

A Report on the 23rd Symposium on Heteroatom Chemistry of the Chemical Society of Japan

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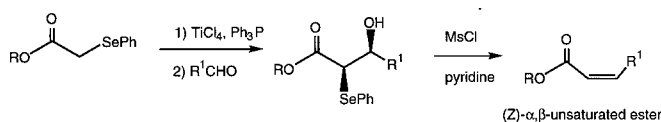
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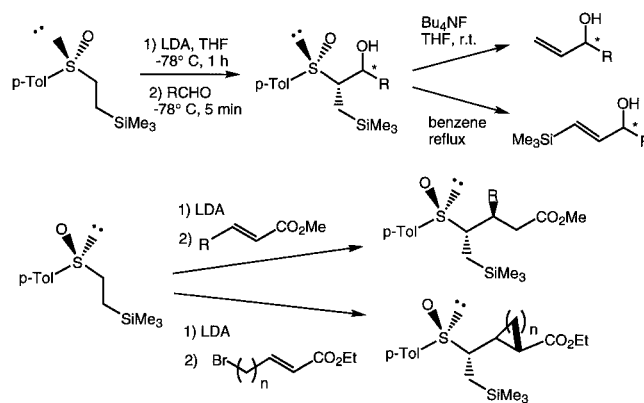
The 23rd domestic Symposium on Heteroatom Chemistry, sponsored by the Chemical Society of Japan, was held at Okayama University Natural Science Research Auditorium on December 12–14, 1996, and all the participants (ca. 280) enjoyed the many lectures. The organizer, Professor Kenji Uneyama of Okayama University, and his staff members deserve much credit for their efforts.

As usual, the meeting began with a plenary lecture entitled "Stereochemical Organic Syntheses Using Sulfur and Selenium Functional Groups," by Professor Takeshi Toru of Nagoya Institute of Technology. The first part of the lecture covered his area of interest as follows:



When an α -seleno carbonyl compound was reacted with an aldehyde in the presence of TiCl_4 and Ph_3P , a highly stereoselective formation of an aldol derivative could be realized. Highly stereoselective reactions of β -trimethylsilylsulfoxides were also described.

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Professor Toru used the reaction to synthesize numerous chiral α -sulfinylenones and utilized them to develop asymmetric radical β -addition reactions.

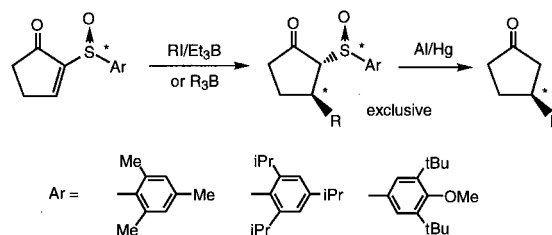
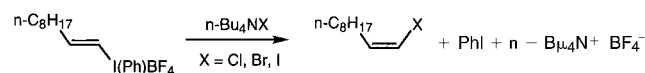


TABLE 1 Relative Leaving Group Abilities

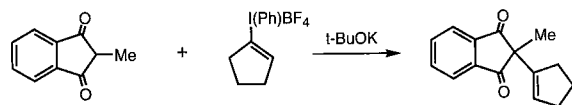
Nucleofuge	k_{rel}	Nucleofuge	k_{rel}
AcO	1.4×10^{-6}	I	9.1×10
Me ₂ S ⁺	5.3×10^{-2}	TsO	3.7×10^4
Cl	1.0	TfO	1.4×10^8
F ₃ CCO ₂	2.5	Ph(BF ₄)I	1.2×10^{14}
Br	1.4×10	p-Cl < 6 H ₄ (BF ₄)I	2.9×10^{14}

The second plenary lecture was “Chemistry of Hypervalent Vinylidanes,” by Professor Masahito Ochiai of Tokushima University. He reported that solvolysis reactions of (1-cyclohexenyl)aryliodanes proceed at reasonable rates even at room temperature. In comparison with other nucleofugic groups, the hypervalent Ph(BF₄)I group can be classified as a hyperleaving group. It has a leaving group ability about 10⁶ times greater than that of the triflate group that itself is regarded to be a superleaving group. Relative leaving group abilities of some common nucleofugic groups are shown in Table 1.

