is the pyramidality of the nitrogen(s), clearly disposing the methyl groups to axial and equatorial positions. We assume the nitrogen(s) are more nearly trigonal in 2 by analogy to most phosphonamides, phosphoramides, and groups to axial and equatorial positions. We assume the nitrogens in 2-0~0-1,3,2-oxazaphosphorinanes unconstrained by small rings.

These structural insights are valuable for the understanding of bonding in these systems and for the rational design of chiral adjuvants. Further studies on the structure and reactivity of P-stabilized anions are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. S.E.D. acknowledges the A. P. Sloan foundation for a Fellowship (1985–1989). We are also grateful to the National Science Foundation (Presidential Young Investigator Award, NSF CHE-8451321) for support. Dr. Scott R. Wilson and Charlotte Stern are thanked for their help with the X-ray structure analysis.

Supplementary Material Available: A listing of crystal and positional parameters, bond lengths, bond angles, and torsional angles for [Li+2-*2THFl2 (24 pages). Ordering information is given on any current masthead page.

Table I. Aldol Reactions of 1 with Representative Aldehydes (Scheme 1)

<table>
<thead>
<tr>
<th>enolatant</th>
<th>RCHO</th>
<th>yield, (%)</th>
<th>ratio 2:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(OTf)2, Et3N</td>
<td>MeCHO</td>
<td>83</td>
<td>95:5</td>
</tr>
<tr>
<td>Sn(OTf)2, Et3N</td>
<td>Me-CHO</td>
<td>&gt;99</td>
<td>&lt;1:99</td>
</tr>
<tr>
<td>Sn(OTf)2, Et3N</td>
<td>Me-CHO</td>
<td>&gt;99</td>
<td>&gt;95:5</td>
</tr>
<tr>
<td>Sn(OTf)2, Et3N</td>
<td>Me-CHO</td>
<td>&gt;99</td>
<td>2:98:3</td>
</tr>
<tr>
<td>Sn(OTf)2, Et3N</td>
<td>Me-CHO</td>
<td>&gt;99</td>
<td>1:99:2:3</td>
</tr>
<tr>
<td>Sn(OTf)2, Et3N</td>
<td>Me-CHO</td>
<td>&gt;99</td>
<td>85:91:11</td>
</tr>
</tbody>
</table>

Notes:

4 Unless noted, 1-1.1 equiv of aldehyde was employed in the reaction.

5 Isolated yield of major diastereomer of >99% purity. Ratios determined by HPLC. Yield obtained by using 3-5 equiv of RCHO.


6 (a) Johnson, F. Chem. Rev. 1968, 68, 375–413.

observed that the Z trichlorotitanium enolate derived from 1 provided exceptional levels of asymmetric induction in the aldol addition to give the all-syn adduct 3. During the course of this study, a highly effective method for the direct generation of these trichlorotitanium enolates was also developed.

In both the Sn(II) and Ti(IV) aldol reactions, ideal 1:1 stoichiometry between enolate and aldehyde can be maintained. Improved yields were noted when excess aldehyde (3–5 equiv) was employed in the aldol reactions of α-methacrolein where competitive aldehyde polymerization was found to be a problem.

Control experiments indicated that the stereochemical outcome of both reactions is dominated by the C3 methyl-bearing stereocenter, with the chirality of the oxazolidone auxiliary playing a subordinate but supporting role. For example, in the aldol addition reactions of the two metal enolates derived from 1 and 2, asymmetric induction was unaltered but the diastereoselection of the enantiomeric chiral auxiliary [4(R)-Bn], the overall sense of chirality transfer is available, the diastereomeric transition states for both Sn(II) and Ti(IV) enolates diminished to 81:19 and 7:93, respectively. Although little concrete information on the details of chirality transfer is available, the diastereomeric transition states depicted in Scheme II are consistent with the observed stereochemical outcome of the reactions.

The aldol adducts 2 and 3 were treated with a variety of reducing agents in order to examine the degree of internal direction in the reduction of the C3 carbonyl function. As shown in Scheme III, either anti or syn 1,3-diol relationships can be obtained from 2 in >20:1 selectivity when reductions are carried out with trichloro(ethylene)borohydride (11) or DBHAl, respectively. Selective syn reduction was also performed on aldol adduct 3, to afford diol 6 with high selectivity.

The combined aldol-reduction sequence described above represents a laboratory analogue of the enzymatic acylation and reduction events that occur in polypropionate biosynthesis and should therefore provide a general tool for the efficient construction of complex polypropionate-derived natural products. For example, as shown in eqs 1 and 2, the use of two iterative Sn(II) aldol reactions facilitates the rapid stereocontrolled assembly of 9b, corresponding to the C1-C13 portion of the polyether antibiotic lonomycin A.

The details of these investigations, as well as the application of this method to the asymmetric total synthesis of natural products, will be reported in due course.

(6) The following metal triflates were examined: manganese triflate, dimethyldistannic triflate, dibutylboron triflate, dicyclopentadienylboron triflate, and 9-BBN triflate. We have noted that boron triflates used in conjunction with tertiary amines provide aldol adducts that are identical with those obtained by using titanium tetrachloride and disopropylethylamine, but in yields and selectivities lower than those obtained with the procedure presented here.

