Registry No. 1, 96452-99-2; 2, 96453-00-8; 2·0.5$CHCl_3$, 96453-01-9; 3, 96453-02-0; 4a, 96453-03-1; 4b, 96453-04-2; 4c, 96453-06-4; 6, 96453-07-5; vdpp, 84494-89-3; Au(CO)Cl, 50960-82-2; CuCl, 7758-89-6; AgCl, 7783-90-6; $AgOCOCH_3$, 563-63-3; $AgBF_4$, 14104-20-2.

Supplementary Material Available: Additional crystal structure data and tables of final anisotropic thermal parameters, H atom parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Synthesis of Optically Active Allyltin Compounds and Their Application to Enantioselective Synthesis of Secondary Homoallyl Alcohols

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Three types of optically active allyltin compounds, $R^*_2Sn(allyl)_2$ (R^* = 2-phenylbutyl, 2-methylbutyl, and 3-phenylbutyl), $R^*R^1Sn(allyl)_2$ (R^* = 2-octyl or 2-phenylbutyl, R^1 = phenyl), and $R^*R^1R^2Sn(allyl)$ (R^* = 2-phenylbutyl, R^1 = phenyl, R^2 = methyl), have been synthesized. On the basis of ^1H NMR spectra, a π-stacking interaction between the 2-phenylbutyl and the allyl groups is suggested. Optically active allyltin compounds thus obtained were subjected to reaction with aldehydes. Among various allyltin compounds, only diallylbis(2-phenylbutyl)tin exhibits good enantioselectivity. The reaction proceeds through addition of the allyl group on the *re* face of aldehydes. The mechanism can be accounted for on the basis of a π-stacking interaction between allyl and phenyl groups.

Introduction

Enantioselective synthesis of secondary homoallyl alcohols from aldehydes and optically active allylmetal compounds has received much attention recently. As templates for chirality transfer, there have appeared three types of organometallics. One of them is based on utilization of an optically active allylic group. Hayashi et al.[1] have synthesized α-substituted allylsilanes in which silicon is directly bonded to an asymmetric α-carbon. These compounds, on treatment with aldehydes, afforded secondary homoallyl alcohols of up to 90% ee. More recently, (α-alkoxycrotyl)tin derivatives have been found to react stereoselectively with benzaldehyde.[2] Employment of a chiral metallic center is the next choice. Unfortunately, however, Paquette et al. have found the reaction of (–)-α-naphthylphenylmethylallylsilane with acetals to give rise to unsatisfactory enantiomeric excess (<6%).[3] The last type which seems to be the most general and has afforded the most successful results thus far is one containing a pure optically active ligand attached to the metal. This method has been applied to boron derivatives first by Hoffmann et al.[4] and later by Midland et al.,[5] resulting in up to ca. 90% ee. More recently, Brown et al. have succeeded in improving the enantiomeric excess up to 96% by employing *B*-allyldiisopinocampheylborane.[6] It should be noted, however, that the method is not successfully applicable to chromium derivatives which lead to less than 17% ee.[7]

Optically active organotin compounds have received considerable attention from a stereochemical standpoint in recent years despite their relatively short history.[8] It is quite surprising, however, that their synthetic application is limited[9] in contrast to the rapidly expanding synthetic utilization of organotin compounds. Among various recently developed applications, allylation of carbonyl compounds by allyltin derivatives is of particular interest.[10] Accordingly, exploitation of optically active allyltin compounds would provide a new method for an enantioselective synthesis of homoallyl alcohols.

Two types of optically active allyltin compounds may be possible. One involved a chiral tin atom which is linked to four different substituents. Although compounds of this type have been most frequently encountered thus far, satisfactory optical purity has not always been attained.[8,11]

(1) (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (b) Hayashi, T.; Konishi, M.; Kumada, M. *Ibid.* **1982**, *104*, 4963. (c) *J. Org. Chem.* **1983**, *48*, 281. (d) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661.

(2) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1984**, 800.

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(4) (a) Herold, T.; Hoffmann, R. W. *Angew. Chem.* **1978**, *90*, 822. (b) Herold, T.; Schrott, U.; Hoffmann, R. W. *Chem. Ber.* **1981**, *114*, 359. (c) Hoffmann, R. W.; Herold, T. *Ibid.* **1981**, *114*, 375.

(5) Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330.

(6) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092.

(7) Cazes, B.; Verniere, C.; Gore, J. *Synth. Commun.* **1983**, *13*, 73.

(8) (a) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 193. (b) Gielen, M.; Simon, S.; Tondeur, Y.; Van de Steen, M.; Hoogzand, C.; Van den Eynde, I. *Isr. J. Chem.* **1976/1977**, *15*, 74.

(9) (a) Optical enrichment of diols with organotin templates: Schanzer, A.; Libman, J.; Gottlieb, H. E. *J. Org. Chem.* **1983**, *48*, 4612. (b) Enantioselective reduction of haloalkanes with optically active organotin hydrides: Schumann, H.; Pachalty, B.; Schutze, B. C.; *J. Organomet. Chem.* **1984**, *264*, 145.

(10) (a) König, K.; Neumann, W. P. *Tetrahedron Lett.* **1967**, 495. (b) Tagliavini, G.; Peruzzo, V.; Plazzogna, G.; Marton, D. *Inorg. Chim. Acta* **1977**, *24*, L47. (c) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Chem. Lett.* **1979**, 977. (d) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7109. (e) Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981**, 1527. (f) Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191.

(11) (a) Folli, U.; Iarossi, D.; Taddei, F. *J. Chem. Soc., Perkin Trans. 2* **1973**, 638. (b) Lequan, M.; Lequan, R. M. *J. Organomet. Chem.* **1982**, *226*, 35. (c) Lequan, M.; Meganem, F. *Ibid.* **1977**, *131*, 231.

