

Synthesis and reactions of new phosphine–boranes

Tsuneo Imamoto

Department of Chemistry, Faculty of Science, Chiba University, Inage, Chiba 263,
Japan

Abstract – Synthesis and reactions of new phosphine–boranes have been studied. Diastereomerically pure menthylphosphine–boranes were prepared from dichlorophenylphosphine. These secondary phosphine–boranes underwent stereospecific alkylation and arylation reactions. It is noted that the stereochemistry of palladium–catalyzed cross-coupling reactions was largely affected by the solvent and the base used. Thus, the reaction in acetonitrile proceeded with net retention of configuration. In sharp contrast, the reaction in THF in the presence of K_2CO_3 occurred with inversion of configuration with high degree of stereospecificity.

The phosphorus–oxygen bond of the resulting phosphine–boranes was reductively cleaved at $-78\text{ }^\circ\text{C}$ by lithium naphthalenide or lithium in liquid ammonia in almost quantitative yields with an excellent degree of stereospecificity. On the other hand, the reactions at elevated temperatures provided the products with almost complete racemization. This racemization was proved to occur via pyramidal inversion of the anionic tricoordinate phosphorus species.

Based on these results, we developed new methods for the synthesis of bidentate phosphine ligands with homochiral phosphine centers. Optically pure bisphosphinoethanes and bisphosphinobutanes possessing phenyl, *t*-butyl, cyclohexyl, *o*-methoxyphenyl, methyl, or 2-methoxyethyl group were prepared via phosphine–boranes.

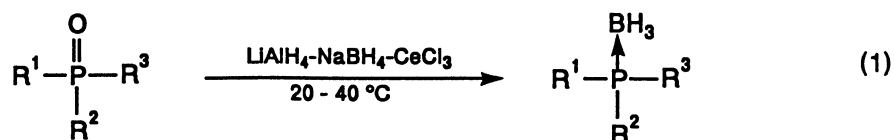
Functionalizations of the boranato group of phosphine–boranes have been investigated. Trimethylphosphine–borane reacted with methanesulfonic acid with evolution of hydrogen. The resulting trimethylphosphine–methylsulfonyloxyborane was subjected to nucleophilic substitution reaction on the boron atom with arenthiols or secondary phosphine–boranes. A new phosphine–borane having a P–B–P–B–P–B–P–B bond linkage was synthesized. Novel boron anion species were generated by the reaction of phosphine–monoiodoboranes with lithium 4,4'-di-*t*-butylbiphenylide.

INTRODUCTION

Phosphine–boranes, adducts of phosphines with borane, have attracted the interest of several research groups for a long time. The previous investigations revealed their peculiar chemical properties as well as the inherent P–B bond nature (ref. 1, 2). We have been interested in the characteristic properties of phosphine–boranes and have worked to develop synthesis and reactions of these compounds with a view to obtaining useful organophosphorus compounds. Our own recent work in this area has focused on (1) synthesis and reactions of achiral phosphine–boranes, (2) synthesis of optically active phosphine–boranes, (3) stereospecific substitution reactions at chiral phosphorus, (4) synthesis of optically active phosphine ligands with homochiral phosphine center, (5) functionalizations of the boranato group of phosphine–boranes. These works will be reviewed in that order.

