Enantioselective Allyltitanation of Aldehydes with Cyclopentadienyldialkoxyallyltitanium Complexes[1]

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Abstract: The preparation, analysis, and reactions of novel, highly stereoselective cyclopentadienyldialkoxyallyltitanium reagents, available in both enantiomeric forms, are described. Chiral monochlorotitanates are readily prepared from $CpTiCl_3$ or Cp^*TiCl_3 and chiral 1,4-diols, which in turn are obtained from tartrate ester acetals by Grignard addition. The resulting stable seven-membered titanacycles have been analyzed by ^1H, ^{13}C, and ^{49}Ti NMR spectroscopy. The structures of two representatives, the complexes **15** and **20**, are confirmed by X-ray diffraction. The allyl reagents are obtained from the chlorides by transmetalation with allyllithium, allylpotassium, or allyl Grignard compounds. For the ensuing reactions with aldehydes these reagents do not have to be isolated or purified. Correlation of X-ray data and Ti NMR line widths with selectivity suggests that asymmetric distortion of the titanium coordination geometry could be essential for enantioface discrimination, rather than direct interactions of reactants with the chiral ligand. By variation of the ligand substituents, allyltitanates derived from chloride **15** (with 2,2-dimethyl-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,3-dioxolane-3,4-dimethanol as the ligand) emerged as the most selective reagents. Excellent regio-, diastereo-, and enantioselectivities (usually ≥95% ee, ≥95% de) are obtained for reactions with various achiral and chiral aldehydes. The NMR spectra of the allyl and the crotyl complexes (*R,R*)-**9** and (*R,R*)-**29** exhibit fast 1,3-shifts, favoring the (*E*) isomer with titanium η^1-bound to the unsubstituted allyl terminus. This equilibration, and also the equilibrations of other aryl-, alkoxy-, and silyl-substituted allyltitanium complexes, restricts this method to the preparation of branched regioisomers with the anti configuration.

Introduction

The asymmetric C–C bond formation is a very attractive synthetic strategy, as the connectivity of a carbon framework and its stereochemistry are established simultaneously. The allylmetalation of aldehydes and ketones, leading to products with a maximum of two new stereocenters and versatile functionality for further transformations, is an important example for acyclic stereocontrol.[4] While a lot of work has been devoted to the development of efficient chiral allylboron reagents,[5] impressive results have been obtained with allylstannanes[6] and allylsilanes[7] as well, especially when the chirality is transferred from the allyl moiety.[4f,8] High enantioface differentiation by a stereogenic metal center has recently been achieved with an η^3-crotyl molybdenum complex.[9] Improvements are, however, still possible because some of these reagents are touchy and tedious to prepare or low solubility, slow reaction rates, and sophisticated chiral auxiliaries hamper large-scale applications. Despite good results with simple aldehydes, the stereodifferentiation is often inadequate in the case of more complex, especially chiral, substrates.

Organotitanium reagents, propagated mainly by Seebach[10] and Reetz,[11] opened new perspectives for chemo-, regio-, and stereoselectivity, as their structural variability allows the necessary adjustment of reactivity. The abundance of titanium, its low toxicity, the ease of transmetalation with organolithium or Grignard compounds, and the enhanced stability are further advantages of organotitanium chemistry. While crotyltitanium compounds emerged as highly diastereoselective reagents,[12] even for unsymmetrical ketones,[12h,13] and high asymmetric induction could be obtained with chiral allyl groups,[14] the enantiofacial differentiation of allyltitanium reagents with chiral alkoxy[15] or bis-cyclopentadienyl ligands[16] is astonishingly low, not exceeding 60% ee.[15c]

The key factor for the first successful enantioselective allyltitanium reagent, complex **1**, which we described a couple of years ago,[3a,17] is a *single cyclopentadienyl ligand*, providing a stable steric arrangement and the appropriate reactivity. A major drawback is, however, that the chiral inductor, diacetone glucose **2**, is readily available in the D form only, thus restricting the enantioface discrimination to the *re* side attack. Therefore, we prepared a variety of such chiral cyclopentadienyldialkoxytitanium(IV) complexes and screened them for enantioselective allyltitanation of benzaldehyde **3** (→ **4**, Scheme I). In most cases a diminished stereoselectivity resulted, however, even from seemingly minor

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(1) Part 7 of Enantioselective Syntheses with Titanium Carbohydrate Complexes; Part 6; ref 2. This work has been partly published in preliminary form[3] and was presented in part at the Fifth IUPAC Symposium on Organometallic Chemistry directed towards Organic Synthesis (OMCOS V), October 1–6, 1989, in Florence, Italy, as well as at the Third Symposium on Organic Synthesis via Organometallics, July 11–14, 1990, in Marburg, Germany.

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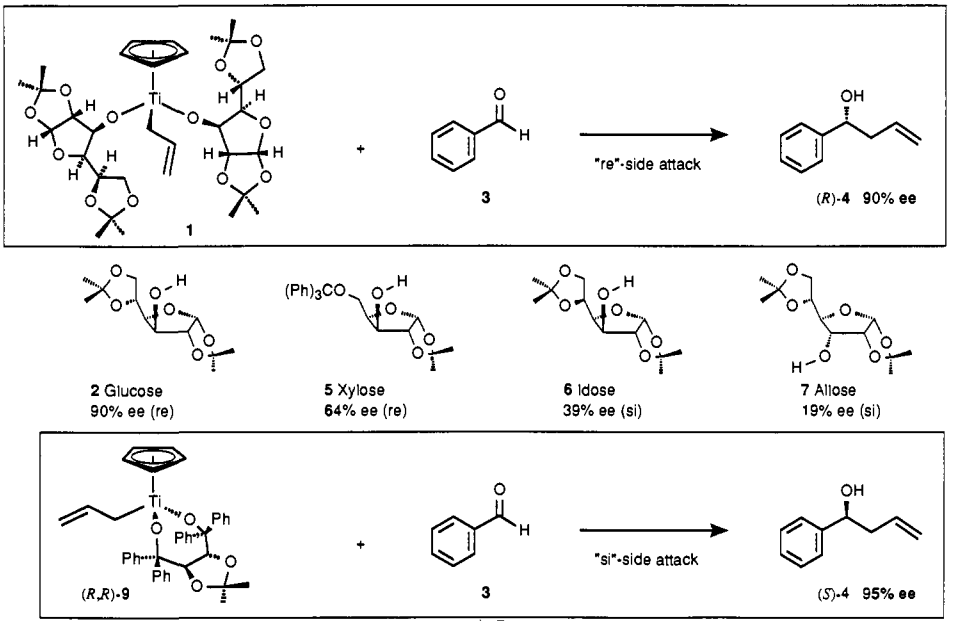
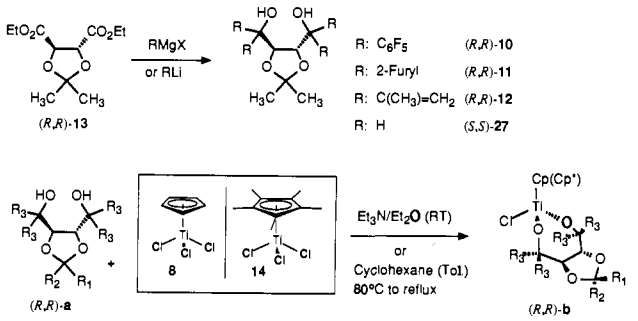
Scheme I



Scheme II. Synthesis of Ligands and Titanium Complexes



List of Cp(Cp*)Ti-Complexes b:

R_1/R_2: CH_3				R_3	C_6H_5	
R_3:	C_6H_5	15 (Cp)	16 (Cp*)	R_1R_2	H	22
R_3:	C_6F_5	17		R_1R_2	H, *t*-Bu	23/24[a]
R_3:	2-Furyl	18		R_1R_2	C_6H_6	25
R_3:	$C(CH_3)=CH_2$	19		R_1R_2	*spiro*-19H]-fluorene	26
R_3:	CH_3	20 (Cp)	21(Cp*)	(a)	4 : 1 ratio of diastereomers	

modifications like replacing diacetone glucose **2** by the xylose acetonide **5**, diacetone idose **6**,[18,19] or diacetone allose **7**. Besides monohydric alkoxy ligands, chiral chelating ligands were also considered, especially those which have already been established

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Table I. Selected Bond Lengths, Bond Angles, and Torsion Angles of Structures **28**, (*R,R*)-**20**, and (*R,R*)-**15** (X-ray Analysis)

28		(*R,R*)-**20**		(*R,R*)-**15**	
		Bond Lengths (pm)			
Ti(1)–Cp^{center}	201.3 (9)	Ti(1)–Cp^{center}	205.0 (1.0)	Ti(1)–Cp^{center}	207.0 (1.0)
Ti(1)–Cl(2)	228.8 (5)	Ti(1)–Cl(2)	229.8 (3)	Ti(1)–Cl(2)	228.4 (3)
Ti(1)–O(8)	180.9 (8)	Ti(1)–O(4)	175.7 (9)	Ti(1)–O(4)	178.3 (6)
Ti(1)–O(26)	178.6 (8)	Ti(1)–O(3)	177.8 (8)	Ti(1)–O(3)	178.8 (1.0)
O(8)–C(9)	143.0 (1.0)	O(4)–C(10)	144.0 (1.0)	O(4)–C(10)	142.0 (1.0)
O(26)–C(27)	141.0 (2.0)	O(3)–C(7)	140.0 (2.0)	O(3)–C(7)	145.0 (1.0)
		Bond Angles (deg)			
O(8)–Ti(1)–Cl(2)	102.0 (4)	O(4)–Ti(1)–Cl(2)	104.1 (4)	O(4)–Ti(1)–Cl(2)	101.6 (2)
O(26)–Ti(1)–Cl(2)	101.3 (3)	O(3)–Ti(1)–Cl(2)	104.0 (3)	O(3)–Ti(1)–Cl(2)	103.0 (2)
Ti(1)–O(8)–C(9)	**145.8 (8)**	Ti(1)–O(4)–C(10)	**148.6 (7)**	Ti(1)–O(4)–C(10)	**155.2 (6)**
Ti(1)–O(26)–C(27)	**153.1 (9)**	Ti(1)–O(3)–C(7)	**148.3 (8)**	Ti(1)–O(3)–C(7)	**145.0 (6)**
O(8)–Ti(1)–O(26)	104.0 (4)	O(4)–Ti(1)–O(3)	97.9 (4)	O(4)–Ti(1)–O(3)	98.4 (3)
O(8)–Ti(1)–Cp^{center}	117.0 (1.0)	O(4)–Ti(1)–Cp^{center}	117.0 (5)	O(4)–Ti(1)–Cp^{center}	120.0 (1.0)
O(26)–Ti(1)–Cp^{center}	118.0 (1.0)	O(3)–Ti(1)–Cp^{center}	118.9 (5)	O(3)–Ti(1)–Cp^{center}	118.0 (1.0)
		Cl(2)–Ti(1)→C(11)[a]	123.3 (5)	Cl(2)–Ti(1)→C(11)[a]	103.4 (5)
		Torsion Angles (deg)			
Cl(2)–Ti(1)–O(8)–C(9)	+115.0 (2.0)	Cl(2)–Ti(1)–O(4)–C(10)	−125.7 (1.4)	Cl(2)–Ti(1)–O(4)–C(10)	−124.6 (1.3)
Cl(2)–Ti(1)–O(26)–C(27)	−124.0 (2.0)	Cl(2)–Ti(1)–O(3)–C(7)	+136.5 (1.4)	Cl(2)–Ti(1)–O(3)–C(7)	+103.0 (1.0)
O(8)–Ti(1)–O(26)–C(27)	+130.0 (2.0)	O(4)–Ti(1)–O(3)–C(7)	+29.8 (1.5)	O(4)–Ti(1)–O(3)–C(7)	−1.0 (1.1)
O(26)–Ti(1)–O(8)–C(9)	−140.0 (2.0)	O(3)–Ti(1)–O(4)–C(10)	−19.1 (1.4)	O(3)–Ti(1)–O(4)–C(10)	−19.3 (1.4)

[a] C(2) of the dioxolane ring (acetonide).

as titanium ligands. While *exo,exo*-camphane-2,3-diol[20] and β-binaphthol[21] gave intractable mixtures upon reaction with $CpTiCl_3$ (**8**) and the corresponding poor performance as reagents, we were pleased to find that complex **9** with a tartrate-derived ligand[15,22] is the complementary reagent to **1**, as (*R,R*)-**9**, obtained from natural tartaric acid, transfers allyl groups with very high *si* face selectivity to aldehydes (Scheme I).

Preparation and Analysis of Titanium Complexes

Preparation of Chlorotitanates. The C_2-symmetric ligand used for the preparation of the chiral reagent (*R,R*)-**9** (Scheme I) and a series of analogous 1,4-diols **a** are obtained from acetal-protected tartrate esters by reaction with Grignard compounds[10b,15a,23] or by hydride reduction.[24] In addition to the known structures, the ligands (*R,R*)-**10**, **-11**, and **-12** have been prepared from diester (*R,R*)-**13** (Scheme II).[25] Cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) chlorotitanates **b** are then formed upon reaction of 1,4-diols **a** with $CpTiCl_3$ (**8**)[26] or Cp^*TiCl_3 (**14**).[27]

The equilibrium between **8** or **14** and the chelates **b** is driven to **b** either by neutralization of HCl with Et_3N or, as we recently discovered, simply by heating in cyclohexane or toluene, removing HCl in a stream of argon through a reflux condenser. As an alternative, HCl can also be bound either internally by molecular sieves (MS adsorb, to some extent, also $CpTiCl_3$ (**8**)) or externally by a vast excess of MgO placed in the thimble of a Soxhlet extractor.

After separation of $Et_3N{\cdot}HCl$, the complexes **b** are either processed further in solution or isolated by precipitation from concentrated solutions or by evaporation of the solvent. Following this method, the complexes **15–26**, listed in Scheme II, could be prepared. Reaction of $CpTiCl_3$ (**8**) with (*S,S*)-2,3-*O*-isopropylidenethreitol **27**[24] gave an intractable mixture of oligomeric species, as indicated by four C_5H_5 (Cp) signals in the ^1H NMR spectrum. Obviously the "Ingold–Thorpe effect"[28] is essential for the closure of the seven-membered titanacycles **b**. A considerable variation of reaction rates is observed for the different structures and methods. With Et_3N, conversions are faster, an indication of base catalysis, and for Cp^*TiCl_3 (**14**) the rates are much slower. The reaction to complex **16** could only be completed by using an excess of Et_3N in boiling toluene. The titanium complexes **b** are generally stable crystalline compounds. Their sensitivity toward hydrolysis is substantially reduced when compared to acyclic analogues, e.g., bis(diacetone glucos-3-*O*-yl)cyclopentadienyltitanium chloride **28**,[3a,17] the precursor of reagent **1**. Quick handling in the open air is therefore possible. The Cp*Ti complexes **16** and **21** are, however, extremely moisture sensitive.

The new titanium complexes **15–26** have been analyzed by ^1H and ^{13}C NMR. In agreement with the assumed monomeric structure **b**, single sets of signals allow a straightforward interpretation of all spectra. ^1H NMR spectroscopy is also the preferred method for monitoring the course and success of complex formation. The number of signals is doubled as the C_2 symmetry of the ligand is lost upon complexation, e.g., the singlet of H-C(4)/H-C(5) of the free ligand **a** becomes an AB system in the complex **b**. The Cp signal is shifted upfield as Ti–Cl bonds are substituted by alkoxy groups. A mixture of two epimeric complexes **23** and **24** in a 1:4 ratio is obtained with the pivalaldehyde-protected ligand lacking C_2 symmetry.

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X-ray Analysis. A definite proof of the proposed structure **b** has been obtained by X-ray analysis of (*R*,*R*)-**15**[29] and (*R*,*R*)-**20**.[30] ORTEP plots[31] (vibrational ellipsoids at the 20% probability level) of (*R*,*R*)-**15**, (*R*,*R*)-**20**, and for comparison **28**[3a,17] are shown in Figure 1. Selected bond lengths, bond angles, and torsion angles are listed in Table I. All three complexes are monomeric, and intermolecular Ti–O interactions can be ruled out. Their coordination geometry is best described as a "three-legged piano stool arrangement". Close values for the Ti–O bond lengths (176–181 pm) and the O–Ti–O (98–104°) and Ti–O–C (145–155°) bond angles in all three structures indicate a minimal strain of the seven-membered titanacycles in **15** and **20**. Of interest is the distortion of the Ti centers induced by the chirality of the ligands, best seen in the difference of the two diastereotopic Ti–O–C bond angles, which is ~10° for **15** and ~7° for **28**, but null for **20**. While this distortion is also reflected in the slightly different O–Ti–Cl angles of **15** and **28**, the corresponding Ti–O bond lengths are insignificantly different. This dissymmetry of the titanium could be responsible for the enantioface discrimination observed for reagents derived from **15**, **20** (see below), and **28**.[2,3a,17a,32] While poor induction is obtained with **20**, the distortions of **15** and **28**, which are enantiomeric to each other, show a suggestive correspondence to the opposite enantiofacial discrimination of their reagents **1** and (*R*,*R*)-**9** (Scheme I). Distinctly different are, however, the dihedral Cl–Ti–O–C angles of **28** and the chelates **15** and **20**. While the O–C(α) bonds of **28** are approximately eclipsed with the Ti–Cp^{center} axis, the O–C(α) bonds of **15** and **20** are eclipsed with the opposite Ti–O bonds (cf. the O–Ti–O–C torsion angles). The fully substituted α-carbons of **15** and **20** and the constraints imposed by the titanacycle preclude the conformation around the Ti–O bond observed for complex **28** with secondary nonchelated alkoxy ligands. The conformation of the seven-membered rings in **15** and **20** is similar. Due to the interactions of phenyl substituents with the Cp ring in **15**, the ring is pushed toward the Cl atom, clearly seen in the smaller angle formed by Cl–Ti and the acetal C(11) in **15** (103.4°) when compared with the value for **20** (123.3°).

