

oriented bilayers allow the anisotropy in both relaxation rates, T_{12}^{-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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(13) (a) Vold, R. L.; Dickerson, W. H.; Vold, R. R. *J. Magn. Reson.* **1981**, *43*, 213-223. (b) Wong, T. C.; Jeffrey, K. R. *Mol. Phys.* **1982**, *46*, 1-12. (c) Dong, R. Y. *J. Magn. Reson.* **1986**, *66*, 422-423.

Unsaturated Transition-Metal Complexes in Solution: Naked $\text{Cr}(\text{CO})_5$ in Cyclohexane Solution Observed by Picosecond IR Transient Absorption

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We have made the first identification of a "naked" square pyramid $\text{Cr}(\text{CO})_5$ 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 $\text{Cr}(\text{CO})_5$, which reacts to add cyclohexane faster than the square pyramid structure. The method used picosecond UV photodissociation of $\text{Cr}(\text{CO})_6$ at 266 nm to generate $\text{Cr}(\text{CO})_5$ and probed the transient species via picosecond IR absorption.

Coordinatively unsaturated organometallic complexes are widely accepted¹⁻³ 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 reported¹⁰⁻¹³ 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

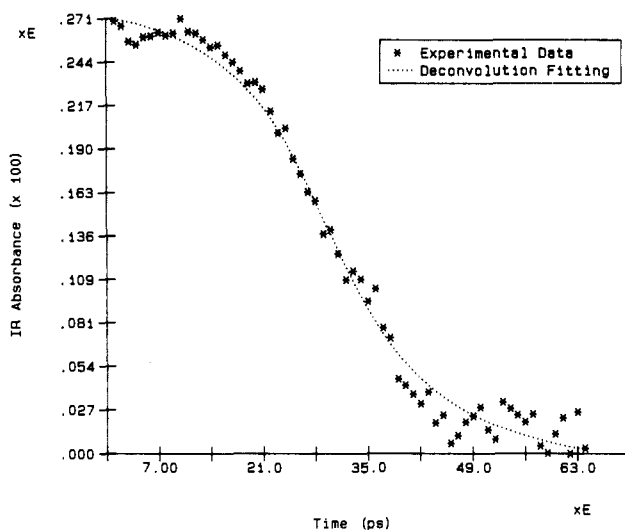


Figure 1. Infrared transient absorption at 1980 cm^{-1} after 266-nm excitation of $\text{Cr}(\text{CO})_6$ at a concentration of $3 \times 10^{-3}\text{ M}$ in cyclohexane solution. The transient is assigned to "naked" square pyramid $\text{Cr}(\text{CO})_5$, and the fit by a kinetic model is shown as a dotted line. The absorbance maximum is consistent with the kinetic model and final product concentration. The 266-nm excitation used $5.4 \times 10^{-2}\text{ J/cm}^2$, and the infrared probe used $1.0 \times 10^{-4}\text{ J/cm}^2$.

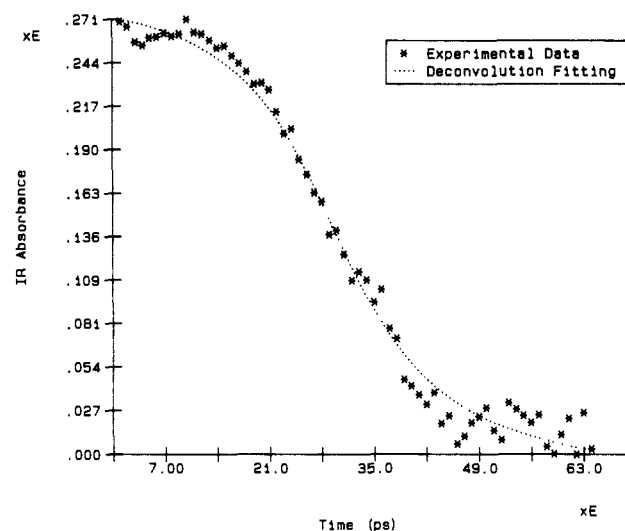


Figure 2. Decrease in infrared absorption at 1986 cm^{-1} by $\text{Cr}(\text{CO})_5$ at $7.5 \times 10^{-4}\text{ M}$. In this figure we plot the predicted decrease for an instantaneous decay rate and a Lorentzian excitation pulse of 20 ps FWHM.

