Cyclic Organotin Lewis Acids

E. Vedejs,* D. E. Erdman, and D. R. Powell

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

Received December 15, 1992

The $Ph_3P{=}O$ IR frequency shift method has been used to compare the Lewis acid strength of several cyclic organotin dichlorides. Structures **3**, **20**, and **4** are relatively weak Lewis acids, less potent than Bu_2SnCl_2, according to the IR criterion. Steric factors appear largely responsible for the decreased Lewis acidity, although bond angle strain may also contribute in the case of **3**. Introduction of electronegative substituents into the aromatic ring of structures related to **4** results in stronger Lewis acids **8** and **18**, both of which are relatively more potent than Ph_2SnCl_2. Methods for the preparation of precursors to the fluorinated **8** and **18** are described, based on the deprotonation of tetrafluoroaryl precursors.

Organotin compounds have been of interest as potential Lewis acids for applications in catalysis and coordination chemistry.[1,2] In contrast to halide-containing Lewis acids derived from a number of other elements, alkyltin halides of the general formula R_nSnCl_m where m = 1 or 2 are relatively easy to isolate and to purify, in part because the Sn–Cl bond is comparable in strength to the Sn–O bond and is not especially sensitive to hydrolysis. They also have the advantage that there are few limitations on the nature of alkyl substituents that can be present at tin. In principle, this feature allows the synthesis of tailor-made Lewis acids that might serve as selective catalysts for organic transformations.[1c] Halides related to Bu_2SnCl_2 or Ph_2SnCl_2 are sufficiently potent Lewis acids to form adducts with a variety of donor molecules.[2] The 1:1 stoichiometry is favored for monodentate ligands in typical solvents, resulting in trigonal bipyramidal complexes, but 1:2 adducts (octahedral geometry) can be present in equilibrium.[2b] The extent of ligand dissociation is related to the Lewis acid strength of the organotin derivative and increases with the electronegativity and decreases with the bulk of the tin substituents.[2] Much of the detailed information regarding the stability of organotin halide adducts is based on calorimetry studies as well as on NMR titration experiments.[2b] However, there is also a simpler technique available that allows the qualitative comparison of the coordinating ability of Lewis acids. The IR frequencies of phosphine oxide or sulfoxide ligands undergo a shift toward lower frequencies in the presence of Lewis acids because coordination of an electrophilic atom at P=O or S=O oxygen electron pairs reduces the double bond character of the P=O or S=O bond.[3] Thus, the $Ph_3P{=}O$ frequency shifts (Table I) suggest an ordering of Lewis acid strengths $SnCl_4 > Ph_2SnCl_2 > Me_2SnCl_2$. This is the logical order according to the electronegativity of substituents and agrees with the results obtained using other criteria.[2] It is not so clear that Ph_3SnCl is in the logical sequence in Table I, but this substance is unique among those listed because it forms a 1:1 complex with $Ph_3P{=}O$. The P=O frequency shift method probably is more reliable within a family of structurally similar Lewis acids. In the case of diorganotin dihalides, it can therefore be expected to correlate with the strength of metal–oxygen coordination and therefore with the Lewis acidity of the test compounds.

An earlier study in our laboratory had been initiated with the expectation that cyclic organotin dichlorides **1**, **3**, and **4** might be useful chiral coordinating agents.[1b] The 5-membered dihalide **1** was a risky choice because this ring system is known to be unstable,[4] and **1** proved to be too labile for convenient handling or for evaluation by the IR method.[1b,5] Stability problems were not encountered with **3** or **4**, but both of these substances were found to be surprisingly feeble Lewis acids by comparison with their acyclic counterparts. The IR frequency shift with $Ph_3P{=}O$ was ca. 10 cm^{-1} smaller for **3** vs Bu_2SnCl_2 and also for **4** vs Ph_2SnCl_2. Stable complexes could not be prepared from **3** using typical monodentate ligands (sulfoxides, phosphine oxides, sulfides, etc), although **4** did afford a reasonably stable crystalline adduct **5** with triphenylphosphine oxide. It became clear that Lewis acidity would have to be increased by introducing more highly electronegative substituents at tin.[6] The purpose of this paper is to explore techniques for the synthesis of fluorinated analogs of **4**

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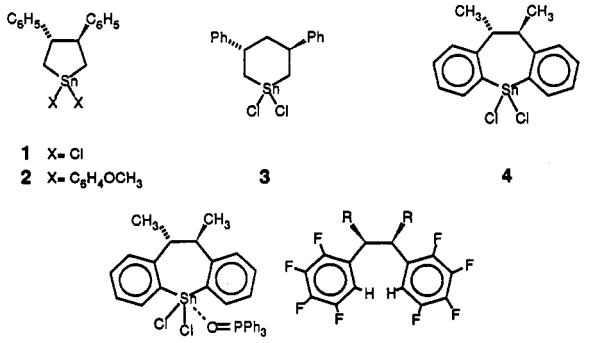
(5) Addition of $Ph_3P{=}O$ to **1** resulted in the formation of an intractable material, presumably via ring cleavage and polymerization. See ref 4b for relevant observations regarding stability of simpler analogues.

0022-3263/93/1958-2840$04.00/0

Table I. Lewis Acidity According to the $Ph_3P{=}O$ Frequency Shift Method (Nujol)

Lewis acid (LA)	LA:$Ph_3P{=}O$	$\Delta\nu$ (cm^{-1})	ref
Me_2SnCl_2	1:2	39	3e
$ZnCl_2$	1:2	41	3b
Ph_3SnCl	1:1	43	3e
Ph_2SnCl_2	1:2	53	3e
$SnCl_4$	1:2	67	3e

and to confirm that they are relatively potent Lewis acids compared to the other cyclic tin dihalides.

