styrene]). Downfield shifts of 0.1-0.3 ppm were observed even when the concentration of alkene was 20 times that of the rhodium(II) carboxylate.

Competitive cyclopropanation reactions of ethyl diazoacetate with two alkenes, cyclohexane and styrene, were performed to evaluate the influence of olefin association on the catalytic function of $Rh_2(pfb)_4$. We have previously shown that relative reactivities in these transformations were dependent on the molar ratio of reactant olefins in reactions catalyzed by copper(I) triflate,[2] which is known to form olefin complexes,[14] but not with rhodium(II) acetate. Schurig has suggested that metal-olefin interactions in rhodium(II) carboxylate catalyzed cyclopropanation reactions should be further scrutinized in view of the propensity of the rhodium(II) compounds to coordinate with olefins.[5] Results similar to those obtained with $Rh_2(OAc)_4$ are observed with $Rh_2(pfb)_4$. There is a linear dependence of the product ratio on the molar ratio of reactants (relative reactivity 0.70), suggesting that olefin coordination is not involved in this transformation, but olefin coordination with $Rh_2(pfb)_4$ does inhibit catalyst turnover as demonstrated by the rate for nitrogen evolution as a function of olefin concentration or olefin coordinating ability. Apparently the coordinated olefin is replaced by the diazo compound and has no directive role in these reactions.

Discussion

Dirhodium(II) tetrakis(trifluoroacetate) and the corresponding perfluorobutyrate form π complexes with alkenes in a 1:1 stoichiometry. Equilibrium constants for olefin coordination in dichloromethane show that the $Rh_2(pfb)_4$-olefin complexes are approximately 3 times more stable than those derived from $Rh_2(OOCCF_3)_4$. The olefin proton NMR spectral shifts resulting from the combination of alkenes with rhodium(II) carboxylates provide further evidence for these olefin complexes. Bonding occurs at the carbon-carbon double bond rather than at oxygen in vinyl ethers, and as suggested by the identical downfield chemical shifts for the two olefinic protons of 2-methoxypropene and α-methoxystyrene, association of these alkenes with $Rh_2(OOCCF_3)_4$ places the two olefinic protons in identical environments. The vinyl ethers examined were more responsive than 2-methyl-2-butene to rhodium(II)-induced vinyl proton chemical shifts, and this could be due to electronic or steric effects on the closeness of axial approach of the carbon-carbon double bond to rhodium or to a combination of these effects.

Rhodium(II) carboxylates are uniquely designed for axial coordination with electron-donor ligands.[15] Adduct formation with n-donor molecules is a two-step process involving initial formation of a 1:1 complex.[16] Once the 1:1 adduct has formed, the second axial ligand is less strongly bound to rhodium at the second coordination site.[17] The formation of only 1:1 adducts between $Rh_2(OOCCF_3)_4$ or $Rh_2(pfb)_4$ and olefins is consistent with these observations.

The spectral changes observed upon successive addition of aliquots of an alkene to $Rh_2(pfb)_4$, particularly those evident in Figure 2, suggest that the initial association of an olefin with the rhodium(II) carboxylate is more complex than simply the combination of the two species (eq 1). If $Rh_2(pfb)_4$ is unassociated in solution, we should have observed a spectral display that exhibited an isosbestic point that included the initial uncomplexed rhodium carboxylate. That we do not observe this condition suggests that the rhodium compound which forms π complexes with alkenes is coordinated either to a weaker electron-donor molecule, such as the solvent dichloromethane, or to itself. Drago and co-workers have established that electron withdrawal from perfluorocarboxylate complexes of rhodium(II) enhances the Lewis acidity of the axial coordination sites.[9,18] However, water is not the "weaker" electron-donor molecule since even traces of water cause a substantial spectral shift to lower wavelengths, and water as a ligand of $Rh_2(pfb)_4$ is not displaced by alkene. In addition, if dichloromethane is the responsible ligand, we would have expected a uniform spectral transition (eq 2) upon addition of the