Titanium NMR. A spectroscopic technique that provides direct information about the metal center participating in the reactions should be an optimal probe for the structure–reactivity and selectivity relation. Despite the scarcity of reports on Ti NMR,[33]

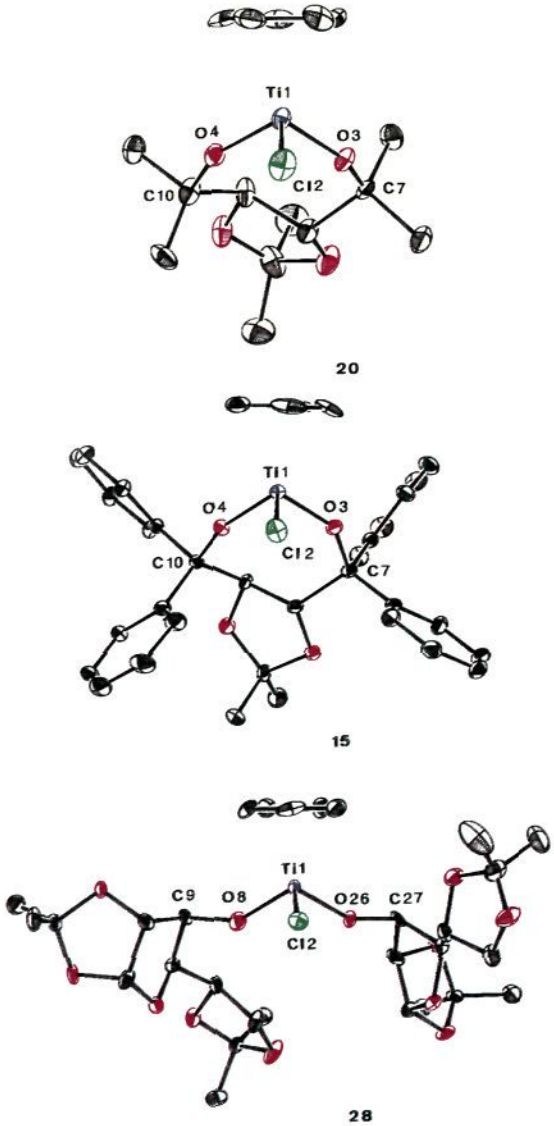

Figure 1. ORTEP plots (vibrational ellipsoids at the 20% probability level) of (*R*,*R*)-**20**, (*R*,*R*)-**15**, and **28**.[17b]

we therefore decided to measure the $^{47/49}$Ti NMR spectra of representative cyclopentadienyldialkoxychlorotitanium complexes and related compounds. Ti NMR measurements are complicated by the fact that the two "NMR-active" isotopes (^{47}Ti, $I = {}^{5}/_{2}$; ^{49}Ti, $I = {}^{7}/_{2}$) have similar NMR properties. With Larmor frequencies of 22.571 (^{47}Ti) and 22.577 MHz (^{49}Ti) at a magnetic field of 9.4 T the separation of the ^{47}Ti and ^{49}Ti chemical shifts is only 266 ppm. Medium-sized quadrupole moments Q, 0.29×10^{-28} (^{47}Ti) and 0.24×10^{-28} m^2 (^{49}Ti), lead to very short relaxation times T_1 and T_2 and therefore to large experimental line widths, especially if the local symmetry at Ti is low. Low natural abundance (^{47}Ti 7.28%, ^{49}Ti 5.51%) and small magnetic moments result in small overall receptivities, which are comparable with ^{13}C NMR. In Table II, chemical shifts (δ ^{49}Ti, based on external $TiCl_4$) and line widths ($\Delta\nu_{1/2}$) measured (22.56 MHz, 9.4 T; 400

(29) Orthorhombic, $P2_12_12_1$, a = 1106.1 (1), b = 1453.1 (1), c = 1920.2 (1) pm, $V = 3.086\ (2) \times 10^9$ pm^3, $Z = 4$, $\rho_{calcd} = 1.317$ g/cm^3. Intensity measurements at 21 °C were carried out on a Philips PW-1100 diffractometer (graphite monochromator, Mo Kα = 71.069 pm, θ range 3–30°). The structure has been solved from 3382 observed independent reflections with $I > 3\sigma(I)$ by the classical heavy atom method. The refinement, according to the least-squares method with anisotropic temperature factors, converged at $R = 0.064$ ($R_w = 0.071$). The hydrogen atoms could not be located. Further details of the crystal structure investigation, numbering of all atoms, positional parameters, bond lengths, bond angles, and measured reflections (h, k, l) are included with the supplementary material. The structural data will also be deposited in the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England), where it will be available on quoting the full citation of the journal.

(30) Monoclinic, P_{2_1}, a = 761.5 (1), b = 959.9 (1), c = 1278.6 (1) pm, β = 98.57 (1)°, $V = 0.924\ (2) \times 10^9$ pm^3, $Z = 2$, $\rho_{calcd} = 1.310$ g/cm^3. Intensity measurements at 21 °C were carried out on a Philips PW-1100 diffractometer (graphite monochromator, Mo Kα = 71.069 pm, θ range 3–30°). The structure has been solved from 964 observed independent reflections with $I > 3\sigma(I)$ by the classical heavy atom method. The refinement, according to the least-squares method with anisotropic temperature factors, converted at $R = 0.049$ ($R_w = 0.059$). The hydrogen atoms could not be located. Further details of the crystal structure investigation, numbering of all atoms, positional parameters, bond lengths, bond angles, and measured reflections (h, k, l) are included with the supplementary material. The structural data will also be deposited in the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England), where it will be available on quoting the full citation of the journal.

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Table II. ^{49}Ti and ^{47}Ti NMR Chemical Shifts[a] and Line Widths ($\nu_{1/2}$) of Selected Cyclopentadienyltitanium(IV) Complexes[b]

complex	solvent	temp (K)	$\delta^{49}Ti$ (ppm)	$\nu_{1/2}(^{49}Ti)$ (Hz)	$\delta^{47}Ti$ (ppm)	$\nu_{1/2}(^{47}Ti)$ (Hz)	enant excess (%)[c]
$Cp(2\text{-}PrO)_2TiCl$ (**42**)	toluene-d_8	373	−917	846			
(*R,R*)-**20** (Cp)	toluene-d_8	373	−889	1080			13
(*R,R*)-**20** (Cp)	$CDCl_3$	320	−896	2430			
(*R,R*)-**19** (Cp)	toluene-d_8	373	−872	1400			71
(*R,R*)-**15** (Cp)	toluene-d_8	373	−854	3460			95
$Cp(DAGO)_2TiCl$ (**28**)[17]	toluene-d_8	373		≥4500			90
(*R,R*)-**21** (Cp*)	toluene-d_8	373	−707	800			87
$TiCl_4$	$CDCl_3$	320	0	4	−266	11	
$CpTiCl_3$	$CDCl_3$	320	−390	60	−657	160	
$(CH_3Cp)TiCl_3$	$CDCl_3$	320	−332	30	−598	90	
$(Me_3SiCp)TiCl_3$	$CDCl_3$	320	−361	70	−627	190	
$((CH_3)_5Cp)TiCl_3$	$CDCl_3$	320	−85	10	−352	27	

[a] δ from external $TiCl_4$. [b] 0.4 M solutions, 22.56 MHz, 9.4 T. [c] Enantiomeric excess (ee) of 1-phenyl-3-butenol (**4**), obtained by allyltitanation of benzaldehyde (**3**) with reagents derived from these titanium chlorides.

MHz for ^1H) of 0.4 M solutions in toluene-d_8 at 373 K are listed together with the enantioselectivities of the corresponding reagents. The ^{47}Ti signals have either been suppressed by an appropriate preacquisition delay or the ^{49}Ti resonance has been assigned to the narrower line in the spectrum (cf. Experimental Section). Not unexpectedly, the resonance frequencies of these closely related complexes are very similar. Furthermore, interpretation of such chemical shifts, especially of d^0 coordination centers, in terms of electron density is difficult and often misleading, because the chemical shifts are dominated by the paramagnetic shielding constant, which is not directly related to the ground-state charge density at the nucleus.[34]

The line width ($\Delta\nu_{1/2}$), on the other hand, provides direct information about the symmetry of the electron distribution around the nucleus (eq 1).[35] For a given nucleus, spin (I) and quadrupole

$$\Delta\nu_{1/2} = \frac{0.3\pi(2I+3)}{I^2(2I-1)}\frac{e^2Q(q_{zz})^2}{h}\left[1+\frac{\eta^2}{3}\right]\tau_C = \frac{1}{\pi T_1} = \frac{1}{\pi T_2} \quad (1)$$

moment (Q) are constant, and $\Delta\nu_{1/2}$ depends only on the correlation time of molecular tumbling (τ_C, a function of the molecular weight, viscosity of the sample, and temperature), the square of the electrical field gradient, $(q_{zz})^2$, and the asymmetry parameter (η, describes the deviation from cylindrical symmetry). Thus, in the case of spherical electron distribution around titanium with $(q_{zz})^2$ and $\eta = 0$, narrow lines are obtained, whereas in a nonspherical environment broad lines are detected. The ^{49}Ti NMR line widths of the structurally related $Cp(RO)_2TiCl$ complexes **15**, **19**, **20**, **21**, **28**, and $Cp(O\text{-}2\text{-}prop)_2TiCl$ **42** can therefore be considered as a rough qualitative measure of the electronic symmetry at the titanium center. This is confirmed by the extremely broad lines of compounds **15** (3500 Hz) and **28** (>4500 Hz) as opposed to the narrower line of complex **20** (1080 Hz), in accordance with their crystal structures where distorted Ti coordination geometry was found for **15** and **28**, but not for **20**. The dependence on solvent and temperature of the correlation time τ_C is demonstrated by the doubled line width when **20** is measured in $CDCl_3$ solution at 320 K. The most salient feature of Table II is the qualitative correlation between line width and enantioselectivity of the corresponding allylating reagents. Provided this relation is significant, the prime factor for enantioface discrimination would be electronic dissymmetry at titanium rather than direct interaction of the substrate with the chiral ligand. It has to be noted that the Cp* complex (*R,R*)-**21** is not fitting in the correlation of the Cp complexes. This is reasonable, if the data of $(RCp)TiCl_3$ complexes with different substituents R at Cp, listed in the lower part of Table II, are considered. The substitution of the Cp group has a decisive effect on the ^{49}Ti line width, and correlations should therefore be restricted to compounds with identical cyclopentadienyl ligands.

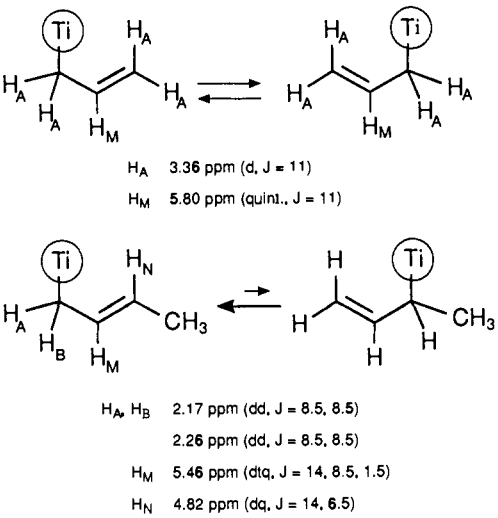
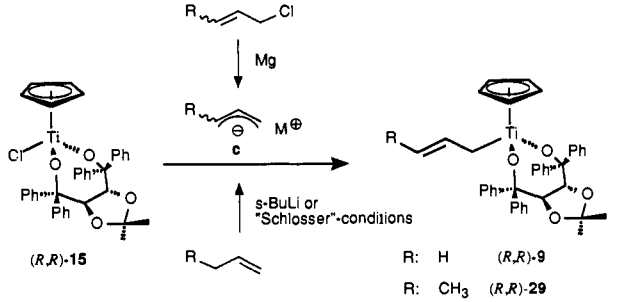


Figure 2. Selected ^1H NMR data of (*R,R*)-**9** and (*R,R*)-**29**.

Scheme III. Preparation of Allyltitanium Reagents



Preparation of Reagents. The allyltitanium reagent (*R,R*)-**9** and Ti complexes with substituted allyl groups are prepared from complex **15** and the analogues **16**–**26** by chloride substitution with allylic anions **c** (Scheme III). Most convenient for this purpose are allyl Grignard compounds, which should, however, be freed of Mg salts by filtration. While Grignard reagents prepared by the Rieke procedure[36] are not suitable, direct allylic metalation with *sec*-butyllithium, *n*-butyllithium/KO(*t*-Bu),[37] or lithium tetramethylpiperidide/KO(*t*-Bu)[38] is successful. The transmetalation conditions, usually 1–5 h at 0 °C, have to be optimized

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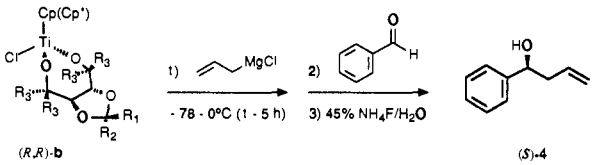
Table III. Allyltitanation of Benzaldehyde (3) with Reagents Derived from Chlorotitanates **b**



b	Cp or Cp*	R_1	R_2	R_3	temp (°C)	4 ee (%)	(config)[a]
(*R*,*R*)-**15**	**Cp**	CH_3	CH_3	C_6H_5	−74	**95**	(*S*)
					−35	93	
					0	89	
(*R*,*R*)-**16**	Cp*	CH_3	CH_3	C_6H_5	−74	87	(*S*)
					0	87	
(*R*,*R*)-**17**	Cp	CH_3	CH_3	C_6F_5	−74	54	(*S*)
(*R*,*R*)-**18**	Cp	CH_3	CH_3	2-furyl	−74	66	(*S*)
(*R*,*R*)-**19**	Cp	CH_3	CH_3	$C(CH_3)=CH_2$	−74	71	(*S*)
(*R*,*R*)-**20**	Cp	CH_3	CH_3	CH_3	−74	12	(*S*)
					0	16	
(*R*,*R*)-**21**	**Cp***	CH_3	CH_3	CH_3	−74	**88**	(*S*)
					0	73	
(*R*,*R*)-**22**	Cp	H	H	C_6H_5	−74	80	(*S*)
(*S*,*S*)-**23**/**24**	Cp	H	*t*-Bu	C_6H_5	−74	82	(*R*)
(*R*,*R*)-**25**	Cp	C_6H_5	C_6H_5	C_6H_5	−74	89	(*S*)
(*R*,*R*)-**26**	Cp	spiro[9*H*]-fluorene		C_6H_5	−74	91	(*S*)
$CpTiCl_3$/**27**[b]	Cp	CH_3	CH_3	H	−74	6	(*S*)

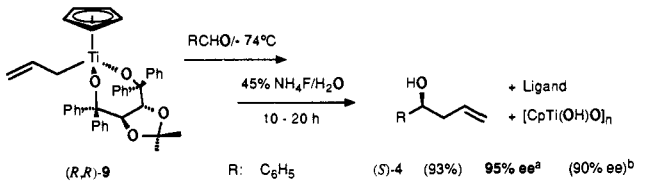
[a] Determined by capillary GLC,[48] derivatization with *N*-isopropyl isocyanate. [b] Mixture of complexes obtained from $CpTiCl_3$ (**8**) and isopropylidenethreitol (*S*,*S*)-**27**.

by quenching aliquots of a reaction mixture after different times with an aldehyde and analyzing the product mixture. For substituted allyl groups, the regio- and stereoselectivity of the titanium reagent are independent of the isomeric composition of the precursor **c**. The use of crotylmagnesium chloride,[39] a mixture of regio and (*E*,*Z*) isomers, or (*Z*)-2-butenyllithium/-potassium[37] leads to the same result, suggesting that the same reagent (*R*,*R*)-**29** is obtained in both cases. The structures of the allyltitanium compounds (*R*,*R*)-**9** and (*R*,*R*)-**29** have therefore been studied by NMR spectroscopy (Figure 2). Contrary to $(Cp)_2Ti^{III}$allyl reagents with η^3-bound allyl substituents,[12a,d,m,16] the ^1H NMR spectrum of (*R*,*R*)-**9** with all terminal protons magnetically equivalent indicates a fast 1,3-shift with bond rotation of an η^1-bound allyl substituent. The ^{13}C NMR spectrum of (*R*,*R*)-**9** shows the same C(1)–C(3) degeneracy. The ^1H NMR spectrum of (*R*,*R*)-**29**, on the other hand, exhibits the pattern of a η^1-bound (*E*)-2-butenyl group. The energetic preference of the (*E*) isomer with titanium bound to the less substituted terminus of the allyl system prevents the observation of dynamic effects in the NMR of (*R*,*R*)-**29**. The rates of this equilibration must be high, as no sign of line-broadening or signal-splitting could be detected in the ^1H and ^{13}C NMR spectra of (*R*,*R*)-**9** measured at 9.4 T (400 MHz for ^1H; 100.6 MHz for ^{13}C) upon cooling to −100 °C. Thus, 3-substituted allyltitanium reagents with the (*E*) conformation can be obtained conveniently from various precursors **c**, unlike in the case of allylboron[5] or allylstannane[6,8] reagents. For the same reason, however, this method is restricted to the preparation of branched regioisomers with the anti configuration (see below). As opposed to the results of Reetz and Sauerwald,[12g] addition of $BF_3{\cdot}Et_2O$ has no effect on the diastereoselectivity of reagent (*R*,*R*)-**29**.

Allyltitanation of Aldehydes

The degree of enantioface discrimination of allyltitanium reagents derived from the chlorotitanates **b** has been assessed by the conversion of benzaldehyde **3** to homoallyl alcohol **4** (Table III). *Si* face attack is preferred for all complexes with ligands derived from (*R*,*R*)-tartrate. Most important for high enantioselectivity is the bulk of R_3. The enantiomeric excess (ee) of

Scheme IV. Allyltitanation of Achiral Aldehydes[a]



R:	C_6H_5	(*S*)-**4**	(93%)	95% ee[a]	(90% ee)[b]
R:	$(CH_2)_8CH_3$	(*R*)-**30**	(94%)[c]	94% ee[a]	(92% ee)[b]
R:	$CH(CH_3)_2$	(*S*)-**31**	(88%)	97% ee[a]	(90% ee)[b]
R:	$C(CH_3)_3$	(*S*)-**32**	(63%)	97% ee[a]	(88% ee)[b]
R:	$CH=CH_2$	(*S*)-**33**	(79%)	95% ee[d]	(86% ee)[b]

[a] (a) Enantiomeric excess determined by capillary GLC,[48] derivatization with *N*-isopropyl isocyanate. (b) Enantiomeric excess obtained with reagent **1**,[17a] opposite enantiomer. (c) Isolated as its *O*-acetyl derivative (*R*)-**30a**. (d) Enantiomeric excess determined by capillary GLC,[48] derivatization with MTPA chloride.[56]

(*S*)-**4** drops from 95% to 12% when $R_3 = C_6H_5$ is replaced by CH_3 (**15**, **20**). Modest to intermediate induction (not optimized) is observed with $R_3 = C_6F_5$, 2-furyl, and isopropenyl (**17**, **18**, **19**). Ligands with acetal protecting groups other than the acetonide of **15** afford reagents with slightly inferior enantioface differentiation (**22**, **23**/**24**, **25**, **26**). Interpretations should therefore be done with caution, but it appears that the conformation of the dioxolane ring, influenced by R_1 and R_2, has no crucial influence on the enantioselectivity (e.g., **23**/**24**: 82% ee). Most interesting is the effect of methyl substitution at the cyclopentadienyl ring (Cp → Cp*). While the influence is small and negative for the optimal system with $R_3 = C_6H_5$ (**15** → **16**), a dramatic increase from 12% to 88% ee is observed for the complexes with the tetramethyl ligand (**20** → **21**). This indicates the importance of cyclopentadienyl–R_3 interactions for the enantioselectivity of these reagents. Such interactions are most probably also responsible for the distortion of the Ti coordination geometry exhibited by the crystal structures of **15** and **28** but not **20** (cf. X-ray analysis, above).[40] The temperature dependence of the enantioface selectivity shows no consistent tendency. While the induction achieved with complex **15** drops from 95% to 89% ee upon raising the temperature from −74 to 0 °C, other systems (**16**, **20**, **21**)

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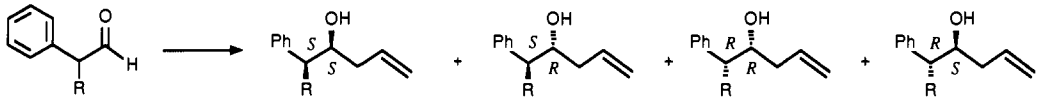
(40) Unfortunately, no crystals suitable for X-ray analysis so far have been grown of the highly soluble and moisture-sensitive complex (*R*,*R*)-**21**.