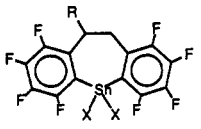


1 X = Cl
2 X = $C_6H_4OCH_3$

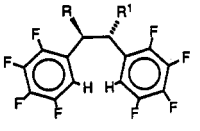
3

4

6 R = H
11 R = CH_3



7 R = H, X = $C_6H_4OCH_3$
8 R = H, X = Cl
17 R = CH_3, X = $C_6H_4OCH_3$
18 R = CH_3, X = Cl

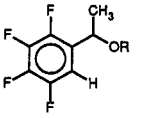


10 R = CH_3, R^1 = CH_3
12 R = CH_3, R^1 = H

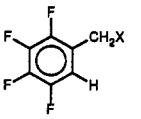
Cyclic organotin structures are usually prepared by the reaction of difunctional organometallic reagents with organotin dihalides.[7] This approach becomes especially convenient for the fluoroaryl series because ortho fluorine activates aromatic C–H bonds for direct metalation.[8] Thus, treatment of 1,2-bis(2,3,4,5-tetrafluorophenyl)ethane (**6**) with butyllithium followed by dianisyltin dichloride produced the dihydrostannepin derivative **7** in a single operation. The electron-rich anisyl groups were then selectively cleaved using HCl in toluene at room temperature to afford the octafluoroorganotin dichloride **8**.

A similar approach was used to prepare chiral analogs of **8**, starting from 1-(pentafluorophenyl)ethanol. Selective ortho-defluorination was accomplished using the hydroxyl-directed $LiAlH_4$ reduction[9] to give the tetrafluorophenylethanol **9**, a potential starting material for the fluorinated bibenzyl derivatives **10** and **12**. Treatment of **9** with the McMurry reagent ($TiCl_3$–$LiAlH_4$)[10a] did produce **10**, but the meso diastereomer **11** was inevitably formed as a major byproduct (**10**:**11** = ca. 1:1). The diasteromers could be separated on small scale by HPLC (ca. 20% recovery), but this approach did not provide sufficient material for detailed study. Fortunately, the monomethyl analog **12** could be prepared easily and allowed access to the chiral stannepin derivative **18**.

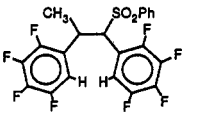
A modified coupling strategy was developed for the synthesis of the monomethylated bibenzyl derivative **12**. Treatment of **9** with CH_3SO_2Cl/Et_3N afforded the mesylate **13** and coupling with the lithium salt of sulfone **15** gave **16** as a mixture of diastereomers (74%). Diastereomer



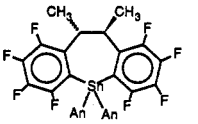
9 R = H
13 R = Ms



14 X = OH
15 X = SO_2Ph



16



19
(An = p-$C_6H_4OCH_3$)

20

21

22

separation was not necessary because desulfonylation with Raney nickel converted both diastereomers into **12** (96%). In anticipation of potential uses for enantiomerically pure **12**, the major diastereomer of **16** was prepared from **9** that had been resolved via the naproxen ester. The enantiomers of **16** from this sequence were formed in a 95:5 ratio (90% ee). Thus, no more than 10% racemization occurs during the mesylate displacement by the sulfone anion.

The conversion from **12** to the dihydrostannepin **17** followed the route used for synthesis of **8**, but careful control of time and temperature variables was necessary in the initial deprotonation step. Best results were achieved when **12** was treated with 2 equiv of *n*-butyllithium at −78 °C for 5 min. The resulting anion was quenched with freshly purified dianisyltin dichloride to produce **17** in 83% yield. Longer deprotonation times gave lower recovery of **17** because the intermediate dianion suffered significant decomposition. Thus, the yield dropped to 20% if the dianisyltin dichloride was added 2 h after the butyllithium. The same procedure was then applied without further optimization to chromatographically purified **10** on small scale. In this system, the C_2-symmetric product **19** was obtained in an acceptable 48% yield. However, the difficulty in preparation of the precursor **10** precluded further investigation of the C_2-symmetric octafluorodibenzodihydrostannepins.

Further conversion from **17** to **18** was performed by using dry HCl in tolune as already described for the synthesis of **8**. The Lewis acid strength of the cyclic fluorinated organotin dichlorides could now be compared with other cyclic tin dihalides using the IR frequency shift method

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Table II. IR Frequency Shifts for $Ph_3P{=}O$ and Cyclic Organotin Dihalides ($CHCl_3$ Solution)

Lewis acid	$\Delta\nu^a$ (cm^{-1})	Lewis acid	$\Delta\nu^a$ (cm^{-1})
3	24[b]	$(C_4H_9)_2SnCl_2$	32[b]
20	26[b]	$(C_6H_5)_2SnCl_2$	42
4	29[b]	8	48
		18	50[c]

[a] Chloroform solution, 0.08 M, 1:1 ratio of $Ph_3P{=}O$/Lewis acid. [b] Reference 1b. [c] Average value of double absorption maximum.

