338)]PF_6. The same procedure was followed as in the synthesis of [CpRu(coum-311)]PF_6 with the exception that the starting materials were 100.0 mg (0.230 mmol) of [CpRu($CH_3CN)_3$]PF_6 and 78.6 mg (0.230 mmol) of coumarin-338 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid 1,1-dimethylethyl ester). Workup of the reaction mixture yielded 48.1 mg (0.0737 mmol) of yellow [CpRu(coum-338)]PF_6 (32% yield). ^1H NMR (methylene-d_2 chloride): δ 8.47 (s, H_4 (unbound ring), 1 H), 6.33 (s, H_5 (bound ring), 1 H), 5.08 (s, Cp, 5 H), 3.41 (m, alkyl CH_2, 2 H), 3.24 (m, alkyl CH_2, 2 H), 2.91 (m, alkyl CH_2, 2 H), 2.91 (m, alkyl CH_2, 2 H), 2.60 (m, alkyl CH_2, 2 H), 2.11 (m, alkyl CH_2, 4 H), 1.58 (s, ester CH_3, 9 H). ^{13}C NMR (methylene-d_2 chloride): δ 20.27, 20.81, 22.42, 26.85, 49.48, 49.85 (alkyl CH_2), 28.00 (ester CH_3), 84.29 (C3), 73.28, 74.71, 83.16, 122.9, 124.39 (aromatic quaternary carbons), 160.5 (C2), 80.81 (Cp), 149.44 (C4), 81.59 (C5). Anal. Calcd for $C_{25}H_{28}NO_4RuPF_6$: C, 46.01; H, 4.33; N, 2.15. Found: C, 45.89; H, 4.54; N, 2.09. IR (cm^{-1}): 1783 s, 1713 m, 1618 m, 1562 s, 1522 w.

[CpRu(coum-6)]PF_6. A 60.5-mg (0.173-mmol) amount of coumarin-6 (3-(2-benzothiazolyl)-7-(diethylamino)coumarin) was dissolved in 20 mL of 1,2-dichloroethane and bubbled with N_2 for 30 min. A 75.0-mg (0.173-mmol) amount of [CpRu($CH_3CN)_3$]PF_6 was added to the laser dye solution under positive N_2 pressure, causing an immediate color change from yellow to an intense dark red. The solution was bubbled with N_2 for another 5 min and then stirred under N_2 for 2 h. Removal of the solvent by rotary evaporation left a dark red residue, which was washed with ether to remove the excess coumarin-6, redissolved in acetone, and eluted on a short diatomaceous earth column. Elution with acetone removed a dark red impurity from the column and left a bright orange solid at the top of the column. The bright orange solid was removed from the column by eluting with acetonitrile. Rotary evaporation of the orange eluant yielded a bright orange solid, [CpRu(coum-6)]PF_6. ^1H NMR (acetonitrile-d_3): δ 8.83 (s, H_4, 1 H), 7.64 (d, H_5, 1 H, J = 9.1 Hz), 7.15 (d, aryl H (bound ring), 1 H, J = 5.4 Hz), 7.04 (d, aryl H (bound ring), 1 H, J = 5.67 Hz), 6.61 (d, H_8, 1 H), 6.83 (d of d, H_6, 1 H, J = 9.1 Hz), 6.05 (m, aryl H (bound ring), 2 H), 5.06 (s, Cp, 5 H), 3.50 (q, ethyl CH_2, 4 H, J = 7.12 Hz), 1.21 (t, ethyl CH_3, 6 H, J = 7.08 Hz). Anal. Calcd for $C_{25}H_{25}N_2O_2SRuPF_6$: C, 45.38; H, 3.50; N, 4.24. Found: C, 45.12; H, 3.55; N, 4.22. IR data (cm^{-1}): 1757 w, 1707 m, 1646 m, 1617 s, 1578 s, 1507 s.

[CpRu(coum-334)]PF_6. To a degassed flask containing 34.4 mg (0.124 mmol) of coumarin-334 (10-acetyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]-benzopyrano[6,7,8-*ij*]quinolizin-11-one) and 58.5 mg (0.134 mmol) of [CpRu($CH_3CN)_3$]PF_6 was added 15 mL of 1,2-dichloroethane. The solution color quickly changed to an intense yellow-brown. The solution was stirred for 2 h, and the solvent was then removed by rotary evaporation. The dark solid was washed with diethyl ether and hexane to remove unreacted ligand to yield 77.6 mg of slightly impure [CpRu(coum-334)]PF_6 (100% yield). The compound was further purified by column chromatography with diatomaceous earth and methylene chloride to give a rusty brown solid, mp 191–193 °C dec. ^1H NMR (methylene-d_2 chloride): δ 2.06 (m, alkyl H, 4 H), 2.61 (s, CH_3, 3 H), 2.77 (m, alkyl H, 4 H), 3.27 (m, H_4, 2 H), 3.42 (m, alkyl H, 2 H), 5.08 (s, Cp, 5 H), 6.32 (s, H_5 (bound ring), 1 H), 8.51 (s, H_4 (unbound ring), 1 H). ^{13}C NMR (methylene-d_2 chloride): δ 20.22, 20.76, 30.11, 49.49, 49.64 (alkyl CH_2) 26.89 (acetyl CH_3), 89.2 (C3), 73.22, 74.78, 83.27, 124.68, 127.07 (quaternary aromatic carbons), 149.77 (C4), 157.20 (C2), 193.61 (acetyl carbonyl), 80.86 (Cp), 81.89 (C5). Anal. Calcd for $C_{22}H_{22}NO_3RuPF_6$: C, 44.45; H, 3.73; N, 2.36. Found: C, 44.36; H, 3.80; N, 2.35. IR data (cm^{-1}): 1767 s, 1700 m, 1655 w, 1602 m, 1563 s, 1521 m.

