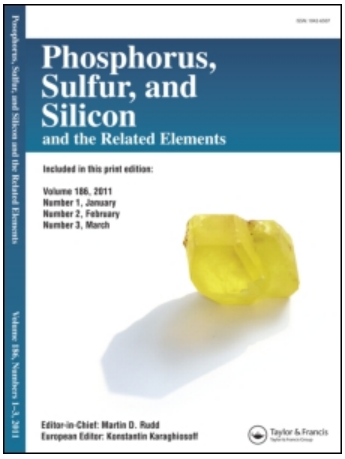

Phosphorus, Sulfur, and Silicon and the Related Elements

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Memoirs of Professor James Cullen Martin

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Memoirs of Professor James Cullen Martin

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Waseda University, Shinjuku-ku, Tokyo, Japan

The invitation by the organizing committee of ISOCS-21, which was held in Madrid, July 2004, to address the memorial speech for the late Professor James C. Martin reminded me at once of his gentle and generous character and his great contributions to the chemistry of hypervalent molecules. Although he died in April 1999, I believe that it is still appropriate to do so and also I am heartily honored by the invitation. As a Japanese chemist, I do not know the formal European tradition of the memorial speech, the memoirs consists of two parts, that is, the first part is dedicated to his personal history and the second one describes short history and back ground of the chemistry of hypervalent compounds and is devoted mainly to the accomplishment of J. C. Martin. Here, all the materials I used for the speech are shown accompanied by some short comments.

Keywords 10-C-5; σ-aromaticity; hypervalent; periodinane; phosphorane; sulfurane; three center-four electron bond

PART I: JAMES CULLEN MARTIN: THE RE-FOUNDER AND THE LEADER OF THE CHEMISTRY OF ORGANIC HYPERVALENT COMPOUNDS (NONMETALS)

Date and Place of Birth: January 14, 1928 Dover, Tennessee, USA
Date and Place of Death: April 20, 1999 Tampa, Florida, USA
Date and Place of Memorial Service: May 7, 1999 Dover, Tennessee, USA

Family: two sisters; married to June and had five sons and five grandchildren

Received June 1, 2005; accepted June 20, 2005.

I heartily acknowledge the help of the Professors Gregory S. Giorami of University of Illinois and Ned A. Porter of Vanderbilt University; they sent me detailed documents on Professor James C. Martin. I also acknowledge the eldest son of J. C., *i.e.*, Professor Joseph V. Martin, who is now at Rutgers University for providing, a variety of private and family photos.

Thank you very much for your kind attention.

Address correspondence to Kin-Ya Akiba, Graduate School and Advanced Research Center, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan. E-mail: akibaky@waseda.jp

Education

U.S. Army, 1946–1950 (stayed in a certain district of Kyoto City, Japan as a cultural liaison after World War II)
BA: Vanderbilt University, 1951
MS: Vanderbilt University, 1952 (Prof. D. E. Pearson)
PhD: Harvard University, 1956 (Prof. P. D. Bartlett)

Professional Experience

Instructor of Organic Chemistry, University of Illinois, 1956–1959
Assistant Professor of Organic Chemistry, University of Illinois, 1959–1962
Associate Professor of Organic Chemistry, University of Illinois, 1962–1965
Professor of Organic Chemistry, University of Illinois, 1965–1982
Distinguished Professor of Chemistry, Vanderbilt University, 1985–1992

Research Activity

Search by SciFinder Scholar: 155 reports
J. Am. Chem. Soc.: 99; *J. Org. Chem.*: 22; *Tetrahedron Letters:* 4; Others: 30 (including *Heteroatom Chem.*: 4; *Science*: 2)
Hence, Professor Martin published most of his research results in journals published by the American Chemical Society.

Classification of Papers According to the Research Theme

The first paper: D.E. Pearson, J.F. Baxter, and J.C. Martin, *J. Org. Chem*., **17,** 1511 (1952) (Vanderbilt: Hammett $\sigma+$ in certain electrophilic reactions)
The second paper: J. C. Martin and P. D. Bartlett, *JACS* **79,** 2533 (1957) (from Harvard Univ.: solvolysis, σ-participation to carbocation in 1,4-endocyclohexanes)
Anchimerically Accelerated Bond Homolysis: 7; from *Chem. & Ind.*, 192 (1959) to *JACS*, **96,** 3319 (1974). The first research project started in Illinois, which laid the fundamental basis of his research.
Sulfuranes: 55 from I, *JACS*, **93,** 2339 (1990) to *JACS*, **112,** 1637 (1990). In 1971, Prof. Martin wrote four communications in *JACS* and started his contribution to the chemistry of hypervalent molecules.
Hypervalent Iodine Compounds: 11 from *JACS*, **100,** 300 (1990) to *Tetrahedron Letters*, **36,** 9117 (1995).

