The spectra of more complex aromatic compounds such as *p*-diphenylbenzene can also be clarified by using these new binuclear complexes. This compound has four sets of equivalent protons; however, the NMR spectrum consists of two complex multiplets. The spectrum obtained after addition of $Yb(fod)_3$ and Ag(fod) is shown in Figure 2b. The silver appears to be bonded at the sterically least encumbered position, with the result that proton A shifts the farthest. Protons A, B, and C exhibit a pattern identical with that observed for the aromatic protons of toluene. Protons D on the center ring are not coupled with the other protons, and the resonance appears as a singlet.

These shift reagents are also capable of inducing substantial shifts in the NMR spectra of olefins and phosphines. A detailed study of other aromatic, olefin, and phosphine-containing compounds will be reported in a future publication.[13]

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Structure and Dynamic Behavior of Transition-Metal Ions in Aqueous Solution: An EXAFS Study of Electron-Exchange Reactions[1]

Sir:

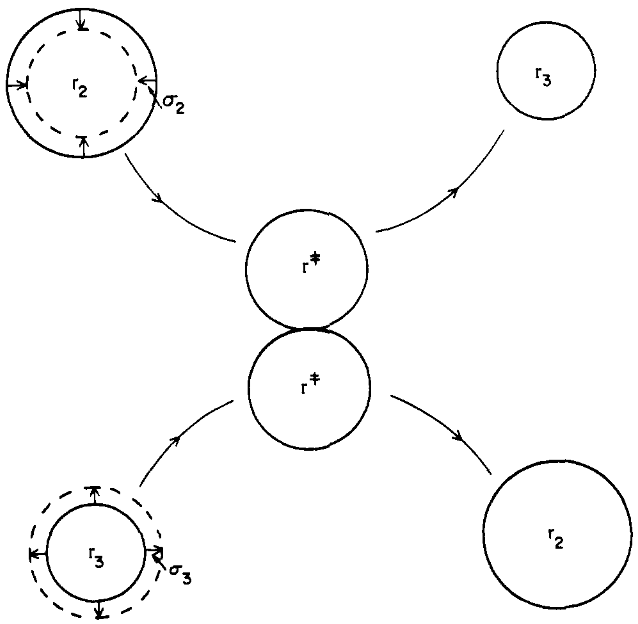

Figure 1. Simplified pictorial representation of $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ electron exchange; the σ values are the root-mean-square displacement amplitudes; arrows indicate the direction of the breathing motion (after Marcus, ref 14).

Table I. Metal-Oxygen Interatomic Distances in $M(H_2O)_6^{n+}$ ($n = 2, 3$)

concn, M	solution			crystal
	M^{n+}	r(EXAFS)[b]	r(X-ray)[c]	r(X-ray)
1	Cr^{3+}	1.966	1.98	
1	Cr^{2+} [a]	1.984		
1	Mn^{2+}	2.177	2.20	
1	Fe^{2+}	2.095	2.12	2.13[d]
1	Fe^{3+}	1.990	2.00	1.99[e]
1	Cu^{2+} [a]	1.940	1.94 (eq) 2.43 (ax)	

[a] In this complex, only the first shell neighbors are considered.[32] [b] These values were measured with solutions acidified with 0.5-1.5 M $HClO_4$. In the cases of Cr^{3+} and Fe^{3+}, the solutions were acidified to 3 M or even 6 M $HClO_4$ to avoid dimer formation. Estimated errors are within ±0.010 Å; k^2 and k^3 weighting gives results within this accuracy. [c] From ref 28-30. [d] Average from ref 20-22. [e] Reference 23.

The extended X-ray absorption fine structure (EXAFS) phenomenon has become a powerful tool for structure determination in the immediate vicinity of an atom of identified Z.[2-13] In this paper, we demonstrate the power of EXAFS for the study of kinetics and reaction mechanisms in solution. Of particular concern here are the metal-ligand bond distances and the associated Debye-Waller factors of $M(H_2O)_6^{n+}$ complexes in aqueous solution. Let us consider $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ (Figure 1); with the bond lengths and Debye-Waller factor information obtained directly from ions in solution, we can estimate the parameters relevant to the kinetics of the electron-exchange reaction (eq 1). Most theories[14-18] which describe such reactions are based

$$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+} \quad (1)$$

on the Franck-Condon principle: there must be formed a transition state in which the coordination shells of the two reactants have adjusted to identical configurations. According to theory,[19] the difference between the Fe-O radii of $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, $r_2 - r_3$, is the most critical parameter. Until now, X-ray crystal structure data[20] have been employed for estimates of this