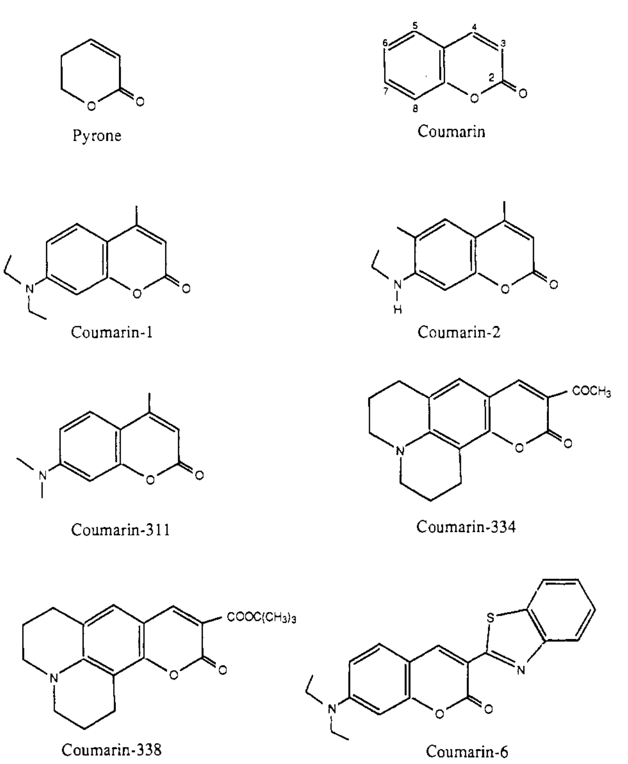

Figure 1. Pyrone, coumarin, and some of its laser dye derivatives.

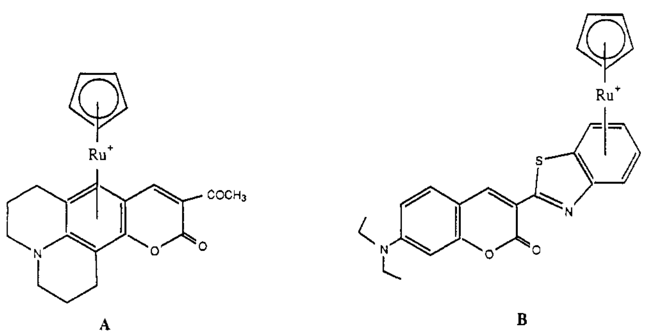

Figure 2. Proposed structures of (A) CpRu(coumarin-334)$^+$ and (B) CpRu(coumarin-6)$^+$.

Emission Quantum Yield Measurement. The emission quantum yield for CpRu(coumarin-6)PF_6 at 25 °C in CH_3CN solution was determined. The emission spectrum of a 2×10^{-6} M acetonitrile solution of the complex was obtained by exciting at the absorption isosbestic point (460 nm). Then a solution of the free dye with the same absorbance at 460 nm was produced by photolysis of the metal complex solution to convert all of the transition-metal complex to CpRu($CH_3CN)_3^+$ and free coumarin-6. A second emission spectrum was then taken, again exciting at 460 nm. From the ratio of the areas of the two corrected emission spectra[7] and the previously determined[8] value of Φ = 0.63 for the emission quantum yield of coumarin-6 in air-saturated acetonitrile solution, we determined the metal complex's emission quantum yield with excellent reproducibility. The emission quantum yield for CpRu(coumarin-6)PF_6 in air-saturated acetonitrile is estimated to be 0.11 ± 0.02.

Results and Discussion

Structural Determination. The CpRu(laser dye)$^+$ complexes reported here were prepared from CpRu($CH_3CN)_3^+$ and the corresponding laser dye. The complexes are analogues of the other CpRu(η^6-arene)$^+$ systems that have been investigated.[2,4,6,9] The laser dye in these compounds is a substituted derivative of the