Hypervalent Phosphorus Compounds: 14 from *JACS*, **100,** 5229 (1990) to *Phosphorus, Sulfur, and Silicon*, **76,** 347 (1993).
Hypervalent Silicon Compounds: 8 from *JACS*, **104,** 309 (1990) to *Tetrahedron*, **53,** 10133 (1997).
Hypervalent Pentacoordinate Carbon: 7 from *JACS*, **95,** 2565 (1990) to *Heteroatom Chem.*, **4,** 137 (1993). Martin kept his interest in stabilizing the transition state of SN_2 for more than 20 years.
σ-Aromaticity: 2 from *JACS*, **110,** 5827 (1990) to *Pure & Appl. Chem.*, **62,** 547 (1990).
Others; Hypervalent Non-Metals; include B, F, Ge, Br, and Te compounds.

Senior Fellowships and Awards

Alfred P. Sloan Foundation Fellow, 1962–1966
John Simon Guggenheim Memorial Fellow, 1966
Alexander von Humboldt Foundation U.S. Senior Scientist Award, 1979
Buck-Whitney Medalist, 1979
Fellow of the American Association for the Advancement of Science, 1980
Fellow of the Japan Society for the Promotion of Science (cooperative research with Kin-ya Akiba, Hiroshima University, supported by NSF and JSPS), 1982
Alexander von Humboldt Foundation, Reinvitation Award, Braunschweig, Germany

SCIENCE/TECHNOLOGY

May 29 and 30, 1992, Vanderbilt University
C & EN News, 1992, September 7, 32

established by use of new types of ligands. Gathered with Martin are (left to right, along wall) Peter Livant of Auburn University; Wesley Bentrude of the University of Utah; Thomas Fisher of Mississippi State University; John Verkade of Iowa State University; William McEwen of the University of Massachusetts; Yohsuke Yamamoto of Japan's Hirosha University; Howard Hargis of Auburn University; Peter Beak of the University of Illinois, Urbana-Champaign; (middle) Alan Cowley of the University of Texas; Gary Schuster of the University of Illinois, Urbana-Champaign; (front) Martin; Anthony Arduengo of Du Pont Central Research Laboratory, Wilmington; and Yorke Rhodes of New York University. Speakers not pictured were James Franz of Battelle Pacific Northwest Laboratory, Richland, Wash.; and Clifford Dykstra of Indiana-Purdue University, Indianapolis.

Symposium honors Vanderbilt's J. C. Martin

Speakers at a symposium titled "From σ Constants to σ Aromaticity" gather around Vanderbilt University professor of chemistry James Cullen Martin, in whose honor the symposium was held. The event, presented by the university's chemistry department, brought together former students, postdoctoral fellows, and friends, who paid tribute to 40 years of publication by Martin. Martin's earlier work in free-radical chemistry gave the first evidence for neighboring-group participation in peroxide decompositions forming radicals. His more recent research has focused on synthesis of novel hypervalent main-group element species, with stability

FIGURE 1 Photo taken at the author's office in Hiroshima and that of J.C. Martin Symposium at Vanderbilt reported in *C & EN News*.

FIGURE 2 Photo taken at Illinois.

Memorial Activity and Articles

From σ constant to σ Aromaticity: A Symposium in honor of 40 years of publication. J.C. Martin, May 29 and 30, 1992, Vanderbilt University, reported in *C & EN News*, September 7, 32 (1992).

Memorial Issue in *Heteroatom Chem.*, **4** (1993).

M. Robert Willcott, Vanderbilt University, [Dedication to J. C. Martin], *Heteroatom Chem.*, **4,** 107 (1993).

Anthony Arduengo, III, University of Alabama, [In Memory of J.C. Martin], *Heteroatom Chem.*, **10,** 349 (1999).

People: Deaths; reported in *C & EN News*, June 28, **76,** 1999.

J. C. Martin Memorial Fellowship Fund, c/o University of Illinois Foundation.

Figure 1 describes J. C. Martin Symposium at Vanderbilt University and Figures 2–4 show his family and some related photos. Figure 5 is a *Waka* to mourn the death of J. C. Martin.

PART II: WHY PROFESSOR JAMES C. MARTIN IS THE REFOUNDER AND LEADER OF THE CHEMISTRY OF HYPERVALENT COMPOUNDS—PRIVATE OPINION

1. The original idea of Staudinger was to prepare homopolar five coordinate nitrogen and phosphorus compounds.

FIGURE 3 Photo taken at Tampa after retirement from Vanderbilt.