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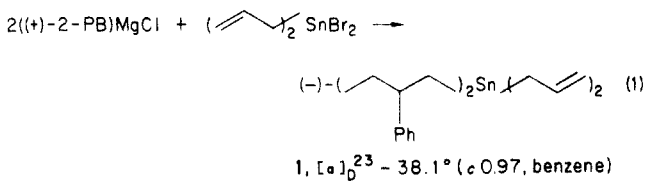
In addition, a lengthy process necessary for the stepwise introduction of each substituent seems to make these compounds impractical as reagents that must be obtainable in quantity.

The alternative involves an optically active substituent attached to tin. Although only a few compounds of this type have been known,[12] they could be prepared in a simpler process if appropriate chiral substituents are available. It may be supposed, however, that the presence of an chiral center remote from an allyl group in these compounds is less favorable for the enantioselective reaction with carbonyl compounds.

In the hope of understanding these problems, we have initiated our program on synthesis and reactions of a variety of optically active allyltin compounds. In this paper, synthesis and characterization of $R^*_2Sn(allyl)_2$, $R^*R^1Sn(allyl)_2$, and $R^*R^1R^2Sn(allyl)$ will be described. Moreover, their reaction with aldehydes was investigated in order to elucidate whether organotins can serve as a suitable template for chirality transfer and what factors control the reaction path.[13]

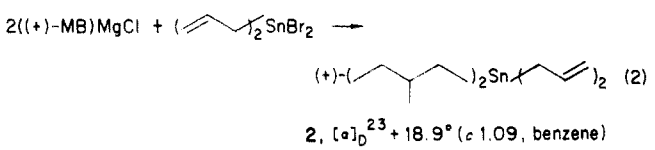
Results and Discussion

Synthesis. Due to the synthetic simplicity, preparation of $R^*_2Sn(allyl)_2$ was undertaken first. For an optically active group attached to tin, 2-phenylbutyl (2-PB) and 2-methylbutyl (MB) groups seemed to be most appropriate since their Grignard reagents had been well studied.[14,15] This is indeed the case. Treatment of ((+)-2-PB)MgCl with diallyltin dibromide (DATB) in THF afforded (−)-diallylbis(2-phenylbutyl)tin (1) in 91% yield. The ^{119}Sn



1, $[\alpha]_D^{23}$ − 38.1° (*c* 0.97, benzene)

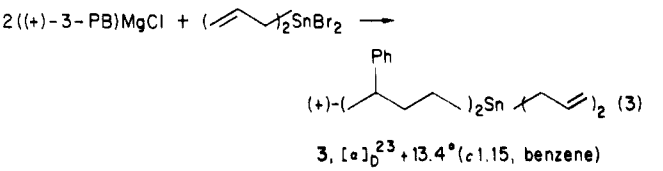
NMR spectrum of this compound exhibits a single peak (δ −39.1) indicative of the absence of diastereomeric isomers since racemic 1 prepared from racemic 2-PBCl gives rise to two singlets at −38.7 and −39.1 ppm.[16] Accordingly, it is apparent that the inherent optical purity of 2-PB group is not reduced during the reaction course. An analogous procedure employing MBCl gave (+)-diallylbis(2-methylbutyl)tin (2) in 53% yield. The ^{119}Sn NMR



2, $[\alpha]_D^{23}$ + 18.9° (*c* 1.09, benzene)

spectrum failed to determine the diastereomeric purity of 2 since even racemic 2 gave rise to a singlet. Nevertheless, the purity of 2 is reasonably expected by analogy with 1.

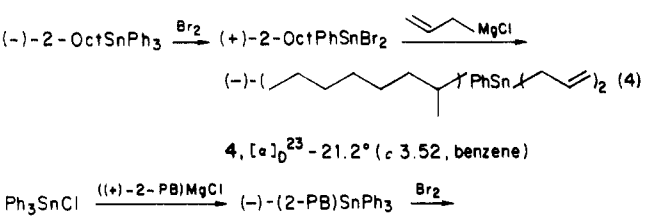
As the chiral carbon atoms in 1 and 2 is separated from tin by two chemical bonds, our next target was synthesis of compounds whose optically active group involves the chiral center one or three bonds away from tin. Preparation of the latter type of compounds was achieved by employing 3-phenylbutyl (3-PB) group according to eq 3.



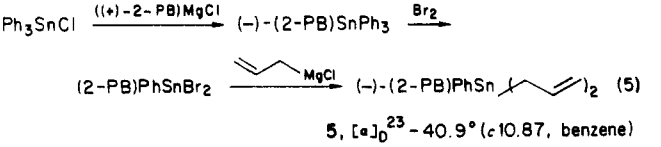
3, $[\alpha]_D^{23}$ + 13.4° (*c* 1.15, benzene)

The procedure requires more detailed comments. The Grignard reaction between 3-PBCl and Mg is initiated at room temperature in THF with difficulty, and heating the reaction mixture induces complex side reactions. The difficulty can be overcome by adding a few drops of methyl iodide before addition of the chloride. The reaction of the resulting Grignard reagent with DATB also should be conducted below 30 °C. Further, the crude product, an oil, 3 must be distilled as quickly as possible since prolonged heating results in decomposition. Preheating of the oven of the Kugelrohr apparatus at 210–220 °C before insertion of distillation bulbs is recommended.

In general, it is difficult to attach a chiral carbon atom to tin directly because of facile epimerization during the Sn–C bond formation.[8] Fortunately, however, San Filippo et al. have already synthesized 2-octyltriphenyltin which is believed to have the maximum rotation value.[12c] Employing this compound as a starting material, we obtained (−)-2-octylphenyldiallyltin (4) according to eq 4. Another $R^*R^1Sn(allyl)_2$ compound was synthesized according to eq 5.

