Table I. Absorption Spectra of Di-5-ASP[a]

solvent	λ_{max}, nm	ϵ_{max}, A/M·cm × 10^{-4}
water	475	2.8
ethanol	494	4.5
butanol	498	3.9
10^{-2} M aqueous sodium dodecyl sulfate	485	3.7
2 mg/mL sonicated egg lecithin	464	3.7
2 mg/mL sonicated dipalmitoyl lecithin	460	4.1

[a] Data obtained on a Cary 118 or a Beckman 25 spectrophotometer over a range of probe concentrations.

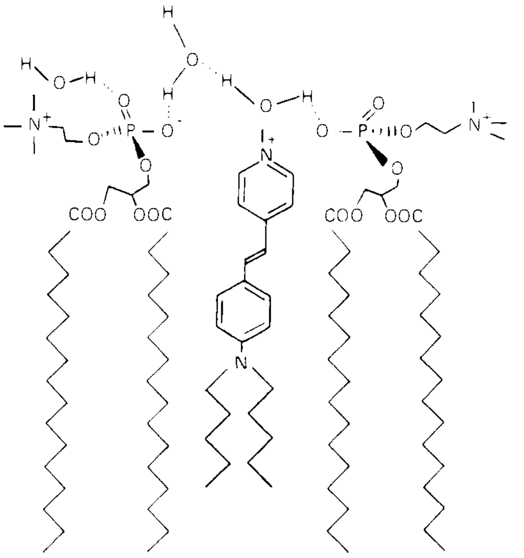

Figure 1. Orientation of di-5-ASP which maximizes stabilizing polar and hydrophobic interactions with adjacent lipid molecules and the aqueous interface in a membrane.

1. The positive charge in the ground state, centered in the pyridinium ring, is in a polar environment; thus, the ground-state stabilization should be comparable with that in H_2O. If the charge migrates to the aniline ring upon excitation, the orientation depicted in Figure 1 places the vertical excited state at a higher energy than it might find itself when simply dissolved in water. The blue shift of di-5-ASP, oriented in the ordered bilayer structure of the membrane, can thus be attributed to a differential solvation which is absent in micelles or homogeneous solution.

Since our explanation rests heavily on the orientation of the chromophore, a polarized fluorescence procedure was devised to verify the presumptions used to formulate Figure 1. The vertically polarized 442-nm line of an He-Cd laser (~5 mW, Liconix 4110H) was focused on either the bottom (B) or the middle (M) of a hemispherical oxidized cholesterol bilayer[6] suspended from a 3-mm polyethylene tube in a 3 μM solution of di-5-ASP in 100 mM aqueous KCl. Membrane fluorescence was collected at 90 °C to the exciting beam through a 570-nm interference filter and a polarizing film which could be oriented either horizontally (H) or vertically (V). A cooled EMI 9558QA photomultiplier tube and a Victoreen 1001 electrometer were used to determine the relative intensities of the four polarized fluorescences: BH, BV, MH, MV. According to an analysis developed by Yguerabide and Stryer in their elegant study of fluorescence from suspended spherical bilayers,[7] BV (δ in ref 7) derives intensity from chromophores with their transition moments perpendicular to the membrane and MV (α in ref 7) derives intensity from chromophores oriented parallel; BH and MH are equivalent for any orientation (these are designated γ in ref 7) and can thus be used to normalize BV and MV for variations in the extent of illumination and the efficiency of light collection at the two positions.

The ratio of the normalized values of BV:MV is 6.1 ± 1.2, indicating a substantial preference for a probe orientation perpendicular to the bilayer surface.[8]

Fluorescence, because of its inherently greater sensitivity, has been a much more popular technique for the study of membrane preparations than absorption spectroscopy. Indeed, the fluorescence properties of di-5-ASP are quite remarkable, showing a 100-fold increase in intensity and a 50-nm blue shift upon binding to egg lecithin vesicles. While these features are generally consistent with our picture of the unique interaction of di-5-ASP with the membrane, an unambiguous interpretation is not possible without additional knowledge of the structure and lifetime of the fully relaxed excited state. Interpretation of the absorption (or, equivalently, excitation) spectra, as exemplified in this work, is simplified by the assurance that only the ground-state structure and environment of the chromophore can contribute to the energies of both the ground and excited states.