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parent molecule coumarin (2*H*-1-benzopyran-2-one; see Figure 1). Each substituted coumarin laser dye contains a six-membered benzenoid ring that can afford η^6-coordination to the metal as well as various Lewis basic sites. Additionally, one of the laser dyes (coumarin-6) has a second potential η^6-arene coordination site (benzothiazolyl group). In each case, with the exception of the coumarin-6 complex, η^6-coordination of the CpRu$^+$ group to the coumarin benzenoid ring, as is shown in Figure 2A for CpRu(coumarin-334)$^+$, is confirmed by ^{1}H and ^{13}C NMR spectroscopy. For example, the ^{13}C resonances of the aliphatic amine carbons of coumarin-334 shift by less than 1 ppm upon complexation to the ruthenium center. The carbonyl carbons in the ketone and lactone functionalities are conjugated with the aromatic ring, and their ^{13}C resonances show a slightly greater change upon complexation, shifting from δ 195.54 and 161.28 in the free dye to δ 193.61 and 157.20 in the metal complex, respectively. By far the greatest change in the ^{13}C spectrum observed on coordination occurs in the aromatic ring carbon resonances. The nonquaternary aromatic carbon of the laser dye (C5 of the coumarin ring system) that appears at δ 127.98 in the uncoordinated dye resonates at δ 81.89 in the metal complex, an upfield shift of 46.09 ppm. The other five quaternary ring carbons experience a similar upfield shift from the free dye that ranges from 24 to 33.4 ppm. These upfield shifts result from large changes in the π system of the arene that occur on coordination to the CpRu$^+$ group. A 40 ppm upfield shift has also been observed for the coordinated anthracene carbons in CpRu(anthracene)$^+$,[10] and similar behavior has been reported for the ^{13}C NMR spectra of CpFe(arene)$^+$ complexes.[11]

The substantial ^{13}C resonance shifts observed exclusively for the aromatic portion of the laser dye on coordination of the metal indicate that the laser dyes are not bound to the ruthenium through the carbonyls, the amino nitrogen, or the lactone ring oxygen but rather in η^6 fashion to the aromatic ring. ^{1}H NMR spectra also support this assignment, but the shifts are smaller. For example the aliphatic protons of the laser dye typically shift by about 0.1 ppm upon complexation, while the aromatic hydrogen on C5 shifts 0.7 ppm upfield on complexation. This net shielding of arene protons is characteristic of coordination with the CpM$^+$ group and has been well documented for both Fe and Ru.[11,12]

In contrast to the other laser dyes used in this study, which can only offer η^6-coordination through the benzenoid ring of the coumarin system, coumarin-6 contains an additional arene in the benzothiazolyl group that is bound to C3 of the coumarin backbone. Decoupled ^{13}C NMR data do not sufficiently differentiate the aromatic carbons of coumarin-6 to make a definite structural assignment,[13] but the ^{1}H NMR spectra clearly distinguish the resonances of the bound and unbound arene rings and unambiguously show that the Ru is bound to the benzothiazole arene ring as is shown in Figure 2b.

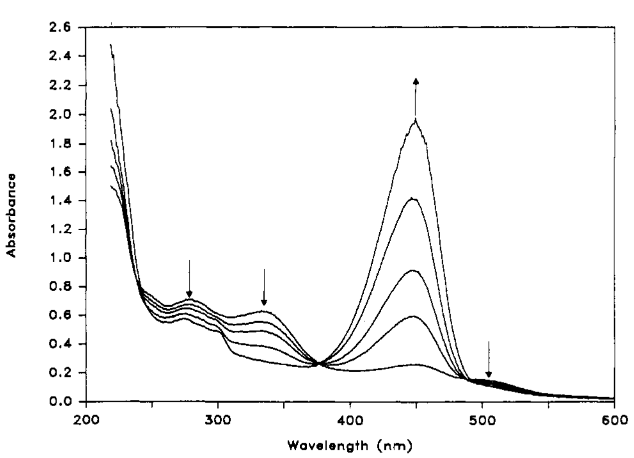

Figure 3. UV–vis spectra recorded during the photolysis ($\lambda > 250$ nm) of a 7×10^{-5} M solution of CpRu(coumarin-334)$^+$ in CH$_3$CN. Absorption bands characteristic of free coumarin-334 grow in intensity while the bands due to the Ru complex decrease as the photoreaction proceeds. Spectra are recorded at approximately 30-s intervals.

The ^{1}H NMR spectrum of CpRu(coumarin-6)$^+$ consists of seven resonances in the aromatic region. The lowest field singlet at δ 8.83 is readily assigned to the pyrone ring proton by comparison with spectra of other substituted coumarins. Of the other six resonances, only three are not shifted upfield with respect to ^{1}H resonances of the free dye: a doublet (1 H, $J = 9.1$ Hz), a doublet (1 H, $J = 9.1$ Hz), and a weakly coupled doublet (1 H). These resonances are shifted slightly downfield (by 0.2, 0.15, and 0.05 ppm, respectively) from similarly coupled peaks in the free-dye spectrum ($J = 8.9$ Hz). These signals are assigned to the protons of C6, C5, and C8 of the coumarin system, respectively. The other three resonances in the complex spectrum have integrations and coupling consistent with their assignment as the four benzothiazole arene ring protons (doublet, 1 H, $J = 5.4$ Hz; doublet, 1 H, $J = 5.67$ Hz; multiplet, 2 H). These signals are shifted upfield from corresponding multiplets in the free coumarin-6 spectrum by 1.9 and 0.3 ppm, consistent with Ru binding of the benzothiazole ring.