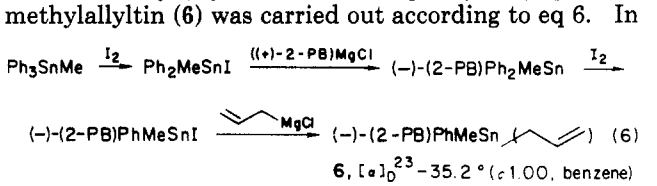


4, $[\alpha]_D^{23}$ − 21.2° (*c* 3.52, benzene)



5, $[\alpha]_D^{23}$ − 40.9° (*c* 10.87, benzene)

Finally, in the hope of obtaining the compound of type $R^*R^1R^2Sn(allyl)$, synthesis of (−)-(2-phenylbutyl)phenylmethylallyltin (6) was carried out according to eq 6. In



6, $[\alpha]_D^{23}$ − 35.2° (*c* 1.00, benzene)

expectation of the highly asymmetric induction at tin, allylation was conducted at −78 °C, but, to our regret,

Table I. Relevant ^1H NMR Spectra of Optically Active Allyltin Compounds

allyltin compd	$CH_2C{=}C$, ppm[a] (Δ)[b]	$CC{=}CH_2$, ppm[a] (Δ)[b]	$CCH{=}C$, ppm[a] (Δ)[b]
$(2\text{-PB})_2Sn(allyl)_2$ (1)	1.06 (−0.67)	4.47 (−0.01)	5.53 (−0.21)
$(MB)_2Sn(allyl)_2$ (2)	1.71 (−0.02)	4.42 (−0.06)	5.61 (−0.13)
$(3\text{-PB})_2Sn(allyl)_2$ (3)	1.73 (0.00)	4.42 (−0.06)	5.64 (−0.10)
$(2\text{-Oct})PhSn(allyl)_2$ (4)	1.92 (+0.19)	4.68 (+0.20)	5.75 (+0.01)
$(2\text{-PB})PhSn(allyl)_2$ (5)	1.69 (−0.04)	4.49 (+0.01)	5.61 (−0.13)
(2-PB)PhMeSn(allyl) (6)	c	4.38 (−0.10)	5.49 (−0.25)
$Bu_3Sn(allyl)$ (7)	1.73	4.48	5.74
$Ph_3Sn(allyl)$ (8)	2.40 (+0.67)	4.77 (+0.29)	5.87 (+0.13)

[a] Chemical shifts of the most intense peak; see text. [b] $\Delta = \delta - \delta(7)$. [c] Obscured by other signals.

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(15) Mosher, H. S.; La Combe, E. *J. Am. Chem. Soc.* **1950**, *72*, 3994.

(16) Otera, J.; Yano, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 387.

Table II. Enantioselective Reaction of Allyltin Compounds with Aldehydes (RCHO)

allyltin compd	R	molar ratio of RCHO/Sn	solv[a]	reactn time, h	homoallyl alcohol yield,[b] %	$[\alpha]^{23}_D$, deg	c	% ee	config[c]
1	C_2H_5	1.5	E	6.5	63	−2.97	10.76 (C_6H_6)	49[d]	*S*
	n-C_3H_7	1.0	E	4.0	50	−6.16	10.22 (C_6H_6)	43[d]	S
		2.0	E	11	54	−5.15	10.22 (C_6H_6)	36[d]	*S*
	i-C_3H_7	1.0	E	4.0	46	+0.75	11.82 (C_6H_6)	20[d]	*R*
		2.0	E	11	48	+0.60	11.82 (C_6H_6)	16[d]	*R*
	t-C_4H_9	1.0	E	4.0	45	+2.39	10.88 (C_6H_6)	21[d]	*R*
	n-C_8H_{17}	1.0	E	6.0	79	−8.45	2.50 (CCl_4)	55[e]	*S*
		1.0	D	3.0	84	−8.79	2.50 (CCl_4)	56[e]	*S*
		1.0	H	3.0	91	−8.00	2.50 (CCl_4)	54[e]	*S*
		2.0	E	11	73	−4.68	2.50 (CCl_4)	26[e]	*S*
	$C_6H_5CH{=}CH$	1.0	E	4.0	96	−8.35	10.08 (Et_2O)	56[d]	*R*
		1.0	D	4.0	94	−7.76	10.08 (Et_2O)	52[d]	*R*
	C_6H_5	1.0	E	3.0	91	+8.10	7.38 (C_6H_6)	17[d]	*R*
		1.0	D	3.0	73	+11.9	7.38 (C_6H_6)	22[d]	*R*
		2.0	E	11	60	+11.0	7.38 (C_6H_6)	23[d]	*R*
2	n-C_8H_{17}	1.4	D	10	89	−0.72	2.50 (CCl_4)	5[e]	*S*
3	n-C_8H_{17}	1.3	D	9.0	99	−1.56	2.50 (CCl_4)	11[e]	*S*
4	n-C_8H_{17}	1.0	E	6.0	80	−2.70	2.50 (CCl_4)	20[e]	*S*
	$C_6H_5CH{=}CH$	1.0	E	6.0	86	−0.60	10.08 (Et_2O)	4[d]	*R*
	C_6H_5	1.0	E	6.0	79	+7.47	7.38 (C_6H_6)	15[d]	*R*
6	n-C_8H_{17}	1.1	D	9.0	63	−1.55	2.50 (CCl_4)	10[e]	*S*

[a] E = ether; D = dichloromethane; H = hexane. [b] Isolated yields based on aldehydes employed. [c] Based on ref 4, 6, and 20. [d] Determined both by ^{1}H NMR spectra in the presence of chiral shift reagent Eu(hfc)$_3$ and comparison with reported $[\alpha]_D$ values.[4,6] [e] Determined by ^{1}H NMR spectra in the presence of Eu(hfc)$_3$.

formation of an equimolar amount of two diastereomers was proved on the basis of the ^{119}Sn NMR spectrum (δ −51.3 and −52.1).