Some reactions illustrating the nucleofugic utility of the Ph(BF₄)I group are as follows:

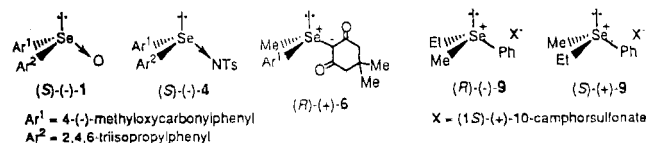


There is evidence that, with Ph(BF₄)I available as the leaving group, S_N2 reactions can take place at a vinyl carbon.

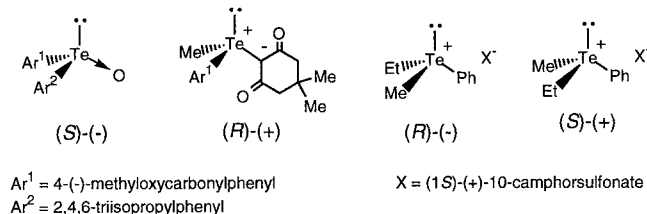


The third plenary lecture was entitled “Synthesis and Stereochemistry of Optically Active Selenium and Tellurium Compounds,” delivered by Professor Nobumasa Kamigata of Tokyo Metropolitan University. He reported that the interest of his research group has recently been focused on chiral tricoordinate selenium and tellurium compounds. Diastereomerically pure selenoxide (S) – (–) 1, selenonium imide (S) – (–) – 4, selenonium ylide (R) – (+) – 6, and selenonium salts (R) – (–) 9 and (S) – (+) – 9 were isolated as stable crystals by resolution of diastereomeric mixtures, and optically ac-

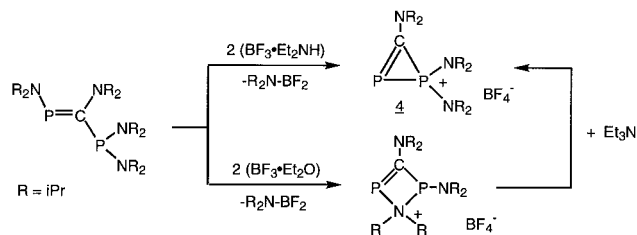
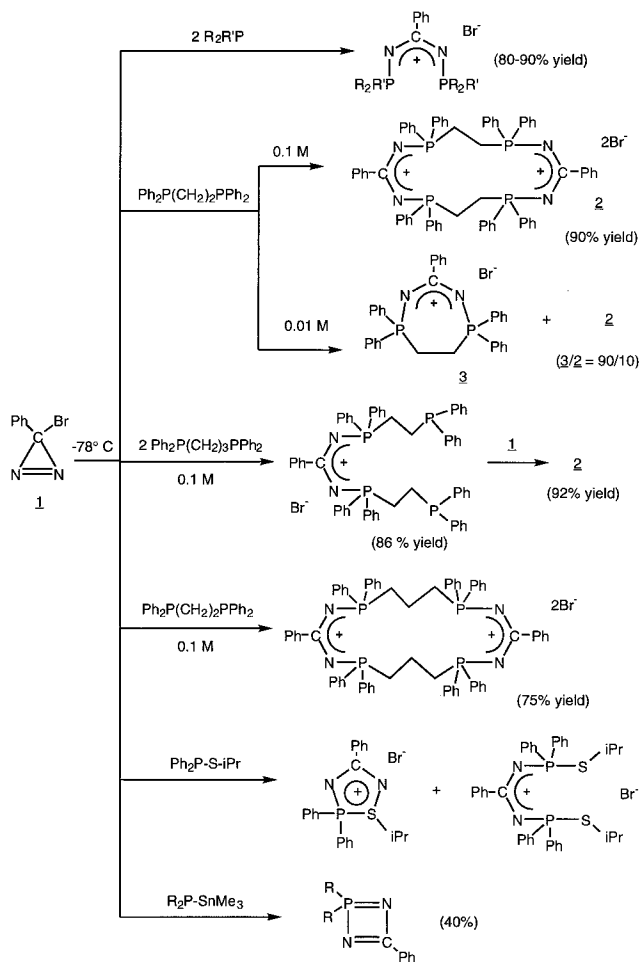
tive selenoxides were also obtained by asymmetric oxidation of the corresponding selenides under Sharpless conditions and chromatographic resolution using an appropriate optically active column. The absolute configurations of these optically pure compounds were determined by X-ray crystallographic analysis and by CD spectroscopy.



