

Ligand coupling reactions of hypervalent species

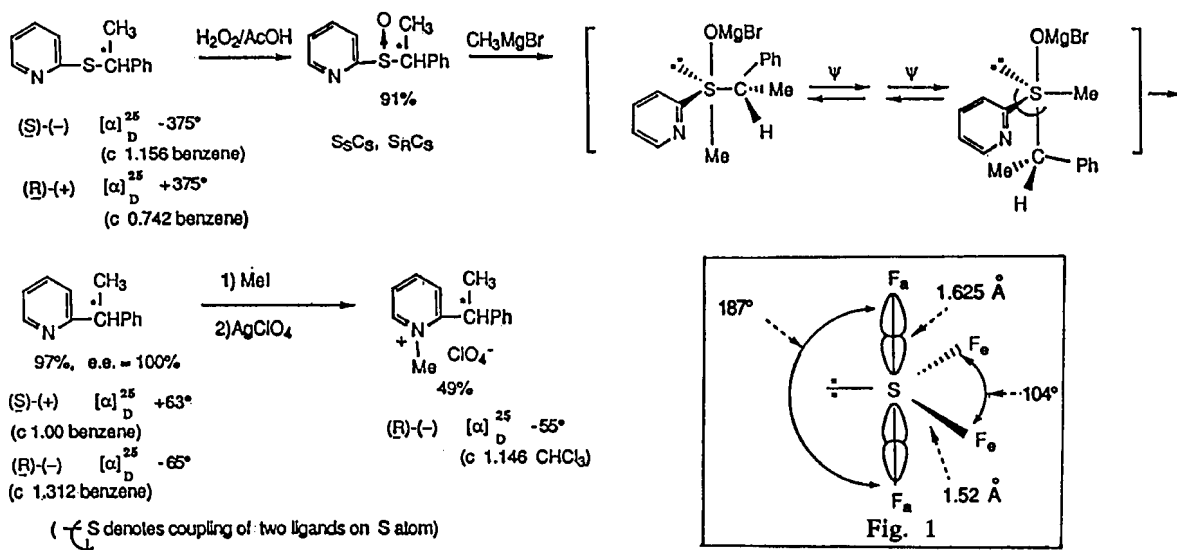
Shigeru Oae

Institute of Heteroatom Chemistry, 2509 Hirao Mihara-cho
 Minamikawachi-gun 587 Japan.

Abstract. The concept of ligand coupling is explained and the actual examples of many important reactions in which not only sulfur and phosphorus centered hypervalent species, but iodine, silicon and copper centered hypervalent ones are presented. It was also mentioned that many other reactions in which the central metal atoms in the nickel triad elements are considered to behave as the catalytic site for ligand coupling reaction, such as the Wäker process and the Heck reaction.

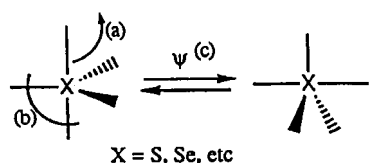
Ever since we found the following reaction,(1) we have extended our concept of ligand coupling(2) and have so many examples of these or similar reactions. However, there were prior many reactions to enable us to postulate the concept.

A typical example of a three-centered, four electron bond, called a hypervalent bond by Musher,(3) can be found in the substance in the structure of quaternary fluorinated sulfur as demonstrated by X-ray analysis by Rundle et al.(4) and Pimentel, (5) in the following figure. (Fig. 1)



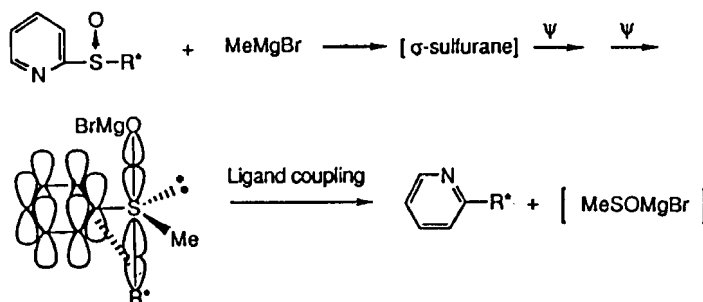
The central atom in a hypervalent species is valence-shell-expanded and tends to extrude one pair of electrons to the normal valency of an octet. This is the driving force of the reaction and there are three conceivable ways for hypervalent species to collapse to form stable octet species; self-decomposition as exemplified by the well-studied Wittig reaction,(6)ligand exchange,(7,8) and ligand coupling.(9-13) It is well known that the equatorial ligands form sp^2 and the axial linkages assume