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(3) A solution of *p*-(dipentylamino)benzaldehyde (1.3 g, 0.005 mol), 1-methyl-4-picolinium iodide (1.18 g, 0.005 mol), and pyrrolidine (0.35 g) in 70 mL of absolute ethanol was heated at reflux for 6 h. Deeply colored orange-red crystals were collected after cooling to 0 °C. Recrystallization from absolute ethanol gave analytically pure di-5-ASP (1.6 g, 67%).

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(8) These considerations are valid only to the extent that the transition moments for absorption and emission are parallel; the polarization spectrum of the probe in a lecithin vesicle suspension is large (0.32 at 465 nm) and essentially constant over the absorption band.

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Electrophile-Induced Disproportionation of the Neutral Formyl (η-C_5H_5)Re(PPh_3)(NO)(CHO). Generation of Cationic Rhenium Carbenes of the Formula [(η-C_5H_5)Re(PPh_3)(NO)(CHX)]$^+$ (X = H, OCH_3, OH)

Sir:

We recently reported the isolation[1] and X-ray crystal structure[2] of the neutral formyl complex (η-C_5H_5)Re(PPh_3)(NO)(CHO) (**1**). In this communication, we describe low temperature reactions of **1** with electrophiles, under which conditions a stoichiometric fraction of the formyl ligands are transformed, *without the addition of a reductant*, into methyl ligands. Furthermore, evidence is presented for the intermediacy of a variety of novel cationic rhenium-carbene complexes in these reactions, several of which have been independently generated.

The treatment of **1** (~0.1 M in toluene) with 1 equiv of CH_3SO_3F at −78 °C, followed by warming to room temperature, resulted in the formation of [(η-C_5H_5)Re(PPh_3)(NO)(CO)]$^+$$SO_3F^-$ (**2**)[1,3] and (η-C_5H_5)Re(PPh_3)(NO)-

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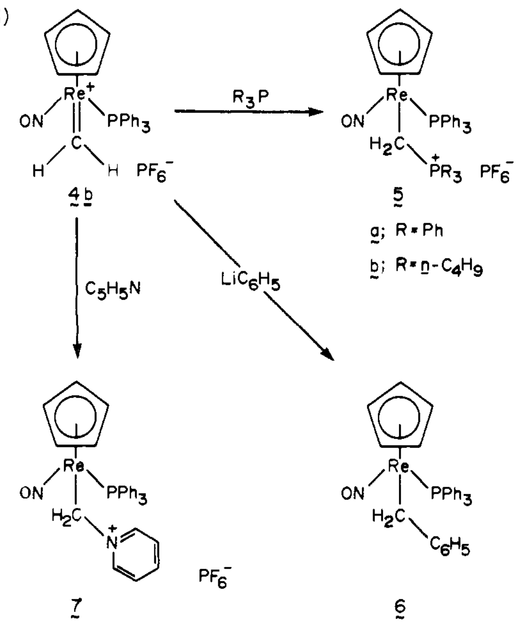
(CH_3) (**3**)[2] in 56 and 29% isolated yields, respectively. Comparable results were obtained with other electrophiles. After adding 1.0 equiv of $(CH_3)_3SiCl$ to **1** (0.20 M in CD_2Cl_2) at −78 °C, followed by warming to room temperature, $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)]^+Cl^-$ (56%), **3** (22%), and $[(CH_3)_3Si]_2O$ (ca. equimolar with **3**) were detected by ^1H NMR.[3,4] A similar reaction of **1** (0.14 M in CD_2Cl_2) with CF_3CO_2H yielded $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)]^+CF_3CO_2^-$ (72%) and **3** (28%).