Table IV. Allyltitanation of α-Phenylpropionaldehyde (**34**) and α-Phenylbutyraldehyde (**35**)



R: CH_3 **34** (*S*)-**36** (*R*)-**38** (*R*)-**36** (*S*)-**38**

R: C_2H_5 **35** (*S*)-**37** (*R*)-**39** (*R*)-**37** (*S*)-**39**

aldehyde	reagent	% yield	product ratio (%)[a] (% ee for main product)		de (%)[b]	product ratio (%)[a] (% ee for main product)		de (%)[c]
			(*S*)-**36**	(*R*)-**38**		(*R*)-**36**	(*S*)-**38**	
(±)-**34**	(allyl)MgCl	quant	33.1 (rac)	17.2 (rac)	31.6	32.5 (rac)	17.2 (rac)	30.8
(±)-**34**	Cp(DAGO)$_2$Ti(allyl) **1**	93	6.9	44.1 (96.4% ee)	73.0	48.2 (75% ee)	0.8	**96.8**
(±)-**34**	(*S*,*S*)-**9**	98	1.3	49.4 (98.4% ee)	**94.8**	48.9 (94% ee)	0.4	**98.4**
			(*S*)-**37**	(*R*)-**39**		(*R*)-**37**	(*S*)-**39**	
(±)-**35**	(allyl)MgCl	70	33.0 (rac)	17.0 (rac)	32.0	33.0 (rac)	17.0 (rac)	32.0
(±)-**35**	Cp(DAGO)$_2$Ti(allyl) **1**	95	10.4	40.0 (98.6% ee)	58.8	49.3 (65.2% ee)	0.3	**98.8**
(±)-**35**	(*S*,*S*)-**9**	94	2.5	48.3 (99.2% ee)	**90.2**	49.2 (90.4% ee)	≤0.2	≥**99.0**
(±)-**35**	(*R*,*R*)-**9**	91	48.7 (90.6% ee)	0.3	**98.8**	2.4	48.6 (98.8% ee)	**90.6**
(*S*)-**35**	(+)-(Ipc)$_2$B(allyl)[43]		97.0	3.0	**94.0**[43]			
(*R*)-**35**	(+)-(Ipc)$_2$B(allyl)[43]					33.0	67.0	34.0[43]
(*S*)-**35**	(−)-(Ipc)$_2$B(allyl)[43]	26.0	74.0	48.0[43]				
(*R*)-**35**	(−)-(Ipc)$_2$B(allyl)[43]					98.0	2.0	**96.0**[43]

[a] Determined by capillary GLC, derivatization with MTPA chloride.[56] [b] Diastereomeric excess of the reactions with (*S*)-**34**/(*S*)-**35**. [c] Diastereomeric excess of the reactions with (*R*)-**34**/(*R*)-**35**.

appear to be temperature insensitive.

The allyltitanation of various aldehydes with reagent (*R*,*R*)-**9** is depicted in Scheme IV. The enantioselectivity is high for all structures (94–97% ee); the chemical yields, which are not optimized, are acceptable to good (63–94%). Reagent (*R*,*R*)-**9** is also distinctly more selective than the diacetone glucose complex **1**[3a,17] (values in parentheses). The use of the (*S*,*S*)-tartrate-derived reagent (*S*,*S*)-**9** instead of **1** for preparing the other enantiomers is therefore worth being considered. It has to be noted that, due to enhanced stability of the chelated ligand system, the time for complete hydrolysis to product, ligand, and oligomeric cyclopentadienyltitanium hydroxo oxides ([CpTi(OH)O]$_n$) is much longer than for the diacetone glucose complex **1**.[3a,17]

Reagents for the highly enantioselective allylboration of simple aldehydes have been developed by Brown,[5i,j,41] Roush,[5n,q] Masamune,[5u] Corey,[5w] and Hoffmann/Stürmer.[5y,42] Some attempts to compare the different reagents[5i,u,43] are, however, ambiguous, as product ratios, resulting from different reaction conditions and determined by different methods in the very critical range of ≥20:1, are correlated rather than thermodynamic constants. Furthermore, it is not of paramount importance whether "easy substrates" like benzaldehyde or isobutyraldehyde can be allylated with 95% or 99% enantiomeric excess. A more reliable and relevant scale of stereoselectivity is obtained from the product distribution of reactions with "difficult", α-chiral substrates. Therefore, we studied the reactions of racemic α-phenylpropionaldehyde (**34**) and α-phenylbutyraldehyde (**35**) with the allyltitanium reagents **1** and **9**. These data and the published product ratios of the conversions of (*S*)- and (*R*)-**35** with both enantiomers of (Ipc)$_2$B(allyl)[43] are listed in Table IV. The reactions with allylmagnesium chloride were used to assign the Cram diastereomers (**36**, **37**) and the anti-Cram diastereomers (**38**, **39**). The enantiomers were assigned by assuming *re* face preference for **1** and (*S*,*S*)-**9** and *si* face preference for (*R*,*R*)-**9** (cf. below, Stereochemical Assignments). It is clearly more difficult to outmatch the influence of the chiral center of **35** than that of **34**. Reaction of aldehyde (*S*)-**35** with reagents **1**, (*S*,*S*)-**9**, or (−)-(Ipc)$_2$B(allyl)[43] leads preferentially to the anti-Cram diastereomer (*R*)-**39**. Of these mismatched pairs, (*S*,*S*)-**9** gives the best diastereoselectivity (90% de, 95:5 ratio), followed by **1** (58% de, 79:21 ratio) and (−)-(Ipc)$_2$B(allyl) (48% de, 74:26 ratio). The same trend with 95% de for (*S*,*S*)-**9** and 73% de for **1** is also observed for the allylation of (*S*)-**34**. When (±)-**34** was treated with 0.5 equiv of **1**, the enantiomer differentiation was low (71.7:28.3).[17a] Other features of the reactions with racemates include the fact that the optical purity of the minor (anti-Cram) diastereomer is generally higher. With a reagent of high enantioface selectivity, such as (*R*,*R*)-**9** and (*S*,*S*)-**9**, the ratio of the diastereomers approaches 1:1 (**36**:**38** = 50.2:49.8; **37**:**39** = 51.7:48.3), and the optical purity of the Cram diastereomer is high as well ((*R*)-**36**, 94.8% ee; (*R*)-**37**, 90.4% ee; (*S*)-**37**, 90.6% ee). The results of Table IV suggest that the allylation of α-phenylbutyraldehyde (**35**) is a very discriminating test for allyltransferring agents, especially recommendable for the high selectivity range.

Chiral α-hydroxy- or α-amino-substituted aldehydes are valuable chiral intermediates. D-Glyceraldehyde acetonide (**40**)[44] and L- or D-*N*-Boc-serine aldehyde acetonide (**41**)[45] are readily accessible compounds that have found many applications.[4f,5p,51,6e,46,47] Conversions of these chiral substrates with the reagents **9**, **29**, and the achiral cyclopentadienylallyltitanium bis(2-propoxide) are depicted in Scheme V. Reaction of glyceraldehyde **40** with allylmagnesium chloride gives a 2:1 mixture of the diastereomers **43** and **44**. By using either (*R*,*R*)-**9** or its enantiomer (*S*,*S*)-**9**, isomer **43** or **44**, respectively, can be prepared with 98% ds (diastereomer ratio). A minor correction of these

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(44) (a) Dumont, R.; Pfander, H. *Helv. Chim. Acta* **1983**, *66*, 814–823. (b) Häfele, B.; Jäger, V. *Liebigs Ann. Chem.* **1987**, 85–87. (c) Schmid, Ch. R.; Bryant, J. D.; Dowlatzedah, M.; Phillips, J. L.; Prather, D. E.; Schantz, R. D.; Sear, N. L.; Vianco, C. S. *J. Org. Chem.* **1991**, *56*, 4056–4058.

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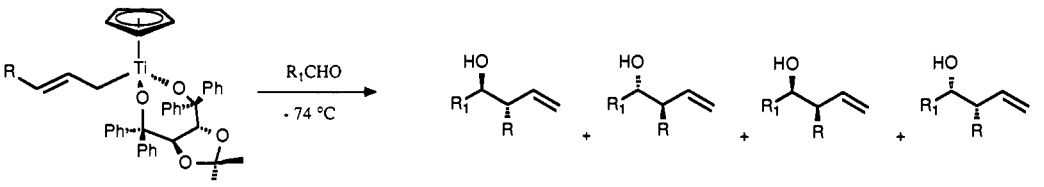
(47) (a) Herold, P. *Helv. Chim. Acta* **1988**, *71*, 354–362. (b) Kiyooka, S.-i.; Nakano, M.; Shiota, F.; Fujiyama, R. *J. Org. Chem.* **1989**, *54*, 5409–5411. (c) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Pedrini, P. *J. Org. Chem.* **1990**, *55*, 1439–1446. (d) Garner, P.; Park, J. M. *J. Org. Chem.* **1990**, *55*, 3772–3787. (e) Casiraghi, G.; Colombo, L.; Rassu, G.; Spanu, P.; Gasparri-Fava, G.; Ferrari-Belicchi, M. *Tetrahedron* **1990**, *46*, 5807–5824. (f) Wagner, R.; Tilley, J. W. *J. Org. Chem.* **1990**, *55*, 6289–6298. (g) Shimamoto, K.; Ohfune, Y. *Tetrahedron Lett.* **1990**, *31*, 4049–4052. (h) Beaulieu, P. L.; Duceppe, J.-S.; Johnson, C. *J. Org. Chem.* **1991**, *56*, 4196–4204. (i) Ibuka, T.; Habashita, H.; Otaka, A.; Fujii, N.; Oguchi, Y.; Uyehara, T.; Yamamoto, Y. *J. Org. Chem.* **1991**, *56*, 4370–4382.

Table V. Allyltitanation of Benzaldehyde (3) and Decanal with Substituted Allyl Reagents



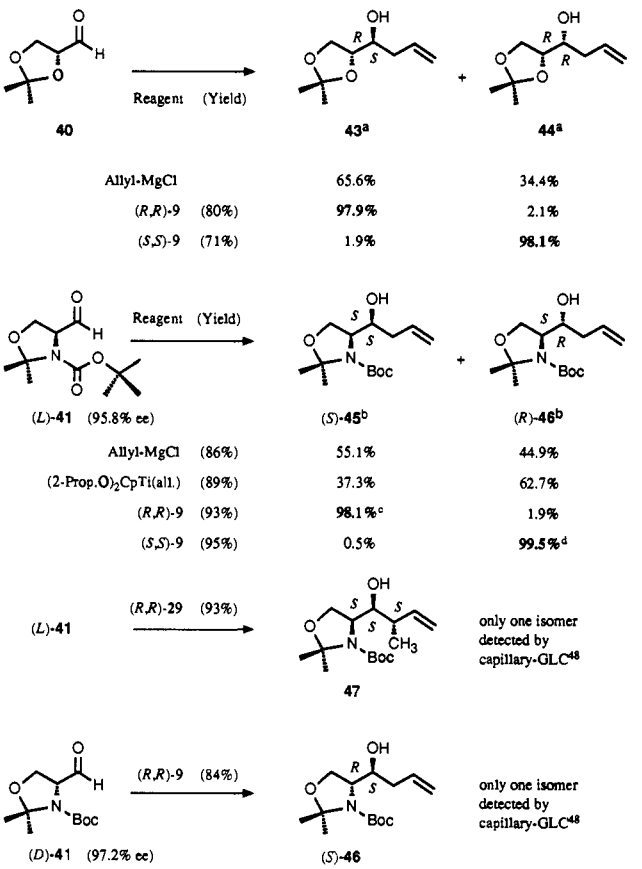
reagent	substituents (total yield, %)	product(s) (% isomer) isomer 1	isomer 2	isomer 3	isomer 4
(*R*,*R*)-**29**	R_1: C_6H_5, R: CH_3 (89)	(*S*)-**52** (97.8)[a] 98% ee	(*R*)-**52** (0.9)[a]	(*S*)-**53** (1.3)[a]	(*R*)-**53** (0)[a]
(*R*,*R*)-**29**	R_1: C_9H_{19}, R: CH_3 (86)	(*R*)-**54** (only one isomer detected)[a]			
(*R*,*R*)-**48**	R_1: C_6H_5, R: C_6H_5 (54)	(*S*)-**55** (98.7)[a] 97% ee	(*R*)-**55** (1.3)[a]		
(*R*,*R*)-**49**	R_1: C_6H_5, R: OEt (77)	(*R*)-**56** (85.5)[a] 95% ee	(*S*)-**56** (2.2)[a]	(*R*)-**57** (10.8)[a] 76% ee	(*S*)-**57** (1.5)[a]
(*R*,*R*)-**49**	R_1: C_9H_{19}, R: OEt (73)	(*R*)-**58** (93.6)[a] 92% ee	(*S*)-**58** (3.7)[a]	(*R*)-**59** (2.0)[a] 48% ee	(*S*)-**59** (0.7)[a]
(*R*,*R*)-**50**	R_1: C_6H_5, R: OPMP[c] (93)	(*R*)-**60** (only one isomer detected)[b]			
(*R*,*R*)-**51**	R_1: C_6H_5, R: $SiMe_3$ (68)	(*R*)-**61** (only one isomer detected)[a]			
(*R*,*R*)-**51**	R_1: C_9H_{19}, R: $SiMe_3$ (69)	(*R*)-**62** (only one isomer detected)[d]			

[a] Determined by capillary GLC,[48] derivatization with *N*-isopropyl isocyanate. [b] Determined by capillary GLC,[48] after oxidative cleavage of the PMP ether; cf. Scheme VI. [c] PMP = *p*-methoxyphenyl. [d] Determined by ^{1}H NMR spectroscopy with the shift reagent TFAF.[51]

product ratios might be necessary, as small amounts of products arising from possible enantiomeric impurity of the glyceraldehyde acetonide **40** have been neglected in the analysis by capillary GLC. The results with serine aldehyde **41** are similar. While the ratio of (*S*)-**45** and (*R*)-**46** obtained with allyl Grignard is close to unity, reaction with the achiral Cp(2-PrO)$_2$Ti(allyl) gives a 2:1 preference for (*R*)-**46**. The conversions with the chiral reagents are again highly diastereoselective and, depending on which enantiomer of **41** and **9** is chosen, (*S*)-**45**, (*S*)-**46**, and (*R*)-**46** could be prepared with very high isomeric purity. As the starting aldehydes L- and D-**41** contained 1–2% of the other enantiomer and not all four stereoisomers could be resolved by capillary GLC (Chirasil-Val column),[48] the diastereomer ratios listed in the Experimental Section might have to be corrected, albeit by less than 1%. Only one isomer of the (*S*,*S*,*S*) configuration (**47**) was isolated when L-**41** was treated with the crotyl reagent (*R*,*R*)-**29**.

In addition to the crotyltitanium reagent (*R*,*R*)-**29**, the complexes with phenyl-, alkoxy-, and trimethylsilyl-substituted allyl groups (*R*,*R*)-**48**–**51** have been prepared as described in Scheme III for (*R*,*R*)-**9** and -**29**. The results of their reactions with benzaldehyde (**3**) and decanal are compiled in Table V. The major or only product of all reactions is the anti diastereomer, obtained by *si* face attack of the substituted allyl terminus ((*S*)-**52**, (*R*)-**54**, (*S*)-**55**, (*R*)-**56**, (*R*)-**58**, (*R*)-**60**, (*R*)-**61**, and (*R*)-**62**). Small amounts of the syn epimer (*si* face preference) are formed in the reaction of benzaldehyde (**3**) with (*R*,*R*)-**29** ((*S*)-**53**, 1.3%) and of decanal with (*R*,*R*)-**49** ((*R*)-**59**, 2.0%; (*S*)-**59**, 0.7%). With 12.3% of the syn isomer **57** the conversion of benzaldehyde (**3**) with (*R*,*R*)-**49** is the only exception of this series. By increasing the bulk of the alkoxy group from ethoxy ((*R*,*R*)-**49**) to *p*-methoxyphenoxy ((*R*,*R*)-**50**), the diastereoselectivity can, however, be greatly increased. The optical purity of the major products, which are obtained in acceptable to good yields, is excellent (in most cases ≥95% ee). The reaction path leading to the minor syn diastereomers appears to be less enantioselective. Incomplete transmetalation can be ruled out, as the regioisomers, resulting from attack of the unsubstituted allyl terminus, could not be detected in the reaction mixtures.

Scheme V. Allyltitanation of Chiral Aldehydes[a]



[a] (a) Ratio determined by GLC,[48] derivatization with MPTA chloride.[56] (b) Ratio determined by GLC,[48] derivatization with *N*-isopropyl isocyanate. (c) Includes ca. 2% of (*S*)-**46** from D-**41** contained in the starting material L-**41**. (d) Most probably includes ca. 2% of (*R*)-**45** from the enantiomeric impurity of L-**41**.

