metal–metal bonds in a number of other molybdenum oligomers[17] lends weight to our hypothesis. The observed essential invariance of the Mo–Mo bond length in the neutral dimer to oxidation may be ascribed to the least stable MO being primarily nonbonding with respect to the two molybdenum atoms. However, a much more plausible explanation (still consistent with our hypothesis of some metal–metal multiple bond character in the oxidized complex) emerges after it is noted that the bridging Mo–S–Mo angles in the neutral dimer are as small as those found in any doubly bridging mercapto system. Hence, it is proposed that these already angularly strained bridging ligands effectively prevent any possible shortening of the Mo–Mo distance on oxidation. These results have a generalized stereochemical importance in ligand-bridged metal–metal bonded systems. The essential invariance of the metal–metal distance in the oxidized form need not imply that there is no increase in multiple bond character between the metal atoms in the oxidized species. The lack of appreciable geometrical change may be due primarily to the particular steric constraints of the bridging ligands in a given architecture.

This study represents the first complete structural determination of this type of binuclear metal complex.[18–22] Our conclusions have prompted a structural investigation of the weakly temperature-dependent paramagnetic vanadium analog $[V(h^5\text{-}C_5H_5)(SCH_3)_2]_2$,[23] which hopefully will provide a further assessment of the interrelationship of the nature of the bridging ligands to the metal–metal distance in a complex apparently containing considerable metal–metal interaction.

Acknowledgment. This research was financially supported by the National Institutes of Health (Grant No. 2-R01-AI07795-4). We were especially indebted to Dr. Robert M. Sweet for his helpful assistance on the crystallographic part of this work. The use of the UNIVAC 1108 computer at the University of Wisconsin Computing Center was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation through the University Research Committee.

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symmetry combinations. It should be noted that one referee has suggested that the narrow esr resonance at room temperature with no apparent hyperfine structure in the $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2^+$ cation may signify that this cation is best regarded as a radical cation with the unpaired electron density located mainly on the sulfur atoms. Low-temperature esr measurements are in progress in an attempt to clarify this possibility.

(17) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969), and references contained therein; (b) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 2698 (1969).

(18) The analogous metal dithiolene complexes $[M(h^5\text{-}C_5H_5)(SCCF_3)]_2$ (M = V, Mo) were prepared and characterized from nmr, ir, and room-temperature magnetic susceptibility data by King,[12,19] who proposed the existence of a Mo–Mo single bond to account for the observed diamagnetism of the molybdenum dimer and a V–V bond of partial double-bond character in the vanadium derivative to explain the observed small magnetic moment. A preliminary X-ray analysis of the molybdenum dimer was carried out by Cox and Baird[20] who, in spite of difficulties encountered in unsuccessful attempts to refine the structure, nevertheless ascertained the gross tetramercapto-bridged geometry proposed by King.[12] A comparison of their determined bond length of 2.62 (2) Å with that of 2.603 (2) Å found for $[Mo(h^5\text{-}C_6H_5)(SCH_3)_2]_2$ makes it likely that the detailed geometries of the corresponding methylthio and dithiolene metal complexes are closely related to each other. Cox and Baird[21] also concluded from similar crystal data (including lattice parameters and space group assignments) that the molybdenum and vanadium dithiolene dimers are isostructural. The corresponding chromium complex, $[Cr(h^5\text{-}C_5H_5)(SCCF_3)_2]_2$, was surprisingly found from an X-ray analysis[21] to have a disulfur-bridged rather than a tetrasulfur-bridged structure. Two derivatives of the same molecular formula $[Mo(h^5\text{-}C_5H_5)S_2C_6H_{10}]_2$, prepared by Treichel and Wilkes,[22] presumably are geometrical isomers with tetrasulfur-bridged and/or disulfur-bridged structures.

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(20) J. W. Cox, Jr., M.S. Thesis, Wake Forrest College, 1965; H. W. Baird, private communication to L. F. Dahl, 1965.

(21) S. F. Watkins and L. F. Dahl, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p 23-O.

