x⁻ = SbCl₆⁻

obtained in equimolar ratio from the addition of **5** to (*E*)-*tert*-butyl-*d₉*-*tert*-butylethylene. Dimethyl disulfide, which can catalyze the interconversion between **10** and **11**, is removed through coprecipitation of the two salts. A substantial secondary kinetic isotope effect ($k_H/k_D = 1.32$) is measured for the migration (in CD_2Cl_2 at 25 °C) of CH_3 in **10** and of CD_3 in **11** (monitoring the nonisochronous NMR *tert*-butyl resonances of the unseparated isotopic isomers). The same ratio is constantly found between selected NMR resonances of the rearranged thietanium ions **12** and **13**. The identity between the ratio of reagent conversion rates and the ratio of product distribution is a strong evidence for the selectivity of the processes described in eq 5 and 6.[12]
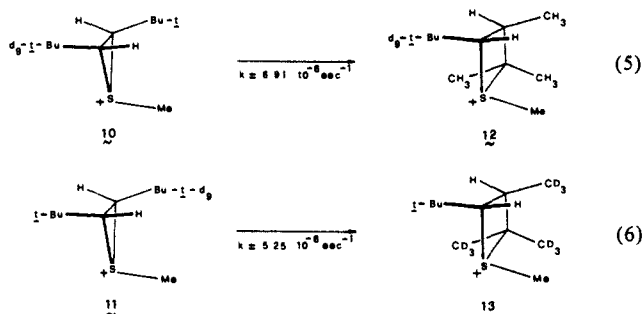
These experimental findings can be rationalized under the following assumptions.

(a) Methide migration and rupture of the C–S bond in thiiranium ion are concerted. A first step consisting in the nonassisted rupture of the C–S bond, i.e., a preequilibrium between thiiranium ion and corresponding open β-thiocarbocation, is inconsistent with the fact that thiiranium ions **6** and **7** do not interconvert and with the observed isotope effect. Furthermore, the methide migration at the level of open β-thiocarbocation would lead both to thietanium ion **8** and to the isomer with *tert*-butyl and migrated methyl on the same ring face.[13]

(b) The migration of methide group therefore occurs under SN2 type conditions. The restriction associated with this mechanism, i.e., the antiperiplanarity of migrating and leaving groups,[2] is not an exhaustive explanation for the observed specificity of the migration, which is limited to those units belonging to groups syn to the *S*-methyl group.

This novel type of selectivity may be associated with the fact that the leaving group, the methylthio moiety, lacks cylindrical symmetry around the bond to be broken, nor can it acquire this symmetry by rotation, which is hindered. This asymmetry is reflected in the region where the migration takes place. Alter-

natively, it may be argued that the methide migration can better assist the rupture of the weaker C–S bond, which is the one that supports the *tert*-butyl and *S*-methyl groups on the same side and hence is subjected to greater steric strain.

Further experimental and theoretical investigations aimed at the rationalization of the rearrangement mechanism are in progress.

Viable Geometries for T₁–S₀ ISC in Alkene Triplets

Richard A. Caldwell,*,† L. Carlacci,‡ C. E. Doubleday, Jr.,*,§
T. R. Furlani,*,⊥ H. F. King,*,‡ and J. W. McIver, Jr.*,‡

*Departments of Chemistry, The University of Texas at
Dallas, Richardson, Texas 75080
State University of Buffalo
Buffalo, New York 14214
Calspan Advanced Technology Center
Buffalo, New York 14225*

Received May 27, 1988

Acyclic alkenes, unless extensively conjugated, are expected to show energy maxima in the ground state and minima in the first triplet state at the perpendicularly twisted geometry (of symmetry D_{2d} for ethylene itself).[1-3] Since in this geometry the energies of S_0 and T_1 must be quite close, it has generally been assumed[4-8] that it represents the geometry at which T_1–S_0 intersystem crossing (isc) occurs if structural constraints do not prevent its attainment. There will be two factors, however, contributing to the rate of a radiationless process, of which energy gap is but one. The other is the intrinsic transition probability, in this case derived from the spin-orbit coupling (SOC) matrix element $\langle \Psi(T_1)|H_{so}|\Psi(S_0)\rangle$. The assumption that a minimized energy gap is the sole figure of merit by which isc rates as a function of geometry should be assessed is equivalent to the assumption of unchanging SOC in the range of feasible geometries. We have performed calculations of T_1–S_0 SOC for ethylene by the CAS-MCSCF technique previously described,[9] by using 2-in-2 CAS and the 3-21G basis set. Not only is the variation of SOC with geometry very large but also SOC *is nil at the D_{2d} geometry*. Since substitutions involving neither heavy atoms nor groups with lone pairs should not vitiate the qualitative trends of SOC with geometry we report here, we believe these results offer a useful framework for analysis of isc of olefin triplets more generally.