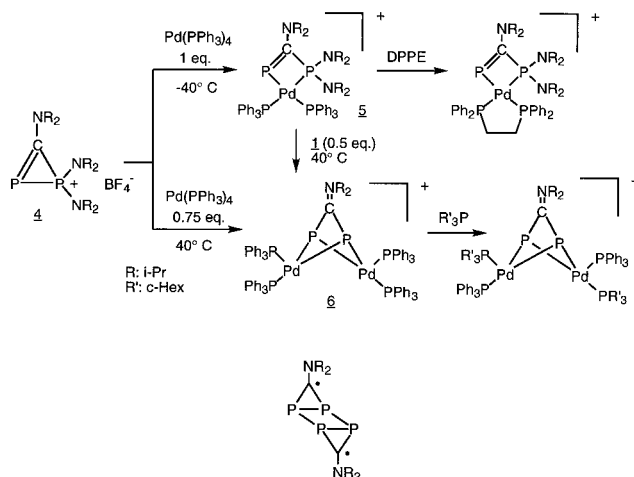
Optically active telluroxides were obtained by chromatographic resolution and were found to be easily racemized in solution. Optically active telluronium ylides and optically pure telluronium salts were obtained by resolution from diastereomeric mixtures. Absolute configurations were determined by X-ray crystallographic analysis and by examination of CD spectra. Diastereomerically pure ethylmethylphenyltelluronium (+)-camphor-sulfonate was converted to enantiomerically pure ethylmethylphenyltelluronium perchlorate by an anion exchange reaction. Some typical structures of chiral tricoordinate compounds that were isolated and studied are the following:



The last plenary lecture was given by Dr. Guy Bertrand of Toulouse University. He is not a stranger here. About 6 years ago, he gave a plenary lecture at the Symposium, and again it was a superb one. He was the first recipient of the ICMGC prize for excellence in main group chemistry research, and Professor Oae, one of the authors of this report, was the representative of ICMGC who presented the award in Canada. The title of his presentation at the 23rd symposium was Group 13 and 15 Elements: From Small Membered Rings to Polymers through Macrocycles,” and the talk was divided into several parts. In the first part, he discussed the role of the bromodiazirine 1 as a building block for many syntheses of interesting compounds, as shown in Scheme 1.



The second portion of his presentation dealt with the chemistry of diphosphirenium salts. It is intriguing that palladium complex (5) reacts with 0.5 equivalent of diphosphirenium salt (1) to give the 1,3-diphospha-2,4-bis[bis(triphenylphosphine)pallada(II)]tricyclo[1.1.1]pentane tetrafluoroborate salt (6) in 25% yield (Scheme 2).



In the last part of his lecture, he discussed the use of the first chiral tetracoordinated aluminum cation as a polymerization catalyst.

In addition to these plenary lectures, there were 74 ordinary talks delivered only in 10 minute sessions plus a few questions, and these presentations lasted three days. On the first day, the symposium continued till 19:00. On the second, there was the banquet that started at 19:00, and on the last day, the meeting finished at 17:00 to allow the participants to travel home at a reasonable hour. The titles and speakers are listed below:

1. "Carbon-bromide Bond Cleavage via Single Electron Transfer from the Selenolate Anion: Generation and Intramolecular Cyclization of the Difluoroalkyl Radical" by T. Yanagiguchi, H. Asai, and K. Uneyama (Okayama University).
2. "Synthesis of Cephalosporins through Sequential Addition/Cyclization of Allenecarboxylates" by H. Tanaka, S. Sumida, H. Tomita, Y. Yamaguchi, and S. Torii (Okayama University).
3. "Synthesis of Optically Active Azirine Derivatives by the Lipase-Catalyzed Resolution" by T. Sakai, I. Kawabata, T. Ema, and M. Utaka (Okayama University).
4. "A Convenient Synthesis of 1,2,3-Triazoles" by K. Harada, M. Oda, A. Matsushita, and M. Shirai (UBE Industries, Ltd.).
5. "A New Synthesis of Benzofurans from *o*-Siloxyacetophenones" by Y. Itoh, T. Aoyama, and T. Shioiri (Nagoya City University).
6. "Synthesis of Optically Pure Cyclopropylstannanes" by T. Itoh, S. Emoto, and M. Kondo (Okayama University).
7. "Generation of Magnesium Akylidene Car-

