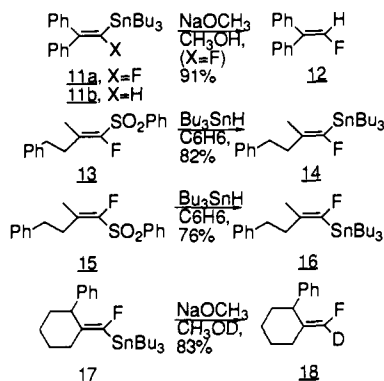


(*E*)-2'-Deoxy-2'-(fluoromethylene)cytidine (**9**) was obtained directly from **6** (CsF/NH₃/CH₃OH). ¹H and ¹⁹F NMR analysis of crude **9** indicated the presence of only the *E* fluoro olefin. Alternatively, **6** was treated with methanolic ammonia to provide **8**,¹³ which upon treatment with CsF yielded **9**. (*Z*)-2'-Deoxy-2'-(fluoromethylene)cytidine (**10**) was obtained from **7** by the "one-pot" procedure, i.e., CsF/NH₃/CH₃OH. The optimum conditions for the stereospecific destannylation reaction depend upon the functionalities present in the molecule. In most cases, refluxing methanolic sodium methoxide is the method of choice over methanolic ammonia or CsF in refluxing methanol.¹⁴ The tributylstannyl group was not removed from nonfluorinated vinylstannane obtained from benzophenone (i.e., **11b**) under conditions (refluxing MeOH/NaOMe, 16 h) where the fluorinated vinylstannane (**11a**) provided 1,1-diphenyl-2-fluoroethylene (**12**)⁸ in 91% yield.



Retention of configuration for the homolytic cleavage of a vinyl phenylsulfonyl group with concomitant replacement by tributyltin is also illustrated with the conversion of the less constrained acyclic (*E*)- and (*Z*)-fluorovinyl sulfones **13** and **15** to (*E*)- and (*Z*)-(fluorovinyl)stannanes **14** and **16**, with greater than 97% retention of configuration.¹⁵ (Fluorovinyl)stannanes provide a convenient entry to deuterated fluoro olefins of defined stereochemistry. Thus, treatment of **17**, obtained exclusively from the corresponding fluorovinyl sulfone,¹⁵ with sodium methoxide in refluxing CH₃OD gave the deuterio olefin **18**.

Compound **9**, administered to L1210 leukemia bearing mice (1 mg/kg, ip) inhibited RDR activity in tumor cells by 80% within 1 h and by 97% within 3 h.¹⁶ Fluoro olefin **9** is a potent cytotoxic agent (IC₅₀ = 58 nM), whereas the geometric isomer **10** is substantially less active (IC₅₀ = 3870 nM).¹⁶ The difference in activity between **9** and **10** is indicative of the importance of the geometry of the fluoro olefin for biological activity.

Acknowledgment. We thank Drs. Boyd Harrison, Esa Jarvi, and Michael Edwards for helpful discussions and Drs. John Paolini and Rose Persichetti for large-scale synthesis.

Supplementary Material Available: Experimental procedures and spectral data for compounds **4**–**18**, the corresponding adenosine and uridine analogues of **9** and **10**, and the fluoro olefins obtained from **14** and **16** and experimental procedures for biochemical results (22 pages). Ordering information is given on any current masthead page.

(12) For a leading reference on the chemistry of vinyl sulfones, see: Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951–6984.

(13) The alkaline reaction conditions caused partial cleavage of the 3',5'-TIPDSi group; see: Markiewicz, W. T.; Nowakowska, B.; Adrych, K. *Tetrahedron Lett.* **1988**, *29*, 1561–1564.

(14) Harpp, D. N.; Gingras, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 7737–7745.

(15) Olefin geometries were based on ¹⁹F–¹³C and Sn–¹³C coupling constants. This will be discussed in more detail in a full paper. The olefin geometry for **9**, **10**, nondeuterated **18**, and the fluoro olefins formed from **14** and **16** were also confirmed by NOE experiments. The structure of the precursor fluorovinyl sulfone to **17** and for **9** were confirmed by X-ray crystallography: Dr. John C. Huffman, Indiana University.