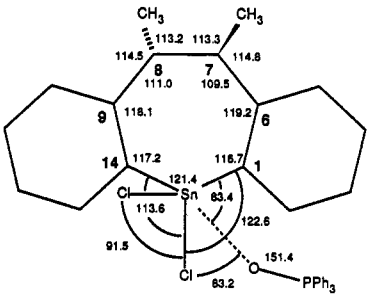
($Ph_3P{=}O$ test ligand). Table II summarizes the data for **3**, the unsubstituted 6-membered ring derivative **20**, the dihydrostannepin **4**, and the fluorine-containing derivatives **8** and **18**. Since stable complexes could not be isolated in all cases, these comparisons were performed using a 1:1 ratio of $Ph_3P{=}O$/diorganotin dichloride in $CHCl_3$ solution at the same molarity to allow systematic comparisons. For that reason, the frequency shifts cannot be compared directly with the values in Table I, and only the relative order of entries in the table is significant. As expected, **8** and **18** are substantially more potent as Lewis acids compared to the other cyclic tin dichlorides. Thus, a cyclic tin environment does not preclude valence shell expansion from tetracoordinated to pentacoordinated tin. However, it is clear that electronegative substituents play an important role in the activation of the stannepin ring system. Further insight into the difference in Lewis acid strength was obtained by comparing the catalytic reactivity of stannepin derivatives **4** and **18** in the hetero-Diels–Alder reaction of Danishefsky's diene with benzaldehyde.[10b] The fluorinated **18** (10 mol %, rt in benzene) induced complete conversion into the dihydropyrone adduct[10b] within 1 h while the nonfluorinated stannepin **4** gave no perceptible rate enhancement over the noncatalyzed reaction. We also considered the possibility that **18** (ca. 90% ee) might catalyze an asymmetric hetero-Diels–Alder reaction. However, the Danishefsky diene–benzaldehyde adduct was virtually racemic, so this line of investigation was not pursued further.

Discussion

A comparison of Tables I and II shows that there is a decrease in Lewis acidity in the 6-membered cyclic organotin dihalides vs acyclic analogues. The decrease can be compensated for by the incorporation of strongly electronegative fluorine substituents. In the absence of fluorine, there is a small improvement from the 6-membered to the 7-membered ring systems, but **4** is less potent relative to the acyclic reference structure Ph_2SnCl_2. Part of the reason for decreased Lewis acidity can be traced to the increased steric bulk of **4**, a factor that is known to destabilize organotin coordination complexes.[2b] Decreased flexibility due to the presence of ring constraints will probably be another contributing factor, one that will tend to maximize steric problems.

The influence of bond angle factors in the cyclic dihalides must also be considered. According to the crystal structure of complex **5** (Table III),[11a] chlorine and $Ph_3P{=}O$ ligands occupy the two apical sites in a trigonal bipyramid. This forces the 7-membered ring to span two equatorial sites, but the endocyclic C–Sn–C bond angle is 121.4°, close to the ideal value of 120°. The other endocyclic bond angles are within ca. 3° of the ideal values for sp^2 or sp^3 hybridized carbon, so the diequatorial 7-membered ring appears to fit comfortably within the trigonal bipyramidal geometry.

Table III. Summary of Structural Data for 5[a]

bond distances (Å)		bond angles (deg)
C_1–Sn	2.123	
C_{14}–Sn	2.109	
Sn–Cl_{eq}	2.339	
Sn–Cl_{ax}	2.457	
C_1–C_6	1.410	
C_6–C_7	1.533	
C_7–C_8	1.578	
C_8–C_9	1.509	
C_9–C_{14}	1.419	
P–O	1.503	
Sn–O	2.309	

Indeed, some driving force from the release of bond angle strain might have been expected because related stannepin derivatives that contain tetrahedral tin have a smaller endocyclic bond angle (ca. 99°) that differs substantially from the tetrahedral angle.[12] Although this factor may not be large, it is safe to conclude that conversion from **4**, **8**, or **18** to pentavalent adducts involves little if any increase in bond angle strain. However, this is not likely in the case of the 6-membered rings **3** and **20**, provided that $Ph_3P{=}O$ coordination occurs in the same way as in **5** (apical oxygen and chlorine). The only reported crystal structure of a compound containing the stannacyclohexane subunit has tetravalent tin and an endocyclic bond angle of 101°.[11b] This is the expected result when the relatively long C–Sn bonds are constrained to a 6-membered ring. Conversion into a trigonal bipyramidal adduct would face the molecule with difficult choices. One option is to place the 6-membered ring in the diequatorial arrangement, a situation that is likely to increase bond angle strain. Another possibility is to place the 6-membered ring in apical and equatorial sites, but the resulting structure would have only one of the electronegative groups in an apical site. Yet another option would be to form a 1:2 adduct having octahedral geometry. Unfortunately, no X-ray structures of relevant adducts in the 6-membered series are available. However, it seems safe to conclude that none of the above alternatives is free of an energy penalty, and the tendency of the 6-membered **3** or **20** to form complexes remains low.

Ring size effects on organotin complexation issues have been encountered in one previous study. It is known that 5-membered cyclic tin alkoxides such as **21** are dimeric in solution because they prefer a pentacoordinated tin environment. Complexation with DMSO is also observed with the 5-membered tin alkoxide.[13] On the other hand, the 6-membered analog **22** is resistant to coordination and exists in solution as the monomer. This difference in behavior has been attributed to bond angle effects.[13] The tetrahedral tin center in the 5-membered **21** is constrained

(11) (a) Atomic coordinates of **2**, **5**, and the $Ph_3P{=}O$ complex **i** derived from a BrSnPh analogue of **18** (SnX_2 = SnBrPh)[1b] have been deposited in the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EW, UK. Adduct **i** has greater stannepin bond angle distortion (endocyclic C–Sn–C bond angle = 110.2°; endocyclic Sn–C–C bond angles = 128.2° and 121.4°), but otherwise the geometry resembles that of **5**. (b) Bokii, N. G.; Yanovskii, A. I.; Struchkov, Y. T.; Shemyakin, N. F.; Zakharin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 380.

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to have an endocyclic bond angle of ca. 90°, and the 5-membered ring is strained. However, the strain can be relieved in pentacoordinated structures where the 5-membered ring spans apical and equatorial sites in the trigonal bipyramid. Neither **21** nor **22** can place the rings into diequatorial sites because of the preference for electronegative oxygen in the apical position and because this would result in additional bond angle strain.

