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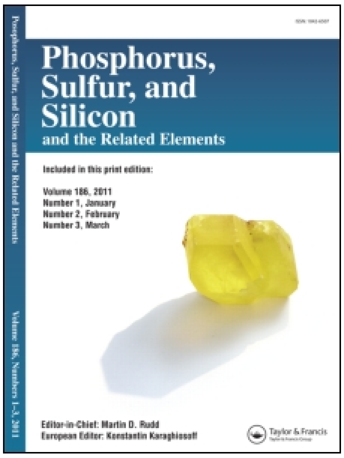

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Retrospect of Se and Te Chemistry

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Retrospect of Se and Te Chemistry

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Retrospect of organoselenium and tellurium chemistry for these 30 years is described focusing on our novel findings in this field: (1) telluroxide elimination leading to alkenes and allylic compounds, (2) Pd-catalyzed or –mediated carbodetelluration for a new C–C bond formation, (3) synthesis of chiral diferrocenyl dichalcogenides and their use as chiral auxiliaries, (4) asymmetric selenoxide elimination for making optically active allenes and alkenes, (5) meta chloroperbenzoic acid (MCPBA) oxidation of organic selenides and tellurides leading to a substitution of a PhSe or PhTe moiety, as well as (6) preparation of chalcogen-bridged diruthenium complexes and their catalytic use for propargylic substitution reactions.

Keywords Asymmetric selenoxide elimination; carbodetelluration; chalcogen-bridged diruthenium complex; chiral diferrocenyl dichalcogenide; imidation; oxidation; telluroxide elimination

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INTRODUCTION

Thallium moiety of organothallium(III) compounds can be replaced by halogen and pseudohalogen by treatment with copper(II) and/or potassium halides and pseudohalides. When an arylthallium(III) compound was treated with $Cu(SeCN)_2$ in a suitable organic solvent, aryl selenocyanate (ArSeCN) was obtained in good yield (Eq. (1)).[1] This is my first encounter with organoselenium chemistry. At that time, the utility of selenium in organic synthesis has been recognized especially by the finding of selenoxide elimination and [2–7]sigmatropic rearrangement of selenoxides for facile preparation of alkenes, allylic alcohols, and allylic ethers.[2–5] I thought to use this newly prepared ArSeCN for preparing synthetically useful organic selenides and eventually disclosed that it

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I would like to express my grateful acknowledgement to all of my collaborators for these works. Without their enthusiastic efforts these works have not been done.

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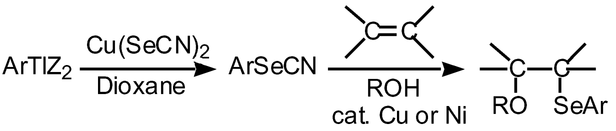
reacted with alkenes in alcohols to give β-alkoxyalkyl aryl selenides in the presence of a catalytic amount of Cu(II) or Ni(II) salt (oxyselenenylation of alkenes, (Eq. (1)).[6] Later, another group reported cyanoselenenylation of various alkenes using ArSeCN.[7,8]



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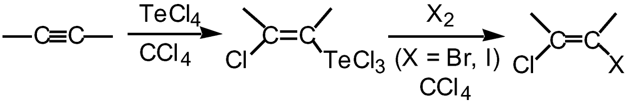
On the other hand, my organotellurium chemistry started when I treated acetylenes with tellurium tetrachloride ($TeCl_4$) in nonpolar solvents to obtain β-chloroalkenyltellurium trichloride (chlorotellurinylation of alkynes) (Eq. (2)).[9] At that time, I have been much devoted to the halogenation of alkenes and alkynes with various metal halides. Chlorotellurinylation itself has long been known, but its stereochemistry has not yet been clear.[10] We could show that this reaction proceeds in a *cis* fashion by examining the product carefully after halogenodetelluration (Eq. (2)). Since the chemistry of the use of tellurium in organic synthesis was much undeveloped compared with that of selenium, I decided to make every effort to develop this field.



