Heteroatom Chemistry
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A Report on the 20th Symposium on Heteroatom Chemistry of the Chemical Society of Japan

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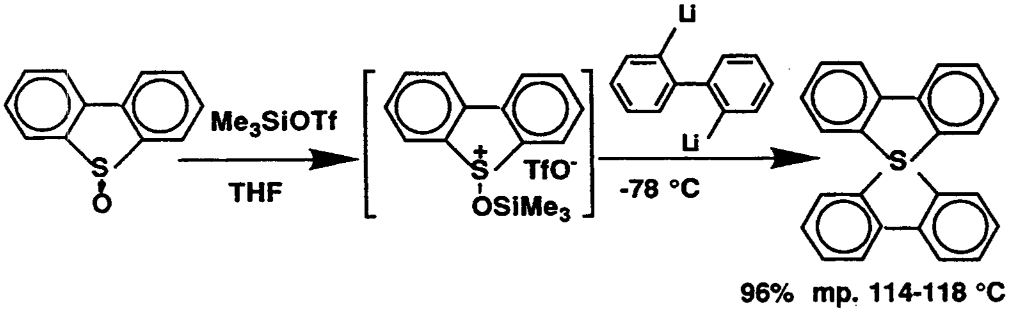
The 20th Symposium on Heteroatom Chemistry was a very successful one. It was organized by Prof. Nobumasa Kamigata of Tokyo Metropolitan University in the western suburb of Tokyo. From this location snow-capped Mt. Fuji can be seen clearly, like Mt. Rainier from Seattle in wintertime. The Symposium attracted about 250 people, despite the economic recession of most of the industries that usually finance the travel expenses of most of the attendees. Many more people came from various academic institutions than in past years, and Prof. N. Kamigata had to arrange five plenary lectures, each of 1 hour, and 58 oral presentations, each of 20 minutes, into exactly 3 days running from 9 A.M. to 6 P.M. each day. We had two foreign plenary lecturers: Prof. J. C. Martin of Vanderbilt University of Nashville, TN, and Prof. R. Steudel of the Technical University of Berlin, Germany. There were also three domestic plenary lecturers: Prof. Naomichi Furukawa of Tsukuba University, Prof. Fumio Ogura of Hiroshima University, and Prof. Tsuneo Imamoto of Chiba University.

Professor Naomichi Furukawa of The University of Tsukuba was the first plenary lecturer, and his topic was "Hypervalent Compounds of Group 16 Elements." He mentioned that, in addition to the isolation of tetraphenylselenium and tetraphenyltellurium derivatives, tetraphenylsulfur could be detected by NMR spectroscopy. He also described the first successful synthesis and isolation of the hypervalent sulfurane, shown below, by the following route.



Thus, hypervalent chalcogen compounds have now been isolated and fully characterized for S, Se, and Te by Prof. N. Furukawa, who also described the differences of ligand exchange and pseudorotation reactions of the three species. When warmed, they underwent ligand coupling readily. As one would expect, the stability of the chalcogen hypervalent species seems to increase as the atomic number of the central atom is increased.

The second plenary lecturer was Prof. Ralf

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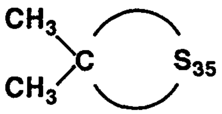
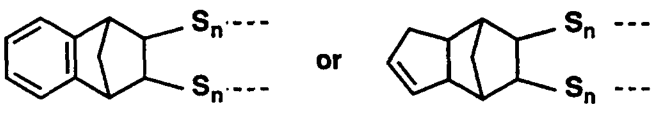
Steudel of the Technical University of Berlin, who spoke on "Novel Organic Compounds with Heteroatoms Si, Ge, P, As, O, S and Se Synthesized from Titanocene Precursors." Using a Cp_2TiS_5 derivative, he could synthesize a ring compound containing 35 atoms of sulfur, as shown below. He also mentioned the synthesis of water-soluble polysulfides, such as the one, R-S_8-R, shown below, where R is sugar moiety.



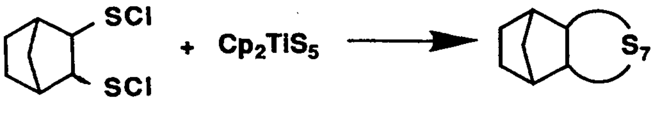
(CH3)2CS35

R-S8-R R = sugar group

Because of the water-tight property of polysulfides, sulfur cement is now made industrially, by incorporating cal 5% of a polysulfide moiety, such as the following, into portland cement.

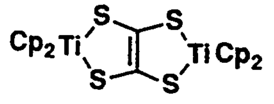


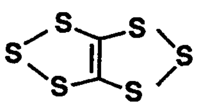
The following type of reaction can be used to make the polysulfides, the starting bis sulfur chloride being synthesized from norbornane-trithiolane by chlorination.

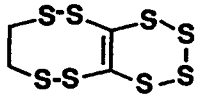


The reactions of the carbonyl complex, $Cp_2Ti(CO)_2$, with organic sulfur compounds are interesting, especially that with CS_2 to form the dinuclear complex, $Cp_2Ti(C_2S_4)TiCp_2$. Many polysulfides which have a C=C bond in the center, such as the following three compounds, were synthesized.