(16) RDR activity was determined by the method of Engstrom et al.: Engstrom, Y.; Eriksson, S.; Thelander, L.; Akerman, M. *Biochemistry* **1979**, *18*, 2941–2948. An IC₅₀ for growth inhibition was determined after a 72-h treatment. Further details are given in the supplementary material.

Intramolecular Dynamics in the Mixed Valence Cluster (CH₃C₅H₄)₄Ru₄S₄²⁺: Observation of Mobile Metal–Metal Bonds

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We wish to describe experiments which probe the movement of metal–metal bonds within a metal cluster.¹ Previous work on the intramolecular dynamics of metal–metal bonds has focused on structural changes coupled to ligand rearrangements.² The dynamic NMR properties of W₄(OⁱPr)₁₂ implicate single bond–double bond isomerization about its metallacyclobutadiene core.³ The present study focuses on the intramolecular bond–no bond dynamics, uncomplicated by changes in ancillary ligation.

The compound (MeCp)₄Ru₄S₄ (**1**, MeCp = η⁵-CH₃C₅H₄) features a distorted tetrahedral Ru₄ core stabilized by a pair of Ru–Ru bonds (2.768 (3) and 2.766 (3) Å) and four triply bridging sulfido ligands.⁴ Cyclic voltammetry of a CH₂Cl₂ solution of **1** shows two one-electron oxidations at the relatively mild potentials of –62 and –183 mV (vs Ag/AgCl).⁴ Previous work has shown that closely spaced pairs of redox steps in metal clusters can be indicative of localized bond breaking/making.⁵ To investigate this point, a salt of the doubly oxidized cubane [**1**]²⁺ was prepared by the addition of 2 equiv of TCNQ (tetracyanoquinodimethane) to a CH₂Cl₂ solution of **1**.⁶ This afforded a purple microcrystalline precipitate of [(MeCp)₄Ru₄S₄](TCNQ)₂·CH₂Cl₂.⁷ A coulometry experiment at 0.0 V (vs Ag/AgCl) confirmed that this salt contains the doubly oxidized cluster.

The structure of [(MeCp)₄Ru₄S₄](TCNQ)₂ was determined by single-crystal X-ray diffraction.⁸ In the lattice the cluster dication is well isolated from the (TCNQ)₂²⁻ anion, whose structure is unexceptional.⁹ The structure of [**1**]²⁺ differs from **1** by the addition of a Ru–Ru bond which gives rise to a chiral

(1) For overviews of the chemistry of metal–metal bonded compounds, see: Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Robert E. Krieger, Ed.; 1982; *Reactivity of Metal–Metal Bonds*; Chisholm, M. H., Ed.; ACS Symposium Series 155; American Chemical Society: Washington, DC, 1981.

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(3) Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 574.

(4) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 14.

(5) Lockemeyer, J. R.; Rauchfuss, T. B.; Rhiengold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5733. Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5960.

(6) For previous work on [cluster](TCNQ)_n salts, see: Green, M. L. H.; Qin, J.; O'Hare, D. *J. Organomet. Chem.* **1988**, *358*, 375. Green, M. L. H.; Qin, J.; O'Hare, D.; Bunting, H. E.; Thompson, M. E.; Marder, S. E.; Chatakondur, K. *Pure Appl. Chem.* **1989**, *61*, 817.

(7) IR (KBr, cm⁻¹) 2180 (s, ν_{CN}). Anal. Calcd for C₄₈H₃₆N₈Ru₄S₄·CH₂Cl₂: C, 43.80; H, 2.83; N, 8.34; S, 9.53. Found: C, 44.07; H, 2.71; N, 8.53; S, 9.25.