Similar arguments can be applied to **3**, **4**, and **8**. The 7-membered rings are sufficiently flexible to span diequatorial sites in a trigonal bipyramid without significant bond angle distortion elsewhere in the ring (Table III). Since electronegative chlorine and a ligand heteroatom (for example, phosphine oxide oxygen) are available to occupy the apical sites, the stannepin-derived Lewis acid complexes easily satisfy the geometric requirements for trigonal bipyramidal tin. The situation is different for the 6-membered organotin dihalides **3** and **20**. Their relatively small endocyclic C–Sn–C bond angle destabilizes adducts having the ring in the diequatorial arrangement, while the alternative of an apical, equatorial 6-membered ring is destabilized because a carbon atom must replace one of the electronegative substituents in an apical position. There is no good trigonal bipyramidal structure available to the 6-membered **3** or **20**, and both of these organotin dihalides are relatively feeble Lewis acids. Pentavalent adducts are formed more easily in the 7-membered rings, and it is conceivable that there would be some decrease in bond angle strain in the trigonal bipyramidal structures by comparison with the tetrahedral precursors. However, the results of Table II argue against this supposition. A comparison of **4**, $(C_6H_5)_2SnCl_2$, and **18** shows that the nonfluorinated stannepin derivative **4** is a weaker Lewis acid compared to the reference structure, diphenyltin dichloride. The difference can be attributed to decreased flexibility in **4** and an increase in steric crowding due to the presence of the 7-membered ring. Both problems are overcome in **18** by the electronegativity effect of fluoraryl substituents, but none of the stannepin dichlorides investigated approaches tin tetrachloride in Lewis acidity.

Experimental Section

2,3,4,5-Tetrafluorobenzaldehyde. Dimethyl sulfoxide (2.8 mL, 40 mmol) was added to a −78 °C solution of oxalyl chloride (2.6 mL, 29 mmol) in 100 mL of methylene chloride, and the bubbling mixture was stirred for 5 min. To this was added a solution of 2,3,4,5-tetrafluorobenzyl alcohol **14**[9] (4.8 g, 27 mmol) in 10 mL of methylene chloride; after 15 min triethylamine (27 mL, 0.19 mol, distilled from CaH_2) was added. The resulting mixture was warmed to room temperature and then poured into saturated aqueous sodium bicarbonate; the layers were separated, and the organics were washed with water (2 × 20 mL), dried ($MgSO_4$), and carefully evaporated (aspirator). The resulting yellow oil was distilled (25 °C, 1.0 Torr, bulb to bulb) to give tetrafluorobenzaldehyde (3.6 g, 74%), identical by NMR comparisons with material reported previously:[14] oil; analytical TLC (silica gel F254), 10% ether/hexane, R_f = 0.55; MS exact mass calcd for $C_7H_2OF_4$ 178.0042, found 178.0047, error = 3.1 ppm; IR ($CHCl_3$, cm^{-1}) C=O, 1710; 200-MHz NMR (CDC_3) δ 10.28 (1 H, d, J = 3 Hz), 7.53 (1 H, dddd, J = 2.4, 5.6, 8, 9.4 Hz).

1,2-Bis(2,3,4,5-tetrafluorophenyl)ethene (Octafluorostilbene). Lithium wire (1.65 g, 0.24 mol) was added to a solution of titanium trichloride (12.1 g, 79 mmol, Aldrich) in 50 mL of dimethoxymethane (distilled from sodium benzophenone) under nitrogen, and the black slurry was heated to reflux for 1 h.[10a] After the mixture was cooled to room temperature, a solution of tetrafluorobenzaldehyde (3.5 g, 20 mmol) in 10 mL of dry dimethoxyethane was added, and the resulting mixture was heated to reflux for 16 h. After being cooled to room temperature, the black slurry was diluted with 100 mL of hexane and filtered through a pad of silica gel. The black filter cake was washed with hexane (2 × 100 mL) and then quenched carefully with methanol and discarded. The hexane filtrate was concentrated, and the resulting oil was purified by chromatography (15 g of silica gel 60, hexane) to give the product octafluorostilbene (2.1 g, 60%) as a mixture of E and Z isomers (10:1): mp 79–84 °C; analytical TLC (silica gel F254), hexane, R_f = 0.32; MS exact mass calcd for $C_{14}H_4F_8$ 324.0185, found 324.0181, error = 1.2 ppm; IR (KBr, cm^{-1}) C=C, 1630; 200-MHz NMR ($CDCl_3$), δ 7.3–6.9 (2 H, m), 7.13 (1.8 H, s, major isomer), 7.26 (0.2 H, s, minor isomer).

1,2-Bis(2,3,4,5-tetrafluorophenyl)ethane (6). Octafluorostilbene (1.8 g, 5.6 mmol, mixture of E,Z) was added to 5% palladium on carbon (0.5 g, Engelhard) in 50 mL of glacial acetic acid. This slurry was placed under 30 psi of hydrogen pressure (Parr apparatus) for 36 h. The resulting slurry was filtered through Celite, and the solvent was evaporated (aspirator). The resulting solid was dissolved in hexane and purified by passing through a small plug of silica gel (7 g) with hexane to give 1,2-bis(2,3,4,5-tetrafluorophenyl)ethane (**6**) (1.78 g, 98%): mp 54–56 °C; analytical TLC (silica gel F254), hexane, R_f = 0.26; MS exact mass calcd for $C_{14}H_6F_8$ 326.0342, found 326.0338, error = 1 ppm; IR ($CHCl_3$, cm^{-1}): ArF, 1220; 200-MHz NMR ($CDCl_3$) δ 6.75 (2 H, dddd, J = 2.6, 6.2, 7.8, 10.4 Hz), 2.91 (4 H, s).

