oriented bilayers allow the anisotropy in both relaxation rates, T_{1Z}^{-1} and T_{1Q}^{-1}, to be measured simultaneously, a well-established approach in liquid crystals[13a-c] but relatively unexploited in lipid bilayers. These T_{1Q} experiments as well as extensions of the approach described herein to other oriented systems, particularly those containing proteins, are the focus of our current investigations.

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Unsaturated Transition-Metal Complexes in Solution: Naked Cr(CO)5 in Cyclohexane Solution Observed by Picosecond IR Transient Absorption

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We have made the first identification of a "naked" square pyramid Cr(CO)5 ground singlet state molecule in cyclohexane solution, which has a vibrational frequency equivalent to the gas phase, and measured its reaction rate with cyclohexane. We tentatively have inferred the reaction rates for another precursor species, probably the trigonal bipyramid triplet state of Cr(CO)5, which reacts to add cyclohexane faster than the square pyramid structure. The method used picosecond UV photodissociation of Cr(CO)6 at 266 nm to generate Cr(CO)5 and probed the transient species via picosecond IR absorption.

Coordinatively unsaturated organometallic complexes are widely accepted[1-3] as reactive intermediates involved in homogeneous catalysis. Photodissociation of transition-metal complexes has been used to generate intermediates in matrices[4,5] and gases.[6-8] True naked intermediates have been characterized by IR absorption in gases, but prior matrix and solution work, including nanosecond resolved spectroscopy in hydrocarbon solution,[9] have always found saturated coordination. Recently, solution phase transient absorption in the visible was reported[10-13] which had very fast transient risetimes of less than 1 ps,[12] which was attributed to fast solvent attachment. Such a conclusion is not compatible with the transient infrared results presented here; although the transient
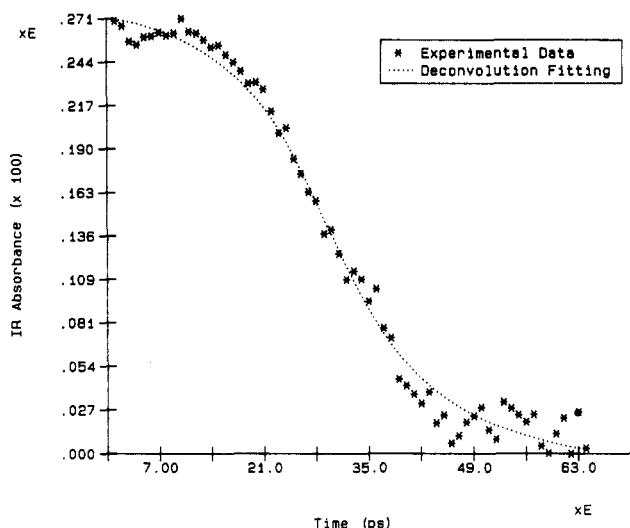
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Figure 1. Infrared transient absorption at 1980 cm^{-1} after 266-nm excitation of Cr(CO)6 at a concentration of 3 × 10^{-3} M in cyclohexane solution. The transient is assigned to "naked" square pyramid Cr(CO)5, and the fit by a kinetic model is shown as a dotted line. The absorbance maximum is consistent with the kinetic model and final product concentration. The 266-nm excitation used 5.4 × 10^{-2} J/cm^2, and the infrared probe used 1.0 × 10^{-4} J/cm^2.

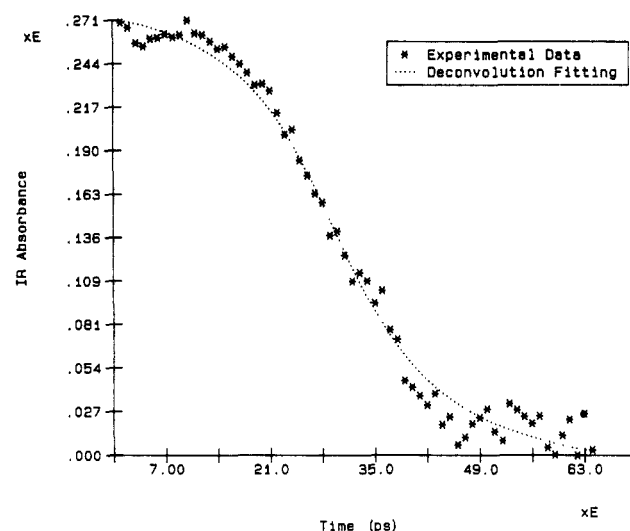**Figure 2.** Decrease in infrared absorption at 1986 cm^{-1} by Cr(CO)6 at 7.5 × 10^{-4} M. In this figure we plot the predicted decrease for an instantaneous decay rate and a Lorenztian excitation pulse of 20 ps FWHM.

shifts in electronic spectra may be a unique probe of continuous bond strength at the metal center, these experiments must separate the effects of multiple species identified in our work. We have used computer simulation to show that spectral overlap in the electronic spectra of *both* intermediates and products of photolysis can create transient absorption signals which are dominated by the fast creation of the initial species and do not necessarily reflect solvent reaction rates. In our experiments we obtained transient infrared absorption spectra, which are sensitive to CO coordination, with a laser developed in our laboratory[14] having a 20 ps pulse width (FWHM) and 5 cm^{-1} of wavelength resolution.

