difference between the various solvents used is polarity. Inspection of Table I shows that a clear ordering exists between the rate of singlet to triplet conversion and the polarity of the solvent, the rate being larger in the less polar solvents. As given in Figure 1, a linear correlation exists between the logarithm of the rate and the empirical solvent polarity parameter, $E_T(30)$.[7,8] We have also found that there is a modest decrease in k_{ST} as the temperature decreases. The observed temperature dependence of k_{ST} is, however, quantitatively accounted for by the change in polarity with temperature. This indicates that there is either no barrier, or a very small one, separating the singlet and triplet states. The absence of a significant activation energy argues against carbene-solvent complexes as a factor in the intersystem crossing process. It is also to be noted that no correlation of k_{ST} with solvent viscosity was found.

To understand the effects of solvent polarity it is helpful to consider the electronic nature of the singlet and triplet states. The singlet state being highly polar (in fact it is often described as zwitterionic[2]) will be strongly stabilized in polar solvents whereas the less polar triplet will only experience a weak stabilization. Thus, it is expected that the singlet-triplet energy gap, ΔE_{ST}, will decrease as the solvent polarity increases. This is confirmed experimentally, where it is found that there is a 1.5 kcal/mol decrease in ΔE_{ST} for DPC in acetonitrile compared to isooctane.[4b] Since intersystem crossing is dependent on the energy gap we note that the solvent polarity affecting ΔE_{ST} will lead to a solvent dependence in k_{ST}. The issue then is to understand the direction of the observed change.

In the domain of small energy gaps there are two potentially opposing factors. One is the density of accepting modes, which increases as the energy increases from 870 to 1400 cm^{-1};[4b] i.e., there are an increasing number of ways to make up the energy gap as well as the availability of new vibrational modes >870 cm^{-1}. Opposing this at some energy are the Franck-Condon factors, which will decrease as the energy increases.[9] The observed increase in k_{ST} as ΔE_{ST} increases argues in favor of the density of accepting modes as winning for this small energy gap case. For larger energy gaps one would anticipate that the Franck-Condon factors would dominate, and thus k_{ST} would decrease as ΔE_{ST} increases in line with what is commonly observed in large molecules.[9]

There is one other factor to be considered in the solvent dependence of k_{ST}, that being the effect of solvent on the expected difference[10] between the singlet and triplet geometries. If the difference between the geometries of the singlet and triplet, e.g., the phenyl-carbonyl-phenyl angle, changes with solvent then the Franck-Condon factors would also change, thus affecting the intersystem crossing rate. That this is probably not a dominant factor in the solvent dependence of k_{ST} is supported by the observed solvent effect (which appears to be similar to the one reported here for DPC) in the case of fluorenylidene,[6] which has a rigid structure.

We expect that the effect of solvent polarity on singlet-triplet energy relaxation will be general for other arylcarbenes in addition to fluorenylidene and diphenylcarbene. It is of interest that this is to our knowledge the only case where the rate of intersystem crossing increases as the energy gap increases, what we might call an inverse gap effect.

Acknowledgment. We acknowledge the generous support of the National Science Foundation, the Air Force Office of Scientific Research, and the Joint Services Electronic Program 29-82-K-0080. We also thank Prof. K. Dimroth and Prof. Chr. Reinchardt for the generous gift of pyridinium *N*-phenoxide betaine dye.

---

[7] (a) Reichardt, C. In "Molecular Interactions"; Ratajcak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; Vol. 3, pp 241-282. (b) Reichardt, C.; Harbusch-Gornert, E. *Leibigs Ann. Chem.* **1983**, 721-743. (c) Kamlet, M. J.; Abbound, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.***1981**, *13*, 485-630. (d) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253-3260.