5,5-Dianisyl-10,11-dihydro-1,2,3,4,6,7,8,9-octafluorodibenzo[*b*,*f*]stannepin (7). A solution of 1,2-bis(2,3,4,5-tetrafluorophenyl)ethane (1.06 g, 3.3 mmol) in 10 mL of THF was added to a −78 °C solution of *n*-butyllithium (3.9 mL, 1.65 M in hexane, 6.5 mmol) in 100 mL of THF, and the resulting mixture was stirred for 90 min. A solution of freshly prepared dianisyltin dichloride[15] (1.3 g, 3.3 mmol) in 20 mL of THF was added, and the resulting mixture was warmed to room temperature and stirred overnight. The solution was then poured into water and extracted with ether (1 × 100 mL); the combined organics were dried ($MgSO_4$) and evaporated (aspirator). The resulting yellow oil was purified by chromatography (30 g of silica 60, hexane) to afford octafluorostannepin **7** (0.637 g, 30%) as a white solid: mp 161–162 °C (crystallized from EtOH); MS exact mass calcd for $C_{28}H_{18}O_2F_8Sn$ 658.0201, found 658.0214, error = 2 ppm; IR ($CHCl_3$, cm^{-1}) Ar, 1625; 200-MHz NMR ($CDCl_3$) δ 7.45 (4 H, d, J = 8.6 Hz; $J^{119}SnH$ = 57 Hz), 6.96 (4 H, d, J = 8.6 Hz), 3.8 (6 H, s), 3.13 (4 H, s).

5,5-Dichloro-10,11-dihydro-1,2,3,4,6,7,8,9-octafluorodibenzo[*b*,*f*]stannepin (8). A steady stream of hydrochloric acid was blown over a room-temperature solution of dianisylstannepin **7** (0.38 g, 0.1 mmol) in 50 mL of toluene for 90 min. The resulting solution was stirred overnight and then evaporated (aspirator) to give a solid. This solid was recrystallized from hexane to give the dichlorostannepin **8** (0.16 g, 53%): mp 129.5–130.5 °C; MS exact mass calcd for $C_{14}H_4Cl_2F_8Sn$ 513.8585, found 513.8576, error = 1.8 ppm; IR ($CHCl_3$, cm^{-1}) ArF, 1220, 1120; 200-MHz NMR ($CDCl_3$) δ 3.2 (4 H, s).

1-(Pentafluorophenyl)ethanol. Pentafluorobenzene (4.4 mL, 40 mmol, Aldrich) was added slowly to a −78 °C solution of *n*-butyllithium (25 mL, 1.61 M in hexane, 40 mmol) in 100 mL of ether. After 2 h at −78 °C a freshly made 50-mL ether solution of magnesium dibromide (1,2-dibromoethane, 3 mL, 35 mmol; Aldrich, excess magnesium) was added via cannula, and the resulting slurry was stirred 30 min. To this was added freshly distilled acetaldehyde (2.2 mL, 40 mmol), and the resulting mixture was warmed to room temperature and then poured into 10% aqueous hydrochloric acid. This two-phase system was extracted with ether (3 × 100 mL), and the combined organics

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were dried ($MgSO_4$) and evaporated (aspirator) to give 1-(pentafluorophenyl)ethanol (8.3 g, 99%) as a pale brown oil, sufficiently pure for the next step. Analytical TLC (silica gel F254), CH_2Cl_2, R_f = 0.34; IR ($CHCl_3$, cm^{-1}) OH, 3610, 3425; 200-MHz NMR ($CDCl_3$) δ 5.27 (1 H, qd, J = 6.8, 7.4 Hz), 2.49 (1 H, d, J = 7.4 Hz), 1.65 (3 H, d, J = 6.8 Hz).

***dl*-1-(2,3,4,5-Tetrafluorophenyl)ethanol (9).** Crude 1-(pentafluorophenyl)ethanol from above (15.5 g, 73 mmol) was added to a solution of lithium aluminum hydride (4 g, 0.1 mole) in 150 mL of ether. This solution was stirred at room temperature for 12 h and then was cooled to −78 °C and carefully quenched with water. The resulting slurry was stirred at room temperature with 50 mL of 10% aqueous hydrochloric acid for 2 h. The resulting clear mixture was extracted with ether (3 × 75 mL), and the combined organics were dried ($MgSO_4$) and evaporated (aspirator) to give 1-(2,3,4,5-tetrafluorophenyl)ethanol (12.8 g, 90%, contaminated by ca. 8% nondefuorinated starting material according to NMR analysis). This material was purified as described in the next step.

