Ongoing studies are aimed at (i) defining and exploiting stress-recognition in greater detail, (ii) clarifying the mechanism by which harpoons induce the release of vesicular CF, and (iii) examining the harpoon-lability of bacteria and also those microorganisms for which stress-recognition may be effectively expressed; e.g., enveloped viruses bearing highly curved outer membranes such as HIV.[14]

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(14) Aloia, R. C.; Jensen, F. C.; Curtain, C. C.; Mobley, P. W.; Gordon, L. M. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 900.

Photoinduced Electron Transfer Mediated by a Hydrogen-Bonded Interface[†]

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Long-range electron transfer (ET) in metalloproteins and enzymes is typically mediated by proton motion. Whereas the importance of proton-coupled electron transfer (PCET) in the primary processes of electron/hole pair separation and storage, as well as the function of a variety of biological assemblies including PS II,[1] cytochrome *c* oxidase,[2] and cytochromes,[3] is recognized, PCET has not been subjected to the rigorous experimental and theoretical treatment that has advanced the knowledge of long-range fixed-distance ET in organic and inorganic compounds,[4] proteins,[5] and enzymes.[6] One approach to assessing the role of proton motion on ET rates is to combine the strategy of photoinduced fixed-distance electron transfer[3-6] with that of photoinduced proton transfer.[7] The propensity of carboxylic acids to form cyclic dimers in low-polarity, non-hydrogen-bonding solvents[8] offers the opportunity to juxtapose an acceptor/donor pair via a hydrogen-bonded interface. We now report the electron-transfer kinetics for **1**, where ET is channeled through a protiated (**1**-H) or deuterated (**1**-D) dicarboxylic acid interface from a photoexcitable Zn^{II}PCOOH porphyrin (PCOOH = 13,17-diethyl-3,7,8,12,18-pentamethylporphine-2-acetic acid)[9] donor to the electron acceptor 3,4-dinitrobenzoic acid (DNBCOOH).

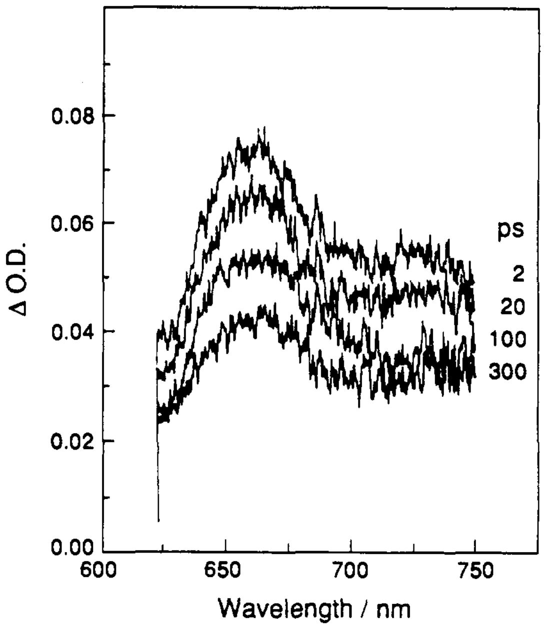
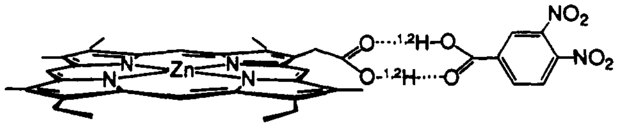


Figure 1. Time evolution of the transient difference spectrum of CH$_2$Cl$_2$ solutions of ZnPCOOCH$_3$ (1.5 × 10^{-3} M) in the presence of 3,5-DNBCOOCH$_2$CH$_3$ (5 × 10^{-2} M).



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Photoexcitation of ZnPCOOH(D) by the amplified output (λ_{exc} = 580 nm) of a Rhodamine 590 synchronously pumped (mode-locked Nd:YAG) dye laser (FWHM = 3 ps, E_p = 300 μJ)[10] produces the emissive $^1\pi\pi^*$ excited state with its characteristic absorption at 660 nm. The singlet decays monoexponentially, with lifetimes of 1.4 and 1.5 ns for ZnPCOOH and ZnPCOOD, respectively, to form a long-lived triplet state (τ_0 = 40 μs). The ZnPCOOH(D) donor is a powerful one-electron reductant from its $^1\pi\pi^*$ and is capable of reacting with a variety of organic acceptors including DNBCOOH(D), for which the driving forces for forward and back electron transfer are −0.73 and −1.37 V, respectively.[11] Indeed, addition of DNBCOOH(D) to dichloromethane solutions of ZnPCOOH(D) leads to the rapid quenching of the $^1\pi\pi^*$ excited state.

