Table I. Kinetics Data for the Epoxidation of Olefins by $[(bpy)_2(py)Ru(O)]^{2+}$ in Acetonitrile at Room Temperature

substrate	product(s)	k(25 °C), $M^{-1}\ s^{-1}$	ΔH^{*}, kcal mol^{-1}	ΔS^{*}, eu
styrene	styrene oxide	1.48×10^{-2}	7.2 ± 2.3	-43 ± 7
trans-stilbene	*trans*-stilbene oxide	1.09×10^{-2}		
cis-stilbene	*cis*-stilbene oxide (95%)[a] *trans*-stilbene oxide (5%)	1.43×10^{-3}		

[a] Yields based on ^1H NMR.

Table II. Catalytic Oxidation of Olefins by $[(trpy)(bpy)Ru(OH_2)]^{2+}/NaOCl$ at pH 10.5[a]

		products	
olefin	% conversion		PhCHO
styrene	60	22	78
trans-stilbene	58	11	71
cis-stilbene	35	trace	99

[a] Conditions as described in text; reaction time of 3 h.

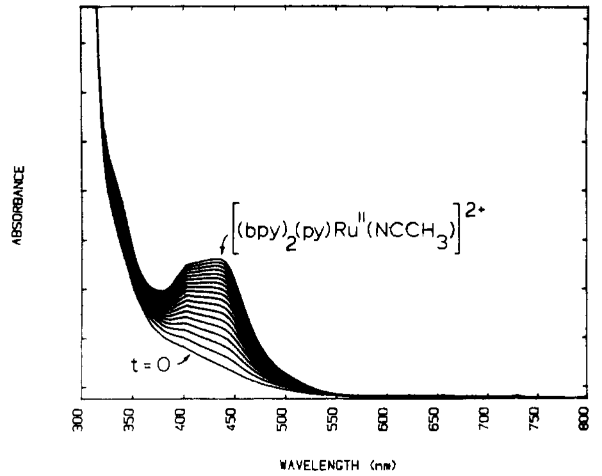

Figure 1. Spectral changes with time in the oxidation of styrene (5×10^{-2} M) by $[(bpy)_2(py)Ru(O)]^{2+}$ (5×10^{-5} M). Spectra were recorded at 1-min intervals. The initial spectrum after mixing is labeled $t = 0$, and the spectrum after 17 min, labeled $[(bpy)_2(py)Ru(NCCH_3)]^{2+}$, has λ_{max} at 440 nm ($\epsilon = 8000\ M^{-1}\ cm^{-1}$).

chromatography. The results of the ^1H NMR analysis are summarized in Table II. In blank experiments without added catalyst only trace amounts of oxidized products appeared. Blank experiments also showed that styrene oxide is stable toward further oxidation under our reaction conditions with or without added catalyst. A high percentage of PhCHO as a product of the NaOCl-catalyzed oxidation of styrene has been found under similar conditions based on RuO_4 or $RuCl_3{\cdot}nH_2O$,[7] and more recently, Eskenazi et al. have reported that the selectivity of epoxidation based on the $RuCl_3{\cdot}nH_2O/NaIO_4$ system can be controlled by the addition of substituted bipyridines or phenanthrolines.[8] We cannot yet account for the change in product distribution and the appearance of PhCHO under catalytic conditions. Even though OCl^- oxidation of the aqua complexes leads to $Ru^{IV}{=}O$ in water, the actual state of the catalyst in the catalytic runs is unknown.

Although simple, quantitative epoxidation is clearly an accessible pathway in dry acetonitrile, it seems clear from observations made here and earlier that there is an extensive chemistry of olefin oxidation by $Ru^{IV}{=}O$: (1) electrocatalytic oxidation of *trans*-$CH_3CH{=}CHOO_2^-$ in water occurs at the allylic position to give the corresponding diacid,[2a] (2) under catalytic conditions in the hypochlorite oxidations a pathway leading to oxidative olefin bond cleavage, eq 4, occurs in competition with epoxidation or,

$$PhCH{=}CHPh + 2OCl^- \rightarrow 2PhCHO + 2Cl^- \qquad (4)$$

perhaps, by further oxidation of *bound* epoxide, and (3) in reactions currently under investigation in acetonitrile, olefins containing α-C–H bonds, e.g., cyclohexene or 2,3-dimethyl-2-butene, undergo allylic oxidation preferentially over epoxidation.