Resolution and Purification of *dl*-1-(2,3,4,5-Tetrafluorophenyl)ethanol (9). A solution of crude *dl*-alcohol **9** (12.8 g, 66 mmol) and 4-(dimethylamino)pyridine (50 mg, 0.4 mmol, Aldrich) in 20 mL of THF was added to a solution of dicyclohexylcarbodiimide (13.6 g, 66 mmol, Aldrich) and (+)-6-methoxy-α-methyl-2-napthaleneacetic acid (naproxen 15.2 g, 66 mmol, Aldrich) in 200 mL of THF. After being stirred for 4 h, this slurry was filtered through Celite and the filtrate was evaporated (aspirator). The resulting solid was purified by passing through a short plug of silica gel (30 g of silica 60, CH_2Cl_2) to give solid naproxen ester (22.0 g, 82%). This ester was dissolved in 600 mL of hot methanol, and the solution was cooled to room temperature. After 3–4 h the resulting crystals were collected (the filtrate was saved), and the solid was recrystallized four more times from methanol to produce pure ester (6.3 g, 47%): mp 127–128 °C; MS exact mass calcd for $C_{22}H_{18}O_3F_4$ 406.1191, found 406.1203, error = 2.9 ppm; IR (KBr, cm^{-1}) C=O, 1740; Ar, 1610; 200-MHz NMR (CDC_3) δ 7.72–7.59 (3 H, m), 7.32–7.13 (3 H, m), 6.35 (1 H, dddd, J = 2.5, 6, 8.5, 10.5 Hz), 6.02 (1 H, q, J = 6.6 Hz), 3.92 (3 H, s), 3.89 (1 H, q, J = 7.1 Hz), 1.57 (3 H, d, J = 7.1 Hz), 1.42 (3 H, d, J = 6.6 Hz). The saved filtrate was concentrated to 400 mL and cooled to room temperature. The resulting crystals were collected (the filtrate saved) and were recrystallized four more times from methanol to give the diastereomeric ester (1.6 g, 12%). The saved filtrate was concentrated to 200 mL, and the resulting solids were collected. Recrystallization of these solids four more times from methanol gave a second crop of diastereomeric ester (1.3 g, 22% total): mp 101–102 °C (crystallized from MeOH); MS exact mass calcd for $C_{22}H_{18}O_3F_4$ 406.1191, found 406.1177, error = 3.5 ppm; IR (KBr, cm^{-1}) C=O, 1730; 200-MHz NMR ($CDCl_3$) δ 7.74–7.13 (6 H, m), 6.85 (1 H, dddd, J = 2.6, 6, 8, 10.5 Hz), 6.03 (1 H, q, J = 6.7 Hz), 3.92 (3 H, s), 3.88 (1 H, q, J = 7.1 Hz), 1.58 (3 H, d, J = 7.2 Hz), 1.40 (3 H, d, J = 6.6 Hz).

The higher melting naproxen ester (7.6 g, 19 mmol) in 100 mL of THF was added to a 100-mL water solution of lithium hydroxide (1.4 g, 62 mmol). This mixture was stirred at room temperature for 12 h. The layers were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The combined organics were dried ($MgSO_4$) and evaporated (aspirator) to give (−)-alcohol **9** (3.7 g, 98%) as an oil: analytical TLC (silica gel F254), CH_2Cl_2, R_f = 0.41; $[\alpha]^{25}_D$ −26.6° (c = 2.3, $CHCl_3$); MS exact mass calcd for $C_8H_6OF_4$ 194.0355, found 194.0355, error = 0.2 ppm; IR ($CDCl_3$, cm^{-1}) OH, 3610; 200-MHz NMR ($CDCl_3$) δ 7.05 (1 H, dddd, J = 2.6, 6.1, 8.2, 10.7 Hz), 5.08 (1 H, q, J = 6.4 Hz), 2.45 (1 H, br s), 1.39 (3 H, d, J = 6.4 Hz).

***meso*- and *dl*-2,3-Bis(2,3,4,5-tetrafluorophenyl)butane (11 and 10).** 1-(2,3,4,5-Tetrafluorophenyl)ethanol (**9**) (97 mg, 0.5 mmol, containing 8% of the pentafluorophenyl derivative) was added to a slurry of McMurry reagent[10] (4:1 $TiCl_3$/LAH, 0.6 g, 0.9 mmol, Aldrich) in 50 mL of dimethoxymethane, and this mixture was heated to reflux overnight. After being cooled to room temperature, the slurry was carefully quenched with 10% hydrochloric acid and then extracted with methylene chloride (2 × 50 mL). The combined organics were dried ($MgSO_4$) and evaporated (aspirator), and the resulting oil was passed through a plug of silica gel 60 (7 g) with hexane. Further purification by HPLC (hexane, 6 mL/min, 5-mg injection, retention time *meso*, 7.8 min; *rac*, 10.3 min) gave *meso*-2,3-bis(2,3,4,5-tetrafluorophenyl)butane (**11**) (10mg, 11%) [analytical TLC (silica gel F254), hexane, R_f = 0.40; MS exact mass calcd for $C_{16}H_{10}F_8$ 354.0654, found 354.0637, error = 4.9 ppm; 200-MHz NMR ($CDCl_3$) δ 6.86 (2 H, dddd, J = 2.5, 6, 7.5, 11.5 Hz), 3.26–3.11 (2 H, m), 1.07 (6 H, d, J = 6.5 Hz)] and *dl*-**10** (10 mg, 11%): analytical TLC (silica gel F254), hexane, R_f = 0.33; IR ($CHCl_3$, cm^{-1}) Ar, 1630; 200-MHz NMR ($CDCl_3$) δ 6.70 (2 H, dddd, J = 2.5, 6, 7.5, 11 Hz), 3.31–3.23 (2 H, m), 1.33 (6 H, d, J = 6.5 Hz).

Phenyl 2,3,4,5-Tetrafluorobenzyl Sulfone (15). Methanesulfonyl chloride (2.5 mL, 33 mmol, Aldrich, distilled from P_2O_5) was added to a 0 °C solution of 2,3,4,5-tetrafluorobenzyl alcohol (**14**)[9] (5 g, 30 mmol) and triethylamine (6.3 mL, 45 mmol, distilled from CaH_2) in 50 mL of methylene chloride. After being stirred 15 min the solution was warmed to room temperature and then poured into water. The layers were separated, and the aqueous phase was extracted with methylene chloride (2 × 50 mL). The combined organics were dried ($MgSO_4$) and evaporated (aspirator), and the resulting oil was passed through a short plug of silica gel (5 g of silica 60, methylene cloride). The mesylate was dissolved in 20 mL of ethanol and added to a 300-mL ethanol solution of sodium thiophenoxide (from 0.68 g, 31 mmol of sodium; and 3.2 mL, 31 mmol thiophenol). The resulting slurry was stirred for 4 h, and then monoperoxyphthalic acid, magnesium salt hexahydrate (30 g, 60 mmol, Aldrich) was added slowly over 15 min. After being stirred for 1 h, this thick slurry was diluted 2-fold with water and then extracted with methylene chloride (2 × 200 mL). The combined organics were washed with 50 mL of saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated (aspirator). The resulting solid was dissolved in 100 mL hot chloroform to give upon cooling phenyl 2,3,4,5-tetrafluorobenzyl sulfone (**15**) (4.8 g, 53%) as a solid: mp 190–191 °C; MS exact mass calcd for $C_{13}H_8O_2F_4S$ 304.0181, found 304.0178, error = 1 ppm; IR (KBr, cm^{-1}) SO_2, 1450; 200-MHz NMR ($CDCl_3$) δ 7.77–7.50 (5 H, m), 7.03 (1 H, dddd, J = 2.6, 6, 7.4, 10.1 Hz), 4.34 (2 H, s).