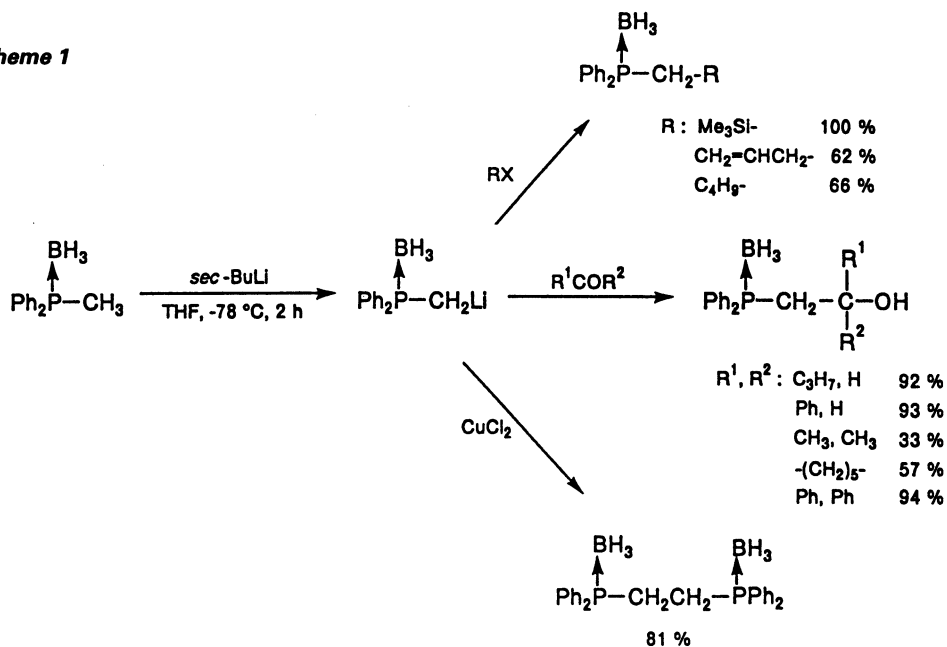
SYNTHESIS AND REACTIONS OF ACHIRAL PHOSPHINE–BORANES

Phosphine–boranes including secondary phosphine–boranes were prepared from phosphine oxides on treatment with $LiAlH_4$ – $NaBH_4$ – $CeCl_3$ (eq. 1). It is noted that this reaction did not proceed in the absence of cerium(III) chloride. Trivalent cerium presumably plays dual roles in this reaction: it activates phosphine oxides by coordination so that the deoxygenation with $LiAlH_4$ proceeds readily, and it activates $NaBH_4$ to facilitate reaction with intermediate phosphines to form phosphine–boranes (ref. 3).



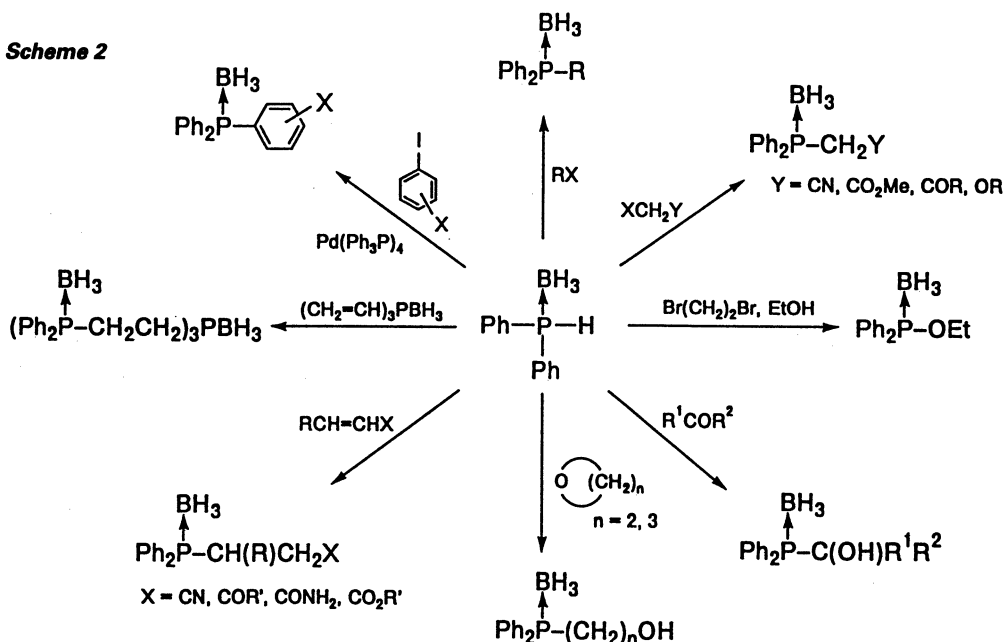
We next examined the synthesis of a variety of functionalized phosphine-boranes by using methyl-diphenylphosphine-borane as a model substrate. The compound was metalated with *s*-butyllithium in THF at $-78\text{ }^\circ\text{C}$. The generated carbanion reacted with various electrophiles to give functionalized phosphine-boranes, as shown in Scheme 1 (ref. 4).

Scheme 1



Our subsequent trial was concerned with reactions of secondary phosphine-boranes. As summarized in Scheme 2, a model substrate, diphenylphosphine-borane, reacted with various electrophiles in the presence of a base. The reactions proceeded under mild conditions to provide a variety of functionalized phosphine-boranes.