p-orbitals. The axial bonds are longer and hold the electronegative substituents, as halogen while the equatorial ones are held with aromatic, olefinic and the negative groups, such as sulfoxide S-O bond. In dealing with the hypervalent species, one has to consider another physicochemical phenomenon, such as the topological transformation, as BPR or TR. The following is the results of stereochemistry, when these hypervalent species are handled.

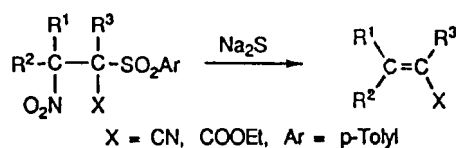
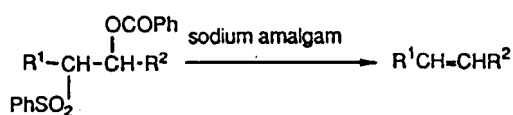


Chemical Phenomenon	Stereochemistry
(a) Ligand Exchange	inversion
+ (c)	retention
(b) Ligand Coupling	retention
(c) Topological Transformation (BPR or TR)	retention or racemization

One of the driving force of ligand coupling is the following effective overlapping, shown by the sulfur-centered reaction, as illustrated below.

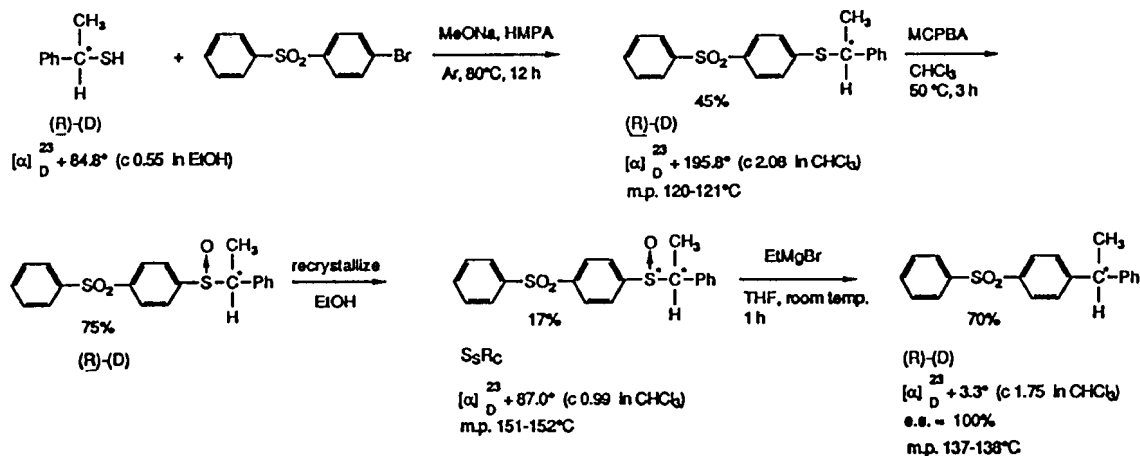


Meanwhile, the expression "reductive elimination" and "oxidative addition" are frequently used in organometallic chemistry. This term is also a mere description of the phenomenon and lacks mechanistic significance. The only two examples are shown below. (14-15)