Attention was directed at the generation of potential intermediates in these disproportionation reactions. When **3** was treated with $Ph_3C^+BF_4^-$ or $Ph_3C^+PF_6^-$ in CH_2Cl_2, or CD_2Cl_2 at −70 °C, the cationic methylidene complex $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CH_2)]^+X^-$ (**4a**, X = BF_4; **4b**, X = PF_6)[4,5] was formed in 88–100% yield. Although unstable at room temperature, **4b** could be efficiently trapped by Ph_3P, $(n\text{-}C_4H_9)_3P$, LiC_6H_5, or pyridine (addition at −78 °C, followed by warming to room temperature). Products **5–7** were isolated in 50–80% yields (eq i).[6] No reaction was observed by ^1H NMR when $(CH_3)_2O$ was added to **4b** in CD_2Cl_2. Of potential relevance to the mechanism by which **3** is formed in the above reactions, an immediate reaction occurred when **4b** was treated with **1** at −78 °C. Subsequently, $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)]^+PF_6^-$ (90%) and **3** (60%) were isolated.

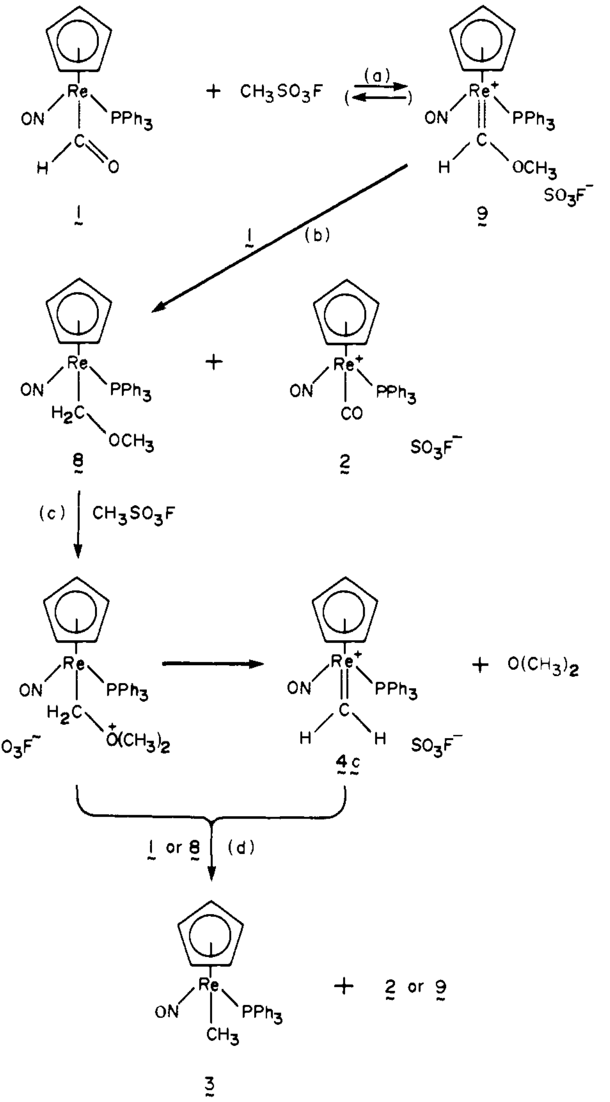
(i)



The reaction of **7** with excess $NaOCH_3$ in CH_3OH (20 °C, 1 h) resulted in the formation of $(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CH_2OCH_3)$ (**8**, isolated in 60–70% yield after recrystallization from CH_2Cl_2-hexane),[7] which is a plausible intermediate in the reaction of **1** with CH_3SO_3F. Significantly, when **8** (0.2 M in $CDCl_3$) was treated with 0.5 equiv of CH_3SO_3F (−60 °C, followed by warming to room temperature), the ^1H NMR spectrum of the reaction mixture indicated the clean formation of **3**, $(CH_3)_2O$, and a new species, $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHOCH_3)]^+SO_3F^-$ (**9**),[8] in a 1.0:1.0:1.1 ratio. Equimolar quantities of **9** (PF_6^- salt) and **3** were also generated when **8** was added to **4b** in CD_2Cl_2 at −70 °C. When **9** (isolated as described)[8] and **1** were reacted in CD_2Cl_2 at −70 °C, **2** (93%) and **8** (100%) formed immediately.