Some reactions of compounds containing Si, Ge, and As atoms are shown below:







$Cp_2Ti(\mu\text{-}S)_2SiR_2 + S_2Cl_2 \rightarrow R_2SiS_5$

$+ Cp_2TiCl_2;\quad R = CH_3, Ph$

$Cp_2Ti(\mu\text{-}S)_2GeR_2 + C_2H_4(SCl)_2 \rightarrow R_2GeS_4C_2H_4$

$+ Cp_2TiCl_2;\quad R = Ph$

$Cp'_2Ti(\mu\text{-}S_2)_2TiCp'_2 + CH_3PCl \rightarrow Cp'_2Ti(\mu\text{-}S_2)_2PCH_3$

$+ Cp'TiCl_2$

$Cp'_2Ti(\mu\text{-}S_2)_2TiCp'_2 + C_6H_5PCl_2 \rightarrow Cp'Ti(\mu\text{-}S)(\mu\text{-}S_3)P(S)C_6H_5$

$+ Cp'_2TiCl_2$

$Cp'_2Ti(\mu\text{-}S_2)TiCp'_2 + CH_3AsCl_2 \rightarrow Cp'_2Ti(\mu\text{-}S_2)_2AsCH_3$

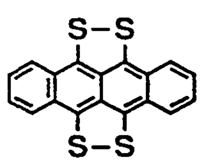
$+ Cp'_2TiCl_2$

In addition, selenium allotropes may be produced by reaction of the above titanocene complexes with various compounds. One of the typical reactions led to the formation of Se_7 whose NMR spectrum shows only one

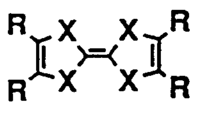
$$Cp_2TiSe_5 + Se_2Cl_2 \rightarrow Se_7 + Cp_2TiCl_2$$

resonance, indicating pseudorotation of the chair-shaped ring. Thus, the use of titanocene complexes as reagents provides a variety of potentially useful heteroatom compounds.

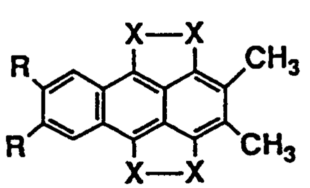
The third plenary lecturer was Prof. Fumio Ogura of Hiroshima University, who lectured on "Design and Synthesis of Electrically Conductive Organic Compounds Containing Heteroatoms." The lecture covered two broad topics: (1) synthesis of new organic electron donors and their CT com-



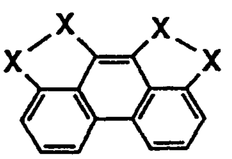
TTT



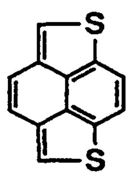
TTF: X=S,R=H
HMTTeF: X =Te,
R,R = -(CH2)3-



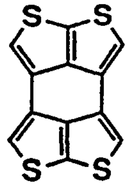
I



II



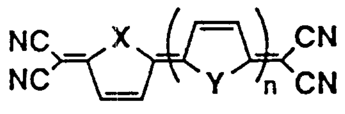
III



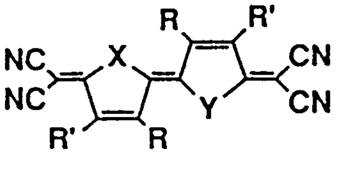
IV

X = S, Se, Te

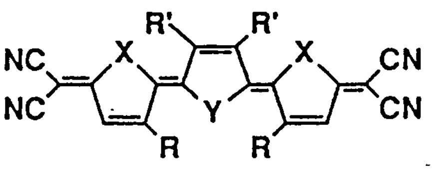
plexes and (2) synthesis of new organic electron acceptors and their CT complexes. Included in the first topic, he mentioned the syntheses of donors, such as TTT and TTF (I–IV), while for the second topic, he mentioned among the acceptors not only TCNQ, but also many similar heteroatom compounds recently synthesized, such as:



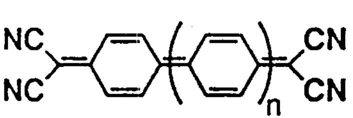
	n=0,	n=1,	n=2
X=Y=O:	F1,	F2,	F3
X=Y=S:	T1,	T2,	T3
X=Y=Se:	S1,	S2,	S3
X=S, Y=Se:		TS	



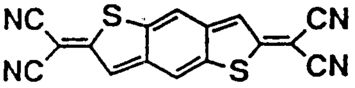
F2-Br: X = Y = O, R = Br, R' = H
T2-Br: X = Y = S, R = Br, R' = H
S2-Br: X = Y = Se, R = Br, R' = H
T2-Br2: X = Y = S, R = R' = Br
T2-Cl: X = Y = S, R = Br, R' = H
TS-Br: X = S, Y = Se, R = Br, R' = H
TS-Cl: X = S, Y = Se, R = Cl, R' = H



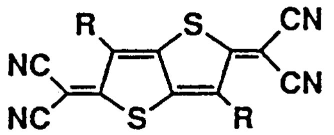
F3-Br: X=Y=O, R = Br, R'= H
F3-Br2: X=Y=O, R = R'= Br
TST: X=S, Y=Se, R = R'= H



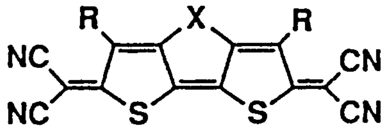
n = 0; TCNQ
n = 1; TCNDQ



CNBDT

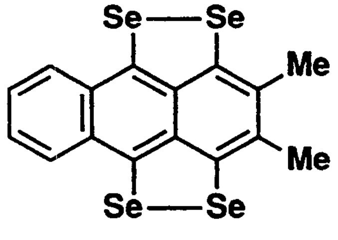


FT2: R = H
FT2-Br: R = Br



FT3: X = S, R = H
FT3-Br: X = S, R = Br
FT3-SO_2: X = SO_2, R = H

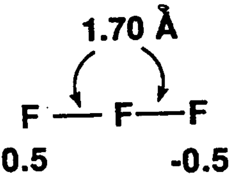
Most of the crystalline complexes were subjected to X-ray diffraction analysis, and some of the complexes were found to conduct electricity as effectively as metals, the value of σ/S cm^{-1} being 4.4 or 4.5 × 10^2 for the complexes shown below:



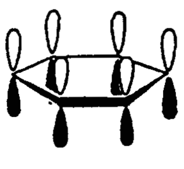
NO_3^- (4.4 x 10^2) , BF_4^- (4.5 x 10^2)

Much of his lecture had been presented at ICHAC-3 in Riccione, Italy, in June of 1992, and one can refer to *Pure and Applied Chemistry*, the official magazine of IUPAC for additional details.