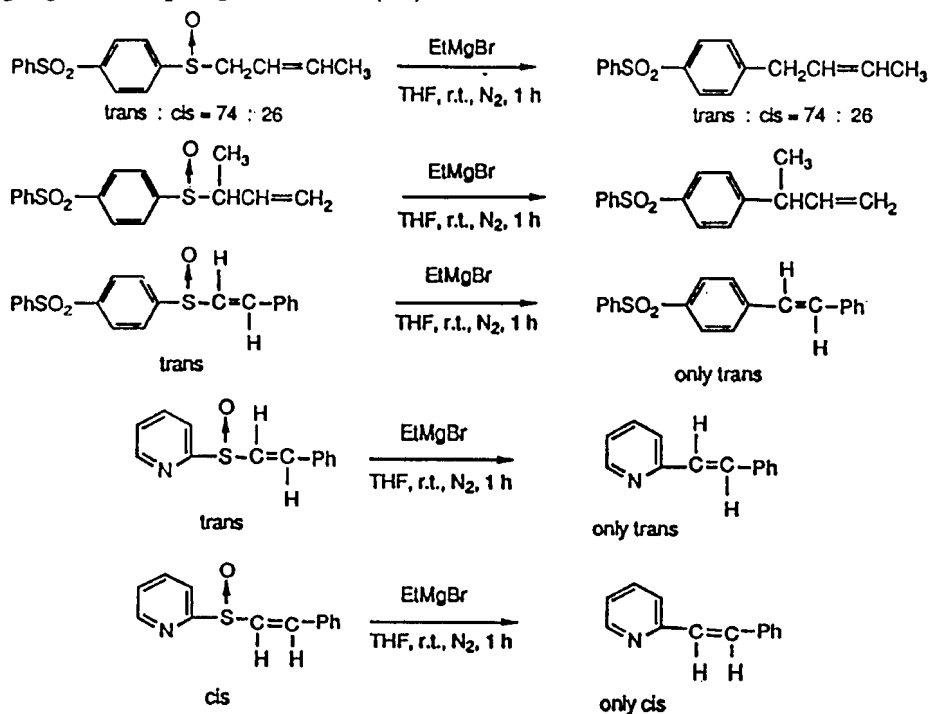


Of course, prior to this assumption, there are many, many experiments and ideas. (16-39)

Another example of stereochemistry is shown below. (40) There is another example



is between optically active 1-phenylethyl 2-quinolyl sulfoxide and methylmagnesium bromide to afford completely retained 1-phenylethyl-2-quinoline in a high yield.(41) In addition, there are a number of stereochemistry of geometrical isomers in the following ligand coupling reactions.(42)

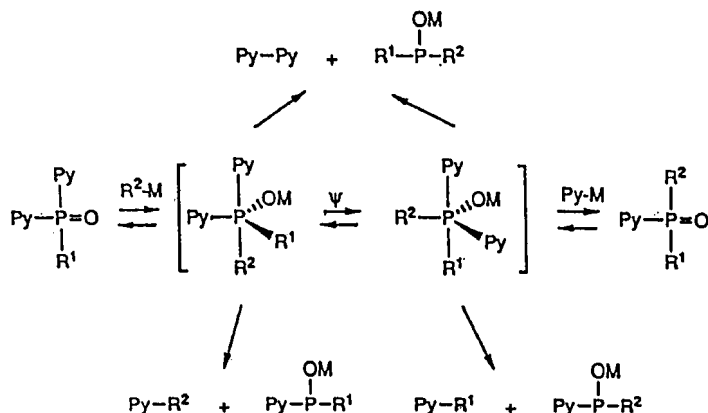


In all the journals, we have found good many examples of ligand coupling reaction, but only a few which we or our friends carried out, are presented.(43-50)

We turn next to the ligand coupling on phosphorus atom. The stereochemistry of the ligand coupling on hypervalent phosphorus atom was carried out by Seyferth et al. accidentally in the following reactions.(51) The yields are good while the stereochemistry in both cases are nearly perfect.

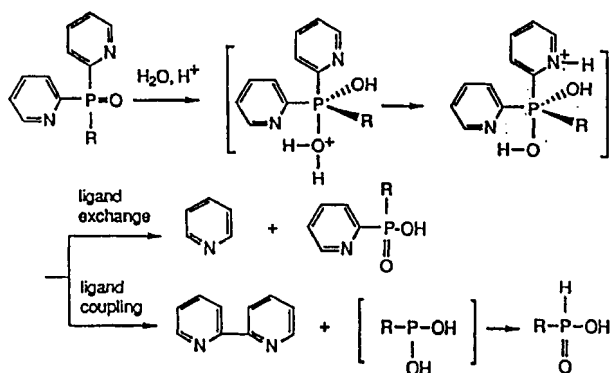


Many examples of the ligand coupling involving 2-pyridyl groups are summarized in the chart, as shown below.(52-55) All these coupling reactions do not require



*Py = 2-pyridyl; R¹ = 2-pyridyl, Ph; R² = Me, Ph, PhCH₂, 4-MeC₆H₄CH₂; M = Li, MgX.

any alkaline condition(56) nor quaternary phosphorus compounds, as shown in the following reaction.

