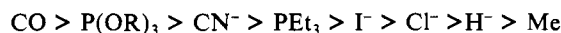


and 2.665 Å) and the $^2J(\text{Pt}_R, \text{Pt}_T)$ values decrease dramatically with increasing Pt-Pt bond length (620 and 1232 Hz), the size of $^2J(\text{Pt}_R, \text{Pt}_T)_{\text{trans}}$ appears to be a good indicator of Pt-Pt bond strength. This correlation of $^2J(\text{Pt}, \text{P})_{\text{trans}}$ with Pt-Pt bond distances in $[\text{L}'-\text{PR}_3]^{n+}$ suggests that the Pt-Pt bond is weakened with increasing trans influence of L'. The Pt-Pt bond distances of other $[\text{L}-\text{L}']^{n+}$ complexes (L \neq PR₃) for which crystal structures have been solved also tend to support this correlation (see Table V) but suggest that other factors may also affect the Pt-Pt bond length (trans influence: CO \approx Cl⁻).

A good correlation of Pt-Pt bond distance with not only $^2J(\text{Pt}, \text{P})_{\text{trans}}$ but also $^2J(\text{Pt}, \text{P})_{\text{cis}}$ is observed. It was proposed that the size of $^2J(\text{Pt}, \text{P})_{\text{cis}}$ in $[\text{L}-\text{L}']^{n+}$ should be a function of Pt-Pt bond strength.²³ Since then, the crystal structures of $[\text{CO}-\text{CO}]^{2+}$,²¹ $[\text{Cl}-\text{PPh}_3]^+$ ⁷ and $[\text{H}-\text{dppm}]^+$ ¹⁹ (see Table V) have been solved. The $^2J(\text{Pt}, \text{P})_{\text{cis}}$ value for $[\text{CO}-\text{CO}]^{2+}$ fits well in the trend of decreasing $^2J(\text{Pt}, \text{P})_{\text{cis}}$ with increasing Pt-Pt bond length as do the values for $[\text{Cl}-\text{PPh}_3]^+$ if one assumes the coupling constants have negative signs.

$^2J(\text{Pt}, \text{P})_{\text{cis}}$ and $^2J(\text{Pt}, \text{P})_{\text{trans}}$ values tend to complement each other as a measure of Pt-Pt bond strength. Although the cis coupling constants should be observed in all Pt(I) dimers of this type, problems are often encountered because it is difficult to determine the sign of these relatively small coupling constants and because the cis satellites are not always well separated from the central resonance. These problems are magnified in highly coupled systems such as complexes containing terminally bound phosphines (e.g., in $[\text{H}-\text{dppm}]^+$), where correlation of $^2J(\text{Pt}, \text{P})_{\text{trans}}$ with Pt-Pt bond length appears to be more useful because of its larger magnitude and greater sensitivity. Therefore, although neither type of coupling constant is observed in all $[\text{L}-\text{L}']^{n+}$ complexes due to the nature of L and L' (e.g., $^2J(\text{Pt}, \text{P})_{\text{trans}}$) or experimental limitations (e.g., $^2J(\text{Pt}, \text{P})_{\text{cis}}$), at least one of these constants is observed for practically all $[\text{L}-\text{L}']$ complexes.

Cis Influence in Pt(I) Dimers. A general conclusion from efforts²⁰ to find a correlation between the strength of a metal-ligand bond and the nature of the cis ligands is that three factors are of comparable importance: σ effects, π effects, and steric factors. (This is in contrast with the trans influence, where the first appears to dominate.) When indirect (i.e., two- or three-bond) coupling constants are used as a measure of the cis influence, cis and trans influences appear to be inversely correlated. Direct (i.e., one-bond) coupling constants are, however, markedly reduced by π bonding to a cis ligand.¹⁴ A cis-influence series, derived¹⁴ from values of $^1J(\text{Pt}, \text{P})$ for Pt(II) complexes, shows that those ligands with large trans and cis influences are those that are π acceptors:



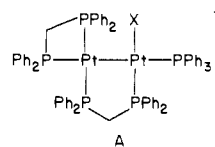
The series of closely related Pt(I) dimers found in Table II follow this trend. The values of $^1J(\text{Pt}_R, \text{Pt}_T)$ in $[\text{Ph}_3\text{P}-\text{L}]^{n+}$ according to cis influence are as follows: L = PPh₃ (2800 Hz) > I (2843) > Cl (2894) > H (3532) \approx Me (3510).