$$Rh_2(pfb)_4(CH_2Cl_2) + \text{olefin} \rightleftharpoons Rh_2(pfb)_4(\text{olefin}) + CH_2Cl_2 \quad (2)$$

alkene. We are left to suggest that $Rh_2(pfb)_4$ is coordinated to itself and exists as an oligomer in solution (eq 3). Such association

$$[Rh_2(pfb)_4]_n + \text{olefin} \rightleftharpoons (n-1)Rh_2(pfb)_4 + Rh_2(pfb)_4(\text{olefin}) \quad (3)$$

has been reported to occur in the solid state for $Rh_2(OOCH)_4$,[19] where the oxygen atom of one rhodium(II) carboxylate unit is an axial ligand for another rhodium(II) carboxylate, but a detailed structure has not appeared. This explanation, coupled with the relative ability of rhodium(II) carboxylates to form complexes with n-donor molecules as opposed to π-electron donors,[6] might account for the absence of observable olefin π complexes with rhodium(II) alkanoates in solution but not on stationary supports in the gas phase.[5]

The association constants for several of the alkenes reported in Table I have also been determined by complexation gas chromatography.[5] A plot of these values shows remarkable linearity and signifies that the same associative processes are being measured by the two methods. The slope of the line is 3.0, which is consistent with the temperature difference between these two measurements and corresponds to $\Delta H_{assoc} = 3$ kcal/mol.

Acknowledgment. The support of the National Science Foundation for this research is gratefully acknowledged. We thank the Johnson Matthey Co. for their loan of rhodium(III) chloride.

Supplementary Material Available: Proton NMR chemical shift data for $Rh_2(OOCCF_3)_4(CH_3C(CH_3)CHCH_3)$ (Figure 3), a plot of relative reactivity data for $Rh_2(pfb)_4$-catalyzed cycloprotonation of cyclohexene/styrene (Figure 4), and a plot of association constants for $Rh_2(pfb)_4$ and selected olefins obtained in dichloromethane and by complexation gas chromatography (Figure 5) (3 pages). Ordering information is given on any current masthead page.

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A Ruthenium Tris(diimine) Complex with Three Different Ligands

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There has been a great deal of recent interest in the chemistry of ruthenium polypyridine complexes.[1] Much of this interest has centered around the utility of such complexes as photocatalysts for the decomposition of water into its elements.[2] The absorption of sunlight by a ruthenium polypyridine catalyst results in the

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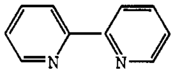
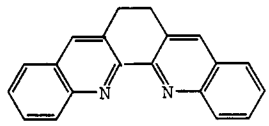
formation of an excited-state species that can then function as an efficient redox catalyst. Useful photocatalytic systems generally incorporate several other components in order to operate effectively.

A considerable amount of the effort expended in this field has been directed toward modification of the polypyridine ligands to increase the catalytic efficiency of the corresponding ruthenium complex. Both electronic and conformational effects have been explored in this regard.[3] Mixed-ligand complexes have also been examined where two different bipyridine derivatives are coordinated to ruthenium.[4] Since ruthenium(II) can accommodate three bidentate ligands, the use of two different ligands A and B leads to the formation of mixed complexes of the types Ru(AAB) and Ru(ABB). Thus far nearly all the mixed bidentate ligand complexes of ruthenium(II) that have been examined have been of these two types.[5] In a number of cases these complexes have properties that differ significantly from those of either of the two parent systems Ru(AAA) or Ru(BBB).

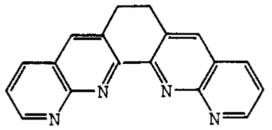
In extending these studies, we wish to report the preparation of a ruthenium(II) complex involving three different ligands: bipyridine (**1**), a biquinoline (**2**), and a bi-1,8-naphthyridine (**3**).



1 (bpy)



2



3

We chose these ligands for several reasons. They are all bidentate chelators that possess a C_2 symmetry axis. Previous work from our laboratory has verified the fact that bi-1,8-naphthyridine chelates through its central two nitrogens.[6] These three ligands have quite different electronic properties and steric requirements. An earlier study has examined these properties with respect to complexes of the type RuL_3^{2+} and $Ru(bpy)_2L^{2+}$ where L = **2** or **3**. Last, the dimethylene bridge in **2** or **3** will aid us in characterization of the complex and in understanding its conformational properties.