Steady-state and time-resolved experiments are consistent with a unimolecular quenching reaction of complex **1**, whose association constant is 552 M^{-1}.[12] The singlet lifetime of ZnPCOOH(D)

[†] A preliminary account of this work was presented at the conference Photoinduced Proton Transfer Dynamics in Chemistry, Biology, and Physics held at Florida State University, Tallahassee, FL, on 6–9 January 1991 in recognition of Michael Kasha's contributions in the area of proton transfer chemistry.

[‡] Alfred P. Sloan Fellow and NSF Presidential Young Investigator.

(1) (a) Babcock, G. T.; Barry, B. A.; Debus, R. J.; Hoganson, C. W.; Atamian, M.; McIntosh, L.; Sithole, I.; Yocum, C. F. *Biochemistry* **1989**, *28*, 9557. (b) Kirmaier, C.; Holten, D. In *The Photosynthetic Bacterial Reaction Center—Structure and Dynamics*; Breton, J., Vermeglio, A., Eds.; Plenum: New York, 1988; p 219. (c) Paddock, M. L.; McPherson, P. H.; Feher, G.; Okamura, M. Y. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 6803. (d) Fox, M. A. *Photochem. Photobiol.* **1990**, *52*, 617.

(2) (a) Morgan, J. E.; Wikstrom, M. *Biochemistry* **1991**, *30*, 948. (b) Wikstrom, M. *Nature* **1989**, *338*, 776. (c) Larsen, R. W.; Li, W.; Copeland, R. A.; Witt, S. N.; Lou, B.-S.; Chan, S. I.; Ondrias, M. R. *Biochemistry* **1990**, *29*, 10135. (d) Maison-Peteri, B.; Malmstrom, B. G. *Biochemistry* **1989**, *28*, 3156.

(3) (a) Therien, M. J.; Selman, M.; Gray, H. B.; Chang, I.-J.; Winkler, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 2420. (b) Onuchic, J. N.; Beratan, D. N. *J. Chem. Phys.* **1990**, *92*, 722.

(4) *Electron Transfer in Biology and the Solid State*; Johnson, M. K., King, R. B., Kurtz, D. M., Kutal, C., Norton, M. L., Scott, R. A., Eds.; Advances in Chemistry Series 226; American Chemical Society: Washington, DC, 1990.

(5) *Metals in Biological Systems*; Sigel, H., Sigel, A., Eds.; Marcel Dekker: New York, 1991; Vol. 27.

(6) Pan, L.-P.; Hazzark, J. T.; Lin, J.; Tollin, G.; Chan, S. I. *J. Am. Chem. Soc.* **1991**, *113*, 5908.

(7) (a) Smith, T. P.; Zaklika, K. A.; Thakur, K.; Barbara, P. F. *J. Am. Chem. Soc.* **1991**, *113*, 4035. (b) Swinney, T. C.; Kelley, D. F. *J. Phys. Chem.* **1991**, *95*, 2430. (c) Held, A.; Plusquellic, D. F.; Tomer, J. L.; Pratt, D. W. *J. Phys. Chem.* **1991**, *95*, 2877.

(8) (a) Chang, Y.-T.; Yamaguchi, Y.; Miller, W. H.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 7245. (b) Davis, J. C., Jr.; Pitzer, K. S. *J. Phys. Chem.* **1960**, *64*, 886. (c) Wenograd, J.; Spur, R. A. *J. Am. Chem. Soc.* **1957**, *79*, 5844.

(9) This porphyrin was synthesized from condensation of 5,5′-dibromo-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethene hydrobromide and 4-(carboxymethyl)-3,3′,4′,5,5′-pentamethyl-2,2′-dipyrrylmethene hydrobromide in formic acid.

(10) A full description of the picosecond transient absorption instrument will be provided at a later time. The temporal calibration (zero time) of the instrument was obtained by overlapping the pump pulse with the red edge of the continuum pulse in our spectral window. In this manner, a signal arising from the effects of group velocity dispersion of the white light traveling through our optics (~2 ps) is observed only prior to zero time (Greene, B. I.; Hochstrasser, R. M.; Weisman, R. B. *J. Chem. Phys.* **1979**, *70*, 1247).