2. The same idea was taken up by Wittig after 30 years, which lead to pentaphenylphosphorane and so on.
3. Theoretical investigations by Musher and colleagues appeared before Martin's work.
4. Martin recognized the idea of the nature of 3 center –4 electron bond (hypervalent bond) and extended the idea to σ-delocalization,

FIGURE 4 Photos taken at Hiroshima (two), Vanderbilt (home), and Kyoto.

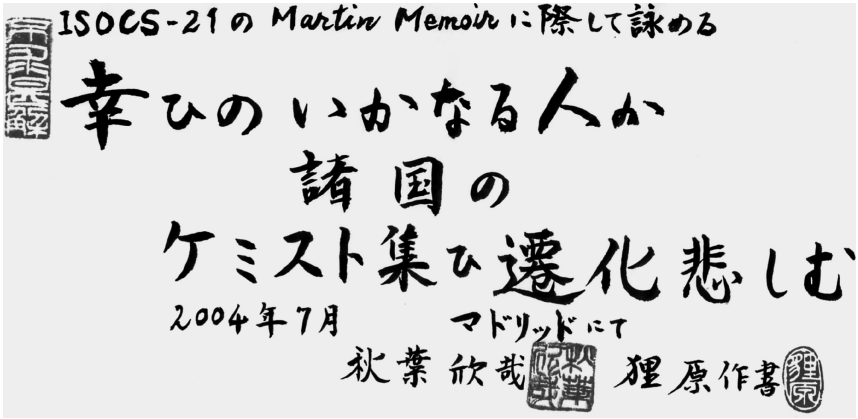


FIGURE 5 This was a *Waka* prepared and written by the author for the ISOCS-21 Conference in Madrid in July, 2004, in memory of Prof. Martin. A *Waka* is a traditional Japanese short poem consisting of 31 phonetic characters. This is based on a well known *Waka* in Mannyosyu, the oldest collections of *Waka*, which is supported by the Emperor. The Japanese reading is shown in the Romanized form, followed by a translation.

Sakiwai no ikanaru hito ka morokuni no kemisuto tudoi sennge kanashimu; What a happy and beloved person he was! Hundreds of chemists from many countries gather to mourn him and to admire his accomplishments in chemistry.

leading to the preparation of a variety of hypervalent nonmetals (main group elements) and σ-aromaticity.

The Origin of the Idea of Hypervalent Compounds

Versuche zur Herstellung neuer Stickstoffverbindungen H., Staudinger, and J. Meyer, *Helv. Chim. Acta*, **2,** 608 (1919).

Staudinger Sagt

Staudinger wrote the following in the above paper, which was not successful, but challenging and impressive.

Nach der Werner'schen Auffassung hat der Stickstoff die koordinationszahl 4; nur 4 Atome oder Atomgruppen koennen direkt an Stickstoff gebunden sein; die fuenfte Valenz ist prinzipiell von den anderen Valenzen verschieden. Es ist deshalb eine theoretisch interessante Frage, ob man nicht doch Stickstoffverbindungen herstellen kann, bei denen 5 Atome oder Atomgruppen gleichartig an Stickstoffgruppen gebunden sind; —-Stickstoff an 5 C Atome gelagert—

*****Resultless Research*****

Ueber neue organische Phosphorverbindungen I, II, III, IV
H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2,** 612, 619, 635, (1919), **4,** 861 (1921) (Hauser, E.).

$$Ph_3P + Ph_2C{=}N{=}N \rightarrow Ph_3P{=}N{-}N{=}CPh_2 \rightarrow Ph_3P{=}CPh_2$$

(+ carbonyl compounds)

$$Ph_3P + Ph{-}N{=}N{=}N \rightarrow Ph_3P{=}N{-}N{=}N{=}Ph \rightarrow Ph_3P{=}NPh$$

(+ carbonyl compounds)

*****Establishment of the prototype of the Wittig reaction*****

Variationen zu einem thema von Staudinger: ein Beitrag zur Geschichte der Phosphororganischen Carbonyl-Olefinierung

G. Wittig, in IUPAC symposium on "Organo-phosphorus Compounds" pp. 245–254, Heidelberg, 1964, Butterwirths, London.

Recognition of the Former Researches

Witting quoted and recognized the former studies as follows. Staudinger Group: 1919 Marvel Group: 1929 Kroehnke: 1936–1950.

Wittig Sagt

Witting wrote the following in the above lecture. Vorwegnehmend moechte ich mit aller Deutlichkeit unterschreichen, dass zu der Zeit, als die zu den Stickstoffyliden und spaeter zur Carbonylolefinierung hinfuehrenden Reaktionen studiert wurden, uns weder die Resultate von Staudinger noch von Marvel bekannt waren und erst nachtraeglich beim Literaturstudium gegenwaertig wurden. Diese Unkenntnis vorausgehender Untersuchungen betrachte ich insofern als eine gluecklicher Fuegung, —-

Unsere erste Zielsetzung war die gleiche wie die von Staudinger und Marvel, naehmlich die Praeparierung von Verbindungen des pentavalenten Stickstoffs.