Stereochemical Assignments

The configurational assignments of compounds (*S*)-**4**, (*R*)-**30**, (*S*)-**31**, (*S*)-**32**, and (*S*)-**33** are based on the relative retention times of the GLC analysis (Chirasil-L-Val column,[48] cf. Experimental Section, general remarks). The absolute configurations of their enantiomers have been assigned before.[17a] The absolute and relative configuration of (*R*)-**39**, obtained from the reaction of 2-phenylbutanal ((±)-**35**) with (*S*,*S*)-**9** (Table IV), was determined by X-ray structure analysis of its (1*S*)-(−)-camphanic acid ester **69** (Scheme VI).[49] The assignment, based on Cram's rule for

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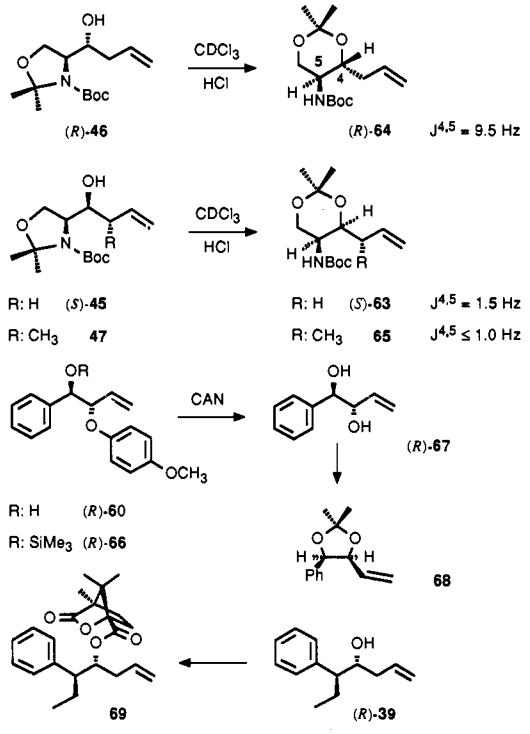
Scheme VI. Transformations for the Configurational Assignments



the relative configuration[50] and on the enantiofacial preference of the chiral reagent (*S,S*)-**9** for the absolute configuration, is thus correct. This assignment confirms at the same time the configuration of the enantiomer (*S*)-**39** and the relative configurations of the diastereomers (*R*)- and (*S*)-**37**. With these premises it is safe to assign the absolute configurations of (*R*)- and (*S*)-**37** by the enantiofacial preferences of the reagents (*R,R*)- and (*S,S*)-**9**, and the configurations of (*R*)- and (*S*)-**36**, as well as (*R*)- and (*S*)-**38**, the products of 2-phenylpropanal ((±)-**34**) (Table IV), by analogy. The structures of **43** and **44** are deduced by comparison of physical data with published values (^{13}C NMR,[46b] $[\alpha]_D$[46d]). The L-serine derivatives (*S*)-**45**, (*R*)-**46**, and -**47** have been converted to the 1,3-acetonides (*S*)-**63**, (*R*)-**64**, and **65** with HCl in chloroform (Scheme VI). The relative configuration of C(4) and C(5) follows from the H–H coupling constant ($J^{4,5}$), which is 9.5 Hz for the trans configuration and ≤1.5 Hz for the cis epimers (cf. ref 47a). The (2′*S*) configuration of **47** ((1′*S*) of **65**) is based on the anti preference of reagent (*R,R*)-**29**.

All four possible diastereomers of the conversions of reagents (*R,R*)-**29**, (*R,R*)-**48**, (*R,R*)-**49**, (*R,R*)-**50**, and (*R,R*)-**51** have been prepared with achiral Grignard, Li, or K/Li reagents. Whenever regioselectivity was a problem, these reagents were transmetalated with $Cp(2\text{-}PrO)_2TiCl$ (**42**). These mixtures served as references for the GLC analyses (Chirasil-L-Val column,[48] cf. Experimental Section, general remarks) and also for ^1H NMR spectroscopy with the chiral solvating agent 2,2,2-trifluoro-1-(9-anthryl)ethanol (TFAE).[51] Preferential formation of one diastereomer usually allowed the assignment of enantiomeric pairs. Comparison with published data confirmed the relative configurations of (*S*)-**52** (δ ^{13}C of $CHCH_3$[5q]), (*R*)-**54** (δ of H-C(3) and H-C(4)[5q]), (*S*)-**55** ($\Delta\delta^{13}C$ of C(1) and C(3) or C(4)[51]), (*R*)-**56** (δ H-C(1) = 4.82 ppm (d, J = 4.5), compared with the methoxy analogue[53]), and (*R*)-**61** (δ H-C(1) in CCl_4 = 4.70 ppm (d, J = 6.5)[54]). The relative configuration of (*R*)-**60** was determined by silylation (→ (*R*)-**66**) followed by cerium(IV) ammonium nitrate (CAN) oxidation and desilylation, affording the *erythro*-diol (*R*)-**67**. Treatment with 2,2-dimethoxypropane and acid gave the dioxolane **68** (Scheme VI). The 4,5-*cis* configuration of **68** follows from $\Delta\delta$ of the C(2) methyl signals (0.19 ppm)[55] and from difference NOE measurements, exhibiting an NOE of the CH_3 at 1.45 ppm with both H-C(4) and H-C(5), but no NOE for the other CH_3 at 1.64 ppm. The configurations of (*R*)-**58** and (*R*)-**62** are based on analogy. The absolute configurations of the products shown in Table V rely on analogy as well. The configuration of **47** has, however, been verified by conversion to **65** (Scheme VI), and the optical rotations of (*S*)-**52** and (*R*)-**54** correspond to the published values: (*S*)-**52** (66% ee), $[\alpha]_D$ = −73.4 (*c* = 2, $CHCl_3$); (*R*)-**54**, $[\alpha]_D$ = +0.5 ($CHCl_3$).[5q]

Conclusions

The well-characterized cyclopentadienyl(1,3-dioxolane-3,4-dimethanolato)chlorotitanium complexes **b** described in this study form the basis for a novel class of highly stereoselective chiral allyl-transferring agents. Asymmetric distortion of the titanium coordination geometry, detected by X-ray analysis and ^{49}Ti NMR line widths, correlates qualitatively with the degree of enantioface discrimination, suggesting that electronic rather than direct steric effects govern the stereoselectivity of these reagents.

These complexes are prepared from readily available nontoxic materials; the source of chirality, tartaric acid, is available in both enantiomeric forms. The reagents derived from natural (*R,R*)-tartaric acid are complementary to those obtained from chloride **28** with diacetone D-glucose ligands,[3a,17] as the opposite face selectivity is observed. Contrary to allylboron[5] or allyltin reagents,[6,8] these allyltitanium compounds can be prepared by transmetalation with a variety of allyl Grignard, allyllithium, and allylpotassium/-lithium compounds, and isolation or purification is not necessary. The chlorides are crystalline, stable compounds, freely soluble in toluene, THF, and chlorinated solvents, moderately soluble in ether, and to some extent (especially Cp*-substituted complexes) even in saturated hydrocarbons. Their potential for large-scale conversions is better than that of any other stoichiometric chiral allyl-transferring reagent known. Complex (*R,R*)-**15** can be prepared conveniently in 1-kg batches; ca. 7 kg have been prepared so far.

The enantioselectivity equals or surpasses the selectivity of the best boron or tin reagents, as far as the results can be compared. Especially rewarding are the results with chiral substrates of synthetic interest. The enantioface discrimination is retained or even improved when the allyl ligand is terminally substituted with alkyl-, aryl-, alkoxy-, or silyl groups. NMR analysis of the allyl and crotyl reagents revealed a fast 1,3-migration of titanium, favoring the (*E*) isomer with titanium η^1-bound to the unsubstituted terminus. This explains the almost exclusive formation of the branched anti diastereomers, a clear restriction of this method, but also a complementarity to the allylboron and allyltin analogues, which give easier access to the corresponding syn diastereomers.

(49) Monoclinic, C_2; a = 2151.0 (1), b = 6131 (1), c = 1673.1 (1) pm; β = 109.60 (1)°; $V = 2.078 \times 10^9$ pm^3; Z = 4; ρ_{calcd} = 1.184 g/cm^3. Intensity measurements at 21 °C were carried out on an Enraf-Nonius CAD-4 diffractometer (154.18 pm, Cu Kα, monochromated, θ range 3° to 75°). The structure has been solved from 2423 observed independent reflections with $I > 3\sigma(I)$ by direct methods. The refinement, according to the full-matrix least-squares method, converged at R = 0.064 (R_w = 0.087). Further details of this crystal structure investigation, numbering of all atoms, positional parameters, general displacement parameter expressions (U's), bond distances, bond angles, and measured reflections (h, k, l) are included with the supplementary material.

(50) According to this rule, the (*RS,RS*) configuration corresponds to the major diastereomers **36** and **37**, respectively, of the reactions of α-phenylpropanal (**34**) and α-phenylbutanal (**35**) with allylmagnesium chloride. The minor products are therefore the (*RS,SR*) epimers **38** and **39**. See: (a) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828–5835. (b) Mulzer, J. *Nachr. Chem. Tech. Lab.* **1984**, *32*, 16–18. (c) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353–3361. (d) Hoffmann, R. W.; Brinkmann, H.; Frenking, G. *Chem. Ber.* **1990**, *123*, 2387–2394.

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The allyltitanium complexes derived from chloride **15** of this study are generally more stereoselective than the corresponding reagents obtained from the previously described[3a,17] diacetone glucose complex **28**. However, preliminary experiments have revealed[3] that the excellent results of the aldol reaction with titanium enolates derived from **28**[2,32] are not paralleled by using chloride **15** or any of the analogues described in this paper. A good *si* face selective titanium enolate based on this methodology is therefore still lacking.

Experimental Section

General Remarks. Specific rotations ($[\alpha]_D$) were measured in a 1-mL microcuvette (10 cm) on a Perkin-Elmer Polarimeter 241 at ambient temperature (20–25 °C). Capillary GLC analyses were done on a Carlo Erba Strumentazione HRGC 5300 chromatograph using Chirasil-Val-III columns[48] (50 m, 0.32-mm diameter, Altech Applied Science Labs, Deerfield, IL 60015, Serial No. 986 L). Considerable variation in retention time (t_R) and separation has been observed for different columns. Before injection, secondary alcohols were either derivatized with *N*-isopropyl isocyanate[48] or, if necessary for separation, with (*R*)-(+)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride[56] (MTPA chloride, see below). The accuracy and reproducibility of such determinations is ±0.1 to ±0.3%. If some variation in the reactions is accounted for as well (most reactions have been carried out only once or twice), the percentages of product ratios should be rounded to 0.5%, as has been done for simple experiments. In more complicated cases with more than two stereoisomeric products, the ratios were rounded to 0.1% in order to report the ratios of minor products as accurately as possible. ^{1}H NMR spectra were recorded on a Bruker AC-250 (250 MHz) or a Bruker AM-400 (400 MHz) instrument at 295 K or at a higher temperature, if indicated. ^{13}C NMR spectra were recorded on a Bruker AC-250 (62.9 MHz) or a Bruker AM-400 (100.6 MHz) spectrometer. The ^{47}Ti and ^{49}Ti NMR spectras at 22.571 and 22.577 MHz, respectively, were measured on a Bruker AM-400 spectrometer with a 10-mm diameter broad-band probe (20–100 MHz). All samples were measured as 0.4 M solutions in 10-mm tubes sealed under argon in toluene-d_8 at 373 ± 1 K or in $CDCl_3$ at 320 ± 1 K. To suppress acoustic ringing and (if necessary) the overlapping ^{47}Ti signal, a preacquisition delay of 140 μs was used. The ^{47}Ti signal can be suppressed efficiently in cases where $\Delta\nu_{1/2}(^{49}\text{Ti}) \geq 1000$ Hz, because $\Delta\nu_{1/2}(^{47}\text{Ti}) \approx 3\Delta\nu_{1/2}(^{49}\text{Ti})$. Errors in line widths and chemical shifts due to temperature differences were avoided by not using ^{1}H decoupling. To optimize the accuracy of peak positions, spectra were Gaussian-broadened between $^1/_5$ and $^1/_{10}$ of their natural line widths. Chemical shifts were recorded on the δ-scale relative to external $TiCl_4$. In a typical case ($\Delta\nu$ = 2400 Hz), a signal-to-noise ratio of 10 was achieved within 25 min of data acquisition.

Cyclopentadienyltitanium trichloride (**8**) was prepared from titanocene dichloride and $TiCl_4$,[26] and (pentamethylcyclopentadienyl)titanium trichloride (**14**) was prepared from pentamethyl(trimethylsilyl)cyclopentadiene and $TiCl_4$;[27] **8** and **14** were freshly sublimed before use. Allylmagnesium chloride in THF was purchased from Alfa Products (1.25 M; usually 0.8 M, when checked by titration[57]). Crotylmagnesium chloride was prepared according to O'Brien et al.,[39a] filtered from precipitated salts, and titrated.[57] KO(*t*-Bu) was freshly sublimed before use, and the content of *n*-butyllithium in hexane (Fluka AG) was determined by titration.[58] THF, diethyl ether (ether), toluene, and saturated hydrocarbons were distilled from Na–benzophenone ketyl for drying. (*R*,*R*)- and (*S*,*S*)-tartaric acid esters were purchased from Fluka AG. D-Glyceraldehyde acetonide (**40**, $[\alpha]_D$ = 75.7 (*c* = 6.66, C_6H_6)) was prepared from 1,2:5,6-di-*O*-isopropylidenemannitol,[44a,b] and *tert*-butyl (4*S*)- and (4*R*)-2,2-dimethyl-4-formyloxazolidine-3-carboxylate (L- and D-**41**) were prepared from L- and D-serine, respectively.[45] The optical purity of **41** was determined by capillary GLC (carrier 50 kPa, 115 °C): D-**41**, t_R = 13.7 min; L-**41**, t_R = 13.9 min.

General Procedure for the Derivatization of Alcohols with *N*-Isopropyl Isocyanate (GLC Analysis). A solution of alcohol (1 drop, 20–50 mg) in CH_2Cl_2 (2 mL) and *N*-isopropyl isocyanate (1 mL) is placed in a screw-cap ampoule with a high-pressure safety valve. After heating for 20 min in an oil bath of 100 °C with magnetic stirring, the volatile components of the cooled mixture are evaporated in a stream of dry argon. The residue is redissolved in CH_2Cl_2 (5 mL), and 0.2 μL of this solution is injected for GLC analysis.

General Procedure for Esterification of Alcohols with MTPA Chloride. To a solution of 45 mg of substrate in 0.7 mL of pyridine (dried with molecular sieves) are added 0.2 mL of (*R*)-(+)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride (MTPA chloride) and a few crystals (5–10 mg) of 4-(dimethylamino)pyridine. After stirring for 16 h at room temperature, 3-(dimethylamino)-1-propylamine (0.5 mL) is added and stirring is continued for 30 min. The mixture is poured into H_2O (25 mL) and 2 N H_2SO_4 (10 mL) and extracted with ether (20 mL, 20 mL, 10 mL). The combined organic extracts are washed with H_2O (20 mL) and saturated brine (20 mL), dried (Na_2SO_4), and evaporated. The residue is subjected to GLC analysis without further purification.

Synthesis of Ligands. 1. (4*R*,*trans*)-2,2-Dimethyl-α,α,α′,α′-tetrakis(pentafluorophenyl)-1,3-dioxolane-4,5-dimethanol ((*R*,*R*)-10). A solution of *n*-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol) was added dropwise over a period of 40 min to a solution of bromopentafluorobenzene (1.25 mL, 10 mmol) in 30 mL of Et_2O at −78 °C. After stirring for 10 min at room temperature, the reaction mixture was recooled to 0 °C, and an ethereal solution (20 mL) of (*R*,*R*)-**13**[24] (0.62 g, 2.5 mmol) was added dropwise. After stirring overnight, the mixture was hydrolyzed with saturated NH_4Cl (20 mL), filtered through Celite and extracted three times with 30 mL of ether. The combined organic phases were dried with Na_2SO_4 and filtered. Evaporation of solvent followed by flash chromatography of the residue (80 g of silica gel, hexane/ether 5:1) afforded 1.06 g (51%) of (*R*,*R*)-**10**: MS *m*/*e* (EI) 811 (M^+ − 15); ^{1}H NMR ($CDCl_3$, 250 MHz) 5.43 (s, H-C(4), H-C(5)), 4.95 (s, 2 O*H*), 1.40 (s, $(CH_3)_2C$). Anal. Calcd for $C_{31}H_{10}F_{20}O_4$: C, 45.06; H, 1.22; F, 45.98. Found: C, 45.20; H, 1.18; F, 46.03.

2. (4*R*,*trans*)-2,2-Dimethyl-α,α,α′,α′-tetra-2-furyl-1,3-dioxolane-4,5-dimethanol ((*R*,*R*)-11). A solution of *n*-BuLi (1.6 M in hexane, 97 mL, 155 mmol) was added via cannula to a precooled solution (−20 °C) of furan (11.62 mL, 60 mmol) in ether (100 mL). After 10 min, the cooling bath was removed, and the reaction mixture was stirred for 4 h at reflux temperature and cooled to 0 °C. After dropwise addition of diethyl (4*R*,*trans*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate[24] ((*R*,*R*)-**13**, 9.84 g, 40 mmol, dissolved in 20 mL of ether), the solution was stirred for 2 h at room temperature and boiled for 16 h under reflux. The reaction mixture was hydrolyzed with saturated aqueous NH_4Cl (300 mL), filtered through Celite, and extracted three times with 200 mL of ether. The combined organic phases were dried with Na_2SO_4 and filtered. Evaporation of the solvent followed by flash chromatography of the residue (800 g of silica gel, toluene/ether 10:1) afforded 5.6 g (33%) of **11**: MS *m*/*e* (EI) 426 (M^+); ^{1}H NMR ($CDCl_3$, 250 MHz) 7.48–7.36 (m, 4 H) and 6.48–6.30 (m, 8 H) (4 2-furyl), 4.20 (s, 2 O*H*), 4.78 (s, H-C(4), H-C(5)), 1.02 (s, $(CH_3)_2C$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 154.3 and 152.9 (2s), 142.4, 110.6, 110.3, 109.8, and 109.3, (5d) (4 2-furyl), 111.5 (s, $(CH_3)_2C$), 80.4 (d, C(4), C(5)), 72.6 (s, 2 *C*(furyl)$_2$O), 26.7 (q, $CH_3)_2C$)). Anal. Calcd for $C_{23}H_{22}O_8$: C, 64.78; H, 5.20. Found: C, 63.93; H, 5.18.

