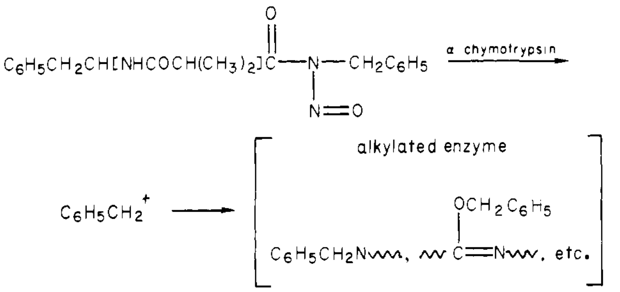
groups and also through alkylation of the amide linkages[34] (eq 7). The sydnone[35,36] and nitrosoamide cases would appear to be related examples of enzyme-activated substrate inhibition.[32,36-38]



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(33) Similar results have been obtained with several nitroso lactams,[32] which, in addition, have been found to inhibit trypsin, elastase, and subtilisin BPN′ (research of Dr. Douglas Hayes).

(34) Reference 32 and unpublished work of Dr. Stephano Donadio.

(35) The enzyme-moderated oxidation of sydnones may involve two one-electron transfers (Silverman, R. B.; Yamasaki, R. B. *Biochemistry* **1984**, *23*, 1322-1333.

(36) We thank Dr. Silverman for preprints of ref 35 and 37.

(37) Silverman, R. B.; Hoffman, S. J. *Med. Res. Rev.*, in press.

(38) Also called mechanism based and suicide inhibition (Colowick, S. P.; Kaplan, N. O. *Methods Enzymol.* **1977**, *46*. Kalman, T. I. "Drug Action and Design"; Elsevier/North-Holland: New York, 1979; Vol 6.

Secondary Deuterium Kinetic Isotope Effect in S_E2 Replacement Reactions[1a]

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In principle, the utility of the hydrogen secondary kinetic isotope effect for investigating S_E2 transition states could be as great as it has been for S_N1 and S_N2 reactions at saturated carbon.[2-4] Here we report the first such determinations associated with bimolecular electrophilic substitution reactions.

Proton and bromine cleavage rank among the most extensively studied electrophilic substitution processes.[5-8] Substantial kinetic and stereochemical evidence has led to the proposal that such reactions occur by a concerted, front-side attack which proceeds through a transition state that involves a pentacoordinate carbon center.[5-9] A similar transition state has been suggested for a variety of elementary electrophilic processes (Figure 1).

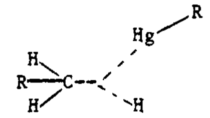

Figure 1. Idealized representation of the rate-limiting transition state proposed for the protonolysis of (n-alkyl)$_2$Hg by HA.

Table I. Deuterium Secondary Isotope Effect for Several Electrophilic Reactions[a]

substrate	electro-phile	solvent	temp, °C	k_{CH_2}/k_{CD_2}[b]
$(C_7H_{15}CL_2)_2Hg$	HCl	dioxane	25	1.191 ± 0.005[e]
	Br_2	CCl_4[c]	0	1.257 ± 0.007
	Br_2	CH_3OH	20	1.223 ± 0.004
$(C_6H_{13}CL_2CH_2)_2Hg$	HCl	dioxane	25	1.008 ± 0.005
$(C_7H_{15}CL_2)Sn-[CH_2C(CH_3)_3]_3$	Br_2	CCl_4[c]	0	1.154 ± 0.007
	Br_2	CH_3OH CH_2Cl_2 (3:1)[d]	20	1.186 ± 0.004

[a] Initial composition: [substrate] = 0.1 M; [electrophile] = 0.01 M. A constant temperature (±0.02 °C) was maintained during the course of all cleavage reactions. The stereoselectivity of electrophilic cleavages has been found to vary substantially with reaction conditions.[5,7] Except where noted, the conditions employed in this study, insofar as possible, duplicate those under which the equivalent reaction employing a chiral substrate is reported to occur with maximum retention of configuration.[5,7] [b] The isotope effect associated with the competitive protic cleavage of **1**-d_0 and **1**-*1,1*-d_2 is given by k_{CH_2}/k_{CD_2} = ([octane-d_2]/[octane-d_0])$_{sc}$([octane-d_0]/[octane-d_2]). The corresponding expression for bromine cleavage is k_{CH_2}/k_{CD_2} = ([bromooctane-d_0]/[bromooctane-d_2])$_{sc}$([bromooctane-d_0]/[bromooctane-d_2]). The subscript sc refers to values obtained from a mixture identical in composition to that of the starting mixture. These ratios were determined by high-precision, whole-molecule mass spectrometry by simultaneously monitoring (for a total of 10 000 scans) the M and M + 2 ions of the octane-d_0 and -d_2 and bromooctane-d_0 and -d_2 mixtures isolated at the completion of each reaction. Since neither octane nor bromooctane exhibit a significant (i.e., >1%) M − 2 ion, a correction for this factor was unnecessary. An ionizing voltage of 70 eV and a constant source pressure of 8.0×10^{-7} torr were employed. [c] Isamyl nitrite (0.01 M) added as a free-radical inhibitor.[7] [d] Reaction mixture was 0.1 M in (n-$C_4H_9)_4NBr$. [e] Indicated error is $\pm\sigma$.