- benoids from 1-Halovinyl Sulfoxides with Grignard Reagent via Ligand Exchange Reactions of Sulfoxides" by T. Satoh, K. Takano, H. Someya, K. Matsuda, and M. Koyama (Science University of Tokyo).
8. "Synthesis and Reactions of 2,2-Dimethyl-2-Silaocetane Derivatives" by O. Hoshino, K. Shimizu, and M. Fukuzawa (Science University of Tokyo).
 9. "Behavior of an Added Stannyl Chloride in the Enolate/Alkyl Halide Reaction System" by M. Suzuki, M. Goto, I.-H. Son, and R. Noyori (Gifu University and Nagoya University).
 10. "Generation and Cycloaddition of an Azomethine Ylide Utilizing Di- or Trifluorosilane" by S. Yokoi, A. Nishi, S. Yamaoka, S. Minakata, I. Ryu, and M. Komatsu (Osaka University).
 11. "A Single-Step Preparation of Crown-Type Cyclophanes via a Bismuth (III) Bromide Catalyzed Reductive Ether Formation" by J. Ishida, N. Komatsu, and H. Suzuki (Kyoto University).
 12. "DMSO Oxidation of Some Benzoines Using Iron(III) Chloride" by J. Yamamoto, M. Tada, and T. Ishiki (Tottori University).
 13. "Oxygen Transfer Reactions of 4-Bromomethylazoxybenzenes in Sulfuric Acid" by J. Yamamoto, T. Oka, and T. Ishiki (Tottori University).
 14. "Syntheses and Properties of Oligoselenophenes and Their Oxidation Species" by H. Nakanishi, S. Inoue, K. Takimiya, Y. Aso, and T. Otsubo (Hiroshima University).
 15. "Selective Anodic Desulfurization of Thiocarbonyl Compounds" by T. Fuchigami and K. Mitomo (Tokyo Institute of Technology).
 16. "Synthesis of Tetrahydronaphthalene Derivatives by Laser Photolyses" by A. Ouchi and Y. Koga (National Institute of Materials and Chemical Research).
 17. "Photolysis of Pyridyl Sulfoxide Derivatives" by H. Kamiyama, M. Takeda, T. Yoshimura, T. Fujii, C. Shimasaki, and H. Morita (Toyo University).
 18. "Synthesis, Physical Properties, and Reactivities of 1,2-Digermacyclohexa-3,5-dienes" by M. Akazawa and K. Mochida (Gakushuin University).
 19. "Photoreaction of Trivalent-Phosphorus Compounds with a Ruthenium Complex: Kinetic Analysis of Single-Electron Transfer Process" by S. Yasui, M. Tsujimoto, K. Shioji, and A. Ohno (Tezukayama College and Kyoto University).
 20. "Reactivity of a Cation Radical Generated from a Trivalent Phosphorus Compound" by K. Shioji, S. Yasui, M. Tsujimoto, and A. Ohno (Kyoto University and Tezukayama College).
 21. "Synthesis and Reactions of Phosphine-Boranes Bearing Functional Groups at the Boron Atom" by T. Imamoto, H. Ohtsuka, E. Hirakawa, K. Asakura, and Y. Yamanoi (Chiba University).
 22. "Reactions of Biheteroaryl Sulfoxides with Heteroarylolithiums-Ligand Coupling and Exchange Reactions" by Y. Inubushi, M. Yoshihara, and S. Oae (Kinki University and Institute of Heteroatom Chemistry).
 23. "Construction of Novel π -Conjugated Systems Composed of Triarylphosphines with Bulky Substituents" by S. Sasaki, F. Murakami, and M. Yoshifuji (Tohoku University).
 24. "Synthesis of New π -Donors Using the Reaction of Ethylenedithiotetrathiafulvalene with Lithium Amide" by H. Suzuki, U. Kux, Y. Kuwatani, S. Sasaki, H. Matsuyama, and M. Iyoda (Tokyo Metropolitan University).
 25. "Synthesis and Reduction of Novel Persilylated π -Electron Systems Derived from Silacyclopentatriene" by T. Matsuo and A. Sekiguchi (University of Tsukuba).
 26. "Synthesis and Properties of Ethylenedithio Modified Naphthalenes" by J. Hohrai, H. Tani, N. Azuma, and N. Ono (Ehime University).
 27. "Permutation of Pentacoordinate Spirophosphoranes and Substituent Effects on the Reactions at Phosphorus" by M. Nakamoto, S. Kojima, and K. Akiba (Hiroshima University).
 28. "Synthesis and Structures of Phosphoranes Bearing a Bidentate Ligand: Relation of Hypervalent Bonds with NMR Chemical Shifts and X-ray Structures" by Y. Yamamoto, K. Nakao, and K. Akiba (Hiroshima University).
 29. "Synthesis of Tellurium Centered Novel Hypervalent Dications" by N. Furukawa, K. Ko-

