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Infrared/Visible/Ultraviolet Spectroscopic Detection of One-Electron- and Two-Electron-Reduction Products of *fac*-$ClRe(CO)_3(4bzpy)_2$ (4bzpy = 4-Benzoylpyridine)

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We wish to report results from a spectroelectrochemical investigation of [*fac*-$ClRe(CO)_3(4bzpy)_2$] (4bzpy ≡ 4-benzoylpyridine). The study concerns the nature of the products from one- and two-electron reduction of the complex (eq 1). Additionally, the study gives insight into the nature of the species formed by electron-transfer quenching of the excited state of [*fac*-$ClRe(CO)_3(4bzpy)_2$] previously demonstrated to be Re → 4bzpy CT in character.[1] Among the issues of interest is the degree of localization of the electron(s) added to the complex. The degree of localization of the electron promoted in the metal-to-ligand charge-transfer (CT) excited state of $[Ru(bpy)_3]^{2+}$ (bpy ≡ 2,2′-bipyridine) has received considerable study.[2-6] $[Ru(bpy)_3]^+$ can be formed electrochemically and is an intermediate in the reductive quenching of photoexcited $[Ru(bpy)_3]^{2+}$. In one respect, the electronic structure of $[Ru(bpy)_3]^+$ has generally been assumed to be similar to that of excited $[Ru(bpy)_3]^{2+}$.[7-9] The results from $[Ru(bpy)_3]^+$ and excited $[Ru(bpy)_3]^{2+}$ reveal that an electron is localized on one of the bipyridines rather than delocalized over all three. [*fac*-$ClRe(CO)_3(4bzpy)_2$] has more than one 4bzpy ligand, an electron acceptor. The degree of localization of the electron(s) added to form reduced species from [*fac*-$ClRe(CO)_3(4bzpy)_2$] is of interest.

$$[fac\text{-}ClRe(CO)_3(4bzpy)_2] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [fac\text{-}ClRe(CO)_3(4bzpy)_2]^- \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [fac\text{-}ClRe(CO)_3(4bzpy)_2]^{2-} \tag{1}$$

The Re → 4bzpy CT excited state of [*fac*-$ClRe(CO)_3(4bzpy)_2$] can quenched by electron donors.[10] In the presence of Et_3N as an electron-donating quencher, the pyridyl ketones of the complex can be photoreduced to alcohols.[10] This process is proposed to involve [*fac*-$ClRe(CO)_3(4bzpy)_2$]$^-$, an intermediate generated from the electron-transfer quenching of photoexcited [*fac*-$ClRe(CO)_3(4bzpy)_2$] (eq 2). Such being the case, [*fac*-$ClRe(CO)_3(4bzpy)_2$]$^-$ may be produced electrochemically to initiate the reduction of the 4bzpy ligand to the corresponding alcohol. Controlled electrochemical reduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] in an optically transparent thin-layer spectroelectrochemical cell[11,12] has enabled us to monitor and characterize the reduced intermediates by IR and UV/vis absorption spectroscopies. The results show that upon one-electron reduction the added electron is localized on the 4bzpy ligand to form one $4bzpy^-$ anion. A two-electron reduction gives a dianionic complex with one electron localized on each pyridyl ketone ligand. With CH_3COOH as a proton source, the complex [*fac*-$ClRe(CO)_3(4bzpy)_2$] can be electrochemically reduced to the bis(alcohol) complex (eq 3).

$$[fac\text{-}ClRe(CO)_3(4bzpy)_2] \xrightarrow{h\nu} [fac\text{-}ClRe(CO)_3(4bzpy)_2]^* \xrightarrow{Et_3N} [fac\text{-}ClRe(CO)_3(4bzpy)_2]^- + Et_3N^{\bullet +} \tag{2}$$

$$[fac\text{-}ClRe(CO)_3(4bzpy)_2] \xrightarrow{4e^-,\ 4H^+} [fac\text{-}ClRe(CO)_3(4bzpy\text{-}OH)_2] \tag{3}$$

Experimental Section

Materials. CH_3CN was distilled from P_2O_5 and stored under Ar. The supporting electrolyte, $[n\text{-}Bu_4N]PF_6$ (Alfa), was recrystallized from EtOH and then dried under vacuum overnight at 80 °C. 4-Benzoylpyridine (Aldrich), $ClRe(CO)_5$ (Pressure Chemical Co.), NH_4PF_6 (Alfa), and CH_3I (Aldrich) were used as purchased.