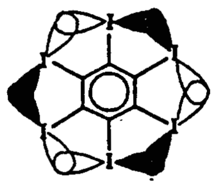
The fourth plenary lecture was presented by Prof. J. C. Martin of Vanderbilt University on "The New Sigma-Delocalized Aromatic Species with Several New Species That Are Now Shown to be Aromatic Ones." He displayed first a hypervalent iodine species and then the F_3^- molecule, which is linear and whose F–F bond distance is longer, 1.70 Å, then the normal F–F bond distance of 1.41 Å. The ionic delocalization is the following:



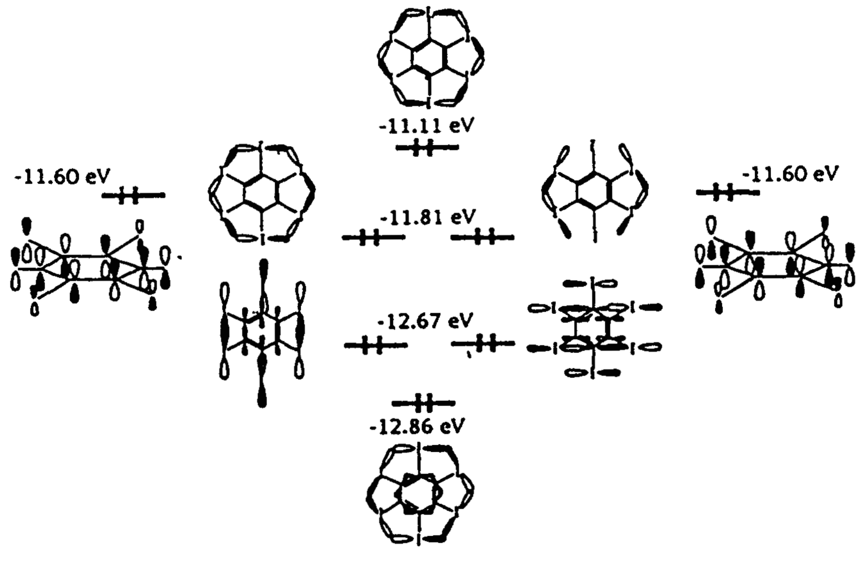
He then mentioned that, based on the aromaticity of the benzene ring related to the (4n + 2) principle, hexaiodobenzene and similar derivatives are worthy of further consideration because of possible sigma-delocalization. Sigma-delocalized MOs are shown in the following manner.



1 (There are 6 electrons in the aromatic group.)

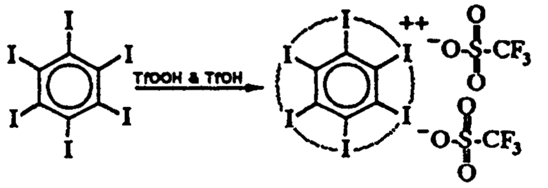


2 (There are 12 electrons in the sigma forms of 6 iodines, that are not aromatic here.)

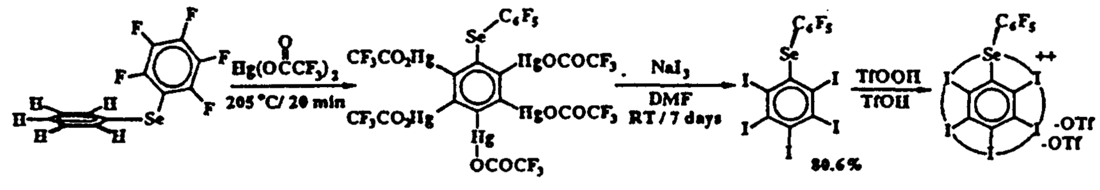


Sigma-delocalized MO's

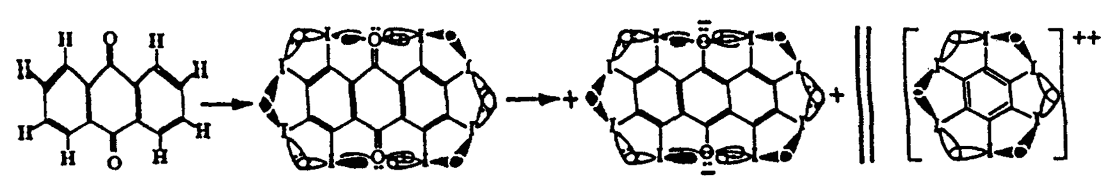
The distance between two iodine atoms in hexaiodobenzene is 3.15 Å. However, by removing two electrons, the species having 10 appropriate electrons, formed as shown below, is aromatic.