(8) X-ray crystallography of C₄₈H₃₆N₈Ru₄S₄·CH₂Cl₂: dark red, opaque crystal: 0.14 × 0.32 × 0.64 mm, triclinic, P1 (C₁, no. 2); a = 10.401 (2) Å, b = 24.166 (6) Å, c = 9.914 (2) Å, α = 100.74 (2)°, β = 100.25 (2)°, γ = 93.19 (2)°, V = 2399 (2) Å³, Z = 2, ρ_{calcd} = 1.797 g/cm³. Diffraction data: mounted in Paratone-N oil (Exxon) at –75 °C, Enraf-Nonius CAD4 automated κ-axis diffractometer, Mo radiation (λ(Kα) = 0.71073 Å), graphite monochromator, 2θ < 46° (±h±k–l), 7242 intensities, 6661 unique (R_i = 0.027), 5966 observed (I > 2.58σ(I)); corrected for anomalous dispersion, absorption, Lorentz, and polarization effects. Solution: direct methods (SHELX-86); Ru and S positions were deduced from an E map; remaining non-hydrogen atoms located by difference Fourier synthesis; hydrogen atoms were included in "idealized" positions. Refinement: full-matrix least squares (SHELX-76), 364 variables against 5966 data converged with R = 0.034 and R_w = 0.049.

(9) Structural studies on other salts of (TCNQ)₂²⁻ have shown that the C–N distances and (methano) carbon–(ring) carbon distances are like those reported for [Nb₂(μ-Cl)₂(C₆Me₆)₃]²⁺(TCNQ)₂²⁻ (Goldberg, S. Z.; Spivack, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Miller, J.; Abkowitz, M. J. *Am. Chem. Soc.* **1977**, *99*, 110) and ((Me₂C₅)₂Fe⁺)(TCNQ)₂²⁻ (Candela, G. A.; Swartzendruber, L. J.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2756).

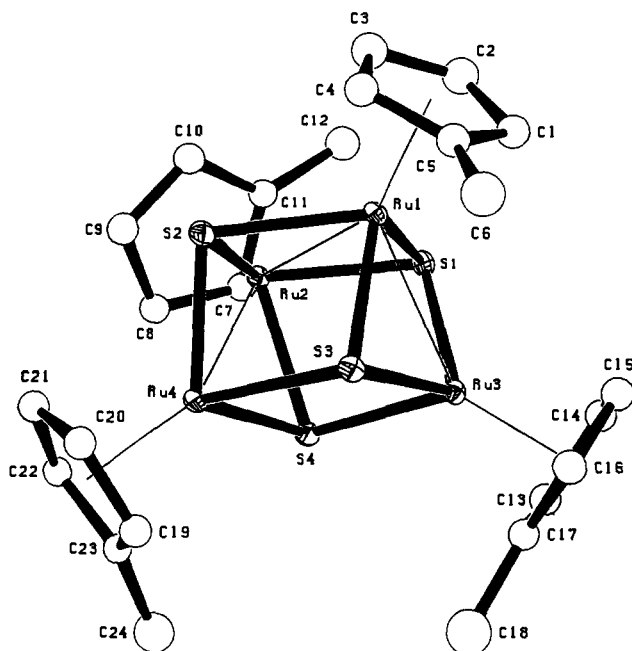


Figure 1. Structure of the dication in $[(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Ru}_4\text{S}_4](\text{TCNQ})_2$ with thermal ellipsoids drawn at the 35% probability level. The ruthenium-sulfur distances (Å) are Ru1-S1, 2.265 (1); Ru1-S2, 2.318 (1); Ru1-S3, 2.358 (1); Ru2-S1, 2.327 (1); Ru2-S2, 2.260 (1); Ru2-S4, 2.346 (1); Ru3-S1, 2.284 (1); Ru3-S3, 2.287 (1); Ru3-S4, 2.351 (1); Ru4-S2, 2.280 (1); Ru4-S3, 2.367 (1); Ru4-S4, 2.286 (1).

cluster of virtual C_2 symmetry (Figure 1).¹⁰ The three bonding Ru-Ru distances are 2.7836 (6), 2.7848 (6), and 2.7937 (6) Å, while the remaining three nonbonding Ru-Ru distances are 3.4646 (7), 3.4832 (6) and 3.5643 (6) Å. Two Ru centers are involved in one Ru-Ru bond each, while the other Ru centers are bound by two Ru-Ru bonds (Scheme I). In contrast, the analogous $[\text{Cp}_4\text{Fe}_4\text{S}_4](\text{PF}_6)_2$ adopts a D_{2d} structure with four equivalent Fe centers interconnected by four moderately short Fe-Fe contacts, each of which is proposed to have 3/4 bond order.¹¹