Thermal and Photochemical Reactivity Studies. All of the laser dye complexes (including the emissive coumarin-6 complex)[14] exhibit reactivity similar to that of previously studied CpRu(arene)$^+$ systems.[2,4,6,9] The complexes are thermally stable in CH$_2$Cl$_2$ solution and undergo very clean ligand substitution of the bound arene upon photolysis in CH$_3$CN solutions.[15] This photochemical reaction generates CpRu(CH$_3$CN)$_3^+$ and the free laser dye. Figure 3 is typical of the large absorbance changes that are observed upon displacement of the laser dye from the complexes. As the coumarin-334 complex is photolyzed in acetonitrile, a metal complex band at 500 nm decreases in intensity while the absorption due to the free laser dye grows in at 450 nm. Less dramatic spectral changes occur in the UV region as the laser dye bands shift to those positions observed for the unbound laser dye transitions (vide infra). The clean isosbestic behavior maintained during the reaction indicates a smooth and quantitative conversion of the complex to free laser dye and CpRu(CH$_3$CN)$_3^+$.

Electronic Structure and Absorption Spectra. Uncoordinated Laser Dyes. Before the electronic structure and absorption spectra of the CpRu(laser dye)$^+$ complexes are discussed, a short discussion of the free laser dyes is in order. The lowest singlet absorption band at 300 nm of the unsubstituted parent compound coumarin (2*H*-1-benzopyran-2-one) was first identified as a π–π^* state that is substantially localized in the pyrone moiety on the basis of band polarization measurements, a MO calculation, and the fluorescence observed for the molecule.[16–18] More recently, Abu-Eittah and El-Tawil have pointed out that the pyrone and arene chromophores interact strongly and constitute a single conjugated π system.[19] Their more refined INDO–MO calcu-

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(10) Unpublished result.

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(13) Analysis of the ^{13}C NMR spectrum of the coumarin-6 complex is complicated because coumarin-6 has seven nonquaternary aromatic carbons, three on the coumarin benzenoid ring and four on the benzothiazole arene ring, which resonate relatively close together in the free dye. Consequently, ^{1}H NMR must be used in this case to unambiguously deduce the structure of the complex. The other dyes studied here have three or fewer nonquaternary aromatic carbons, making assignment of the ^{13}C peaks in the aromatic region of the NMR spectra much simpler.

(14) It is interesting that the emissive coumarin-6 complex undergoes the photochemical arene release reaction in CH$_3$CN solutions. We plan variable-temperature emission and lifetime studies to address the question of the orbital parentage of the photochemically reactive state. At this time, we speculate that the photochemically reactive state lies at slightly higher energy than the emissive ICT state. In CH$_2$Cl$_2$ solutions, thermal population of this state leads to nonradiative decay but to no net photoreaction.

(15) The quantum yields for arene release from the laser dye complexes have not been measured but are of the same order as for the previously studied CpRu(bz)$^+$ system.[6]

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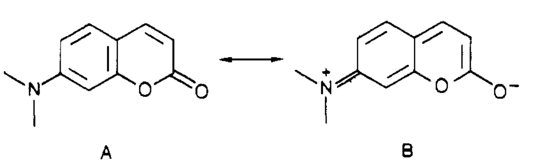
Table I. Spectral Data (λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})) for Substituted Coumarins and CpRu(coumarin)$^+$ Complexes

	MLCT	ICT	$\pi-\pi^*$ 1	$\pi-\pi^*$ 2	$\pi-\pi^*$ 3	$\pi-\pi^*$ 4
coumarin[a]	*b*	*b*	310 (6000)	274 (10 500)	238	210 (11 700)
1,2-pyrone[a]	*b*	*b*	300 (5000)	*c*	*c*	*c*
coumarin-1	*b*	368 (26 000)	*b*	310 (5000)	239 (14 000)	208 (34 000)
coumarin-2	*b*	356 (27 000)	*b*	310 (6000)	234 (21 000)	209 (48 000)
coumarin-311	*b*	360 (25 000)	*b*	310 (5000)	237 (16 000)	208 (37 000)
coumarin-334	*b*	447 (50 000)	*b*	295 (5000)	272 (8000)	218 (23 000)
coumarin-338	*b*	428 (47 000)	*b*	295 (4000)	260 (9000)	218 (30 000)
coumarin-6	*b*	457 (86 000)	*b*	274 (13 000)	250 (sh)	214 (66 000)
CpRu(coum-1)$^+$	360 (2600)	*d*	300 (10 000)	*e*	265 (13 000)	216 (24 000)
CpRu(coum-2)$^+$	360 (1100)	*d*	298 (8000)	*e*	260 (11 000)	213 (22 000)
CpRu(coum-311)$^+$	360 (1300)	*d*	295 (10 000)	*e*	255 (14 000)	215 (24 000)
CpRu(coum-334)$^+$	450 (8000)	*d*	332 (9000)	*e*	277 (11 000)	218 (22 000)
CpRu(coum-338)$^+$	505 (4000)	*d*	330 (8000)	*e*	280 (12 000)	220 (18 000)
CpRu(coum-6)$^+$	*d*	483 (91 000)	320 (sh)	282 (8000)	250 (sh)	<220 (sh)

[a] Data taken from ref 17. [b] Not applicable. [c] Not reported. [d] Not observed. [e] Obscured by $\pi-\pi^*$(1).

lation supports the assignment of the UV bands of coumarin to four $\pi-\pi^*$ transitions of this π system.