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 laboratory¹⁴ having a 20 ps pulse width (FWHM) and 5 cm^{-1} of wavelength resolution.

Figure 1 shows evidence for a "naked" $\text{Cr}(\text{CO})_5$ molecule in cyclohexane at $22\text{ }^\circ\text{C}$. The transient absorption at 1980 cm^{-1} corresponds to the E symmetry carbonyl vibrational mode of "naked" $\text{Cr}(\text{CO})_5$ which we have inferred by comparison with gas-phase assignment⁷ of this frequency to a square pyramid structure of C_{4v} symmetry. Other vibrational modes (A symmetry)

(1) Taqui Khan, M.; Martell, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic Press: New York, 1974.

(2) Parshall, G. W. *Homogeneous Catalysis: The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes*; John Wiley & Sons Inc.: New York, 1980.

(3) *Fundamental Research in Homogeneous Catalysis*; Proceedings of the Fourth International Symposium on Homogeneous Catalysis, Leningrad, USSR, Sept. 24-28, 1984, Shilov, A. E., Ed.; Gordon and Breach Science Publishers: 1986.

(4) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1.

(5) Turner, J. J.; Poliakov, M.; Simpson, M. B. *J. Mol. Struct.* **1984**, *113*, 359.

(6) Weitz, E. *J. Phys. Chem.* **1987**, *91*, 3945.

(7) Seder, T. A.; Church, S. P.; Weitz, E. *J. Am. Chem. Soc.* **1986**, *108*, 4721.

(8) Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1986**, *108*, 1686.

(9) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakov, M. *Organometallics* **1987**, *6*, 2600.

(10) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53.

(11) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751.

(12) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538.

(13) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941.

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

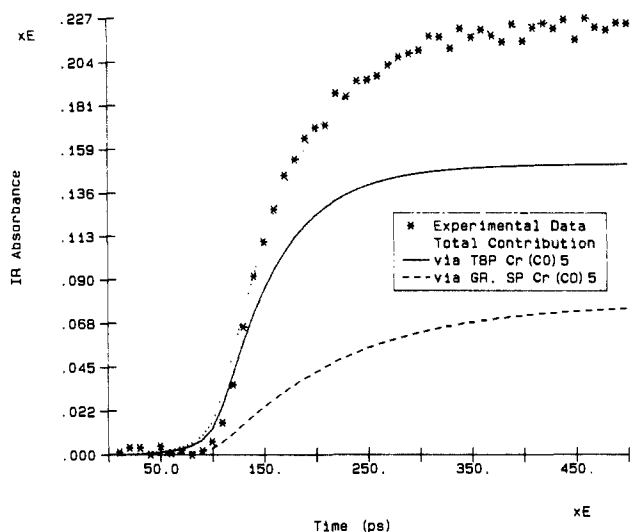


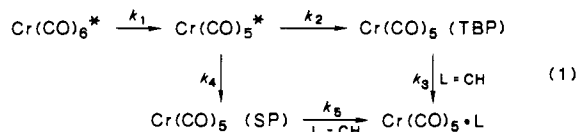
Figure 3. Increase in infrared absorbance at 1961 cm^{-1} by $\text{Cr}(\text{CO})_5$ cyclohexane. The calculated individual contributions of ground state square pyramid (SP) and trigonal bipyramid (TBP) geometries are shown separately.

of $\text{Cr}(\text{CO})_5$ (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 $\text{Cr}(\text{CO})_6$ 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 $\text{Cr}(\text{CO})_5(\text{CH})$ (CH = cyclohexane) with E symmetry.¹⁵ The risetime is faster than the decay rate for "naked" $\text{Cr}(\text{CO})_5$, which suggests that another channel exists for formation of $\text{Cr}(\text{CO})_5(\text{CH})$.