For use in ^1H NMR studies, the diamagnetic salt $[(\text{MeCp})_4\text{Ru}_4\text{S}_4](\text{PF}_6)_2$ was prepared by oxidation of a tetrahydrofuran solution of **1** with 2 equiv of $[(\text{MeCp})_2\text{Fe}]\text{PF}_6$, followed by recrystallization of the resulting precipitate from acetonitrile-tetrahydrofuran.^{12a} The 200 MHz ^1H NMR spectrum of a CD_3CN solution (20 °C) of $[\mathbf{1}](\text{PF}_6)_2$ consists of one methyl resonance and a pair of $\text{CH}_3\text{C}_5\text{H}_4$ signals. A more complex spectrum reflecting the presence of two nonequivalent MeCp groups is anticipated based on the crystallographic results on $[\mathbf{1}](\text{TCNQ})_2$. The 500 MHz ^1H NMR spectrum (20 °C) of $[\mathbf{1}](\text{PF}_6)_2$ also features only one methyl singlet although the $\text{CH}_3\text{C}_5\text{H}_4$ signals are broadened.¹³ At lower temperatures, the

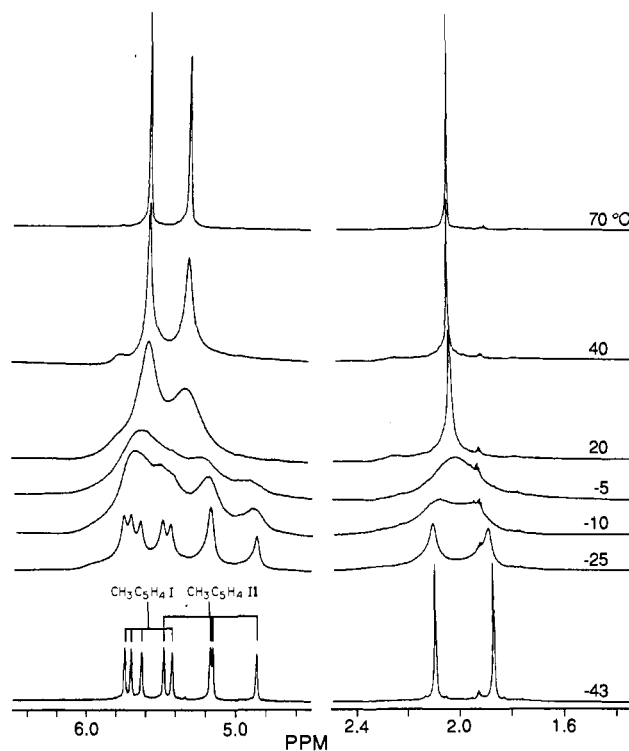


Figure 2. The variable-temperature 500 MHz ^1H NMR spectra of $[(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Ru}_4\text{S}_4](\text{PF}_6)_2$ in the $\text{CH}_3\text{C}_5\text{H}_4$ and the $\text{CH}_3\text{C}_5\text{H}_4$ regions. The spectra are referenced to CD_2HCN , whose chemical shift shows a small temperature dependence. The spectra are scaled differently for clarity.

methyl singlet splits into two equally intense resonances (Figure 2). Furthermore, at -43 °C, eight equally intense $\text{CH}_3\text{C}_5\text{H}_4$ signals are observed, consistent with a chiral structure. With two-dimensional chemical shift correlation spectroscopy (COSY) the eight $\text{C}_5\text{H}_4\text{Me}$ resonances were shown to consist of two ABCD patterns. On the basis of coalescence temperature ($T_c = -8$ °C) of the methyl resonances ($\delta\nu = 113$ Hz at -43 °C), the dynamic process occurs with an activation energy (ΔG^\ddagger) of 52 kJ/mol.¹⁴

The coalescence of the methyl resonances in $[\mathbf{1}]^{2+}$ requires equilibration of the two types of Ru centers, indicating that the Ru-Ru bonds are mobile within the cluster. The observation of two sharp $\text{CH}_3\text{C}_5\text{H}_4$ resonances at high temperatures (70 °C) rules out a chiral rearrangement pathway, a D_{2d} intermediate (Scheme I) analogous to Dahl's $\text{Cp}_4\text{Fe}_4\text{S}_4^{2+}$ is consistent with the NMR results.¹¹