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(23) R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

Organometallic Chalcogen Complexes. XX. Stereochemical Characterization of an Oxidized Iron–Sulfur Dimer, $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$. A Paramagnetic Cation Effectively Containing a One-Electron Metal–Metal Bond[1]

Sir:

As part of a systematic investigation of redox effects on the geometries of various types of organometallic oligomers which gain and/or lose electrons without rupture of their atomic frameworks,[1] we wish to report the structural characterization of an $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2^+$ cation (R = CH_3) which, in conjunction with the known architectures of the neutral phenylmercapto analog[2] and other stereochemically related complexes,[3–10] provides definitive evidence that the iron–iron interaction in the above cation can be essentially described as a *one-electron metal–metal bond.* These results are of particular importance in that they imply the possibility that the geometries of the plant-like or bacterial-type ferredoxins, which have been shown to possess either *dimeric* or one (or two) *tetrameric* iron-sulfur systems,[11] may be markedly different with regard to the iron–iron distances in the oxidized and reduced forms.

This work was greatly stimulated by the extensive electrochemical studies of Dessy and coworkers[12] who

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(1) Previous paper in this series: N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7470 (1970).

(2) G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Commun.*, 1165 (1968).

(3) R. F. Bryan, P. T. Greene, D. S. Field, and M. J. Newlands, *ibid.*, 1477 (1969).

(4) O. S. Mills, *Acta Crystallogr.*, **11**, 620 (1958).

(5) N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, **91**, 5173 (1969).

(6) A. J. Carty, T. W. Ng, W. Carter, G. J. Palenik, and T. Birchall, *Chem. Commun.*, 1477 (1969).

(7) K. K. Joshi, O. S. Mills, P. L. Pauson, and B. W. Shaw, *ibid.*, 181 (1965).

(8) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(9) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.*, **11**, 599 (1958).

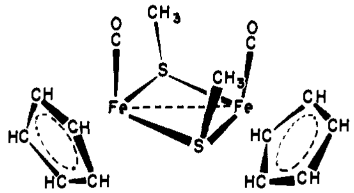
(10) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **91**, 761 (1969); **92**, 3342 (1970).

(11) (a) J. C. M. Tsibris, R. L. Tsai, I. C. Gunsalus, W. H. Orme-Johnson, R. E. Hansen, and H. Beinert, *Proc. Nat. Acad. Sci. U. S.*, **59**, 959 (1968); (b) W. H. Orme-Johnson, R. E. Hansen, H. Beinert, J. C. M. Tsibris, R. C. Matholomaus, and I. C. Gunsalus, *ibid.*, **60**, 368 (1968); (c) J. Kraut, G. Strahs, and S. T. Freer in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, New York, 1968, p 55; (d) D. O. Hall and M. C. W. Evans, *Nature (London)*, **223**, 1342 (1969); (e) W. H. Orme-Johnson, R. M. Sweet, M. Sundralingam, L. F. Dahl, and H. Beinert, submitted for publication.

showed that a number of ligand-bridged organometallic dimers (including $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2$) undergo reversible one-electron redox reactions. The resulting species were electrochemically generated and their properties determined in solution by Dessy, *et al.*[12] The $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$ cation was first chemically prepared and characterized by King and Bisnette[13] as the hexafluoroantimonate and hexafluorophosphate salts by oxidation of the neutral dimer with the corresponding silver salts. Our preparation of this cation was accomplished with either $AgBF_4$ or iodine to give on recrystallization from polar solvents dark green crystals as the BF_4^- or I_3^- salts. Solutions of these cationic complexes are moderately stable to air but slowly reduce on standing to the neutral complex. On addition of $NaBH_4$, however, reduction of the cation back to the neutral molecule is rapid. Elemental analysis and conductivity measurements in acetone are in good agreement with the formulation of this dimeric cation as a monocharged species. The infrared spectrum of the $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2I_3$ salt in KBr pellet exhibits a very strong carbonyl absorption band at 1998 cm^{-1} which expectedly is at a higher frequency than that of 1947 cm^{-1} (also from KBr pellet) for the neutral dimeric species. The solid-state magnetic moment of 1.70 ± 0.05 BM per dimer at ambient room temperature[14] is a normal spin-only value for a first-row transition metal complex containing one unpaired electron. In addition, the esr spectral parameters measured in CH_2Cl_2 solution are in good agreement with those of Dessy and coworkers,[12] the isotropic g value being 1.998 and the line width 7 G.