The carbonyl ligand, a strong π acceptor but only a moderate σ donor, has the highest cis influence but an intermediate trans influence in accord with these generalizations. This is illustrated by the Pt-P bond distances and $^1J(\text{Pt}, \text{P})$ coupling constants in Table IV for the series $[\text{CO}-\text{CO}]^{2+}$ ($d = 2.320$ Å, $J = 2390$ Hz), $[\text{Cl}-\text{CO}]^+$ (2.295 and 2.306, 2591 and 2711), $[\text{Cl}-\text{PPh}_3]^+$ (2.277, 2872), and $[\text{Cl}-\text{Cl}]$ (2.268, 2936). It is evident that the Pt-P bonds cis to CO are weakened considerably by its π -accepting ability. Even a cis-located CO three bonds away from the phosphorus in question can compete effectively with it for potential π -electron density. The three-bond cis influence through the Pt-Pt bond parallels that for the normal two-bond effect, CO > PPh₃ > Cl in $[\text{L}-\text{Cl}]^{n+}$.

A dpdm-bridged Pt-Pt bond has a cis influence, as well as a trans influence, very similar to that of a hydride. That is illustrated by data in Table IV for the series of *trans*- $[\text{Pt}(\text{PR}_3)_2(\text{L})\text{Cl}]$ complexes with L = PPh₃ ($d = 2.354$ Å, $^1J_{\text{Pt}, \text{P}} = 2233$ Hz), Cl (2.314, 2400), L'-Pt (2.280, 2838; average of three compounds),

and H (2.268, 2723). The low cis influences of hydride and of Pt(I) are due in part to their inability to accept π -electron density from the adjacent Pt center. In fact, the shortest Pt-P bond and the largest coupling constant occur when both Pt(I) and hydride are cis to Pt-P bonds.

Summary. Because of the wide range of values possible for platinum-phosphorus coupling constants, they have proven in the past¹⁷ and continue to be sensitive indicators of not only the structure and stereochemistry of platinum phosphine complexes (e.g., in the structural determination of A)²³ but also the electronic



and steric influences of the ligands in such complexes.

These results and correlation suggest the following: (1) the Pt-Pt bond in $[\text{L}-\text{L}']^{n+}$ has trans and cis influence similar to those of a hydride; (2) because of the sensitivity of $^1J(\text{Pt}, \text{P})$ to Pt-P bond length, a value for the Pt-PPh₃ bond length in $[\text{PPh}_3-\text{PPh}_3]^{2+}$ can be estimated; (3) both $^2J(\text{Pt}, \text{P})_{\text{cis}}$ and $^2J(\text{Pt}, \text{P})_{\text{trans}}$ are sensitive to the Pt-Pt bond strength in complexes containing the $[\text{Pt}_2(\mu\text{-dpdm})_2]^{2+}$ core; (4) ligands with a large trans influence appear to weaken the Pt-P bond when they are bound trans to it; (5) the cis influence of ligands in Pt(I) dimers parallels that in Pt(II) monomers and can be transmitted through three bonds via the Pt-Pt bond in the dimers; (6) the Pt-Pt bond exhibits a very low cis influence.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82.

Registry No. ¹⁹⁵Pt, 14191-88-9.

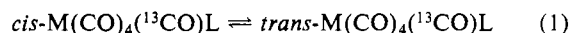
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

Intramolecular Ligand Rearrangements in Anionic Group 6 Metal Pentacarbonyl Hydride Derivatives

Donald J. Darensbourg,* Marcetta Y. Darensbourg,* Robert L. Gray, Debra Simmons, and Larry W. Arndt

Received July 11, 1985

Several research groups have reported ligand rearrangements in six-coordinate, low-valent metal carbonyl derivatives that occur without loss of bound ligands, i.e., via intramolecular pathways.¹ Cis \rightleftharpoons trans isomerization processes involving $\text{M}(\text{CO})_4\text{LL}'$ complexes comprise the bulk of the instances investigated. In general, these processes are thermodynamically driven due to the electronic and/or steric site preferences of the noncarbonyl ligands L and L'. Earlier we examined *intramolecular* ligand rearrangements in phosphine and phosphite derivatives of Cr and W pentacarbonyl (eq 1) that have been stereoselectively labeled with ¹³C-substituted



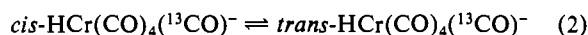
carbon monoxide, where there is no thermodynamic driving force for isomerization.^{2,3} Similarly, Dombek and Angelici have studied

- (1) (a) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407. (b) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508 and references therein. (c) Fischer, H.; Fischer, E. O.; Werner, H. *J. Organomet. Chem.* **1974**, *73*, 331. (d) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680. (e) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14. (f) Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307. (g) Fischer, H.; Motsch, A.; Markel, R.; Ackermann, K. *Organometallics* **1985**, *4*, 726. (h) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.