With independently generated samples of **4**, **8**, and **9** in hand, their intermediacy in the reaction of **1** with CH_3SO_3F could be tested by low-temperature ^1H NMR monitoring. Accordingly, the addition of 1 equiv of CH_3SO_3F to **1** (0.15 M in CD_2Cl_2) at −70 °C resulted in a slow reaction. After warming to −40 °C, **1**, **3**, **2**, **8**, and CH_3SO_3F were present in a 0.5:0.3:1.4:1.0:1.0 ratio; remaining **1** disappeared within 15 min. With further warming, the reaction mixture became heterogeneous. However, commencing at −10 °C and proceeding more rapidly upon additional warming, **8** disproportionated to **9** and **3**, and $(CH_3)_2O$ (δ 3.27) formed. Methoxycarbene **9** was also obtained as a minor product (cocrystallizing with **2**) in some preparative runs. The precise distribution of products obtained should reasonably be a sensitive function of reactant ratios and concentrations, order of reactant addition, and reaction temperature and time.

Scheme I. Proposed Mechanism for the Generation of **3** upon Treatment of **1** with CH_3SO_3F.



From these data, we propose that **3** is formed from **1** and CH_3SO_3F by the mechanism depicted in Scheme I. The conversion of **1** into **9** (step a) is not directly observed by ^1H NMR, but this is understandable in view of the previously noted rapid reaction of **1** and **9** at −70 °C (step b). Furthermore, CH_3SO_3F has been shown to methylate numerous transition metal acyls to cationic methoxycarbene complexes.[9] The conversion of **8** into **4c** (step c) is not directly observed because of the rapid subsequent reaction (independently demonstrated) of **4** with **8** (or **1**, step d). However, excellent precedent exists for the formation of cationic alkylidene complexes upon treatment of isoelectronic metal-$CHROCH_3$ species with electrophiles.[10]

Although the characterization of intermediates and products is less complete, available evidence indicates that $(CH_3)_3SiCl$ and CF_3CO_2H react with **1** by qualitatively similar pathways. In CD_2Cl_2 at −70 °C, a species believed to be $[(\eta\text{-}C_5H_5)$-

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$Re(PPh_3)(NO)(CHOH)]^+CF_3CO_2^-$ (**10**)[11] is generated cleanly and quantitatively from **1** and CF_3CO_2H. Complexes containing carbene ligands of the formula $=CHOH$ have not been previously generated, although the intermediacy of such a ligand type in the Fischer-Tropsch process was first considered in 1951.[12] Upon warming, **10** disproportionates to the product mixture quoted above, suggesting that the protonation of **1** is reversible.

The recent study of Cutler[13] bears comment in light of this work. Upon treatment of cationic iron alkoxycarbenes of the formula $[(\eta\text{-}C_5H_5)FeL(CO)(CHOCH_3)]^+PF_6^-$ (**11**) with I^- (1.0-0.5 equiv), equimolar quantities of $[(\eta\text{-}C_5H_5)FeL(CO)_2]^+PF_6$ and $(\eta\text{-}C_5H_5)Fe(CO)_2(CH_2OCH_3)$ were generated. Our data provide additional support for the postulated intermediacy of neutral iron formyls in these reactions, which would rapidly donate hydride to unreacted **11**.

Only one other well-characterized nonbridging methylidene complex, $(\eta\text{-}C_5H_5)_2Ta(CH_3)(CH_2)$ (**12**),[14] has been described in the literature. Whereas the methylidene ligand in **12** is nucleophilic, undergoing ready reaction with $(CH_3)_3SiBr$ and CD_3I, precisely the opposite reactivity is observed with **4** (eq i). Numerous carbene complexes have been observed to form related stable phosphine and amine adducts.[15] As observed with **12**, our ^1H NMR data[5] indicate restricted rotation about the methylidene-metal bond in **4**.

Finally, the facile electrophile-induced disproportionation of formyl **1** may have significant mechanistic relevance to Fischer-Tropsch chemistry.[12] There is substantial hydride mobility associated with homogeneous formyl complexes.[16] Hence, on a Fischer-Tropsch catalyst layered with CO, the generation of low concentrations of catalyst-bound formyls might be accompanied by a similar, electrophile-induced disproportionation.