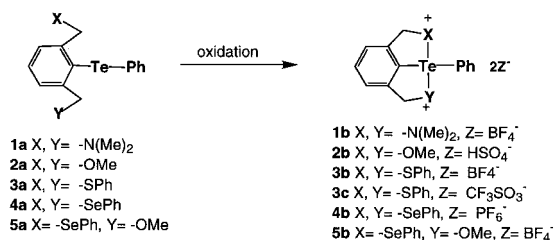
- bayash, S. Sato, A. B. Bergholt, E. Horn, and O. Takahashi (University of Tsukuba).
30. "Oxirane Formation Reactions from Novel Oxetanes Containing a Highly Coordinate Group 16 Element" by F. Ohno, T. Kawashima, and R. Okazaki (University of Tokyo).
 31. "Reaction of Thiobenzophenones with Benzynes" by K. Okuma, T. Sotoyama, K. Shiki, T. Kitamura, and Y. Fujiwara (Fukuoka University and Kyushu University).
 32. "Generation of Allenyliodanes and Their Reactions as Propynyl Cation-Equivalent Species" by M. Kida, T. Sueda, M. Ochiai, and T. Okuyama (University of Tokushima and Osaka University).
 33. "Synthesis of Oligomers Including Hypervalent Iodine" by T. Kitamura, T. Nakamura, and Y. Fujiwara (Kyushu University).
 34. "Cyclic Alkoxylation and Amination onto Aromatic Rings with (Diacyloxyiodo)arenes" by H. Togo, Y. Hoshina, T. Muraki, H. Nakayama, and M. Yokoyama (Chiba University).
 35. "Mechanism for Sequential Pericyclic Reactions of Unsaturated Xanthates" by M. Eto and K. Harano (Kumamoto University).
 36. "Non-Berry Pseudorotation and Ligand Coupling of Chalcogenuranes" by O. Takahashi, S. Sato, and N. Furukawa (University of Tsukuba).
 37. "Ab Initio MO Studies of Hypervalent Species of Heteroatom Elements" by A. Maki, N. Kambe, N. Sonoda, T. Sugino, and Y. Shimizu (Osaka University and Osaka National Research Institute).
 38. "Synthesis and Stereochemistry of Penta-thiepanes with a Propellane Structure" Y. Sugihara, H. Takeda, A. Ishii, S. Kumakura, and J. Nakayama (Saitama University).
 39. "Synthesis, Reactivities and Conformational Analysis of New Cyclic Polysulfides, 6,10-Di-substituted [1,2,3]Tri-thiolo[h]benzopentathiepin Derivatives" by T. Kimura, M. Hanazawa, S. Ogawa, and R. Sato (Iwate University).
 40. "Synthesis and Reactions of Lead-Sulfur Doubly-Bonded Compounds, Plumbanethiones" by N. Kano, N. Tokitoh, and R. Okazaki (University of Tsukuba).
 41. "Synthesis and Structure of Heterohelicenes Containing Phenolic Hydroxy Groups" by K. Tanaka, Y. Kitahara, H. Osuga, K. Some-miya, T. Kume, T. Takimoto, H. Suzuki, and Y. Kawai (Kyoto University).
 42. "Synthesis and Highly Selective Ag⁺ Binding Capability of Cyclophanes Containing Sulfur Atoms" by T. Nabeshima, T. Aoki, Y. Yano, and E. Horn (University of Tsukuba and Gunma University).
 43. "Se—F Intramolecular Interaction in Organic Selenium Compounds Containing Fluorine" by H. Komatsu, M. Iwaoka, and S. Tomoda (University of Tokyo).
 44. "Asymmetric [2,3] Sigmatropic Rearrangement of Chiral Selenonium Compounds Bearing the 2-exo-Hydroxy-10-bornyl Group" by N. Kurose, T. Takahashi, and T. Koizumi (Toyama Medical and Pharmaceutical University).
 45. "Synthesis of Chiral 2-Sulfur-Substituted 1,1'-Binaphthyl Compounds and Synthetic Utilities" by H. Kosugi, R. Hatsuda, M. Kato, T. Hattori, and S. Miyano (Tohoku University).
 46. "Asymmetric Recognition of Sulfoxides by Crystalline Dipeptides" by M. Akazome, O. Tanaka, M. Noguchi, A. Sumikawa, T. Uchida, and K. Ogura (Chiba University).
 47. "Cycloaddition of Imines with Allene. Formation Mechanism of Azetidine Ring" by T. Matsuoka and K. Harano (Kumamoto University).
 48. "Chiral Bis(oxazoline)-Copper Catalyzed Enantioselective Imidation of Sulfides" by H. Takada, Y. Nishibayashi, K. Ohe, and S. Uemura (Kyoto University).
 49. "Asymmetric Radical β -Addition to Chiral α -Sulfinylenones" by N. Mase, Y. Watanabe, Y. Ueno, and T. Toru (Nagoya Institute of Technology).
 50. "Participation of Chiral Sulfinyl Ligands in Transition Metal-Catalyzed Reactions" by Y. Suzuki, I. Abe, A. Seo, F. Kato, and K. Hiroi (Tohoku College of Pharmacy).
 51. "Synthesis and Structure of Organotin Chalcogenocarboxylates" by R. Yamada, O. Niyomura, M. Nomura, T. Kanda, T. Murai, and S. Kato (Gifu University).
 52. "New Synthesis, Structure and Reactivity of Selenoamides" by T. Ezaka, N. Niwa, Y. Kimura, T. Murai, T. Kanda, and S. Kato (Gifu University).