Phenyl 1,2-Bis(tetrafluorophenyl)-1-propyl Sulfone (16). Methanesulfonyl chloride (1.1 g, 14 mmol, Aldrich, distilled from P_2O_5) was added to a 0 °C solution of (−)-1-(2,3,4,5-tetrafluorophenyl)ethanol (**9**) (2.45 g, 12.6 mmol) and triethylamine (2.6 mL, 19 mmol, distilled from CaH_2) in 50 mL of methylene chloride. After 15 min this mixture was warmed to room temperature and poured into 25 mL of aqueous saturated sodium bicarbonate. The layers were separated, the aqueous phase was extracted with methylene chloride (2 × 50 mL), and the combined organics were dried ($MgSO_4$) and evaporated (aspirator). The resulting oil was purified by passing through a short plug of silica gel (7 g silica 60, CH_2Cl_2) to give crude mesylate **13** as a clear oil.

n-Butyllithium (7.2 mL, 1.68 M in hexane, 12 mmol) was then added to a 0 °C slurry of phenyl 2,3,4,5-tetrafluorobenzyl sulfone (**15**) (3.7 g, 12 mmol) in 100 mL of ether. To the resulting clear red anion solution was added a 25-mL ether solution of mesylate **13**. After 3 h at 0 °C the resulting slurry was poured into 50 mL of water and extracted with ether (2 X 75 mL). The combined organics were dried ($MgSO_4$) and evaporated (aspirator). The resulting solid was purified by chromatography (100 g of silica 60, 10% ether/hexane) to give sulfone **16** (4.5 g, 74%) as a 2:1 mixture of diastereomers. Both sulfones were taken on to the next step without further purification. For characterization, the major diastereomer was recrystallized from methanol: mp 153–154 °C; MS M − 141 (loss of $PhSO_2$) 340.0495, calcd 340.0498, error = 0.9 ppm, formula $C_{21}H_{12}O_2F_8S$; analytical TLC (silica gel F254) R_f = 0.28, 10% ether/hexane; IR (KBr, cm^{-1}) SO_2, 1320; Ar, 1640; 200-MHz NMR ($CDCl_3$) δ 8.7–7.4 (6 H, m), 6.85 (1 H, dddd, J = 2.5, 6, 8, 11 Hz), 5.05 (1 H, d, J = 9.5 Hz), 3.9 (1 H, dq, J = 7, 9.5 Hz), 1.2 (3 H, d, J = 7 Hz). Minor diastereomer: oil; analytical TLC (silica gel F254) R_f = 0.17, 10% ether/hexane; 200-MHz NMR ($CDCl_3$) δ 7.7–7.4 (5 H, m), 7.25–7.1 (1 H, m), 6.74 (1 H, dddd, J = 2.5, 6, 8, 10 Hz), 4.83 (1 H, d, J = 11 Hz), 4.16 (1 H, dq, J = 6.5, 11 Hz), 1.8 (3 H, d, J = 6.5 Hz). In a separate experiment to assay enantiomeric purity, the (+)-1-(2,3,4,5-tetrafluorophenyl)ethanol was taken through the same sequence to the major sulfone diastereomer. Thus, (+)-(tetrafluorophenyl)ethanol with $[\alpha]^{25}_D$ +28° (c = 2.3, $CHCl_3$) gave sulfone with $[\alpha]^{25}_D$ −40° (c = 0.77, $CHCl_3$). Addition of chiral

shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium (III) resolved the doublet at 1.2 ppm and showed that this sulfone was a 95:5 mixture of enantiomers, 90% ee through the coupling step.

1,2-Bis(2,3,4,5-tetrafluorophenyl)propane (12). W-2 Raney nickel (ca. 6 g, slurry in ethanol) was added to a slurry of (+) sulfone diastereomers **16** (0.82 g, 1.7 mmol) in 50 mL of dry ethanol. The resulting mixture was heated to reflux for 4 h and then cooled to room temperature and poured onto a large pad of Celite in a fritted funnel. This slurry was covered with another 2 cm of Celite, vacuum filtered, and washed with several portions of methylene chloride. (**Caution**: do not allow nickel catalyst to go dry!). The filtrate was evaporated and purified by passing through a short plug of silica gel (7 g of silica 60, hexane) to give (+)-1,2-bis(2,3,4,5-tetrafluorophenyl)propane (**12**) (0.56 g, 96%): $[\alpha]^{25}_D$ +58° (c = 1.7, $CHCl_3$); oil; analytical TLC (silica gel F254), hexane, R_f = 0.37; MS exact mass calcd for $C_{15}H_8F_8$ 340.0498, found 340.0497, error = 0.3 ppm; IR ($CHCl_3$, cm^{-1}) Ar, 1635; 200-MHz NMR ($CDCl_3$) δ 6.81 (1 H, dddd, J = 2.4, 6, 8.2, 10.4 Hz), 6.67 (1 H, dddd, J = 2.7, 6, 8.5, 10.1 Hz), 3.36 (1 H, sextet, J = 7.3 Hz), 2.87 (2 H, dd, J = 0.8, 7.6 Hz), 1.29 (3 H, d, J = 7.0 Hz).