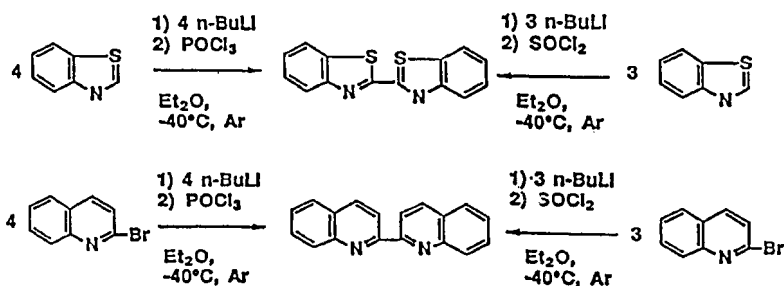


The uses of phosphorus trichloride, phosphorus oxychloride and thionyl chloride were found to undergo coupling reaction with many heterocycles.(57)(Table. I) The following examples are also interesting to note.

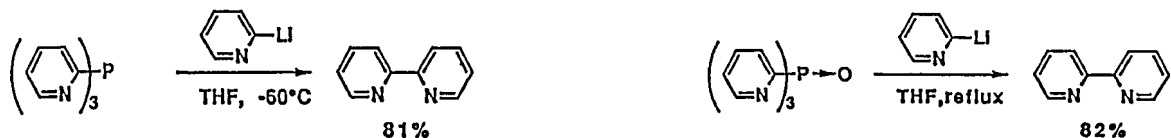
TABLE 1 Reactions of Heterocyclic Aryllithium Compounds with PCl₃, POCl₃, and SOCl₂

Starting Material	Ligand Coupling Product Yield (%) ^a		
	PCl ₃	POCl ₃	SOCl ₂
	50	51	55
	45	58	47
	16	62	63
	35	58	75
	16	70	77
		55	40
		44	43

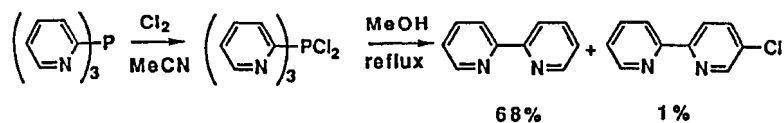
^aIsolated yields were calculated based on PCl₃, POCl₃, and SOCl₂



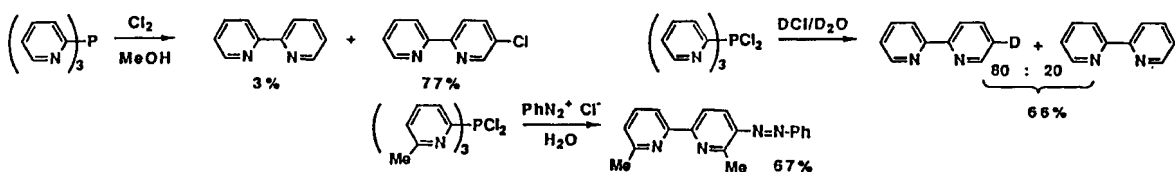
The involvement of 2-pyridyllithium in the ligand coupling is known in the following example.(58)



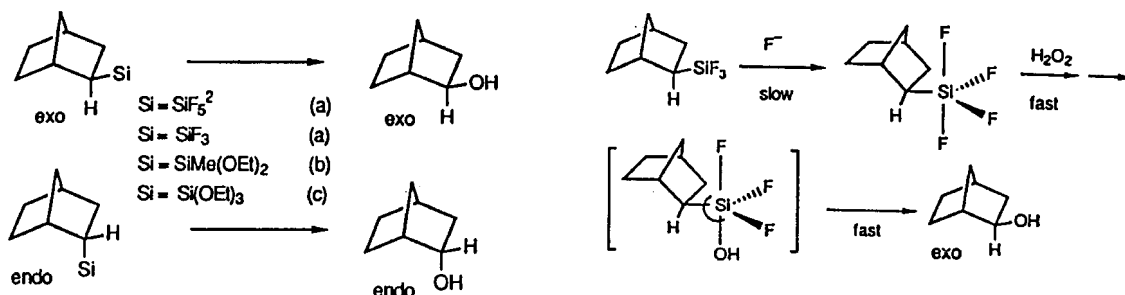
Meanwhile, the following electrophilic substitution by chlorine was found to occur.(59)



The use of the protic solvent is preferable. Chlorination, bromination, deuteration and diazocoupling are achieved,(60) as shown below. We believe that these are typical electrophilic substitutions, since the phosphorus atom in such a pentacoordinate species, especially 3-position of the axial pyridine ligand, is susceptible to the electrophilic substitution.