(23) Blau, R. J.; Espenson, J. H., submitted for publication.

the analogous process starting with *trans*-W(CO)₄(¹³CO)CS.⁴ The fact that specifically ¹³CO-labeled derivatives are isolable emphasizes the slow reaction rates experienced for these type processes; kinetic parameters were determined by conventional means.

Recently, we reported that the CO ligands in HCr(CO)₅⁻ undergo rapid reversible intramolecular site exchange (eq 2) when compared to their chemical shift difference (166 Hz at 50.3 MHz).^{5,6} The present contribution describes the kinetic parameters,



obtained from DNMR spectroscopy, determined for ligand rearrangement in this anionic hydride complex. Comparisons of these data with those obtained for Cr(CO)₅PR₃ derivatives and the HW(CO)₅⁻ analogue are provided.

Experimental Section

General Procedure. All operations were carried out under nitrogen with standard Schlenk techniques or in an argon atmosphere glovebox. Solvents were dried and degassed as described below. Infrared spectra were recorded on a Perkin-Elmer 283B or an IBM FTIR/85 spectrophotometer using 0.1-mm CaF₂ cells. ¹³C NMR spectra were measured on a XL200 Varian spectrometer and referenced against benzene-*d*₆.

Materials. Tetrahydrofuran (THF) and hexane were distilled under nitrogen from sodium/benzophenone. Diethyl ether was freshly distilled from lithium aluminum hydride. Nitrogen was predried over molecular sieves prior to use. ¹³CO was purchased from Prochem, BOC Ltd., London. [PPN][W(CO)₅Cl] was prepared according to the literature.⁷ All other reagents were purchased from standard vendors as reagent grade and used without further purification.

Preparation of W(¹³CO)₆. Into a 100-mL Schlenk flask was introduced 4.00 g (4.46 mmol) of [PPN][W(CO)₅Cl]. A 50-mL portion of the THF was added to the flask via syringe. The system was evacuated and back-filled with ¹³CO. The solution was stirred for 4 days. At 1 day intervals the system was evacuated and refilled with ¹³CO. The solvent was removed under vacuum to yield ¹³C-enriched W(CO)₆Cl⁻. The yellow solid was dissolved in 50 mL of MeOH and stirred for 2 additional days under a ¹³CO atmosphere. The mother liquor was removed via cannula and the white solid washed twice with MeOH. The dried solid was sublimed at 50 °C and 10⁻² torr to yield a white crystalline solid, which weighed 1.10 g (3.08 mmol) for a 69% yield.

Preparation of W(¹³CO)₅NMe₃. A 1.00-g (2.80-mmol) sample of W(¹³CO)₆ was introduced into a 150-mL water-jacket-cooled photovessel. A 90-mL portion of the THF was added to the reactor via cannula. The mixture was photolyzed for 1 h. Trimethylamine gas was bubbled through the freshly prepared W(¹³CO)₅THF solution for 5 min. The solution was then transferred into a 100-mL Schlenk flask and the solvent removed under vacuum. The yellow crystalline product was sublimed at 50 °C and 10⁻² torr for 2 h to rid the product of excess W(¹³CO)₆. The bright yellow solid weighed 1.02 g (2.63 mmol), a 94% yield.

Preparation of Cr(CO)₄(¹³CO)pip. To a 150-mL water-jacket-cooled photovessel was introduced 1.00 g (4.55 mmol) of Cr(CO)₆. A 90-mL portion of the THF was added via cannula under nitrogen pressure. The mixture was photolyzed (450-W Hg-vapor lamp) for 1 h or until >90% conversion to Cr(CO)₅THF was produced based on the infrared spectrum: $\nu(\text{CO}) = 2074 \text{ w}, 1938 \text{ s}, 1894 \text{ m cm}^{-1}$. A steady stream of nitrogen bubbling through the solution during photolysis assists in removal of CO. The photovessel was then evacuated and back-filled with ¹³CO. The solution was shaken and allowed to react for 1 h, during which time the yellow color faded. The freshly prepared Cr(CO)₅(¹³CO) was then photolyzed again according to the procedure described above. After Cr(CO)₄(¹³CO)THF was generated, the mixture was transferred into a 100-mL Schlenk flask. A 0.450-mL (4.55-mmol) portion of piperidine was added to the flask via syringe. The solution was stirred for 30 min and the solvent removed under vacuum. The title complex was dissolved in hexane and transferred to another 100-mL Schlenk flask. After removal of the solvent under vacuum, the solid was placed in a sublimator