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Registry No. $[(bpy)_2(py)Ru(O)]^{2+}$, 67202-43-1; $[(bpy)_2(py)Ru(OH_2)]^{2+}$, 70702-30-6; $[(trpy)(bpy)Ru(OH_2)]^{2+}$, 20154-63-6; NaOCl, 7681-52-9; styrene, 100-42-5; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8.

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Reduction of Dirhodium(II) Complexes of the Type $[Rh_2(O_2CCH_3)_3(L)]^+$. An ESR Investigation

Sir:

The electrooxidation of dirhodium complexes of the forms $Rh_2(O_2CR)_4$[1-7] and $Rh_2(O_2CCH_3)_n(RNOCR')_{4-n}$[8-13] where RNOCR′ is the anion of acetamide or acetanilide has been a subject of numerous publications. However, very few studies have reported electroreductions for these type complexes. The scarcity of such studies is due to the fact that the electroreductions of all $Rh_2(O_2CR)_4$ complexes are irreversible[7] while $Rh_2(O_2CCH_3)_n(RNOCR')_{4-n}$ complexes show no reduction waves within the range of investigated electrochemical solvents.

Until recently, reversible reductions had not been reported for any dirhodium complexes, nor was there any spectral characterization of the chemical or electrochemical reduction products.

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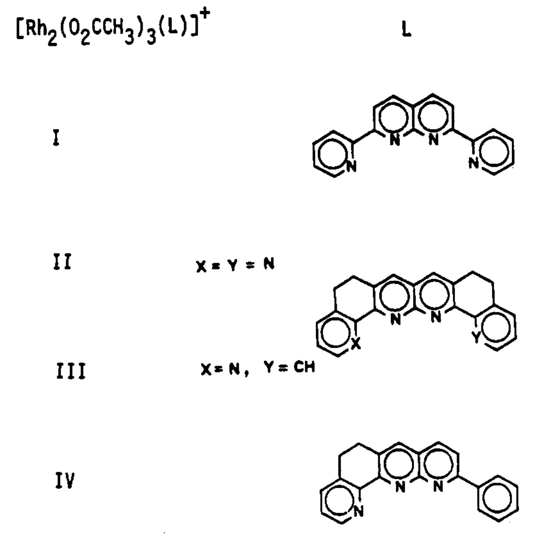

Figure 1. Structures of ligands L in dirhodium complexes I–IV of formula $[Rh_2(O_2CCH_3)_3(L)]^+$.

However, two types of dirhodium complexes are now known to undergo reversible electroreductions. These reductions are given by eq 1 for a neutral dirhodium complex[14] containing four *N*,*N'*-diphenylbenzamidine bridging ligands and by eq 2 for a series of positively charged dirhodium species.[15-17] In eq 2, L is a neutral multidentate ligand containing a 1,8-naphthyridine fragment.[15,16]

$$Rh_2(PhC(NPh)_2)_4 + e^- \rightleftarrows [Rh_2(Ph_2C(NPh)_2)_4]^- \qquad (1)$$

$$[Rh_2(O_2CCH_3)_n(L)_{4-n}]^{(4-n)+} + e^- \rightleftarrows [Rh_2(O_2CCH_3)_n(L)_{4-n}]^{(3-n)+} \qquad (2)$$

The reduction product of $Rh_2(PhC(NPh)_2)_4$ has been examined by ESR spectroscopy.[14] The potential for reaction 1 is −1.58 V vs. SCE in CH_2Cl_2 and −1.52 V vs. SCE in CH_3CN, and the one-electron addition has been shown to be metal-based, yielding a formal $Rh^{II}Rh^{I}$ species. Reaction 2 occurs at potentials between $E_{1/2}$ = −0.57 and −0.72 V vs. SCE in CH_3CN.[16] The exact potential depends upon the nature of the L group and the value of *n* (either 2 or 3). The site of electron transfer in reaction 2 was not identified in previous studies, but the possibility that the reductions occurred at the aromatic ligands was suggested.[16]

Complexes (I–IV) having the formula $[Rh_2(O_2CCH_3)_3(L)]^+$ have been reported where L is one of the neutral multidentate ligands shown in Figure 1. These dirhodium complexes are reduced between $E_{1/2}$ = −0.57 and −0.68 V vs. SCE in CH_3CN.[16,17] A second one-electron reduction also occurs at potentials ranging between −1.21 and −1.36 V, and this reduction is given by reaction 3. The potentials for these reductions are summarized in Table I.