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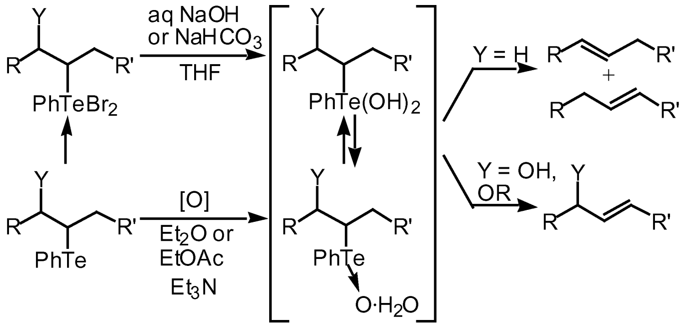
In this article, I would like to present the results of several novel findings in organoselenium and tellurium chemistry such as telluroxide elimination, Pd-catalyzed or -mediated carbodetelluration, synthesis of chiral diferrocenyl dichalcogenides, asymmetric selenoxide elimination, MCPBA oxidation of organic selenides, and tellurides as well as preparation of chalcogen-bridged diruthenium complexes and their catalytic use for organic transformations.

TELLUROXIDE ELIMINATION

In contrast to the selenoxide elimination leading to double-bond formation, little was known in the telluroxide elimination. We have found that sec-alkyl phenyl telluroxides, prepared via treatment of the corresponding organotellurium dibromides with NaOH or $NaHCO_3$, readily decompose to afford alkenes, allylic alcohols and allylic ethers under mild conditions (Eq. (3)).[11] Soon it also was disclosed that similar elimination occurs even by direct oxidation of alkyl phenyl tellurides with such oxidants as MCPBA, H_2O_2 and *t*-BuOOH, especially in the presence of Et_3N (Eq. (3)).[12,13] This finding disclosed a new characteristic feature of telluroxides and also showed their utility for alkene and allylic compound syntheses, a reaction which previously appeared to be of little value.



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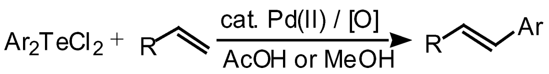
Pd-CATALYSED OR–MEDIATED CARBO-DETELLURATION

Aryltellurium(IV) compounds reacted with alkenes to give the corresponding arylated alkenes in the presence of a stoichiometric amount of Pd(II) salt or a catalytic amount of it if a suitable oxidant is present (Eq. (4)).[14] In the absence of alkenes, the corresponding biaryls were formed. Transmetallation of Te with Pd is a key step of the reaction. At that time, a synthetically useful C—C bond forming reaction using organotellurium compounds (carbodetelluration) has been limited to only two cases, namely, the syntheses of biaryls by Raney Ni reduction of diaryltellurium(IV) dibromides[15] and the carbonylation of aryltellurium(IV) chlorides with $Ni(CO)_4$.[16] When a similar reaction was carried out in the presence of atmospheric pressure of CO in place of alkenes, the corresponding carboxylic acids were obtained also via transmetallation between Te and Pd (Eq. (5)).[17]



(4)

$$Ph_2Te + CO \xrightarrow[MeCN]{Li_2PdCl_4} \xrightarrow{H_3O^+} PhCO_2H \qquad (5)$$

SYNTHESIS OF CHIRAL DIFERROCENYL DICHALCOGENIDES

I have been interested in the introduction of asymmetric methodology to the branch of Se and Te chemistry because it may be possible to obtain optically active organochalcogen compounds having a chiral center

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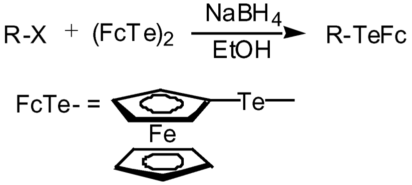
on a chalcogen atom (Ch). We undertook the introduction of a chiral ferrocenyl group as an aryl moiety of arylchalcogen compounds, since the compounds having a ferrocene planar chirality have been known to be very important in the field of catalytic asymmetric synthesis.[18] Another reason was that I was familiar with handling ferrocenyltellurium compounds because I have synthesized many new ferrocenyl organyl tellurides, especially air-stable cinnamyl and benzyl-ferrocenyl tellurides, by using diferrocenyl ditelluride (Eq. (6)).[19] We eventually succeeded in preparation of a variety of optically active [*R*, *S*; *R*, *S*] and [*S*, *R*; *S*, *R*]-diferrocenyl dichalcogenides (Eq. (7)).[20–22]