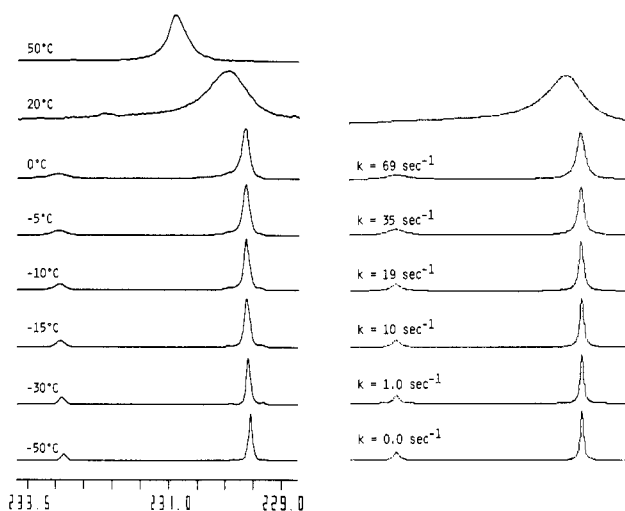
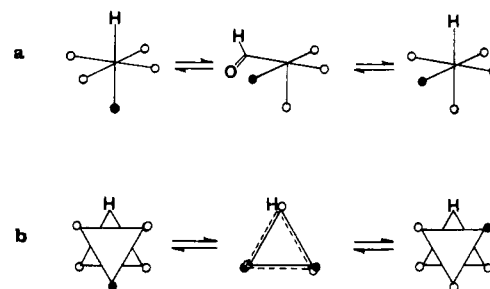


Figure 1. Observed and computed ¹³C DNMR spectra of [PPN][HCr(CO)₅] in tetrahydrofuran.

Scheme I



to sublime out excess Cr(CO)₆. The yellow crystalline solid weighed 1.10 g (3.98 mmol), an 88% yield.

Preparation of [PPN][HCr(CO)₄(¹³CO)]. The title compound was prepared as described in an earlier report.¹⁰ To a 100-mL Schlenk flask was introduced 1.10 g (3.98 mmol) of Cr(CO)₄(¹³CO)pip generated as above and 2.30 g (3.98 mmol) of PPNBH₄. The flask was evacuated and flamed to remove moisture and back-filled with nitrogen. A 80-mL portion of THF was added to the flask via syringe. The solution was stirred for 45 min and the solvent concentrated to 20 mL. A 50-mL portion of Et₂O was added to precipitate any unreacted PPNBH₄ and the solution transferred via cannula into a Schlenk filter stick containing Celite. The solution was concentrated to 10 mL, and hexane was slowly added while the mixture was agitated to precipitate a fine yellow powder. The mother liquor was removed and the yellow solid washed twice with hexane. The dried solid weighed 2.10 g (2.87 × mmol), a 72% yield.

Preparation of [PPN][HW(¹³CO)₅].¹⁰ The title compound was prepared in the same manner as HCr(CO)₄(¹³CO)⁻ described above.

Nuclear Magnetic Resonance Measurements. ¹³C NMR measurements were carried out in sealed 10-mm tubes in tetrahydrofuran-*d*₈ solvent. Spectra were recorded on a Varian XL-200 spectrometer at temperature intervals from -50 to +50 °C.

Results and Discussion

An examination of the variable-temperature ¹³C NMR spectra of [PPN][HCr(CO)₅] in tetrahydrofuran depicted in Figure 1 clearly shows a broadening of resonances representing the two carbonyl sites.¹¹ At the slow-exchange limit the *trans* and *cis* carbonyl resonances appear at 232.9 and 229.6 ppm, respectively. Coalescence into one symmetrical peak at 230.9 ppm occurred at temperatures greater than 50 °C. Spectra measured at six different temperatures between -50 and +20 °C were simulated by the density matrix procedure of Kaplan¹² and Alexander¹³ for the exchange process. The best fit for the permutation of axial

(2) (a) Darensbourg, D. J.; Baldwin, B. J. *J. Am. Chem. Soc.* **1979**, *101*, 6447. (b) Darensbourg, D. J.; Kudasroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488.

