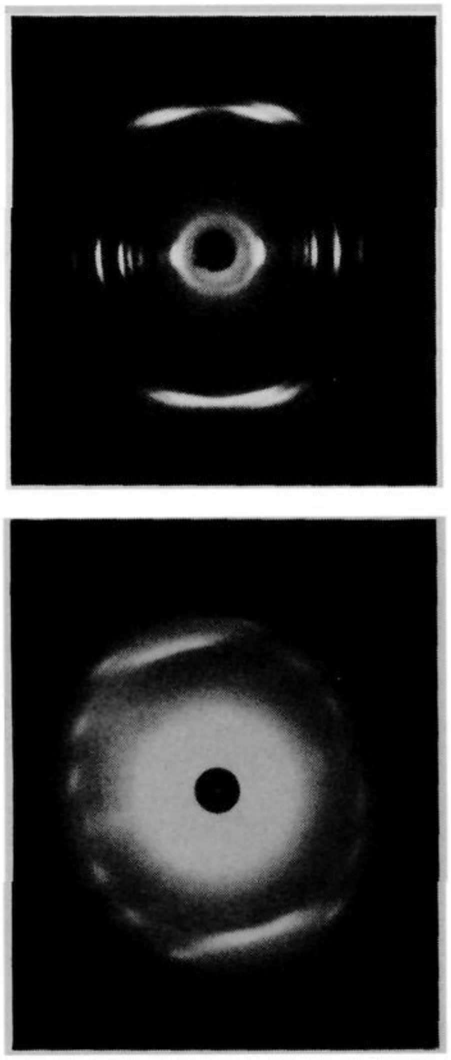

Figure 2. Room temperature, wide-angle X-ray diffraction (WAXD) pictures of stretch-oriented samples of PDHS (upper) and PDPS (lower).

that the molecular structure of the two polymers is different. Since the backbone conformation of PDHS below its transition temperature (~41 °C) is predominantly planar zigzag, the narrow line width and upfield position of the PDPS signal at comparable temperatures suggest a regular, *albeit* nonplanar, backbone conformation. At 87 °C, which is above the respective phase transition temperature of both polymers, the silicon signal of each sample becomes a narrow, time-averaged resonance around −23.5 ppm.

Fiber diffraction patterns for a stretch-oriented sample of PDPS (lower photograph, Figure 2) show sharp reflections out to ~4 Å. Similar studies on samples of PDHS (upper photograph, Figure 2) revealed defined reflections to ~1.5 Å which were consistent with side-chain crystallization.[20] For PDPS, instead of a layer line spacing indicative of a planar zigzag backbone conformation (4.07 Å) as observed for PDHS, the layer line spacing was found to be 13.8 Å, clearly representative of a helical conformation of the polymer. Strong near-meridional reflections occurred on the third-layer line. Both these reflections and the *c*-axis repeat were found to be consistent with a 7/3 helical conformation of the polymer backbone. In addition, a meridional reflection in diffraction patterns from a tilted fiber sample was observed on the seventh-layer line at 1.9–2.0 Å. The strongest reflection, which appeared on the zero-layer line, was about 11.8 Å and corresponds to the interchain backbone spacing. Interestingly, fiber patterns of PDPS taken above the transition temperature are comparable to those recorded for PDHS at 50 °C. In this regard, the strongest reflection for each remained sharply defined on the zero-layer line. This and other spectral information suggest that all molecular order is not lost above the respective transition temperatures.

In summary, spectroscopic evidence indicates that PDPS exists in the solid state at room temperature in a regular 7/3 helical conformation. This is in contrast to PDHS which has been demonstrated to prefer a planar zigzag conformation below 41 °C. A stable helical conformation is also in accord with recent calculations.[21] Our studies imply that PDHS and higher homologues adopt a trans planar backbone conformation in the solid state primarily due to the side-chain crystallization. Comparison of the UV and WAXD data for PDPS and PDHS shows conclusively for the first time that significant deviation from the trans backbone geometry, even for regular structures, results in a large blue shift (~60 nm) in the UV absorption spectrum.