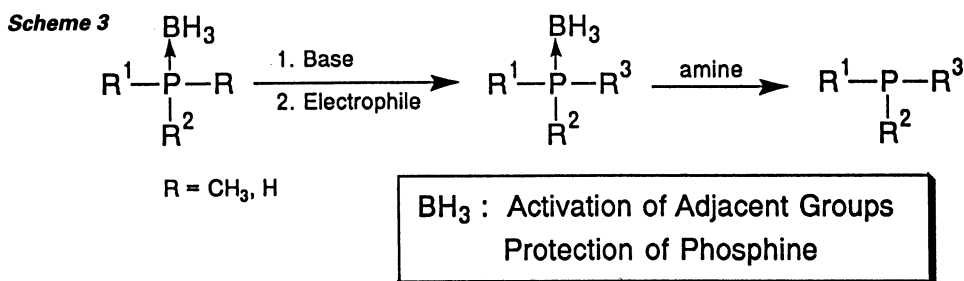
Scheme 2



It was found that the boranato group of phosphine-boranes was removed on treatment with a large excess of an amine such as morpholine or diethylamine. This reaction has been proven to proceed in a stereospecific manner with retention of configuration (eq. 2).

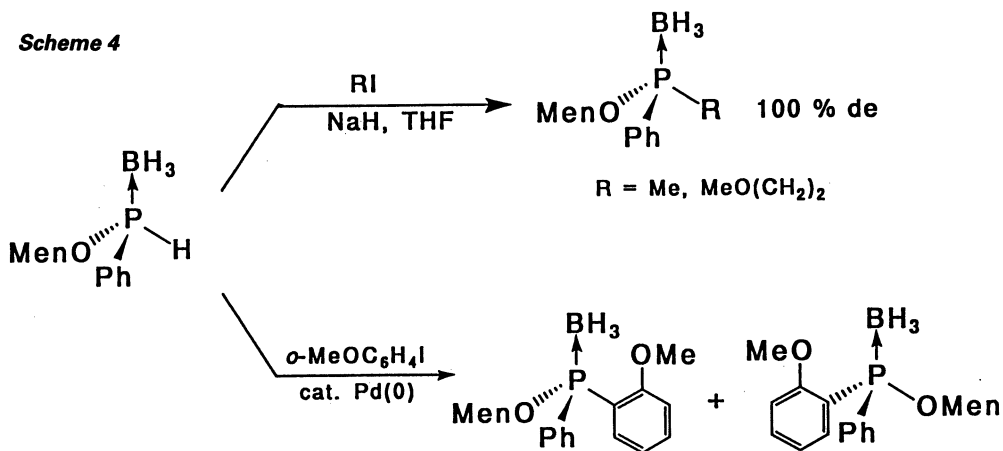


The reactions mentioned above may offer a possible route to such phosphine derivatives that are not easily accessible by the other previously existing methods (Scheme 3). It is particularly worth mentioning that in these reaction sequences the boranato group acts both as an activating group and a protecting group.

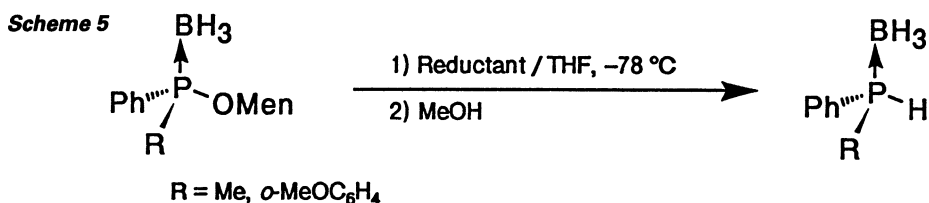


SYNTHESIS OF OPTICALLY ACTIVE PHOSPHINE-BORANES

Optically active phosphine-boranes possessing a P-H bond were prepared from dichlorophosphine, and they were allowed to react with alkyl iodides or aryl iodides (ref. 4, 5). The reactions with alkyl iodides in the presence of NaH proceeded with complete retention of configuration. On the other hand, the stereospecificity of palladium(0)-catalyzed arylation reaction depended largely on the solvent and the base used (Scheme 4, ref. 5). Thus, the reaction in acetonitrile proceeded with almost complete retention of configuration. In sharp contrast, inversion of configuration was observed in ethereal solvents or toluene. In particular, the reactions in THF in the presence of K₂CO₃ or CH₃CO₂K proceeded with a remarkably high degree of stereospecificity.