The particular coumarin dyes used in our study have a substituted amino group in the 7-position as a common feature. The chromophore in these N-substituted dyes is significantly different from that of coumarin. The ground and lowest excited singlet states are described as mixtures of the mesomeric structures A and B.[20] For these N-substituted dyes, the ground state is adequately described by structure A, while the lowest excited singlet state is believed to have a large contribution from a polar, intramolecular charge transfer (ICT) state that more closely resembles the resonance structure B. The assignment of the lowest singlet excited state to this mesomeric form is supported by correlation of solvent polarity and the nature of the amino substituents on the position of the lowest energy absorption band[19] and MO calculations.[21] Recently this polar, mesomeric form has been directly observed through the use of picosecond time-resolved fluorescence measurements on 7-hydroxy-4-methylcoumarin,[22] a molecule that is very similar to the 7-aminocoumarin laser dyes discussed here. As is the case for pyrone and coumarin, the higher energy bands of the 7-aminocoumarin laser dyes are assigned to other $\pi-\pi^*$ transitions of the chromophore.



Laser Dye Metal Complexes. Band positions, assignments, and extinction coefficients for pyrone, coumarin, the free laser dyes, and the new complexes are given in Table I. The absorption spectra of the metal complexes can be tentatively assigned with the aid of the qualitative MO diagram shown in Figure 4. The diagram shown is constructed for the five complexes with the Ru atom bound directly to the coumarin benzenoid ring. As can be seen in Table I, many of the spectral features present in the uncomplexed dyes are also present in the complexes; additionally, new bands due to dπ(Ru) → π^*(pyrone) (MLCT) transitions are also observed. The weak d–d bands localized on Ru that have been observed[6] at 320 nm in CpRu(benzene)$^+$ are obscured in these complexes by the more intense $\pi-\pi^*$ and MLCT bands and have not been observed for any of the new compounds.

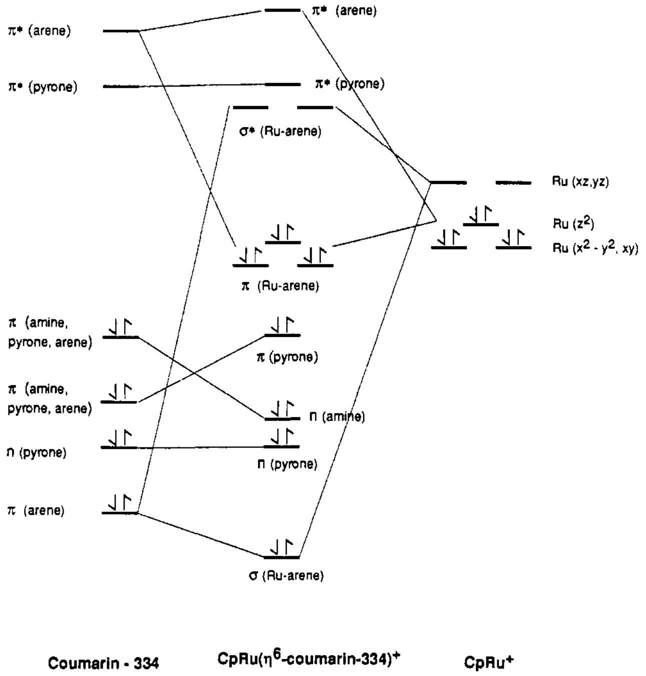


Figure 4. Qualitative molecular orbital diagram for the CpRu$^+$ group bound to a 7-aminocoumarin chromophore π system. This diagram is not applicable to the complex of coumarin-6 (see the text for details).

Complexation of the coumarin benzenoid moiety of the laser dye results in the disappearance of the low-energy n(N) → π^*(pyrone) intramolecular charge transfer (ICT) band and the appearance of a new band not present in the free dyes. This band occurs at 330 nm for compounds that have an acyl substituent in the 3-position or at about 300 nm for those with a hydrogen atom in the 3-position. The energy of the new band in the complexes is very nearly the same as that of the $\pi-\pi^*$(pyrone) transition in uncomplexed, unsubstituted coumarin and in the parent species 1,2-pyrone. The ICT band disappears upon complexation of the π-arene electrons because complexation partially localizes the π electrons to form the Ru–arene σ bonds and destabilizes the polar tautomer, which features conjugation of the nitrogen lone pair into the arene and hence the pyrone system. Partial localization of the arene π electrons disrupts the net amine–pyrone conjugation and replaces the low-energy ICT chromophore with an essentially unsubstituted pyrone function that absorbs at about 300 nm.