3. (4*R*,*trans*)-2,2-Dimethyl-α,α,α′,α′-tetra-2-propenyl-1,3-dioxolane-4,5-dimethanol ((*R*,*R*)-12). Magnesium turnings (13.8 g, 575 mmol) were suspended in 50 mL of THF, and 43.7 mL (500 mmol) of 2-bromopropene were added dropwise during a period of 1.5 h. After stirring for 2 h at room temperature, the reaction mixture was stirred for 1 h at reflux temperature and cooled to 0 °C. Dropwise addition of a solution of (*R*,*R*)-**13**[24] (24.6 g, 100 mmol) dissolved in 50 mL of Et_2O was followed by stirring for 10 h at room temperature. The reaction mixture was then hydrolyzed with 2 N H_2SO_4 (250 mL), filtered through Celite, and extracted three times with 200 mL of ether. The combined organic phases were dried with Na_2SO_4 and filtered. Evaporation of the solvent followed by flash chromatography of the residue (1000 g of silica gel, hexane/ether 5:1) afforded 6.1 g (19%) of (*R*,*R*)-**12**: MS *m*/*e* (EI) 322 (M^+); ^{1}H NMR ($CDCl_3$, 250 MHz) 5.28, 5.21, 5.14, and 5.03 (4s, split by small couplings, 4 CH_2=C), 4.40 (s, H-C(4), H-C(5)), 3.10 (bs, 2 O*H*), 1.80 and 1.73 (2s, 4 CH_3C=), 1.40 (s, $(CH_3)_2C$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 146.1 and 145.7 (2s, 4 CH_3C=), 114.3 and 113.7 (2t, 4 CH_2=C), 98.4 (s, $(CH_3)_2C$), 80.2 (d, C(4), C(5)), 79.1 (s, 2 CH_2=C(CH_3)COH), 27.2 (q, $(CH_3)_2C$), 21.0 and 19.4 (2q, 4 CH_3C=CH_2). Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 71.09; H, 9.61.

Preparation of Titanium Complexes. 1. Cyclopentadienyl[(4*R*,*trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*′]titanium Chloride ((*R*,*R*)-15). (a) Neutralization with Et_3N. A solution/suspension of freshly sublimed cyclopentadienyltitanium trichloride ($CpTiCl_3$, **8**)[26] (11 g, 50 mmol) in Et_2O (400 mL, distilled from Na/benzophenone) was treated with (4*R*,*trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol[15a] (23.3 g, 50 mmol) under argon with exclusion of moisture. After 2 min at room temperature (RT), a solution of NEt_3 (12.65 g, 110 mmol) in 125 mL of Et_2O was added dropwise to the stirred mixture over 1 h (efficient stirring is essential). After additional stirring for 12 h, Et_3N·HCl (13.8 g) was filtered off under argon and washed three times with ca. 50 mL of Et_2O. This solution (610 mL) was assumed to be 82 mM and can be used directly if desired. Crystals of (*R*,*R*)-**15** will, however, separate after

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a few days if this solution is stored. *Isolation*: The solution was concentrated under reduced pressure to ca. 75 mL, and 300 mL of hexane was added. After stirring for 30 min, the suspension was filtered, and the residue was washed three times with 10 mL of hexane, yielding 26.8 g (87%) of analytically pure (*R,R*)-**15**.

(b) Evaporation of HCl. A solution/suspension of freshly sublimed $CpTiCl_3$ (**8**)[26] (2.195 g, 10 mmol) in 200 mL of absolute cyclohexane was treated with 4.655 g (10 mmol) of (4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol.[15a] The reaction apparatus was fitted with a Soxhlet extractor containing 8.0 g of MgO (activated for 4 h at 300 °C). After the mixture was stirred for 12 h under reflux temperature, the solvent was evaporated. The residue was twice dissolved in 100 mL of absolute ether, stirred for 15 min, and concentrated, yielding 6.0 g (98%) of analytically pure (*R,R*)-**15**: ^{1}H NMR (CD_2Cl_2, 400 MHz) 7.65–7.27 (m, 20 H, aryl), 6.43 (s, C_5H_5), 5.16 and 4.95 (2d, *J* = 7.0, H-(C4), H-C(5), 0.94 and 0.50 (2s, $(CH_3)_2C$); ^{13}C NMR (CD_2Cl_2, 100 MHz) 148.87, 146.72, 142.86, and 142.72 (4s), 129.75, 129.08, 128.60, 128.36, 127.99, 127.92, 127.73, 127.68, 127.59, 127.57, 127.55, 127.49 (12d) (4 C_6H_5), 117.48 (d, C_5H_5), 111.71 (s, C(2)), 98.65 and 98.06 (2s, 2 $C(Ph)_2O$), 82.12 and 81.67 (2d, C(4), C(5)), 27.60 and 27.00 (2q, $(CH_3)_2C$).

2. Cyclopentadienyl[(4*S,trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium chloride (*S,S*)-15 was prepared from (4*S,trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol[15a] according to the procedure described above for the synthesis of (*R,R*)-**15**.

3. (Pentamethylcyclopentadienyl)[(4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-16). A solution of Cp^*TiCl_3 (**14**)[27] (1.37 g, 6.0 mmol) in 75 mL of toluene was treated with 2.80 g (6.0 mmol) of (4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol.[15a] After 5 min at room temperature, a solution of NEt_3 (1.212 g, 12 mmol, in 15 mL of toluene) was added over 45 min to the stirred mixture. The reaction mixture was boiled for 6 days under reflux; another portion of NEt_3 (0.177, 1.75 mmol) had been added after 3 days. The reaction was cooled to RT, and 1.48 g (90%) of Et_3N·HCl was removed by filtration. The solvent was evaporated under reduced pressure to yield 3.89 g of crude product, which was contaminated with 14% of unreacted ligand according to ^{1}H NMR spectroscopy. An analytically pure sample was obtained by recrystallization from chloroform at −30 °C: ^{1}H NMR (C_6D_6, 250 MHz) 7.82–7.54 (m, 8 H), 7.28–6.95 (m, 12 H), 5.60 and 5.54 (2d, *J* = 7.0, H-(C4), H-C(5)), 1.90 (s, $C_5(CH_3)_5$), 0.65 and 0.60 (2s, $(CH_3)_2C$); ^{13}C NMR (C_6D_6, 62.89 MHz) 148.40, 147.07, 144.71, and 144.51 (4s), 130.74, 130.28, 129.11, 128.43, 128.11, 127.99, 127.74, 127.56, 127.52, 127.47, 127.30, 127.14 (12d) (4 C_6H_5), 128.40 (s, $C_5(CH_3)_5$), 112.70 (s, C(2)), 96.79 and 96.53 (2s, 2 $C(Ph)_2O$), 81.85 and 80.29 (2d, C(4), C(5)), 28.07 and 27.97 (2q, $(CH_3)_2C$), 12.4 (q, $C_5(CH_3)_5$).

4. Cyclopentadienyl[(4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetrakis(pentafluorophenyl)-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-17). $CpTiCl_3$ (**8**)[26] (1.23 g, 5.59 mmol) in ether (60 mL) was treated with (4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetrakis(pentafluorophenyl)-1,3-dioxolane-4,5-dimethanol ((*R,R*)-**10**) (5.13 g, 5.59 mmol) and NEt_3 (1.23 g, 12.3 mmol, in 25 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 130 mL of a solution which was assumed to be 43 mM (used directly for further reactions).

5. Cyclopentadienyl[(4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetra-2-furyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-18). $CpTiCl_3$ (**8**)[26] (0.88 g, 4.0 mmol) in ether (60 mL) was treated with (4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetra-2-furyl-1,3-dioxolane-4,5-dimethanol ((*R,R*)-**11**) (1.70 g, 4.0 mmol) and NEt_3 (0.89 g, 8.8 mmol, in 16 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 120 mL of a solution which was assumed to be 31 mM (used directly for further reactions).

6. Cyclopentadienyl[(4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetra-2-propenyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-19). $CpTiCl_3$ (**8**)[26] (0.88 g, 4.0 mmol) in ether (60 mL) was treated with (4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetra-2-propenyl-1,3-dioxolane-4,5-dimethanol ((*R,R*)-**12**) (1.29 g, 4.0 mmol) and NEt_3 (0.89 g, 8.8 mmol, in 16 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 120 mL of a solution which was assumed to be 31 mM. For analytical purposes, 5 mL of this solution was evaporated under reduced pressure, affording 25 mg of (*R,R*)-**19**: ^{1}H NMR ($CDCl_3$, 250 MHz) 6.49 (s, C_5H_5), 5.34, 5.26, 5.22, and 5.16 (4s, split by small couplings, 4 CH_2=C), 5.13, 5.11, 5.09, and 4.96 (4dq, *J* = 1.0, 1.0, 4 CH_2=C), 4.67 and 4.35 (2d, *J* = 7.0, H-C(3), H-C(4)), 1.72, 1.69, 1.65, and 1.50 (4s, split by small couplings, 4 CH_3C=), 1.27 and 1.25 (2s, $(CH_3)_2C$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 146.3, 145.5, 145.4, and 144.0 (4s, 4 CH_3C=), 117.1, 114.4, 112.9, and 112.8 (4t, 4 CH_2=C), 116.4 (d, C_5H_5), 109.9 (s, C(2)), 99.8 and 99.3 (2s, 2 CH_2=$C(CH_3)CO$), 81.4 and 80.8 (2d, C(3), C(4)), 27.5 and 27.4 (2q, $(CH_3)_2C$), 22.6, 22.3, 19.0, and 18.9 (4q, 4 CH_3C=CH_2).

7. Cyclopentadienyl[(4*R,trans*)-2,2,α,α,α′,α′-hexamethyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-20). $CpTiCl_3$ (**8**)[26] (1.10 g, 5.0 mmol) in ether (75 mL) was treated with (4*R,trans*)-2,2-dimethyl-α,α,α′,α′-tetramethyl-1,3-dioxolane-4,5-dimethanol[15a] (1.09 g, 5.0 mmol) and NEt_3 (1.10 g, 11.0 mmol, in 10 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 120 mL of a solution which was assumed to be 41 mM. For analytical purposes, 5 mL of this solution was evaporated under reduced pressure, affording 40 mg of (*R,R*)-**20**: ^{1}H NMR ($CDCl_3$, 250 MHz) 6.48 (s, C_5H_5), 4.05 and 3.60 (2d, *J* = 8.0, H-C(4), H-C(5)), 1.35 (s, 2 CH_3), 1.34 and 1.29 (2s, 2 CH_3), 1.26 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$, 62.89 MHz) 115.4 (d, C_5H_5), 107.7 (s, C(2)), 91.6 and 91.5 (2s, 2 $C(CH_3)_2O$), 82.6 and 81.9 (2d, C(4), C(5)), 29.0, 28.7, 27.5, 27.4, 21.45, and 22.25 (6q, 6 CH_3).

8. (Pentamethylcyclopentadienyl)[(4*R,trans*)-2,2,α,α,α′,α′-hexamethyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-21). Cp^*TiCl_3 (**14**)[27] (0.724 g, 2.5 mmol) in 40 mL of ether was treated with (4*R,trans*)-2,2,α,α,α′,α′-hexamethyl-1,3-dioxolane-4,5-dimethanol[15a] (0.545 g, 2.5 mmol) and NEt_3 (0.55 g, 5.5 mmol, in 20 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 90 mL of a solution which was assumed to be 25 mM and was used directly for further reactions. For analytical purposes, 5 mL of this solution was evaporated under reduced pressure, affording 60 mg of (*R,R*)-**21**: ^{1}H NMR ($CDCl_3$, 250 MHz) 3.90 and 3.60 (2d, *J* = 7.0, H-(C4), H-C(5)), 2.01 (s, $C_5(CH_3)_5$), 1.30, 1.28, 1.24, 1.21, 1.20, and 1.18 (6s, 3 $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 62.89 MHz) 126.49 (s, $C_5(CH_3)_5$), 108.11 (s, C(2)), 89.74 and 89.62 (2s, 2 $C(CH_3)_2O$), 82.80 and 82.68 (2d, C(4), C(5)), 27.89 and 27.75 (2q, $(CH_3)_2C$), 31.31, 29.00, 23.32, and 21.92 (4q, 2 $C(CH_3)_2O$), 12.18 (q, $C_5(CH_3)_5$).

9. Cyclopentadienyl[(4*R,trans*)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-22). $CpTiCl_3$ (**8**)[26] (2.20 g, 10.0 mmol) in ether (125 mL) was treated with (4*R,trans*)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol[15a] (4.38 g, 10.0 mmol) and NEt_3 (2.12 g, 21 mmol, in 20 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 170 mL of a solution which was assumed to be 58 mM. For analytical purposes, 5 mL was evaporated under reduced pressure, affording 180 mg of (*R,R*)-**22**: ^{1}H NMR ($CDCl_3$, 250 MHz) 7.85–7.18 (m, 20 H, 4 C_6H_5), 6.48 (s, C_5H_5), 5.05 and 4.02 (2d, *J* = 0.5, 2 H-C(2)), 4.94 and 4.86 (2d, *J* = 5.0, H-C(4), H-C(5)).

10. Cyclopentadienyl[(4*S,trans*)-2-*tert*-butyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*S,S*)-23/24). $CpTiCl_3$ (**8**)[26] (0.55 g, 2.5 mmol) in 50 mL of ether was treated with (4*S,trans*)-2-*tert*-butyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol[15a] (1.24 g, 2.5 mmol) and NEt_3 (0.55 g, 5.5 mmol) in 10 mL of ether according to the synthesis of (*R,R*)-**15**, yielding 90 mL of a solution which was assumed to be 27 mM. For analytical purposes, 5 mL of this solution was evaporated under reduced pressure, affording 30 mg of (*S,S*)-**23/24** as a 4:1 mixture of C(2) epimers according to ^{1}H NMR analysis. *Main isomer*: ^{1}H NMR (CD_2Cl_2, 400 MHz) 7.20–7.70 (m, 4 C_6H_5), 6.26 (s, C_5H_5), 4.86 and 4.79 (2d, *J* = 6.5, H-C(4), H-C(5)), 3.43 (s, H-C(2)), 0.84 (s, $C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2, 100 MHz) 147.22, 146.79, 142.83, and 142.17 (4s), 128.73, 128.59, 128.24, 128.08, 127.99, 127.92, 127.91, 127.89, 127.59, 127.53, 127.47, 127.33 (12d) (4 C_6H_5), 117.32 (d, Cp), 109.42 (d, C(2)), 97.88 and 97.27 (2s, 2 $C(Ph)_2O$), 83.83 and 80.30 (2d, C(4), C(5)), 35.51 (s, $C(CH_3)_3$), 24.74 (q, $C(CH_3)_3$). *Minor isomer*: ^{1}H NMR (CD_2Cl_2, 400 MHz) 7.20–7.70 (m, 4 C_6H_5), 6.56 (s, C_5H_5), 5.03 and 4.78 (2d, *J* = 7.5, H-C(4), H-C(5)), 3.44 (s, H-C(2)), 0.61 (s, $C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2, 100 MHz) 146.49, 146.45, 142.53, and 142.06 (4s), 129.25, 128.84, 128.63, 128.53, 128.16, 128.07, 127.99, 127.92, 127.88, 127.55, 127.46, and 127.17 (12d) (4 C_6H_5), 117.80 (d, Cp), 109.85 (d, C(2)), 97.52 and 97.40 (2s, 2 $C(Ph)_2O$), 80.83 and 80.01 (2d, C(4), C(5)), 35.30 (s, $C(CH_3)_3$), 24.38 (q, $C(CH_3)_3$).

11. Cyclopentadienyl[(4*R,trans*)-2,2,α,α,α′,α′-hexaphenyl-1,3-dioxolane-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-25). $CpTiCl_3$ (**8**)[26] (1.04 g, 4.73 mmol) in ether (60 mL) was treated with (4*R,trans*)-2,2,α,α,α′,α′-hexaphenyl-1,3-dioxolane-4,5-dimethanol[23c] (2.79 g, 4.73 mmol) and NEt_3 (1.0 g, 9.9 mmol, in 10 mL of ether) according to the synthesis of (*R,R*)-**15**, yielding 105 mL of a solution which was assumed to be 45 mM. For analytical purposes, 5 mL was evaporated under reduced pressure, affording 170 mg of (*R,R*)-**25**: ^{1}H NMR ($CDCl_3$, 250 MHz) 7.68–6.40 (m, 6 C_6H_5), 6.32 (s, C_5H_5), 5.33 and 5.18 (2d, *J* = 7.0, H-(C5), H-C(4)); ^{13}C NMR ($CDCl_3$, 62.89 MHz) 146.40, 146.27, 144.03, 143.44, 141.32, and 140.23 (6s), 129.3–125.2 (18d) (6 C_6H_5), 116.80 (d, C_5H_5), 112.24 (s, C(2)), 98.39, and 97.80 (2s, $C(Ph)_2O$), 84.27 and 83.47 (2d, C(5), C(4)).

12. Cyclopentadienyl[(4*R,trans*)-α,α,α′,α′-tetraphenylspiro[1,3-dioxolane-2,9′-(9*H*)-fluorene]-4,5-dimethanolato-*O,O*′]titanium Chloride ((*R,R*)-26). $CpTiCl_3$ (**8**)[26] (1.12 g, 5.1 mmol) in ether (65 mL) was

treated with (4*R*,*trans*)-α,α,α′,α′-tetraphenylspiro[1,3-dioxolane-2,9′-(9*H*)-fluorene]-4,5-dimethanol[23c] (3.28 g, 5.1 mmol) and NEt_3 (1.08 g, 10.7 mmol, in 10 mL of ether) according to the synthesis of (*R*,*R*)-**15**, yielding 105 mL of a solution which was assumed to be 48 mM. For analytical purposes, 2 mL was evaporated under reduced pressure, affording 70 mg of (*R*,*R*)-**26**: ^{1}H NMR ($CDCl_3$, 250 MHz) 7.60–7.05 (m, 24 H), 6.76 and 6.70 (2ddd, *J* = 7.0, 7.0, 0.5, *H*-C(2′), *H*-C(7′), fluorenyl), 6.55 (s, C_5H_5), 5.58 and 5.29 (2d, *J* = 7.5, H-(C5), H-C(4)), 5.28 and 5.22 (2d, *J* = 7.0, *H*-C(1′), *H*-C(8′), fluorenyl); ^{13}C NMR ($CDCl_3$, 62.89 MHz) 146.6, 145.6, 143.4, 143.3, 142.6, 142.5, 139.3, and 139.1 (8s), 129.8, 129.7, 129.6, 129.3, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 127.2, and 126.9 (12d), 124.3, 124.0 (2d, C(1′), C(8′), fluorenyl), 119.1, 119.0 (2d, C(4′), C(5′), fluorenyl), 117.3 (d, C_5H_5), 113.4 (s, C(2)), 98.2 and 98.1 (2s, $C(Ph)_2O$), 81.2 and 80.6 (2d, C(4), C(5)).