Nucleophilic substitution reaction has also been studied. Less sterically hindered organolithium reagents afforded inversion products with high stereospecificity. The reactions of sterically hindered reagents such as *o*-methoxyphenyllithium resulted in the formation of racemized products (ref. 6). Reductive removal of the menthyl group was accomplished by the use of lithium naphthalenide or lithium in liquid ammonia. Optically active secondary or tertiary phosphine-boranes were obtained by quenching the reaction with water or alkyl halides, respectively (Scheme 5, ref. 7, 8).



SYNTHESIS OF OPTICALLY ACTIVE PHOSPHINE LIGANDS WITH HOMOCHIRAL PHOSPHINE CENTER

Based on the results mentioned above we tried to synthesize new phosphine ligands whose chirality exists at phosphorus atom. A typical example is illustrated in Scheme 6 (ref. 4) In a similar manner various ligands were synthesized via optically active phosphine-boranes (Fig. 1, ref. 9).

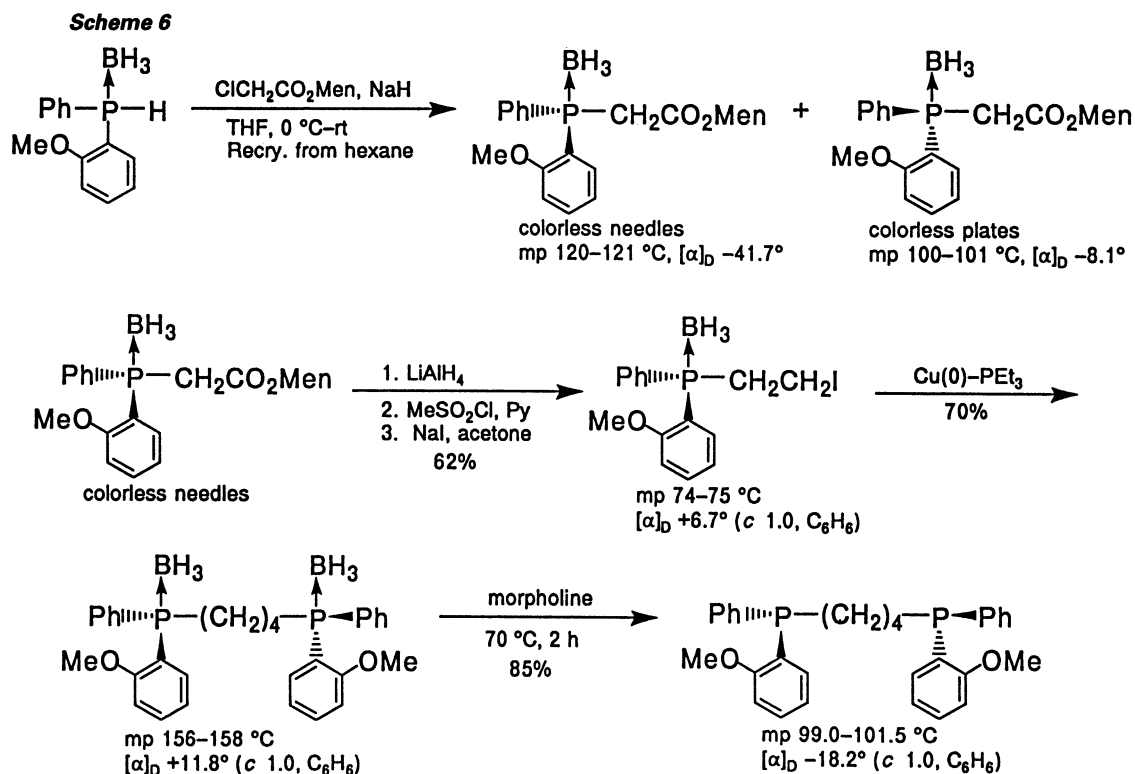
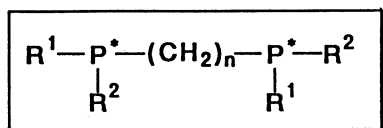
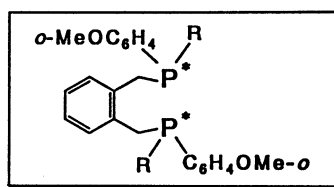