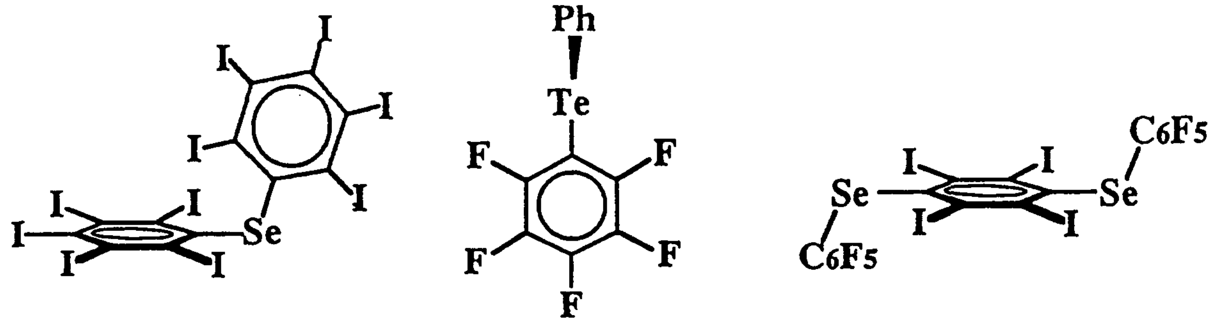
His group synthesized a pentafluoro molecule by a complex route and found that the last compound with 10 appropriately located sigma electrons is aromatic.



Mention was made of possible aromatic compounds having 18 appropriately located sigma electrons that fit the (4*n* + 2) principle. The NMR spectrum did not indicate the presence of a normal C=O group for the product of the following reaction owing to the delocalization.

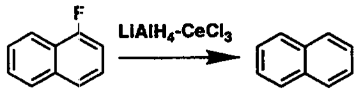


He also mentioned that, by removing two electrons, they could make aromatic cations from the three following compounds:

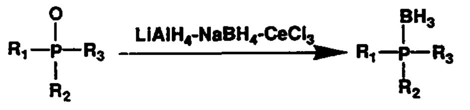


The last plenary lecture was presented by Prof. Tsuneo Imamoto of Chiba University, who spoke on "Synthesis and Reactions of Phosphine-Boranes." This covered much more of his work than he had presented at ICHAC-3 in Riccione last June. He briefly told us how he had gotten into the work by trying to carry out $CeCl_3$-catalyzed reduction reactions of organic fluorides. He mentioned that, with the use of $LiAlH_3$-$CeCl_3$, one can reduce both aliphatic and aromatic fluoro compounds.

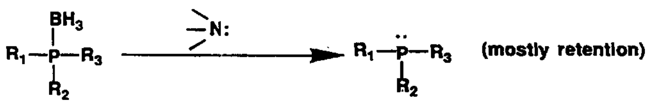
$$\text{R-F} \xrightarrow{\text{LiAlH}_4\text{-CeCl}_3} \text{R-H}$$



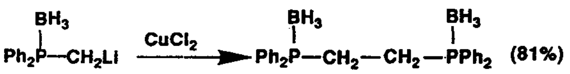
Imamoto and his co-workers found that, in the following reaction of a phosphine oxide, the use of $LiAlH_4$-$NaBH_4$-$CeCl_3$ can lead directly to the formation of a phosphine-borane.



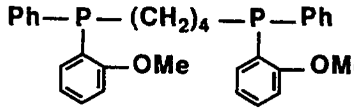
The P–B bond of phosphine-boranes can be cleaved easily by treatment with amines, giving the original phosphine.



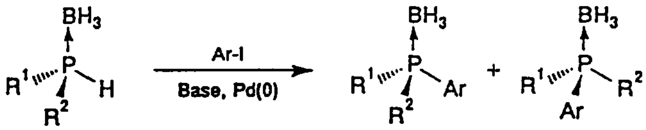
Other new and useful reactions were developed, such as the one shown below.



Imamoto et al. prepared many optically active phosphines, and an especially useful optically active compound is the following one, which has been used extensively by many workers for various applications since the specific rotation of the compound is very high.



Optically active phosphine-boranes could be prepared, and the following electrophilic arylation reaction was studied. Acetonitrile was found to be a retention solvent, while the use of K_2CO_3 in THF led to inversion of the configuration.



Other syntheses and reactions of optically active phosphine-boranes have been investigated. Optically active secondary phosphine-boranes, (S_P)- and (R_P)-menthyloxyphenylphosphine-boranes and (S)-methylphenylphosphine-borane, underwent palladium(0)-catalyzed electrophilic arylation with o-, m-, or p-iodoanisole. The stereochemistry of this arylation was largely dependent on the solvent and the base used. The reaction in acetonitrile proceeded with almost complete retention of configuration at the chiral phosphorus, whereas inversion of configuration was observed in ethereal solvents or toluene. The phosphorus-oxygen bond of (R_P)-menthyloxy(methyl)phenylphosphine-borane and (S_P)-menthyloxy(o-methoxyphenyl)-phenylphosphine-borane was reductively cleaved at −78°C by lithium naphthalenide or Li/NH_3 with net retention of configuration at phosphorus, providing secondary or tertiary phosphine-boranes in excellent yields. New synthetic routes to optically pure C_2-symmetric bisphosphine-boranes possessing chirality at phosphorus have been developed on the basis of these stereochemical studies.

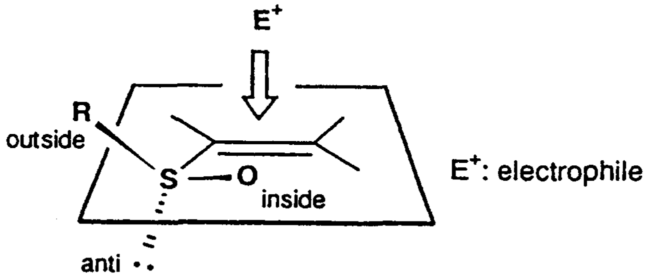
In addition to these plenary lectures, there were many relatively short oral presentations.