Wittig tried to generate ammonium ylide and phosphonium ylide by using organolithium compounds.

$$[(CH_3)_3M{-}CH_3]Br + RLi\ (Me\ or\ Ph) \rightarrow (CH_3)_3M^+{-}CH_2^- + RH + LiBr$$

$$(CH_3)_3M{-}CH_2 + Ph_2C{=}O \rightarrow (CH_3)_3M^+{-}CH_2{-}C(-O^-)Ph_2M{:}\ N,\ P$$

$$[Ph_3P - CH_3]Br + RLi\ (Me\ or\ Ph) \rightarrow Ph_3P^+{-}CH_2^- + RH + LiBr$$

$$\rightarrow\ Ph_3P^+{-}CH_2^- + R_1R_2C{=}O \rightarrow R_1R_2C{=}CH_2 + Ph_3P{=}O$$

Wittig Reaction: Witting wrote only eight papers on the Witting reaction.

Ueber phosphin-alkylene als olefinbildende Reagenzien I—VIII, from *Ber.*, **87** (1954) to *Ber*,, **96** (1963).

These facts show, I think, that what Wittig said can be believed.

Pentaphenylhypervalent typical elements

$$Ph_4MI + PhLi \rightarrow Ph_5M \text{ M:P, As, Sb, Bi } \textit{Ann}, \mathbf{562}, 187 \text{ (1949).}$$

Ann, **577**, 26 (1952).

Pentaarylierte Spiro Compounds: Preparation of stereoisomers

Ann, **578,** 136 (1953); *Ber.*, **97,** 741 (1964); M: P, As, Sb, Bi;

Pentamethylarsenic and bismuth

$$(CH_3)_4AsI + CH_3Li \rightarrow (CH_3)_5As : (CH_3)_3SbBr_2 + 2CH_3Li \rightarrow (CH_3)_5Sb$$

Acta Chem. Scandinavia, **7,** 1293–1301 (1953).

Homopolar pentavalent compounds were prepared by witting. They are the first and original hypervalent organic compounds! However, Wittig did not know the TBP structure without X-ray analysis.

Theoretical Investigations

Theoretical investigations related to hypervalent molecules are cited below.

I—I—I: a stable linear molecule; In order to explain the stability of the molecule, a proposal of 3center-4 electron bond was made by Pimentel and Rundle independently. G.C. Pimental, *J. Chem. Phys.*, **19,** 446 (1951).

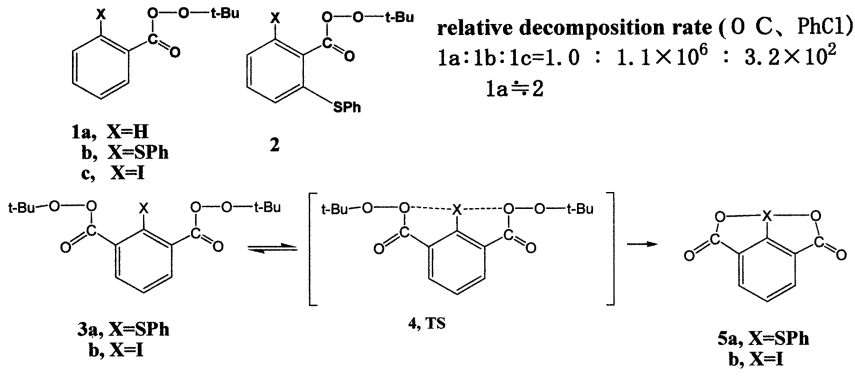
The Chemistry of Hypervalent Molecules: J. I. Musher, *Angew. Chem. Int. Ed.*, **8,** 54 (1969). (definition of hypervalent compounds, 3c–4e bond)

The Structure and Stability of the 10-F-2 Trifluoride Ion, a Compound of a Hypervalent First Row Element: P. A. Cahill, C. E. Dykstra, and J. C. Martin, *J. Am. Chem. Soc.*, **107,** 6359 (1985).

Bonding between Nonbonded Sulfur and Oxygen Atoms in Selected Organic Molecules (A Quantum Chemical Study): J. G. Angyan, R. A. Poirier, A. Kucsman, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **109,** 2237 (1987).

Chemical Bonding in Hypervalent Molecules: The Dominance of Ionic Bonding and Negative Hyperconjugation over d-Orbital Participation: A. E. Reed, and P. von R. Schleyer, *J. Am.Chem. Soc.*, **112,** 1434 (1990)

Hypervalent Compounds: M. Lattman, *Encyclopedia of Inorganic Chemistry*, 1496 (1994).