Complexation also produces new, low-lying absorptions due to MLCT dπ(Ru) → π^*(pyrone) transitions.[23,24] These transitions

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(19) Abu-Eittah, R. H.; El-Tawil, B. A. H. *Can. J. Chem.* **1985**, *63*, 1173.

(20) Drexhage, K. H. In *Dye Lasers*; Schäfer, F. P., Ed.; Topics in Applied Physics 1; Springer-Verlag: West Berlin, 1973; Chapter 4.

(21) Sairam, R.; Ray, N. K. *Indian J. Chem.* **1980**, *19B*, 989.

(22) Kobayashi, T. *J. Phys. Chem.* **1978**, *82*, 2277.

(23) A reviewer has suggested that the bands we assign as MLCT could alternatively be assigned to a ligand-localized singlet–triplet transition enhanced through a heavy-atom effect. This possibility is unlikely because the proposed singlet–triplet band in several cases would have an intensity nearly as large as the corresponding singlet–singlet transition (labeled as $\pi-\pi^*$ in Table I). The extinction coefficient ($\epsilon \approx 450$ M^{-1} cm^{-1})[24] for the *largest* heavy-atom-enhanced singlet–triplet transition observed is still 1 order of magnitude smaller than those observed for the bands in question.

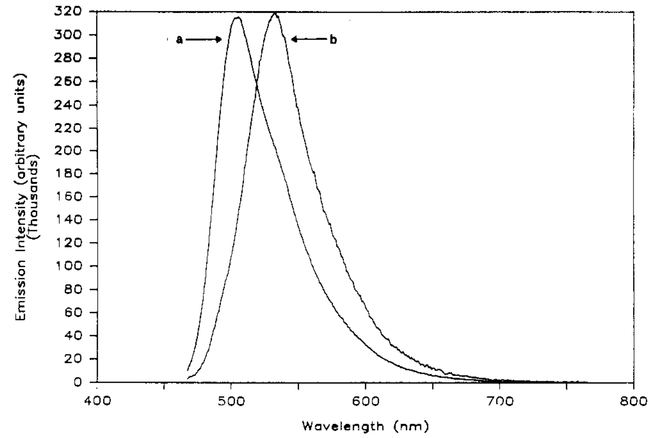

Figure 5. Emission spectra of coumarin-6 (curve a) and CpRu(coumarin-6)PF_6 (curve b) recorded at room temperature as CH_3CN solutions. Excitation was at 460 nm. The intensity of curve b was multiplied by 5.2.

are similar in intensity to bands observed in complexes of several polyaromatic hydrocarbons[4] that do not have ICT bands. The lowest energy visible absorptions observed in the spectrum of CpRu(coumarin-334)$^+$ are assigned to these $d\pi(Ru) \rightarrow \pi^*$(pyrone) MLCT transitions. These bands are partially obscured in the other complexes because they occur at energies similar to those of other π–π^* bands of the coordinated laser dye.

As previously discussed, the coumarin-6 complex differs in structure from the other five laser dye complexes investigated here. As expected, the absorption spectrum of CpRu(coumarin-6)$^+$ also shows substantial differences when compared to the other complexes. In this complex, the CpRu$^+$ moiety is η^6-bound to the electron-withdrawing benzothiazolyl substituent attached to the coumarin backbone and does not interfere with the formation of the polar tautomer when the coumarin chromophore is excited. The low-energy ICT band in this complex is not replaced by the 300-nm π–π^*(pyrone) transition at higher energy but rather is shifted 25 nm to the red side of the free-dye ICT band. This shift to lower energy is caused by the additional inductive effect the electropositive CpRu$^+$ group has on the coumarin chromophore when it is bound to the benzothiazolyl group. The positively charged metal center withdraws electron density from the benzothiazolyl group and further stabilizes the polar ICT excited state. This result is consistent with previously observed red shifts of the lowest absorption band for uncomplexed coumarin laser dyes that undergo stabilization of the polar excited state by increased solvent polarity or by substitution of the coumarin dye at the 4-position with electron-withdrawing groups.[8,19]

In summary, direct complexation of the coumarin benzenoid ring replaces the strongly emitting, low-lying ICT state with a $d\pi(Ru) \rightarrow \pi^*$(pyrone) transition or an unobserved, Ru-localized d–d state while complexation of the substituent benzothiazolyl group leaves the ICT band as the lowest absorption and slightly red-shifts it from the position for the free dye. These proposed assignments are consistent with the emissive properties of the complexes, which will be discussed next.