1. "Asymmetric Synthesis of Azalactams Utilizing Optically Active Vinyl Sulfoxides," by Nobuhiro Itoh, Haruo Matsuyama, Masato Yoshida, Nobumasa Kamigata, and Masahiko Iyoda (Tokyo Metropolitan University).
2. "Highly Enantioselective Protonation of Prochiral Enolates Using Chiral β-Hydroxy Sulfoxides," by Kunihide Hoshino, Hiroshi Kosugi, and Hisashi Uda (Tohoku University).
3. "The Syntheses and Reactions of 2-(1-Dimethylaminoethyl)phenyl Alkyl Sulfoxides," by Makoto Shimazaki, Mizue Yoshimura, and Akihiro Ohta (Tokyo College of Pharmacy).
4. Stereoelectronic Effects of a Sulfinyl Group in Electrophilic Addition Reactions to Vinylic Sulfoxides," by Makoto Fujita, Masahiro Takahashi, Yoichi Ihori, Keiichiro Manako, Hiroshi Tomori, Michio Ishida, and Katsuyuki Ogura (Chiba University).
5. "Cyclization of Polyenic Compounds Containing a Chiral Sulfinyl Group," by Hiroshi Kosugi, Osamu Kannno, Kunihide Hoshino, and Hisashi Uda (Tohoku University).
6. "Asymmetric Selenoxide Elimination: Application to the Synthesis of Chiral Cyclohexylidene Derivatives," by Naoki Komatsu, Yasuhiro Haseba, Yoshiaki Nishibayashi, Toshio Sugita, and Sakae Uemura (Kyoto University).
7. "Lewis Acid-Catalyzed Intramolecular Asymmetric Ene Reactions of Chiral Vinyl Sulfoxides," by Kunio Hiroi and Masayuki Umemura (Tohoku College of Pharmacy).
8. "A Facile Stereocontrol for the Synthesis of *cis* and *trans* Thiirane Thiolcarbamates Using Dithiocarbamate Salts," by Masaaki Yoshida, Hideyuki Ishida, Naoko Hashimoto, and Takashi Toda (Utsunomiya University).
9. "Stereoselective Formation of (Z)-Vinyl Derivatives by Nucleophilic Ring-Opening Reactions of 1-Arylbenzo[b]thiophenium Salts," by Tsugio Kitamura, Shin-ichi Soda, and Hiroshi Taniguchi (Kyushu University).
10. "Reaction of Nucleophiles with the Corey-Kim Reagent," by Sadamu Katayama, Toshio Watanabe, and Masashige Yamuchi (Josai University).
11. "Specific Reactivity of Naphthalene-Bisulfonates in Their Intramolecular Cyclization and Substitution Reactions," by Shigeki Sano, Masanobu Suzuki, Tetsuo Yagi, Yoshimitsu Nagao (Tokushima University), and Motoo Shiro (Rigaku Co).
12. "Reactivity of Sulfenamides and Their Derivatives," by Isao Shibuya, Katsumi Yonemoto, Masahiko Yasumoto, Yoichi Taguchi, and Akihiko Oishi (National Chemical Laboratory for Industry).
13. "Remarkably Selective Binding of Silver Ion by Thiolariat Ether," by Tatsuya Nabeshima, Naoko Tsukada, and Yumihiko Yano (Gunma University).
14. "Synthesis and Properties of Ethylenedithio-Substituted Pyracylene and Its Radical Cation Salts," by Kazunori Masumoto, Hiroyuki Tani, Nagao Azuma, and Noboru Ono (Ehime University).
15. "Regioselective Anodic Monofluorination of Organo Selenium Compounds," by Toshio Fuchigami, Toshiaki Hayashi, Akinori Konno, and Tsutomu Nonaka (Tokyo Institute of Technology).
16. "Synthesis and Reactions of Selenabenzenes," by Tadashi Kataoka, Yasuhiro Ohe, Tatsunori Iwamura (Gifu Pharmaceutical University).
17. "C-Carbonylation of Carbonyl Compounds with Selenium and Carbon Monoxide," by Akira Nishiyama, Shin-ichi Fujiwara, Tsutomu Shin-ike, Nobuaki Kambe, and Noboru Sonoda (Osaka University).
18. "Novel Synthesis of Benzimidazolones by Reductive Carbonylation of 2-Nitroanilines with Ammonium Formate and Elemental Sulfur," by Toshiyuki Miyata, Takumi Mizuno, Ikuzo Nishiguchi, Tsuneaki Hirashima, and Noboru Sonoda (Osaka Municipal Technical Research Institute and Osaka University).
19. Diselenoic Acid Esters: "Synthesis, Isolation, and Reactions," by Tomoyoshi Mizutani, Takahiro Kanda, Toshiaki Murai, Hideharu Ishihara, and Shinzi Kato (Gifu University).
20. "Generation and Reaction of Active Oxidizing Species in Photosensitized Oxygenation of Organosulfur Compounds," by Takeshi Aksaka, Masayuki Haranaka, and Wataru Ando (Tsukuba University).
21. "Photochemical Oxygen Migration from Benzotrithiole 2-Oxides to Benzotrithiole 1-Oxides," by Ryu Sato, Naoki Yomoji, Shin-ichi Satoh, and Satoshi Ogawa (Iwate University).