Chem. & Ind. 192 (1959), *JACS*, 96, 3319 (1974).

FIGURE 6 Anchimeric acceleration of homolytic bond cleavage: simultaneous participation of three neighboring groups.

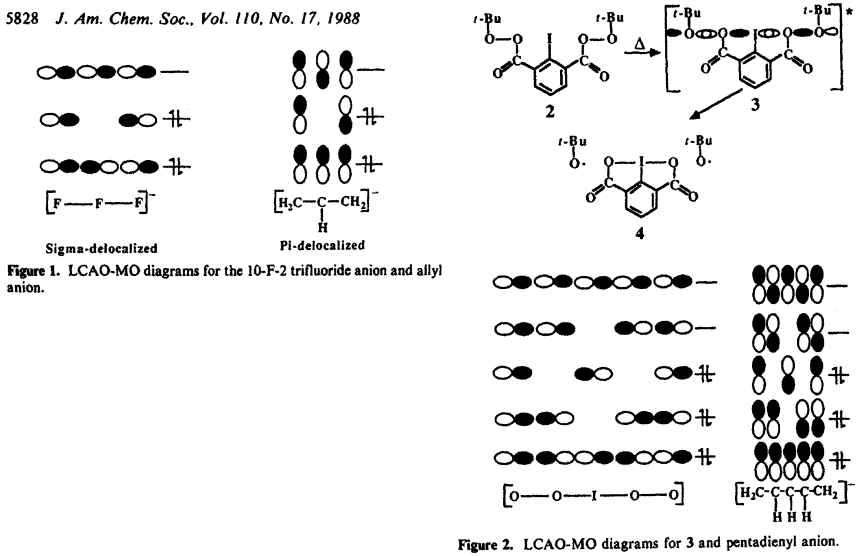


FIGURE 7 Molecular orbitals of 3c–4e and 5c–6e bonds.

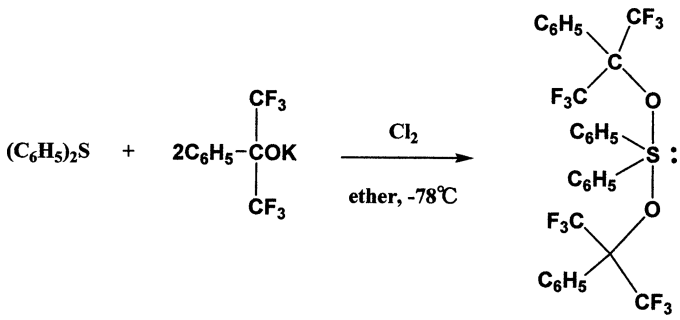


FIGURE 8 Sulfuranes: Diaryldialkoxy sulfurane.

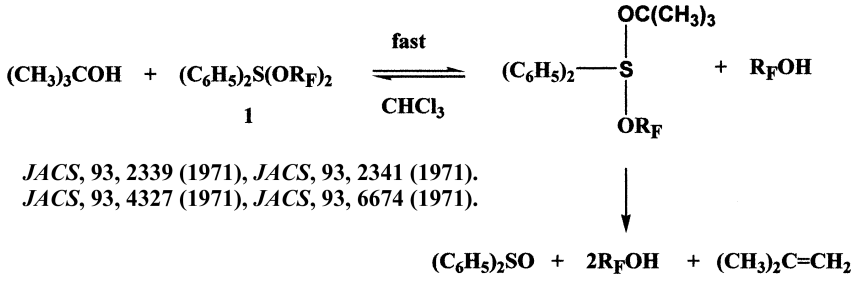


FIGURE 9 Sulfuranes: Dehydrating reagent.

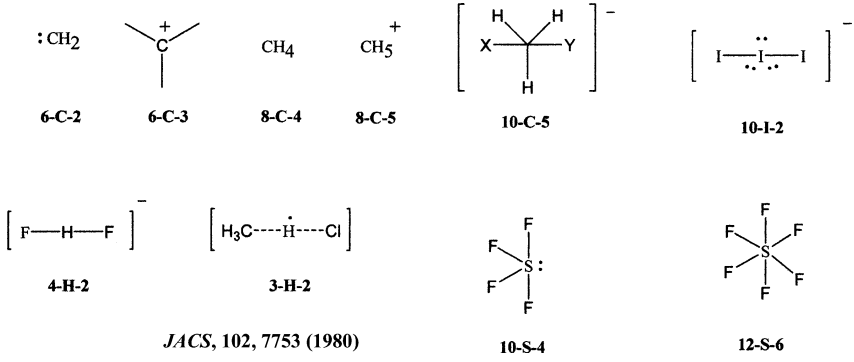


FIGURE 10 N-X-L designation: Fundamental formalizm. *X*: the central atom of any kind; *N*: the number of valence shell electrons formally associated directly with atom *X*; *L*: the number of ligand directly bonded to *X*.