(3) Darensbourg, D. J.; Gray, R. L. *Inorg. Chem.* **1984**, *23*, 2993.

(4) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4110.

(5) Darensbourg, M. Y.; Slater, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

(6) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.

(7) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068.

(8) Maher, J. N.; Beatty, R. P.; Cooper, N. J. *Organometallics*, **1982**, *1*, 215.

(9) Darensbourg, D. J.; Murphy, M. A. *Inorg. Chem.* **1978**, *17*, 884.

(10) Slater, S.; Darensbourg, M. Y. *Inorg. Synth.* **1983**, 181.

(11) A mono-¹³C-enriched sample was employed in these studies in order to avoid line shape complications due to ¹³C-¹³C coupling.

(12) Kaplan, J. I. *J. Chem. Phys.* **1958**, *28*, 278; **1958**, *29*, 462.

(13) Alexander, S. J. *J. Chem. Phys.* **1962**, *37*, 967, 974; **1963**, *38*, 1787; **1964**, *40*, 2741.

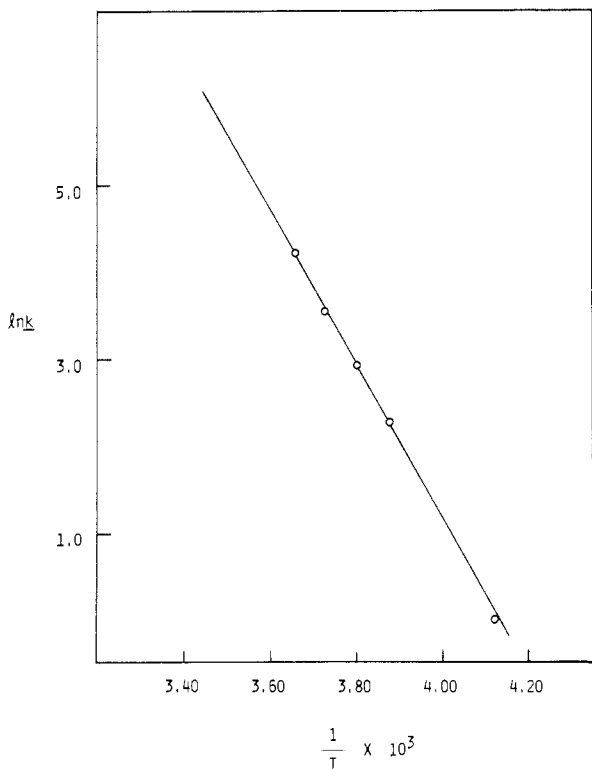


Figure 2. Arrhenius plot for the intramolecular CO ligand exchange process in [PPN][HCr(CO)₅] in tetrahydrofuran.

and equatorial CO groups is shown in Figure 1. The values used for the relative site populations were varied slightly from the ideal to offset the observed differential nuclear Overhauser effects.¹⁴

An Arrhenius plot (Figure 2) yielded an activation energy of 18.5 ± 0.5 kcal/mol with $\Delta H^\ddagger = 18.0 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = 14.0 \pm 2$ eu, and $\Delta G^\ddagger_{298} = 13.8 \pm 0.5$ kcal/mol. Error limits represent 90% confidence limit. Two specific mechanisms to explain the solution dynamic behavior of the HCr(CO)₅⁻ anion can be proposed: Scheme Ia, a trigonal-twist mechanism, with or without substantial metal-ligand bond breaking in the transition state;^{3,15} Scheme Ib, a hydride migration mechanism.¹⁶

A twist mechanism that provides a pathway for intramolecular axial-equatorial CO exchange is favored. This mechanism would be consistent with that proposed for the related M(CO)₅PR₃ (M = Cr, W) derivatives.³ The more facile exchange process observed in HCr(CO)₅⁻ as compared with Cr(CO)₅PR₃ species most likely reflects the large angle between axial and equatorial MCO vectors observed both in the solid state (95.4°) and in solution (94.9°) for the hydride complex.¹⁷ The alternative, the hydride migration mechanism, is less favored from the viewpoint of chemical precedence (supported by thermodynamic considerations).¹⁸ Furthermore, the rate of methyl migration in CH₃Cr(CO)₅⁻ is a relatively slow process.¹⁹ Since hydride migration would be anticipated to be even slower,²⁰ this latter process (Scheme Ib)

can be ruled out as a pathway for rapid axial-equatorial CO exchange. It should as well be reiterated here that intermolecular CO exchange does not readily occur under the conditions of this rearrangement process.