Figure 1 shows evidence for a "naked" Cr(CO)5 molecule in cyclohexane at 22 °C. The transient absorption at 1980 cm^{-1} corresponds to the E symmetry carbonyl vibrational mode of "naked" Cr(CO)5 which we have inferred by comparison with gas-phase assignment[7] of this frequency to a square pyramid structure of C_{4v} symmetry. Other vibrational modes (A symmetry)

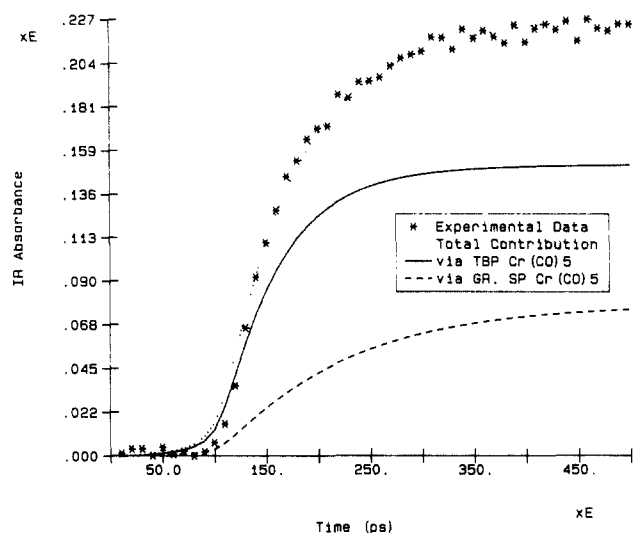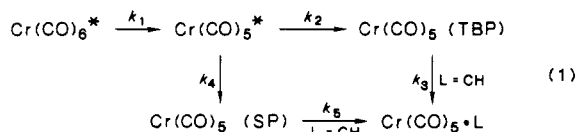(14) Spears, K. G.; Zhu, X.; Yang, X.; Wang, L. *Optics Commun.* **1988**, *66*, 167.

Figure 3. Increase in infrared absorbance at 1961 cm⁻¹ by Cr(CO)₅·cyclohexane. The calculated individual contributions of ground state square pyramid (SP) and trigonal bipyramid (TBP) geometries are shown separately.

of Cr(CO)₅ (SP) which are equal to the gas-phase frequencies[6,7] also have been observed in our experiment with the same time transient.

Figure 2 shows that the rate of Cr(CO)₆ disappearance in cyclohexane solution is at the resolution limit of the apparatus. This absorption at 1986 cm⁻¹ is similar to the gas-phase frequency, and the transient decay is significantly faster than the final product appearance rate.

Figure 3 shows the transient absorption at 1961 cm⁻¹ which is the reported frequency of Cr(CO)₅·(CH) (CH = cyclohexane) with E symmetry.[15] The risetime is faster than the decay rate for "naked" Cr(CO)₅, which suggests that another channel exists for formation of Cr(CO)₅·(CH).

We propose that reaction mechanism 1 is compatible with both polarized light photolysis[16] and a theoretical model of dissociation.[17] In this model the excited state of Cr(CO)₆ correlates with an excited state of Cr(CO)₅ which decays to triplet trigonal bipyramid (TBP) and singlet square pyramid species (SP).

$$Cr(CO)_6^* \xrightarrow{k_1} Cr(CO)_5^* \xrightarrow{k_2} Cr(CO)_5 \text{ (TBP)}$$

$$\downarrow k_4 \qquad\qquad k_3 \downarrow L = CH \qquad (1)$$

$$Cr(CO)_5 \text{ (SP)} \xrightarrow[L=CH]{k_5} Cr(CO)_5 \cdot L$$

The curves in Figures 1-3 and another transient at 1920 cm⁻¹ (not shown) were fit with a self-consistent set of rate constants by a response function deconvolution fitting procedure. We report the fitting results as first order or pseudo-first-order rate constants (s⁻¹) with standard deviation estimates of about 30%. The rate constants for k_1, k_2, k_3, k_4, and k_5 are $\geq 4.2 \times 10^{11}$, 2.5×10^{11}, 2.0×10^{10}, 1.3×10^{11}, and 8.6×10^9, respectively.

In addition, we tentatively have assigned a transient signal at a frequency of 1920 cm⁻¹ for triplet state Cr(CO)₅ (TBP) that is compatible with the proposed kinetics. The 2.3 times faster reactivity of triplet state Cr(CO)₅ (TBP) than (SP) is interesting and suggests that the geometry or electronic configuration of unsaturated coordination is important in reactivity.

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Stereoselective Synthesis of (±)-Indolizidines 167B, 205A, and 207A. Enantioselective Synthesis of (−)-Indolizidine 209B

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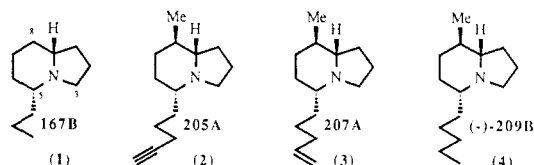
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A large number of alkaloids have been isolated in minute quantity from the skin extracts of neotropical poison-dart frogs (family Dendrobatidae).[1] The scarcity of natural material, coupled with the intriguing biological activity of those compounds which have been studied,[1] makes these alkaloids ideal targets for total synthesis.[2] The 5,8-disubstituted indolizidines, for which no syntheses have been reported, have a structural similarity to the cardiotonic pumiliotoxins.[3] In this communication we now report the synthesis of indolizidines 167B (**1**), 205A (**2**), and 207A (**3**) by a general route involving the intramolecular dipolar cy-

cloaddition of the (Z)-N-alkenylnitrone **8** to give the isoxazolidine **9** as the only isolated product (Scheme I).[4] The unique aspect of this approach is the rapid construction of the indolizidine skeleton from relatively simple molecules with a high degree of stereocontrol at C-5, C-8, and C-8a. Thus the homochiral hydroxylamine precursor **7d** can be used to prepare the enantiomerically pure indolizidine (−)-209B (**4**). A notable use of the intramolecular nitrone approach to all-cis 2,3,6-trisubstituted piperidines had previously been reported by LeBel and Balasu-

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