[*fac*-$ClRe(CO)_3(4bzpy)_2$] was prepared[1] by refluxing $ClRe(CO)_5$ with a 2-fold excess of 4-benzoylpyridine in hexane for 45 min, collecting the precipitate, and washing with copious amounts of hot hexane. ^1H NMR (250 MHz, $(CD_3)_2CO$): δ 9.10 (m, 4 H), 7.85 (m, 8 H), 7.74 (m, 2 H), 7.59 (m, 4 H).

1-Methyl-4-benzoylpyridinium hexafluorophosphate was prepared by refluxing 1.83 g of 4-benzoylpyridine and 1.5 mL of MeI in CH_3CN overnight, cooling, and collecting the precipitate. The precipitate was dissolved in H_2O, and addition of NH_4PF_6 to the solution caused precipitation of the white product. The product was recrystallized from EtOH; yield 2.55 g (75%). ^1H NMR (250 MHz, $(CD_3)_2CO$): δ 9.27 (d, 2 H, *J* = 6.5 Hz), 8.43 (d, 2 H, *J* = 6.1 Hz), 7.90 (m, 2 H), 7.79 (m, 1 H), 7.62 (m, 2 H), 4.70 (s, 3 H). MS: $(M - PF_6)^+$ *m/e* 198.0890 (obsd), 198.0919 (calcd); composition $C_{13}H_{12}NO$.

Electrochemistry. Electrochemical measurements were made with a PAR Model 173 potentiostiat and Model 175 voltage programmer. Cyclic voltammograms were recorded with a Houston Instrument Model 2000 X-Y recorder. Measurements were done in Ar-purged CH_3CN with $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte by using a Pt-wire working electrode, a Pt-flag counter electrode, and a SCE reference electrode.

Thin-layer cell[12] IR and UV-vis spectroelectrochemical experiments were carried out with a cell made from two NaCl plates. Two pieces of Pt gauze in the cell served as a spacer as well as a working electrode and a counterelectrode. The edges of the NaCl plates were sealed with epoxy. The path length of the cell was about 0.2 mm. The cell was placed in a holder that resembles that of an ordinary IR solution cell, which allows the holes to be sealed with septa. An Ag wire was introduced through the septum as a quasi-reference electrode. The IR spectra were taken on a Nicolet Model 60SX FTIR spectrometer and the UV/vis absorption spectra were recorded on a HP 8451 diode array spectrometer by using the same electrochemical equipment as for the cyclic voltammetry.

Electrolysis of [*fac*-$ClRe(CO)_3(4bzpy)_2$] to form the bis(alcohol) complex was done in a two-compartment cell. The catholyte consisted of 0.1 M CH_3COOH, 10 mM [*fac*-$ClRe(CO)_3(4bzpy)_2$], and 0.1 M $[n\text{-}Bu_4N]PF_6$ in CH_3CN, and the anolyte consisted of 0.1 M $[n\text{-}Bu_4N]PF_6$ in CH_3CN. A Hg pool was used as the working electrode, Pt gauze as counterelectrode, and SCE as reference electrode. The potential was controlled at −1.4 V vs SCE. At the end of electrolysis, the solution in the catholyte was withdrawn and combined with 100 mL of CH_2Cl_2. The resulting solution was washed with concentrated aqueous Na_2CO_3 solution and dried over anhydrous Na_2SO_4. Then the solvent was removed by evaporation, and the product was extracted from the residue by a mixture of hexane and EtOH. ^1H NMR ($CDCl_3$): δ 8.53 (d, 4 H, *J* = 7 Hz), 7.28 (m, 14 H), 5.74 (s, 2 H), 3.66 (br, 2 H). After 1 drop of D_2O was added to the solution, the peak at δ 3.66 diminished, showing that this proton is a hydroxyl proton. MS: M^+ *m/e* 676.0776