The $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2BF_4$ salt crystallizes with four formula species in a unit cell of dimensions $a = 12.106$ (1), $b = 11.859$ (1), $c = 12.832$ (2) Å. Systematic absences denote the allowable space groups as either $Aba2$ (C_{2v}^{17}, no. 41) (alternative nonstandard axial orientation, $C2ca$) or $Cmca$ (D_{2h}^{18}, no. 64). The intensities of 642 independent reflections were collected on a General Electric four-circle diffractometer by the θ–2θ scan technique with Mo Kα radiation. The noncentrosymmetric space group $Aba2$ was found from the structural determination to be the correct one with each of the four $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$ cations and each of the four BF_4^- anions per cell possessing crystallographic site symmetry C_2-2; this latter constraint is achieved by a crystal order–disorder phenomenon in which a crystallographic twofold axis is coincident with a threefold axis of each tetrahedral tetrafluoroborate anion. The mixed anisotropic–isotropic least-squares refinement has yielded an unweighted R_1 discrepancy value of 6.4% based on 581 absorption-corrected data with $I > 2.0\sigma(I)$.

The structure (Figure 1) of the $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2^+$ cation ($R = CH_3$) is comprised of two crystallographically identical $Fe(h^5\text{-}C_5H_5)(CO)$ moieties symmetrically linked to each other by two bridging mercapto ligands such that the two carbonyl groups and two sulfur-attached methyl groups are both cisoid.



$[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$

Figure 1. Architecture of the $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$ cation possessing crystallographic site symmetry C_2-2; its geometry experimentally has C_{2v}-$2mm$ symmetry. Important bond lengths are Fe–Fe, 2.925 (4); Fe–S, 2.233 (4) and 2.235 (4); Fe–CO, 1.79 (2); C–O, 1.16 (2); and S–CH_3, 1.84 (2) Å. The Fe–S–Fe and S–Fe–S angles are 81.8 (1) and 95.4 (1)°, respectively. The Fe–S–CH_3 angles are 112.4 (4) and 112.7 (5)°.

With the assumption of cylindrical symmetry for each cyclopentadienyl ring, the configuration of this cation experimentally conforms to C_{2v}-$2mm$ symmetry. This gross geometry is found to be similar to that previously determined by X-ray analysis[2] at $-160°$ for the neutral geometrical isomer $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2$ ($R = C_6H_5$). As also occurs in this neutral phenylmercapto molecule, the Fe_2S_2 system in the cation is somewhat nonplanar. The torsional angle between the two planes in the Fe_2S_2 system each formed by the two bridging S atoms and one Fe atom is 153°; the other torsional angle defined by the two planes each formed by two Fe atoms and one S atom is 156° in the cation compared to the reported values[2] of 161 and 164° for the two crystallographically independent molecules in crystalline $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2$.

The most striking difference between the geometries of the neutral and cationic species is the shortening of the iron–iron distance from a nonbonding value of 3.39 Å in the diamagnetic $[Fe(h^5\text{-}C_5H_5)(CO)(SC_6H_5)]_2$ molecule (*i.e.*, a closed-shell electronic configuration is achieved without the necessity of any Fe–Fe single-bond interaction) to a value of 2.925 (4) Å in the $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$ cation. This drastic decrease of 0.46 Å in the iron–iron distance is also reflected in a large distortion of the bridging Fe–S–Fe angle by 16° from a normal obtuse value of 98° in the neutral species to an acute angle of 81.8 (1)° in the paramagnetic cation.[15] It is especially significant that the iron–iron distance of 2.925 (4) Å in the cation in turn is 0.4 Å longer[16,17] than the iron–iron distances in the structurally related cisoid $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$

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[12] R. E. Dessy, R. Kornmann, C. Smith, and R. Hayter, *J. Amer. Chem. Soc.*, **90**, 2001 (1968); R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *ibid.*, **88**, 471 (1966).

[13] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

[14] Faraday magnetic measurements were kindly performed by Mr. Michael Camp.

[15] A general comparison of ligand-bridged molecules containing four-membered M_2B_2 bridged systems with and without M–M interactions has emphasized that metal–metal electron-pair interactions (as normally demonstrated by magnetic behavior) in ligand-bridged organometallic dimers generally give rise to significant molecular deformations detected by much sharper M–B–M bridging angles for such complexes compared to those for corresponding complexes not containing metal–metal interactions: L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

[16] A somewhat shorter metal–metal distance in carbonyl-bridged dimers compared to corresponding *electronically equivalent* mercapto-bridged dimers is expected due to the differences in size and in effective electronegativity[15,17] between the two-electron donating carbonyl carbon atoms *vs.* the three-electron donating mercapto sulfur atoms (*i.e.*, an expected contraction of approximately 0.1 Å is not unreasonable), but certainly not the observed decrease of 0.4 Å between the nonelectronically equivalent $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$ cation and the corresponding neutral carbon-bridged iron dimers. Hence, this Fe–Fe bond length shortening must be ascribed to the presence of the extra unpaired electron primarily in an *antibonding* metal σ-orbital combination in the cation.