[8] An equally good correlation is found by using a different solvent polarity index parameter, namely the *Z* solvent parameter that is based on the pyridinium iodide solvatochromic dye, as developed by Kosower.[7d]

[9] There can be an initial increase in the Franck-Condon factor with increasing energy prior to the expected decrease. For a general discussion of radiationless transitions some references are: (a) Robinson, C. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962-1973; *Ibid.* **1963**, *38*, 1187-1203. (b) Jortner, J.; Rice, S. A.; Hochstrasser, R. M. *Adv. Photochem.* **1969**, *7*, 149-309. (c) Heury, B. R.; Siebrand, W. In "Organic Molecular Photophysicis"; Birks, B. J., Ed.; Wiley: New York, 1973; Vol. 1, p 153. (d) Freed, K. In "Topics in Applied Physics", Fong, F. K., Ed., Springer-Verlag, 1976; Vol. 15, p 23.

[10] (a) Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 634-639. (b) Hoffman, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485-1499.

Unusual Metal-Metal Bonding in Transition-Metal Carbonyl Cluster Compounds. The Synthesis, Reactivity, and Crystal and Molecular Structure of $[Os_3(CO)_8(\mu_3\text{-}S)_2]_2$

Richard D. Adams* and István T. Horvath

Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received November 28, 1983

The 18-electron rule is widely recognized as one of the most fundamental precepts for understanding electronic structure and bonding in organometallic compounds.[1,2] In metal carbonyl cluster compounds the metal atoms usually achieve 18-electron configurations through the formation of metal-metal bonds in which a pair of electrons is shared between two nuclei.[3,4] However, recent studies of higher nuclearity clusters have revealed a growing number of compounds in which the bonding cannot be explained by these basic principles. The polyhedral skeletal electron pair theory has been developed[3-5] and can explain the bonding of most of these anomalies, yet all new examples of this unusual bonding are a source of curiosity, in general, and a challenge to both the theorist and the practicing chemist.

We now wish to report the synthesis, structure, and some reactions of the new compound $[Os_3(CO)_8(\mu_3\text{-}S)_2]_2$ (I) which exhibits this anomalous bonding in a most surprising and dramatic fashion. Compound I is formed in 34% yield when solutions of $Os_3(CO)_9(\mu_3\text{-}S)_2$,[6] (II) are exposed to UV irradiation under a rapid purge with nitrogen. The molecular structure of I was determined by single-crystal X-ray diffraction techniques,[8,9] and an ORTEP diagram of it is shown in Figure 1.[10] The molecule consists of an extended array of six osmium atoms with four triply bridging sulfido ligands. A central group of four metal atoms, Os(1)-Os(4),

---

[1] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; Chapters 3 and 25.

[2] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 2.

[3] Johnson, B. F. G.; Benfield, R. E. In "Topics in Inorganic and Organometallic Stereochemistry"; Geoffroy, G., Ed.; Wiley: New York, 1981.

[4] Wade, K. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: Chichester, 1980.

[5] Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1.

[6] Adams, R. D.; Horvath, I. T.; Segmuller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301.

[7] Compound 1 is dark green and was isolated in 34% yield by TLC on silica gel with hexane/CH_2Cl_2 (90/10) solvent. IR ν(CO) cm^{-1} in CH_2CL_2: 2093 vs, 2078 vs, 2030 vs, 2021 sh, 2013 m, 2009 m, 1923 w.

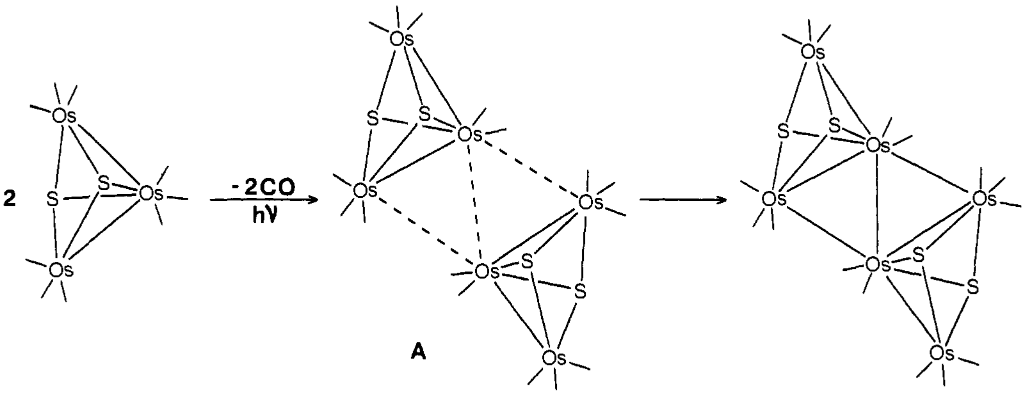
[8] Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer by using MO $K\bar{\alpha}$ radiation and the ω-scan technique. All calculations were performed on a Digital Equipment Corp. PDP 11/45 computer by using the Enraf-Nonius SDP program library, version 18.

