opportunity to achieve selectivity for metalloradical reactions. The large steric demands of (TTEPP)Rh prohibit formation of the two-carbon bridged complex, and the reaction proceeds to give a four-carbon alkene coupling product, **1**, which relieves the steric congestion. Alkene oligomerization stops at the dimer because further radical reaction requires homolysis of a relatively strong Rh–CH_2 bond. We are currently evaluating reactions for a wide variety of metalloradicals and alkenes in an effort to determine the generality and efficacy of this type of controlled radical process.

Acknowledgment. We are indebted to Dr. Alan E. Sherry for the synthesis of the (TTiPP)Rh–CH_3 and (TTEPP)Rh–CH_3 compounds used in this study to generate the metalloradicals. This work was supported by the National Science Foundation through Grant CHE-87-16691. Additionally, we thank the Science and Engineering Research Council, United Kingdom, for a studentship (to A.G.B.).

Sub-Picosecond $\Delta S = 2$ Intersystem Crossing in Low-Spin Ferrous Complexes

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In this communication, we present observations on two $\Delta S = 2$ intersystem crossing processes for Fe^{II} complexes, namely, the $^1MLCT \rightarrow {}^5T_2$ and $^5T_2 \rightarrow {}^1A_1$ conversions. Intersystem crossing where $\Delta S = 2$ has previously been examined for several Fe^{II} complexes.[1,2] For spin-crossover Fe^{II} complexes where the $^1A_1$ and $^5T_2$ "ligand-field" states are in close energy proximity ($\Delta E < 1000$ cm^{-1}), excited-state relaxation times have been found to be in the range of 40–120 ns and assigned as $^5T_2 \rightarrow {}^1A_1$. The excited-state characteristics of low-spin Fe^{II} polypyridyl complexes have also been examined in detail.[3] The $[Fe(bpy)_3]^{2+}$ complex is first photoexcited from the $^1A_1$ ground state to a singlet metal-to-ligand charge-transfer excited state, ^1MLCT, where picosecond time-resolved studies[3c,d] suggest that the ^1MLCT state is depopulated in ≤10 ps. By ground-state bleaching recovery experiments, a 0.81 ± 0.07 ns state of $[Fe(bpy)_3]^{2+}$ has been identified[3a,c] and tentatively assigned[3e] as a $^5T_2$ ligand-field state. In this work, results are presented which definitively establish the $^5T_2$ nature of the long-lived excited state in Fe^{II} spin-crossover complexes and that depopulation of the ^1MLCT state occurs in <1 ps.

Previously we reported[4] that $[Fe(tpen)](ClO_4)_2$, where tpen is the hexadentate ligand tetrakis(2-pyridylmethyl)-1,2-ethylenediamine, is a spin-crossover complex both in the solid state and in solution. Following $^1MLCT \leftarrow {}^1A_1$ excitation of a 3.36×10^{-4} M H_2O solution of $[Fe(tpen)](ClO_4)_2$ at 440 nm at 290 K, transient bleaching was monitored at $\lambda = 430$ nm to determine a relaxation time of 18 ± 2 ns ($k = (5.6 \pm 0.6) \times 10^7$ s^{-1}) (Figure 1).[5] The corresponding $^5T_2$ lifetime of 20 ± 2 ns is nearly a factor of 2 shorter than that reported for any other Fe^{II} spin-crossover complex. Probe wavelengths in the 266–440 nm range were employed to establish as definitively as possible the identity of the excited state as the $^5T_2$ ligand-field state.[6] A change from transient absorption to transient bleaching was found at ~300 nm (i.e., $\Delta OD_{\lambda=300nm} \approx 0$). This wavelength coincides with an isosbestic point determined from variable-temperature static electronic absorption spectra.[7] Furthermore, a single kinetic species was observed in the picosecond experiment for all delay times spanning the instrument-limited response time (~50 ps)