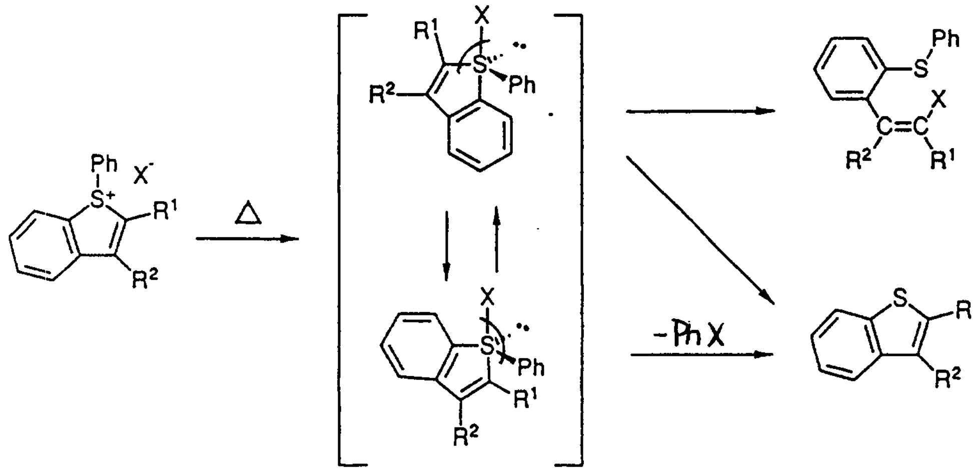
22. "Importance of Hypervalent Selenium Species on Glutathione Peroxidase Activity," by Michio Iwaoka and Shuji Tomoda (Tokyo University).
23. "Reactions of Alkynylphenyliodonium Tosylates with Various Nucleophiles," by Makoto Sakurai, Ryuichi Tanaka, Tugio Kitamura, Hiroshi Taniguchi (Kyushu University), and Peter J. Stang (Utah University).
24. "Synthesis and Reactions of 2-Silatetralin Derivatives. Synthesis of Polycyclic Silicon Compounds," by Osamu Hoshino, Akihisa Hirokawa, and Atsuhiro Tatsuno (Tokyo Science University).
25. "Synthesis and Properties of 9,10-Disilatriptycenes," by Ken Hatano, Masaki Takahashi, Yuzo Kawada, and Gen Koga (Ibaraki University).
26. "Generation and Cycloaddition of 1,3-Dipoles via Thermal Rearrangement of Silicon onto a Heteroatom," by Mitsuo Komatsu, Haruhisa Tanaka, Seiji Yokoi, Mitsuru Ohno, Shinobu Itoh, and Yoshiki Ohshiro (Osaka University).
27. "Synthesis of Novel Organolead Compounds from Bulky Organolithiums and Lead-Containing Electrophiles and Their Reactions," by Kazusato Shibata, Norihiro Tokitoh, and Renji Okazaki (Tokyo University).
28. "Palladium-Catalyzed Double Germilation of Unsaturated Compounds with Digermanes," by Noriyoshi Unehara, Yoshimi Miyazawa, Chikako Hodota, Kunio Mochida, Hiroshi Yamashita, and Masato Tanaka (Gakushuin University).
29. "Synthesis of Germamacrocycles. Synthesis of Lewis Acid Hosts and Anion Transport Capability," by Shigenobu Aoyagi, Tatsumi Tanaka, Keiichiro Ogawa, and Yoshito Takeuchi (Tokyo University).
30. "Synthesis of Organobismuth(III) Compounds with Bidentate Ligand and Inversion at Bismuth: Evidence for an Edge Inversion Mechanism," by Xinag Chen, Matsuko Kitano, Satoshi Kojima, Yohsuke Yamamoto, and Kin-ya Akiba (Hiroshima University).
31. "Synthesis and X-ray Crystallographic Analysis of a Pentacoordinate 1,2-Oxaphosphetane Bearing a 3-Carbonyl Functionality," by Katsuhiro Kato, Takayuki Kawashima, and Renji Okazaki (Tokyo University).
32. "Preparation of a Phosphorane Compound Containing a $C_5H_5(CO)_2Fe$ Fragment as a Ligand, $C_5H_5(CO)_2FeP(OC_6H_4NH)_2$," by Kazuyuki Kubo, Hiroshi Nakazawa, and Katsuhiko Kiyoshi (Hiroshima University).
33. "On Charge-Transfer in the Formation of Molecular Complexes of Diorganyl Chalcogenides with Halogens-Contribution of the $\sigma(X_2)$-$\pi^*(C=C)$ Type Charge-Transfer in Phenyl and Vinyl Chalcogenides," by Waro Nakanishi, Satoko Hayashi (Wakayama University), and Hiroshi Kihara (Hyogo University of Teacher Education).
34. "Unusual Reactions of Carboxylic Acids with Triarylbismuthes," by Takuji Ogawa, Tetsuya Hikasa, Noboru Ono (Ehime University), and Hitomi Suzuki (Kyoto University).
35. "Hypervalent Intermediates in Nucleophilic Substitution of Sulfinate Esters," by Tadashi Okuyama (Osaka University).
36. "Ligand Coupling and Ligand Exchange of Heteroaromatic Compounds," by Shigeru Oae (Institute of Heteroatom Chemistry), Youichi Inubushi, and Masakuni Yoshihara (Kinki University).
37. "Telluroxide Elimination by Oxidation of Alkyl Aryl Tellurides," by Yoshiaki Nishibayashi, Naoki Komatsu, and Sakae Uemura (Kyoto University).
38. "Addition Reactions of Acetylenes and Conjugated Olefins with Benzenetellurinic Mixed Anhydride," by Takahiro Fukumoto, Akinori Kawachi, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura (Hiroshima University).
39. "A Generation of Telluroaldehydes by [3,3]Sigmatropic Rearrangement of Allyl Vinyl Tellurides," by Kazuaki Shimada, Seiji Oikawa, and Yuji Takikawa (Iwate University).
40. "Synthesis and Properties of Bis(N,N-diethylamino)carbeniumdithio-carboxylate and 4,8-Bis[bis(N,N-diethylamino)ethylidene]-1,2,3,5,6,7-hexaselenacyclooctane," by Isao Akiyama, Juzo Nakayama (Saitama University), and Takehiko Nishio (Tsukuba University).
41. "Synthesis of the Group 14 Cage Compounds with Chalcogen Atoms," by Atsushi Watanabe, Tetsuji Kadowaki, Yoshio Kabe, Toshio Shimizu, Nami Choi, and Wataru Ando (Tsukuba University).
42. "Generation of Reactive Species with Chalcogen-Heteroatom (N, S, P, etc.) Double Bonds," by Hitoshi Karino, Masahito Segi, and Tadashi Nakajima (Kanazawa University).