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(3) Carbonyl cations $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)]^+X^-$ were identified by characteristic ^1H NMR resonances (δ 5.85–6.08, s, 5H) and IR absorbances (ν_{CO} 2000–2030 cm^{-1}, ν_{NO} 1760 cm^{-1}).

(4) ^1H NMR spectra were recorded at 200.04 MHz and ^{13}C NMR spectra were recorded at 50.32 MHz on a spectrometer provided by a NSF departmental instrument grant (CHE 76-05926). Probe temperatures were ambient unless noted, and chemical shifts were measured relative to $(CH_3)_4Si$.

(5) ^1H NMR (**4b,** δ, CD_2Cl_2, −70 °C)[4] 15.67 (m, unresolved ABX system, 1 H; at 10 °C: t, $J_{H-H'} = J_{H-P} = 4$ Hz), 15.42 (br d, $J_{H'-H} = 4$, $J_{H'-P} \leq 1$ Hz), 6.03 ppm (s, 5 H); ^{13}C NMR (**4a,** CD_2Cl_2, −70 °C, gated decoupled) 290.3 (t, $J_{C-H} = 151$ Hz), 100.5 (d, $J_{C-H} = 190$ Hz) ppm. Phenyl proton and carbon resonances were obscured by Ph_3CH.

(6) Satisfactory C, H, N, and P analyses were obtained for **5a**, **5b**, **6**, and **7**. Spectroscopic data follow.[4] **5a:** ^1H NMR (δ, CD_3CN) 7.58–7.50 (m, 30 H), 4.68 (s, 5 H), 3.23 (m, part of ABXY system, $J_{H-H'} = 14$, $J_{H-P} = 11$, $J_{H-P'} = 8$ Hz, 1 H), 2.68 (m, $J_{H'-H} = 14$, $J_{H'-P} = 16$, $J_{H'-P'} = 1$ Hz, 1 H); ^{13}C NMR (CD_3CN) 91.4, −28.6 (d, $J = 31$ Hz) ppm, and phenyl carbons; IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1650; mp >280 °C. **5b:** ^1H NMR (δ, CD_2Cl_2) 7.51–7.29 (m, 15 H), 5.17 (s, 5 H), 2.15 (m, part of ABXY system, $J = 14$, 12, 9 Hz, 1 H) 2.00–1.20 (m, 18 H + 1 H), 0.94 (t, $J = 7$ Hz, 9 H); ^{13}C NMR (CD_2Cl_2) 90.6, −33.5 (d of d, $J_{C-P} = 16$, $J_{C-P'} = 3$ Hz) ppm, and phenyl and butyl carbons; IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1647; mp 229–235 °C. **6:** ^1H NMR (δ, $CDCl_3$) 7.49–7.09 (m, 20 H), 4.74 (d, $J = 1$ Hz, 5 H) 3.50 (d of d, $J = 12$, 8 Hz, 1 H) 2.89 (d of d, $J = 12$, 3 Hz, 1 H); IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1626; mp 180–182 °C. **7:** ^1H NMR (δ, $CDCl_3$) 8.82 (d, $J = 6$ Hz, 2 H) 8.14 (t, $J = 8$ Hz, 1 H), 7.75 (d of d, $J = 6$, 8 Hz, 2 H) 7.53–7.30 (m, 15 H), 5.08 (s, 5 H), 5.81 (d of d, $J = 12$, 2 Hz, 1 H), 5.67 (d of d, $J = 12$, 7 Hz, 1 H); IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1640; mp 180 °C dec.

(7) Anal. ($C_{25}H_{25}NO_2PRe$) C, H, N, P. ^1H NMR (δ, $CDCl_3$)[4] 7.40–7.25 (m, 15 H), 5.04 (d, $J = 0.5$ Hz, 5 H) 5.09 (d of d, $J = 11$, 6 Hz, 1 H), 5.45 (d of d, $J = 11$, 2 Hz, 1 H), 3.16 (s, 3 H); IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1625; mp 175–177 °C.