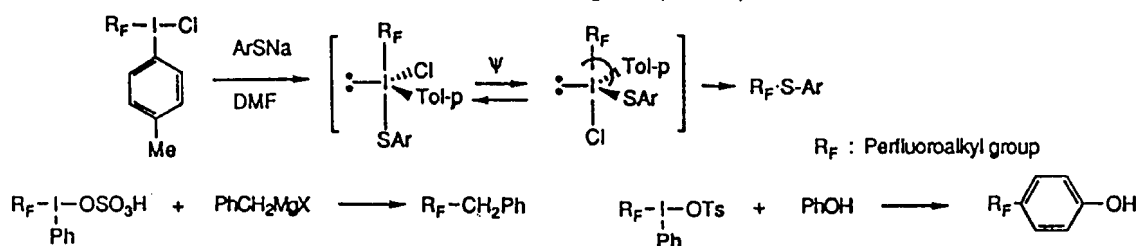


We then turn to the hypervalent silicon species and only one example is sited below. (61,62)

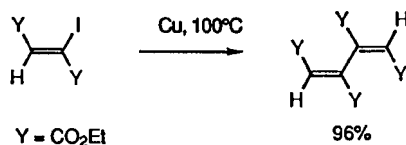


*Reaction conditions: (a) MCPBA/DMF/room temperature; (b) 30% $\text{H}_2\text{O}_2/\text{KHF}_2/\text{DMF}/60^\circ\text{C}$; (c) 30% $\text{H}_2\text{O}_2/\text{NaHCO}_3/\text{MeOH}/\text{THF}/60^\circ\text{C}$.

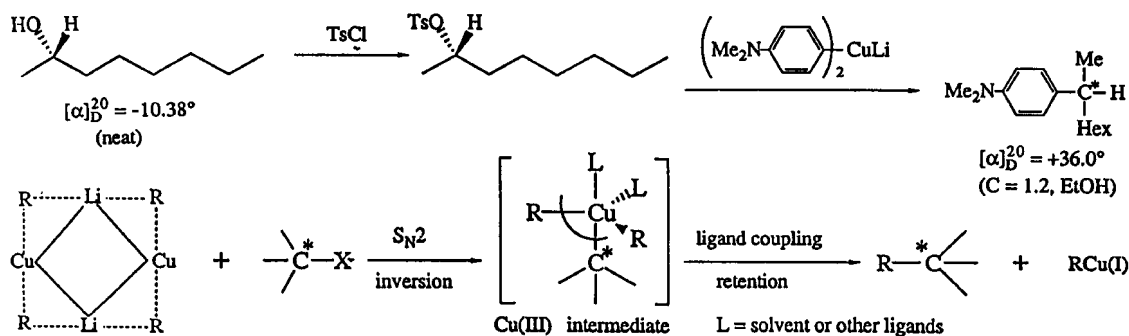
What about the central iodine atom? There are so many and I do not want to go in detailed discussions but cite only a few examples.(63,64)



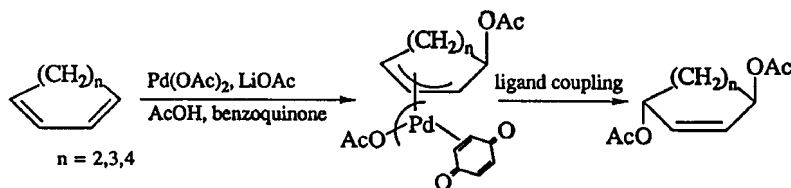
As we said earlier(2,30), many reactions involving organic copper reagents, such as the Ullmann type reaction shown below,(66) and the following one is a few typical