13. Reaction of $CpTiCl_3$ (8) with (4*S*,*trans*)-2,2-Dimethyl-1,3-dioxolane-4,5-dimethanol ((*S*,*S*)-27). $CpTiCl_3$ (**8**)[26] (0.55 g, 2.5 mmol) in ether (30 mL) was treated with **27**[24] (0.41 g, 2.5 mmol) and NEt_3 (0.53 g, 5.25 mmol, in 10 mL of ether) according to the synthesis of (*R*,*R*)-**15**, yielding (105 mL) of a stock solution which was assumed to be 48 mM. For analytical purposes, 10 mL of the solution was evaporated under reduced pressure affording, according to NMR analysis, 90 mg of a product mixture (oligomers): ^{1}H NMR ($CDCl_3$, 250 MHz) 6.58, 6.56, 6.54, 6.52 (4s, 4 C_5H_5), 4.82–4.36 (m), 4.32–3.60 (m), 1.55–1.40 (m); ^{13}C NMR ($CDCl_3$, 62.89 MHz) 118.0, 117.6, 117.2, and 116.9 (4d, C_5H_5), 109.85, 109.6, 109.55, 109.2, (4s, 4 C(2)), 81.0, 80.6, 80.2, 79.4, 79.0, 78.8, 78.5 (7t), 79.5, 78.7, 78.3, 78.1, 77.1, 77.1, 77.0 (7d), 29.6, 28.1, 27.5, 27.1 (4q).

14. Cyclopentadienyl[(4*R*,*trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*′]-2-propenyltitanium ((*R*,*R*)-9). Allylmagnesium chloride in THF (1.8 mL of a 1.25 M solution, 2.25 mmol) was added dropwise at 0 °C under argon to 30 mL of a 82 mM ethereal solution of (*R*,*R*)-**15** (2.46 mmol) over 10 min. After stirring for 1 h, the reaction mixture was filtered under argon, and the solvent was removed under reduced pressure, affording 1.28 g (93%) of (*R*,*R*)-**9**: ^{1}H NMR (CD_2Cl_2, 250 MHz, RT) 7.65–7.27 (m, 4 C_6H_5), 6.15 (s, C_5H_5), 5.85 (quint, *J* = 11.5, H-C(2′)), 5.40 and 4.78 (2d, *J* = 7.0, H-C(4), H-C(5)), 3.36 (d, *J* = 11.5, 2 *H*-C(1′) and 2 *H*-C(3′)), 0.72 and 0.58 (2s, 2 CH_3); ^{13}C NMR (CD_2Cl_2, 62.9 MHz, RT) 148.48, 147.86, 143.85, and 143.23 (4s), 129.8–127.5 (12 d) (C_6H_5), 143.4 (d, C(2′)), 115.25 (d, C_5H_5), 112.10 (s, C(2)), 94.90 (2s, 2 $C(Ph)_2O$), 88.0 (t, C(1′), C(3′)), 82.30, 82.25 (2d, C(4), C(5)), 27.67, 27.64 (2q, 2 CH_3). (Upon cooling to −100 °C, the dynamic process was still in the fast exchange limit, even for ^{13}C NMR at a spectrometer frequency of 100.6 MHz.)

15. Cyclopentadienyl[(4*R*,*trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*′]-(*E*)-but-2-enyltitanium ((*R*,*R*)-29). Crotylmagnesium chloride (10 mL, 10 mmol, 1 M in ether) was added dropwise at 0 °C under argon to a solution of (*R*,*R*)-**15** (6.29 g, 10.25 mmol) in 125 mL of ether over 10 min. After stirring for 1 h at 0 °C, the reaction mixture was filtered under argon. Evaporation of the solvent afforded 4.93 g (78%) of (*R*,*R*)-**29**: ^{1}H NMR (CD_2Cl_2, 250 MHz, RT) 7.65–7.15 (m, 4 C_6H_5), 6.08 (s, C_5H_5), 5.46 (dtq, *J* = 14.0, 8.5, 1.5, H-C(2′)), 4.82 (dq, *J* = 14.0, 6.5, H-C(3′)), 5.38 and 4.75 (2d, *J* = 7.0, H-C(4), H-C(5)), 2.26 and 2.17 (2dd, *J* = 8.5, 8.5, 2 H-C(1′)), 1.67 (dd, *J* = 8.5, 1.5, $CH_3C(3')$), 0.68 and 0.58 (2s, 2 CH_3).

Allyltitanation of Aldehydes. 1. (1*S*)-1-Phenyl-3-buten-1-ol ((*S*)-4). **(a) With Complex (*R*,*R*)-15.** Allylmagnesium chloride in THF (5.3 mL of a 0.8 M solution, 4.25 mmol) was added dropwise over 10 min at 0 °C under argon to a solution of (*R*,*R*)-**15** (3.06 g, 5 mmol) in 60 mL of ether. After stirring for 1.5 h at 0 °C, the slightly orange suspension was cooled to −74 °C, and benzaldehyde (**3**, 403 mg, 3.8 mmol, dissolved in 5 mL of ether) was added over 2 min. Stirring at −74 °C was continued for 3 h. The reaction mixture was then treated with 20 mL of aqueous 45% NH_4F solution, sitrred for 12 h at room temperature, filtered through Celite, and extracted twice with ether (50 mL). The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated. The solid residue was stirred with 50 mL of pentane. Subsequent filtration furnished 1.68 g of white crystalline (4*R*,*trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (ligand). Chromatography of the residue of the filtrate (1.54 g, 200 g of silica gel, CH_2Cl_2/hexane/ether 4:4:1) finally afforded 521 mg (93%) of (*S*)-**4** (95% ee), as determined by capillary GLC (carrier 70 kPa, 160 °C, after derivatization with *N*-isopropyl isocyanate): (*R*)-**4** 2.5%, t_R = 14.9 min; (*S*)-**4** 97.5%, t_R = 15.3 min; $[\alpha]_D$ = −47.9 (*c* = 5.0, C_6H_6).

Addition of benzaldehyde at −35 °C and additional stirring for 2 h at this temperature afforded (*S*)-**4** of 93% ee. The same reaction at 0 °C gives (*S*)-**4** of 89% ee.

(b) With Complex (*R*,*R*)-16. Allylmagnesium chloride (3.44 mmol) in THF (4 mL) was added to a solution of (*R*,*R*)-**16** (2.63 g, 3.85 mmol) in ether (60 mL) at 0 °C. After the solution was stirred for 2 h at 0 °C, approximately one-third of the reaction mixture was transferred via cannula into a separate Schlenk tube, cooled to −74 °C, and treated with benzaldehyde (**3**, 0.12 g, 1.14 mmol, reaction I). The remaining solution of reagent (*R*,*R*)-**9** was stirred for an additional 3 h at 0 °C before it was divided as before into two equal parts. While the first part was treated at 0 °C with benzaldehyde (**3**, 0.12 g, 1.14 mmol, reaction II), the second was quenched at −74 °C with **3** (0.12 g, 1.14 mmol, reaction III). Workup as described above gave a total of 86% of (*S*)-**4**, 84% ee from reaction I and 87% ee from reactions II and III.

(c) With Complex (*R*,*R*)-17. Reaction of benzaldehyde (**3**, 61 mg, 0.58 mmol) with the complex prepared from allylmagnesium chloride (0.58 mmol) and 15 mL of a 43 mM ethereal solution of (*R*,*R*)-**17** (0.645 mmol) according to preparation a afforded 53 mg (62%) of (*S*)-**4**, 54% ee, as determined by capillary GLC.

(d) With Complex (*R*,*R*)-18. Reaction of benzaldehyde (**3**, 341 mg, 3.22 mmol) with the complex prepared from allylmagnesium chloride (3.60 mmol) and 120 mL of a 31 mM ethereal solution of (*R*,*R*)-**18** (3.7 mmol) according to preparation a afforded 300 mg (63%) of (*S*)-**4**, 66% ee, as determined by capillary GLC.

(e) With Complex (*R*,*R*)-19. Reaction of benzaldehyde (**3**, 337 mg, 3.19 mmol) with the complex prepared from allylmagnesium chloride (3.6 mmol) and 120 mL of a 33 mM ethereal solution of (*R*,*R*)-**19** (4.0 mmol) according to preparation a afforded 250 mg (53%) of (*S*)-**4**, 71% ee, as determined by capillary GLC.

(f) With Complex (*R*,*R*)-20. Allylmagnesium chloride (1.4 mmol) was added to 39 mL of a 41 mM ethereal solution of (*R*,*R*)-**20** (1.6 mmol). After stirring for 2 h at 0 °C, approximately one-half of the reaction mixture was transferred via cannula in a separate Schlenk tube and treated immediately with benzaldehyde **3** at −78 °C (0.75 mg, 0.71 mmol, reaction I), whereas the same amount of **3** was added at 0 °C to the other part of the reagent solution (reaction II). Usual workup gave a total of 0.14 g (66%) of (*S*)-**4**, with 14% ee from reaction I and 11% ee from reaction II.

(g) With Complex (*R*,*R*)-21. Reaction of benzaldehyde (**3**, 211 mg, 1.99 mmol) with the complex prepared from allylmagnesium chloride (2.25 mmol) and 85 mL of a 27 mM ethereal solution of (*R*,*R*)-**21** (2.36 mmol) according to preparation a afforded 260 mg (88%) of (*S*)-**4**, 88% ee, as determined by capillary GLC.

(h) With Complex (*R*,*R*)-22. Reaction of benzaldehyde (**3**, 340 mg, 3.2 mmol) with the complex prepared from allylmagnesium chloride (3.6 mmol) and 74 mL of a 58 mM ethereal solution of (*R*,*R*)-**22** (4.3 mmol) according to preparation a afforded 460 mg (97%) of (*S*)-**4**, 80% ee, as determined by capillary GLC.

(i) With Complex (*S*,*S*)-23/24. Reaction of benzaldehyde (**3**, 211 mg, 1.99 mmol) with the complex prepared from allylmagnesium chloride (2.25 mmol) and 2.5 mmol of (*S*,*S*)-**23/24** in 80 mL of ether according to preparation a afforded 165 mg (56%) of (*R*)-**4**, 82% ee, as determined by capillary GLC.

(j) With Complex (*R*,*R*)-25. Reaction of benzaldehyde (**3**, 338 mg, 3.19 mmol) with the complex prepared from allylmagnesium chloride (3.6 mmol) and 96 mL of a 43 mM ethereal solution of (*R*,*R*)-**25** (4.3 mmol) according to preparation a afforded 458 mg (97%) of (*S*)-**4**, 89% ee, as determined by capillary GLC.

(k) With Complex (*R*,*R*)-26. Reaction of benzaldehyde (**3**, 338 mg, 3.19 mmol) with the complex prepared from allylmagnesium chloride (3.6 mmol) and 90 mL of a 43 mM ethereal solution of (*R*,*R*)-**26** (4.3 mmol) according to preparation a afforded 448 mg (95%) of (*S*)-**4**, 91% ee, as determined by capillary GLC.

(l) With the Complex Mixture Obtained from $CpTiCl_3$ (8) and Isopropylidenethreitol (*S*,*S*)-27. Reaction of benzaldehyde (**3**, 211 mg, 1.99 mmol) with a reagent prepared from allylmagnesium chloride (2.0 mmol) and the solution of the conversion of $CpTiCl_3$ (2.46 mmol) with **27** (2.46 mmol) in ether (90 mL) according to preparation a afforded 59 mg (20%) of (*S*)-**4**, 6% ee, as determined by capillary GLC.

2. (4*R*)-1-Tridecen-4-ol ((*R*)-30). Allylmagnesium chloride in THF (10.6 mL of a 0.8 M solution, 8.5 mmol) was added dropwise over 10 min at 0 °C under argon to 120 mL of a 82 mM solution of (*R*,*R*)-**15** (9.84 mmol). After stirring for 1 h at 0 °C, the slightly orange suspension was cooled to −74 °C, and decanal (1.188 g, 7.6 mmol, dissolved in 5 mL of ether) was added over 2 min. The mixture was stirred for 3 h at −74 °C. After hydrolysis with 45% aqueous NH_4F solution (20 mL, 12 h, RT), the reaction mixture was filtered through Celite and extracted twice with ether (50 mL). The combined extracts were washed with brine, dried with $MgSO_4$, and concentrated. Trituration with pentane (25 mL) and separation of precipitated (4*R*,*trans*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-3,4-dimethanol (2.2 g, ligand) furnished 2.22 g of crude (*R*)-**30**, a small sample of which was derivatized with *N*-isopropyl isocyanate for GLC analysis (carrier 50 kPa, 160 °C): (*S*)-**30** 2.8%, t_R = 35.3 min; (*R*)-**30** 97.2%, t_R = 36 min, 94.4% ee. The remaining crude (*R*)-**30** was purified by acetylation (Ac_2O/pyridine, 15 h at 0 °C). Removal of reagents by azeotropic distillation with hexanes

(2 × 500 mL) and chromatography (250 g of silica gel, hexane/ether 20:1) finally afforded 1.72 g (94%) of (*R*)-1-tridecen-4-yl acetate ((*R*)-**30a**).

3. (4*S*)-5-Methylhexen-4-ol ((*S*)-31). Allylmagnesium chloride in THF (2.9 mL of a 1.25 M solution, 3.6 mmol) was added to 80 mL of a 63 mM ethereal solution of (*R*,*R*)-**15** (5.0 mmol). Reaction with 2-methylpropionaldehyde (288 mg, 4.0 mmol) according to the procedure described above for the synthesis of (*R*)-**30**, usual workup, and chromatography (80 g of silica gel, pentane/ether 5:1) afforded 400 mg (88%) of (*S*)-**31**, 97% ee, as determined by capillary GLC (carrier 50 kPa, 110 °C, derivatization with *N*-isopropyl isocyanate): (*S*)-**31** 98.6%, t_R = 18.82 min; (*R*)-**31** 1.4%, t_R = 19.1 min; 97.2% ee.

4. (3*S*)-2,2-Dimethyl-5-hexen-3-ol ((*S*)-32). Allylmagnesium chloride in THF (3.4 mL of a 1.25 M solution, 4.25 mmol) was added to 72 mL of a 63 mM ethereal solution of (*R*,*R*)-**15** (4.5 mmol). Reaction with trimethylacetaldehyde (330 mg, 3.8 mmol) according to the procedure described above for the synthesis of (*R*)-**30** but extending the reaction time from 3 to 18 h at −74 °C, usual workup, Kugelrohr distillation (150 °C, 20 mbar), and chromatography (38 g of silica gel, pentane/ether 4:1) afforded 307 mg (63%) of (*S*)-**32**, 97% ee, as determined by capillary GLC (carrier 50 kPa, 110 °C, derivatization with *N*-isopropyl isocyanate): (*S*)-**32** (98.54%, t_R = 21.5 min; (*R*)-**32** 1.46%, t_R = 22.0 min; 97.1% ee.

5. (3*S*)-1,5-Hexadien-3-ol ((*S*)-33). Allylmagnesium chloride in THF (3.6 mL of a 1.25 M solution, 4.5 mmol) was added to 80 mL of a 63 mM ethereal solution of (*R*,*R*)-**15** (5.0 mmol). Reaction with acrolein (225 mg, 4.0 mmol) according to the procedure described above for the synthesis of (*R*)-**30**, usual workup, and chromatography (250 g of silica gel, pentane/ether 5:1) afforded 448 mg (79%) of (*S*)-**33**, 95% ee, as determined by capillary GLC (carrier 50 kPa, 140 °C, derivatization with MTPA chloride): (*R*)-**33** 2.4%, t_R = 16.8 min; (*S*)-**33** 97.6%, t_R = 17.4 min; 95.2% ee.

6. Reaction of (2*RS*)-2-phenylpropanal ((±)-34) with allylmagnesium chloride gave a 65.6:34.4 mixture of (4*RS*,5*RS*)-5-phenyl-1-hexen-4-ol ((±)-**36**) and (4*RS*,5*SR*)-5-phenyl-1-hexen-4-ol ((±)-**38**), as determined by capillary GLC (carrier 50 kPa, 200 °C, derivatization with MTPA chloride): (4*S*,5*R*) isomer, (*S*)-**38** 17.2%, t_R = 22.5 min; (4*R*,5*S*) isomer, (*R*)-**38** 17.2%, t_R = 23.1 min; (4*S*,5*S*) isomer, (*S*)-**36** (33.1%, t_R = 24.3 min; (4*R*,5*R*) isomer, (*R*)-**36** (32.5%, t_R = 24.6 min; 31.2% de.

7. Reaction of (2*RS*)-2-Phenylpropanal ((±)-34) with CP-(DAGO)$_2$Ti(allyl) (1). Allylmagnesium chloride in THF (7.0 mL of a 0.8 M solution, 5.6 mmol) was added at 0 °C to chloride **28** (68 mL of a 91.7 mM solution, 6.25 mmol) in ether[2,17,32] and stirred for 1.5 h. The reaction mixture was cooled to −78 °C, and (±)-**34** (6.71 mg, 5.0 mmol, dissolved in 5 mL of ether) was added. After stirring for 3 h at −78 °C, the reaction mixture was hydrolyzed for 12 h by adding 10 mL of THF/H_2O (1:1). Filtration through Celite and chromatography (160 g of silica gel, hexane/ether 4:1) afforded 815 mg (93%) of a 55.1:44.9 mixture of (*R*)-**36** (containing 12.5% of (*S*)-**36**, 75% ee) and (*R*)-**38** (containing 1.8% of (*S*)-**38**, 96.4% ee), as determined by capillary GLC (see above): (*S*)-**38**, 0.8%; (*R*)-**38**, 44.1%; (*S*)-**36**, 6.9%; (*R*)-**36**, 48.2%.

8. Reaction of (2*RS*)-2-Phenylpropanal ((±)-34) with (*S*,*S*)-9. Allylmagnesium chloride in THF (10.6 mL of a 0.8 M solution, 8.5 mmol) was added to 125 mL of a 78 mM ethereal solution of (*S*,*S*)-**15** (9.8 mmol), and (±)-**34** (1.02 g, 7.6 mmol, dissolved in 5 mL of ether) was added to the resulting reagent (*S*,*S*)-**9**, according to the procedure described for the synthesis of (*R*)-**30**. Chromatography (160 g of silica gel, hexane/ether 10:1) afforded 1.31 g (98%) of a 50.2:49.8 mixture of (*R*)-**36** (containing 2.6% of (*S*)-**36**, 94.8% ee) and (*R*)-**38** (containing 0.8% of (*S*)-**38**, 98.4% ee), as determined by capillary GLC (see above): (*S*)-**38**, 0.4%; (*R*)-**38**, 49.4%; (*S*)-**36**, 1.3%; (*R*)-**36**, 48.9%.

