spectroscopy time scale and is again fluxional on the slower NMR time scale. These results demonstrate that in BrF_6^- the bromine free valence electron pair is sterically inactive, while in IF_6^- the iodine free valence electron pair is sterically active. This difference is attributed to the smaller size of the bromine central atom, which with its maximum coordination number of 6 toward fluorine cannot accommodate a seventh ligand. The observation of fluxionality for both BrF_6^- and IF_6^- is not surprising in view of the fact that the ease of delocalization of the free valence electron pair can provide a low energy path for the deformation of these ions.

The failures to prepare a stable ClF_6^- anion[15] are not attributed to steric effects since the maximum coordination number of chlorine toward fluorine is the same as for bromine, i.e. 6, as shown by the existence of the ClF_6^+ cation[16,17] and the fact that ClF_5 undergoes rapid exchange with either CsF[18] or FNO[19] in ^{18}F radiotracer experiments. This conclusion is obviously based on the assumption that by analogy with BrF_6^- the chlorine free valence electron pair in ClF_6^- can be accommodated in a sterically inactive, centrosymmetric orbital. In our opinion, the instability of ClF_6^- is most likely due to the expected decrease in Lewis acidity in the series $IF_5 > BrF_5 > ClF_5$. By analogy to BrF_6^-, the free ClF_6^- anion should also be octahedral, contrary to previous predictions of C_{3v} symmetry made on the basis of the VSEPR rules[1,2] and the Laplacian of the calculated electronic charge distribution.[20]

Finally, we would like to emphasize the need for fast time scale methods when searching for the actual structures of fluxional molecules, while the slower methods can yield valuable information on the dynamics of the intramolecular motions. For ions it is desirable to study, whenever possible, the free ions and not the solids in order to avoid crystal field effects, which can impose either order or disorder on fluxional ions.[3]

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Registry No. BrF_6^-, 56713-48-5; IF_6^-, 27931-77-7; $CsBrF_6$, 26222-92-4; $CsIF_6$, 20115-52-0.

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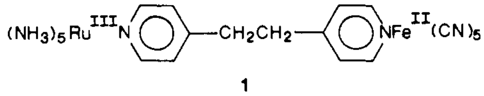
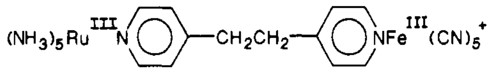
An Example of Intramolecular Electron-Transfer Assistance in a Bimolecular Redox Reaction: Peroxydisulfate Oxidation of (μ-1,2-Bis(4-pyridyl)ethane)pentaammineruthenium(III) Pentacyanoferrate(II) via Its Electronic Isomer

We report herein the first example of intramolecular electron-transfer assistance in a bimolecular redox reaction, namely, the oxidation of **1**, the title compound (1,2-bis(4-pyridyl)ethane



1

= BPA), by peroxydisulfate. Reactivity patterns for the peroxydisulfate oxidations of mono- and binuclear BPA complexes of pentacyanoferrate(II) and pentaammineruthenium(II) provide strong evidence that the oxidation of **1** to **2** (eq 1,2) does not

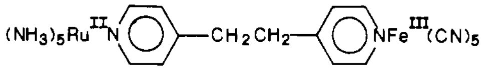


2

$$\mathbf{1} + S_2O_8^{2-} \rightarrow \mathbf{2} + SO_4^{2-} + SO_4^{\bullet -} \quad \text{slow, } k_1 \qquad (1)$$

$$\mathbf{1} + SO_4^{\bullet -} \rightarrow \mathbf{2} + SO_4^{2-} \quad \text{fast} \qquad (2)$$

proceed by direct oxidation of the Fe(II) center in **1**. Instead, the electronic isomer of **1**, **1′**, postulated to be present in small concentrations and in rapid equilibrium with **1**, is the reactive species.