Emission and Excitation Spectra. Fluid solutions of all five of the CpRu(laser dye)$^+$ complexes that have η^6-coumarin coordination exhibit emission bands that are due to small amounts of the corresponding free laser dye as an impurity. We calculate that a 0.0001% free-dye impurity in each complex would suffice to cause the emission observed from these solutions. Additionally, the excitation spectra of these five complexes are in each case identical with the excitation spectra of the corresponding free laser dye. Finally, fluorescence lifetime measurements of the representative complex [CpRu(coumarin-311)]PF_6 and its parent free laser dye gave identical results. We conclude that none of these five complexes emit appreciably under the conditions of our measurements; however, authentic emissive behavior *is* observed for the CpRu(coumarin-6)$^+$ complex, in which the ICT transition localized in the bound laser dye is apparently the lowest excited singlet electronic state in the molecule. The emission observed (see Figure 5) from solutions of this complex at λ_{max} = 532 nm is distinct from that of solutions of the unbound coumarin-6. First, the excitation maximum for CpRu(coumarin-6)$^+$ is red-shifted (25 nm) to the same position as the ICT band in the absorption spectrum of the complex, which is also red shifted by 25 nm. Further, evidence for an emissive complex was obtained by following the changes in the excitation spectrum of acetonitrile solutions of the complex induced by photolysis (Figure 6).[14] CpRu(coumarin-6)$^+$ undergoes clean photochemical substitution of the bound arene in acetonitrile to yield a solution of CpRu$(CH_3CN)_3^+$ and free coumarin-6. The clean isosbestic behavior that is observed in the excitation spectra obtained during the photolysis indicates that the initial emissive species (the complex) is cleanly converted to a new emissive species (free dye). The clean photochemical conversion of CpRu(coumarin-6)$^+$ into CpRu$(CH_3CN)_3^+$ and the free dye suggested that the emission quantum yield of CpRu(coumarin-6)$^+$ could be estimated by comparison with that of the free coumarin-6 dye. Emission spectra of a solution (initially of the complex) were obtained before and after photolysis quantitatively produced the free dye. This solution was excited at the isosbestic point of the solution (460 nm). From these emission spectra and the known coumarin-6 quantum yield (Φ = 0.63), the emission quantum yield of the complex was determined to be 0.11 ± 0.02.

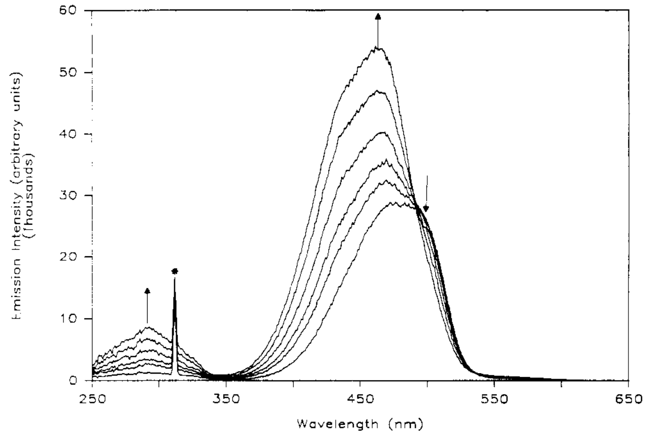

Figure 6. Excitation profile of emitted light at 625 nm recorded during the photolysis of an acetonitrile solution of CpRu(coumarin-6)$^+$; arrows indicate the direction of change. Excitation bands characteristic of free coumarin-6 grow in at 290 and 460 nm. The starred peak at 312 nm arises from scattering of the excitation beam.

Conclusions

We have found that complexation of the coumarin laser dyes in complexes of the form [CpRu(η^6-laser dye)]$^+$ significantly alters the spectroscopic properties of the laser dye system without significantly affecting the photochemical reactivity of the Ru–arene system. Photolysis in CH_3CN efficiently forms the free dye and CpRu$(CH_3CN)_3^+$. Complexation of the metal directly to the coumarin chromophore inhibits reorganization of the dye to its polar form in the ICT excited state and results in nonemissive complexes in which MLCT or d–d excited states are lowest. In contrast, the CpRu(coumarin-6)$^+$ complex with the CpRu$^+$ group bound to a side-chain substituent retains the low-lying ICT chromophore with both the intense, long-wavelength absorption and the efficient emission (Φ = 0.11) properties characteristic of the dye.

The behavior we have observed for the coumarin-6 complex is consistent with that observed for the recently synthesized complex of rubrene in which a Cp*Ru$^+$ (Cp* = η^5-pentamethylcyclopentadienyl) is bound to each of the four phenyl substituents of the naphthacene core.[25] This rubrene complex

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[24] Donckt, E. V.; Vogels, C. *Spectrochim. Acta* **1971**, *27A*, 2157.

[25] Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981.

is structurally similar to the CpRu(coumarin-6)$^+$ system in that the Cp*Ru$^+$ groups are not bound to the main π system of the highly fluorescent rubrene group but rather to electron-withdrawing substituent groups. In this case as well, complexation of the rubrene caused a significant red shift in both the absorption and emission maxima.

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Registry No. [CpRu(coum-1)]PF$_6$, 120546-44-3; [CpRu(coum-2)]PF$_6$, 120546-46-5; [CpRu(coum-311)]PF$_6$, 120546-48-7; [CpRu(coum-334)]PF$_6$, 120546-50-1; [CpRu(coum-338)]PF$_6$, 120546-52-3; [CpRu(coum-6)]PF$_6$, 120546-54-5; [CpRu(CH$_3$CN)$_3$]PF$_6$, 80049-61-2; coumarin-1, 91-44-1; coumarin-2, 26078-25-1; coumarin-311, 87-01-4; coumarin-334, 55804-67-6; coumarin-338, 62669-75-4; coumarin-6, 38215-36-0.