In a control experiment, the 500 MHz ^1H NMR spectrum of **1** (CD_2Cl_2 solution) was found to be essentially unchanged over the range 30 to -50 °C. It is of course possible that the pair of Ru-Ru bonds in **1** are mobile, but our experiment would not have detected this. When the concentration of $[\mathbf{1}](\text{PF}_6)_2$ was lowered by a factor of approximately 10, T_c was unchanged. The dynamics therefore result from an intramolecular process. The dynamic properties of CD_3CN solutions of $[(\text{MeCp})_4\text{Ru}_4\text{E}_4](\text{PF}_6)_2$ (E = Se, Te)¹² were preliminarily investigated by 500 MHz ^1H NMR spectroscopy. The temperature-dependent ^1H NMR spectra for the selenium analogue of $[\mathbf{1}](\text{PF}_6)_2$ resemble those for the sulfide ($T_c = -21$ °C), but the slow exchange limit was not achieved. The T_c for the telluride cluster is lower still, with only slight broadening at -40 °C.

(13) General Electric GN-500 NMR spectrometer with a Doric Trendicator 410A temperature controller (calibrated by MeOH and ethylene glycol standards) was used for the variable-temperature NMR measurements. All spectra were collected with 32 pulses and 64 000 data points, a 1-s delay time, and 0.2-Hz line broadening. Ca. 15 mg of the samples was dissolved in 0.8 mL of CD_3CN (99.96+% d, Aldrich) which had been dried over 4 Å molecular sieves for 12 h.

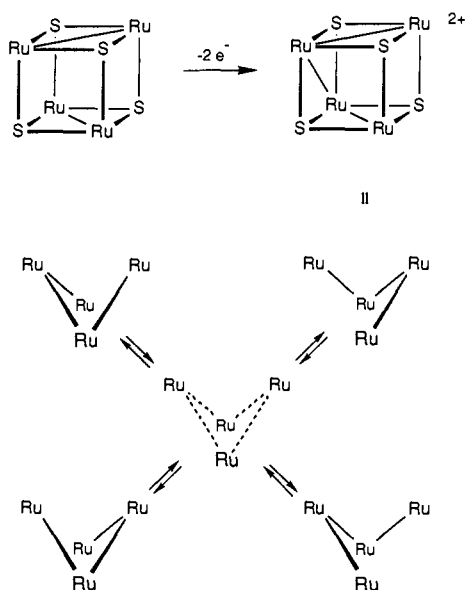
(14) On the basis of ΔG^\ddagger (kJ/mol) = $(1.914 \times 10^{-2}) T[9.972 + \log(T/\delta\nu)]$. Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 77-123.

(10) Leading references on chiral metal clusters: Edidin, R. T.; Zyzyck, L. A.; Norton, J. R. *J. Chem. Soc., Chem. Commun.* **1979**, 580. Vahrenkamp, H. *J. Organomet. Chem.* **1989**, 370, 65.

(11) Trinh-Toan; Teo, B. K.; Ferguson, J. A.; Meyer, T. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, 99, 408. Ogino, H.; Satoh, A.; Shimoi, M. *Bull. Chem. Soc. Jpn.* **1990**, 63, 2314. For work on the analogous $\text{Cp}_4\text{Fe}_4\text{Se}_4^{2+}$ clusters, see: Ogino, H.; Tobita, H.; Yanagisawa, K.; Shimoi, M.; Kabuto, C. *J. Am. Chem. Soc.* **1987**, 109, 5847.