(11) The redox potential of excited-state donor, $E_{1/2}$(ZnP$^{+/*}$), is −1.30 V as calculated from $E(^1\pi\pi^*)$ = 2.1 eV and $E_{1/2}$(ZnP$^{+/0}$) = 0.80 V vs NHE (Kalyasundaram, K.; Newman-Spallart, M. *J. Phys. Chem.* **1982**, *86*, 5163), and that for the acceptor, $E_{1/2}$(DNB$^{0/-}$), is −0.57 V vs NHE (Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Marcel Dekker: New York, 1970).

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is only marginally affected by addition of the acceptor to concentrations of 5.0 × 10^{-2} M, whereas the intensity of the fluorescence decreases by an order of magnitude. This observation of static quenching is explained by the hydrogen-bonded association of ZnPCOOH(D) with DNBCOOH(D).[13] In accordance with this contention, static quenching is not observed when the carboxylic acid network is disrupted by the addition of hydrogen-bonding solvents and when the carboxylate functionalities of the acceptor/donor pair are esterified. Figure 1 shows the transient absorption spectrum of $ZnPCOOCH_3$ (1.5 × 10^{-3} M) in the presence of ethyl 3,5-dinitrobenzoate. The singlet decays monotonically, and no prominent absorptions for the radical cation,[14a] which displays an absorption peak at 670 nm (ϵ = 5100 M^{-1} cm^{-1}) with a high-energy shoulder at 640 nm,[14b] are observed on the picosecond time scale. These results are consistent with the inability of the esters to form acceptor/donor bound pairs, whereas in **1**-H and **1**-D static quenching can occur by association of the acceptor and donor through the hydrogen-bonded interface.

The kinetics for quenching of the hydrogen-bonded acceptor/donor pair is conveniently monitored by picosecond transient absorption spectroscopy. The disappearance of the 660-nm absorption of the $^1\pi\pi^*$ soon after laser excitation is accompanied by the concomitant appearance of an absorption feature at 675 nm for **1**-H and **1**-D. For the latter, this absorption evolves on a slow enough time scale to be easily monitored. Figure 2a shows the time evolution of the transient of **1**-D from 0 to 5 ps. A pronounced absorption of the $^1\pi\pi^*$ excited state at 660 nm is observed at zero time. A strong absorption feature at 675 nm, with a shoulder at 655 nm, is clearly observed within 5 ps of the excitation pulse. These absorptions are representative of the Zn(II) porphyrin cation radical.[15] The singlet disappears monoexponentially, with a rate constant of 3.0 (3) × 10^{10} s^{-1}, to produce the cation radical, which subsequently decays by charge recombination with a rate constant of 6.2 (3) × 10^9 s^{-1} (Figure 2b). Transient absorption spectra of **1**-H exhibit an acceleration in both the quenching of the $^1\pi\pi^*$ excited state and the decay of the cation. From the disappearance of the singlet transient, we infer that the forward electron transfer rate constant is 5.0 (5) × 10^{10} s^{-1}; the rate constant for charge recombination is 1.0 (2) × 10^{10} s^{-1}. As expected for an intramolecular process, the rates for quenching of the $^1\pi\pi^*$ excited state and disappearance of the cation radical are concentration independent in the ranges [ZnPCOOH] = 1.0–1.5 × 10^{-3} M with [DNBCOOH] = 5.0–40 × 10^{-3} M.[16]