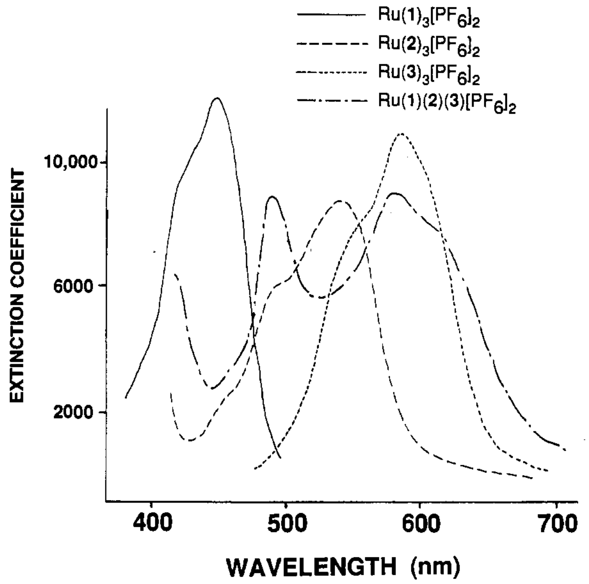


Figure 1. Ultraviolet absorption spectra of ruthenium tris(diimine) complexes.

Table I. Half-Wave Potentials for $Ru(\mathbf{1})(\mathbf{2})(\mathbf{3})^{2+}$ and Related Ruthenium Complexes[a]

	$E_{1/2}$, V			
		redn		
complexes	Ru^{2+}/Ru^{3+}	Ru^{2+}/Ru^{+}	Ru^{+}/Ru^{0}	Ru^{0}/Ru^{-}
$Ru(\mathbf{1})(\mathbf{2})(\mathbf{3})^{2+}$	+1.26	-0.65	-1.01	-1.69
$Ru(\mathbf{1})_3^{2+}$	+1.30	-1.33	-1.52	-1.77
$Ru(\mathbf{2})_3^{2+}$	+1.51	-0.80	-1.08	-1.68
$Ru(\mathbf{3})_3^{2+}$	+1.01	-0.82	-1.07	-1.40
$Ru(\mathbf{1})_2(\mathbf{2})^{2+}$	+1.34	-0.90	-1.37	-1.66
$Ru(\mathbf{1})_2(\mathbf{3})^{2+}$	+1.18	-0.76	-1.26	-1.83

[a] Potentials are given vs. SCE, and all waves were reversible; solutions were 0.1 M in TBAP; the solvent was acetonitrile; $T = 25 \pm 1$ °C.

Treatment of $[Ru(bpy)Cl_3]_n$[7] with 1 equiv of ligand **2** in refluxing aqueous ethanol provides an intermediate complex **4** where

$$[Ru(\mathbf{1})Cl_3]_n \xrightarrow{\mathbf{2}} \underset{\mathbf{4}}{Ru(\mathbf{1})(\mathbf{2})X_2} \xrightarrow{\mathbf{3}} \underset{\mathbf{5}}{Ru(\mathbf{1})(\mathbf{2})(\mathbf{3})[PF_6]_2}$$

X represents chloride or solvent.[11] This material is not isolated or characterized but instead reacted directly with 1 equiv of **3** and the product is precipitated as its PF_6 salt and purified by chromatography and recrystallization to provide a 57% yield of **5**. The complex gave a satisfactory elemental analysis and showed a parent peak in the thermospray interfaced LC-MS at *m*/*e* 824 for the singly charged positive ion as well as major peaks corresponding to the mass of each of the three ligands.