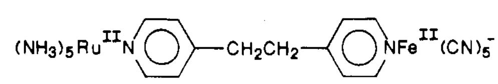
1′

Aqueous solutions[1] containing substantial concentrations of **1** ((2-5) × 10^{-5} M, 25 °C, I = 0.10 M (NaCl), pH = 5.5 with $H_2EDTA^{2-}/CH_3CO_2^-$) were prepared by one of two procedures. In the first, equimolar solutions of $Fe^{II}(CN)_5OH_2^{3-}$[2] and $Ru^{III}(NH_3)_5BPA^{3+}$[3] were mixed anaerobically and allowed to equilibrate[4] according to eq 3. The resulting solutions display a MLCT

$$Ru^{III}(NH_3)_5BPA^{3+} + Fe^{II}(CN)_5OH_2^{3-} \rightleftharpoons \mathbf{1} \quad k_3, k_{-3} \qquad (3)$$

band at 368 nm ($\epsilon = 4.3 \times 10^3\ M^{-1}\ cm^{-1}$, corrected for incomplete reaction). By comparing this band with those of related Ru and Fe complexes (Table I), we infer that the oxidation states of the metal centers are as indicated in **1**. Additional supporting evidence comes from IR studies of the solid: the CN^- stretch at 2036 cm^{-1} and the NH_3 deformation at 1327 cm^{-1} are diagnostic[5] of Fe(II) and Ru(III), respectively. It is noteworthy that electron-withdrawing effects (on spectroscopic and electrochemical properties) associated with substitution on the remote N are not transmitted through BPA.[6,7] On the basis of this information and by comparison with similar unsymmetrical mixed-valence complexes,[7] it is apparent that **1** is a valence-trapped species.[8] Because of the competing outer-sphere electron-transfer reaction[4] between the reactants in eq 3, k_3 was measured by utilizing equal concentrations of Ru(III) and Fe(II) complexes. From absorbance increases at 367 nm, $k_3 = (4.0 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$. Values of $k_{-3} = (3.1 \pm 0.1) \times 10^{-3}\ s^{-1}$ were obtained by adding 0.20 M 4-acetylpyridine to solutions of **1** and following the subsequent absorption increase at 490 nm.[2,9] Solutions of **1** treated with excess $S_2O_8^{2-}$ ((5.0-50) × 10^{-4} M) exhibit first-order absorbance decreases at 380 nm, which yield $k_1 = (3.9 \pm 0.2) \times 10^2\ M^{-1}\ s^{-1}$.

In the second procedure, **1** was generated as a transient by oxidation of **3** with $S_2O_8^{2-}$. First, solutions containing **3** at (2-5)



3

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(1) Solutions of **1** are metastable. Even at low concentrations (2 × 10^{-5}), slight turbidities (undetectable to the eye but observed by shining the beam of a HeNe laser through the solution) develop after several minutes.
(2) Toma, H.; Malin, J. M. *Inorg. Chem.* **1974**, *13*, 1772.
(3) Prepared by reaction of $Ru(NH_3)_5OH_2^{2+}$ with excess BPA in the presence of amalgamated zinc, followed by oxidation of $Ru(NH_3)_5BPA^{2+}$ with bromine and isolation of $[Ru(NH_3)_5BPAH](ClO_4)_4$.
(4) These solutions also contain ~1% of $Fe^{III}(CN)_5OH_2^{2-}$ and $Ru^{II}(NH_3)_5BPA^{2+}$ formed by outer-sphere electron transfer. When Ru(III) is in excess, then detectable amounts of Ru(II) are produced.
(5) Yeh, A.; Haim, A.; Tanner, M.; Ludi, A. *Inorg. Chim. Acta* **1979**, *33*, 51.
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(8) Because of the expected[6] internal ion pair configuration of **1**, we are searching for a MM′CT band.
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Table I. MLCT Bands, Rate Constants for Peroxydisulfate Oxidation, and Reduction Potentials of Complexes of $Ru(NH_3)_5$ and $Fe(CN)_5$ with BPA[a]