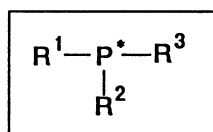
Fig. 1



- 1 : R¹ = Ph, R² = *o*-MeOC₆H₄, n = 2
- 2 : R¹ = Ph, R² = *o*-MeOC₆H₄, n = 3
- 3 : R¹ = Ph, R² = *o*-MeOC₆H₄, n = 4
- 4 : R¹ = *t*-Bu, R² = Ph, n = 2
- 5 : R¹ = Me, R² = Ph, n = 2
- 6 : R¹ = Me, R² = Ph, n = 3
- 7 : R¹ = Me, R² = Ph, n = 4
- 8 : R¹ = MeO(CH₂)₂, R² = Ph, n = 2
- 9 : R¹ = MeO(CH₂)₂, R² = Ph, n = 3
- 10 : R¹ = MeO(CH₂)₂, R² = Ph, n = 4
- 11 : R¹ = *t*-Bu, R² = *o*-MeOC₆H₄, n = 2
- 12 : R¹ = *o*-C₆H₁₁, R² = *o*-MeOC₆H₄, n = 2



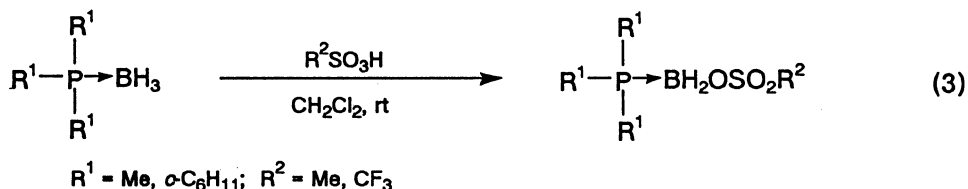
- 1 : R = *o*-C₆H₁₁
- 2 : R = *t*-C₄H₉



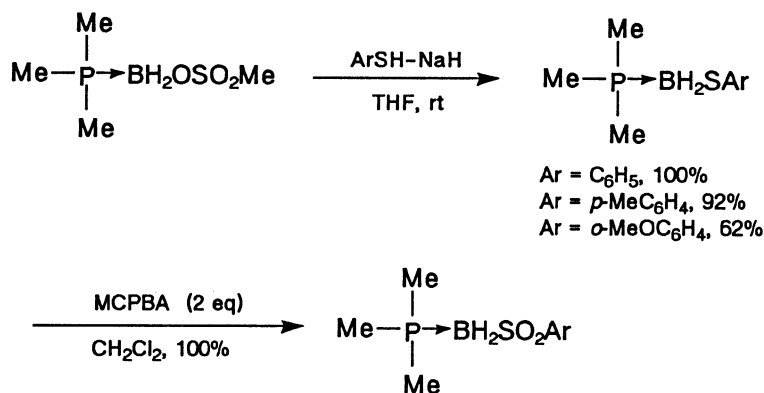
- 1 : R¹ = Me, R² = Ph, R³ = MeO(CH₂)₂
- 2 : R¹ = Me, R² = *o*-MeOC₆H₄, R³ = *t*-Bu
- 3 : R¹ = Me, R² = *o*-MeOC₆H₄, R³ = *o*-C₆H₁₁

FUNCTIONALIZATIONS OF THE BORANATO GROUP OF PHOSPHINE-BORANES

Phosphine-boranes reacted with methanesulfonic acid or trifluoromethanesulfonic acid in dichloromethane with evolution of hydrogen to give the corresponding sulfonate (eq. 3, ref. 10, 11). The resulting sulfonates reacted with various nucleophiles such as arethiols and secondary phosphine-boranes to give substitution products. A representative example for the conversion of trimethylphosphine-methylsulfonyloxyborane to sulfone analogues is shown in scheme 7 (ref. 10).