(12) (a) The $[(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Ru}_4\text{E}_4](\text{PF}_6)_2$ (E = S, Se, Te) salts were prepared in this manner. $[(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Ru}_4\text{S}_4](\text{PF}_6)_2$: FABMS (m/z , ^{101}Ru , ^{32}S): 851 (P^+), 771 ($\text{P}^+ - \text{MeCp}$). ^1H NMR (CD_3CN , δ) 2.07 (s, 3 H), 5.32 (s, 2 H), 5.57 (s, 2 H). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_{12}\text{P}_2\text{Ru}_4\text{S}_4$: C, 25.31; H, 2.48. Found: C, 25.66; H, 2.59. $[(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Ru}_4\text{Se}_4](\text{PF}_6)_2$: FABMS (m/z , ^{101}Ru , ^{79}Se): 1038 (P^+), 960 ($\text{P}^+ - \text{MeCp}$). ^1H NMR (CD_3CN) 2.08 (s, 3 H), 5.19 (s, 2 H), 5.43 (s, 2 H). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_{12}\text{P}_2\text{Ru}_4\text{Se}_4$: C, 21.73; H, 2.13. Found: C, 21.82; H, 2.13. $[(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Ru}_4\text{Te}_4](\text{PF}_6)_2$: FABMS (m/z , ^{101}Ru , ^{130}Te): 1233 (P^+), 1155 ($\text{P}^+ - \text{MeCp}$). ^1H NMR (CD_3CN) 2.13 (s, 3 H), 4.99 (2 H), 5.35 (s, 2 H). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_{12}\text{P}_2\text{Ru}_4\text{Te}_4$: C, 18.95; H, 1.86. Found: C, 19.09; H, 1.91. (b) A full report on the synthesis, structure, and electrochemistry of the neutral $[(\text{MeCp})_4\text{Ru}_4\text{E}_4]$ clusters is in preparation: Houser, E. J.; Amarasekara, J.; Dev, S.; Rauchfuss, T. B.; Wilson, S. R. to be submitted for publication.

Scheme I



In summary, the clusters $[(\text{MeCp})_4\text{Ru}_4\text{E}_4]^{2+}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) have dynamic structures which arise from mobile Ru-Ru bonds. The dynamic process was monitored through the ^1H NMR signals of the MeCp ligands which report on the time-averaged stereochemical environment about each metal. The manipulation of dynamic metal-metal bonds presents some novel opportunities in stereochemistry.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE 87-11460. Dr. Mary Frances Leopold is thanked for her assistance with the NMR measurements.

Supplementary Material Available: For $[\text{1}](\text{TCNQ})_2$ tables of bond distances and angles and positional and thermal parameters and an ORTEP drawing for the $(\text{TCNQ})_2^{2-}$ anion (9 pages); table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

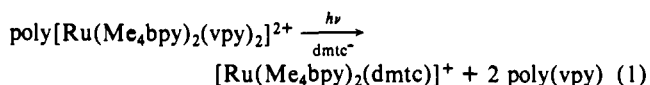
Size-Selective Electrochemistry

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In a recent paper we reported that photochemical loss of 4-vinylpyridine (vpy) from $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ (Me_4bpy is 4,4',5,5'-tetramethyl-2,2'-bipyridine), reaction 1, occurred in thin polymeric films prepared by reductive electropolymerization of *cis*- $[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ on Pt electrodes.^{1,2} As a result

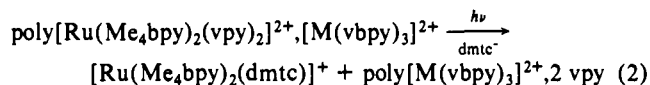


of the photochemistry, the cross-linking fragment $[-\text{Ru}(\text{Me}_4\text{bpy})_2]^{2+}$ was removed from the films, which led to a loss of

the polymer from the electrode and provided a means for creating images and novel microstructures.² We report here that photolysis of copolymeric films of $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$, $[\text{Ru}(\text{vbpy})_3]^{2+}$ (vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine) leads to the selective removal of the fragment $[-\text{Ru}(\text{Me}_4\text{bpy})_2]^{2+}$. The $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}$ film that remains acts as a size-selective transport barrier toward diffusion, which creates a basis for size-selective electrochemistry at the underlying electrode.

