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 $^1H$ NMR shifts and FWHM as a function of concentration; IR spectra of ZnPCOOH and DNBCOOH as a function of concentration, $\nu$(CO) and $\nu$(OH) frequencies, calculated association constants for $ZnP(COOH)_2ZnP$ and $DNB(COOH)_2DNB$, and plot utilized to obtain the association constant of $ZnP(COOH)_2DNB$ (9 pages). Ordering information is given on any current masthead page.

(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.

$$2MX_3L_3 \underset{+2L}{\overset{-2L}{\rightleftharpoons}} M_2X_6L_4 \underset{+L}{\overset{-L}{\rightleftharpoons}} M_2X_6L_3$$
MONO ESBO FSBO

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.

(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.

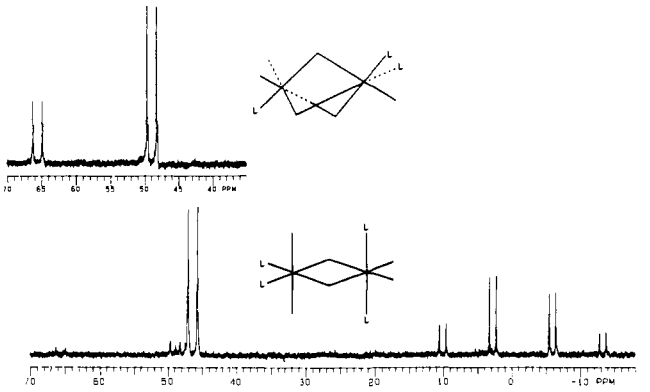
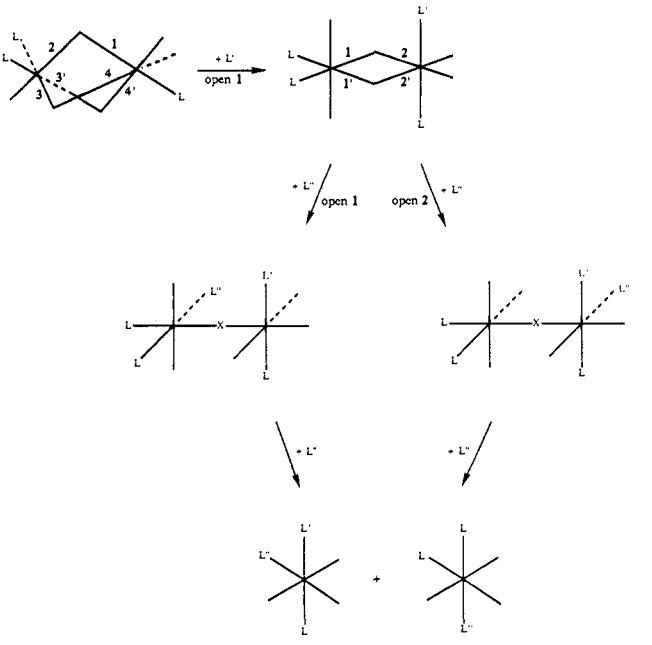


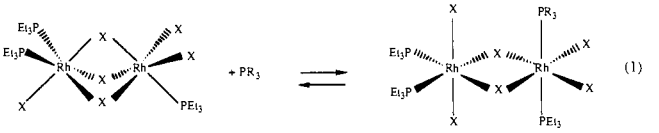
**Figure 1.** $^{31}P\{^1H\}$ NMR spectra (81 MHz). Upper: *anti*-$Rh_2Br_6(PEt_3)_3$. Lower: After addition of $PMe_3$.

**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*-$Rh_2X_6(PEt_3)_3$ shows no tendency to isomerize at or below room temperature and, upon treatment with slightly more than 1 molar equiv of $PR_3$ ($R_3$ = $Et_3$, $Me_3$, $Me_2Ph$), is converted *exclusively* to the *ax,ax,eq,eq*-$Rh_2X_6(PEt_3)_3PR_3$ isomer, as demonstrated in Figure 1[3] and summarized in eq 1.