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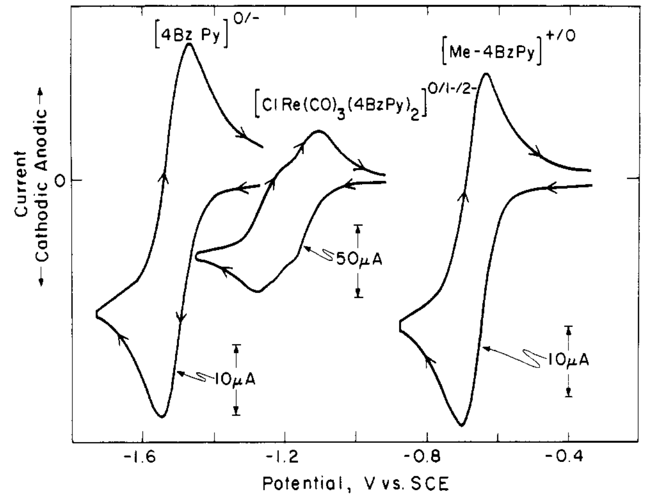

Figure 1. Cyclic voltammetry of ~1 mM 4bzpy, [*fac*-ClRe(CO)$_3$-(4bzpy)$_2$], and Me-4bzpy$^+$. All voltammograms were taken at 100 mV/s in CH_3CN/0.1 M [*n*-Bu_4N]PF_6 at 25 °C. The peak current in the cyclic voltammograms is proportional to (sweep rate)$^{1/2}$, consistent with diffusion-limited redox processes.

Table I. Cyclic Voltammetric Determination of $E_{1/2}$ for Relevant Species[a]

redox couple	$E_{1/2}$, V vs SCE
4bzpy$^{0/-}$	-1.51
[*fac*-ClRe(CO)$_3$(4bzpy)$_2$]$^{0/-/2-}$	-1.14, -1.25
Me-4bzpy$^{+/0}$	-0.67

[a] Data are from cyclic voltammograms recorded at 25 °C in CH_3CN/0.1 M [*n*-Bu_4N]PF_6. The $E_{1/2}$ values given are the average position of the cathodic and anodic current peaks; cf. Figure 1.

(obsd), 676.0777 (calcd); composition $C_{27}H_{22}ClN_2O_5Re$.

Results and Discussion

Electrochemistry of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$]. The cyclic voltammetry of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] at 100 mV/s in CH_3CN/0.1 M [*n*-Bu_4N]PF_6 exhibits two closely spaced, chemically reversible, one-electron-reduction waves with $E_{1/2}$ at -1.14 and -1.25 V vs SCE, as shown in Figure 1. The number of electrons in the reduction of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] was established by comparing the cyclic voltammetry waves to those for ferrocene as an internal standard. The fact that the one-electron- and two-electron-reduction potentials are nearly the same is consistent with the fact that the two lowest unoccupied molecular orbitals of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] are the two independent π^* orbitals of each 4bzpy ligand. Apparently, the first electron added is primarily localized on one of the 4bzpy ligands while the second electron added is primarily localized on the other, and the dianion is presumably a diradical. The reduction wave of 4bzpy with an $E_{1/2}$ at -1.51 V vs SCE and that of 1-methyl-4-benzoylpyridinium (Me-4bzpy$^+$) with an $E_{1/2}$ at -0.67 V vs SCE are also shown in Figure 1. Comparing the reduction potentials of [*fac*-ClRe-(CO)$_3$(4bzpy)$_2$], 4bzpy, and Me-4bzpy$^+$ reveals that coordination of 4bzpy, via the nonbonding electron pair of the nitrogen, to the metal causes a perturbation in the π^* orbital of 4bzpy which results in behavior intermediate between that for the free ligand and that for the methylated ligand, Me-4bzpy$^+$. Table I gives the reduction potentials of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$], 4bzpy, and Me-4bzpy$^+$.