The ^{1}H NMR spectra of these compounds exhibit a marked change in the chemical shifts of the allyl group protons. The typical examples are illustrated in Figure 1 along with that of allyltributyltin (7) as a reference, and all of the results are summarized in Table I in which the magnitude of the shifts with reference to the chemical shifts in 7 is given as Δ. For olefinic protons, the 60- or 100-MHz NMR spectra failed to give precise chemical shifts. Accordingly, the chemical shifts of the most intense peaks of respective terminal methylene and vinylic protons which are indicated by arrows in Figure 1 were compared. The Δ values thus obtained are, we believe, satisfactory, at least for the qualitative estimation. Apparently, 1 gave rise to a significant high field shift of allylic protons as well as olefinic protons as compared with those of 7. This may be accounted for by the π-stacking interaction[17] between allyl and phenyl groups as depicted in Figure 2a. That 2 gives rise to small shifts is consistent with this postulate. High field shifts of olefinic protons also were observed for 3, but to a much lesser extent, suggesting the occurrence of a weak π-stacking interaction. Apparently, each plane of the allyl and phenyl groups is more separated in 3 than in 1 since the phenyl group in 3 is located at the 3-position of a butyl group. The molecular model clearly indicates that allylic protons are situated out of the periphery of the phenyl ring. This explains why a small shift was observed for allylic protons. By contrast, a low field shift was observed for 4. This may be ascribed to a phenyl group directly attached to tin since exertion of low field shifts by this group is evident from the results of allyltriphenyltin (8). Other compounds, 5 and 6, which possess both 2-phenylbutyl and phenyl groups exhibit no definite direction of shift, a result which may be attributed to compensation of a π-stacking effect and a deshielding effect of the phenyl groups. However, the interaction in these compounds may be weaker than that in 1 which possesses two pairs of interacting groups.

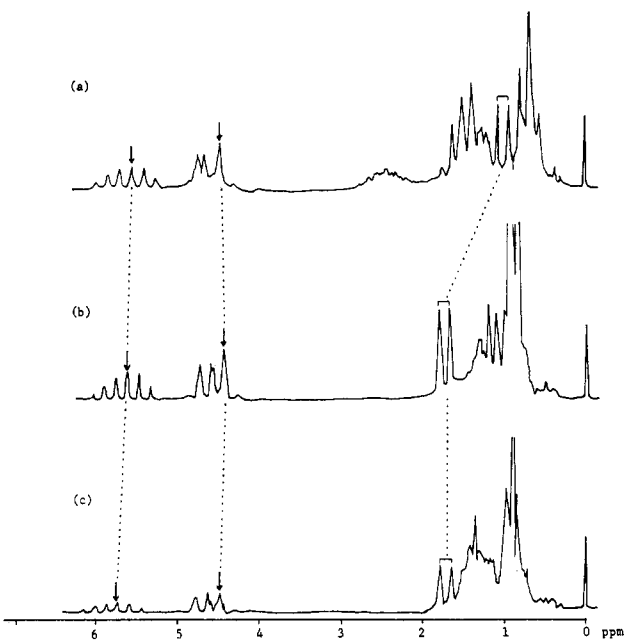
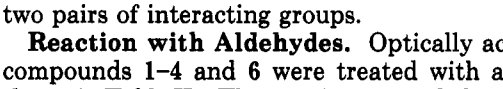


Figure 1. ^{1}H NMR spectra of representative allyltin compounds: (a) (2-PB)$_2$Sn(allyl)$_2$ (1), (b) MB$_2$Sn(allyl)$_2$ (2), and (c) Bu$_3$Sn(allyl) (7).

Reaction with Aldehydes. Optically active allyltin compounds 1–4 and 6 were treated with aldehydes as shown in Table II. The reaction proceeded in the presence of BF_3·OEt_2 at −78 °C[10c,d] (eq 7). Other Lewis acids such



(7)

as $SnCl_4$ and $TiCl_4$ caused complex side reactions. The values of enantiomeric excess and absolute configuration of the resulting secondary homoallyl alcohols were readily determined by comparison of $[\alpha]_D$ with the reported data[4,6,20] and by ^{1}H NMR spectra with a chiral shift reagent

(17) The intramolecular π-stacking between the phenyl group and an ene[18] or dienic[19] moiety has been suggested.
(18) Oppolzer, W.; Kurth, M.; Reichlin, D.; Chapuis, C.; Mohnhaupt, M.; Maffatt, F. *Helv. Chim. Acta* **1981**, *64*, 2802.
(19) (a) Trost, B. M.; O'Krongly, D.; Belletire, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7595. (b) Dauben, W. G.; Bunce, R. A. *Tetrahedron Lett.* **1982**, *23*, 4875.

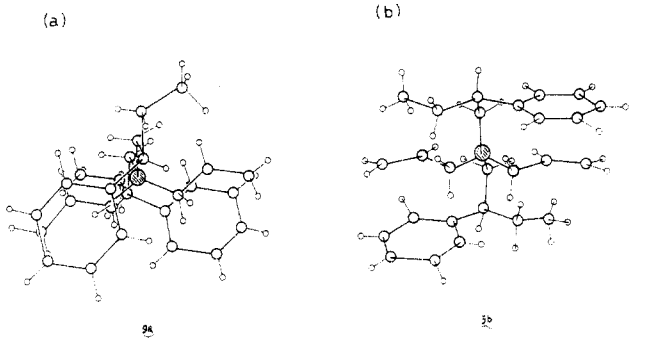


Figure 2. Proposed configuration for 1: (a) **9a** and (b) **9b**.

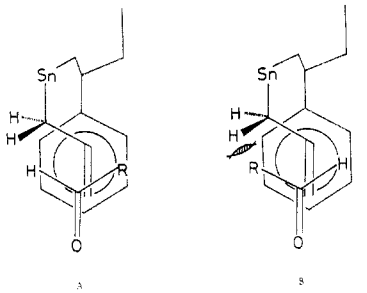
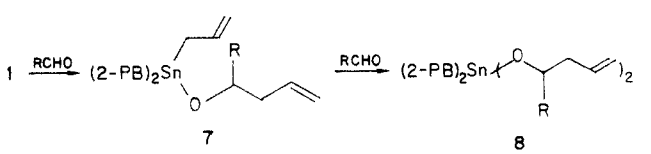


Figure 3. Transition state of the reaction of 1 with an aldehyde.