53. "Syntheses and Properties of 1- and 3-Benzoheteroepines Containing Group 14, 15 and 16 Heavier Elements" by S. Yasuike, T. Kiharada, J. Kurita, and T. Tsuchiya (Hokuriku University).
54. "Novel Synthesis of Dialkenyl Dichalcogenides, and Conversion of Dialkenyl Diselenides to the Corresponding Selenophenes by Thermal Reaction" by K. Shimada, M. Asahida, K. Takahashi, S. Aoyagi, and Y. Takikawa (Iwate University).
55. "Synthesis of Aromatic Sulfoximines by the Friedel-Crafts Reaction" Y. Okada, Y. Furucho, and T. Takata (Osaka Prefecture University).
56. "Introduction of Chalcogen Atoms into Vinylcyclopropanes by Use of Dichalcogenide— $h\nu$ Systems and Its Application" by I. Ogawa, A. Ogawa, T. Hirao, and N. Sonoda (Osaka University).
57. "Synthesis and Reactions of N,N-Bis(acylthio)methylanilines—Mercaptomethylation of Aromatic and Carbonyl Compounds via Acylthiomethyl Intermediates" by T. Izawa, Y. Terao, and K. Suzuki (University of Shizuoka).
58. "Regioselective Carbon–Selenium Bond Forming Reactions Using Zirconacyclopentene Derivatives" by T. Suzuki, M. Segi, and T. Nakajima (Kanazawa University).
59. "Novel Intramolecular Oxyselenenylation Using Benzeneselenocyanate" by H. Inoue and S. Murata (Nagoya University).
60. "Reactions of Alkynyl- and Alkenylselenonium Salts with Nucleophiles" by T. Kataoka, S. Watanabe, Y. Banno, T. Iwamura, and H. Shimizu (Gifu Pharmaceutical University).
61. "The Reaction of Tellurium(IV) Compounds with a Phosphite in the Presence of a Nucleophile" by Y. Watanabe, S. Inoue, and A. Fukushima (Ehime University).
62. "Reactions of Sulfonyl Chlorides with Silyl Enol Ethers Catalyzed by a Transition Metal Complex" by M. Yoshikawa, K. Udodaira, T. Shimizu, and N. Kamigata (Tokyo Metropolitan University).
63. "Radical Substitution in Metalladithiolene Rings" by A. Sugimori, G. Hagino, N. Tachiya, M. Kajitani, and T. Akiyama (Sophia University).
64. "Reactivity of Mo Phosphenium Complexes—Migration of OR, SR, and NR₂ on Tertiary Phosphorus Compounds to a Phosphenium Ligand" by H. Nakazawa, Y. Yamaguchi, and K. Miyoshi (Hiroshima University).
65. "Lewis-Acid-Catalyzed Intramolecular [2 + 2] Cycloaddition Reaction of Dienyl- and Trienylphosphonates" by T. Kakiuchi, N. Kitamura, T. Okauchi, J. Ichikawa, and T. Minami (Kyushu Institute of Technology).
66. "Palladium-Catalyzed Regio- and Stereoselective Phosphorylation of Alkynes" by L. Han, M. Tanaka, and N. Choi (National Institute of Material and Chemical Research).
67. "Amide-Type Phosphate Protecting Groups for Phosphoamino Acids" by M. Ueki, J. Okumura, M. Goto, and M. Igarashi (Science University of Tokyo).
68. "Reagent Design Directed Toward the Synthesis of a Stereodefined Isoxazolidinone Framework" by T. Ishikawa, K. Nagai, T. Kudoh, A. Tatsukawa, and S. Saito (Okayama University).
69. "Novel [2,3]-Sigmatropic Rearrangement of O-Allylic Hydroxylamines and Its Synthetic Applications" by T. Ishikawa, M. Fukui, T. Kohara, A. Yamashita, K. Sigemori, and S. Saito (Okayama University).
70. "Synthesis and Properties of C-Azanucleosides" by M. Yokoyama, A. Momotake, Y. Ochiai, T. Akiba, and H. Togo (Chiba University).
71. "Synthesis of Novel Glycoside and Nucleoside Derivatives of Phospha Sugar Analogs" by Y. Kato, K. Suzuki, T. Oshikawa, and M. Yamashita (Shizuoka University).
72. "A Preparation of a Phospholane Oxide from a 4-Bromobutylphosphinate Derivative and Application to the Synthesis of Phospha-Sugars" by T. Hanaya, S. Kawase, H. Kawamoto, and H. Yamamoto (Okayama University).
73. "Synthesis of Optically Active Carbocyclic nucleosides" by J. Nokami, Y. Ozaki, N. Imai, H. Matsuura, and S. Torii (Okayama University of Science and Okayama University).
74. "Synthesis of 4'-Thioribonucleosides" by J. Nokami, Y. Mae, K. Nakaniwa, N. Imai, H. Matsuura, S. Torii (Okayama University of Science and Okayama University).