complex	λ, nm	$10^{-3}\epsilon$, $M^{-1}\ cm^{-1}$	k, $M^{-1}\ s^{-1}$	$E°$, V vs NHE
$Fe^{II}(CN)_5BPA^{3-}$	365[b]	4.7	0.10	0.440
$Ru^{II}(NH_3)_5BPA^{2+}$[c]	410	7.2	1.0×10^5	0.293
$(NH_3)_5Ru^{III}(BPA)Fe^{II}(CN)_5$	368	4.3	4.3×10^2	
$(NH_3)_5Ru^{II}(BPA)Fe^{II}(CN)_5^-$	408, 368[d]	8.7, 5.7	5.0×10^4[e]	
$(NH_3)_5Ru^{III}(BPA)Fe^{III}(CN)_5^+$	415, 365	1.4, 1.3		0.447,[f] 0.290[g]
$(NH_3)_5Rh^{III}(BPA)Fe^{II}(CN)_5$	367	3.3	0.50	0.440
$(NH_3)_5Co^{III}(BPA)Fe^{II}(CN)_5$	365[b]	4.5		
$(NH_3)_5Ru^{II}(BPA)Co^{III}(CN)_5$[h]	403			

[a] At 25 °C, $I = 0.10$ M (NaCl), pH = 5.5 ($H_2EDTA^{2-}/CH_3CO_2^-$). [b] Reference 6. [c] In 0.10 M HCl. [d] Shoulder. [e] Oxidation of Ru^{II}. [f] Reduction of **2** to **1**. [g] Reduction of **1** to **3**. [h] In KBr pellet; solution studies precluded by insolubility of complex.

$\times 10^{-5}$ M were obtained by reduction of **1** with ascorbic acid[10] or via eq 4 by mixing equimolar solutions of $Ru^{II}(NH_3)_5BPA^{2+}$

$$Ru^{II}(NH_3)_5BPA^{2-} + Fe^{II}(CN)_5OH_2^{3-} \rightleftharpoons \mathbf{3} \quad k_4, k_{-4} \quad (4)$$

(prepared by reduction of $Ru^{III}(NH_3)_5BPA^{3+}$ with ascorbic acid or with zinc amalgam) and $Fe^{II}(CN)_5OH_2^{3-}$. Solutions of **3** display the MLCT bands of both Ru(II) and Fe(II) centers (Table I). Values of $k_4 = (2.1 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$ were measured by a competitive method (490 nm) with [4-acetylpyridine] = 2.3×10^{-3} M and $[Ru^{II}(NH_3)_5BPA^{2+}] = (1.5–10) \times 10^{-3}$ M.[11] Values of $k_{-4} = (1.9 \pm 0.1) \times 10^{-3}\ s^{-1}$ were measured by the same procedure as for k_{-3}. When solutions of **3** are mixed with excess $S_2O_8^{2-}$, biphasic kinetics are observed at 410 nm. The first, rapid change corresponds to oxidation of **3** to **1** with a rate constant of $(5.0 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$. The second, slower changes corresponds to oxidation of **1** to **2**[12] with $k_1 = (4.6 \pm 0.3) \times 10^2\ M^{-1}\ s^{-1}$, in acceptable[13] agreement with the value reported above.

Rate constants for the peroxydisulfate oxidations of $Ru^{II}(NH_3)_5BPA^{2+}$, $Fe^{II}(CN)_5BPA^{3-}$, and $(NH_3)_5Rh^{III}(BPA)Fe^{II}(CN)_5$[14] and relevant reduction potentials (cyclic voltammetry) are presented in Table I.