[9] Space group $P2_1/n$, $a = 13.880$ (4) Å, $b = 12.061$ (4) Å, $c = 18.168$ (5) Å, $\beta = 106.43$ (2)°, $V = 2917$ (3) Å^3, $Z = 4$, $\rho_{calc} = 3.91$ g/cm^3. The structure was solved by direct methods (MULTAN, 220 reflections, $E \geq 2.05$). After correction for absorption, full-matrix least-squares refinement (2942 reflections, $F^2 \geq 3.0\sigma(F^2)$ yielded the residuals $R = 0.067$, $R_w = 0.079$.

[10] Selected interatomic distances (Å) and angles (deg) for I are as follows: Os(1)-Os(2) = 2.834 (1), Os(1)-Os(3) = 2.973 (1), Os(1)-Os(4) = 2.941 (1), Os(2)-Os(3) = 2.957 (1), Os(2)-Os(4) = 2.971 (1), Os(1)-Os(5) = 2.789 (1), Os(2)-Os(6) = 2.792 (1); Os(3)-Os(1)-Os(4) = 109.60 (4), Os(3)-Os(2)-Os(4) = 109.23 (4), Os(3)-Os(1)-Os(5) = 132.00 (4), Os(4)-Os(2)-Os(6) = 132.09 (4).

0002-7863/84/1506-1869$01.50/0

Scheme I



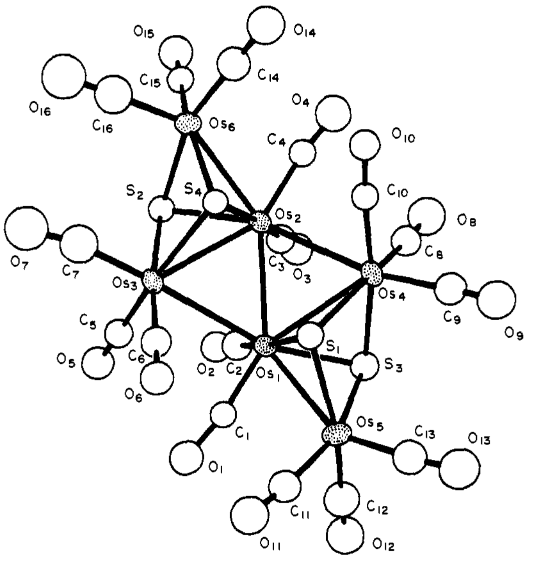


Figure 1. ORTEP diagram of $[Os_3(CO)_8(\mu_3\text{-}S)_2]_2$ (I) showing 50% probability thermal ellipsoids.

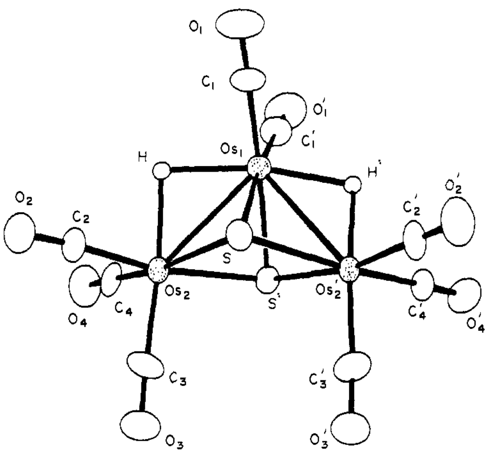


Figure 2. ORTEP diagram of $H_2Os_3(CO)_8(\mu_3\text{-}S)_2$ (III) showing 50% probability thermal ellipsoids.