[17] L. F. Dahl, W. R. Costello, and R. B. King, *J. Amer. Chem. Soc.*, **90**, 5422 (1968).

isomer (2.533 Å),[3,18] in the transoid $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$ isomer (2.49 (2) Å),[4,18] in the cisoid $[Fe(h^5\text{-}C_5H_5)(CO)(COAl(C_2H_5)_3)]_2$ adduct (2.49 (1) Å),[5,18] in the acetylenic diphosphine derivative $[Fe_2(h^5\text{-}C_5H_5)_2(CO)_3]_2[(C_6H_5)_2PC_2P(C_6H_5)_2]$ (2.54 Å),[6,18] and in the cisoid $[Fe_2(h^5\text{-}C_5H_5)_2(CO)_3(CNC_6H_5)]$ isomer (2.53 Å).[7,18] Expectedly, the Fe–Fe bond length is also longer and the bridging Fe–S–Fe angles are larger in the cation than those in the dimercapto-bridged $[Fe(CO)_3(SC_2H_5)]_2$ dimer (2.54 (1) Å, 68°),[8] in the dimercapto-bridged $[Fe(NO)_2(SC_2H_5)]_2$ dimer (2.720 (3) Å, 74°),[9] and in the dimercapto- and dithioxanthate-bridged $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$ dimer (2.61 (1) Å; bridging mercapto ligands, 72°).[10] In each of these above molecules a two-electron iron–iron bond is in accord with the observed diamagnetism.

This study thereby provides an operational test of our hypothesis (which motivated this research) that one may expect a dramatic decrease in the metal–metal distance of a dimeric complex containing no electron-pair metal–metal bond to a value intermediate between that of a "no bond" distance and a two-electron bond distance if the electron is removed from an MO which is *strongly* antibonding with respect to the two metal atoms. Hence from a qualitative viewpoint the $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2^+$ cation may simply be regarded as having *two* electrons in a *bonding* metal σ orbital combination and *one* electron in the corresponding antibonding combination. The resulting net metal–metal bond order (based on the Coulson definition[19]) is thereby 0.5, which, in valence-bond terminology, corresponds to a *one-electron metal–metal bond.*[20]

Acknowledgment. The authors are most pleased to acknowledge the financial support of this research by the National Institutes of Health (Grant No. 2-R01-AI07795-4). The use of the UNIVAC 1108 computer at the University of Wisconsin Computing Center was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation through the University Research Committee.

(18) The two crystalline isomers[3,4] of $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$ are cisoid and transoid with respect to the two terminal carbonyl groups (and two cyclopentadienyl rings). The $[Fe(h^5\text{-}C_5H_5)(CO)(COAl(C_2H_5)_3)]_2$ complex,[5] an aluminum triethyl adduct of $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$, has the two terminal carbonyl groups in a cisoid arrangement with an $Al(C_2H_5)_3$ coordinated to each of the two bridging carbonyl oxygen atoms. The $[Fe_2(h^5\text{-}C_5H_5)_2(CO)_3]_2[(C_6H_5)_2PC_2P(C_6H_5)_2]$ molecule[6] consists of two identical $Fe_2(h^5\text{-}C_5H_5)_2(CO)_3$ moieties each linked to a different phosphorus atom of the bridging $(C_6H_5)_2PC_2P(C_6H_5)_2$ ligand such as to give molecular symmetry C_i-1; the phosphorus atom and one terminal carbonyl group of each $Fe_2(h^5\text{-}C_5H_5)_2(CO)_3P$ fragment are cisoid. The $Fe_2(h^5\text{-}C_5H_5)_2(CO)_3(CNC_6H_5)$ isomer[7] possesses a cisoid orientation of two terminal carbonyl groups with one bridging carbonyl and one bridging isonitrile group. Each of these above five complexes, which differ in constitution from the $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2$ dimer by the replacement of the bridging mercapto three-electron donors with carbon-bridging two-electron donors (*viz.*, bridging CO, $COAl(C_2H_5)_3$, or isonitrile ligands), requires a two-electron Fe–Fe bond in order for each iron atom to achieve a closed-shell electronic configuration.