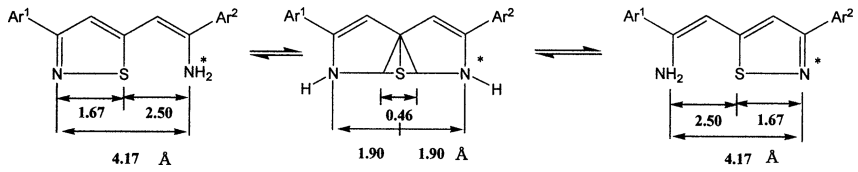


FIGURE 11 Ring transformation equilibrium (bond switch) in the 5-(2-aminovinyl) isothiazole system via hypervalent sulfurane.
K.-y. Akiba, K. Kashiwagi, Y. Ohyam, Y. Yamamoto, and K. Ohkata, *Angew. Chem. Int. Ed.*, **18,** 166 (1979), *JACS*, **101,** 5857 (1979), *JACS*, **107,** 2721 (1985).

"Organic Compounds of Hypervalent Nonmetallic Elements"
The U.S.-Japan Corperative Science Program Supported by NSF and JSPS for 1987–1988.
U.S.: Professor J. C. Martin, Vanderbilt Univercity
Japan: Professor Kin-ya Akiba, Hiroshima Univercity

Based on our common research interests in hypervalent compounds over ten years, the above cooperative science program was approved.

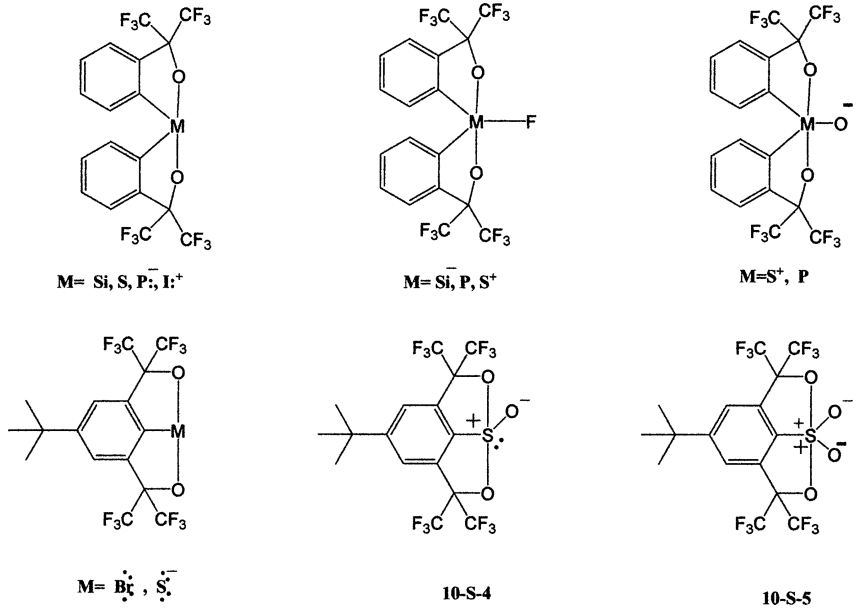


FIGURE 12 "Frozen" transition states: Pentavalent carbon et al., *Science*, **221,** 509 (1983). Stabilization of Hypervalent Compounds by "Martin Ligand".

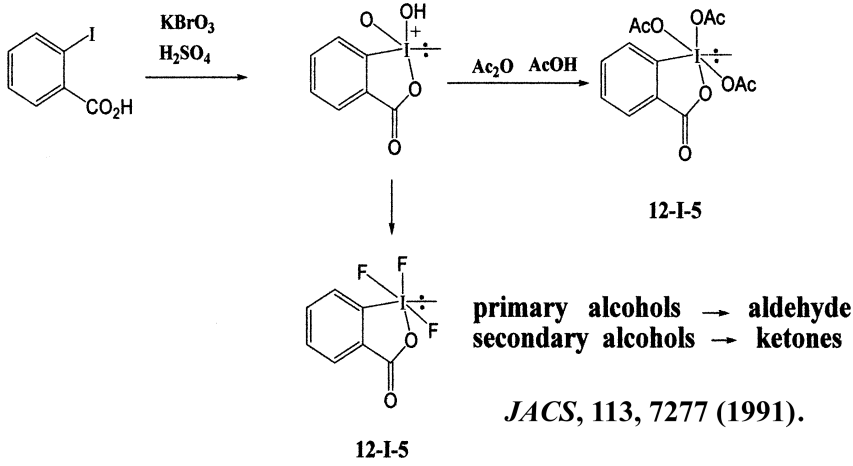


FIGURE 13 Dess-Martin Periodinane. A useful 12-I-5 triacetoxyperiodinane (Dess-Martin periodinane) for the selective oxidation of primary or secondary alcohols and variety of related 12-I-5 species.