The secondary deuterium kinetic isotope effect associated with the competitive protonolysis of (di-n-octyl-*1,1*-d_0)mercury- - -(di-n-octyl-*1,1*-d_2)mercury, (**1**-d_0 and **1**-*1,1*-d_2, respectively) and (di-n-octyl-*2,2*-d_0)mercury- - -(di-n-octyl-*2,2*-d_2)mercury (**1**-d_0 and **1**-*2,2*-d_2, respectively) by anhydrous hydrogen chloride in dioxane is presented in Table I. Also listed are the corresponding data

$$[CH_3(CH_2)_6CH_2]_2Hg + [CH_3(CH_2)_6CD_2]_2Hg \xrightarrow[\text{dioxane}]{\text{HCl}} CH_3(CH_2)_6CH_3 + CH_3(CH_2)_6CD_2H$$

from the competitive bromine cleavage of **1**-d_0 and **1**-*1,1*-d_2, together with the equivalent data for trineopentyl(n-octyl-*1,1*-d_0)tin (**2**-d_0) and trineopentyl(n-octyl-*1,1*-d_2)tin (**2**-d_2). These data reveal (i) that a normal α-deuterium KIE prevails, i.e., $k_H/k_D > 1$, corresponding in this instance to ca. 1.10 per deuterium at 25 °C, (ii) that neither solvent nor the size or polarizability of the entering or leaving groups appear to have any significant influence on the magnitude of this effect, and (iii) that the corresponding β-deuterium isotope effect is negligible.

α-Deuterium secondary isotope effects arise in major part from the difference between the bending force constants at the isotopic center in the ground-state reactant and in the transition state.[2-4] This effect will the inverse ($k_D > k_H$) if the force constants are

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(1) (a) Supported by the NSF, Grant CHE 83-12730-01. (b) Jilin University, Changchun, Peoples' Republic of China.

(2) Shiner, V. J., Jr. "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nonstrand Reinhold: New York, 1970; Chapter 2.

(3) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980; Chapter 6.

(4) Gray, C. H.; Coward, J. K.; Schowen, K. B.; Schowen, R. L. *J. Am. Chem. Soc.*, **1979**, *101*, 4351 and references therein.

(5) Jensen, F. R.; Rickhorn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968.

(6) Matteson, D. S. "Organometallic Reaction Mechansms"; Academic Press: New York, 1974.

(7) McGahey, L. F. Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 4397 and references therein.

(8) Nugent, N. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5979 and references therein.

(9) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.

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greater in the transition state than in the reactant and normal ($k_H > k_D$) if the reverse is true. Although experimental values for the C–H force constants at a positively charged, pentacoordinate carbon center are not generally available, extensive molecular orbital studies of the geometries and the energies of CH_5^+ predict several possible structures for this species including a lowest energy structure of C_s symmetry, which is further distinguished by the fact that all of the C–H bond distances for this structure are calculated to be *greater* than that observed for methane.[10] [Two of the theoretical bond lengths calculated for this structure are between 0.25 and 0.30 Å longer than the experimentally determined C–H bond length in methane.[10b]] If these gas-phase calculations can be qualitatively extended to positively charged, pentacoordinate transition-state structures in solution, it is possible to appreciate how such increases in C–H bond length would result in a *reduction* in the C–H force constants associated with such transition states, and, therefore, to a value of $k_H/k_D > 1$.

Finally, it is significant that there is no β-effect. This finding suggests that, although the overall bonding at C is looser in the transition state, there is no appreciable accumulation of positive charge at this carbon center for if there were, then by analogy to S_N1 solvolysis reactions, a substantial normal β-effect would be anticipated as a result of hyperconjugation.[2]

Confirmation of the generality of these observations to S_E2 reactions as a class must await the results of model calculations as well as further studies, currently under way, designed to more fully establish the scope of the influence of entering and leaving groups, the structure of the carbon center, and the role of solvent effects.

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(10) (a) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. V. R. *Ibid.* **1981**, *103*, 5649.