Registry No. PDPS (SRU), 96228-24-9; PDPS (homopolymer), 97036-66-3.

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[20] Jones, A. T. *Makromol. Chem.* **1964**, *71*, 1.

[21] Farmer, B. L.; Rabolt, J.; Miller, R. D. *Macromolecules*, in press.

Interactions of a Diarylmagnesium Compound with Cryptands and Crown Ethers: Formation of Ar_3Mg^-, $ArMg(cryptand)^+$, and Threaded Ar_2Mg(crown ether)

Herman G. Richey, Jr.,* and Diana M. Kushlan

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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Three new species result from treating Tol_2Mg (Tol = *p*-methylphenyl) with cryptands and crown ethers. We believe that the ^1H NMR spectrum in Figure 1 of a solution prepared by stirring benzene with a 2:1 mixture of solid Tol_2Mg (itself insoluble in benzene) and 2,2,1-cryptand is of $TolMg(2,2,1\text{-cryptand})^+$ and Tol_3Mg^-.[1] The spectrum shows two kinds of tolyl groups in a 3:1 ratio and one cryptand for four tolyl groups. The three multiplets (each representing two H's) in the δ 1.1–1.5 region, though remarkably upfield, are due to cryptand H's.[2] Spectra of solutions prepared by using initial Tol_2Mg to cryptand ratios less than about 2 are similar except for the presence of additional absorptions identical with those exhibited by the cryptand alone.[3]

Arylmagnesium ions such as Ar_3Mg^- and $ArMg^+$ have not previously been observed.[4] The disproportionation (eq 1) that

$$2(\mathrm{Tol})_2\mathrm{Mg} + \text{cryptand} \rightarrow \mathrm{TolMg(cryptand)}^+ + \mathrm{Tol_3Mg}^- \quad (1)$$

forms these ions is analogous, however, to that recently observed for dialkylmagnesium compounds (R_2Mg). Structures of solid $NpMg(2,1,1\text{-cryptand})^+ Np_3Mg^-$ (Np = neopentyl) and $[EtMg(2,2,1\text{-cryptand})^+]_2 Et_6Mg_2^{2-}$ were determined,[5] and ^1H NMR spectra of solutions prepared from several R_2Mg's and cryptands show absorptions attributed to similar species.[5,6] R_2Mg's form $RMg(crown)^+$ ions with 15-crown-5, though disproportionation never is as complete as in eq 1.

Tol_2Mg and crown ethers lead to organomagnesium species of composition Tol_2Mg(crown) that we think have "threaded" structures (**1**), in which the crown ether surrounds the Mg in an equatorial fashion and the aryl groups occupy apical positions.

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[1] The anion could instead be $Tol_6Mg_2^{2-}$ if its tolyl groups become equivalent on the NMR time scale.

[2] When the δ 2.5 region was irradiated in a coupling experiment, the δ 1.13 and 1.50 doublets collapsed to singlets.

[3] As initial Tol_2Mg to 2,2,1-cryptand ratios are increased much above 3, absorptions due to cryptand residues and tolyl groups are progressively weaker, indicating that little material has dissolved. Cryptand and tolyl absorptions also are weak in benzene solutions prepared from combinations of Tol_2Mg and 2,1,1- or 2,2,2-cryptand.

[4] A solid of composition Ph_3MgLi has been prepared from Ph_2Mg and PhLi (Wittig, G.; Meyer, F. J.; Lange, G. *Justus Liebigs Ann. Chem.* **1951**, *571*, 167), and ^1H NMR studies of diethyl ether solutions have been interpreted to indicate the presence of species of composition Ph_3MgLi and Ph_4MgLi_2 (Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1602). It is likely that even in solution, however, the Li's are involved significantly in C–Li covalent bonds, as found in the crystal structure of $Ph_6Mg_2Li_2$(tetramethylethylenediamine)$_2$ (Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726), so that there are not the "free" magnesiate ions that must be present when the cation is $TolMg(cryptand)^+$.

[5] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

[6] Kushlan, D. M., Pajerski, A. D. The Pennsylvania State University, unpublished observations.