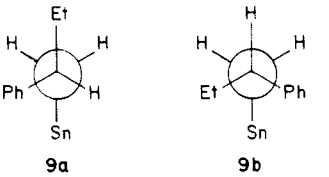
$Eu(hfc)_3$.[21] In the comparative reactions with nonanal, only 1 gave rise to good enantioselectivity while much decreased enantiomeric excess values were obtained with other allyltins. A possible explanation for these results may be put forth by taking the rigidity of the molecular configuration into account. As suggested above, a π-stacking interaction operates more effectively in 1 as compared with other compounds, resulting in a stiffening of the molecular configuration and thus preventing a decrease in the molecular asymmetry.

More detailed investigations were carried out by using 1. *n*-Alkylaldehydes gave rise to higher enantiomeric excess values than branched alkylaldehydes, though the reason for this unusual result is not clear at present. In general, little solvent effect was observed except for 3 and 6. In these cases, when ether is used as a solvent, addition of $BF_3{\cdot}OEt_2$ to the reaction mixture induces the formation of white precipitates with a significant decrease in product yield. Dichloromethane is preferable as reaction medium since the reaction mixture stays homogeneous. Even if 2 equiv of aldehydes (except nonanal) was employed, only a little of the second equivalent of aldehyde was consumed while consumption of more than one equivalent of nonanal was observed with a striking decrease in enantiomeric excess. It is well recognized that the reaction of allyltin with aldehydes proceeds via homo(allyloxy)tin intermediates 7 and 8 (eq 8).[22] The present results indicate that the reaction rate of the second step is slower than the first step and enantioselectivity of the second step is extensively reduced.



(8)

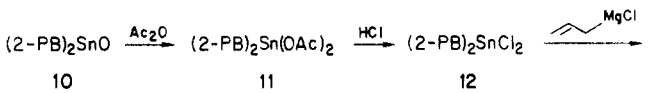
The absolute configuration of homoallyl alcohols thus obtained is consistent with the addition of the allyl group on the *re* face of aldehydes. The mechanism may be accounted for on the basis of the π-stacking configuration of 1. As depicted in Figure 2, the π-stacking interaction leads to two rotamers with respect to the asymmetric carbon, **9a** and **9b**. It is seen that the terminal ethyl group



9a **9b**

in the 2-phenylbutyl is located trans to the Sn–C bond in **9a** as shown.[23] On the other hand, the ethyl group occupies a *gauche* position in **9b** in which the ethyl group approaches the allyl group to a considerable extent, thus resulting in a significant steric repulsion. It is, therefore, reasonably assumed that **9a** is sterically favored. The reaction of aldehydes with 1 is visualized in Figure 3. In the reaction of allyltins with aldehydes in the presence of a Lewis acid catalyst, an anti acyclic transition state is highly probable.[10d] Addition of the allyl group on the *re* face of aldehydes leads to transition state A which is more favored than transition state B since in the latter there is a steric repulsion between the R of the aldehyde and the allylic protons.

Finally, it is noteworthy that 1 can be recovered from the reaction mixture in substantial yield according to eq 9. Treatment of the oxide **10** that is recovered from the



1 (9)

reaction mixture with HCl failed to give **12** directly. The chloride **12** was therefore obtained via the acetate **11**. Allylation of **12** afforded 1 in 60–70% overall yields. The successful recovery of 1 as well as a simple preparative method for 1 employing readily available starting materials may be promising for a large scale reaction.

Experimental Section

The reactions were conducted under a nitrogen atmosphere. Solvents were purified by standard methods. Preparation of optically active 2-PBCl and MBCl is described in the literature.[14,15] Optically active 3-PBCl ($[\alpha]_D^{23}$ +78.2° (neat)) was prepared by the analogous method for 2-PBCl from (+)-3-phenylbutyric acid.[24] Aldehydes were distilled before use.

^1H NMR and ^{119}Sn NMR spectra were obtained by using Hitachi R-24B (60 MHz) and JEOL FX-100 (100 MHz) spectrometers in CCl_4 or $CDCl_3$ solution with Me_4Si or Me_4Sn as an internal standard. Optical rotation was measured on a Union Giken PM-101 automatic digital polarimeter with a 10-cm cell.

(−)-Diallylbis(2-phenylbutyl)tin (1). To a THF solution (20 mL) of (2-phenylbutyl)magnesium chloride[14] prepared from (+)-1-chloro-2-phenylbutane (18.0 g, 107 mmol) was added DATB (12.8 g, 36 mmol) at room temperature. The reaction mixture was stirred at this temperature for 1 h and subsequently heated under reflux for 30 min. Hexane (100 mL) was added to the mixture which was then filtered. The filtrate was evaporated to leave an oil, distillation of which yielded 1: yield 15.1 g (90%); bp 210 °C (0.15 mm) (Kugelrohr bath temperature); ^1H NMR

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(21) The ee values of 1-dodecen-4-ol reported previously[13] have been found not to be correct on the basis of NMR spectra.
(22) Gambaro, A.; Marton, D.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1981**, *204*, 191.
(23) It is fully confirmed that the 2-phenylbutyl group employed in this study possesses the *R* configuration.[14]
(24) "Optical Resolution Procedures for Chemical Compounds"; Newnan, P., Ed.; Optical Resolution Information Center, Manhattan College: Riverside, N.Y., 1981; Vol. 2, p 470.

(CCl_4) δ 0.69 (t, 6 H, J = 6.6 Hz), 1.06 (d, 4 H, J = 8.0 Hz), 0.87–1.93 (m, 8 H), 2.02–2.85 (m, 2 H), 4.40–4.88 (m, 4 H), 5.16–6.03 (m, 2 H), 7.17 (br s, 10 H); ^{119}Sn NMR ($CDCl_3$) δ −39.1; $[\alpha]^{23}_D$ −38.1° (c 0.97, benzene). Anal. Calcd for $C_{26}H_{36}Sn$: C, 66.83; H, 7.77. Found: C, 67.17; H, 7.94.