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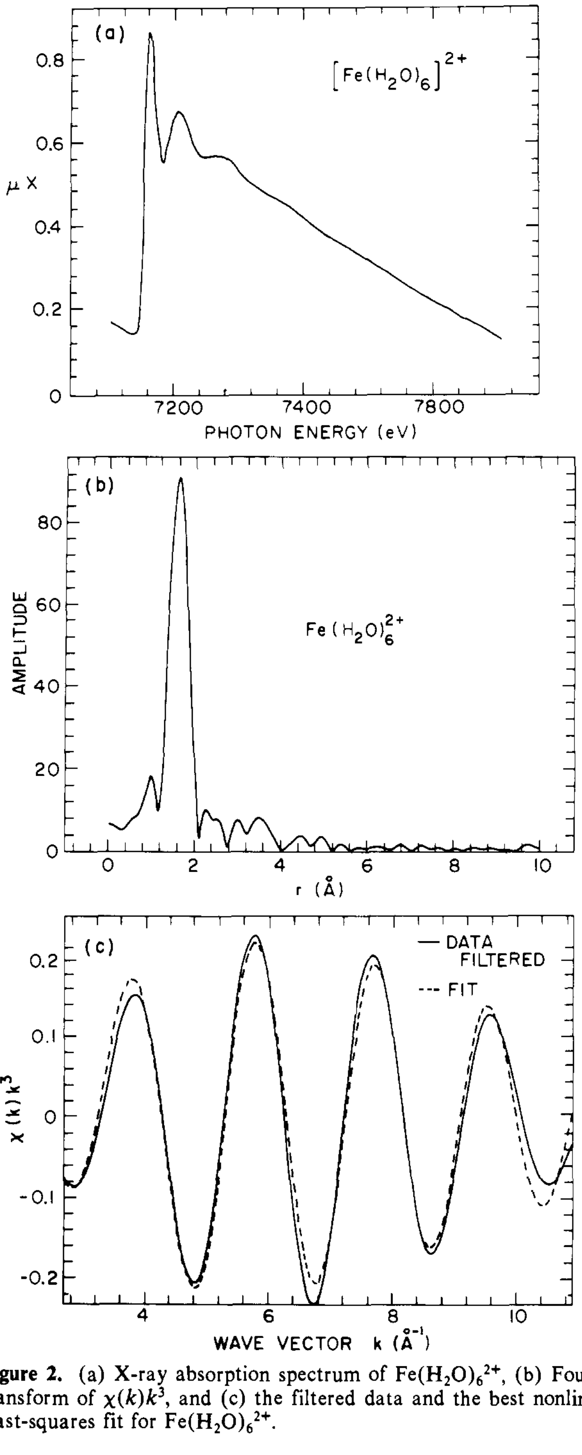

Figure 2. (a) X-ray absorption spectrum of $Fe(H_2O)_6^{2+}$, (b) Fourier transform of $\chi(k)k^3$, and (c) the filtered data and the best nonlinear least-squares fit for $Fe(H_2O)_6^{2+}$.

parameter despite the fact that the $Fe–OH_2$ distance varies among different Fe^{2+} complexes in the lattices from 2.12 to 2.15 Å.

The EXAFS, $\chi(k)$, of an atom is given[2-5] by eq 2, where μ is the absorption coefficient, μ_0 is the smoothed absorption of an isolated atom, k is the electron wavenumber ($k = [2m(E - E_0)]^{1/2}/h$), E is the photon energy above the ionization threshold,

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} = \sum \frac{-N_i|f(\pi,k)|}{kr_i^2} e^{-2\sigma_i^2k^2} e^{-2r_i/\lambda} \sin\,[2kr_i + \phi(k)] \tag{2}$$

E_0, N_i is the coordination number, σ_i^2 is the root-mean-square deviation of r_i, and λ is the electron mean free path. It is apparent from eq 2 that with knowledge of the phase $\phi(k)$ and the amplitude $f(\pi,k)$ of the absorbing and the scattering atoms, r_i and σ_i^2 can be extracted from the experimentally obtained $\chi(k)$.[4,24,25]

K edge spectra were recorded in transmission at the Stanford Synchrotron Radiation Laboratory[26] for perchlorate solutions of Cr^{3+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, and Cu^{2+}. A typical spectrum is given[27] in Figure 2a. Data were analyzed with the filtered Fourier transform and fitting techniques.[5-7] Theoretical amplitudes and phases were used to fit the data to eq 2 with E_0 as a parameter.[24,25] A typical Fourier transform and fit are shown in Figure 2b,c. Results, including those from solution X-ray scattering experiments[28-31] and single-crystal diffraction work,[20-23] for $Fe(H_2O)_6^{n+}$ are given in Table I. Although it appears from Table I that for these ions in solution the EXAFS r values are slightly smaller than those from diffraction measurements, the differences are within experimental error.[31] It is not clear at present whether or not this observation is an indication of a real difference. Cr^{2+} and Cu^{2+}, Jahn–Teller distorted complexes, will be discussed elsewhere.[32]

