

constant is *ca.* 10⁶). Secondly, the $\pi d-\pi^*$ transition except for the matter of intensity for [2,3] is so like that of the [2,2].

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Intervalence Transfer in Unsymmetrical, Ligand-Bridged Dimeric Complexes of Ruthenium

Sir:

The properties of the mixed-valence ions, $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{5+}$ and $[(\text{bipy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{3+}$ (pyz is pyrazine; bipy is 2,2'-bipyridine).¹⁻⁴ are consistent with the presence of discrete ruthenium(II) and ruthenium(III) sites. For the pentaammine mixed-valence dimer, an intense, near-infrared band has been found which has been assigned to an intervalence transfer (IT) transition.^{1,2} However, the half-width and solvent dependence of the band are not consistent with the model developed by Hush.^{5,6} For the 2,2'-bipyridine mixed-valence dimer, no band attributable to an IT transition has been found.³

We have prepared dimeric, mixed, pentaammine-2,2'-bipyridine complexes in order to compare their mixed-valence and IT properties with the symmetric dimers. The complexes, $[(\text{NH}_3)_5\text{Ru}(\text{L})\text{RuCl}(\text{bipy})_2]^{3+}$ (L is pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE), and 1,2-bis(4-pyridyl)ethane (BPA)), were prepared by the reactions between $[\text{Ru}$

Table I. Intervalence Transfer Bands for the Transition

$$[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{L})\text{Ru}^{\text{II}}\text{Cl}(\text{bipy})_2]^{4+} \xrightarrow{h\nu} [(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}\text{Cl}(\text{bipy})_2]^{4+*}$$

Ion	kK	λ_{max} , ^a nm	ϵ
$[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{4+}$	10.4	960	530
$[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NO}_2)(\text{bipy})_2]^{4+}$	12.7	790	
$[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{CH}_3\text{CN})(\text{bipy})_2]^{5+}$	13.3 (sh)	750 (sh)	
$[(\text{NH}_3)_5\text{Ru}(4,4'\text{-bipy})\text{RuCl}(\text{bipy})_2]^{4+}$	14.4 (sh)	695 (sh)	>300
$[(\text{NH}_3)_5\text{Ru}(\text{BPE})\text{RuCl}(\text{bipy})_2]^{4+}$	14.7 (sh)	680 (sh)	>300
$[(\text{NH}_3)_5\text{Ru}(\text{BPA})\text{RuCl}(\text{bipy})_2]^{4+}$	—	—	—

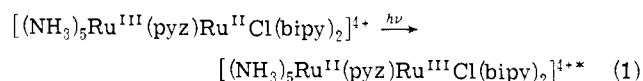
^a In deaerated acetonitrile, ± 3 nm.

$(\text{NH}_3)_5\text{H}_2\text{O}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ and $[\text{Ru}(\text{bipy})_2(\text{L})\text{Cl}](\text{PF}_6)_8$ in acetone. The complexes were isolated as hexafluorophosphate salts and had satisfactory elemental analyses.

Voltammetry at a Pt-bead electrode in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}](\text{PF}_6)$ -acetonitrile solutions showed that the dimeric complexes undergo two, reversible, one-electron oxidations. From the available spectral and electrochemical data, the initial site of oxidation in the one-electron oxidized dimers, $[(\text{NH}_3)_5\text{Ru}(\text{L})\text{RuCl}(\text{bipy})_2]^{4+}$, is localized largely on the pentaammine end giving $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{L})\text{Ru}^{\text{II}}\text{Cl}(\text{bipy})_2]^{4+}$. Localized oxidation at the pentaammine end is the expected result since, on the average, monomeric $[\text{Ru}(\text{bipy})_2(\text{L})\text{Cl}]^+$ complexes are more difficult to oxidize than $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ by ~ 0.4 V.⁹ Solutions containing the mixed-valence +4 ions in acetonitrile can be prepared by stoichiometric oxidation using Br₂ or Ce(IV).

For the BPA-bridged dimers, $[(\text{NH}_3)_5\text{Ru}(\text{BPA})\text{RuCl}(\text{bipy})_2]^{4+/3+}$ there is no evidence for even weak metal-metal interactions across the bridging ligand. For example, the spectra of the +3 and +4 ions are virtually the sum of the spectra of the monomeric components, $[\text{Ru}(\text{bipy})_2(\text{BPA})\text{Cl}]^+$ and $[\text{Ru}(\text{NH}_3)_5\text{BPA}]^{2+}$ or $[\text{Ru}(\text{NH}_3)_5\text{BPA}]^{3+}$. No metal-metal interaction occurs in the BPA dimers because of the saturated $-\text{CH}_2\text{CH}_2-$ linkage; when the bridging ligand has an intact π system (pyz, 4,4'-bipy, or BPE), the effects of weak metal-metal interactions are observed in spectral and reduction potential data and in the appearance of IT bands for the mixed-valence ions.

Intervalence transfer bands found for the mixed-valence, dimeric complexes are given in Table I. No bands are observed for the +3 ions in this spectral region. The assignment of the near-infrared bands to IT transitions for the pyrazine-bridged complexes is based on several lines of evidence. By replacing Cl⁻ in $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{4+}$ by NO₂⁻ or CH₃CN, the IT band maximum shifts to higher energies. The IT transition (eq 1) is expected to



shift to higher energies since the bis-2,2'-bipyridine center is more difficult to oxidize when Cl⁻ is replaced by NO₂⁻ or CH₃CN.¹¹ Band half-widths on the order of 4–8 kK are expected for IT bands.^{5,6,10} A band half-width of 5.8 kK is found for the IT band in $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{4+}$ which is in reasonable agreement with the half-width predicted in an equation given by Hush.^{6,7} Hush has suggested that the energy of IT bands should vary with $(1/n^2 - 1/D)$ where n is the index of refraction and D the static dielectric constant for a given solvent.⁶ The IT band for the ion, $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{4+}$, has the expected solvent dependence (using acetonitrile, nitrobenzene, and dilute, aqueous perchloric acid).