(+)-Diallylbis(2-methylbutyl)tin (2). To a THF solution (20 mL) of (2-methylbutyl)magnesium chloride[15] prepared from (+)-1-chloro-2-methylbutane (1.42 g, 13.3 mmol) was added DATB (1.19 g, 3.3 mmol). After being stirred for overnight at room temperature, the reaction mixture was evaporated. The resulting residue was extracted with hexane repeatedly. The hexane solution was evaporated to leave an oil that was purified by column chromatography (silica gel, 100:1 hexane–ether) to give **2**: yield 0.56 g (53%); ^{1}H NMR (CCl_4) δ 0.74–1.38 (m, 22 H), 1.71 (d, 4 H, J = 8.0 Hz), 4.34–4.87 (m, 4 H), 5.28–6.08 (m, 2 H); ^{119}Sn NMR ($CDCl_3$) δ −33.2; $[\alpha]^{23}_D$ +18.9° (c 1.09, benzene). Anal. Calcd for $C_{16}H_{32}Sn$: C, 56.02; H, 9.33. Found: C, 56.44; H, 9.02.

(+)-Diallylbis(3-phenylbutyl)tin (3). To a 100-mL reaction vessel containing magnesium turnings (146 mg, 6 mmol) and iodine (a few milligrams) was added THF (20 mL) and a few drops of methyl iodide. On stirring the mixture at room temperature, the reaction initiated and the color of iodine disappeared. Then, (+)-1-chloro-3-phenylbutane (505 mg, 3 mmol) was slowly added to this solution so as to keep the reaction mixture below 30 °C. After completion of the addition, the mixture was stirred for 3 h at room temperature and DATB (360 mg, 1 mmol) was added dropwise to this mixture. The mixture was stirred overnight and then was evaporated. The residue was extracted repeatedly with dry hexane. Evaporation of hexane yielded an oil that was distilled (Kugelrohr). The oven of the Kugelrohr must be preheated at 210–220 °C. Distillation should be completed as quickly as possible (within 10 min) because **3** is easily hydrolyzed in air and decomposes on prolonged heating. Distillation of the crude oil afforded pure **3**: yield 336 mg (72%); bp 210–220 °C (0.1 mm) (Kugelrohr bath temperature); ^{1}H NMR (CCl_4) δ 0.55–0.93 (m 4 H), 1.04–1.27 (m, 6 H), 1.44–1.90 (m, 4 H), 1.73 (d, 4 H, J = 7.8 Hz), 2.04–2.73 (m, 2 H), 4.40–4.90 (m, 4 H), 5.33–6.03 (m, 2 H), 7.00 (br s, 10 H); $[\alpha]^{23}_D$ +13.4° (c 1.15, benzene). Anal. Calcd for $C_{26}H_{36}Sn$: C, 66.83; H, 7.77. Found: C, 66.79; H, 7.79.

(−)-2-Octylphenyldiallyltin (4). To a CCl_4 solution (50 mL) of (−)-2-octyltriphenyltin[12c] (11.7 g, 25.3 mmol) was added dropwise bromine (8.1 g, 50.6 mmol) at 0 °C. After it had been stirred for 1 h at room temperature, the reaction mixture was evaporated to give pure (+)-2-octylphenyltin dibromide: yield 11.6 g (98%); $[\alpha]^{23}_D$ +20.1° (c 4.0, benzene). Anal. Calcd for $C_{14}H_{22}Br_2Sn$: C, 35.87; H, 4.73. Found: C, 35.41; H, 4.74.

To an ether solution (20 mL) of allylmagnesium chloride prepared from allyl chloride (1.04 g, 13.6 mmol) was added (+)-2-octylphenyltin dibromide (1.06 g, 2.27 mmol) at −10 °C. After it had been stirred for 30 min at room temperature, the reaction mixture was heated at reflux for 1 h and concentrated to 5 mL. The residue was diluted with hexane and filtered. Evaporation of the filtrate followed by distillation gave **4**: yield 795 mg (90%); bp 175–195 °C (0.5 mm) (Kugelrohr bath temperature); ^{1}H NMR (CCl_4) δ 0.67–0.93 (m, 3 H), 1.00–1.69 (m, 14 H), 1.92 (d, 4 H, J = 8.6 Hz), 3.96–4.92 (m, 4 H), 5.44–6.21 (m, 2 H), 6.96–7.29 (m, 5 H); $[\alpha]^{23}_D$ −21.2° (c 3.5, benzene). Anal. Calcd for $C_{20}H_{32}Sn$: C, 61.40; H, 8.25. Found: C, 61.40; H, 8.29.

(−)-(2-Phenylbutyl)phenyldiallyltin (5). To a THF solution (50 mL) of (+)-(2-phenylbutyl)magnesium chloride (20.7 mmol) was added triphenyltin chloride (5.0 g, 13 mmol) in THF (20 mL). The reaction mixture was heated at reflux for 1 h and evaporated. The residue was diluted with hexane and filtered. Evaporation of the filtrate followed by column chromatography (silica gel, 50:1 hexane–ether) afforded (2-phenylbutyl)triphenyltin ($[\alpha]^{23}_D$ −27.2° (c 12.2, benzene)). Bromination of this compound in CCl_4 at 0 °C gave (2-phenylbutyl)phentyltin dibromide. To an ether solution (60 mL) of allylmagnesium chloride (25 mmol) was added an ether solution (20 mL) of (2-phenylbutyl)phenyltin dibromide (5.3 g, 10.9 mmol) at −10 °C. The reaction mixture was heated at reflux for 1 h and evaporated. The residue was extracted with hexane. Evaporation and distillation of the hexane solution gave **5**: yield 4.46 g (85%); bp 180–200 °C (0.1 mm) (Kugelrohr bath temperature); ^{1}H NMR (CCl_4) δ 0.74 (t, 3 H, J = 7.0 Hz), 0.94–1.58 (m, 3 H), 1.69 (d, 4 H, J = 8.4 Hz), 2.09–2.85 (m, 2 H), 4.42–4.85 (m, 4 H), 5.78–5.93 (m, 2 H), 6.78–7.28 (m, 10 H); $[\alpha]^{23}_D$ −40.9° (c 10.87, benzene). Anal. Calcd for $C_{22}H_{28}BrSn$: C, 64.28; H, 5.12. Found: C, 64.59; H, 5.22.

