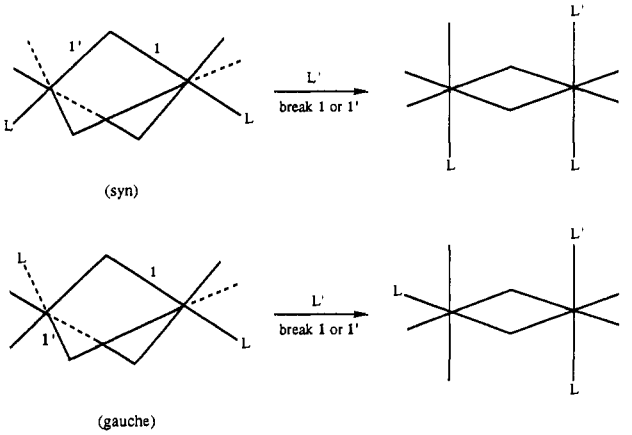
**Scheme II**




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.