According to Salem,[10] T–S spin-orbit coupling in biradicals (we consider ethylene excited states as biradicaloids) requires both nonparallel orbitals and an ionic contribution to the singlet wave function, since with either parallel orbitals or a purely covalent

(1) Mulliken, R. S. *Phys. Rev.* **1932**, *41*, 751.
(2) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.
(3) Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys.* **1976**, *9*, 75. Brooks, B. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 307.
(4) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; p 25.
(5) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1196.
(6) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.
(7) Bonneau, R.; Herran, B. *Laser Chem.* **1984**, *4*, 151 and references therein.
(8) Goerner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835.
(9) Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577. Carlacci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. To include all three triplet sublevels we report SOC = $[|SOC(m_s = 1)|^2 + |SOC(m_s = 0)|^2 + |SOC(m_s = -1)|^2]^{1/2}$. This quantity both is invariant to the coordinate frame in which the calculation is done (the components, of course, are not) and is that which would be used (subject to a statistical factor of $1/(3^{1/2})$) in a Golden Rule calculation of the rate of isc of an equilibrated set of triplet sublevels.
(10) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

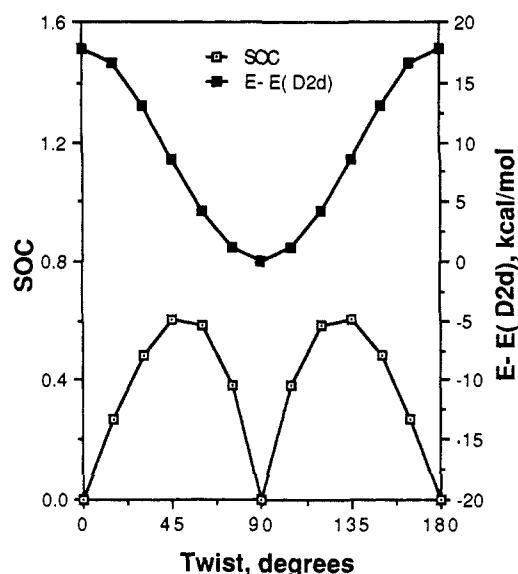6902   *J. Am. Chem. Soc., Vol. 110, No. 20, 1988*

Communications to the Editor

Figure 1. Spin orbit coupling (cm^{-1}) and MCSCF energy of T_1 as a function of the dihedral angle between the HCH planes. $R(C–C) = 1.48$ Å, $R(C–H) = 1.08$ Å, $\angle(HCH) = 120°$.

Figure 2. Spin orbit coupling (cm^{-1}) and MCSCF energy of T_1 as a function of pyramidalization away from the D_{2d} geometry at one center. Angle given is that between the HCH plane at the pyramidalized terminus and the C–C bond. Other geometries as in Figure 1.

singlet there can be no net change of orbital angular momentum as a result of the transition. Ionic character should increase with increasing overlap.[11] Although for ethylene D_{2d} singlet the orbitals of interest are perpendicular, a frequently unrecognized feature is that its wave function is purely covalent as a consequence of the symmetry and their orthogonality; T_1–S_0 SOC must therefore be zero for D_{2d} geometries.[12] Our calculations fully bear this out, the value of ca. 10^{-6} cm^{-1} we calculate being negligible and most likely representative of the roundoff errors in these numerically intensive computations.

Figure 1 summarizes our calculations for twisting. Zero SOC occurs at $0°$ (D_{2h}) and $90°$ (D_{2d}) twist angles. A maximum of ca. 0.6 cm^{-1} at ca. $50°$ twist represents the best tradeoff between achieving orbital perpendicularity and retaining ionic character to the singlet wave function. However, both the MCSCF triplet energy and the T_1–S_0 energy gap increase substantially as twisting diminishes. The latter is not shown but generally is 4–5 times $E - E(D_{2d})$. Achieving isc purely by torsion then would involve both low Boltzmann populations and large energy gaps for geometries in which SOC is largest.