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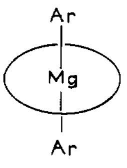

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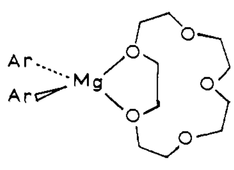

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Figure 2 shows the ^{1}H NMR spectrum of a solution prepared by stirring benzene and a 1:1 mixture of solid Tol_2Mg and 15-crown-5. This spectrum shows only one set of tolyl absorptions but two crown ether absorptions. In this spectrum and those of solutions prepared by using other initial Tol_2Mg to 15-crown-5 ratios, the ratio of tolyl groups to the crown ethers responsible for one of the absorptions is 2:1. The other crown ether absorption is similar in position to that of the crown ether alone and its relative size decreases with increasing initial Tol_2Mg to crown ether ratio. Solutions prepared with 18-crown-6 have similar spectra.[7]

Several observations support the assignment of a threaded structure (**1**) to Tol_2Mg(crown). (1) The ^{1}H NMR absorption of the crown ether is a singlet.[8] If this species had a structure in which Mg was over one face of the crown ether or, as in **2**, bonded to only some of the crown ether oxygens, then the crown ether absorption would be more complex unless appropriate Mg–O bonds were rapidly broken and formed. Although exchange of oxygens attached to Mg often is rapid, the observation of independent crown ether absorptions indicates that equilibration between free crown ether and that in Tol_2Mg(crown) is slow on the NMR time scale. Therefore if the crown ether of Tol_2Mg(crown) is unsymmetrical but that is not evident in the ^{1}H NMR spectrum because of rapid exchange of Mg–O bonds, then that equilibration occurs without interchange of bound and free crown ether. (2) In nuclear Overhauser difference spectra of Tol_2Mg(crown), irradiation of the absorption of the bound crown ether significantly enhances the absorptions due to the tolyl H's ortho to Mg,[9] indicating that the ortho and crown ether H's are in proximity. (3) Reaction of a benzene solution of Tol_2Mg(18-crown-6) and acetophenone takes hours.[10] Such unusual lack of reactivity[11] is consistent with structure **1** and the proposal, reasonable and often made but for which evidence has been scanty, that coordination of Mg to the carbonyl group is important in additions of organomagnesium compounds to ketones.

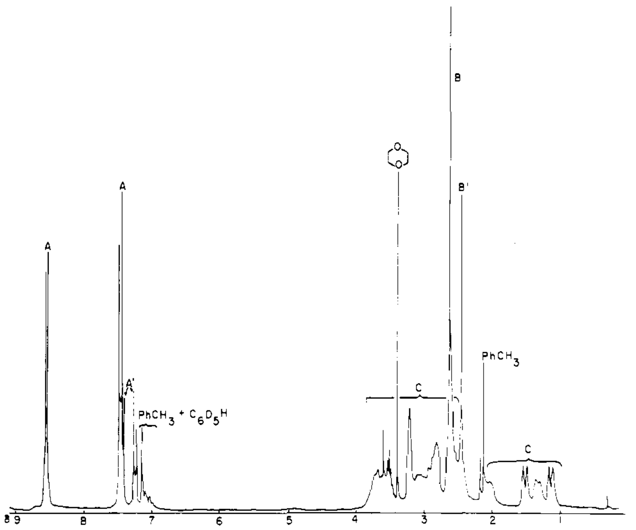

Figure 1. ^{1}H NMR spectrum, 200 MHz, in C_6D_6 of a solution formed from Tol_2Mg and 2,2,1-cryptand. Chemical shifts are relative to benzene (δ 7.15). The aryl H doublets labeled A and the CH_3 singlet labeled B are assigned to Tol_3Mg^-. The corresponding absorptions labeled A′ and B′ plus the cryptand absorptions (C) are assigned to $TolMg^+$(cryptand). The dioxane was introduced in the preparation of Tol_2Mg from TolMgBr and not totally removed.