adopts the form of a butterfly tetrahedron. The dihedral angle between the planes Os(1), Os(2), Os(3) and Os(1), Os(2), Os(4) is 136.3°. The two remaining metal atoms are linked to the central cluster at the "hinge" atoms, one to each, via a metal–metal bond and the bridging sulfido ligands. The shortest metal–metal bonds are those involving the external metal atoms, Os(1)–Os(5) = 2.789 (1) and Os(2)–Os(6) = 2.792 (1) Å. The shortest metal–metal bond in the central cluster is the hinge bond Os(1)–Os(2) = 2.834 (1) Å. The metal–metal bonds around the periphery of the central cluster are significantly longer and range from 2.941 (1) to 2.973 (1) Å. The Os–Os bond distance in $Os_3(CO)_{12}$ is 2.877 (3) Å.[11] The triply bridging sulfido ligands are arranged in pairs along diametrically opposed edges of the central cluster and extend to each of the external metal atoms. The hinge atoms of the cluster each contain two linear terminal carbonyl ligands. The other metal atoms each have three.

An alternative way of describing I is that of tail-to-tail coupling A, of two $Os_3(CO)_8(\mu_3\text{-}S)_2$ units formed by the loss of a carbonyl ligand from the central metal atom of II (Scheme I). The two triosmium units are then joined through the formation of *three* new osmium–osmium bonds. In compound II all the metal atoms contain 18-electron configurations; however, these configurations cannot be maintained in I if the newly formed bonds are of a two-center two-electron type. The bonding could be rationalized by a delocalization process which places the two "excess" electrons in a low-lying antibonding orbital. Indeed, the greater length of the four metal–metal bonds around the periphery of the central cluster could be an indicator of this.[12] Electronically, the cluster $(C_5H_5)_3Co_3(\mu_3\text{-}S)_2$ also contains two electrons in excess of the requirements of the 18-electron rule. It was proposed that these electrons occupy a low-lying antibonding orbital, and it was also observed that the Co–Co distances were approximately 0.2-Å longer than those of related electron precise clusters.[13] The UV-vis spectrum of II contains a low-energy absorption at 600 nm (ϵ = 1260), which is not present in the spectrum of I and could be a result of the delocalized metal–metal bonding.

It has been found that compound I is an unusually reactive molecule and readily engages in reactions that lead to cleavage of the three unsupported metal–metal bonds. For example, in heptane solution I reacts with CO (1 atm/98 °C, 3 h) to regenerate II quantitatively. At 110 °C I reacts with H_2 (1 atm) to form the new compound $H_2Os_3(CO)_8(\mu_3\text{-}S)_2$ (III).[14] The molecular structure of III was determined by single-crystal X-ray diffraction techniques, and an ORTEP diagram of it is shown in Figure 2.[8,15] This molecule consists of an "open" triangle of three osmium atoms with two triply bridging sulfido ligands.[16] A

---

[11] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[12] The central cluster of four metal atoms contains 64 electrons. The observed geometry is in accord with the skeletal electron pair theory if the shape of this cluster is viewed as a pentagonal bipyramid with three vertices missing. However, this theory does not account for the selective lenghening of the metal–metal bonds about its periphery.

[13] Frish, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082.

[14] Compound III is yellow and was obtained in 66% yield from solutions of I refluxed in heptane under 1 atm H_2 for 6 h. III was isolated by TLC on silica gel using hexane/CH_2Cl_2 (85/15) solvent. IR ν(CO) in CH_2Cl_2: 2116 w, 2096 s, 2033 vs, 2026 sh, 1964 w. ^1H NMR ($CDCl_3$) −13.65 ppm.

[15] Space group $C2/c$, a = 12.019 (4) Å, b = 12.323 (8) Å, c = 11.217 (4) Å, β = 115.41 (3)°, V = 1500 (2) Å^3, Z = 4, ρ_{calcd} = 3.81 g/cm^3. The structure was solved by direct methods (MULTAN, 144 reflections, $E \geq 1.79$). After correction for absorption, full-matrix least-squares refinement (903 reflections, $F^2 \geq 3.0\sigma(F^2)$ yielded the residuals R = 0.048 and R_w = 0.063.