We propose that reaction mechanism 1 is compatible with both polarized light photolysis¹⁶ and a theoretical model of dissociation.¹⁷ In this model the excited state of $\text{Cr}(\text{CO})_6$ correlates with an excited state of $\text{Cr}(\text{CO})_5$ which decays to triplet trigonal bipyramid (TBP) and singlet square pyramid species (SP).



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 $\text{Cr}(\text{CO})_5$ (TBP) that is compatible with the proposed kinetics. The 2.3 times faster reactivity of triplet state $\text{Cr}(\text{CO})_5$ (TBP) than (SP) is interesting and suggests that the geometry or electronic configuration of unsaturated coordination is important in reactivity.

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(15) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1985**, *24*, 418.

(16) Burdett, J. K.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1978**, *17*, 147.

(17) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2411.

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

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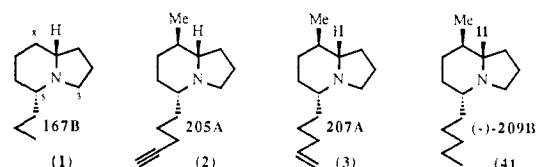
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A large number of alkaloids have been isolated in minute quantity from the skin extracts of neotropical poison-dart frogs (family Dendrobatidae).¹ The scarcity of natural material, coupled with the intriguing biological activity of those compounds 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 cardiotoxic 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*-alkenylnitron 8 to give the isoxazolindine 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 nitron approach to all-cis 2,3,6-trisubstituted piperidines had previously been reported by LeBel and Balasu-

(1) (a) Daly, J. W.; Spande, T. F. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; Wiley: New York, 1986; Vol. 4, Chapter 1, pp 1-274. (b) Daly, J. W.; Myers, C. W.; Whittaker, N. *Toxicol.* **1987**, *25*, 1023-1095. (c) Tokuyama, T.; Nishimori, N.; Shimada, A.; Edwards, M. W.; Daly, J. W. *Tetrahedron* **1987**, *43*, 643-652.

(2) Indolizidine 223AB has been synthesized by more than one strategy, and its structure and absolute stereochemistry have been defined as (3*R*,5*R*,8*aR*)-3-butyl-5-propylindolizidine: (a) MacDonald, T. L. *J. Org. Chem.* **1980**, *45*, 193-194. (b) Hart, D. J.; Tsai, Y.-M. *J. Org. Chem.* **1982**, *47*, 4403-4409. (c) Broka, C. A.; Eng, K. K. *J. Org. Chem.* **1986**, *51*, 5043-5045. (d) Iida, H.; Watanabe, Y.; Kibayashi, C. *J. Am. Chem. Soc.* **1985**, *107*, 5534-5535. (e) Royer, J.; Husson, H.-P. *Tetrahedron Lett.* **1985**, *26*, 1515-1518.

(3) (a) Overman, L. E.; Bell, K. L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *106*, 4192-4201. (b) Overman, L. E.; Goldstein, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 5360-5361. (c) Overman, L. E.; Lin, N.-H. *J. Org. Chem.* **1985**, *50*, 3669-3670. (d) Overman, L. E.; Sharp, M. J. *Tetrahedron Lett.* **1988**, *29*, 901-904. (e) Daly, J. W.; McNeal, E. T.; Overman, L. E.; Ellison, D. H. *J. Med. Chem.* **1985**, *28*, 482-486. (f) Daly, J. W.; McNeal, E. M.; Gusovsky, F.; Ito, F.; Overman, L. E. *J. Med. Chem.* **1988**, *31*, 477-480.

(4) (a) Tufariello, J. J. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 2, Chapter 12, pp 277-406. Confalone, P. N.; Huie, E. M. *Org. React.* **1988**, *36*, 1-173. (b) For related intramolecular nitron cycloadditions, see: Oppolzer, W.; Siles, S.; Snowden, R. L.; Bakker, B. H.; Petrzilka, M. *Tetrahedron Lett.* **1979**, *20*, 4391-4394. Oppolzer, W.; Siles, S.; Snowden, R. L.; Bakker, B. H.; Petrzilka, M. *Tetrahedron* **1985**, *41*, 3497-3509. Holmes, A. B.; Swithenbank, C.; Williams, S. F. *J. Chem. Soc., Chem. Commun.* **1986**, 265-266.