(8) When this reaction was conducted in toluene, **9** precipitated after stirring overnight. ^1H NMR (δ, CD_2Cl_2)[4] 13.58 (s, 1 H), 7.58–7.18 (m,), 5.85 (s, 5 H), 3.94 (s, 3 H); ^{13}C NMR ($CDCl_3$) 288.4, 96.6, 72.2 ppm, and phenyl carbons; IR (cm^{-1}, CD_2Cl_2) ν_{NO} 1711. After 4 days of vacuum drying, **9** still contained absorbed toluene (10:4 ratio by ^1H NMR). Anal. ($C_{25}H_{24}FNO_5PSRe + 0.33C_7H_8$) C, H, N, P.

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(11) ^1H NMR (δ, CD_2Cl_2, −50 °C)[4] 17.80 (br s, 1 H), 14.80 (s, 1 H), 7.64–7.34 (s, 15 H), 5.57 (s, 5 H); ^{13}C NMR (CD_2Cl_2, −60 °C) 277.8, 95.7 ppm, and phenyl, $CF_3CO_2^-$ carbons. In the reaction of 1 with $(CH_3)_3SiCl$ in CD_2Cl_2, a species believed to be the analogous carbene $\{(\eta\text{-}C_5H_5)Re(PPh_3)(NO)\text{-}[CHOSi(CH_3)_3]\}^+Cl^-$ was formed at −70 °C (δ 15.06 (s, 1 H), 5.91 (s, 5 H); 0.29 (s, 9 H)), along with **3** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+Cl^-$.

(12) See Masters, C. *Adv. Organomet. Chem.* **1979,** *17*, 61, and references therein.

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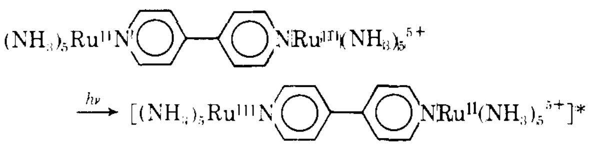
Direct Measurement of the Rate of Intramolecular Electron Transfer in a Diruthenium Mixed-Valence Complex

Sir:

The physical properties of class II mixed-valence ions[1] may be of utility in assessing barriers to electron transfer.[2] Mixed-valence complexes in which the degree of interaction between the two metal sites is moderate (not negligible, but not so large that the sites are equivalent) manifest intervalence transfer absorption[3-6] (e.g., eq 1 for $[(NH_3)_5Ru]_2$-4,4′-bpy^{5+} [7,8]) at energies (E_{op}) which are related by theory to the barriers for thermal electron transfer (E_{th}) within these ions. For the general case in which the two metal coordination spheres are not identical, eq 2 applies:[2]



(1)

$$E_{th,f} = [(E_{op})^2/4(E_{op} - E_0)] - H_{12} \qquad (2)$$

Here $E_{th,f}$ is the barrier for the process endothermic by E_0, the equilibrium energy difference between the two electronic isomers, and H_{12} is the delocalization energy. The intervalence spectra of binuclear species have been extensively characterized,[3-6] and intramolecular electron-transfer rates have been obtained for species which do not manifest intervalence transfer absorption.[9-11] Here we report the rate of intramolecular electron transfer in the mixed-valence ion $(NH_3)_5Ru^{II}pzRu^{III}(edta)^+$ (pz = pyrazine, edta = ethylenediaminetetraacetate) which does exhibit intervalence transfer absorption. As a consequence we are able to test eq 2 directly. Our results suggest a revised model for the electron-transfer process in systems in which the activation barriers arise largely from solvent reorganization.

When $Ru^{II}(NH_3)_5pz^{2+}$ [12] (λ_{max} 472 nm) in pH 5 acetate buffer is mixed with an equivalent amount of yellow $Ru^{III}(Hedta)H_2O\cdot 4H_2O$,[13,14] the pink product I (λ_{max} 520 nm (ϵ_{max} 1.72×10^4 M^{-1} cm^{-1})) results.[15] A class II (trapped-valence) description of the binuclear ion is suggested by its physical properties.[16] No pronounced special stability is associated with