$$Rh_2(O_2CCH_3)_3L + e^- \rightleftarrows [Rh_2(O_2CCH_3)_3L]^- \qquad (3)$$

Figure 2 shows the frozen-glass (<−150 °C) ESR spectra of complexes II and IV after controlled-potential reduction in CH_3CN under a nitrogen atmosphere. The spectrum of the singly reduced complex IV (Figure 2b) is isotropic with g = 1.99. While there appears to be some anisotropy in the spectrum of the singly reduced complex II (Figure 2a), the g value of this signal is also 1.99. Reduction of complex III also yields an isotropic signal with g = 1.99. Finally, isotropic spectra with g values of 1.99 were also obtained at room temperature by in situ generation of the singly reduced ESR-active species from complexes II–IV in a flat cell.

Table I. Reduction Potentials[a] and ESR Parameters for Neutral and Singly Reduced Dirhodium(II) Complexes in CH_3CN Containing 0.1 M TBAP

complex	$E_{1/2}$, V (sc. SCE)		g^c
	1st redn	2nd redn	
$Rh_2(O_2CCH_3)_4$	−1.08[b]		
I	−0.57	−1.21	
II	−0.68	−1.36	1.99[d]
III	−0.66	−1.30	1.99
IV	−0.64	−1.29	1.99
$Rh_2(PhC(NPh)_2)_4$	−1.52		$g_\perp$ = 2.181,[e] $g_\parallel$ = 2.003[e]

[a] Potentials for I–IV are taken from ref 17 while those for $Rh_2(O_2CCH_3)_4$ and $Rh_2(PhC(NPh)_2)_4$ are taken from ref 7 and 14, respectively. [b] Irreversible reduction. [c] g values are from a frozen-glass ESR spectra taken after the first one-electron reduction. [d] Slightly anisotropic signal. See Figure 2a. [e] Reference 14.

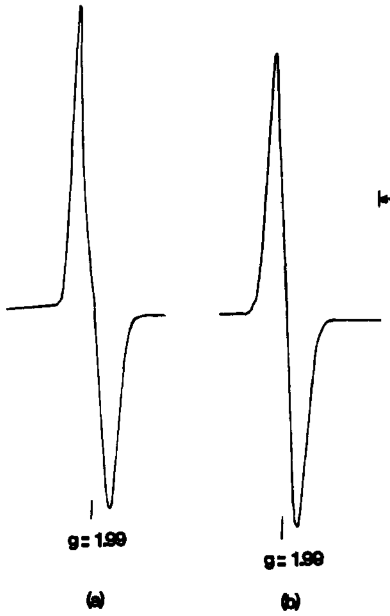

Figure 2. Frozen-glass ESR spectra of (a) compound II and (b) compound IV in CH_3CN.

The fact that the isotropic signals at room temperature have g = 1.99 and no hyperfine splitting due to ^{103}Rh ($I = {}^1/_2$) is indicative of an unpaired electron on $Rh_2(O_2CCH_3)_3(L)$, which is largely ligand-based. The signals are quite broad ($\Delta_{pp} \simeq$ 10 G),[18] suggesting a delocalized radical, most probably on the aromatic ligand. Complex I has essentially the same structure as other members of the series (II–IV) and may be expected to give similar results.

The second reduction (reaction 3) of complexes I–IV may be expected to be metal-based. However, reaction 3 of compounds III and IV is complicated by the presence of irreversible follow-up chemical reactions.[17] Reaction 3 is reversible for II on a cyclic voltammetric time scale, but on a bulk electrolysis time scale the reaction products appears to decompose, thus prohibiting further studies.

In conclusion, it appears now that the LUMO of the $[Rh_2(O_2CCH_3)_3(L)]^+$ complexes is a mainly ligand-based orbital, unlike that found in the case of reduced $Rh_2(PhC(NPh)_2)_4$. Ligand radical formation is especially interesting since reduction of the 2,7-bis(2-pyridyl)-1,8-naphthyridine ligand (L in complex

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I) is nearly 0.9 V more negative than reduction of complexes I-IV.[10] However, the uniqueness of the $Rh^{II}Rh^{I}$ formation in $Rh_2(PhC(NPh)_2)_4$[14] must remain unexplained in the absence of clear characterizations for reaction 3.