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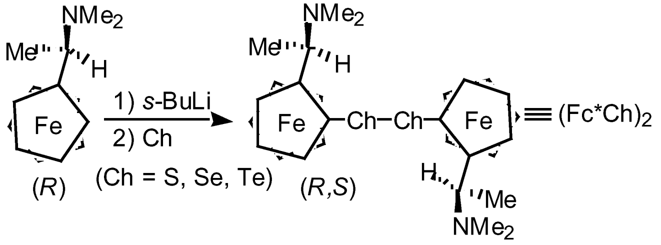

(7)

These compounds were employed as reagents for new asymmetric reactions such as selenoxide elimination, [2,3]sigmatropic rearrangement of chiral selenoxides, selenimides and telluroxides, and intramolecular selenenylation of alkenes. These also worked as chiral ligands in the Rh- and Ir-catalyzed asymmetric hydrosilylation and transfer hydrogenation of ketones.[23–26]

ASYMMETRIC SELENOXIDE ELIMINATION

During our investigation of asymmetric oxidation of organic selenides, we came across the first successful enantioselective elimination of chiral selenoxides by using either Sharpless oxidants or Davis oxidants to obtain optically active allenes (Eq. (8)) and cyclohexylidenemethyl ketones (Eq. (9)).[27,28] When suitable selenides having a chiral ferrocenyl group described above were oxidized with *meta*-chloroperbenzoic acid (MCPBA), chiral selenoxides were diastereoselectively formed which

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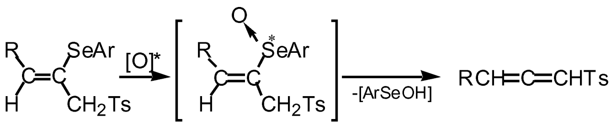
underwent *in situ* selenoxide elimination to afford optically active compounds (Eq. (10)).[20]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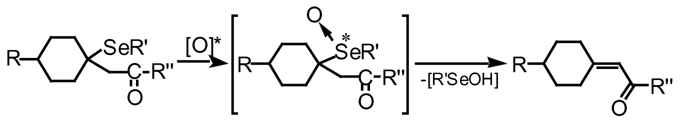
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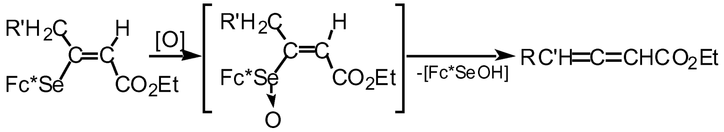
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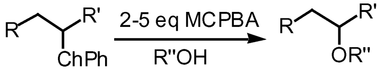
MCPBA OXIDATION OF SELENIDES AND TELLURIDES