Dianisyltin Dichloride. Freshly distilled (from P_2O_5) tin(IV) chloride (0.13 mL, 1.1 mmol) was added to freshly prepared tetraanisyltin (0.6 g, 1.1 mmol)[15a] and slowly heated neat to 150 °C over ca. 20 min. This temperature was maintained for another 2 h, the oil bath was removed, and the flask was cooled to room temperature. The resulting off-white solid (a deep red color indicated a failed reaction) was dissolved in 50 mL of hot hexane and filtered hot. The filtrate was then cooled to give dianisyltin dichloride[15b,c] (0.68 g, 76%): solid; mp 84–85 °C (lit.[15c] mp 75.5–76.5 °C).

(−)-5,5-Dianisyl-10-methyl-10,11-dihydro-1,2,3,4,6,7,8,9-octafluorodibenzo[*b,f*]stannepin (17). A solution of (+)-1,2-bis(tetrafluorophenyl)propane (**12**) (1.1 g, 3.2 mmol) in 20 mL of THF was added via cannula to a −78 °C solution of n-butyllithium (3.85 mL, 1.68 M in hexane, 6.5 mmol) in 50 mL of THF. After 5 min, a solution of freshly prepared dianisyltin dichloride[15] (1.3 g, 3.2 mmol) in 20 mL of THF was added slowly over 5 min via cannula. The solution was then warmed to room temperature for 30 min, poured into 30 mL water, and extracted with ether (2 × 100 mL). The combined organics were dried ($MgSO_4$) and evaporated (aspirator). The resulting glass was purified by passing through a short plug of silica (7 g silica 60, 1:1 hexane/CH_2Cl_2) to give (−)-dianisylstannepin **17** (1.8 g, 83%) as a solid: mp 145–146.5 °C; $[\alpha]^{25}_D$ −64% (c = 3.0, $CHCl_3$); analytical TLC (silica gel F254), 20% ether/hexane, R_f = 0.43; MS exact mass calcd for $C_{29}H_{20}O_2F_8Sn$ 672.0357, found 672.0362, error = 0.7 ppm; IR (KBr, cm^{-1}) Ar, 1630, 1590; 200-MHz NMR ($CDCl_3$) δ 7.48 (2 H, d, J = 8.5 Hz; J^{119}SnH = 55 Hz), 7.42 (2 H, d, J = 8.5 Hz; J^{119}SnH = 55 Hz), 7.0 (2 H, d, J = 8.5 Hz), 6.95 (2 H, d, J = 8.5 Hz), 4.15–3.95 (1 H, m), 3.8–3.7 (1 H, m), 3.81 (3 H, s), 3.8 (3 H, s), 2.8 (1 H, br d, J = 15.5 Hz), 1.05 (3 H, d, J = 7.5 Hz).

(−)-5,5-Dichloro-10-methyl-11-hydro-1,2,3,4,6,7,8,9-octafluorodibenzo[*b,f*]stannepin (18). Gaseous HCl was gently bubbled for 15 min into a solution of (−)-dianisylstannepin **17** (0.67 g, 1 mmol) in 100 mL of toluene. This solution was stirred for 1 h and then resubjected to gaseous HCl for 15 min. After the mixture was stirred for another hour, this HCl treatment cycle was repeated for a total of 5 h. The toluene was then evaporated (aspirator), and the resulting brown oil was dissolved in 50 mL hexane and filtered. Evaporation of the hexane (aspirator) gave (−)-**18** (0.44 g, 83%): mp 129–132 °C (recrystallized from hexane); $[\alpha]^{25}_D$ −74° (c = 0.66, $CHCl_3$); MS exact mass calcd for $C_{15}H_6Cl_2F_8Sn$ 527.8742, found 527.8728, error = 2.5 ppm; IR (KBr, cm^{-1}) Ar, 1630, 1605; 200-MHz NMR ($CDCl_3$) δ 4.25–4.0 (1 H, m), 3.9 (1 H, br dd, J = 11.0, 16.3 Hz), 2.81 (1 H, br d, J = 16.3 Hz), 1.03 (3 H, d, J = 7.3 Hz).

5,5-Dianisyl-10,11-dimethyl-10,11-dihydro-1,2,3,4,6,7,8,9-octafluorodibenzo[*b,f*]stannepin (19). n-Butyllithium (0.22 mL, 1.61 M in hexane, 0.4 mmol) was added to a −78 °C solution of 1,2-bis(tetrafluorophenyl)butane (**9**) (62 mg, 0.2 mmol) in 25 mL of THF. After 5 min, a 20-mL THF solution of freshly prepared dianisyltin dichloride (70 mg, 0.2 mmol) was added via cannula. The resulting solution was warmed to room temperature for 30 min, poured into 30 mL of water, and extracted with ether (2 × 100 mL). The combined organics were dried ($MgSO_4$) and evaporated (aspirator). The resulting oil was further purified by chromatography on silica gel to give **19** (58 mg, 48%) as an oil: analytical TLC (silica gel F254), 20% ether/hexane, R_f = 0.51; MS exact mass calcd for $C_{30}H_{22}O_2F_8Sn$ 686.0514, found 686.0566, error = 7.6 ppm; IR ($CDCl_3$, cm^{-1}) Ar, 1630, 1590; 200-MHz NMR ($CDCl_3$) δ 7.37 (4 H, d, J = 8 Hz; J^{119}SnH = 57.5 Hz), 6.88 (4 H, d, J = 8 Hz), 4.15–4.0 (2 H, m), 3.73 (6 H, s), 1.10 (6 H, br d, J = 5.5 Hz).

Acknowledgment. This work was supported by the National Institutes of Health (CA17918).

Supplementary Material Available: ^{1}H NMR spectra (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.