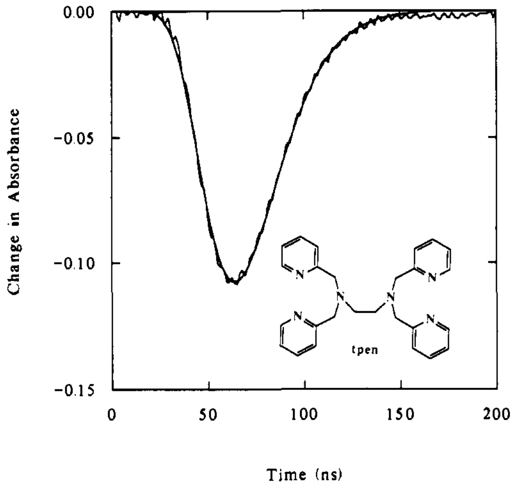

Figure 1. Transient bleaching observed at 430 nm for a 3.36×10^{-4} M aqueous solution of $[Fe(tpen)](ClO_4)_2$ following excitation at 440 nm. The fit represents a convolution of the instrument response function with a single exponential decay ($\tau = 18 \pm 2$ ns).

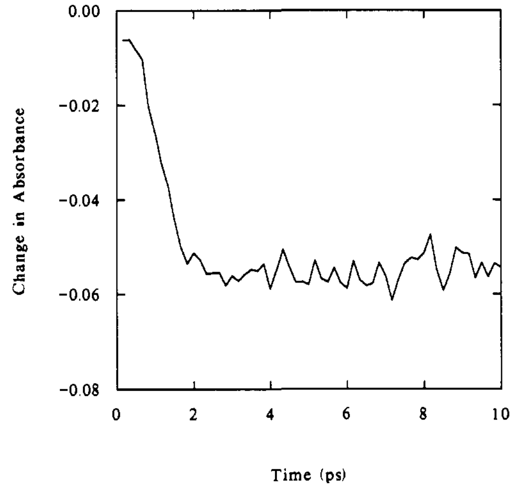

Figure 2. Plot of the change in absorbance [ΔOD] as a function of time in steps of 167 fs following $^1MLCT \leftarrow {}^1A_1$ excitation of a 1.52×10^{-3} M aqueous solution of $[Fe(tpen)](ClO_4)_2$ at 314 nm. The width of the excitation pulse was ~500 fs.

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0002-7863/92/1514-6919$03.00/0

out to several nanoseconds; the longest delay times overlap with the data shown in Figure 1. We believe this to be the strongest spectroscopic evidence to date for establishing the $^5T_2$ state as the "long-lived" excited state following photoperturbation of low-spin Fe^{II} complexes.

The analogous complex $[Fe(tptn)](ClO_4)_2$, where tptn is tetrakis(2-pyridylmethyl)-1,3-propylenediamine, has its $^5T_2$ excited state at a somewhat higher energy than the tpen complex. For this near-to-spin-crossover complex we find a $^5T_2 \rightarrow {}^1A_1$ relaxation time of 1.6 ± 0.1 ns. Careful redeterminations of the $^5T_2 \rightarrow {}^1A_1$ relaxation times of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in aqueous solution gave values at room temperature of 676 ± 30 and 687 ± 30 ps, respectively.

Definitive evidence for the sub-picosecond formation of the $^5T_2$ state following excitation to the ^{1}MLCT state was obtained. Figure 2 shows a plot of ΔOD versus time for a 1.52×10^{-3} M aqueous solution of $[Fe(tpen)](ClO_4)_2$ measured in increments of 167 fs following excitation at 314 nm with a ~500-fs laser pulse.[8] It can be seen that the kinetics are essentially time-independent on this time scale, again establishing the presence of a single kinetic species over the time interval from ≤700 fs to ca. 1 μs. Deconvolution of the data in Figure 2 reveals that the rise time of the transient bleach is indistinguishable from the instrumental response. This sets a lower limit on the rate of formation of the $^5T_2$ state of $\geq 1.5 \times 10^{12}$ s^{-1}. Identical results were obtained from studies on aqueous solutions of $[Fe(tptn)]^{2+}$, $[Fe(bpy)_3]^{2+}$, and $[Fe(phen)_3]^{2+}$.