9. Reaction of (2*RS*)-2-phenylbutanal ((±)-35) with allylmagnesium chloride gave a 66:34 mixture of (4*RS*,5*RS*)-5-phenyl-1-hepten-4-ol ((±)-**37**) and (4*RS*,5*SR*)-5-phenyl-1-hepten-4-ol ((±)-**39**), as determined by capillary GLC (carrier 50 kPa, 200 °C, derivatization with MTPA chloride): (4*S*,5*R*) isomer, (*S*)-**39** 17%, t_R = 24.1 min; (4*R*,5*S*) isomer, (*R*)-**39** 17%, t_R = 25.6 min; (4*S*,5*S*) isomer, (*S*)-**37** 33%, t_R = 26.3 min; (4*R*,5*R*) isomer, (*R*)-**37** 33%, t_R = 26.8 min; 32% de. The diastereomers can be separated by chromatography (silica gel, hexane/ether 5:1). (4*RS*,5*SR*)-5-Phenyl-1-hepten-4-ol ((±)-**39**, eluted first): ^{1}H NMR ($CDCl_3$, 250 MHz) 7.28–7.08 (m, C_6H_5), 5.87–5.67 (m, H-C(2)), 5.06–4.94 (m, H-C(1)), 3.88–3.66 (m, H-C(4)), 2.44 (ddd, *J* = 10.0, 5.0, 5.0, H-C(5)), 2.30–2.15 (m, H-C(3)), 1.96 (ddd, *J* = 14.0, 8.0, 8.0, H-C(3)), 1.83–1.53 (m, 2 H, H-C(6)), 1.46 (bs, OH), 0.69 (t, *J* = 7.0, CH_3); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 141.02 (s, C_6H_5), 135.11 (d, C(2)), 128.98, 128.22, and 126.48 (3d, C_5H_5), 117.38 (t, C(1)), 73.61 (d, C(4)), 53.13 (d, C(5)), 39.49 (t, C(3)), 24.75 (t, C(6)), 12.09 (q, C(7)). (4*RS*,5*RS*)-5-Phenyl-1-hepten-4-ol ((±)-**37**, eluted second): ^{1}H NMR ($CDCl_3$, 250 MHz) 7.28–7.05 (m, C_6H_5), 5.77–5.61 (m, H-C(2)), 5.08–4.90 (m, H-C(1)), 3.72–3.62 (m, H-C(4)), 2.42 (ddd, *J* = 11.0, 8.0, 4.0, H-C(5)), 2.08–1.78 (m, 3 H, H-C(3), H-C(6)), 1.64 (d, *J* = 4.0, OH), 1.64–1.44 (m, H-C(6)), 0.67 (t, *J* = 7.0, CH_3); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 142.19 (s, C_6H_5), 135.06 (d, C(2)), 128.48, 128.37, and 126.41 (3d, C_5H_5), 118.14 (t, C(1)), 74.25 (d, C(4)), 53.10 (d, C(5)), 38.83 (t, C(3)), 24.26 (t, C(6)), 12.05 (q, C(7)).

10. Reaction of (2*RS*)-2-Phenylbutanal ((±)-35) with CP-(DAGO)$_2$Ti(allyl) (1). Allylmagnesium chloride in THF (7.0 mL of a 0.8 M solution, 5.6 mmol) was added at 0 °C to chloride **28** in ether (68 mL of a 91.7 mM solution, 6.25 mmol)[2,17,32] and stirred for 1.5 h. The reaction mixture was cooled to −78 °C, and (±)-**35** (6.71 mg, 5.0 mmol, dissolved in 5 mL of ether) was added. After stirring for 3 h at −78 °C, the reaction mixture was hydrolyzed for 12 h by adding 10 mL of THF/H_2O (1:1). Filtration through Celite and chromatography (160 g of silica gel, hexane/ether 4:1) afforded 907 mg (95%) of a 59.7:40.3 mixture of (*R*)-**37** (containing 17.4% of (*S*)-**37**, 65.2% ee) and (*R*)-**39** (containing 0.7% of (*S*)-**39**, 98.6% ee), as determined by capillary GLC (see above): (*S*)-**39**, 0.3%; (*R*)-**39**, 40.0%; (*S*)-**37**, 10.4%; (*R*)-**37**, 49.3%.

11. Reaction of (2*RS*)-2-phenylbutanal ((±)-35) with (*S*,*S*)-9 as described below for (*R*,*R*)-**9** afforded a 51.5:48.5 mixture of (*R*)-**37** (containing 4.8% of (*S*)-**37**, 90.4% ee) and (*R*)-**39** (containing ≤0.5% of (*S*)-**39**, ≥99% ee), as determined by capillary GLC (see above): (*S*)-**39**, ≤0.2%; (*R*)-**39**, 48.3%; (*S*)-**37**, 2.5%; (*R*)-**37**, 49.2%. An analytically pure sample of (*R*)-**39** was isolated by flash chromatography (silica gel, hexane/ether 5:1) ((*R*)-**39** eluted first), $[\alpha]_D$ = +9.0 (*c* = 6.21, C_6H_6).

12. (1*S*)-3-Oxo-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptane-1-carboxylic Acid (4*R*,5*S*)-5-Phenylhept-1-en-4-yl Ester (69). To a solution of (*R*)-**39** (66 mg, 0.35 mmol) in 10 mL of pyridine was added slowly (1*S*)-(−)-camphanic chloride (120 mg, 0.50 mmol) at 0 °C. After the mixture was stirred for 16 h at RT, 30 mL of CH_2Cl_2 was added. The organic phase was washed four times with 20 mL of cold 2 N HCl and once with 20 mL of saturated $NaHCO_3$ solution, dried with $MgSO_4$, and filtered. Evaporation of the solvent followed by flash chromatography (20 g of silica gel, hexane/ether 5:1) afforded 120 mg (93%) of **69**. Crystals suitable for X-ray analysis were grown at 0 °C from an ether solution: $[\alpha]_D$ = −2.35 (*c* = 0.765, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) 7.28–7.09 (m, Ph), 5.80–5.60 (m, H-C(2)), 5.07–4.95 (m, 2 H-C(1)), 5.33 (ddd, *J* = 7.0, 7.0, 4.5, H-C(4)), 2.66 (ddd, *J* = 10.5, 7.0, 4.5, H-C(5)), 2.46–2.32 (m, H-C(3)), 2.21 (ddd, *J* = 14.5, 8.0, 8.0, H-C(3)), 2.09–1.94 (m, 1 H), 1.80–1.40 (m, 5 H), 0.99, 0.86, 0.64 (3s, 3 CH_3), 0.69 (t, *J* = 7.0, $H_3C(7)$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 178.1 (s), 166.9 (s), 140.5 (s), 133.4 (d), 128.8 (d), 128.3 (d), 126.7 (d), 118.3 (t), 91.1 (s), 54.8 (s), 53.8 (s), 50.9 (d), 37.2 (t), 30.7 (t), 28.9 (t), 25.2 (t), 16.7 (q), 16.3 (q), 11.9 (q), 9.6 (q).

13. Reaction of (2*RS*)-2-Phenylbutanal ((±)-35) with (*R*,*R*)-9. Allylmagnesium chloride in THF (7 mL of a 0.8 M solution, 5.6 mmol) was added to 80 mL of a 78 mM ethereal solution of (*R*,*R*)-**15** (6.25 mmol), and the resulting (*R*,*R*)-**9** was brought to reaction with (±)-**35** (787 mg, 5.0 mmol, dissolved in 5 mL of ether) according to the procedure described for the synthesis of (*S*)-**30**. Chromatography (160 g of silica gel, hexane/ethyl acetate 6:1) afforded 864 mg (91%) of a 51.1:48.9 mixture of (*S*)-**37** (containing 4.7% of (*R*)-**37**, 90.6% ee) and (*S*)-**39** (containing 0.6% of (*R*)-**39**, 98.8% ee), as determined by capillary GLC (see above): (*S*)-**39**, 48.6%; (*R*)-**39**, 0.3%; (*S*)-**37**, 48.7%; (*R*)-**37**, 2.4%.

14. (2*R*,3*S*)-1,2-*O*-Isopropylidene-5-hexene-1,2,3-triol (43). Allylmagnesium chloride in THF (11.25 mL of a 0.8 M solution, 9 mmol) was added dropwise over 10 min at 0 °C under argon to 122 mL of a 82 mM ethereal solution of (*R*,*R*)-**15** (9.8 mmol) according to the general procedure. Reaction of the resulting (*R*,*R*)-**9** with (4*R*)-2,2-dimethyl-4-formyl-1,3-dioxolane (D-glyceraldehyde acetonide (**40**),[44] 1.04 g, 8.0 mmol, dissolved in 5 mL of ether) at −74 °C (4 h), usual workup, and chromatography (80 g of silica gel, pentane/ether 1:2) afforded 1.104 g (80%) of **43** ($[\alpha]_D$ = 16.6 (*c* = 1.1, C_6H_6); $[\alpha]_D$ = 15.5 (*c* = 1.1, $CHCl_3$); lit.[46d] $[\alpha]_D$ = 17.4 (*c* = 3.4, $CHCl_3$)), 95.8% de according to GLC analysis (carrier 50 kPa, 150 °C, derivatized with MTPA chloride): (2*R*,3*S*) isomer **43** (97.9%, t_R = 53.5 min; (2*R*,3*R*) isomer **44** 2.1%, t_R = 61.2 min; ^{13}C NMR ($CDCl_3$, 62.9 MHz, signals with significant shift differences compared to **44** are italicized) 133.94 (d, C(5)), 118.31 (t, C(6)), 109.00 (s, $C(CH_3)_2$), 78.05 (d, C(3)), *70.35* (d, C(2)), *65.16* (t, C(1)), *37.56* (t, C(4)), 26.52 and 25.24 (2q, $C(CH_3)_2$).

15. (2*R*,3*R*)-1,2-*O*-Isopropylidene-5-hexene-1,2,3-triol (44). Allylmagnesium chloride in THF (11.25 mL of a 0.8 M solution, 9 mmol) was added dropwise over 10 min at 0 °C under argon to 122 mL of an 82 mM ethereal solution of (*S*,*S*)-**15** (9.8 mmol) according to the general procedure. The resulting (*S*,*S*)-**9** was then brought to reaction with D-glyceraldehyde acetonide (**40**)[44] (1.04 g, 8.0 mmol, dissolved in 5 mL of ether) at −74 °C and stirred for 4 h at this temperature. Usual workup and chromatography (80 g of silica gel, pentane/ether 1:2) afforded 980 mg (71%) of **44** ($[\alpha]_D$ = 19.3 (*c* = 1.5, C_6H_6); $[\alpha]_D$ = 10.6 (*c* = 1.0, $CHCl_3$); lit.[46d] $[\alpha]_D$ = 12.7 (*c* = 1.5, $CHCl_3$)), 96.2% de according to GLC analysis (carrier 50 kPa, 150 °C, derivatized with MTPA chloride):

(2*R*,3*S*) isomer, **43** 1.9%, t_R = 53.5 min; (2*R*,3*R*) isomer, **44** 98.1%, t_R = 61.2 min; ^{13}C NMR ($CDCl_3$, 62.9 MHz, signals with significant shift differences compared to **43** are italicized) 117.52 (t, C(6)), 109.14 (s, *C*$(CH_3)_2$), 78.37 (d, C(3)), *71.37* (d, C(2)), *65.77* (t, C(1)), *37.96* (t, C(4)), 26.38 and 25.14 (2q, C(*C*$H_3)_2$).

16. Reaction of D-glyceraldehyde acetonide (40) with allylmagnesium chloride afforded a 65.6:34.4 mixture of **43** and **44**, as determined by capillary GLC (see above).

17. *tert*-Butyl (4*S*,1′*S*)-2,2-Dimethyl-4-(1′-hydroxy-3′-butenyl)oxazolidine-3-carboxylate ((*S*)-45). Allylmagnesium chloride in THF (5.6 mL of a 0.8 M solution, 4.5 mmol) was added dropwise over 10 min at 0 °C under argon to a solution of (*R*,*R*)-**15** (3.06 g, 5.0 mmol) in 60 mL of ether. After stirring for 1 h at 0 °C, the reaction mixture was cooled to −78 °C, and a solution of *tert*-butyl (4*S*)-2,2-dimethyl-4-formyloxazolidine-3-carboxylate (L-**41**,[45] 95.8% ee, 917 mg, 4.0 mmol) in ether (5 mL) was added over 5 min. Stirring at −78 °C for 3 h, hydrolysis, usual workup, and chromatography (250 g of silica gel, hexane/ethyl acetate 3:1) afforded 1.007 g (93%) of (*S*)-**45** ($[\alpha]_D$ = −17.0° (*c* = 0.95, C_6H_6)), 96% de, as determined by capillary GLC (carrier 50 kPa, 190 °C, derivatization with *N*-isopropyl isocyanate): (4*S*,1′*R*) diastereomer, (*R*)-**46** 1.9%, t_R = 19.0 min; (4*S*,1′*S*) diastereomer, (*S*)-**45** and ca. 2% of (4*R*,1′*S*) diastereomer, (*S*)-**46** 98.1%, t_R = 19.4 min; MS *m*/*e* (EI) 271 (M^+), 256 (1), 201 (10), 200 (10), 174 (3), 156 (5), 144 (20), 100 (60), 57 (100); IR 3400 w, 2980 m, 2920 w, 2880 w, 1700 s, 1660 s, 1400 s, 1380 s, 1360 s; ^{1}H NMR (C_6D_6, 250 MHz, 340 K) 5.92 (dddd, *J* = 17.0, 10.0, 7.0, 6.5, H-C(3′), 5.08–4.97 (m, 2 H-C(4′)), 3.96–3.84 (m, H-C(4), H-C(1′)), 3.73–3.59 (m, 2 H-C(5)), 2.30 (ddddd, *J* = 14.0, 6.5, 3.0, 1.0, 1.0, H-C(2′)), 2.10 (ddddd, *J* = 14.0, 7.0, 7.0, 1.0, 1.0, H-C(2′)), 1.62 (s, C$(CH_3)_3$), 1.45 and 1.39 (2s, $(CH_3)_2$C(2)); ^{13}C NMR (C_6D_6, 62.9 MHz, 340 K) 153.8 (s, *C*OO-*t*-Bu), 135.7 (d, C(3′)), 117.0 (t, C(4′)), 94.3 (s, C(2)), 80.4 (s, *C*$(CH_3)_3$), 72.3 (d, C(1′)), 64.6 (t, C(5)), 61.9 (d, C(4)), 38.2 (t, C(2′)), 28.4 (q, C(*C*$H_3)_3$), 27.0 and 24.1 (2q, $(CH_3)_2$C(2)). Anal. Calcd for $C_{14}H_{25}NO_4$ (271.36): C, 61.97; H, 9.29; N, 5.16; O, 23.58. Found: C, 62.12; H, 9.10; N, 5.00; O, 23.67.

18. *tert*-Butyl *N*-[(4*S*,5*S*)-2,2-Dimethyl-4-(2′-propenyl)-1,3-dioxan-5-yl]carbamate ((*S*)-63). Oxazolidine (*S*)-**45** (20 mg, 0.07 mmol) was dissolved in $CDCl_3$ (1 mL) containing traces of HCl. After 48 h at RT, it had rearranged to dioxane (*S*)-**63**: ^{1}H NMR ($CDCl_3$, 250 MHz) 5.75 (ddt, *J* = 17.0, 10.0, 7.0, H-C(2′)), 5.29 (d, *J* = 10.0, NH), 5.06 (dd, *J* = 17.0, 2.0, H-C(3′)), 5.02 (dd, *J* = 10.0, 2.0, H-C(3′)), 4.02 (dd, *J* = 12.0, 2.0, H-C(6)), 3.91 (td, *J* = 6.5, 1.5, H-C(4)), 3.71 (dd, *J* = 12.0, 2.0, H-C(6)), 3.49 (dddd, *J* = 10.0, 2.0, 2.0, 1.5, H-C(5)), 2.17 (dd, *J* = 7.0, 6.5, 2 H-C(1′)), 1.42 and 1.36 (2s, $(CH_3)_2$C(2)), 1.41 (s, C$(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 156.2 (s, *C*OO-tBu), 133.7 (d, C(2′)), 117.6 (t, C(3′)), 99.0 (s, C(2)), 79.3 (s, *C*$(CH_3)_3$), 71.3 (d, C(4)), 65.3 (t, C(6)), 46.4 (d, C(5)), 36.2 (t, C(1′)), 29.6 (q, CH_3C(2)), 28.3 (q, C(*C*$H_3)_3$), 18.5 (q, CH_3C(2)).

19. *tert*-Butyl (4*S*,1′*R*)-2,2-Dimethyl-4-(1′-hydroxy-3′-butenyl)oxazolidine-3-carboxylate ((*R*)-46). Reaction of L-**41**[45] (95.8% ee) with (*S*,*S*)-**9**, as described above for the preparation of (*S*)-**45**, afforded 95% of (*R*)-**46** ($[\alpha]_D$ = 4.4 (*c* = 1, C_6H_6)), 99% de, as determined by capillary GLC (see above): (*R*)-**46** and ca. 2% of the (4*R*,1′*R*) isomer, (*R*)-**45** 99.5%, t_R = 19.0 min; (*S*)-**45** 0.5%, t_R = 19.4 min; ^{1}H NMR (C_6D_6, 250 MHz, 340 K) 5.90 (dddd, *J* = 17.0, 10.0, 6.5, 6.5, H-C(3′)), 5.12–4.97 (m, 2 H-C(4′)), 3.92–3.80 (m, H-C(1′), H-C(4), H-C(5)), 3.63 (dd, *J* = 9.0, 6.5, H-C(5)), 2.20 (dd, *J* = 6.5, 6.5, 2 H-C(2′), 1.62 and 1.46 (2s, $(CH_3)_2$C(2)), 1.39 (s, C(*C*$H_3)_3$); ^{13}C NMR (C_6D_6, 62.9 MHz, 340 K) 153.8 (s, *C*OO-*t*-Bu), 135.9 (d, C(3′)), 116.9 (t, C(4′)), 94.4 (s, C(2)), 80.1 (s, *C*$(CH_3)_3$), 72.0 (d, C(1′)), 64.5 (t, C(5)), 62.0 (d, C(4)), 38.9 (t, C(2′)), 28.4 (q, C(*C*$H_3)_3$), 27.0 and 24.2 (2q, $(CH_3)_2$C(2)). Anal. Calcd for $C_{14}H_{25}NO_4$ (271.36): C, 61.97; H, 9.29; N, 5.16; O, 23.58. Found: C, 62.33; H, 9.31; N, 4.95.