Starting from the planar geometry, C_{2v} pyramidalization of $20°$ at both termini affords large SOC (1.36 cm^{-1}). Effectively, the AO's are hybrid orbitals and are no longer parallel. C_{2h} pyramidalization would retain the parallel feature and afford negligible SOC; our computations indeed give $<10^{-6}$ cm^{-1} for pyramidalization angles up to $60°$. The best geometry for isc in olefins constrained within five-membered or smaller rings thus resembles the former (sketched below), but of course the very large T_1–S_0 gap in such cases is well known to cause relatively slow isc regardless.

Pyramidalizations near the D_{2d} geometry of one or both of the termini give rise to modest SOC, as shown for one center pyramidalization in Figure 2. The very low energies associated with these motions demonstrate how flexible such species must be. S_0 and T_1 energy increases differ little upon pyramidalization. On energy and energy gap arguments, therefore, pyramidalizations represent potentially good geometric changes for inducing isc.
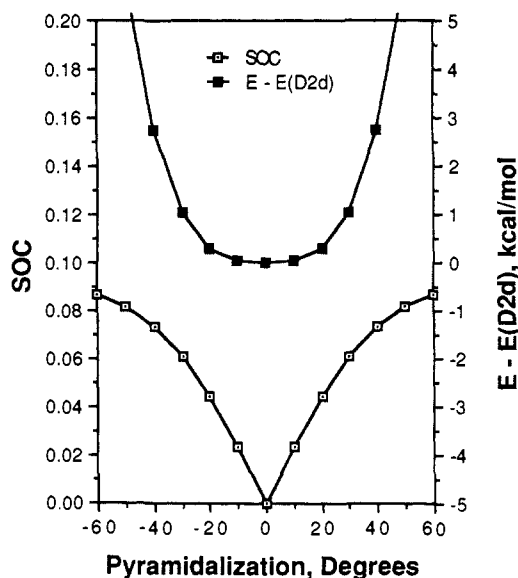
However, since even small changes from the D_{2d} twist angle induce larger SOC, we suggest that both modes usually contribute. For example, at $75°$ twist and $20°$ pyramidalization SOC is 0.48 cm^{-1}, the MCSCF energy is only ca. 1.3 kcal/mol above the D_{2d} geometry, and $E(T_1) - E(S_0)$ is only 5.2 kcal/mol. All pure twists between ca. $80°$ and $90°$ and all pyramidalizations away from D_{2d} up to ca. $25°$ at one end or $20°$ at both give $E - E(D_{2d}) < kT = 600$ cal/mol and $E(T_1) - E(S_0) < 3$ kcal/mol, which suggests a reasonable range of geometries for isc of unconstrained alkene triplets. It is well to remember that zero-point vibration will provide a non-D_{2d} geometry and thus SOC even at absolute zero.

While absolute predictions of ISC rates would be desirable, they depend on a complex Franck–Condon calculation and are not yet available. We do, however, note that the analysis of Salem and Rowland,[10] which associates SOC in the range of 0.1–1 cm^{-1} with intersystem crossing rates of 10^{-8}–10^{-6} s^{-1} for isc between arene excited states and for isc in $1,3$-^{9} and $1,4$-biradicals, could be applied to alkene T_1–S_0 isc also. Since known isc rates in alkene triplets are in just this range,[4–8] the magnitude of SOC we find is reasonably in accord with experiment.

The premise that intersystem crossing requires distortion away from a perpendicular structure of the triplet demands study of constrained species for validation. There are some results in the literature already, however, which lend it support. The trend to longer alkene triplet lifetime with increasing substitution at the double bond[5,6] could be due to steric restriction, which increases with substitution, of torsion away from perpendicularity and/or of pyramidalization. The remarkably short (250 ns) lifetime of the norbornene triplet and the large energy associated with its relaxation[13] might have to do with pyramidalization, suggested by Arnold and Abraitys[14] to rationalize chemical processes of norbornene triplet. Finally, the substantial yield of trans isomer (0.36) in the decay of phenylcyclohexene triplet[15] and the rather short (67 ns) lifetime cannot be accommodated by twisting since the ring constraints prohibit a $90°$ twist angle. However, pyramidalization as shown below provides both SOC and a geometry in which the T_1–S_0 gap should be small. In this geometry the molecule is able with only slight distortion of the phenyl-bearing center to decay either to cis or trans.
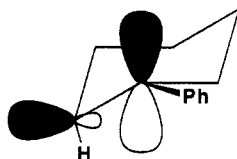
(11) The relevance of ionic character in CAS-MCSCF calculations was discussed briefly in ref 9.