(19) C. A. Coulson, *Proc. Chem. Soc., Ser. A*, **169**, 413 (1938).

(20) It is noteworthy that the corresponding monocharged $[Mn(h^5\text{-}C_5H_5)(CO)(SR)]_2^-$ anion is isoelectronic with the $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2^+$ cation. Detailed stereochemical comparisons of these and other isoelectronic cations and anions are needed to give further insight concerning the correlation of the observed molecular features with electronic bonding models.

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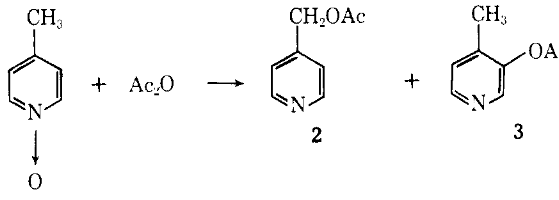
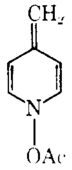
The Mechanism of the Reaction of 4-Picoline *N*-Oxide with Acetic Anhydride Studied by Nuclear Magnetic Resonance Spectroscopy

Sir:

Attempts to delineate the mechanism of the reaction between 4-picoline *N*-oxide (**1**) and acetic anhydride have so far not been completely successful.[1] According to the recent tracer studies utilizing ^{18}O-labeled acetic anhydride,[2] it appears almost conclusive that in the absence of solvents or in acetic acid, 4-acetoxymethylpyridine (**2**) and 3-acetoxy-4-methylpyridine (**3**) are formed by intermolecular rearrangement with nucleophilic attack of an acetate anion on the intermediate anhydro base **4**, as originally suggested by Berson and Cohen.[3] With the use of an equimolar amount of acetic anhydride in tenfold molar amounts of aromatic solvents, however, results were obtained which suggest operation of the predominantly intramolecular radical-pair process.[4] More recently, similar ester-forming rearrangement encountered in the reaction of **1** with phenylacetic anhydride was considered to indicate the nonradical paths,[5] because a phenylacetoxyl radical is even less stable than the exceedingly unstable acetoxyl radical and it is extremely unlikely that the former is capable of existence.[6] Cohen and Deets claimed further to have demonstrated the ionic mechanism by trapping the cationic intermediates in anisole and benzonitrile.[7]



1 **2** **3**



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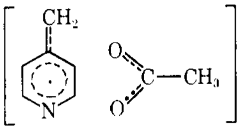

5

In this communication we report the observation of the chemically induced nuclear spin polarization during the reaction of **1** with acetic anhydride to give direct evidence for the radical pair **5**.[8]

(1) H. J. Shine, "Aromatic Rearrangements," Elsevier, Amsterdam, 1967, p 284; E. Ochiai, "Aromatic Amine N-Oxides," Elsevier, Amsterdam, 1967; A. R. Katritzky, *Quart. Rev., Chem. Soc.*, **10**, 395 (1956).

(2) S. Oae, T. Kitao, and Y. Kitaoka, *J. Amer. Chem. Soc.*, **84**, 3362 (1962).

(3) J. A. Berson and T. Cohen, *ibid.*, 77, 1281 (1955).

(4) S. Oae, Y. Kitaoka, and T. Kitao, *Tetrahedron*, **20**, 2685 (1964); V. J. Traynelis and A. I. Gallagher, *J. Amer. Chem. Soc.*, **87**, 5710 (1965).

(5) T. Cohen and J. H. Fager, *ibid.*, **87**, 5701 (1965).

(6) M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1962, p 156; L. Herk, M. Feld, and M. Swarc, *J. Amer. Chem. Soc.*, **83**, 2998 (1961); T. C. Vogt and W. H. Hamill, *J. Phys. Chem.*, **67**, 292 (1963); M. J. Goldstein, *Tetrahedron Lett.*, 1601 (1964).

(7) T. Cohen and G. L. Deets, *J. Amer. Chem. Soc.*, **89**, 3939 (1967).

(8) For a brief review, see H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969). More recent works: G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969); G. L. Closs and L. E. Closs, *ibid.*, **91**, 4549 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970); G. L. Closs, C. E. Double-