It is difficult to choose a few from 74 talks for additional attention since most of these talks are worthy of presentation as plenary lectures. Imamoto's talk (21) concerning the synthesis and properties of

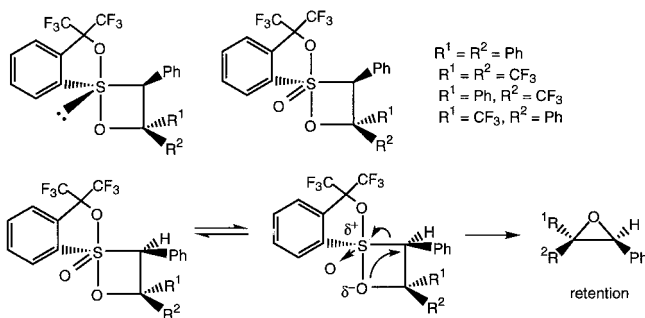
phosphine-boranes was outstanding. For example, he presented results of the reactions of the tricyclohexylphosphine-trifluoromethanesulfonyloxyborane complex with nucleophiles to give products substituted at the boron atom, as seen from Table 2.

He also reported the first example of a B-chiral phosphine-borane, tricyclohexylphosphine-chloro(trifluoromethanesulfonyloxy)borane, synthesized from tricyclohexylphosphine-monochloroborane and trifluoromethanesulfonic acid.



SCHEME 3

Professor N. Furukawa and co-workers (29) presented "Synthesis of Tellurium Centered Novel Hypervalent Dications." The first examples of dicationic tellurane species have been synthesized and isolated. A typical structure was established by X-ray crystallography (Scheme 3).



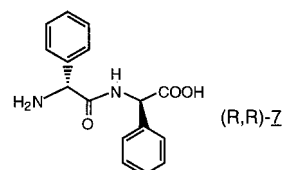
SCHEME 4

The lecture on oxirane formation reactions from novel oxetanes containing a highly coordinate group 16 element presented by F. Ohno, T. Kawashima, and R. Okazaki (30) was stimulating. As shown by the

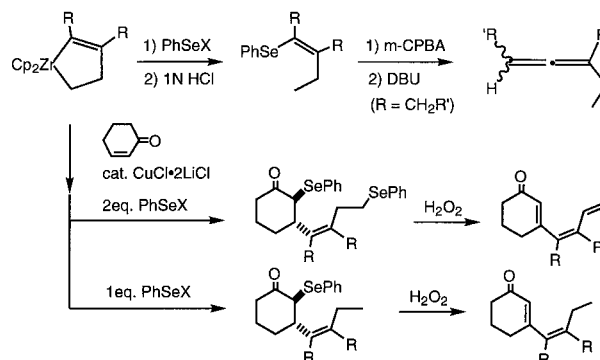
structures in Scheme 4, the four-membered intermediates are interesting. Probably the chemistry depicted in the equation is a ligand coupling reaction.

Another outstanding lecture was that of (46) presented by Professor K. Ogura, on "Asymmetric Recognition of Sulfoxides by Crystalline Dipeptides". It is summarized in Table 3.