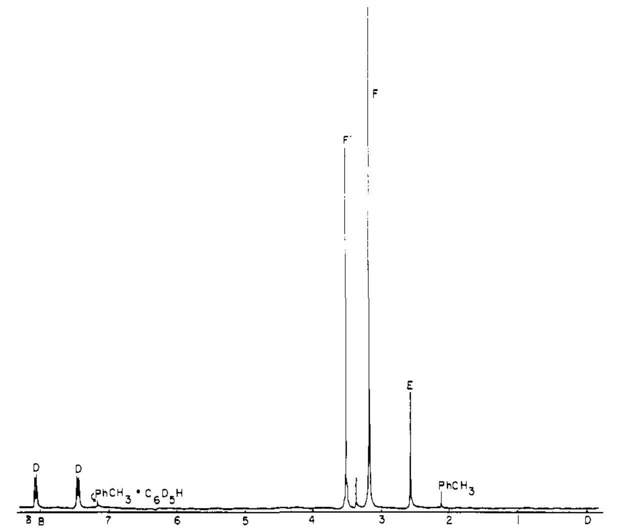

Figure 2. ^{1}H NMR spectrum, 200 MHz, in C_6D_6 of a solution formed from Tol_2Mg and 15-crown-5. Chemical shifts are relative to benzene (δ 7.15). The aryl doublets (D), the CH_3 singlet (E), and the crown ether (F) absorption are assigned to Tol_2Mg(crown). The absorption labeled F′ is assigned to free crown ether.

By contrast to the slow reaction of Tol_2Mg(18-crown-6), immediate precipitation when acetophenone is added to a solution of Tol_2Mg(15-crown-5) suggests a much more rapid reaction; reaction is complete by the time (<5 min) of the first NMR observation.[12] This reactivity difference, however, is not reflected in a significant difference in formation constants for the complexes. The equilibrium constant for the equilibration in eq 2 is approximately 1.0 in benzene at 25 °C.[13]

$$\mathrm{Tol_2Mg(15\text{-}C\text{-}5) + 18\text{-}C\text{-}6 \rightleftarrows Tol_2Mg(18\text{-}C\text{-}6) + 15\text{-}C\text{-}5} \quad (2)$$

A cryptand causes complete disproportionation of Tol_2Mg to a coordinated organomagnesium cation and a magnesiate anion. Crown ethers, however, convert Tol_2Mg to Tol_2Mg(crown) species, probably having threaded structures, without accompanying formation of disproportionation products.

Acknowledgment. We are indebted to the National Science

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[7] Solutions prepared by using initial ratios of Tol_2Mg to 18-crown-6 of greater than about 2 show no free crown ether absorption. All spectra prepared with 15-crown-5, however, exhibit an absorption for at least some free crown ether. Absorptions due to uncoordinated Tol_2Mg are not observed in any solutions prepared with 15-crown-5 or 18-crown-6. Just as observed with the cryptand preparations, tolyl and crown ether absorptions are progressively weaker as the initial ratio of Tol_2Mg to crown ether is increased above about 3.

[8] The absorptions of toluene-d_8 solutions prepared from Tol_2Mg and 15-crown-5 or 18-crown-6 do not broaden significantly when the temperature is lowered to −60 °C.

[9] The enhancement of the δ 8.04 absorption of Tol_2Mg(15-crown-5) is 28% and of the δ 8.16 absorption of Tol_2Mg(18-crown-6) is 18%. Irradiation of the free crown ether absorption in the 15-crown-5 solution also enhances (13%) the δ 8.04 absorption, probably because of some incidental irradiation of the nearby absorption of the crown ether of Tol_2Mg(crown).

[10] Only one-half of the Tol_2Mg(18-crown-6) in a benzene solution approximately 0.06 M in this species and 0.19 M in acetophenone disappeared within 90 min.

[11] A solution containing Tol_2Mg in the presence of an excess of the excellent coordinating agent $Me_2NCH_2CH_2NMe_2$ reacts rapidly with acetone.

[12] That Tol_2Mg(15-crown-5) reacts considerably more rapidly can be verified by ^{1}H NMR observations after adding acetophenone to solutions that contain both Tol_2Mg(15-crown-5) and Tol_2Mg(18-crown-6).