43. "Photolysis and Thermolysis of 1,9-Substituted Dibenzothiophenes and Dibenzoselenophenes," by Takeshi Kimura, Yasuhiro Ishikawa, and Naomichi Furukawa (Tsukuba University).
44. "Pt, Pd and Rh Complexes with a Metalapentalene Framework," by Masanori Yasui, Satoshi Yoshida, Fujiko Iwasaki (Electro-Communications University), Noboru Matsumura, and Hiroo Inoue (Osaka Prefectural University).
45. "Electrophilic Substitution Reactions at Cobaltadithiolene Rings. Aromaticity of Dithiolene Rings," by Genjiro Hagino, Tetsuji Fujita, Masami Sakurada, Minako Tamada, Masatsugu Kajitani, Takeo Akiyama, and Akira Sugitani (Sophia University).
46. "The Reaction of Pentacarbonyltungsten (0) Complexes of Thiobenzaldehydes and Substituted Thiocinnamaldehydes with Dienes and Vinyl Ethers," by Motomu Muraoka, Tatsuo Yamamoto, Hiroyuki Takani, and Hitoshi Chiba (Josai University).
47. "Synthesis of Optically Active Heterohelicenes by the Use of Bicyclic Aminoalcohols," by Kazuhiko Tanaka, Hideji Osuga, Hajime Abe, Koji Koyama, and Hitomi Suzuki (Kyoto University).
48. "Highly Selective Aldol Reactions of α-(Phenylseleno)carbonyl Compounds under $TiCl_4/R_3N$ Conditions," by Takeshi Toru, Tatsuya Nishi, Yoshihiko Watanabe, and Yoshio Ueno (Nagoya Institute of Technology).
49. "First Synthesis, Structure, and Reactions of a Dithiirane S-Oxide Derivative," by Akihiko Ishii, Toru Akazawa, Meng-Xin Ding, Juzo Nakayama, and Masamatsu Hoshino (Saitma University).
50. "A New General Method for the Synthesis of Chiral Organobismuth Compounds Based on the Intramolecular Coordination by a Sulfonyl Group," by Toshihiro Murafuji, Yoshihiro Matano, and Hitomi Suzuki (Kyoto University).
51. "A New Synthesis of Cyclic Terpenoids via an Intramolecular Ene Reaction of Vinylphosphonates," by Tomohisa Utsunomiya, Michiharu Ohkubo, Junji Ichikawa, and Toru Minami (Kyushu Institute of Technology).
52. "Synthesis of Vinylphosphonium Salts from Epoxides," by Kentaro Okuma, Masaaki Ono, Koumei Kari, and Hiroshi Ohta (Fukuoka University).
53. "Stereoselective Preparation and Structure of Phosphono Sugars Derived from Phospholenes," by Akihiro Yabui, Yasushi Miyamoto, Mitsuji Yamashita, Tatsuo Oshikawa, Tadashi Hanaya, and Hiroshi Yamamonto (Shizuoka University).
54. "Dehalogenation with a Phosphite-Containing Redox System and Its Application," by Toshikazu Hirao, Keisuke Hirano, Takeya Hasegawa, Isao Ikeda, and Yoshiki Ohshiro (Osaka University).
55. "Photochemical Reactions of Naphthyl Phosphate and Phosphonate Derivatives," by Yoshiki Okamoto, Koichi Sawasaki, and Setsuo Takamuku (Osaka University).
56. "Preparation of Novel Sterically Protecting Groups Bearing Electron Donating Groups at the o-Position and its Synthetic Applications to Phosphorus Compounds in Low Coordination States," by Kozo Toyota, Masaru Hirano, and Masaaki Yoshifuji (Tohoku University).
57. "Synthesis of Cyclopentanones Using Allylidenetriphenylphosphoranes and 2-Oxoalkylidenetriphenylphosphoranes," by Minoru Hatanaka, Yasuhiro Tanaka, Ritsuo Imashiro, and Ikuo Ikeda (Osaka University).
58. "A New Reaction of Phosphine Borane Complexes: Insertion of Carbenes into the Boron Hydrogen Bond," by C. P. Bedel, A. Foucaud, and Atsuyoshi Ohno (Kyoto University).

Among these, a few particularly noteworthy works were selected and are shown here. The work of Prof. K. Ogura (No. 4) on the high selectivities on an electronic model of vinyl sulfoxide, shown below, is interesting, since most of the electrophiles, such as Br_2, CH_3I, and BH_3SMe_2, underwent reactions with high selectivities (over 95%).

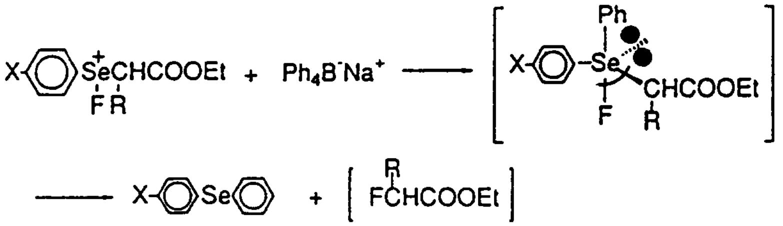


Professor Taniguchi's work (No. 9), especially the ring-opening reaction, is interesting. A similar open chain sulfonium salt is known to undergo ligand coupling.