[16] Selected interatomic distances (Å) and angles (deg.) for III are as follows: Os(1)–Os(2) = 2.802 (1), Os(2)···Os(2′) = 3.707 (1), Os(1)–S = 2.428 (4), Os(2)–S = 2.414 (4), Os(2)–S′ = 2.425 (4); Os(2)–Os(1)–Os(2′) = 82.84 (3).

hydride ligand bridges each of the two metal–metal bonds.

The details of the nature of the delocalized bonding in clusters such a I remains to be established, but this bonding could have an important influence on the reactivity of the compounds and could lead to the development of new reaction processes that are characteristic of multinuclear metal centers.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract DE-AC02-78ER04900. We thank Engelhard Industries for a loan of osmium tetraoxide.

Supplementary Material Available: Tables of final fractional atomic coordinates, thermal parameters, interatomic distances, angles and structure factor amplitudes are available for structures I and II (26 pages). Ordering information is given on any current masthead page.

Remarkable, Contrasteric, Electrocyclic Ring Opening of a Cyclobutene[1]

William R. Dolbier, Jr.,* and Henryk Koroniak

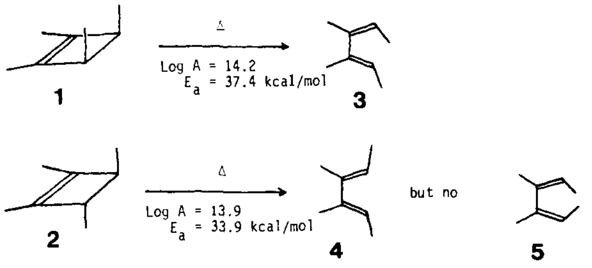
Department of Chemistry, University of Florida
Gainesville, Florida 32611

Donald J. Burton,* A. R. Bailey, G. S. Shaw, and S. W. Hansen

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

Received December 1, 1983
Revised Manuscript Received February 4, 1984

The earliest examples of electrocyclic cyclobutene ring opening, which demonstrated unambiguously the orbital symmetry control of such reactions, derived from Criegee's elegant studies of the *cis*- and *trans*-1,2,3,4-tetramethylcyclobutenes (**1** and **2**).[2] In the case of the cis isomer, **1**, the *E*,*Z*-diene **3** was the only product



that could have been formed by conrotatory ring opening. On the other hand, conrotatory ring-opening of the trans isomer, **2**, could have formed either the observed *E*,*E*-isomer **4** or the unobserved *Z*,*Z*-isomer **5**. The exclusive formation of **4** has been uniformly attributed to probable repulsive steric interactions that would be present in the transition state for formation of **5** due to the two methyl substituents rotating simultaneously inward. This argument has been uniformly applied to rationalize similar results in virtually all electrocyclic ring-opening reactions of cyclobutenes.

We wish to report kinetic and thermodynamic studies of the *cis*- and *trans*-perfluoro-3,4-dimethylcyclobutene system (**6** and **7**), which open this interpretation to serious doubt since the trans isomer, **7**, ring opens to the *Z*,*Z*-diene **9** with an activation energy ~18 *kcal less* than it ring opens to the *E*,*E*-diene **10** ($k_{ZZ}/k_{EE} = 1.9 \times 10^9$ at 111.5 °C).

Table I. Thermodynamic Parameters[a]

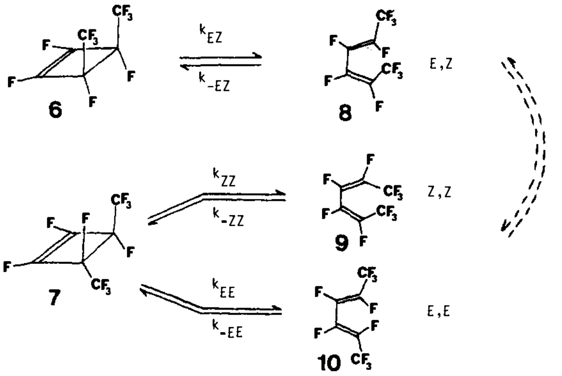
	6 (cis)	7 (trans)	8 (*E*,*Z*)	9 (*Z*,*Z*)	10 (*E*,*E*)
$\Delta H°$ [b]	2.5	0	7.7	7.2	8.3
ΔS [c]	0.5	0	12.8	11.0	12.1

[a] All thermodynamic parameters are given relative to 7. [b] In kcal/mol. [c] In cal/deg.