Axial-equatorial carbon monoxide exchange in the HW(CO)₅⁻ anion is a much less rapid process than that reported upon herein for the HCr(CO)₅⁻ species. That is, only a slight broadening of the two CO resonances (211.0 (CO_{axial}), 207.2 ppm (CO_{equatorial})) was noted at +50 °C in tetrahydrofuran. Intramolecular CO scrambling in the W(CO)₅PR₃ derivatives are similarly less facile than in the chromium analogues.³

Acknowledgment. Support for this work from the National Science Foundation, Grant Nos. CHE83-08281 (to D.J.D.) and CHE83-04162 (to M.Y.D.), is greatly appreciated.

Registry No. [PPN][HCr(CO)₅(¹³CO)], 100243-50-3; W(¹³CO)₆, 25941-11-1; W(¹³CO)₅NMe₃, 100228-87-3; Cr(CO)₄(¹³CO)pip, 100348-10-5; [PPN][HW(¹³CO)₅], 100243-52-5.

(20) For example, the second-order rate constant for ¹³CO incorporation in CH₃Mn(CO)₅ (a process where methyl migration is indicated) is $9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, whereas the analogous process involving HMn(CO)₅, where H migration is proposed, has a rate constant of $1.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at ambient temperature.¹⁶

Contribution from the Department of Chemistry, Clemson University, Clemson, South Carolina 29631

The Next Generation of (Polyazine)ruthenium(II) Complexes

Karen J. Brewer, W. Rorer Murphy, Jr., Stanford R. Spurlin, and John D. Petersen*

Received November 7, 1985

In the past, a vast body of work has focused on the excited-state electron-¹⁻⁶ and energy-transfer⁷⁻¹¹ reactions of Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) and its derivatives for the capture, storage, and utilization of solar energy. This interest in Ru(bpy)₃²⁺ stems from the fact that the complex absorbs visible light, is sufficiently long-lived in fluid solution at room temperature to undergo spontaneous emission ($\tau = 600$ ns),⁶ has favorable potentials for both excited-state oxidation and reduction reactions of water,³ and is thermally stable in the +3, +2, and +1 oxidation states. While considerable progress has been made in the understanding of such processes, practical utilization of the considerable energy available in the excited state of Ru(bpy)₃²⁺ has been hampered by such problems as a back-reactions, diffusion-control limitations, parasitic side-electron-transfer reactions, and long-term instability of the photocatalyst.^{2,6,12-14}

- (14) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411. The two populations in this study were varied from 0.215/0.785 to 0.230/0.770, with the ideal population being 0.200/0.800.
- (15) (a) Brown, T. L. *Inorg. Chem.* **1968**, *7*, 2673. (b) Butler and co-workers have recently reported a 2-D NOE ³¹P NMR study of Cr(CO)₅-n-(CX)[(RO)₃P]_n (R = alkyl, aryl; X = O, n = 2,3; X = S, Se, n = 1-3), which illustrates that intramolecular rearrangement in these derivatives occurs via a trigonal-prismatic pathway. Ismail, A. A.; Sauriol, F.; Sedman, J.; Butler, I. S. *Organometallics* **1985**, *4*, 1914.
- (16) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.
- (17) Darensbourg, M. Y.; Bau, R.; Marks, M. W.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961.
- (18) Casey, C. P.; Neumann, S. M. *Adv. Chem. Ser.* **1979**, No. 173, 131.
- (19) (a) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463. (b) The ¹³C NMR spectrum of [CH₃Cr(CO)₅][PPN] in THF exhibits two sharp signals in the CO region (228.9 (CO_{ax}) and 224.9 ppm (CO_{eq})) in the temperature range -50 to +60 °C. Wiegrefe, Philip, unpublished observations from our laboratories.

- (1) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238.
- (2) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.
- (3) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.
- (4) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, No. 168, 1.
- (5) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.
- (6) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159.
- (7) Sabbatini, N.; Balzani, V. *J. Am. Chem. Soc.* **1972**, *94*, 7587.
- (8) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 1800.
- (9) Kane-Maguire, N. A. P.; Langford, C. H. *J. Am. Chem. Soc.* **1972**, *94*, 2125.
- (10) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. A. *Coord. Chem. Rev.* **1975**, *15*, 321.
- (11) Lin, C.-T.; Botcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.
- (12) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.
- (13) Brugger, P.-A.; Infelta, P. O.; Brown, A. M.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320.