[13] The ^{1}H NMR absorptions of the free crown ethers are separated by somewhat less than 0.01 ppm. For that reason, determinations of the relative amounts of the free crown ethers from areas of their absorptions in 200 MHz spectra have considerable error and the equilibrium constant of 1.0 probably is accurate only to ±50%. Because of this experimental problem, there has been no critical test that the data fit the equilbrium expression for eq 2.

Foundation for support of this research and for aiding in the purchase of the NMR spectrometer. We thank Professor Lloyd Jackman for helpful discussions, Alan Freyer for assistance with the NMR observations, and a referee for helpful comments.

$SnCl_4(4\text{-}t\text{-}BuC_6H_4CHO)_2$. X-ray Crystal Structure, Solution NMR, and Implications for Reactions at Complexed Carbonyls[1a]

Scott E. Denmark,*[1b] Brad R. Henke, and Eric Weber[1c]

Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

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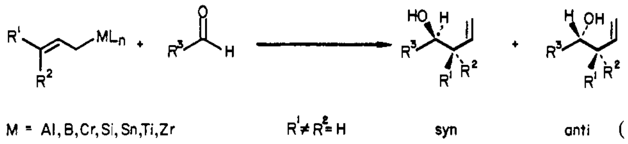
The reaction of allylic organometallic reagents with aldehydes (eq 1) has emerged as one of the more synthetically useful methods



(1)

for acyclic steroselection.[2] It is also a reaction that has aroused considerable interest in mechanistic detail since it shows divergent behavior depending upon the metal, double-bond geometry, and reaction conditions. We have recently reported the results of studies with models **1a** and **1b** which were desigened to clarify the origins of stereoselectivity in these reactions[3] (Scheme I). Specifically, those models allowed an unambiguous correlation between product stereochemistry and transition-state geometry. Thus, the syn alcohol **2** and the anti alcohol **3** arise from synclinal and antiperiplanar transition states, respectively. For **1a** we noted variable syn selectivity (47–99%) with a strong dependence on the nature of the Lewis acid. This was interpreted in terms of the bulk of the Lewis acid–aldehyde complex (assumed to be of *E* configuration). We describe herein several studies on the effects of experimental variables (concentration, stoichiometry, and "spectator groups") on the stereoselectivity of cyclization. These data support our earlier hypothesis on the nature of Lewis acid–aldehyde complexation (and its importance in stereocontrol) with evidence from X-ray crystallography and NMR.[4]

All of the studies were carried out on model **1a** with $SnCl_4$ as the Lewis acid. We were puzzled by the poor selectivity with this reagent (syn/anti 47/53) in our earlier work and suggested that the well-known 1:2 complexation stoichiometry ($SnCl_4$/Lewis base)[5] was responsible for the greater "effective steric bulk" of the Lewis acid. Given this hypothesis we investigated the effects of those experimental factors which might be expected to influence the nature of that complex and observed the changes in stereoselectivity. The results of concentration effects on stereochemistry are summarized in Table I. As the solution became more dilute, we noted than an increasing proportion of the syn product **2** was forming in preference to **3** to the point where $SnCl_4$ and $BF_3{\cdot}OEt_2$ gave the same ratio. We interpret this trend in terms of the expected increase in the relative amount of the 1:1 complex at higher dilution. This complex should be kinetically competent and significantly less bulky.[6] The lesser bulk provides for a less

Scheme I

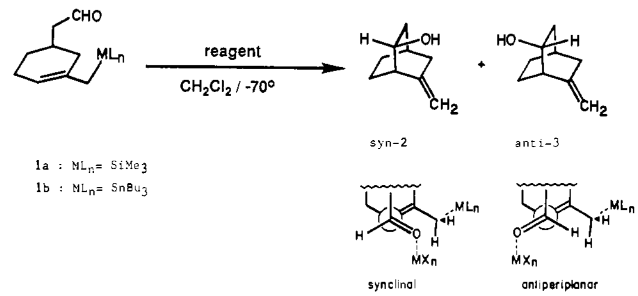


Table I. Concentration Effects on Stereochemistry in Conversion of **1a** → **2**/**3**[a]

entry	Lewis acid	concn of **1a**, M	% convsn[b]	syn (**2**)/anti (**3**)[c]
1	$SnCl_4$	0.25	89	44/56
2	$SnCl_4$	0.05	82	56/44[d]
3	$SnCl_4$	0.005	85	64/36
4	$SnCl_4$	0.0005	100	86/14
5	$BF_3{\cdot}OEt_2$	0.28	89	82/18
6	$BF_3{\cdot}OEt_2$	0.05	87	79/21
7	$BF_3{\cdot}OEt_2$	0.005	93	84/16