Table II, Kinetic Parameters

	Log *A*	E_a [a]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	mean *T*, °C
k_{ZZ}	12.6 (0.3)	30.5 (0.5)	29.8	−3.1	93.8
k_{-ZZ}	10.2 (0.3)	23.2 (0.5)	22.5	−14.0	93.8
k_{EE}	14.2 (0.4)	49.7 (0.8)	48.6	3.5	257.8
k_{-EE}	11.6 (0.4)	41.4 (0.8)	40.4	−8.6	257.8
K_{EZ}	14.6 (0.2)	39.6 (0.4)	38.7	5.5	207.8
k_{-EZ}	11.9 (0.1)	34.4 (0.3)	33.5	−6.9	207.8

[a] In kcal/mol. [b] In cal/deg.



The thermal equilibrations **6** ⇄ **8**, **7** ⇄ **9**, and **7** ⇄ **10** were examined kinetically over the temperature ranges 199.25–217.0, 76.5–111.5, and 240.75–272,5 °C, respectively, yielding the thermodynamic and kinetic parameters in Tables I and II. All equilibria were actually examined starting from the respective dienes[3] since in each case the cyclobutenes were strongly favored thermodynamically. Rate data for the *leakage* process from the **7**, **9**, **10** system to the **6**, **8** system could not be determined with great precision, but the approximated E_a (42 kcal/mol) is consistent with the process involving a double-bond isomerization process (**10** ⇄ **8**).[6]

The contrast of these results with those of the methyl-substituted cyclobutenes is both dramatic and remarkable. Moreover there is not a simple explanation for this anomaly. Since the results are clearly contrary to expectations based upon the oft-quoted "steric" argument, the whole use of steric effects to explain the methyl-derivative results must be called into question. Theoreticians have projected a probable cisoid but skewed geometry, with

---

[1] Taken in part from: Shaw, G. S. Ph.D. Thesis, University of Iowa, Iowa City, Ia, 1981. Reported in part (D. J. Burton, G. S. Shaw, and S. W. Hansen) at the 6th Winter ACS Fluorine Conference, Daytona Beach, Florida, Feb 1983.

[2] (a) Criegee, R.; Noll, K. *Liebigs Ann. Chem.* **1959**, *627*, 1; *Chem. Ber.* **1965**, *98*, 2339. (b) Branton, G. R.; Frey, H. M.; Skinner, R. F. *Trans. Faraday Soc.* **1966**, *62*, 1546.

[3] Dienes **8**, **9**, and **10** were synthesized by coupling of (*E*)- and (*Z*)-perfluoroprop-1-enylcopper reagents with (*E*)- and (*Z*)-perfluoro-1-iodopropene.[4] They were characterized by their ^{19}F NMR, IR, and UV spectra, with the unambiguous *E* vs. *Z* determination deriving from the well-precedented[5] and distinctive 145 and 5.1 Hz $J_{F_2F_3}$ values obtained for **10** and **9**, respectively.

[4] Burton, D. J., Bailey, A. R., unpublished results.

[5] (a) Hirao, K.; Nakatsuji, H.; Kato, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1972**, *94*, 4078. (b) Flynn, G. W.; Matsushima, M.; Baldeschwieler, J. D.; Craig, N. C. *J. Chem. Phys.* **1963**, *38*, 2295.

[6] (a) Rabinovitch, B. S.; Michel, K. W. *J. Am. Chem. Soc.* **1959**, *81*, 5065. (b) Schlag, E. W.; Kaiser, E. W., Jr. *Ibid.* **1965**, *87*, 1171. (c) Doering, W. v. E.; Beasley, G. H. *Tetrahedron* **1973**, *29*, 2231.