(−)-(2-Phenylbutyl)phenylmethylallyltin (6). To a dichloromethane solution (100 mL) of methyltriphenyltin (3.66 g, 10 mmol) was slowly added a dichloromethane solution (50 mL) of iodine (2.55 g, 10 mmol) at 0 °C. After it had been stirred for 10 h at room temperature, the reaction mixture was evaporated. The residue was crystallized from hexane at −78 °C to give pure methyldiphenyltin iodide which melts to an oil at room temperature: yield 2.57 g (62%); ^{1}H NMR (CCl_4) δ 1.12 (s, 3 H), 6.88–7.46 (m, 10 H). Anal. Calcd for $C_{13}H_{13}ISn$: C, 37.63; H, 3.13. Found: C, 37.52; H, 3.33.

To a THF solution (25 mL) of (+)-(2-phenylbutyl)magnesium chloride (3.5 mmol) was added methyldiphenyltin iodide (1.4 g, 3.38 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 5 h and extracted with hexane–ammonium chloride solution. Drying ($MgSO_4$) and evaporation of the hexane layer afforded an oil which was subjected to column chromatography (alumina, hexane) yielding (−)-(2-phenylbutyl)methyldiphenyltin: yield 1.01 g (71%); ^{1}H NMR (CCl_4) δ 0.12 (s, 3 H), 0.77 (t, 3 H, J = 5.1 Hz), 1.45–1.78 (m, 4 H), 2.36–2.90 (m, 1 H), 6.84–7.18 (m, 15 H); $[\alpha]^{23}_D$ −37.6° (c 1.76, benzene).

This compound was allowed to react with iodine as described above. Recrystallization of the reaction product from hexane gave (−)-(2-phenylbutyl)phenylmethyltin iodide as faintly pale yellow crystals: yield 64%; ^{1}H NMR (CCl_4) δ 0.47 (s, 3 H), 0.75 (t, 3 H, J = 6.2 Hz), 1.35–2.01 (m, 4 H), 2.43–2.93 (m, 1 H), 6.86–7.18 (m, 10 H); $[\alpha]^{23}_D$ −44.9° (c 1.27, benzene). Anal. Calcd for $C_{17}H_{21}ISn$: C, 43.35; H, 4.46. Found: C, 42.97; H, 4.50.

To an ether solution (10 mL) of allylmagnesium chloride (5 mmol) was slowly added (−)-(2-phenylbutyl)phenylmethyltin iodide (980 mg, 2.08 mmol) in ether (10 mL) at −78 °C over a period of 1 h. After it had been stirred at this temperature for 4 h, the reaction mixture was warmed to room temperature and evaporated. The residue was diluted with hexane and filtered. Evaporation of the filtrate, followed by distillation, gave **6**: yield 426 mg (53%); bp 110–130 °C (0.1 mm) (Kugelrohr bath temperature); ^{1}H NMR (CCl_4) δ −0.03 (s, 3 H), 0.34–0.99 (m, 5 H), 1.27–1.73 (m, 4 H), 2.29–2.85 (m, 1 H), 4.30–4.73 (m, 2 H), 5.18–5.83 (m, 1 H), 6.70–7.17 (m, 10 H); ^{119}Sn NMR ($CDCl_3$) δ −51.3, −52.1. Anal. Calcd for $C_{20}H_{26}Sn$: C, 62.39; H, 6.76. Found: C, 62.30; H, 6.83.

Reaction of Optically Active Allyltins with Aldehydes. The following procedure is representative. To an ether solution (20 mL) of **1** (5.05 g, 10.8 mmol) and 1.06 mL of 47% ether solution of BF_3·OEt_2 (5.4 mmol) was added propanal (0.94 g, 16.2 mmol) at −78 °C. The reaction mixture was stirred at this temperature for 6.5 h and then was shaken with 0.5 N NaOH solution (30 mL). The organic layer was separated, washed with 1 N HCl solution and water, and dried ($MgSO_4$). After distillation of ether, the residue was carefully distilled to give (−)-5-hexen-3-ol (1.02 g, 63%). The distillation residue (4.5 g) was dissolved in acetic anhydride (10 mL). The mixture was heated under reflux for 1 h followed by evaporation of acetic anhydride. The resulting oil was stirred in 1:2 methanol–3 N HCl overnight. Extraction of this mixture with dichloromethane and evaporation of the organic layer yielded $(2\text{-PB})_2SnCl_2$.[16] The chloride thus obtained was treated with the allyl Grignard reagent (30 mmol) in ether (50 mL) at −10 °C followed by heating at reflux for 1 h. Workup and distillation afforded **1** (3.28 g, 65%).

Reactions of other aldehydes were carried out analogously. The resulting secondary homoallyl alcohols were purified by distillation except when nonanal, cinnamaldehyde, and benzaldehyde were employed. In these cases, the homoallyl alcohols were purified by column chromatography on silica gel.