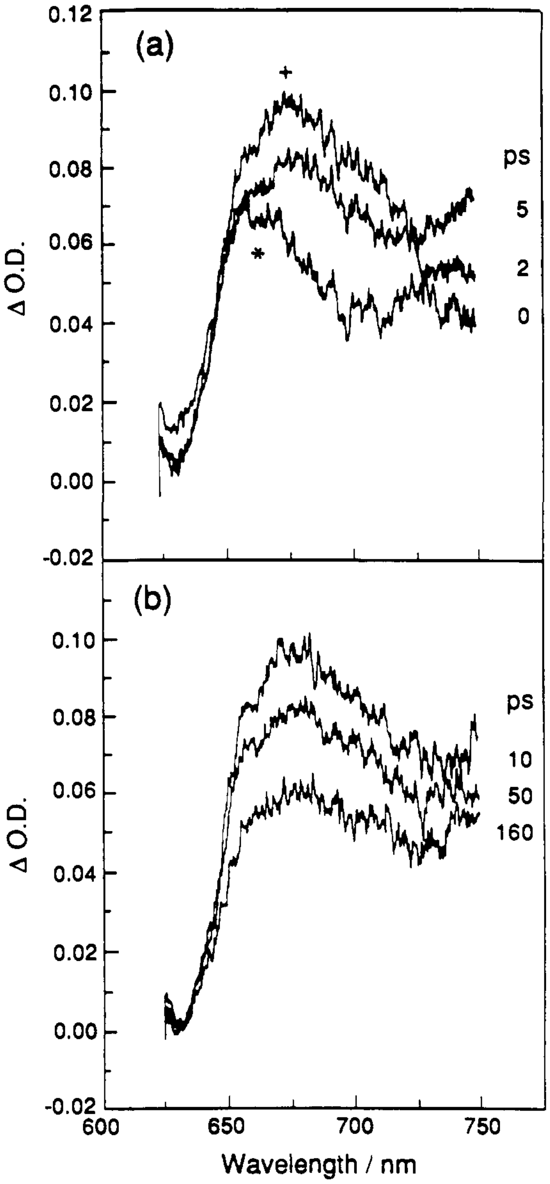

Figure 2. (a) Time evolution for the disappearance of the $^1\pi\pi^*$ absorption and the growth of the cation radical absorption of ZnPCOOD. The singlet absorption is designated by * and that of the radical cation by +. (b) The time evolution for the disappearance of the radical cation transient spectrum of ZnPCOOD.

Our experimental observations show that ET through hydrogen-bonded interfaces is fast. The ET rates reported here appear to be only slightly slower than those of covalently linked Zn(II) porphyrin/acceptor systems of similar separation and driving force. Electron-transfer rate constants of k_{CS} = 2.5 × 10^{11} s^{-1} and k_{CR} = 1.2 × 10^{11} s^{-1} are interpolated from Wasielewski's data on (Zn porphyrin)–L–(quinone) (L = rigid polycyclic cage) systems at driving forces equivalent to the charge separation and recombination reactions of **1**-H.[17] Inasmuch as the porphyrin/acceptor edge-to-edge distance of the (Zn porphyrin)–L–(quinone) system is 10.5 Å as compared to the 9.4-Å distance of **1**-H, the electronic coupling of the acceptor/donor pair spaced by a covalent linkage appears to be greater than that for a $-(COOH)_2-$ spacer. Nonetheless the ET rates of the two systems are of similar orders of magnitude, thereby establishing that hydrogen-bonded pathways for ET can be competitive to covalent bond routes, as recently predicted by Beratan et al.[18] Moreover, the importance of proton

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(12) Dimer **1** in CH_2Cl_2 was characterized by NMR and IR spectroscopy; relevant spectra have been included as supplementary material. The association constant was measured from the IR absorptions of the CO and OH stretching vibrations according to standard methods (Affsprung, H. E.; Christian, S. D.; Melnick, A. M. *Spectrochim. Acta* **1963**, *20*, 285. Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker, Inc.: New York, 1974).

(13) The association constant calculated from static quenching (Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F. *Coord. Chem. Rev.* **1975**, *15*, 321) of the ZnPCOOH fluorescence agrees with that measured from IR spectroscopy (K_{assoc} = 698 and 316 M^{-1} for **1**-H in *o*-dichlorobenzene and **1**-D in CH_2Cl_2, respectively).

(14) (a) The appearance and subsequent decay of the transient absorption spectrum of the $^1\pi\pi^*$ excited state of $ZnPCOOCH_3$ in the absence of quencher is shown in the supplementary material. (b) The $ZnPCOOCH_3{}^+$ transient absorption spectrum was obtained by irradiating a CH_2Cl_2 solution of $ZnPCOOCH_3$ (1 × 10^{-5} M) and TCNE with a 10-ns pulse from a frequency-doubled Nd:YAG laser instrument, which has been described previously (Jackson, J. A.; Turrõ, C.; Newsham, M. D.; Nocera, D. G. *J. Phys. Chem.* **1990**, *94*, 4500).

(15) (a) Rodriguez, J.; Kirmaier, C.; Johnson, M. R.; Friesner, R. A.; Holten, D.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1652. (b) Batteas, J. D.; Harriman, A.; Kanda, Y.; Mataga, N.; Nowak, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 126.