[a] All reactions employed 1.1 equiv of Lewis acid in CH_2Cl_2 solution at −78 °C. [b] The conversions are calculated for products by comparison to decane as an internal standard. **1a** was completely consumed in all runs. [c] Averages of at least three runs with ratios ±3%. [d] This measurement was less reproducible ranging from 46/54 to 63/37.

Table II. Stoichiometry Effects on Stereochemistry of Conversion of **1a** → **2**/**3**[a]

entry	Lewis acid	equiv	% convsn[b]	syn (**2**)/anti (**3**)[c]
1	$SnCl_4$	0.25	83	51/49
2	$SnCl_4$	0.55	89	42/58
3	$SnCl_4$	1.10	82	56/44[d]
4	$SnCl_4$	10.0	93	60/40
5	$SnCl_4$	25.0	90	75/25
6	$BF_3{\cdot}OEt_2$	0.55	85	92/8
7	$BF_3{\cdot}OEt_2$	1.00	87	79/21
8	$BF_3{\cdot}OEt_2$	10.0	86	80/20

[a] All reactions were run at 0.05 M in **1a** in CH_2Cl_2 at −78 °C. [b] Calculated for products by comparison to decane as an internal standard. [c] See Table I. [d] See Table I.

Table III. Dummy Ligand Effects on Stereochemistry of Conversion of **1a** → **2**/**3**[a]

entry	equiv	time, min	% convsn[b]	syn (**2**)/anti (**3**)[c]
1	1.1	10	41	90/10
2	1.1	60	80	87/13
3	1.1	360	88	72/28
4	5.0	360	97	70/30

[a] The Lewis acid used was $SnCl_4{\cdot}(SMe_2)_2$ (1.0 M in CH_2Cl_2). All reactions were run at 0.05 M concentration in CH_2Cl_2 at −78 °C. [b] Calculated for products by comparison to decane as an internal standard. [c] See Table I.

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[1] (a) Presented at the 20th Great Lakes Regional Meeting, Milwaukee, WI, June 1986, ORGN 322. (b) Fellow of the Alfred P. Sloan Foundation (1985–1987); NSF Presidential Young Investigator (1985–1990). (c) Taken in part from: Weber, E. J. Ph.D. Thesis, University of Illinois, Urbana, 1985.

[2] Reviews: (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. (c) Hiyama, T. *J. Synth. Org. Chem. Jpn.* **1981**, *39*, 81. See also: (d) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron*, **1984**, *40*, 2239. (e) Young, D.; Kitching, W. *Aust. J. Chem.* **1985**, *38*, 1767. (f) Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927.

[3] (a) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (b) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655.

[4] For studies on the importance of Lewis acid–carbonyl complexation on stereocontrol, see: (a) reference 2f. (b) Benner, J. P.; Gill, G. B.; Parrott, S. J.; Wallace, B.; Begley, M. J. *J. Chem. Soc., Perkin Trans 1* **1984**, *315*. (c) Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667. (d) Heathcock, C. H.; Norman, M. H.; Uehling, D. E. *Ibid.* **1985**, *107*, 2797. (e) Danishefsky, S. J.; Pearson, W. H.; Harvey, D. F.; Maring, C. J.; Springer, J. P. *Ibid.* **1985**, *107*, 1256 and reference cited therein. (f) Keck, G. E.; Castellino, S. *Ibid.* **1986**, *108*, 3847. (g) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556.

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[6] (a) The "effective bulk" of the 1:2 vs. 1:1 complexes clearly depends on the geometry of complexation around oxygen and tin. (b) Zahrobsky, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 3313.

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