(7) General titanium tetrachloride mediated aldol procedure: The 8-keto imide 1 was dissolved in dry CH2C12 (0.25 M) under N2, and the solution is cooled to –10 °C, tiCl4 (1.1 equiv) is added dropwise. The reaction mixture is stirred at –10 °C for 1 h. The enolate solution is then cooled to –78 °C, and freshly distilled aldehyde (1.1 equiv) is added dropwise. The reaction mixture is stirred at –78 °C for 30 min and then allowed to come to –40 °C over a 1-h period. Upon warming to 0 °C, the reaction is quenched by the addition of pH 7 buffer (1.6 mL/mmol). After stirring for an additional 5 min at 0 °C, the solution is transferred into CH2C12 and the product is isolated as described above (footnote 5) for the analogous Sn(II) enolate reactions.

(8) The trichlorotitanium enolate derived from 1 may be generated by precomplexing 1.1 equiv of TiCl4 with 1 (–10 °C, CH2C12) followed by enolization with disopropylethylamine. This enolization protocol was based upon related experiments reported by Harrison: Harrison, C. R. Tetrahedron Lett. 1987, 28, 4135–4138. The generality of this reaction for other substrates will be reported shortly.

(9) Oxazolidinone auxiliaries derived from (S)-valine and (1S,2R)-norephedrine, as well as the parent unsubstituted case, have also been examined, and similar results in reaction diastereoselection have also been observed with these systems.
Metal complexes have played central roles in the initiation and propagation of many important polymerization reactions. Studies of the reactions of metal carbonyl cluster complexes with epoxides have shown sulfur transfer and alkene elimination to be the preferred reaction pathway (e.g., eq 1). Although thirane, C₅H₆S₂, is able to serve as a ligand through coordination of the sulfur atom, very little is known about the nature of the ring opening and eventual elimination of alkene in these reactions. The desulfurization of thirane on a clean molybdenum (110) surface is believed to occur by an intramolecular elimination of ethylene without the formation of a thiolate intermediate. We have now investigated the reactions of Os₆(CO)₁₆(NCMe)S with 19 mg (0.03 mmol) of (CH₂)₄S₆ in 50 mL of CH₂Cl₂ solvent at reflux for 50 min. From this mixture, we have isolated by TLC 4.6 mg of the known compound Os₆(CO)₁₆(μ₄-S)(S)₃, 13% yield; and 1.8 mg of the new compound Os₆(CO)₁₆(μ₄-S(CH₂CH₂S)₃)(S)₄, 26% yield.  

Figure 1. An ORTEP diagram of Os₆(CO)₁₆(μ₄-S(CH₂CH₂S)₃)(S)₄ (4) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are Os(1)-Os(3) = 2.872 (2), Os(1)-Os(5) = 2.880 (2), Os(2)-Os(6) = 2.814 (2), Os(3)-Os(4) = 2.778 (2), Os(3)-Os(5) = 2.725 (2), Os(3)-Os(6) = 2.897 (2), Os(4)-Os(5) = 2.862, Os(5)-Os(6) = 2.894 (2), Os(1)-S(1) = 2.380 (7), Os(2)-S(1) = 2.355 (7), Os(2)-S(2) = 2.389 (7), Os(6)-S(1) = 2.324 (7), Os(6)-S(2) = 2.401 (7).

Figure 2. An ORTEP drawing of Os₆(CO)₁₆(μ₄-S(CH₂CH₂S)₃)(S)₄ (7) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are Os(1)-Os(2) = 2.728 (2), Os(1)-Os(3) = 2.870 (2), Os(2)-Os(3) = 2.767 (1), Os(2)-Os(4) = 2.820 (1), Os(2)-Os(6) = 2.587 (2), Os(3)-Os(4) = 2.980 (2), Os(4)-Os(6) = 2.977 (1), Os(5)-Os(6) = 2.930 (1), Os(5)-S(1) = 2.404 (6), Os(5)-S(2) = 2.432 (6), Os(5)-S(4) = 2.424 (6).

Compound 4 was characterized by IR, ¹H NMR, and single-crystal X-ray diffraction analysis. An ORTEP drawing of 4 is shown in Figure 1. Four of the six molybdenum atoms, Os(3), Os(4), Os(5), and Os(6), are arranged in the shape of a closed tetrahedron. The Os(3)-Os(5) edge of this group is bridged by an Os(CO)₃ group, Os(1), and a second Os(CO)₃ group, Os(2), is bonded to the cluster at Os(6). An ethanedithiolate group bridges the reactions of metal carbonyl cluster complexes with epoxides have shown sulfur transfer and alkene elimination to be the preferred reaction pathway (e.g., eq 1). Although thirane, C₅H₆S₂, is able to serve as a ligand through coordination of the sulfur atom, very little is known about the nature of the ring opening and eventual elimination of alkene in these reactions. The desulfurization of thirane on a clean molybdenum (110) surface is believed to occur by an intramolecular elimination of ethylene without the formation of a thiolate intermediate. We have now investigated the reactions of Os₆(CO)₁₆(NCMe)S with 19 mg (0.03 mmol) of (CH₂)₄S₆ in 50 mL of CH₂Cl₂ solvent at reflux for 50 min. From this mixture, we have isolated by TLC 4.6 mg of the known compound Os₆(CO)₁₆(μ₄-S)(S)₃, 13% yield; and 1.8 mg of the new compound Os₆(CO)₁₆(μ₄-S(CH₂CH₂S)₃)(S)₄, 26% yield.


(6) Thirane was purified by distillation before use and was shown to be pure by ¹H NMR spectroscopy.


(8) Compound 4 was isolated by TLC on silica gel by elution with a hexane/CH₂Cl₂ 3/1 solvent mixture. For 4; IR (ν(CO) cm⁻¹ in CH₂Cl₂) 2100 (w), 2081 (m), 2067 (v), 2024 (s, br); ¹H NMR (in CD₂CN) 3.26 (s, br). Significant elemental analyses for C and H have been obtained.