We now return to the relationship connecting the EXAFS parameters and the electron-exchange reaction. The rate constant for electron exchange, k_{ex}, is given[16] by eq 3, where $\Delta G^{\ddagger}$, the free energy of activation of the reaction, is a sum of several contributions (eq 4). Here, w_r, the work required to bring the two reactants together, is small, $\Delta G_{trans}^{\ddagger}$ is the free energy of formation of the precursor complex of separate reactants, and $\Delta G_o^{\ddagger}$ and $\Delta G_i^{\ddagger}$, the free energies required to reorganize the outer- and inner-coordination spheres of the reactants, are the dominant terms and are related to the $Fe^{2+}–OH_2$ and $Fe^{3+}–OH_2$ distances.[16]

$$k_{ex} = \frac{kT}{h} \exp[-\Delta G^{\ddagger}/RT] \tag{3}$$

$$\Delta G^{\ddagger} = w_r + \Delta G_{trans}^{\ddagger} + \Delta G_o^{\ddagger} + \Delta G_i^{\ddagger} \tag{4}$$

The EXAFS r_2 and r_3 results may be used to evaluate $\Delta G_i^{\ddagger}$, $\Delta G_o^{\ddagger}$, and $r^{\ddagger}$. Following the approximations considered by Sutin,[16] we find that $r^{\ddagger} = 2.030$ Å, $\Delta G_i^{\ddagger} = \Delta H_i^{\ddagger} \simeq 4.7$ kcal/mol^{-1}, and $\Delta G_o^{\ddagger} = \Delta H_o^{\ddagger} \simeq 6.5$ kcal/mol^{-1}. Further, following Sutin's calculation of w_r and $G_{trans}^{\ddagger}$ in eq 4,[16] we obtain $G^{\ddagger} = 14.7$ kcal/mol^{-1}, a value in reasonable agreement with that observed, 16.6 kcal/mol^{-1}.

The Debye–Waller factor[34] derived from the EXAFS data also contains important bonding information. For the ions in solution, one may consider contributions to σ_i due to static disorder (σ_{stat}), to first shell H_2O and solvent H_2O exchange (σ_{exch}), and to thermal vibration (σ_{vib}). Thus, $\sigma_i^2 = \sigma_{stat}^2 + \sigma_{exch}^2 + \sigma_{vib}^2$. In the limit of spherical screening of the octahedral complex by the solvent, σ_{stat} vanishes, and it is reasonable to argue on the basis of the crystal data[20-23] that in these aqueous solutions σ_{stat} is quite small relative to σ_{vib}. Further, the slow ligand-exchange rate[18] makes σ_{exch}^2 small. Therefore, the dominant contribution to σ_i as observed in EXAFS should be the average of all the vibrational M–O amplitudes in the respective complex.[35] The EXAFS σ_i values are 0.081 ± 0.010 Å for $Fe(OH)_6^{2+}$ and 0.055 ± 0.010 Å for

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$Fe(H_2O)_6^{3+}$. The latter is in good agreement with the X-ray scattering results[29] for iron(3+) perchlorate solution, $\sigma_i \sim 0.055(5)$ Å.

One may derive σ_{vib} values from the Raman frequencies, ν, from the relation shown in eq 5, in which μ is the reduced mass. With

$$\sigma_{vib}^2 = \frac{h\nu}{8\pi^2\mu\nu}\coth\left(\frac{h\nu}{2kT}\right) \qquad (5)$$

the vibrational frequencies for crystals used by Sutin,[16] we obtain σ_{vib} values of 0.0233 and 0.0194 Å, corresponding to the totally symmetric stretching modes for the Fe–O bonds in $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively, at room temperature.[35] These σ values are small compared with the EXAFS σ_i values, not a surprising result since σ_i includes all the vibrational modes. It is interesting to note that the $r_2 - r^*$ and $r^* - r_3$ differences, 0.065 and 0.040 Å, respectively are greater than the σ_{vib} values for the totally symmetric vibration, indicating that electron transfer requires much greater activation energy than the energy present on the average in the breathing motions of the complexes at room temperature.

Acknowledgments. We thank Drs. N. Sutin, M. Newton, and S. Heald for discussions and M. Chou for preparing some of the samples. We thank Dr. B. K. Teo for sending us some preprints prior to their publication. EXAFS spectra were measured at the Stanford Synchrotron Radiation Laboratory, which is supported by the National Science Foundation (under Contract DMF77-27489), in cooperation with SLAC and DOE. Work at Brookhaven National Laboratory was performed under the auspices of the Department of Energy.