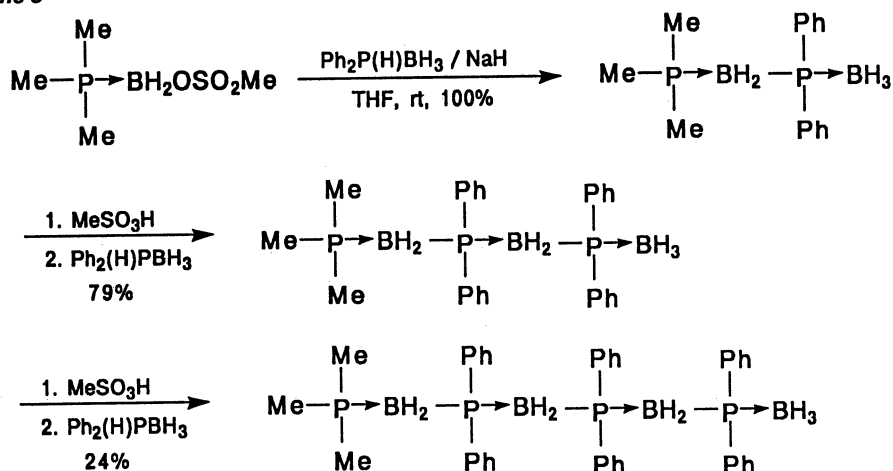


Scheme 7



By utilizing the substitution reaction on boron atom, we tried to synthesize a new class of phosphine-boranes possessing a P-B bond linkage. A typical example is illustrated in scheme 8 (ref. 10, 12).

Scheme 8



Tricoordinate boron species possessing a dinegative formal charge at the boron atom have an isoelectronic relationship with tricoordinate carbanions. We have been interested in this class of chemical species, particularly with respect as to whether or not they exhibit reactivities similar to those of carbanions. We succeeded in the generation of this kind of species by the reduction of phosphine-moniodoboranes with 4,4'-di-*t*-butylbiphenylide. The generated species reacted with various electrophiles such as water or diphenyldisulfide (ref. 13).

Acknowledgement

I wish to express my sincere appreciation to co-workers, whose names appear in the references, for their efforts and valuable contribution. This work was supported by a Grant-in-Aid from Scientific Research on a Priority Area of Organic Unusual Valency No. 02247104 from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. For representative reviews, see: H. Schmidbaur, *J. Organomet. Chem.*, **200**, 287 (1980); B. A. Arbuzov and G. N. Nikonov, *Rev. Heteroatom. Chem.*, **3**, 1 (1990); P. P. Power, *Angew. Chem. Int. Ed. Engl.*, **29**, 449 (1990).
2. For representative recent works dealing with phosphine-boranes, see: R. Köster, G. Seidel, G. Müller; R. Böse and B. Wrackmeyer, *Chem. Ber.* **121**, 1381 (1988); R. Köster, G. Seidel, R. Böse and B. Wrackmeyer, *Chem. Ber.* **121**, 1941 (1988); H. Schmidbaur, E. Weiss and W. Graf, *Organometallics*, **4**, 1233 (1985); H. Schmidbaur, T. Wimmer, A. Grohmann, O. Steigelmann and G. Müller, *Chem. Ber.*, **122**, 1607 (1989); H. J. Bestmann, T. Röder and K. Sühs, *Chem. Ber.*, **121**, 1509 (1988); A. Sood, B. F. Spielvogel and B. R. Shaw, *J. Am. Chem. Soc.* **111**, 9234 (1989); A. Sood, B. R. Shaw and B. F. Spielvogel, *J. Am. Chem. Soc.* **112**, 9000 (1990); H. V. Rasika Dias and P. P. Power, *J. Am. Chem. Soc.*, **111**, 144 (1989). E. Juaristi and M. A. Aguilar, *J. Org. Chem.*, **56**, 5919 (1991).
3. T. Imamoto, T. Kusumoto, N. Suzuki and K. Sato, *J. Am. Chem. Soc.* **107**, 5301 (1985).
4. T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto and K. Sato, *J. Am. Chem. Soc.* **112**, 5244 (1990).
5. T. Oshiki and T. Imamoto, *J. Am. Chem. Soc.*, **114**, 3975 (1992).
6. T. Oshiki and T. Imamoto, *Bull. Chem. Soc. Jpn.*, **63**, 3719 (1990).
7. T. Oshiki, T. Hikosaka and T. Imamoto, *Tetrahedron Lett.* **32**, 3371 (1991).
8. Y. Koide, A. Sakamoto and T. Imamoto, *Tetrahedron Lett.* **32**, 3375 (1991).
9. T. Imamoto, T. Oshiki, M. Matsuo, T. Hikosaka and M. Yanagawa, *Heteroatom. Chem.*, in press.
10. T. Imamoto and T. Oshiki, *Tetrahedron Lett.* **30**, 383 (1989).
11. T. Imamoto, M. Yanagawa and K. Kishikawa, unpublished results.
12. T. Oshiki and T. Imamoto, *Bull. Chem. Soc. Jpn.* **63**, 2846 (1990).
13. T. Imamoto and T. Hikosaka, submitted for publication.