(16) The solution contains, in addition to **1**, dimers of $ZnP(COOH)_2ZnP$ and $DNB(COOH)_2DNB$, with association constants of 1090 M^{-1} and 200 M^{-1}, respectively (supplementary material). The formation of $ZnP(COOH)_2ZnP$ dimers in solution is inconsequential to our transient absorption experiments because the driving force for charge separation in $ZnP(COOH)_2ZnP$ is endogenic (ΔG = +0.07 V); in accordance with these energetics, transient absorption spectra of CH_2Cl_2 solutions of ZnPCOOH and ZnPCOOD exhibit only the singlet spectrum. For the case of $DNB(COOH)_2DNB$ pairs, the chromophores absorb light at much higher energy than that of our excitation pulse.

(17) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080.

(18) Beratan, D. N.; Betts, J. N.; Onuchic, J. N. *Science (Washington, D.C.)* **1991**, *252*, 1285.

motion on the electronic coupling of the acceptor/donor pair is in evidence from the pronounced deuterium isotope effect of k_H/k_D = 1.7 (3) and 1.6 (4) for the charge separation and recombination rates, respectively. This observation is consistent with the 1.7–2.0 deuterium isotope effects measured for the oxidation of a soluble analog of vitamin E by organochloro peroxides.[19] In this latter system, the rate-determining step has been proposed to involve the transfer of an electron from substrate to the peroxy radical via a hydrogen-bonding network formed from the incipient hydroperoxide and solvent. Thus, our results show that hydrogen-bonding interfaces not only are important in the supramolecular preorganization of acceptor/donor pairs for energy[20] and electron[21] transfer but also may directly mediate the electron-transfer event.

Acknowledgment. We thank Jeffrey M. Zaleski for obtaining time-correlated single photon counting measurements and Lawrence E. Bowman for his contributions to the assembly of the picosecond amplification system. The financial support of the National Institutes of Health (GM 47274) is gratefully acknowledged.

Supplementary Material Available: Transient absorption spectrum of ZnPCOOCH$_3$ NMR spectra of ZnPCOOH/DNBCOOH solutions and tables of ^{1}H NMR shifts and FWHM as a function of concentration; IR spectra of ZnPCOOH and DNBCOOH as a function of concentration, ν(CO) and ν(OH) frequencies, calculated association constants for ZnP(COOH)$_2$ZnP and DNB(COOH)$_2$DNB, and plot utilized to obtain the association constant of ZnP(COOH)$_2$DNB (9 pages). Ordering information is given on any current masthead page.

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(19) Neta, P.; Huie, R. E.; Maruthamuthu, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 7654.

(20) (a) Harriman, A.; Magda, D.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 1530. (b) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408.

(21) (a) Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 388. (b) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ososhi, H. *J. Am. Chem. Soc.* **1991**, *113*, 6233.

Stereospecific and Regiospecific Ligand Substitution Reactions of Mononuclear and Dinuclear Rhodium(III) Phosphine Complexes

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It is known[1] that for several transition metals mononuclear octahedral (MONO), edge-sharing bioctahedral (ESBO), and face-sharing bioctahedral (FSBO) complexes all exist and are interconvertible, as in the following scheme, where X = halide and L = a tertiary phosphine.

$$\underset{\text{MONO}}{2MX_3L_3} \xrightleftharpoons[+2L]{-2L} \underset{\text{ESBO}}{M_2X_6L_4} \xrightleftharpoons[+L]{-L} \underset{\text{FSBO}}{M_2X_6L_3}$$

This scheme, as written, omits the fact that stereoisomerism is possible at all three stages, there being two MONO isomers and (considering only 1,1,2,2 or 1,1,2 regioisomers, and counting each pair of enantiomers as one) nine ESBO and two FSBO isomers. Very little is known about the mechanisms and/or stereospecificities pertinent to the interconversion of these species.