Contribution from Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, New Jersey 08801, and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Comparison of the Electronic Structures of Homo- and Heteronuclear Butterfly Clusters Containing Carbide, Nitride, and Oxide Ligands. Crystal and Molecular Structure of [PPN][$Ru_4N(CO)_{12}$]

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The electronic structures of several butterfly clusters containing carbon, nitrogen, and oxygen atoms have been studied by using Fenske–Hall molecular orbital calculations. Comparison of the calculated electronic structures of $[Fe_4X(CO)_{12}]^{n-}$ (X = C, N, O) shows that the major effect of substituting the smaller N and O atoms is a weakening of the X–wingtip Fe bond. These results suggest that the O–Fe interactions may not be strong enough to maintain the same butterfly cluster geometry as that observed for $[Fe_4C(CO)_{12}]^{2-}$ and $[Fe_4N(CO)_{12}]^-$. The coordinates for the homonuclear ruthenium nitride cluster were obtained from the single-crystal X-ray crystallographic analysis of [PPN][$Ru_4N(CO)_{12}$] [$P\bar{1}$ space group, a = 10.815 (2) Å, b = 14.185 (2) Å, c = 16.433 (9) Å, α = 91.98 (3)°, β = 94.68 (3)°, γ = 97.79 (2)°, Z = 2], which established that it was isomorphous with the tetrairon nitrido cluster. The major difference between the electronic structure of $[Fe_4N(CO)_{12}]^-$ and that of $[Ru_4N(CO)_{12}]^-$ is the stronger metal–metal bonding in the Ru_4N cluster. Calculations for the two isomers of $[FeRu_3N(CO)_{12}]^-$ show that substitution of Fe into the Ru_4 framework of $[Ru_4N(CO)_{12}]^-$ results in relatively small perturbations of the electronic structure of the cluster.

Introduction

The so-called butterfly structure found in many four-metal-atom clusters is capable of binding a wide variety of substrates. Among the more actively studied compounds are those containing a single main-group atom such as C,[1] N,[2] and O.[3] Much of the effort in studying the structure and reactivity of these atoms exposed along the edge of a cluster stems from the interest in comparing them to surface-coordinated atoms.[4] The availability of such a set of isoelectronic and isostructural compounds makes them attractive subjects for detailed comparisons of the bonding.

Previous studies on the electronic structure of butterfly clusters containing carbide and related carbon-bound ligands have established the basic patterns of the orbital interactions and their relative energies.[5-7] In the study presented here we consider the changes affected first by moving from carbide to nitride and oxide ligands and then by replacing a 3d metal (Fe) with a 4d metal (Ru). We first compare the electronic structures of $[Fe_4C(CO)_{12}]^{2-}$, $[Fe_4N(CO)_{12}]^-$, and the model cluster $Fe_4O(CO)_{12}$. This is followed by a description of the molecular structure of [PPN][$Ru_4N(CO)_{12}$] and a comparison of the electronic structures of $[Ru_4N(CO)_{12}]^-$ and $[Fe_4N(CO)_{12}]^-$. Finally, the electronic structure of the heterometallic cluster $[FeRu_3N(CO)_{12}]^-$ is discussed.

Experimental Section

X-ray Crystallographic Study. Orange crystals of [PPN][$Ru_4N(CO)_{12}$][8] were grown from an ether/hexane solution. Details of the structural analysis (Table I) are similar to those of closely related compounds studied in our laboratory.[9] A preliminary peak search indicated the crystal was triclinic, and the $P\bar{1}$ space group was chosen. The cell data were very similar to those found for the analogous iron cluster,[10] suggesting that they were isomorphous. The Ru structure was solved by using the coordinates from the Fe structure. All atoms in the cluster and the P and N atoms of the cation were refined with the use of anisotropic temperature factors. The hydrogen atom positions were calculated and

Table I. Summary of Crystallographic Data

Crystal Parameters	
cryst syst	triclinic
space group	$P\bar{1}$
formula	$C_{48}H_{30}N_2P_2O_{12}Ru_4$
fw	1293.0
a, Å	10.815 (2)
b, Å	14.185 (2)
c, Å	16.433 (9)
α, deg	91.98 (3)
β, deg	94.68 (3)
γ, deg	97.79 (2)
V, Å^3	2487 (2)
Z	2
ρ(calcd), g cm^{-3}	1.73
temp, °C	23
abs coeff, cm^{-1}	12.92
cryst dimens, mm	0.04 × 0.12 × 0.25
transmissn factors, max–min, %	100–85.9
abs cor applied	empirical (Ψ scans)
Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite cryst
programs used	Enraf-Nonius CAD-4-SDP programs
scan type	ω–2θ
scan range, deg	$0 \le 2\theta \le 48$
reflns measd	$+h,\pm k,\pm l$
no. of unique reflns	7787
no. of reflns used	5354
no. of variables	613
cutoff	2σ
p	0.03
extinction coeff	2.62×10^{-8}
R	0.031
R_w	0.033
error in observn of unit wt	1.131

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