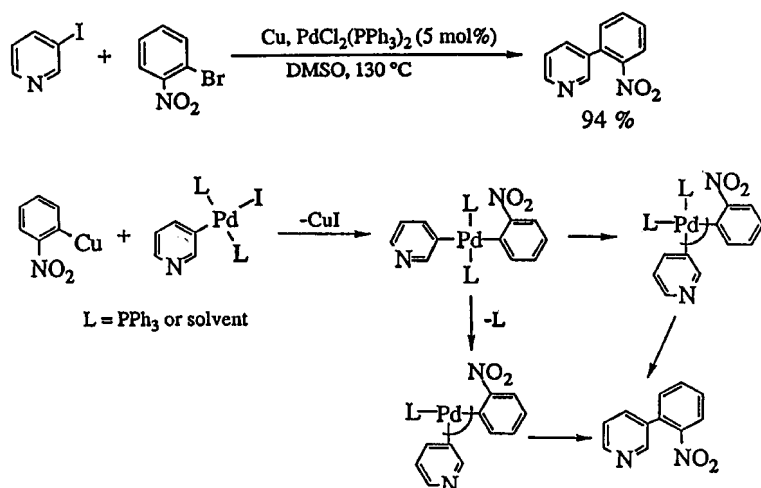
example of the fast ligand coupling within the hypervalent copper(III) intermediate after a typical $\text{S}_{\text{N}}2$ process, as shown below.(67)



There are a number of examples of ligand coupling within hypervalent species of the nickel triad.(68) We are going to present only one stereospecific example to form the trans-acetoxypalladium, eventually giving the final trans product.(69)



Another example is a typical Ullmann cross-coupling reaction shown below.(70)



Acknowledgement. Many colleagues have collaborated in pursuing this work. Professors N. Furukawa, Y. H. Kim who is the chief organizer of this ICHAC-4 T. Aida, T. Yoshimura when I was at Osaka City University. In the University of Tsukuba, Professor N. Furukawa, Dr. T. Kawai and when I was in Okayama University of science Professors S. Wakabayashi and J. Uenishi and Dr. T. Takeda. After that, Professors Y. Uchida, K. Negoro and M. Yoshihara have done many important works; especially Dr. Y. Inubushi and Mr. H. Ishihara have done so much contributions in this Institute. I can by no means forget many useful comments and opinions of my friends who have kindly suggested in pursuing the interesting works.

REFERENCES

1. S. Oae, T. Kawai, N. Furukawa, *Tetrahedron Lett.*, **25**, 65 (1984); S. Oae, T. Kawai, N. Furukawa, F. Iwasaki, *J. Chem. Soc., Perkin Trans.*, **3**, (1987) 405.
2. S. Oae, *Croat. Chem. Acta*, **59**, 129 (1986); S. Oae, *Phosphorus and Sulfur*, **27**, 13 (1986).
3. J. I. Musher, *Angew. Chem. Int. Ed. Engl.*, **8**, 54 (1969).
4. R. J. Hoh, R. E. Rundle, *J. Am. Chem. Soc.*, **71**, 48 (1951).
5. G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).
6. G. Wittig, *Pure Appl. Chem.*, **9**, 245 (1964); G. Wittig, H. Fritz, *Liebigs Chem.*, **577**, 39 (1952).
7. R. R. Holmes, "Pentacoordinated Phosphorus", ACS Monographs 175 and 176 Am. Chem. Soc., Washington, D.C., Vols., I and III (1977).
8. S. Oae, "Organic Sulfur Chemistry-Structure and Mechanism" CRC Press Florida (1991), Chapter 5; T. Kawai, N. Furukawa, S. Oae, *Tetrahedron Lett.* **25**, 2549 (1984).
9. Y. H. Khim, S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 1968 (1969).
10. B.M. Trost, R. La Rochelle, R. C. Atkins, *J. Am. Chem. Soc.*, **91**, 2175 (1969); **93**, 6077 (1972).
11. M. Hori, T. Kataoka, H. Shimizu, *Chem. Pharm Bull.*, **22**, 1711, 2004, 2014, 2020, 2030 (1974).
12. W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 5597 (1973)