The 300-MHz ^1H NMR spectrum of **5** showed an extremely complex downfield region since all 26 aromatic protons are chemically nonequivalent. This region integrated correctly, however, against the eight bridge protons in the upfield region. The bridge protons showed a complex overlapping multiplet from 3.3 to 2.8 ppm. The complexity of this region is consistent with conformational rigidity of the ligands **2** and **3**. Since **5** has no

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(6) Draux, M.; Bernal, I.; Lefoulon, F.; Thummel, R. P. *Inorg. Chim. Acta* **1985**, *104*, 203.

(7) This reagent is prepared according to the method of Krause,[8] who identified it as $Ru(bpy)Cl_4$. Anderson and Seddon[9] later characterized this material as $Ru(bpy)Cl_3$, which was first reported by Dwyer and co-workers in 1963.[10] The material is probably not monomeric and is best represented as $[Ru(bpy)Cl_3]_n$.

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symmetry element, this rigidity leads to nonequivalence of all four bridge protons in ligands **2** and **3**. In a previous study of $\mathrm{Ru}(\mathbf{2})_3^{2+}$ and $\mathrm{Ru}(\mathbf{3})_3^{2+}$, we found that in the former case the coordinated ligand **2** was rigid while in the latter case the coordinated ligand **3** was mobile.[3e]

The complex **5** showed a long wavelength absorption in its electronic spectrum consisting of two principal bands centered at 490 and 577 nm. Figure 1 illustrates this spectrum along with the spectra of $\mathrm{Ru}(\mathbf{1})_3^{2+}$, $\mathrm{Ru}(\mathbf{2})_3^{2+}$, and $\mathrm{Ru}(\mathbf{3})_3^{2+}$. These three curves are all very similar in shape, consisting of a major band and a shoulder at shorter wavelength, and are associated with a metal-to-ligand charge transfer (MLCT) state. The shift of this MLCT band to longer wavelength with increased delocalizing ability of the ligand is a well-documented phenomena.[12] The absorption curve for **5** shows essentially no component for charge transfer into the bpy ligand. We have shown that the energy for this transition for complexes of the type $\mathrm{Ru(bpy)_2L}$ remains invariant as the electronegativity of L increases.[4a] For MLCT into the biquinoline ligand we observe the band at 490 nm, which corresponds to the shoulder of the major band for the complex $\mathrm{Ru}(\mathbf{2})_3^{2+}$. For MLCT into the binaphthyridine ligand we observe the band at 577 nm, which corresponds to the major band of $\mathrm{Ru}(\mathbf{3})_3^{2+}$. Since these transitions have yet to be unequivocally assigned, we cannot read too much into these results except to note that MLCT is apparently allowed only for certain transitions in these complexes.

The half-wave potentials for complex **5** as determined by cyclic voltammetry are summarized in Table I along with those of other related ruthenium complexes. The oxidation potential of +1.26 V demonstrates with surprising exactness that ligands **2** and **3** share equally in mediating the ease with which the complex loses an electron. This value represents the average oxidation potential for the complexes $\mathrm{Ru}(\mathbf{2})_3^{2+}$ and $\mathrm{Ru}(\mathbf{3})_3^{2+}$ as well as the average value for $\mathrm{Ru}(\mathbf{1})_2(\mathbf{2})^{2+}$ and $\mathrm{Ru}(\mathbf{1})_2(\mathbf{3})^{2+}$. The implication is that fine tuning of the oxidation potential of complexes of the type $\mathrm{Ru(bpy)LL'^{2+}}$ may be accomplished in a readily predicted fashion. Since the oxidation potential is a reflection of the energy of the highest filled t_{2g} level of ruthenium, it is also apparent that the energy of this level is affected in a very regular fashion by the attached ligands. Data from additional systems is clearly needed to lend more certainty to these conclusions.