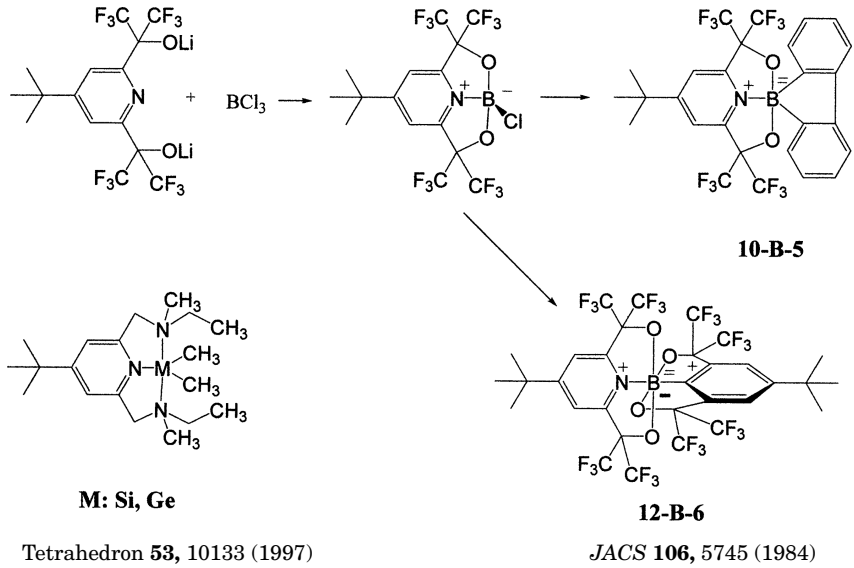


FIGURE 14 Examples of tridentate ligand.

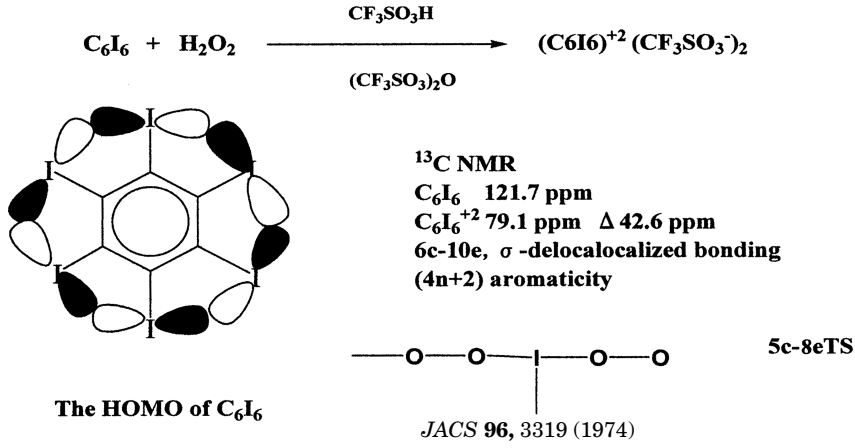
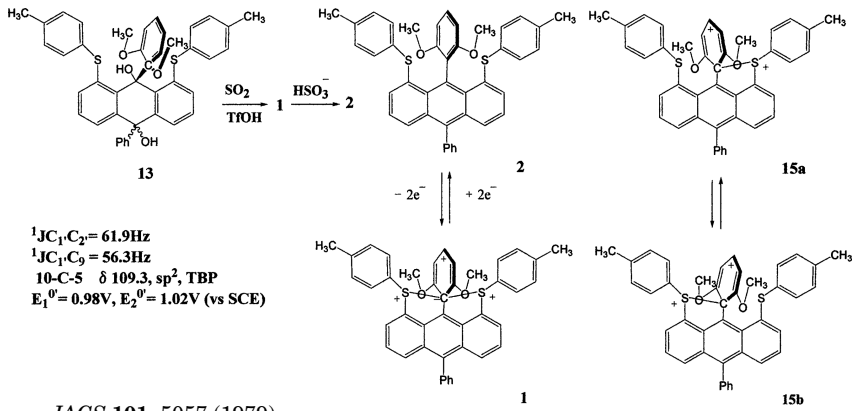
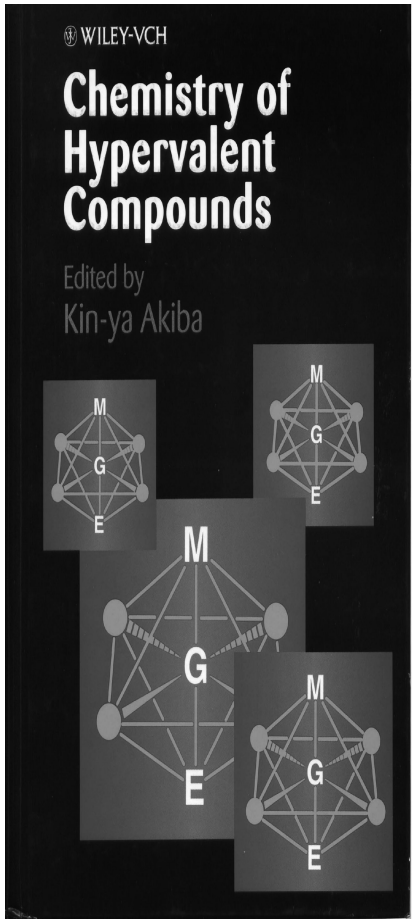