(12) These facts were alluded to briefly in ref 10.

(13) Barwise, A. J. G.; Gorman, A. A.; Rodgers, M. A. J. *Chem. Phys. Lett.* **1976**, *38*, 313.

(14) Arnold, D. R.; Abraitys, V. Y. *Mol. Photochem.* **1970**, *2*, 27.

(15) Goodman, J. L.; Peters, K. S.; Misawa, H.; Caldwell, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 6803. See also ref 7.

Further computational studies of SOC in substituted olefins are underway, as are experimental studies of constrained olefins which the present calculations point out as good tests. In particular the role of pyramidalizations deserves more scrutiny than it has hitherto received.

Transition-Metal-Based Reagents for Molecular Recognition: Hydrogen-Bonding Properties of Tungsten(II) *cis*-Amino Halides

Carolyn E. Osterberg, Atta M. Arif, and Thomas G. Richmond*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received May 16, 1988

Hydrogen bonding frequently plays a central role in the process of molecular recognition. This is evidenced in numerous biochemical systems as well as in attempts by synthetic chemists to elucidate the molecular basis for recognition.[1] The design of new types of receptors has largely involved organic molecules[2] although literature reports noting the occurrence of hydrogen bonding in transition-metal coordination[3] and organometallic compounds[4] have appeared. Herein we report that the bifunctional hydrogen bonding capabilities of a series of tungsten(II) *cis*-amino halides provide a binding site for complementary organic substrates such as lactams and nucleosides. The interactions of metal complexes with biological molecules are important in the design and elucidation of the chemotherapeutic action of selective metal-based drugs.[5]

We have previously reported the preparation of seven-coordinate tungsten(II) complexes by chelate assisted oxidative addition of aromatic C–X (X = F, Cl, Br, I) bonds to tungsten(0).[6]

Scheme I

1: X = F, R = F
3: X = Cl, R = H

Spectroscopic and crystallographic analysis of **1** suggested that the coordinated fluoride could function as a hydrogen bond acceptor and that the relatively acidic hydrogens on the primary amine could act as hydrogen bond donors. This is evidenced in the head-to-tail dimerization observed in the solid-state structure of **1**·THF.[6a]

We have investigated the ability of **1** to bind complementary organic substrates in solution by recording ^{1}H and ^{19}F NMR spectra as a function of substrate concentration. For solubility reasons, experiments were conducted in the relatively polar solvent acetone. The concentration independent chemical shifts of **1** in acetone indicate that **1** is monomeric in solution. Upon addition of δ-valerolactam (val),[7] the NH protons of **1** and val shift downfield and the ^{19}F NMR resonance of the fluoride bound to tungsten shifts upfield as the val concentration is increased and **1**·val is formed (Scheme I). Binding constants were calculated from ^{19}F NMR titration data by using an iterative nonlinear least-squares procedure.[8] Linear Scatchard plots[9] for the fluorine resonance and for the proton resonance H_a covering the observable (ca. 80%) portion of the binding isotherm are consistent with the formation of a 1:1 adduct with K_1 = 4.5 M^{-1} at 25 °C. Variable temperature equilibrium measurements[9e] gave ΔH = −2.1 ± 0.4 kcal/mol and ΔS = −3.9 ± 0.2 eu. This simple model is undoubtedly perturbed by interaction of free val with H_b and by val self-association.[7] However, the related *N*-phenyl-substituted complex **2**[10] shown below exhibits similar binding parameters. The

2 · val

K_2 (25 °C) = 2.1 M^{-1}
ΔH = −1.8 ± 0.1 kcal/mole
ΔS = −4.6 ± 0.1 eu

(1) (a) Rebek, J., Jr. *Science (Washington, D. C.)* **1987**, *235*, 1478. (b) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (c) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039. (d) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487.
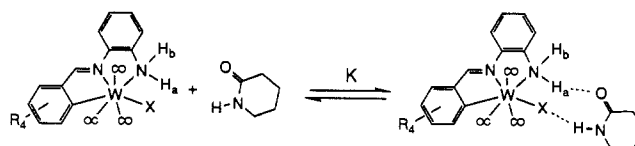
(2) (a) Kilburn, J. D.; MacKenzie, A. R.; Still, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 1307. (b) Chang, S. K.; Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 1318. (c) Wilcox, C. S.; Greer, L. M.; Lynch, V. *J. Am. Chem. Soc.* **1987**, *109*, 1865.