The first reduction potential of **5** is more positive than those of any of the three related symmetrical $\mathrm{RuL_3^{2+}}$ complexes or the mixed complexes $\mathrm{Ru(bpy)_2L^{2+}}$, implying that the π^* orbital, which is the LUMO for this system, is unusually low in energy. The lowering of this π^* level may be associated with the lack of symmetry of complex **5** as compared with the $\mathrm{RuL_3^{2+}}$ complexes, which have D_3 symmetry, and the $\mathrm{Ru(bpy)_2L^{2+}}$ complexes, which have C_2 symmetry. The second and third reduction potentials appear to be less affected.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Nicolet NT-300 WB spectrometer in $\mathrm{CD_3CN}$ with chemical shifts reported in parts per million downfield from $\mathrm{Me_4Si}$. Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. LC-MS measurements were performed on a Biospec mass spectrometer with a thermospray ionization interface. Elemental analyses were performed by the Canadian Microanalytical Service ltd., New Westminister, BC, Canada. The preparation of ligands **2** and **3** has been previously described.[13] The $[\mathrm{Ru(bpy)Cl_3}]_n$ was prepared according to a procedure described by Krause.[8]

Cyclic voltammograms were recorded by using a PAR Model 174A polarographic analyzer, a PAR Model 175 universal programmer, and a Houston Instruments, Omnigraphic 2000 X-Y recorder. A three-electrode system was employed, consisting of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high-purity nitrogen through the solution for 5 min and maintaining a blanket of nitrogen over the solution while measurements were made. Reagent grade acetonitrile was distilled twice from $\mathrm{P_2O_5}$ under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc/hexane, dried, and stored in a desiccator. Half-wave potentials were calculated as an average of the cathodic and anodic peak potentials. The criteria for reversibility was that the separation of the anodic and cathodic peaks is equal to less than 60 mV for a one-electron process and that the ratio of anodic to cathodic current is unity.[14]

Preparation of $\mathrm{Ru}(\mathbf{1})(\mathbf{2})(\mathbf{3})[\mathrm{PF_6}]_2$ (5). A solution of 47.4 mg (0.118 mmol) of $[\mathrm{Ru(bpy)Cl_3}]_n$ and 33.5 mg (0.118 mmol) of 3,3′-dimethylene-2,2′-biquinoline (**2**) in 15 mL of 1:1 $\mathrm{EtOH/H_2O}$ was refluxed for 24 h. The solution was cooled, 34 mg (0.118 mmol) of 3,3′-dimethylene-2,2′-binaphthyridine (**3**) was added, and then reflux was continued another 48 h. After cooling, an aqueous solution of $\mathrm{NH_4PF_6}$ (2 equiv) was added. The resulting blue precipitate was collected, dried, and chromatographed on 20 g of alumina eluting with 1:1 acetonitrile/toluene. Slow evaporation of acetonitrile from the eluent provided 67 mg (57%) of **5** as purple crystals. Anal. Calcd for $\mathrm{C_{48}H_{34}F_{12}N_8P_2Ru}$: C, 51.75; H, 3.05; N, 10.06. Found: C, 51.92; H, 3.21; N, 9.74.

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^{31}P NMR Studies of $[\mathrm{Au_2}(\mu\text{-dppe})]^{2+}$ Antitumor Complexes. Conversion into $[\mathrm{Au(dppe)_2}]^+$ Induced by Thiols and Blood Plasma

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We have recently reported the unusual stability of tetrahedral Au(I) complexes with chelated diphosphine ligands.[1,2] The most common coordination geometry for Au(I) is linear, and in previous studies of Au(I) complexes with flexible diphosphine ligands chelation has not been considered important.[3-5] Diphosphine-bridged-digold complexes $\mathrm{ClAu(Ph_2P(CH_2)_{\mathit{n}}PPh_2)AuCl}$ are readily converted into the bischelated species in the presence of added diphosphine ligand. Chelated complexes of the type $[\mathrm{Au(R_2P(CH_2)_{\mathit{n}}PR'_2)_2]Cl}$ form readily when R and R′ are phenyl and n = 2 or 3 and also with the more rigid ligand *cis*-$\mathrm{Ph_2PCH{=}CHPPh_2}$.[2]

A number of diphosphine-bridged-digold complexes, $\mathrm{XAu(Ph_2P(CH_2)_{\mathit{n}}PPh_2)AuX}$, have been reported to have good antitumor activity in animal models.[6,7] Activity was maximized for

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