He also clarified the mechanism of the reaction leading to high enantioselectivity and the dependence of the preferred absolute configuration of the sulfoxides on the substituents of the dipeptides as a host.



The results of research carried out by Professor M. Segi and Professor T. Nakajima (58) and their colleagues at Kanazawa University on "A Regioselective Carbon-Selenium Bond Forming Reaction Using Zirconacyclopentene Derivatives" was intriguing. These workers uncovered the regioselective reaction of zirconacyclopentenes or their derivatives with phenylselenenyl halide and the subsequent conversion into conjugated olefins or allenes via elimination of phenylseleno groups, as shown in Scheme 5.

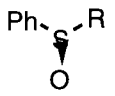


SCHEME 5

TABLE 2 Products Substituted at the Boron Atom

Reagent	Conditions	Product	Yield/%
LiAlD ₄	0°C, 0.5 h	Cy ₃ PBH ₂ D	86
CeCl ₃	50°C, 5 h	Cy ₃ PBH ₂ Cl	89
LiBr	RT, 0.5 h	Cy ₃ PBH ₂ Br	88
LiCN	RT, 1 h	Cy ₃ PBH ₂ CN	45
PhSH/NaH	0°C, 0.5 h	Cy ₃ PBH ₂ SPh	82
Me ₃ SiC≡CLi	RT, 6 h	Cy ₃ PBH ₂ C≡CSiMe ₃	81
(CH ₃) ₂ Cu(CN)Li ₂	RT, 2 h	Cy ₃ PBH ₂ CH ₃	28
(n-C ₄ H ₉) ₂ Cu(CN)Li ₂	-20°C, 1 h; 0°C, 0.5 h	Cy ₃ PBH ₂ C ₄ H ₉ -n	78
(s-C ₄ H ₉) ₂ Cu(CN)Li ₂	-30°C, 2 h; 0°C, 0.5 h	Cy ₃ PBH ₂ C ₄ H ₉ -s	89

TABLE 3 Inclusion of Alkyl Phenyl Sulfoxide by (*R,R*)-7

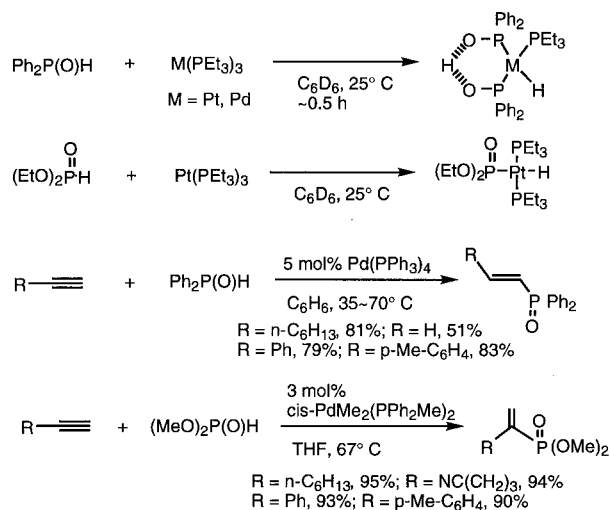
	Method A: Sorption		Method B: Crystallization	
	<i>ee</i> /%	Inclusion ^a /%	<i>ee</i> /%	Inclusion ^a /%
<i>t</i> -Bu	37(<i>S</i>)	89	90(<i>S</i>)	100
<i>i</i> -Pr	86(<i>S</i>)	100	87(<i>S</i>)	100
Et		N.I. ^b	91(<i>S</i>)	95
Me	92(<i>R</i>)	95	93(<i>R</i>)	100

^a Inclusion means the percentage of the included guest based on the dipeptides. Determined by ¹H NMR.

^b N.I. means no formation of the inclusion complex.

Dr. M. Tanaka's group (66) reported on a novel and useful reaction, "Palladium-Catalyzed Regio- and Stereoselective Phosphorylation of Alkynes." They reported the facile oxidative addition involving the P-H bonds of diphenylphosphine oxide and secondary phosphites to Pd and Pt complexes generating H-M-P(O) (M = Pd, Pt) species. The efficient Pd-catalyzed regio- and stereoselective additions of X₂P(O)H (X = Ph, OR) to alkynes affording alken-

ylphosphine compounds were also described (Scheme 6).



SCHEME 6

The next Symposium will be held in Sendai at about the same season as the present. However, the number of talks is getting so large that a poster session will have to be introduced. We can now look forward with pleasure to the 24th Domestic Symposium on Heteroatom Chemistry.