During the investigation of selenoxide and telluroxide eliminations, I unexpectedly came across facile oxidative transformation of a C—Ch (Ch=Se, Te) bond of alkyl phenyl selenides and tellurides to C—O bond. MCPBA and methanol were revealed to be the most appropriate oxidant and solvent, respectively, and the fundamental reaction is a substitution of a PhSe or PhTe moiety with a methoxy group instead of β-elimination (Eqs. (11) and (12)).[20–31] The oxidation has been applied to the selective formation of dialkyl ethers, epoxides, ketones or acids, and the type of products depending strongly on the structure of the starting selenides and tellurides (Eq. (13)).[32–34] The key intermediate of the reaction is the MCPBA-addition product to an alkyl phenyl selenone or tellurone where a PhSe(VI) or PhTe(VI) moiety works as a very good leaving group.[35]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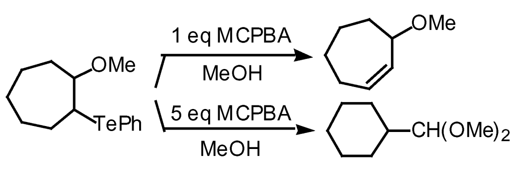
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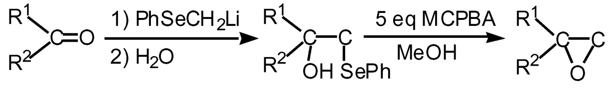
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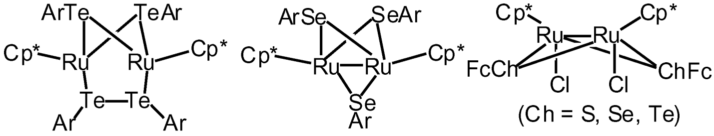
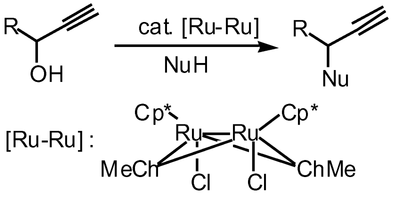
CHALCOGEN-BRIDGED DIRUTHENIUM COMPLEXES

As a series of thiolate-bridged dinuclear (η^5-C_5Me_5)Ru complexes have been known, I investigated synthesis and reactivities of similar dinuclear Ru family having bridging Se or Te ligands (Scheme 1).[36,37] In my continuing studies on these complexes, I found that a methylthio-bridged complex works especially as a good catalyst for propargylic substitution reactions (Eq. (14)).[38] Quite recently, I prepared the corresponding methylseleno- or methyltelluro-bridged complex as well and compared their catalytic activity for the above reactions. As a result, it was revealed that the Se-bridged complex is a quite effective catalyst similar to the S-complex, while the Te-complex does not show any catalytic activity.[39]



SCHEME 1



(14)

CONCLUSION

In conclusion, I described main results of my organoselenium and tellurium chemistry of these 30 years during which period I have published about 110 original articles and 20 review articles. When the reactivity of organochalcogen compounds (S, Se, Te) is compared, that of Se seems to resemble to that of S in some cases, while in some other cases it is quite close to that of Te. Although it is difficult to conclude what the main reason of the reactivity difference is between these compounds, the difference of either bond length and strength of C-chalcogen atoms or electronegativity of chalcogen atoms surely contributes to it as generally accepted. Most electropositive Te atoms in organotellurium compounds has a most metallic character to be easily replaced with transition metals to afford the corresponding organometallic species.

During these three decades, organic chemistry concerning Se and Te has been much explored, but the development of more novel catalytic reactions using Se and Te compounds is still waited which might greatly contribute to organic synthesis from the viewpoint of environmentally friendly green and sustainable chemistry.