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Proton-Induced Ring Opening of a Dimetallacyclopropane-Type μ-Methylene-rhodium Compound. A Straightforward Novel Route to Halo(methyl) Complexes[1]

Sir:

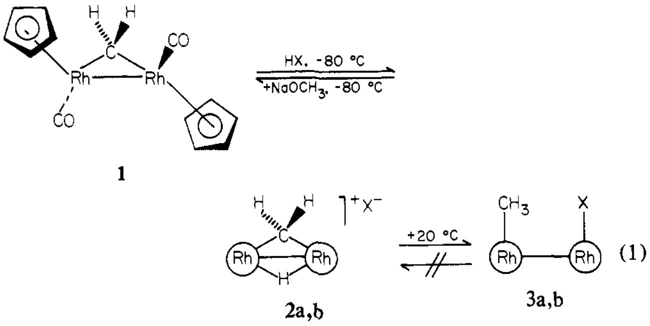
Transition-metal methylene complexes containing unsubstituted metal-to-metal methylene (CH_2) bridges have attracted considerable attention since the first examples of this class of compounds were reported in 1975.[2] Although they meanwhile have been thoroughly investigated by spectroscopic methods,[3,4] X-ray[4a,5,6] as well as neutron-diffraction techniques,[6] Hückel MO calculations,[7] and a representative experimental electron density determination,[8] very little is known about their chemistry to date. Both photochemically and thermally remarkably stable and also synthetically easily available, the dinuclear μ-methylene-rhodium complex μ-$CH_2[(\eta^5$-$C_5H_5)Rh(CO)]_2$ (**1**)[5] represents a neat example of the dimetallacyclopropane-type compounds structurally characterized by a methylene function which bridges a pronounced electron-rich metal–metal bond. Recently, we demonstrated that strong protic acids such as tetrafluoroboric acid initiate clean clusterification of **1**, yielding novel trinuclear μ_3-methylidine derivatives of high thermal stability.[9] Bearing the obvious catalytic importance of simple, metal-bound hydrocarbon fragments and their mechanistic fate in mind,[10] we now report, for the first time, on the proton-induced ring opening of the three-membered Rh–CH_2–Rh skeleton of **1** and the molecular structure of the final product.

Table I. Selected Bond Lengths and Angles of 3b[a]

	bond lengths, pm		bond angles, deg
Rh(1)–Rh(2)	266.0 (3)		
Rh(1)–Br[a]	250.4 (13)	C(2)–Rh(1)–Rh(2)	102.3 (13)
Rh(2)–Br[a]	254.1 (6)	C(1)–Rh(1)–Rh(2)	48.1 (6)
Rh(1)–C(1)	199.5 (20)	C(1)–Rh(1)–C(1′)	91.1 (11)
Rh(2)–C(1′)	199.3 (20)	Rh(1)–C(1)–Rh(2)	83.7 (9)
Rh(2)–C(2)[a]	234.1 (48)	Rh(1)–C(1)–O(1)	137.7 (15)
Rh(1)–C(2)[a]	248.6 (54)	Rh(2)–C(1)–O(1)	138.6 (15)
Rh(1)–C(4)	228.8 (32)	C(5)–C(4)–C(5′)	104.6 (26)
Rh(1)–C(5)	229.5 (21)	C(4)–C(5)–C(6)	111.2 (20)
Rh(1)–C(6)	222.3 (16)	C(5)–C(6)–C(6′)	106.1 (12)
Rh(2)–C(7)	208.4 (38)	Br–Rh(2)–Rh(1)	100.3 (1)
Rh(2)–C(8)	217.8 (38)	C(1)–Rh(2)–Rh(1)	48.2 (6)
Rh(2)–C(9)	222.4 (25)	C(1)–Rh(2)–C(1′)	91.3 (12)
C(4)–C(5)	142.4 (29)	C(8)–C(7)–C(8′)	108.1 (47)
C(5)–C(6)	144.5 (31)	C(7)–C(8)–C(9)	108.1 (36)
C(6)–C(6′)	145.0 (41)	C(8)–C(9)–C(9′)	107.7 (23)
C(7)–C(8)	123.2 (45)		
C(8)–C(9)	130.2 (48)		
C(9)–C(9′)	120.4 (69)		

[a] The positions of C(2) and Br are statistically disordered.

If the μ-methylene-rhodium complex **1** is allowed to react with dry hydrogen halides such as HCl or HBr, brown, slightly air-sensitive, neutral compounds **3a** and **3b**, respectively, are quickly formed according to eq 1 in near quantitative yields.[11] In a typical



1

2a,b

3a,b

Ⓡⓗ = $(\eta^5$-$C_5H_5)Rh(CO)$
X = Cl (a), Br (b)

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(1) Transition Metal Methylene Complexes, 13. This work is being supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Degussa (Hanau), and the Hoechst Aktiengesellschaft. Part 12: W. A. Herrmann, J. Plank, and D. Riedel, *J. Organomet. Chem.*, **190**, C 47 (1980).

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