IR Spectral Changes upon One- and Two-Electron Reduction of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$]. Figure 2 shows the IR spectral changes in the CO stretching region for [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] upon electrochemical reduction in CH_3CN/0.36 M [*n*-Bu_4N]PF_6 in an optically transparent thin-layer spectroelectrochemical cell. [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] exhibits a characteristic three-band IR spectrum in the CO stretching region at 2027, 1923, and 1895 cm^{-1}. Moreover, the complex has a ketone carbonyl stretching absorption at 1672 cm^{-1} (1670 cm^{-1} for 4bzpy, 1678 cm^{-1} for Me-4bzpy$^+$) with integrated intensity twice that for the free ligand at the same concentration. Upon one-electron reduction the IR absorption bands in the CO stretching region for [*fac*-ClRe-(CO)$_3$(4bzpy)$_2$] diminish, and new bands appear at 2013, 1903, and 1881 cm^{-1} corresponding to [*fac*-ClRe(CO)$_3$(4bzpy)$_2$]$^-$. Further the absorption of the ketone carbonyl stretch decreases in intensity to half its original value *but does not shift in energy*. When the electrode potential is moved more negative, [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] becomes two-electron reduced. The carbonyl absorptions of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$]$^-$, including the ketone stretch at 1672 cm^{-1}, disappear, concomitant with the growth of three bands at 2001, 1886, and 1865 cm^{-1} corresponding to the dianion [*fac*-ClRe(CO)$_3$(4bzpy)$_2$]$^{2-}$. When the potential is swept positive of the reduction potential the new bands disappear and the original bands of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] are regenerated, clearly showing that the species obtained upon reduction are associated with the two, reversible, one-electron reductions shown by the cyclic voltammetry in Figure 1. Table II summarizes the IR data for the relevant species.

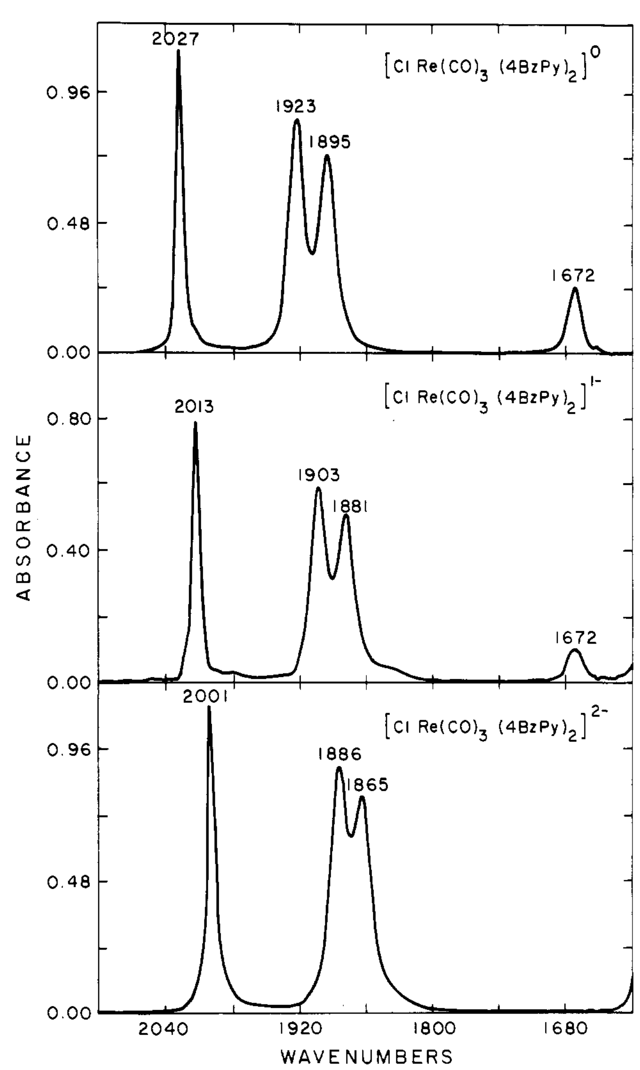

Figure 2. IR spectral changes resulting from one- and two-electron reduction of 10 mM [*fac*-ClRe(CO)$_3$(4bzpy)$_2$] in CH_3CN/0.36 M (*n*-Bu_4N][PF_6. $E_{1/2}$ values for the redox processes are given in Table I.

It should be appreciated that the $E_{1/2}$ values for the one- and two-electron reductions, eq 1, are sufficiently close, Table I, that the one-electron species cannot be cleanly obtained owing to rapid disproportionation. The IR data shown in Figure 2 show, however, that *fairly* clean samples of the one-electron-reduced species can be obtained. In any case, the two-electron-reduced species can be cleanly generated and shows unique IR bands that are well-resolved from both the starting complex and the intermediate one-electron-reduced state.