REFERENCES

[1] S. Uemura, A. Toshimitsu, and M. Okano, *Bull. Chem. Soc. Jpn.*, **48,** 1925 (1975).
[2] K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95,** 2697 (1973).
[3] H. J. Reich, I. L. Reich, and J. M. Renga, *J. Am. Chem. Soc.*, **95,** 5813 (1973).
[4] K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94,** 7154 (1972).
[5] H. J. Reich, *J. Org. Chem.*, **40,** 2570 (1975).
[6] A. Toshimitsu, S. Uemura, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 166 (1977).
[7] S. Tomoda, Y. Takeuchi, and Y. Nomura, *Chem. Lett.*, 1733 (1982); *idem., Tetrahedron Lett.*, **23,** 1361 (1982).
[8] *idem., J. Chem. Soc., Chem. Commun.*, 871 (1982).
[9] S. Uemura, H. Miyoshi, and M. Okano, *Chem. Lett.*, 1357 (1979).
[10] M. de M. Campos and N. Petragnani, *Tetrahedron*, **18,** 527 (1962).
[11] S. Uemura and S. Fukuzawa, *J. Am. Chem. Soc.*, **105,** 2748 (1983).
[12] S. Uemura, K. Ohe, and S. Fukuzawa, *Tetrahedron Lett.*, **26,** 895 (1985).
[13] Y. Nishibayashi, N. Komatsu, K. Ohe, and S. Uemura, *J. Chem. Soc., Perkin Trans.*, **1,** 1133 (1993).
[14] S. Uemura, M. Wakasugi, and M. Okano, *J. Organomet. Chem.*, **194,** 277 (1980).
[15] J. Bergman, *Tetrahedron*, **28,** 3323 (1972).
[16] J. Bergman and L. Engman, *J. Organomet. Chem.*, **175,** 233 (1979).
[17] K. Ohe, H. Takahashi, S. Uemura, and N. Sugita, *J. Organomet. Chem.*, **326,** 35 (1987).
[18] A. Togni and T. Hayashi (Eds.), *Ferrocenes*, VCH, Weinheim, 1995.
[19] Y. Nishibayashi, T. Chiba, J. D. Singh, and S. Uemura, *J. Organomet. Chem.*, **473,** 205 (1994).
[20] Y. Nishibayashi, J. D. Singh, S. Uemura, and S. Fukuzawa, *Tetrahedron Lett.*, **35,** 3115 (1994).
[21] Y. Nishibayashi, J. D. Singh, S. Fukuzawa, and S. Uemura, *J. Org. Chem.*, **60,** 4114 (1995); *idem., J. Chem. Soc., Perkin Trans.*, **1,** 2871 (1995).
[22] T. Chiba, Y. Nishibayashi, J. D. Singh, K. Ohe, and S. Uemura, *Tetrahedron Lett.*, **36,** 1519 (1995).
[23] S. Uemura, *Phosphorus, Sulphur and Silicon*, **136–138,** 219 (1998).
[24] Y. Nishibayashi and S. Uemura, *Rev. Heteroatom. Chem.*, **14,** 83 (1996).
[25] Y. Nishibayashi, J. D. Singh, K. Segawa, S. Fukuzawa, and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 1375 (1994).
[26] Y. Nishibayashi, K. Segawa, J. D. Singh, S. Fukuzawa, K. Ohe, and S. Uemura, *Organometallics*, **15,** 370 (1996).
[27] N. Komatsu, Y. Nishibayashi, T. Sugita, and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 46 (1992).
[28] N. Komatsu, M. Matsunaga, T. Sugita, and S. Uemura, *J. Am. Chem. Soc.*, **115,** 5847 (1993).

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[29] S. Uemura, S. Fukuzawa, and A. Toshimitsu, *J. Chem. Soc., Chem. Commun.*, 1501 (1983).

[30] S. Uemura and S. Fukuzawa, *Tetrahedron Lett.*, **24,** 4347 (1983).

[31] *idem., J. Chem. Soc., Perkin Trans.*, **1,** 471 (1985).

[32] S. Uemura, K. Ohe, and N. Sugita, *J. Chem. Soc., Chem. Commun.*, 111 (1988).

[33] S. Uemura, S. Fukuzawa, T. Yamauchi, K. Hattori, S. Mizutaki, and K. Tamaki, *J. Chem. Soc., Perkin Trans.*, **1**, 1983 (1986).

[34] S. Uemura, *Rev. Heteroatom. Chem.*, **3,** 105 (1990).

[35] M. Tiecco, L. Testaferri, M. Tingoli, D. Chianeli, and D. Bartoli, *Gazz. Chim. Ital.*, **117,** 423 (1987).

[36] H. Matsuzaka, T. Ogino, M. Nishio, M. Hidai, Y. Nishibayashi, and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 223 (1994).

[37] H. Matsuzaka, J.-P. Qü, T. Ogino, M. Nishio, Y. Nishibayashi, Y. Ishii, S. Uemura, and M. Hidai, *J. Chem. Soc., Dalton Trans.*, 4307 (1996).

[38] Y. Nishibayashi, I. Wakiji, Y. Ishii, S. Uemura, and M. Hidai, *J. Am. Chem. Soc.*, **123,** 3393 (2001).

[39] Y. Nishibayashi, H. Imajima, G. Onodera, M. Hidai, and S. Uemura, *Organometallics*, **22,** 26 (2004).

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