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Registry No. I, 101652-69-1; I^+, 84810-83-3; I^-, 101652-70-4; II, 101652-66-8; II^+, 101348-72-5; II^-, 101652-71-5; III, 101652-67-9; III^+, 101652-65-7; III^-, 101652-72-6; IV, 101652-68-0; IV^+, 101348-74-7; IV^-, 101652-73-7; $Rh_2(O_2CCH_3)_4$, 15956-28-2; $Rh_2(O_2CCH_3)_4^-$, 94342-85-5; $Rh_2(PhC(NPh)_2)_4$, 99148-26-2; $Rh_2(PhC(NPh)_2)_4^-$, 99148-28-4.

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Articles

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Interligand Repulsion Energy and the Twisting of Hexadentate Chelating Ligands

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The simple repulsion energy model, which has quite successfully explained the observed twist angles of tris-bidentate complexes, has been applied to 24 complexes of six hexadentate ligands having C_3 symmetry. The mean difference between observed and calculated twist angles is between 2 and 3°.

Kepert[1,2] and Avdeef and Fackler[3] have demonstrated that the twist angle[1,4] (ϕ) of tris-bidentate complexes can be predicted given the ratio of the chelate bite distance to the metal-ligand atom distance (bite/r). The ligand atoms are represented by point charges, and ϕ is found such that the total computed repulsion energy among the charges is a minimum. (The metal-ligand atom distance and the chelate bite distance are assumed to be fixed as the complex is twisted.) The computed ϕ corresponding to this "repulsion" minimum is usually within a few degrees of the ϕ observed in the complexes.[1,3,5-8] In the cases of several complexes where ϕ(found) is more than 2° different from ϕ(calcd), steric interactions among ligands have been postulated as the cause of the deviation.[9-12] In addition to the six-coordinate tris-bidentate complexes, the minimum repulsion energy model has been applied to four-, five-, seven-, eight-, nine-, ten- and twelve-coordinate complexes.[13-17]

It was of interest to us to further test the efficacy of the repulsion model by applying it to chelates containing hexadentate ligands. One such set of complexes, briefly discussed elsewhere[18], contains $EDTA^{4-}$ and similar ligands. The following discussion is addressed to chelates of C_3 symmetry where the ligands have the general topology illustrated in Figure 1. Although such ligands give rise to complexes closely related to the tris-bidentate chelates, there are two differences of interest here: for these "C_3" chelates two bite distances (not one) must be considered, and two metal-ligand atom distances may be characteristic of a complex instead of one. The two bites are BITE, which is the L1-L4 distance (assumed to be equal to L2-L5 and L3-L6), and TOP, which is the L1-L2 distance (equal to L2-L3 and L1-L3). The metal-ligand distances are M-L1 (equal to M-L2 and M-L3) and M-L4 (equal to M-L5 and M-L6).

In the tris-bidentate chelates the repulsions to be minimized (see Figure 2) are the six pairs L1-L2 and equivalents, the three pairs L1-L5 and equivalents, and the three pairs L1-L6 and equivalents, whereas in the "C_3" chelates the repulsions to be minimized are the three pairs L4-L5 and equivalents, the three pairs L1-L5 and equivalents, and the three pairs L1-L6 and equivalents (Figure 3).

Figures 3 and 4 show the spherical polar coordinate system used to describe the "C_3" chelates. Each point represents a ligand atom i having coordinates r_i, θ_i, and ϕ_i, where r_i is the metal-ligand distance, θ_i is the azimuthal angle (from the polar axis, Figure 4) and ϕ_i is the third coordinate (Figure 3). Assuming C_3 symmetry, the M-L1, M-L2, and M-L3 distances are r_1 and the M-L4, M-L5, and M-L6 distances are r_4. Similarly, θ_1 is the azimuthal angle for L1, L2, and L3, and θ_4 is the azimuthal angle for L4, L5, and L6.

Given r_1, r_4, BITE, and TOP, the value of θ_1 is unambiguously determined from eq 1, and the problem then is to find the sets

$$\theta_1 = \sin^{-1}\left[(\mathrm{TOP})/(3^{1/2}r_1)\right] \qquad (1)$$

of specific values of θ_4 and ϕ attainable with the given values for r_1, r_4, BITE, TOP, and θ_1 and then to find that set corresponding to the minimum total Coulombic repulsion energy.

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