When one electron is added to the lowest unoccupied molecular orbital of [*fac*-ClRe(CO)$_3$(4bzpy)$_2$], two limiting possibilities represent the description: (1) the electron will be delocalized over

Table II. IR and UV/Vis Data for Relevant Compounds

species[a]	abs max (ϵ, M^{-1} cm^{-1})[c] IR, cm^{-1}	abs max (ϵ, M^{-1} cm^{-1})[c] UV/vis, nm
[*fac*-$ClRe(CO)_3(4bzpy)_2$]	2027 (4300)	320 (9500)
	1923 (3000)	260 (24 300)
	1895 (2800)	
	1672 (940)	
[*fac*-$ClRe(CO)_3(4bzpy)_2$]$^-$	2013 (4320)	604 (6700)
	1903 (3200)	350 (17 500)
	1881 (2830)	260 (20 200)
	1672 (500)	
[*fac*-$ClRe(CO)_3(4bzpy)_2$]$^{2-}$	2001 (4330)	612 (13 000)
	1886 (3420)	352 (26 100)
	1865 (3000)	
[*fac*-$ClRe(CO)_3(bpy)$][b]	2019 (5800)	
	1914 (4370)	
	1893 (4300)	
[*fac*-$ClRe(CO)_3(bpy)$]$^-$[b]	1994 (5630)	
	1880 (4220)	
	1862 (4480)	
Me-4bzpy$^+$	1687 (450)	348 (140)
		272 (10 250)
Me-4bzpy		508 (5600)
		330 (12 500)
4bzpy	1670 (490)	336 (120)
		258 (11 100)
4bzpy$^-$		696 (5600)
		324 (10 700)

[a] In CH_3CN/0.36 M [*n*-Bu_4N]PF_6, except where noted otherwise. [b] In DMF/0.36 M [*n*-Bu_4N]PF_6, from ref 13. [c] Absorptivities have been determined accurately for the oxidized complex, ligand, and methylated ligand by using solutions of known concentration and cells of known path length. Absorptivities for reduced species are measured by assuming a quantitative yield of the reduced species in the spectroelectrochemical cell; cf. Figures 2 and 3.

the two 4bzpy ligands with a net increase of half of an electron per 4bzpy, or (2) the electron will be localized on one 4bzpy thus forming one 4bzpy$^-$ anion and one neutral 4bzpy on the resulting [*fac*-$ClRe(CO)_3(4bzpy)_2$]$^-$ anion. IR spectra of the one-electron-reduced species from [*fac*-$ClRe(CO)_3(4bzpy)_2$] give a clear distinction between these two limiting possibilities. In the case of two-electron reduction two equivalent 4bzpy ligands are expected in the reduced product. Since the electrons are being added to π^* orbitals of the 4bzpy's, one would expect a decrease in energy of the CO stretch of the ketones as the electron density in these orbitals increases. Thus, in the delocalized model, one would expect to see the IR absorption band of the ketones at 1672 cm^{-1} disappear (i.e. shift to lower energy) with the addition of the first electron. In the localized model one neutral 4bzpy still exists when the first electron is added, so the absorption at 1672 cm^{-1} remains, but decreases in intensity to half of its original value. Our result is that upon one-electron reduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] the IR absorption of ketone stretching still remains at 1672 cm^{-1}, consistent with an electron localized on one of the 4bzpy ligands. Unfortunately, the IR absorption of the reduced ketone could not be determined. The IR absorptions of the CO groups bonded to Re establish the distinctiveness of the one-electron- and two-electron-reduced species. The CO data exclude the possibility that the decrease in intensity of the ketone carbonyl stretch to half its original value upon one-electron reduction (without shift in energy) of [*fac*-$ClRe(CO)_3(4bzpy)_2$] is attributable to a solution of a mixture of [*fac*-$ClRe(CO)_3(4bzpy)_2$] and [*fac*-$ClRe(CO)_3(4bzpy)_2$]$^{2-}$.