13. T. Aida, N. Furukawa, S. Oae, *Chem. Lett.* 805 (1973), 29 (1975); *J. Chem. Soc., Perkin Trans.* II 1438 (1976).
14. P. J. Kocienski, B. Lythgoe, I. Waterhuse, *J. Chem. Soc., Perkin Trans.* 1, 1045 (1980).
15. N. Ono, R. Tamura, J. Hayami, A. Kaji, *Tetrahedron Lett.*, 763 (1978).
16. S. Oae, T. Aida, N. Furukawa, *Chem. Pharm. Bull.*, 3011 (1975); *Int'l. J. Sulfur Chem.*, 401 (1973).
17. S. Oae, T. Yoshimura, N. Furukawa, *Bull. Chem. Soc. Jpn.*, 45, 2019 (1972).
18. T. Takeda, Ph.D. Thesis, Okayama University of Science (1989).
19. S. Oae, T. Takeda, T. Kawai, N. Furukawa, *Phosphorus and Sulfur*, 34, 133; T. Kawai, Y. Koderu, N. Furukawa, S. Oae, M. Ishida, T. Takeda, S. Wakabayashi, *ibid.*, 34, 139 (1987).
20. S. Oae, "Yukiokagaku / Organic Sulfur Chemistry", Kagaku Dojin, Kyoto, Chapter 3, 4 (1982).
21. S. Oae, N. Furukawa, "Sulfur Compounds and Related Derivatives" ACS Monograph 179, Am. Chem. Soc. (1983).
22. S. Oae, "Historical Development of Sulfur Bonding" in "Organic Sulfur Chemistry", edited by F. Bernardi, I. G. Csizmadia, A. Mangini, Elsevier, Amsterdam (1985).
23. S. Oae, T. Kawai, N. Furukawa, *Phosphorus and Sulfur*, 34, 123 (1987).
24. S. Wakabayashi, M. Ishida, T. Takeda, S. Oae, *Tetrahedron Lett.* 29, 4441 (1988).
25. S. Oae, T. Takeda, S. Wakabayashi, *Heterocycles*, 28, 99 (1989).
26. S. Wakabayashi, T. Takeda, Y. Kubo, J. Uenishi, S. Oae, *Bull. Chem. Soc. Jpn.*, 62, 3848 (1989).
27. S. Wakabayashi, Y. Kubo, T. Takeda, J. Uenishi, S. Oae, *Bull. Chem. Soc. Jpn.*, 62, 2338 (1989).
28. J. Uenishi, T. Tanaka, S. Wakabayashi, S. Oae, H. Tsukube, *Tetrahedron Lett.*, 31, 4625 (1990).
29. S. Oae, N. Furukawa, "Heteroaromatic Sulfoxides and Sulfones: Ligand Exchange and Coupling in Sulfuranes and Ipso-Substitutions", in *Advances in Heterocyclic Chem.* (Ed.) by A. R. Katritzky (Academic Press), 48, 1-63 (1990).
30. S. Oae, *Reviews on Heteroatom Chem.*, 1, 304, (1988).
31. S. Oae, Y. Uchida, *Reviews on Heteroatom Chem.*, 2, 76 (1989).
32. S. Oae, *Reviews on Heteroatom Chem.*, 4, (1991).
33. J. Uenishi, T. Tanaka, K. Nishiwaki, S. Wakabayashi, S. Oae, H. Tsukube, *J. Org. Chem.*, 58, 4382 (1993).
34. H. Tsukube, J. Uenishi, H. Higaki, K. Kikukawa, T. Tanaka, S. Wakabayashi, S. Oae, *J. Org. Chem.*, 58, 4389 (1993).
35. S. Wakabayashi, Y. Kiyohara, S. Kameda, J. Uenishi, S. Oae, *Heteroatom Chem.*, 1, 225 (1990).
36. K. S. Kim, I. B. Jung, Y. H. Kim, S. Oae, *Tetrahedron Lett.*, 30, 1087 (1989).
37. S. Oae, Y. Inubushi, M. Yoshihara, *Heteroatom Chem.* 4, 185 (1993); 5, 223 (1994); S. Oae, Y. Inubushi, M. Yoshihara, *Phosphorus, Sulfur and Silicon*, (in print).
38. S. Oae, H. Ishihara, M. Yoshihara, *Zhur. Org. Khim.*, (in print).