Reduction Chemistry of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ and Selective Synthesis of Isomeric Doubly Bridged Methylene–Tetraphenylbiphosphine and Diphenylphosphido–Methylenediphenylphosphine Complexes

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Considerable interest has developed in the chemistry of phosphido-bridged binuclear transition-metal complexes.[1] Such complexes are generally stable with respect to fragmentation, and this property renders them particularly useful for studies of cooperative effects in bimetallic systems. This communication focuses on the preparation of new phosphido-bridged diiron nitrosyl anions and on their application in the selective synthesis of unusual isomeric (CH_2, Ph_2PPPh_2)-bridged and (PPh_2, CH_2PPh_2)-bridged bimetallic complexes, as shown in Scheme I.

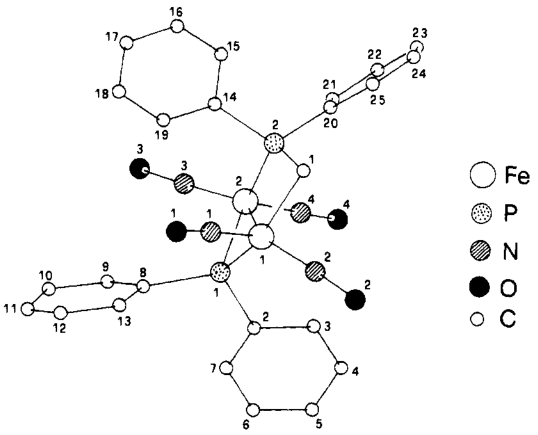
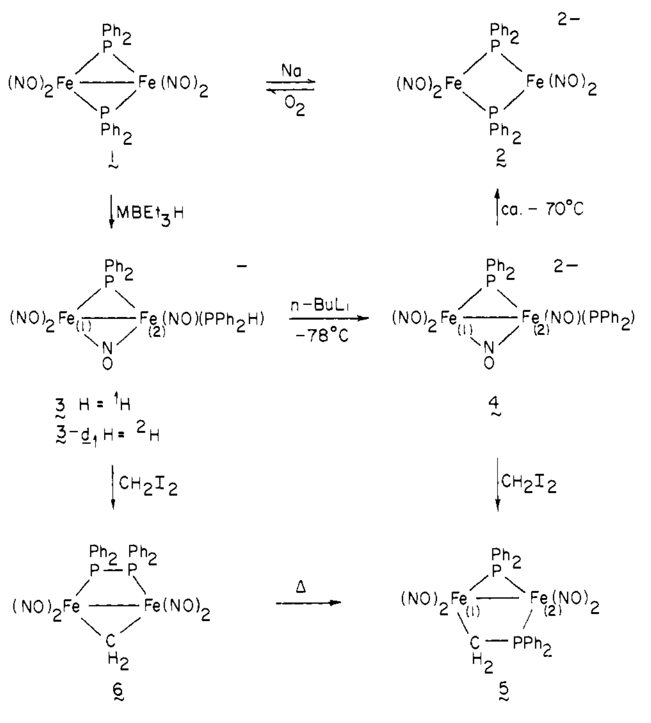


Figure 1. Molecular structure of one of two crystallographically independent molecules of **5**.

Scheme I



Chemical reduction of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ proceeds either to $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^{2-}$ or to $[(CO)_3Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_2(PPh_2H)]^-$ depending on the reagent employed.[2,3] We now find that such dual behavior extends to the reduction of the isoelectronic nitrosyl complex $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$[4] (**1**). Thus, on treatment with Na dispersion in THF, a red slurry of **1** gradually changes to a dark brown solution of $(Na^+)_2$**2**. The proposed structure of **2** is based on its spectroscopic properties[5] and on its extremely rapid and essentially quantitative oxidation by air back to **1**. The dianion **2**, which was originally prepared electrochem-

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* Inquiries concerning the X-ray crystallographic work should be directed to the Trieste address.

(1) Leading references: (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163; (b) *Pure Appl. Chem.* **1982**, *54*, 113. (c) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349. (d) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846. (e) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 1069. (f) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *Ibid.* **1981**, *103*, 1394. (g) Finke, R. G.; Gaughan, G.; Pierpont, C.; Noordik, J. H. *Organometallics* **1983**, *2*, 1481. (h) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Ibid.* **1983**, *2*, 1437. (i) McKennis, J. S.; Kyba, E. P. *Ibid.* **1983**, *2*, 1249. (j) Huttner, G.; Schneider, J.; Müller, H. D.; Mohr, G.; von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76. (k) Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Ibid.* **1979**, *18*, 690. (l) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. (m) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47. (n) Zolk, R.; Werner, H. *Ibid.* **1983**, *252*, C53.

(2) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

(3) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

(4) (a) Hayter, R. G.; Williams, L. F. *Inorg. Chem.* **1964**, *3*, 717. (b) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 1626.

(5) $(Na^+)_2$**2**: IR (THF) $\nu_{N\equiv O}$ 1672 s, br cm^{-1}; $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ −32.9 (s), indicating the presence of equivalent bridging PPh_2 groups with no supporting Fe–Fe bond.[1a] Similar data were obtained for $(Li^+)_2$**2**.

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