Registry No. 1, 96292-65-8; racemic 1, 96346-84-8; 2, 96292-66-9; racemic 2, 96346-85-9; 3, 96292-67-0; 4, 96292-68-1; 5, 96292-69-2; 6 isomer I, 96306-36-4; 6 isomer II, 96292-70-5; 7, 24850-33-7; 8, 76-63-1; (+)-2-PBCl, 38554-58-4; (±)-2-PBCl, 96391-80-9; DATB, 17381-88-3; (+)-MBCl, 40560-29-0; (+)-3-PBCl, 74259-58-8; C_2H_5CHO, 123-38-6; n-C_3H_7CHO, 123-72-8; i-C_3H_7CHO, 78-84-2; t-C_4H_9CHO, 630-19-3; n-$C_8H_{17}CHO$, 124-19-6; C_6H_5-CH=CHCHO, 104-55-2; C_6H_5CHO, 100-52-7; (S)-H_2C=$CHCH_2CH(OH)R$ (R = C_2H_5), 62959-96-0; (S)-H_2C=

$CHCH_2CH(OH)R$ (R = n-C_3H_7), 85520-72-5; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ (R = i-C_3H_7), 88691-75-2; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ (R = t-C_4H_9), 88691-76-3; (*S*)-$H_2C{=}CHCH_2CH(OH)R$ (R = n-C_8H_{17}), 88691-77-4; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ (R = $C_6H_5CH{=}CH$), 88763-79-5; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ (R = C_6H_5), 85551-57-1; (–)-2-octyltriphenyltin, 82823-89-0; (+)-2-octylphenyltin dibromide, 96306-48-8; allyl chloride, 107-05-1; triphenyltin chloride, 639-58-7; (2-phenylbutyl)triphenyltin, 96292-71-6; (2-phenylbutyl)triphenyltin dibromide, 96292-72-7; methyltriphenyltin, 1089-59-4; methyldiphenyltin iodide, 1015-39-0; (–)-(2-phenylbutyl)methyldiphenyltin, 96292-73-8; (–)-(2-phenylbutyl)phenylmethyltin iodide, 96306-49-9.

Early–Late Transition Metal Heterobimetallic Compounds Linked by a Heterodifunctional (Diphenylphosphino)cyclopentadienyl-Bridging Ligand

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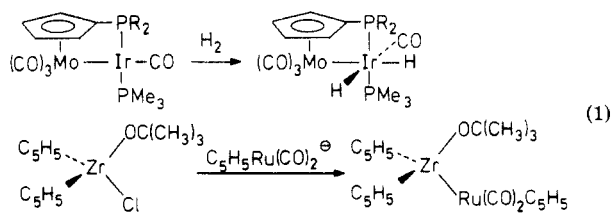
Reaction of $Li^+C_5H_4P(C_6H_5)_2^-$ with $C_5H_5ZrCl_3$ gave $(C_5H_5)[C_5H_4P(C_6H_5)_2]ZrCl_2$, **1**. Reaction of $K^+OC(CH_3)_3^-$ with **1** gave $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Cl$, **2**. Reaction of $K^+(C_5H_5)Fe(CO)_2^-$ with **2** gave $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Fe(CO)_2(C_5H_5)$, **3**. Photolysis of **3** led to expulsion of CO and formation of $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Fe(CO)(C_5H_5)$, **4**, in which Zr and Fe are linked by a metal–metal bond and by the heterodifunctional (diphenylphosphino)cyclopentadienyl ligand. Photolysis of **2** and $Na^+Co(CO)_4^-$ led directly to $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Co(CO)_3$, **5**.

Introduction

One of our long-range goals is the synthesis of a heterobimetallic dihydride with one hydridic M–H bond to an early transition metal, one acidic M–H bond to a late transition metal, and a heterodifunctional ligand joining the two metals. We believe that such compounds would be powerful reducing agents for polar molecules including CO. Since synthetic methods for preparing the desired precursors with directly bonded early and late transition metals are only in their infancy, we initially concentrated on preparing bimetallic compounds linked by heterodifunctional ligands in which the electronegativities of the metals were similar. In this regard, we prepared a series of Mo–Mn,[1] Mo–Re,[1] Mo–Ir,[2] and Mo–Rh[2] compounds in which the metals were linked by a (di-*p*-tolylphosphino)cyclopentadienyl ligand. Of these compounds, only the Mo–Ir compounds[2] reacted with H_2, and they produced iridium dihydrides instead of the desired heterobimetallic dihydrides. In related work, we have synthesized new compounds with directly bonded Zr–Fe[3] and Zr–Ru[3,4] units, but in these cases the metals were not joined by a heterodifunctional ligand (eq 1).



(1)

Here we report our initial attempts to combine these two approaches by preparing early–late heterobimetallic compounds linked by a heterodifunctional ligand. In this work, we have succeeded in synthesizing new Zr–Fe and Zr–Co complexes linked by a heterodifunctional ligand.

Results

The isolability and stability of compounds with directly bonded Zr–Ru and Zr–Fe units encouraged us to try to synthesize early–late transition metal bonded compounds of zirconium linked by a heterodifunctional ligand. The (diphenylphosphino)cyclopentadienyl ligand was chosen because we had used it successfully to prepare Mo–Mn and Mo–Ir compounds[2,3] and because Rausch[5] and Leblanc[6] had used it as a ligand on titanium. Our first synthetic goal was the synthesis of the zirconium complex **1** possessing one C_5H_5 and one $C_5H_4P(C_6H_5)_2$ ligand. With a sequence of reactions similar to that employed by Rausch[5] for the preparation of $(C_5H_5)[C_5H_4P(C_6H_5)_2]TiCl_2$, we reacted $Li^+C_5H_4P(C_6H_5)_2^-$ with $(C_5H_5)ZrCl_3{\cdot}2THF$ in THF at room temperature and isolated $(C_5H_5)[C_5H_4P(C_6H_5)_2]ZrCl_2$ (**1**) as white crystals in 47% yield.

In earlier work with Zr–Ru and Zr–Fe compounds, we had found that *tert*-butoxy groups on zirconium led to more stable and more easily isolated complexes than derivatives with Zr–Cl or Zr–CH_3 groups.[3] Therefore, we reacted the dichloride complex **1** directly with potassium *tert*-butoxide and isolated white crystalline $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Cl$ (**2**) in 45% yield based on $C_5H_5ZrCl_3$.

Reaction of this *tert*-butoxy-substituted zirconium compound **2** with $K^+(C_5H_5)Fe(CO)_2^-$ in THF at room temperature led to the isolation of the directly bonded Zr–Fe compound **3** as bright yellow crystals in 58% yield.

The zirconium atom of **3** is an asymmetric center since it has four different groups bonded to it in a roughly tetrahedral array. Because of this asymmetric zirconium

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