The implication of these results for the mechanism of intersystem crossing can be understood as follows. The Fe–N stretching mode, which has been presumed to be involved in the dynamics of spin-state interconversion,[1,9] has a frequency of ~380 cm^{-1} for low-spin Fe^{II} and Fe^{III} and ~230 cm^{-1} for high-spin Fe^{II} when bound to a pyridyl-based ligand system.[10] These frequencies correspond to vibrational periods of ~88 and ~145 fs, respectively. Given the fact that excitation at 314 nm instills some 8000 cm^{-1} of excess vibrational energy into the ^{1}MLCT state of $[Fe(tpen)]^{2+}$ (λ_{max} = 414 nm), we conclude that the conventional picture[1-3] of vibrational cooling followed by internal conversion and intersystem crossing cannot be accurate in view of the rapid formation of the $^5T_2$ state. Rather, we suggest that intersystem crossing in low-spin Fe^{II} complexes proceeds via direct ^{1}MLCT → $^5T_2$ conversion at or near the configuration of the Franck–Condon state following photoexcitation.[11] There is simply insufficient time for the system to relax in the charge-transfer state, undergo internal conversion to lower lying singlet ligand-field states, and then repeat the process through the $S = 1$ manifold to reach the $^5T_2$ state in ≤700 fs. Furthermore, the system must rapidly relax down the $^5T_2$ potential surface, spending appreciable time only in the lower energy vibrational levels, in order to achieve thermalization within the observed ~2 ps. An experimental probe for this mechanism would require excitation with a sufficiently short laser pulse at variable wavelengths so that the rise time of the $^5T_2$ state could be measured. If conversion occurs from the Franck–Condon state, we would anticipate that the observed rise time will be relatively independent of λ_{pump}. In any event, it seems clear that the excited-state dynamics of these systems is quite distinct from that observed in organic systems with respect to the relative rates of vibrational cooling and internal conversion/intersystem crossing. We believe this to be a very general result for these types of transition-metal systems, and further details of our work will be reported elsewhere.[12]

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(8) Sub-picosecond experiments were performed using a colliding-pulse mode-locked ring dye laser amplified at 10 Hz through a four-stage amplifier using a Q-switched, frequency-doubled Nd:YAG laser as previously described (Jongeward, K. A.; Magde, D.; Taube, D. J.; Marsters, J. C.; Traylor, T. G.; Sharma, V. S. *J. Am. Chem. Soc.* **1988**, *110*, 380). The system has been modified by the introduction of two prisms to partially compensate for group velocity dispersion through the amplifier chain, and the detector is now an amplified diode array (Princeton Instruments). The duration of the frequency-doubled excitation pulse (λ = 314 nm) is ~500 fs FWHM.

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Mixed-Valence Lanthanum Titanium(III/IV) Oxosilicate $La_4Ti_9Si_4O_{30}$. A Novel Perrierite-Related Compound, $La_4Ti(Si_2O_7)_2(TiO_2)_{4m}$ (m = 2), with a Quasi-Two-Dimensional Rutile-Based Structure

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A novel oxo compound[1] with a quasi-two-dimensional (2D) structure is reported for the first time in the reduced first row early transition metal containing systems. The structural composition, $La_4Ti_9Si_4O_{30}$, reveals that this phase is a mixed-valence lanthanum titanium(III/IV) oxosilicate. The title compound may offer an opportunity for experimental and theoretical studies of the behavior of delocalized electrons in a confined lattice because of its quasi-two-dimensionality. Compounds with quasi-low-dimensional structures, such as the bronzes, show interesting anisotropic electrical and magnetic properties.[2] However, the weak interchain or interlayer electron interaction, due to a small separation gap, often complicates the interpretation of the observed physical phenomena. The newly discovered reduced oxosilicate compound may rectify this situation and shed light on the possibility of designing a new series of structural models for systematic studies of electrical conduction mechanisms.

The title compound possesses an interesting quasi-2D structure that is characterized by double layers of fused titanium(III/IV) oxide octahedral slabs. Until now, the synthesis of reduced titanium oxo compounds has led to the formation of mixed frameworks that consist of either isolated TiO_6 octahedra,[3] face-sharing Ti_2O_9 double-octahedra,[4] or pseudo-one-dimensional, edge-shared TiO_6 octahedral chains.[5] In contrast, a large col-

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(1) By the term oxo compound, we mean phases that have quasi-one-dimensional chain or two-dimensional layer transition metal oxide structures which are preserved and isolated by closed-shell, nonmagnetic groups, such as silicate and phosphate anions. Structurally, the discovery of new families of oxosilicates as well as oxophosphates is significant because the preserved metal–oxygen–metal (M–O–M) and metal–metal (M–M) linkages are common features observed in metallic transition metal oxide frameworks and are deemed important to the mechanistic studies of the transport properties which are induced by conduction electrons.

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