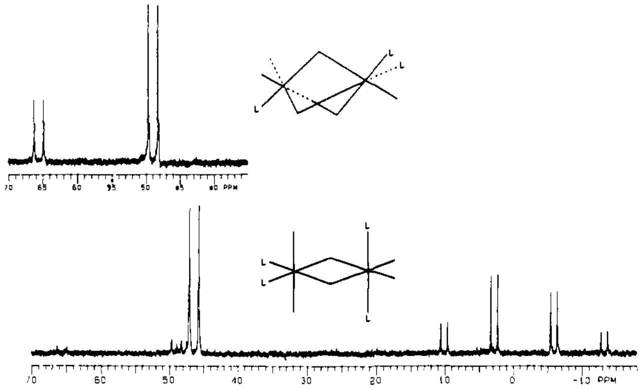
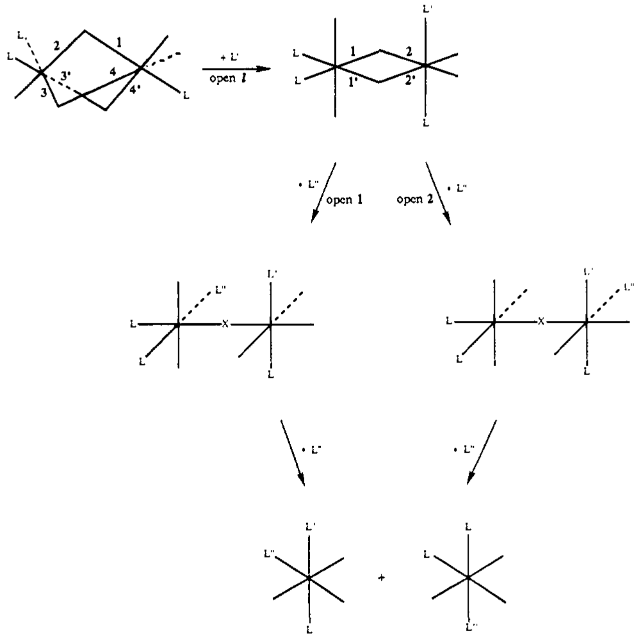


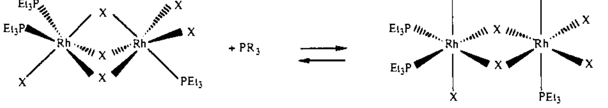
Figure 1. ^{31}P{^{1}H} NMR spectra (81 MHz). Upper: *anti*-Rh$_2$Br$_6$(PEt$_3$)$_3$. Lower: After addition of PMe$_3$.

Scheme I



By virtue of the capacity of rhodium(III) chloride and bromide phosphine complexes to afford uniquely informative NMR data, we have been able to learn a great deal about these processes for rhodium(III) compounds and have found that there is strict stereo- and regiospecificity throughout. This in turn allows the assignment of unique, simple, and reasonable mechanisms. We present here illustrative highlights of a broad study that is still in progress.

A solution[2] of *anti*-Rh$_2$X$_6$(PEt$_3$)$_3$ shows no tendency to isomerize at or below room temperature and, upon treatment with slightly more than 1 molar equiv of PR$_3$ (R$_3$ = Et$_3$, Me$_3$, Me$_2$Ph), is converted *exclusively* to the *ax*,*ax*,*eq*,*eq*-Rh$_2$X$_6$(PEt$_3$)$_3$PR$_3$ isomer, as demonstrated in Figure 1[3] and summarized in eq 1.



(1)

Because J_{P-Rh} values are always in the ranges 103–120 Hz for P trans to X and 70–90 Hz for P trans to P for Rh(III) complexes containing only phosphine and halide ligands,[4] the spectra of the

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(1) (a) Chacon, S. T.; Chisholm, M. H.; Streib, W. E.; van der Sluys, W. *Inorg. Chem.* **1989**, *28*, 5. (b) Poli, R.; Mui, H. D. *J. Am. Chem. Soc.* **1990**, *112*, 2446. (c) Poli, R.; Mui, H. D. *Inorg. Chem.* **1991**, *30*, 65. (d) Cotton, F. A.; Matusz, M.; Torralba, R. C. *Inorg. Chem.* **1989**, *28*, 1516. (e) Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 2196. (f) Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 4392.

(2) The solvent is CH$_2$Cl$_2$ in all experiments mentioned here.

(3) In *anti*·Rh$_2$Br$_6$(PEt$_3$)$_3$: doublets of relative intensity 1:2 at 65.5 ppm (J_{P-Rh} = 115 Hz) and 48.5 ppm (J_{P-Rh} = 115 Hz). Chemical shifts externally referenced to H$_3$PO$_4$. In Rh$_2$Br$_6$(PEt$_3$)$_3$(PMe$_3$): doublet at 46.0 (J_{P-Rh} = 111 Hz), quartet of doublets (J_{P-Rh} = 79 Hz) at 9.7, 2.3, −6.3, −13.6 ppm. J_{P-P} ≈ 595 Hz for trans phosphines, and the chemical shift difference for the phosphorus atoms of the trans PEt$_3$ and PMe$_3$ ligands in the complex is of similar magnitude (ca. 15 ppm).

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