Upon reduction of [*fac*-$ClRe(CO)_3(bpy)$], the energy of CO stretching absorptions of the complex shifts to lower energy but the three-band pattern still remains. The average of the energy shift of the carbonyl absorptions upon the addition of the first electron is ~16 cm^{-1}, similar to that caused by the addition of the second electron, ~14 cm^{-1}. It is interesting to note that the energies of CO stretching absorptions of [*fac*-$ClRe(CO)_3(bpy)$] (bpy ≡ 2,2′-bipyridine), which has a Re → bpy CT lowest excited state, shift ~30 cm^{-1} to lower energy upon one-electron reduction and the reduced species becomes very substitution labile.[13] The lifetime of the reduced product is 2.5 min in the presence of entering ligand, Ph_3P. In contrast, the one- and two-electron-reduced [*fac*-$ClRe(CO)_3(4bzpy)_2$] species give no detectable substitution reaction in 60 min in the presence of 1 M Ph_3P. The substitution lability of [*fac*-$ClRe(CO)_3(bpy)$]$^-$ compared to [*fac*-$ClRe(CO)_3(4bzpy)_2$]$^{-/2-}$ is consistent with the fact that the added electron in the bpy complex has relatively more electron density at the metal center, increasing π-back-bonding to CO and promoting loss of Cl^-, while the added electron(s) of the reduced product(s) of [*fac*-$ClRe(CO)_3(4bzpy)_2$] is (are) mainly localized on the 4bzpy ligands.

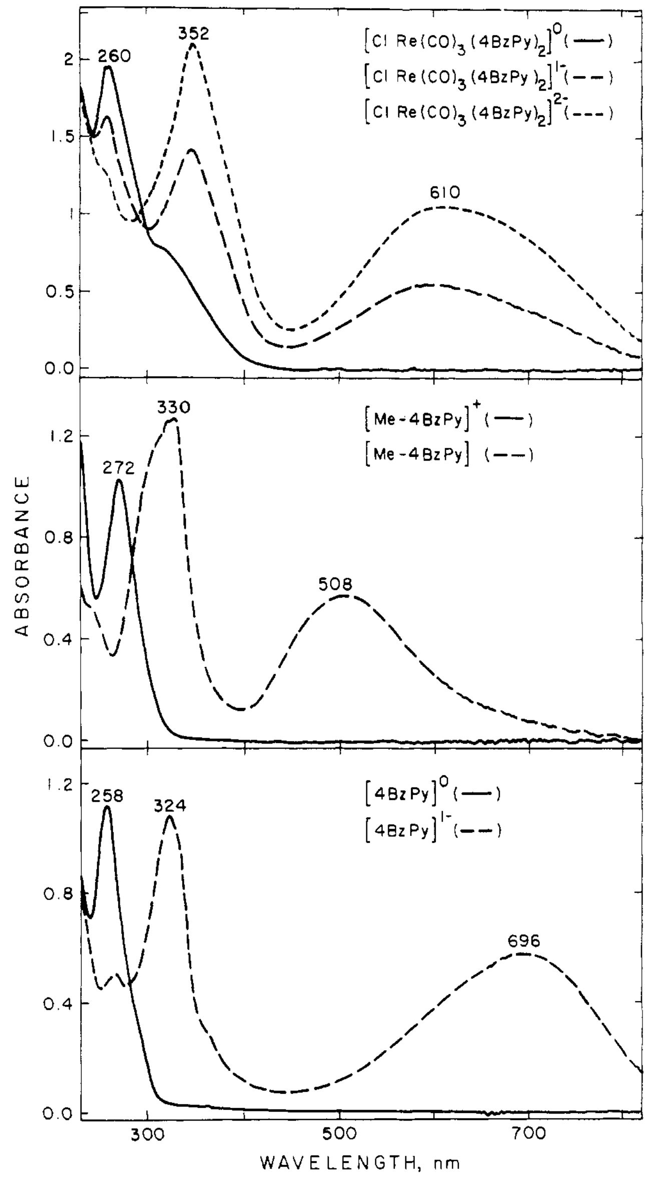

Figure 3. UV/vis absorption spectra of [*fac*-$ClRe(CO)_3(4bzpy)_2$] (4 mM), Me-4bzpy$^+$ (5 mM), 4bzpy (5 mM), and their reduced species. All are measured in CH_3CN/0.36 M [*n*-Bu_4N]PF_6. $E_{1/2}$ values for the redox processes are given in Table I.