Peroxydisulfate discriminates by a factor of 10^6 in its reactions with $Ru^{II}(NH_3)_5BPA^{2+}$ and $Fe^{II}(CN)_5BPA^{3-}$ (Table I). Therefore, the oxidation of **3** to **1**, which proceeds at a rate comparable with that of $Ru^{II}(NH_3)_5BPA^{2+}$, undoubtedly involves electron loss from Ru(II).[12] On the basis of present and earlier[12] reactivity patterns, it is apparent that the oxidation of **1** proceeds at an anomalously high rate for removal of an electron from a Fe(II) center. The ca. 10^3 difference between **1** and $(NH_3)_5Rh^{III}(BPA)Fe^{II}(CN)_5$ is particularly noteworthy since the two complexes have equal charges, geometry, and $E°$ values. We propose that the oxidation of **1** proceeds *via* rapid and reversible isomerization to **1′** (eq 5) and is followed by reaction of **1′** with $S_2O_8^{2-}$

$$(NH_3)_5Ru^{III}(BPA)Fe^{II}(CN)_5 \rightleftharpoons (NH_3)_5Ru^{II}(BPA)Fe^{III}(CN)_5 \quad K_5 \quad (5)$$

(eq 6). In this interpretation, $k_1 = K_5k_6$. K_5, estimated from

$$\mathbf{1'} + S_2O_8^{2-} \rightarrow \mathbf{2} + SO_4^{\bullet-} + SO_4^{2-} \quad k_6 \quad (6)$$

$E°$ values of 0.44 and 0.29 V for reduction of Fe(III) and Ru(III) centers, respectively, is 2.9×10^{-3}. Therefore, $k_6 = 1.5 \times 10^5\ M^{-1}\ s^{-1}$, a perfectly reasonable value for oxidation of a Ru(II) center. The key finding herein, namely, that the electron to be lost from a given site is first transferred (in a rapid preequilibrium) to a site which is oxidized more readily, could have important implications in biological electron-transport chains.

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(12) Freshly prepared solutions of **2** could be reduced to **3** with ascorbic acid. But after several minutes, less than quantitative formation of **3** was observed. Evidently, solutions of **2** undergo decomposition upon aging, a phenomenon previously observed for the corresponding pyrazine complex: Yeh, A.; Haim, A. *J. Am. Chem. Soc.* **1985**, *106*, 369.

(13) Solutions of **1** and **3** contain small and variable amounts of $Ru(NH_3)_5BPA^{3+/2+}$, which are extremely efficient catalysts for the peroxydisulfate oxidation of Fe(II) complexes.

(14) Prepared by reaction of $Fe^{II}(CN)_5OH_2^{2+}$ with $Rh^{III}(NH_3)_5BPA^{3+}$ which in turn was prepared by reaction of $Rh(NH_3)_5OH_2^{3+}$ with BPA following the procedure for making $[Rh(NH_3)_5py](ClO_4)_3$: Petersen, J. D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3188. Rate constants for formation and dissociation of $(NH_3)_5Ru^{III}(BPA)Fe^{II}(CN)_5$ are $(3.0 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$ and $(3.2 \pm 0.2) \times 10^{-3}\ s^{-1}$, respectively.

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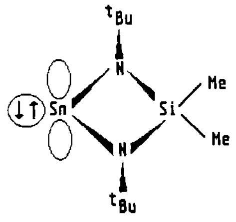
Facile Substitution of Triphenylphosphine in Wilkinson's Catalyst by $Sn(N^tBu)_2SiMe_2$. Syntheses and Molecular Structures of Square-Planar and Homoleptic Trigonal-Bipyramidal Stannylene Complexes of Rhodium(I)

It has been known for some time that certain tin(II) compounds, such as $SnCl_3^-$,[1] $Sn(acac)_2$,[2] and $Sn[N(SiMe_3)_2]_2$,[3] are excellent ligands for late transition elements—particularly those of the platinum-metal group. The monomeric, divalent tin species bear some resemblance, both in structure and reactivity, to carbenes and thus the name stannylene has been proposed for these compounds.[4]

A considerable portion of the research in our group has been concerned with synthesis and chemical characterization of the cyclic bis(amino)stannylene **1** and its lighter and heavier homologues.[5] The presence of both a filled σ-donor orbital and an



1

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