39. Y. Inubushi, Ph. D. Thesis, Kinki University, (1995).
40. S. Oae, T. Takeda, S. Wakabayashi, F. Iwasaki, N. Yamazaki, Y. Katsube, *J. Chem. Soc., Perkin Trans.*, 2, 273 (1990).
41. J. Uenishi, A. Yamamoto, T. Takeda, S. Wakabayashi, S. Oae, *Heteroatom Chem.*, 3, 73 (1992).
42. S. Oae, T. Takeda, S. Wakabayashi, *Tetrahedron Lett.*, 29, 4445 (1988).
43. C. R. Johnson, C. W. Schroeck, J. R. Shauklin, *J. Am. Chem. Soc.* 95, 7424 (1973).
44. J. Kiji, M. Iwamoto, *Tetrahedron Lett.*, 2749 (1966).
45. S. Oae, Y. Tsuchida, K. Tsujihara, N. Furukawa, *Bull. Chem. Soc. Jpn.*, 45, 2856 (1972).
46. H. Yoshida, H. Teketani, T. Ogata, S. Inakawa, *Bull. Chem. Soc. Jpn.*, 49, 3124 (1976), 50, 3302 (1977).
47. T. Aida, Ph. D. Thesis at Osaka City University, (1974).
48. R. L. Smorada, W. E. Truce, *J. Org. Chem.*, 44, 3444 (1979).
49. G. H. Wiegant, W. E. McEwen, *J. Org. Chem.*, 33, 2971 (1966).
50. S. Ogawa, private communications.
51. D. Seyferth, J. Fogel, J. K. Heeren, *J. Am. Chem. Soc.*, 88, 2207 (1966).
52. Y. Uchida, K. Onoue, K. Tada, F. Nagano, S. Oae, *Tetrahedron Lett.*, 30, 567 (1989).
53. Y. Uchida, H. Kozawa, S. Oae, *Tetrahedron Lett.*, 30, 6365 (1989).
54. Y. Uchida, Y. Takaya, S. Oae, *Heterocycles*, 55, 347 (1990).
55. Y. Uchida, K. Onoue, N. Tada, F. Nagao, H. Kozawa, S. Oae, *Heteroatom Chem.*, 1, 295 (1990); Y. Uchida, H. Kawai, H. Masauji, S. Oae, *Heteroatom Chem.*, 4, 421 (1993).
56. G. R. Newkome, D. C. Hager, *J. Am. Chem. Soc.*, 100, 5567 (1978).
57. Y. Uchida, N. Echikawa, S. Oae, *Heteroatom Chem.*, 5, 409 (1994).
58. Y. Uchida, R. Kajita, Y. Kawasaki, S. Oae, *Phosphorus, Sulfur and Silicon*, 93(1-4) & 94(1-4) 403 (1994).
59. Y. Uchida, R. Kajita, Y. Kawasaki, S. Oae, *Tetrahedron Lett.*, 36, 4077 (1995).
60. Y. Uchida, S. Oae, XIII ICPC Abstract, Jerusalem, July (1995).
61. K. Tamao, T. Hayashi, Y. Ito, *Nippon Kagaku Kaishi*, 509 (1990); *Tetrahedron Lett.*, 31, 2925 (1990).
62. K. Tamao, T. Hayashi, Y. Ito, unpublished, cited in 61.
63. V. V. Lyalim, V. V. Orda, L. A. Alekseeva, L. M. Yagpolskii, *Zhur. Org. Khim.*, 7, 1473 (1971); *Synthesis*, 835 (1978).
64. T. Umemoto, Y. Kuriu, *Tetrahedron Lett.*, 22, 5197 (1981); *Bull. Chem. Soc. Jpn.*, 57, 3361 (1984).
65. T. Umemoto, Yuki Gosei Kagaku Kyokaishi, 41, 251 (1981).
66. T. Cohen, T. Poeth, *J. Am. Chem. Soc.*, 94, 4363 (1972).
67. K. Negoro, S. Oae, *Reviews on Heteroatom Chem.*, 9, 123 (1993).
68. K. Negoro, S. Oae, *Reviews on Heteroatom Chem.*, 13, (in print).
69. J.-E. Backvall, *Acc. Chem. Res.*, 16, 335 (1983).
70. N. Shimizu, T. Kitamura, K. Watanabe, T. Yamaguchi, H. Shigyo, T. Ohta, *Tetrahedron Lett.*, 34, 3421 (1993).