(3) (a) Chatt, J.; Duncanson, L. A.; Venanzi, L. M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 67. (b) Massa, W.; Babel, D. *Chem. Rev.* **1988**, *88*, 275. (c) Perry, D. L.; Ruben, H.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1980**, *19*, 1067. (d) Strauss, S. H.; Abney, K. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 2806. (e) van Driel, G. J.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 2919. (f) Hughes, D. L. *Acta Crystallogr., Sect. B* **1981**, *37*, 557. (g) Aoyama, Y.; Yamagishi, A.; Asagawa, M.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1988**, *110*, 4076. (h) Antolini, L.; Benedetti, A.; Fabretti, A. C.; Giusti, A. *Inorg. Chem.* **1988**, *27*, 2192. (i) van Staveren, C. J.; van Eerden, J.; van Veggel, F. C. J. M.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4994.
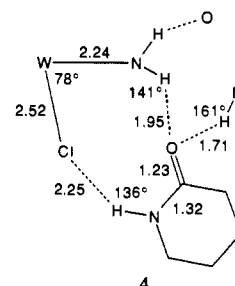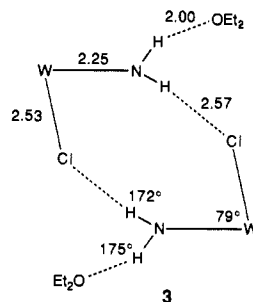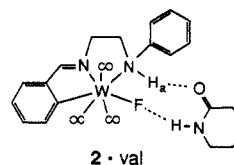
(4) (a) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803. (c) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7238. (d) Andrews, M. A.; van Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7245. (e) Sartorelli, U.; Garlaschelli, L.; Ciani, G.; Bonora, G. *Inorg. Chem. Acta* **1971**, *5*, 1971. (f) Fawzi, R.; Hiller, W.; Lorenz, I. P.; Mohyla, J.; Zeiher, C. *J. Organomet. Chem.* **1984**, *262*, C43.

(5) (a) Kopf-Maier, P.; Kopf, H. *Chem. Rev.* **1987**, *87*, 1137. (b) Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153. (c) Dervan, P. B. *Science (Washington, D. C.)* **1986**, *232*, 464. (d) Barton, J. K. *Science (Washington, D. C.)* **1986**, *232*, 727. (e) Basile, L. A.; Barton, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7548.

(6) (a) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091. (b) Richmond, T. G.; King, M. A.; Kelson, E. P.; Arif, A. M. *Organometallics* **1987**, *6*, 1995. (c) Poss, M. J.; Arif, A. M.; Richmond, T. G. *Organometallics* **1988**, *7*, 1669.

(7) Self-association of δ-valerolactam has been investigated in nonpolar solvents: (a) Tsuboi, M. *Bull. Chem. Soc. Jpn.* **1951**, *24*, 75. (b) Purcell, J. M.; Susi, H.; Cavanaugh, J. R. *Can. J. Chem.* **1969**, *47*, 3655. (c) Klemperer, W.; Cronyn, M. W.; Maki, A. H.; Pimentel, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 5846. (d) Krikorian, S. E. *Spectrochimica Acta* **1981**, *37A*, 745.

(8) (a) Shepodd, T. J.; Petti, M. A.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1983. (d) Barrans, R. E., Jr.; Dougherty, D. A., personal communication, **1988**.

(9) (a) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044. (b) Scatchard, G. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 660. (c) Connors, K. A. *Binding Constants*; Wiley: New York, 1987. (d) Binding isotherms and Scatchard plots are included as Supplementary Material. We report equilibrium constants obtained from ^{19}F NMR measurements since the NH resonances of 1–3 in the ^{1}H NMR are broad and at times obscured by the large excess of val present. (e) Determined over the temperature range −40 to 25 °C; uncertainty limits quoted are three standard deviations.

(10) Prepared by Dr. M. A. King, University of Utah, unpublished results, 1988.