UV/Vis Spectral Changes upon Reduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$]. Reduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] can also be followed by UV/vis spectroscopy. Figure 3 shows the UV/vis spectral changes for [*fac*-$ClRe(CO)_3(4bzpy)_2$] upon reduction, and Table II gives relevant spectral data for the compounds studied. Upon one-electron reduction the π–π^* absorption (λ_{max} at 260 nm) of the 4bzpy in the complex decreases, and two absorption bands (λ_{max} at 352, 610 nm) due to [*fac*-$ClRe(CO)_3(4bzpy)_2$]$^-$ appear. When the potential of the cell is moved more negative, the UV/vis absorption spectrum of [*fac*-$ClRe(CO)_3$-

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$(4bzpy)_2]^{2-}$ is obtained. The spectral transition from [*fac*-$ClRe(CO)_3(4bzpy)_2$] to [*fac*-$ClRe(CO)_3(4bzpy)_2]^{2-}$ is smooth. One-electron- and two-electron-reduced species exhibit nearly the same absorption maxima in the UV/vis region, but the intensity of the absorption band at 610 nm of the dianion is twice that of the monoanion. The UV/vis spectra of the reduced 4bzpy and Me-4bzpy$^+$ have been measured also. The π–π^* absorptions (λ_{max} at 258 nm for 4bzpy, λ_{max} at 272 nm for Me-4bzpy$^+$) disappear upon reduction and two new bands appear (λ_{max} at 324 and 696 nm for 4bzpy$^-$, λ_{max} at 330 and 508 nm for Me-4bzpy^0). The reduced forms of the complexed ligand, the free ligand, and the methylated ligand have the same absorption pattern in the UV/vis region.

The number, position, structure, and intensity of the observed UV/vis spectral features indicate that the electrons added to [*fac*-$ClRe(CO)_3(4bzpy)_2$] are localized on the 4bzpy ligands. The first electron added produces one 4bzpy$^-$ anion, and the second electron added produces the second 4bzpy$^-$ anion. Therefore, the one-electron- and the two-electron-reduced species have the same UV/vis absorptions, but for the two-electron-reduced product, the intensity of the absorption band at 610 nm, attributable to the absorption of the Re-bound 4bzpy$^-$ ligand, is twice that of the one-electron-reduced product. The UV/vis spectra again support the view that the added electrons are localized on the 4bzpy.

Reduction of Bound Ketone to Bound Alcohol. In the presence of CH_3COOH as a proton source, reduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] becomes chemically irreversible. [*fac*-$ClRe(CO)_3(4bzpy)_2$] can be electrochemically reduced to the bis(alcohol) complex in CH_3CN/0.1 M [*n*-$Bu_4N]PF_6$ with 0.1 M CH_3COOH by using a mercury pool as the working electrode of which the potential is controlled at −1.4 V vs SCE (eq 3). The result is consistent with the mechanism proposed for the photoreduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] where the first step in the photoreduction is one-electron reduction of the Re complex.[10] It is well-known that ketones can be electrochemically reduced to alcohol,[14] and [*fac*-$ClRe(CO)_3(4bzpy)_2$] is unexceptional in this regard.

Conclusions

The spectroelectrochemical studies of [*fac*-$ClRe(CO)_3(4bzpy)_2$], a complex having a lowest excited state corresponding to a Re to 4bzpy charge-transfer transition, allow comparison of IR and UV/vis spectra of the one-electron- and the two-electron-reduced products. The spectral and electrochemical data obtained are uniformly consistent with the conclusion that the reduced metal complex has the electron(s) localized on the 4bzpy ligand(s).

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(Pentafluoro-λ^6-sulfanyl)(fluorosulfonyl)ketene

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In an attempt to find pathways to potentially useful compounds containing the unique pentafluorothio (SF_5) and fluorosulfonyl (SO_2F) groups, the new ketene $F_5SC(SO_2F){=}C{=}O$ (**1**) was synthesized. Recently, we found that SF_5-containing sultones were effective precursors to a number of derivatives potentially useful as acid electrolytes, surface-active agents, and ion-exchange resins.[1-3] It is anticipated that the new ketene and its derivatives will also serve in this role.