FIGURE 15 Sigma-delocalized aromatic species formed from cyclic arrays of hypervalent main-group element species. *Pure & Appl. Chem.*, **62,** 547 (1990). Dication of Hexaiodobenzene: σ-Delocalized Dication, *J. Am. Chem. Soc.*, **110,** 5827 (1988).



JACS **101,** 5057 (1979)
Heteroatom Chem., **4,** 113 (1993)

FIGURE 16 An observable model for the S_N2 transition state: hypervalent pentacoordinate carbon species (10-C-5).



To Former Professor James C. Martin of the University of Illinois, Urbana-Champaign, and Vanderbilt University
And to my wife Yoko

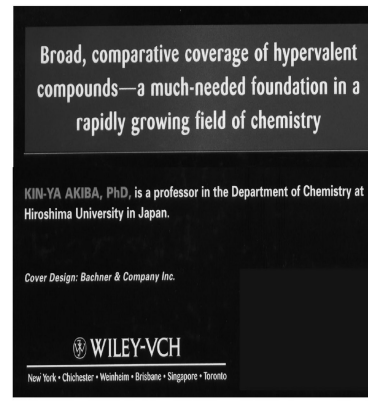


FIGURE 17 Front and rear covers of the book on *Chemistry of Hypervalent Compounds*.

Summary of Research by Prof. James. C. Martin and his Group

When I edited a book on [Chemistry of Hypervalent Compounds] in 1999 from Wiley-VCH, I dedicated the book for Dr. James C. Martin in order to show my appreciation heartily to him personally and scientifically.

The second Waka below is also based on a well-known one in Mannyosyu. As is stated, I deeply wish his holly rest in the heaven and also the future development of the field of hypervalent chemistry, which he reopened, developed, and loved.

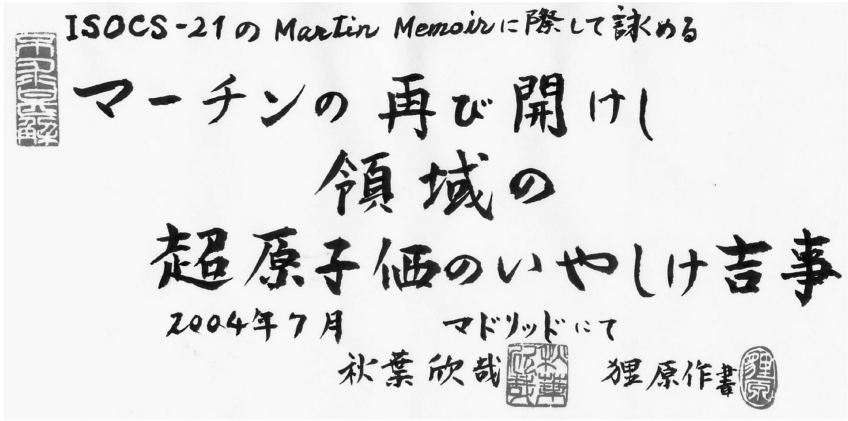


FIGURE 18 This *Waka* in memory of Prof. Martin was written by the author for the ISOCS-21 Conference in Madrid in July, 2004. The Japanese reading is shown in the Romanized form, followed by a translation.

Martin no hatutabi akeshi pryouiki no tyougennshika no iyashike yogoto, Dr. Martin reopened the field of the chemistry of hypervalent compounds. May the field be developing and prosperous in the future!

I hope this speech read by a Japanese chemist will add additional evidence to show that Dr. J. C. Martin was highly recognized and loved internationally.