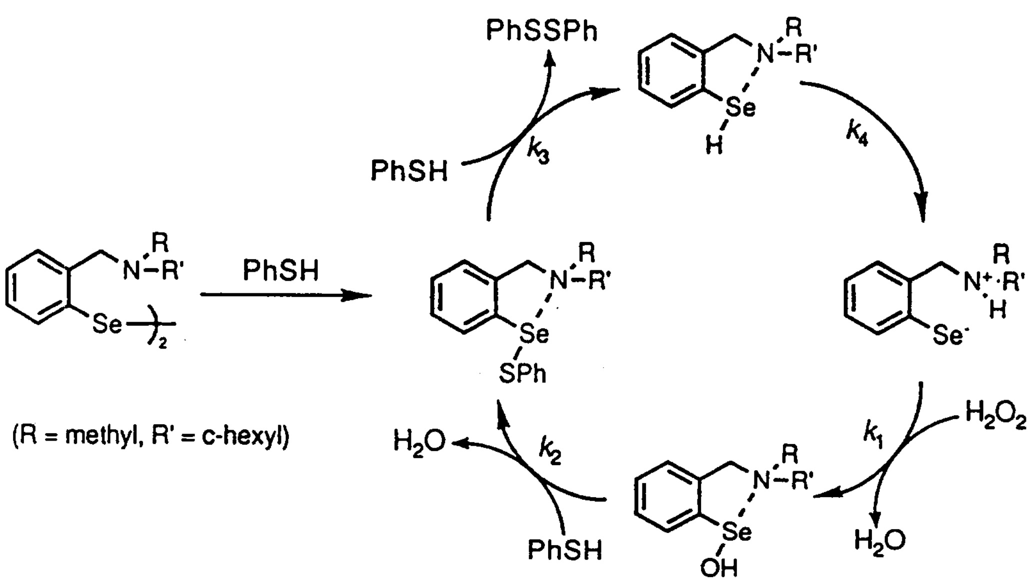


Professor Toshio Fuchigami's electron transfer leading to ligand coupling is indeed an interesting interpretation. He has also shown that anodic fluorination is very similar to the Pummerer reaction (No. 15).

The importance of glutathione peroxidase was emphasized by Prof. S. Tomoda (No. 22), and the enzyme capable of forming a hypervalent selenium moiety was thought to be responsible for the reactivity. Tomoda also showed that the o-aminophenyl-selenyl derivative is a very good catalyst, as shown below.

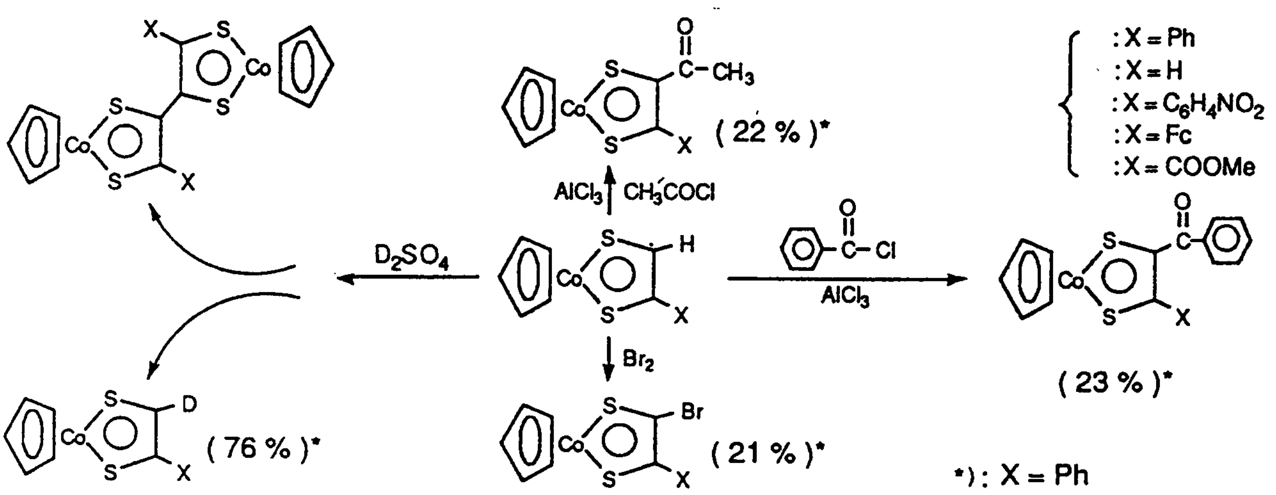


X	R	Yield of 5 (%)
H	Me	41
H	C_5H_{11}	66
Cl	CH_2Ph	17



(R = methyl, R' = c-hexyl)

The aromatic character of cobaltdithiolene rings has been shown by Prof. Akira Sugimori's group by the occurrence of the electrophilic aromatic substitution reactions shown below (No. 45).



The interesting nature of the chemistry of small-size cyclic disulfides was shown by the group of Prof. J. Nakayama, who isolated an interesting three membered thiosulfinate, as shown below (No. 49).

We now look forward to the 21st Symposium of Heteroatom Chemistry in December of this year in Toyama which will be organized by Prof. Toru Koizumi of the Toyama Medical and Pharmaceutical University. He chose the second week of December, simply because he wants to avoid the probable heavy snow fall in January. We have never held the Symposium at any Hokuriku area of this country. Therefore, it will be an interesting experience, and we look forward to the nice fresh-fish meals in Hokuriku.