In order to obtain $F_5SC(SO_2F){=}C{=}O$ (**1**), it was necessary to prepare the new ester $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ (**2**) via reaction of the sultone $F_5S\overline{CHCF_2OSO_2}$ with 2-propanol in the presence of sodium fluoride:

$$F_5S\overline{CHCF_2OSO_2} + (CH_3)_2CHOH + NaF \rightarrow \underset{\mathbf{2}}{F_5SCH(SO_2F)C(O)OCH(CH_3)_2} + NaHF_2 \quad (1)$$

Treatment of the ester with P_4O_{10} and heat resulted in the formation of the new compound (pentafluoro-λ^6-sulfanyl)(fluorosulfonyl)ketene (**1**):

$$F_5SCH(SO_2F)C(O)OCH(CH_3)_2 + P_4O_{10} \xrightarrow{\Delta} \underset{\mathbf{1}}{F_5SC(SO_2F){=}C{=}O} \quad (2)$$

This procedure resulted in some contamination of **1** with $SF_5CH_2SO_2F$, and although the yields varied from 49 to 89%, it was found that they decreased upon attempts to prepare larger amounts (e.g. from 8.7 g of ester, only about 1 g of the ketene could be collected). Due to these problems, an alternate procedure was sought that involved dehydrofluorination of $F_5S\overline{CHCF_2OSO_2}$ or its rearranged isomer, $F_5SCH(SO_2F)COF$. Interestingly, with the comparatively weak base NaF, the sultone underwent rearrangement and partial dehydrofluorination to produce a mixture (14:86) of the ketene **1** and $F_5SCH(SO_2F)COF$, respectively. Sodium fluoride failed to give pure **1** even upon warming to 135 °C (15 h); under this condition some COF_2 and a 50:50 mixture of **1** and $F_5SCH(SO_2F)COF$ were produced. It was found, however, that treatment of the original mixture (14:86) with $BF_3{\cdot}N(C_2H_5)_3$ resulted in essentially quantitative conversion to pure ketene **1**. Overall, the reaction sequence is summarized as

$$F_5S\overline{CHCF_2OSO_2} + NaF \rightarrow SF_5C(SO_2F){=}C{=}O/SF_5CH(SO_2F)COF \quad (3)$$

$$SF_5C(SO_2F){=}C{=}O/SF_5CH(SO_2F)COF + BF_3{\cdot}N(C_2H_5)_3 \rightarrow SF_5C(SO_2F){=}C{=}O \quad (4)$$

The ketene could not be directly prepared in pure form from the sultone and $BF_3{\cdot}N(C_2H_5)_3$. Ketene **1** fumes slightly in air and has a faintly pleasant odor. It reacts readily with alcohols and water according to the equations

$$F_5SC(SO_2F){=}C{=}O + ROH \rightarrow F_5SCH(SO_2F)C(O)OR \qquad R = CF_3CH_2,\ (CH_3)_2CH \quad (5)$$

$$F_5SC(SO_2F){=}C{=}O + H_2O \rightarrow F_5SCH_2SO_2F + CO_2 \quad (6)$$

The proposed acid intermediate $F_5SCH(SO_2F)C(O)OH$ is not stable and decarboxylates spontaneously.[2] With diethylamine the corresponding amide was produced:

$$F_5SC(SO_2F){=}C{=}O + (CH_3CH_2)_2NH \rightarrow F_5SCH(SO_2F)C(O)N(CH_2CH_3)_2 \quad (7)$$

(Pentafluoro-λ^6-sulfanyl)(fluorosulfonyl)ketene is thermally stable; it can be recovered (98%) after heating (4 h) to 220 °C.

Compounds containing SF_5 or SO_2F groups show characteristic infrared bands; the pentafluorothio group shows very strong absorption bands in the region from 820 to above 900 cm^{-1} (SF stretching modes) and absorption bands of medium strength in the region of 600 cm^{-1} (SF deformation modes).[4] Likewise, compounds with an SO_2 group exhibit a strong asymmetric stretching band in the region 1400–1470 cm^{-1} and a strong symmetric stretching band in the region 1200–1300 cm^{-1}. The S–F

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