The IT bands for the mixed-valence ions containing BPE or 4,4'-bipy are at higher energies, and therefore appear as well-defined shoulders on the tail of the lowest d(Ru) \rightarrow

π^* (bipy) transitions at λ_{\max} 480–490 nm. Qualitative observations indicate that the bands have the expected solvent dependence. However, reliable estimates for band half-widths and molar extinction coefficients cannot be easily made because of distortions in the band shapes caused by the $d \rightarrow \pi^*$ bands.

The IT transitions are at higher energies for the larger 4,4'-bipy and BPE ligands. This can be predicted from the Hush model since the intersection region between the potential surfaces for the Ru(II)–Ru(III) and Ru(III)–Ru(II) states (and therefore the energy of the IT transition) is a function of the distance separating the metal centers.

The energies of the IT transitions for the $[(\text{NH}_3)_5\text{Ru}^{(\text{II})}(\text{pyz})\text{Ru}^{(\text{III})}\text{X}(\text{bipy})_2]^{4+}$ complexes are at higher energies than the transition for the pentaammine Creutz and Taube ion, as expected, because of the energetically unsymmetrical nature of the light-induced electron transfer process (eq 1). However, the IT band for the unsymmetrical complex ($\text{X} = \text{Cl}$) shows the band width and solvent dependence predicted by Hush, which is in contrast to the Creutz and Taube ion. The oscillator strength of the IT transition for $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{4+}$ is lower by a factor of ~ 2 than the value found for the Creutz and Taube ion indicating less metal–metal interaction.^{2,6} The appearance of a moderately intense IT band for the unsymmetrical dimer is in marked contrast to the $[(\text{bipy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{3+}$ ion where if an IT band exists in the region 700–2500 nm, ϵ must be less than $5 \text{ M}^{-1} \text{ cm}^{-1}$.¹¹ It is interesting to note that although the intervalence transfer properties of the symmetrical pentaammine and 2,2'-bipyridine mixed-valence ions are unusual, the properties of the IT bands for the unsymmetrical mixed-valence ions are in good agreement with the Hush theory.

A noteworthy feature of the data in Table I is that the properties of the IT transitions are dependent upon both bridging and nonbridging ligand effects. From the treatment given by Hush for the properties of IT transitions, it follows that the extent of metal–metal interaction and rates of thermal electron transfer between the metal centers in the mixed-valence ions can be controlled in a systematic way by varying these molecular features.

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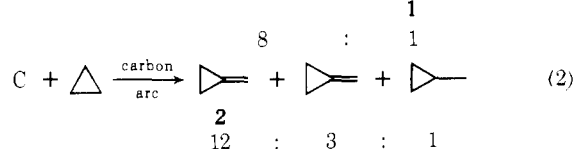
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Reaction of Chemically Generated ^{14}C Atoms with Cyclopropane

Sir:

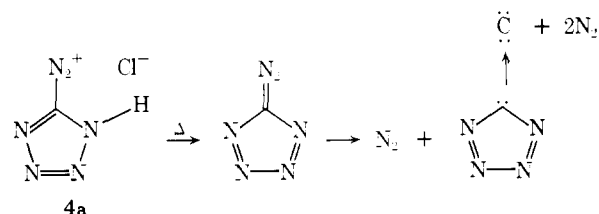
One of the most intriguing aspects of carbon atom chemistry is the reaction of atomic carbon with cyclopropane. Nucleogenic carbon-11 reacts with cyclopropane to produce acetylene- ^{11}C along with smaller amounts of 1,3-butadiene (**1**) (eq 1).^{1,2} In contrast, the major product formed when arc generated carbon atoms are allowed to react with cyclopropane is methylenecyclopropane (**2**) (eq 2).^{3,4}



The formation of acetylene and **1** in the ^{11}C reaction is consistent with a mechanism involving an initial C–H insertion to generate cyclopropyl carbene, **3**. This carbene is known to fragment to ethylene and acetylene, as well as rearrange to cyclobutene and subsequently to **1**.^{5–7} It should be noted that in the ^{11}C system acetylene is also generated by an intermolecular reaction, the mechanism of which has not been resolved.⁸

Inasmuch as **3** is not known to rearrange to **2**, the formation of this product in the reaction of carbon with cyclopropane is surprising. It may be that **2** results from a spectroscopic state of carbon (or intermediate carbene) that is not produced in the nucleogenic reaction. Alternately, the higher energy of the nuclear system may preclude the isolation of labile products such as **2** in the reactions of ^{11}C .

We have recently shown that atomic carbon can be conveniently generated by the thermal decomposition of 5-tetrazoyldiazonium chloride (**4a**).^{9,10} These chemically generated carbon atoms, which possess little excess kinetic energy, are ideally suited for a study of the reaction of carbon with cyclopropane. We now report the results of such a study.



These studies are carried out by coating **4** on the walls of a flask, as described previously,⁹ and thermally (120°) decomposing it in the presence of gaseous cyclopropane. Low product yields presented an initial problem in this reaction. These low yields are due to competing processes such as reaction of atomic carbon with starting material on the walls of the flask and dimerization of the carbon atoms. In order to circumvent the problem of low yields and increase the sensitivity of product analysis, we have employed ^{14}C atoms in this study.

The ^{14}C atoms were generated by the thermolysis of 5-tetrazoyldiazonium- ^{14}C chloride (**4b**). This radioactive car-