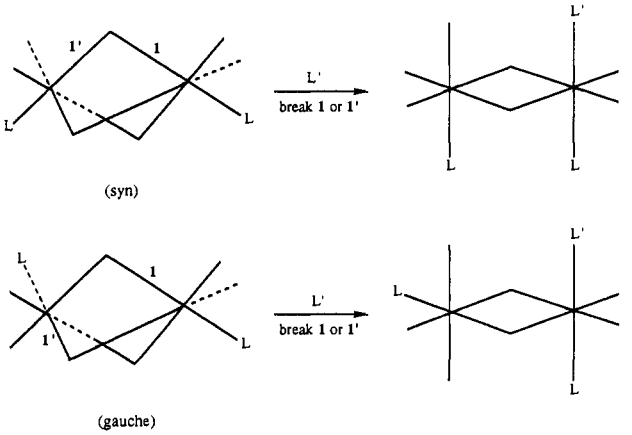
(1)

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

(2) The solvent is $CH_2Cl_2$ in all experiments mentioned here.
(3) In *anti*-$Rh_2Br_6(PEt_3)_3$: 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 $H_3PO_4$. In $Rh_2Br_6(PEt_3)_3(PMe_3)$: 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).

0002-7863/92/1514-4015$03.00/0 

**Scheme II**




ESBO products show unequivocally that only the isomer shown in eq 1 (and none of the other eight) is formed. When the ESBOs $Rh_2X_6(PEt_3)_4$ are heated to 60 °C under vacuum, *anti*-$Rh_2X_6(PEt_3)_3$ is re-formed quantitatively and exclusively. Similar results were obtained with *anti*-$Rh_2Br_6(P\text{-}nPr_3)_3$.

The addition of 2.5 equiv of $PEt_3$ to *ax,ax,eq,eq*-$Rh_2Br_6(PEt_3)_4$ produces quantitatively and exclusively the *mer* isomer of $RhBr_3(PEt_3)_3$.[5]

(4) (a) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 704. (b) Grim, S. O.; Ference, R. A. *Inorg. Chim. Acta* **1970**, *4*, 277. (c) Allen, F. H.; Gabuji, K. M. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 833.

All of these results are consistent with the pathways shown in Scheme I, where the key elements of stereochemical control are that (1) bonds trans to L break preferentially[6] and (2) there is regiospecificity in the formation of the ESBOs. X-ray crystallographic studies have been carried out on most of the compounds studied by NMR, and the Rh–X bonds trans to $PR_3$ are always much (ca. 0.2 Å) longer than those trans to X, as was the case with previously reported crystal structures of dinuclear Rh(III)[7] complexes.

Finally, we report that the $[Rh_2Br_7(PEt_3)_2]^-$ ion has been obtained as both syn and gauche isomers.[8] These do not interconvert or equilibrate in solution at or below room temperature, and each reacts with additional phosphine in a strictly stereospecific manner which we believe to be as shown in Scheme II. Once again, the $^{31}P$ NMR spectra allow us to establish that there is stereospecificity, i.e., the production of only one isomer in each case, cleanly and unambiguously.

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(5) $^{31}P\{^1H\}$ NMR: doublet of triplets at 18.5 ppm with $J_{P\text{-}P}$ = 22.9 Hz and $J_{P\text{-}Rh}$ = 109.2 Hz; doublet of doublets at −2.4 ppm with $J_{P\text{-}P}$ = 22.9 Hz and $J_{P\text{-}Rh}$ = 82.8 Hz in 1:2 intensity ratio.

(6) As shown in Scheme I, this assumption is unnecessary in the ESBO → MONO process since the result is the same regardless of which type of bridge bond is opened.

(7) (a) Muir, J. A.; Baretty, R.; Muir, M. M. *Acta Crystallogr.* **1976**, *B32*, 315. (b) Muir, J. A.; Muir, M. M.; Rivera, A. C. *Acta Crystallogr.* **1974**, *B30*, 2062.

(8) For several compounds the isomer has been verified by X-ray crystallography.

# *Additions and Corrections*

**Electrophilic Catalysis Can Explain the Unexpected Acidity of Carbon Acids in Enzyme-Catalyzed Reactions** [*J. Am. Chem. Soc.* **1991**, *113*, 9667]. JOHN A. GERLT,* JOHN W. KOZARICH, GEORGE L. KENYON, and PAUL G. GASSMAN*

Page 9667: The equation in footnote 29 relating **k**, the rate of transfer of the proton from the substrate carbon acid to the base, to $\Delta G^{\ddagger}$, the activation energy for an isoergonic proton transfer, and $\Delta pK_a$, the difference in $pK_a$ values for the acid and base, neglected the effect of the Bronsted coefficient for the transfer. This omission does not alter the conclusions reached in the communication since the $\Delta pK_a$ will remain consistent with the observed rates of enzyme-catalyzed reactions.