Copolymeric films of $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$, $[\text{M}(\text{vbpy})_3]^{2+}$ (M is Ru^{II} or Os^{II}) were prepared on Pt disk electrodes by reductive electropolymerization.³ The ratio was varied by controlling the compositions of the solutions used for electropolymerization. In most cases the composition of the copolymeric films was the same as that of the solutions from which they were prepared. In cyclic voltammograms of the films, reversible $\text{Ru}^{\text{III/II}}$ couples for $\text{poly}[\text{Ru}(\text{vbpy})_3]^{3+/2+}$ (+0.91 V) and $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{3+/2+}$ (+0.80 V) appeared as a single, unresolved wave at $E_{1/2} = +0.88$ V vs Ag/AgNO₃,⁴ and the $\text{Os}^{\text{III/II}}$ couple for $\text{poly}[\text{Os}(\text{vbpy})_3]^{2+}$ appeared at +0.42 V. For $\text{M} = \text{Ru}^{\text{II}}$ there were reversible, bipyridine-based reductions at -1.66 V for $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}$ and an overlapping reduction at -1.88 V for $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}$ and $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ (-1.86 V) and $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ (-1.88 V). For $\text{M} = \text{Os}^{\text{II}}$ there were reversible, bipyridine-based reductions at -1.60 V for $\text{poly}[\text{Os}(\text{vbpy})_3]^{2+}$ and an overlapping reduction at -1.85 V for $\text{poly}[\text{Os}(\text{vbpy})_3]^{2+}$ (-1.76 V) and $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$.

Photolysis of ~1:1 copolymeric films (H_2O , 0.1 M in sodium dimethyldithiocarbamate with a 200-W high-pressure Hg lamp for 45 min, followed by rinses in water and acetonitrile) led to equal peak currents for the ligand-based reduction waves. For $\text{M} = \text{Ru}^{\text{II}}$, the peak current for the $\text{Ru}^{\text{III/II}}$ wave decreased by about half. For $\text{M} = \text{Os}^{\text{II}}$, the $\text{Ru}^{\text{III/II}}$ wave disappeared. Under these conditions, films of $\text{poly}[\text{M}(\text{vbpy})_3]^{2+}$ are photoinert. These observations are consistent with reaction 2. Analysis of the



copolymeric films by X-ray photoelectron spectroscopy (XPS) before and after photolysis confirmed that the Ru^{II} complex was lost from the films as a result of the photochemical reaction. A typical spectrum for a copolymeric film of $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$, $[\text{Os}(\text{vbpy})_3]^{2+}$ exhibited peaks for the Ru 3d, N 1s, and Os 4f photoelectrons. After photolysis, the peaks for Ru 3d were significantly attenuated, indicating that species had been lost from the polymer. The existence of free vpy sites in the films after photolysis was shown independently by chemical binding studies; see below. From the results of initial angle-dependent XPS studies on ~1:1 $\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$, $[\text{Os}(\text{vbpy})_3]^{2+}$ (surface coverage $(\Gamma) = 6.6 \times 10^{-10}$ to 8.4×10^{-10} mol/cm²), the films had decreased in thickness by 0-10% after photolysis. Profilometry experiments on thick films ($\Gamma = 0.7 \times 10^{-8}$ to 1.5×10^{-8} mol/cm²) suggested decreases of 20-40%.

The photochemical reaction changes the transport properties of the films. The ability of the resulting microstructure to discriminate between ferrocene derivatives on the basis of molecular volume was investigated by oxidation at a rotated disk electrode. The data were treated by using eq 3, which describes the limiting current at a rotated disk electrode by assuming that mass transport through the films can be treated as a membrane-diffusional process.⁵ This equation relates the limiting current (i_{lim}) to the

$$\frac{1}{i_{\text{lim}}} = \frac{1}{0.62nFAD_s^{2/3}\nu^{-1/6}\omega^{1/2}C_s} + \frac{1}{nFAD_{s,\text{pol}}PC_s/d} \quad (3)$$

(3) (a) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153. (b) Abruña, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (c) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151.

(4) The reference was Ag/0.01 M AgNO₃ in 0.1 M $[\text{NEt}_4](\text{ClO}_4)/\text{acetonitrile}$. The potential of this electrode is +0.3 V vs the saturated sodium chloride calomel electrode.

(1) (a) Gleria, M.; Minto, F.; Beggiato, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1978**, 285. (b) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860. (c) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

(2) Gould, S.; O'Toole, T. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9490.