20. *tert*-Butyl-*N*-[(4*R*,5*S*)-2,2-Dimethyl-4-(2′-propenyl)-1,3-dioxan-5-yl]carbamate ((*R*)-64). Oxazolidine (*R*)-**46** (20 mg, 0.07 mmol) was dissolved in $CDCl_3$ (1 mL) containing traces of HCl. After 48 h at RT, it had rearranged to dioxane (*R*)-**64**: ^{1}H NMR (C_6D_6, 250 MHz, 340 K) 5.89 (dddd, *J* = 17.0, 10.0, 6.75, 6.75, H-C(2′)), 5.06 (dddd, *J* = 17.0, 2.0, 1.25, 1.25, H-C(3′)), 5.02 (dddd, *J* = 10.0, 2.0, 1.25, 1.25, H-C(3′)), 4.0 (m, NH), 3.75 (dd, *J* = 11.0, 5.0, H-C(6)), 3.56 (dddd, *J* = 9.5, 8.5, 8.5, 5.0, H-C(5)), 3.40 (ddd, *J* = 9.5, 6.75, 6.75, H-C(4)), 3.25 (dd, *J* = 11.0, 8.5, H-C(6)), 2.34 (ddddd, *J* = 14.0, 6.75, 6.75, 1.25, 1.25, H-C(1′)), 2.23 (ddddd, *J* = 14.0, 6.75, 6.75, 1.25, 1.25, H-C(1′)), 1.38 (s, C$(CH_3)_3$), 1.33 and 1.24 (2s, $(CH_3)_2$C(2)); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 155.0 (s, *C*OO-tBu), 134.2 (d, C(2′)), 116.9 (t, C(3′)), 98.7 (s, C(2)), 79.7 (s, *C*$(CH_3)_3$), 72.4 (d, C(4)), 63.3 (t, C(6)), 49.1 (d, C(5)), 37.0 (t, C(1′)), 28.3 (s, C(*C*$H_3)_3$), 28.0 and 19.9 (2q, $(CH_3)_2$C(2)).

21. Reaction of L-41 with Allylmagnesium Chloride. Allylmagnesium chloride in THF (6.25 mL of a 0.8 M solution, 4.5 mmol) was added dropwise over 10 min at 0 °C under argon to a solution of L-**41**[45] (1.008 g, 4.4 mmol, 95.8% ee) in ether (60 mL), and the mixture was stirred for 2 h at 0 °C. After hydrolysis with 10 mL of 1 N HCl, the reaction mixture was extracted twice with ether (40 mL). Chromatography (80 g of silica gel, hexane/ether 2:1) afforded 1.03 g (86%) of a 55.1:44.9 mixture of (*S*)-**45** and (*R*)-**46**, according to GLC analysis (see above).

22. Reaction of L-41 with Cp(2-PrO)$_2$Ti(allyl). Allylmagnesium chloride in THF (5.63 mL of a 0.8 M solution, 4.5 mmol) was added dropwise over 10 min at 0 °C under argon to a solution of diisopropoxycyclopentadienylchlorotitanate **42**[32c] (1.33 g, 5.0 mmol) in ether (80 mL). After stirring for 75 min at 0 °C, the reaction mixture was cooled to −78 °C, and a solution of L-**41**[45] (917 mg, 4.0 mmol, 95.8% ee) in ether (5 mL) was added over 2 min. Stirring for 5.5 h at −74 °C, the usual workup, and chromatography (80 g of silica gel, hexane/ether 2:1) afforded 964 mg (89%) of a 37.3:62.7 mixture of (*S*)-**45** and (*R*)-**46**, according to GLC analysis (see above).

23. *tert*-Butyl (4*R*,1′*S*)-2,2-Dimethyl-4-(1′-hydroxy-3′-butenyl)oxazolidine-3-carboxylate ((*S*)-46). Reaction of D-**41**[45] with (*R*,*R*)-**9**, as described above for the reaction of L-**41**, afforded 84% of (*S*)-**46**. GLC analysis (carrier 50 kPa, 190 °C, derivatization with *N*-isopropyl isocyanate) showed a single peak (t_R = 19.4 min) with the same t_R as observed for (*S*)-**45**.

24. *tert*-Butyl (4*S*,1′*S*,2′*S*)-2,2-Dimethyl-4-(2′-methyl-1′-hydroxy-3′-butenyl)oxazolidine-3-carboxylate (47). Crotylmagnesium chloride in THF (11.25 mL of a 0.2 M solution, filtered through Celite, 2.25 mmol) was added at −74 °C to a solution of (*R*,*R*)-**15** (1.53 g, 2.5 mmol) in ether (40 mL). The reaction mixture was stirred for 2 h at −74 °C before the temperature was slowly raised to RT. After cooling to −74 °C, L-**41**[45] (0.459 g, 2.0 mmol, 98% ee) was added, and stirring was continued for 3 h. Usual workup and chromatography (180 g of silica gel, hexane/ether 3:1) afforded 0.51 g (93%) of **47**, ≥98% de according to GLC analysis (carrier 45 kPa, 140 °C, derivatized with *N*-isopropyl isocyanate): (4*S*,1′*S*,2*S*′) isomer, **47** t_R = 73.30 min; (4*S*,1′*R*,2′*R*) isomer, (t_R = 72.36 min (obtained from a test reaction with (*S*,*S*)-**29**, not detected); (4*S*,1′*S*,2′*R*) isomer and (4*S*,1′*R*,2′*S*) isomer, t_R = 72.00 and 72.32 min (obtained as additional diastereomers in a test reaction with crotylmagnesium chloride, not detected); ^{1}H NMR ($CDCl_3$, 250 MHz) 5.85 (ddd, *J* = 17.0, 10.0, 9.0, H-C(3′)), 5.03 (dd, *J* = 10.0, 2.0, H-C(4′)), 4.94 (dd, *J* = 17.0, 2.0, H-C(4′)), 4.25 (bs, OH), 3.99 (ddd, *J* = 9.0, 6.0, 1.5, H-C(4)), 3.85 (dd, *J* = 9.0, 6.0, H-C(5)), 3.63 (dd, *J* = 9.0, 1.5, H-C(5)), 3.52 (m, H-C(1′)), 2.19 (dq, *J* = 9.0, 6.0, H-C(2′)), 1.52 (s, $(CH_3)_2$C(2)), 1.45 (s, C(*C*$H_3)_3$), 1.10 (d, *J* = 7.0, *C*H_3C(2′)); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 153.8 (s, *C*OOC$(CH_3)_3$), 138.63 (d, C(3′)), 116.01 (t, C(4′)), 93.99 (s, C(2)), 81.39 (s, *C*$(CH_3)_3$), 77.82 (d, C(1′)), 64.82 (t, C(5)), 60.79 (d, C(4)), 42.03 (d, C(2′)), 28.32 (q, C(*C*$H_3)_3$), 27.21 and 24.27 (2q, $(CH_3)_2$C(2)), 17.99 (q, *C*H_3C(2′)). Anal. Calcd for $C_{15}H_{27}NO_4$ (285.49): C, 63.10; H, 9.55; N, 4.93; O, 23.58. Found: C, 63.15; H, 9.59; N, 4.82.

25. *tert*-Butyl *N*-[(4*S*,5*S*,1′*S*)-2,2-Dimethyl-4-(1′-methyl-2′-propenyl)-1,3-dioxan-5-yl]carbamate (65). Oxazolidine **47** (20 mg, 0.07 mmol) was dissolved in $CDCl_3$ (1 mL) containing traces of HCl. After 48 h at RT, it had rearranged to dioxane **65**: ^{1}H NMR (C_6D_6, 250 MHz, 340 K) 6.06 (ddd, *J* = 17.0, 10.0, 7.0, H-C(2′)), 5.50 (bs, NH), 5.19 (dd, *J* = 17.0, 2.0, H-C(3′)), 5.17 (dd, *J* = 10.0, 2.0, H-C(3′)), 3.89–3.72 (m, H-C(5), 2 H-C(6)), 3.51 (d, *J* = 9.0, H-C(4)), 2.53 (ddq, *J* = 9.0, 7.0, 6.0, H-C(1′)), 1.62 (s, C$(CH_3)_3$), 1.44 and 1.30 (2s, $(CH_3)_2$C(2)), 1.18 (d, *J* = 6.0, CH_3C(1′)); ^{13}C NMR (C_6D_6, 62.9 MHz) 155.0 (s, *C*OOC$(CH_3)_3$), 141.3 (d, C(2′)), 113.8 (t, C(3′)), 99.1 (s, C(2)), 79.0 (s, *C*$(CH_3)_3$), 75.7 (d, C(4)), 65.6 (t, C(6)), 46.2 (d, C(5)), 38.8 (d, C(1′)), 28.5 (q, C(*C*$H_3)_3$), 29.7 and 18.50, (2q, $(CH_3)_2$C(2)), 14.8 (q, C(1′)-*C*H_3).

26. (1*S*,2*S*)-1-Phenyl-2-methyl-3-buten-1-ol ((*S*)-52). (a) (*R*,*R*)-29 Prepared from Crotylmagnesium Chloride. Crotylmagnesium chloride in THF (23 mL of a 0.39 M solution, filtered through Celite, 9 mmol) was added at −78 °C to a solution of (*R*,*R*)-**15** (6.125 g, 10 mmol) in ether (150 mL). After 30 min at this temperature, the reaction mixture was stirred for 3 h at 0 °C and recooled to −78 °C, and benzaldehyde **3** (0.848 g, 8 mmol) was added. Stirring was continued for 4 h. Usual workup, chromatography (150 g of silica gel, hexane/ether 5:1), and bulb-to-bulb distillation (50 °C/0.001 mm) afforded 1.157 g (89%) of a 98.7:1.3 mixture of (*S*)-**52** (containing 0.9% of (*R*)-**52**, 98.2% ee) and (*S*)-**53** ((*R*)-**53** was not detected), as determined by capillary GLC (carrier 50 kPa, 130 °C, derivatized with *N*-isopropyl isocyanate): (1*S*,2*R*) isomer, (*S*)-**53** 1.3%, t_R = 83.03 min; (1*R*,2*S*) isomer, (*R*)-**53** not detected, t_R = 85.98 min; (1*S*,2*S*) isomer, (*S*)-**52** 97.8%, t_R = 86.63 min; (1*R*,2*R*) isomer, (*R*)-**52** 0.9%, t_R = 89.73 min; $[\alpha]_D$ = −115.4 (*c* = 1.5, $CHCl_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 142.4 (s), 128.1, 127.5, 126.7 (3d) (C_6H_5), 140.6 (*C*H=CH$_2$), 116.5 (CH=*C*H$_2$), 77.7 (CHOH), 46.1 (*C*HCH_3), 16.4 (CH_3).

(b) (*R*,*R*)-29 Prepared by Metalation of (*Z*)-2-Butene. To a solution of 2,2,6,6-tetramethylpiperidine (0.51 mL, 3.0 mmol) in THF (20 mL) was added dropwise *n*-butyllithium (1.88 mL of a 1.6 M solution in

hexane, 3.0 mmol) at −74 °C. After 10 min, KO(*t*-Bu) (0.34 g, 3.0 mmol, freshly sublimed) was added slowly. The reaction mixture was stirred for 2 h at −74 °C before (*Z*)-2-butene (0.34 g, 6.0 mmol) was introduced by condensation. After stirring for 1 min at −74 °C, the reaction mixture was transferred via cannula to a solution of (*R,R*)-**15** (2.02 g, 3.3 mmol) in ether (50 mL), precooled to −74 °C, and stirring was continued for 15 min at −78 °C and 30 min at 0 °C. Benzaldehyde (**3**, 0.27 mL, 2.75 mmol) was then added at −74 °C to the red-brown solution. Usual workup after 2 h and chromatography (80 g of silica gel, hexane/ether 5:1) afforded 77 mg (17%) of a 98.85:1.15 mixture of (*S*)-**52** (97.7% ee) and (*S*)-**53**, as detected by GLC analysis (see above).

27. (3*S*,4*R*)-3-Methyl-1-tridecen-4-ol ((*R*)-54). Reaction of decanal (150 mg, 0.96 mmol) with (*R,R*)-**29** as described above for benzaldehyde (**3**) and purification by chromatography (80 g of silica gel, hexane/ether 3:1) afforded 0.175 g (86%) of (*R*)-**54**, containing no other isomers according to GLC analysis (carrier 45 kPa, 140 °C, derivatized with *N*-isopropyl isocyanate): (3*R*,4*S*) isomer ((*S*)-**54**), (3*R*,4*R*) isomer, and (3*S*,4*S*) isomer (not detected, t_R = 112.53, 114.75, and 118.0 min); (3*S*,4*R*) isomer, (*R*)-**54** 100%, t_R = 115.84 min; $[\alpha]_D$ = 0.5 (*c* = 0.19, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz) 5.83–5.68 (m, H-C(2)), 5.14–5.06 (m, 2 H, H-C(1)), 3.40 (m, H-C(4)), 2.22 (dq, *J* = 7.0, 7.0, H-C(3)), 1.56 (d, *J* = 4.0, OH), 1.58–1.15 (m, 16 H), 1.03 (d, *J* = 7.0, CH_3C(3)), 0.86–0.92 (m, CH_3C(12)).

28. (1*S*,2*R*)-1,2-Diphenyl-3-buten-1-ol ((*S*)-55). *n*-Butyllithium in hexane (2.8 mL, 1.6 M, 4.5 mmol) was added dropwise at −30 °C to a solution of allylbenzene (0.59 mL, 4.5 mmol) in THF (50 mL). The dark red reaction mixture was stirred for 30 min at −30 °C and 1 h at 20 °C and was then transferred via cannula to a solution of (*R,R*)-**15** (3.06 g, 5.0 mmol) in ether (70 mL, precooled to 0 °C). Stirring for 1 h at 0 °C (→ (*R,R*)-**48**) preceded the addition of benzaldehyde (**3**, 0.424 g, 4.0 mmol) at −74 °C. After 2 h at −74 °C, the mixture was worked up as usual. Chromatography of the residual oil (80 g of silica gel, hexane/ether 9:1) gave 0.487 g (54%) of (*S*)-**55** ($[\alpha]_D$ = −12.5 (*c* = 3.4, $CHCl_3$)), 97.4% ee, as determined by capillary GLC (carrier 70 kPa, 190 °C, derivatization with *N*-isopropyl isocyanate): (1*RS*,2*RS*) diastereomer t_R = 35.94 and 36.82 min (obtained by reaction of **3** with lithiated allylbenzene, not detected); (1*R*,2*S*) isomer, (*R*)-**55** 1.3%, t_R = 38.20 min; (1*S*,2*R*) isomer, (*S*)-**55** 98.7%, t_R = 39.20 min; ^1H NMR ($CDCl_3$, 250 MHz) 7.00–7.40 (m, 2 C_6H_5), 6.24 (ddd, *J* = 17.0, 10.0, 8.0, H-C(3)), 5.27 (dd, *J* = 10.0, 2.0, H-C(4)), 5.19 (dd, *J* = 17.0, 2.0, H-C(4)), 4.82 (d, *J* = 8.0, H-C(1)), 3.54 (dd, *J* = 8.0, 8.0, H-C(2)), 2.40 (bs, OH); ^{13}C NMR ($CDCl_3$, 62.896 MHz) 141.82, 140.59, (2s), 128.27, 127.82, 127.30, 126.60, 126.50 (5d) (2 C_6H_5), 137.79 (d, C(3)), 118.25 (t, C(4)), 77.14 (d, C(1)), 59.06 (d, C(2)).

29. Reaction of Benzaldehyde (3) with (*R,R*)-49. A solution of allyl ethyl ether (0.258 g, 3 mmol) in THF (5 mL) was added slowly at 0 °C to a solution of KO(*t*-Bu) (0.224 g, 2 mmol, freshly sublimed) in THF (15 mL) followed by *n*-butyllithium in hexane (1.25 mL, 1.6 M, 2 mmol) at −74 °C (exothermic reaction!). After stirring for 15 min at −74 °C, the reaction mixture was transferred via cannula to a solution of (*R,R*)-**15** (1.286 g, 2.1 mmol) in ether (30 mL, precooled to −74 °C). Stirring at −74 °C was continued for 30 min, and benzaldehyde (**3**, 0.17 g, 1.6 mmol) was added to the dark brown solution of (*R,R*)-**49**. The reaction was worked up as usual, after stirring for 3 h at −74 °C. Chromatography (80 g of silica gel, hexane/ether/CH_2Cl_2 3:1:1) afforded 0.24 g (77%) of a 87.7:12.3 mixture of (1*R*,2*S*)-1-phenyl-2-ethoxy-3-buten-1-ol ((*R*)-**56**, 95% ee) and (1*R*,2*R*)-1-phenyl-2-ethoxy-3-buten-1-ol ((*R*)-**57**, 75.6% ee), as determined by capillary GLC (carrier 60 kPa, 160 °C, derivatized with *N*-isopropyl isocyanate): (1*S*,2*R*) isomer, (*S*)-**56** 2.2%, t_R = 32.97 min; (1*R*,2*S*) isomer, (*R*)-**56** 85.5%, t_R = 33.47 min; (1*S*,2*S*) isomer, (*S*)-**57** 1.5%, t_R = 36.63 min; (1*R*,2*R*) isomer, (*R*)-**57** 10.8%, t_R = 37.41 min; ^1H NMR ($CDCl_3$, 250 MHz, signals of (*R*)-**56** only) 7.20–7.40 (m, C_6H_5), 5.68 (ddd, *J* = 17.5, 10.5, 7.5, H-C(3)), 5.22 (dd, *J* = 10.5, 2.0, H-C(4)), 5.15 (dd, *J* = 17.5, 2.0, H-C(4)), 4.82 (dd, *J* = 4.5, 4.0, H-C(1)), 3.85 (dd, *J* = 7.5, 4.5, H-C(2)), 3.58 and 3.37 (2 dq, *J* = 9.5, 7.5, OCH_2CH_3), 2.78 (d, *J* = 4.0, O*H*), 1.17 (dd, *J* = 7.5, 7.5, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 62.896 MHz, signals of **56**) 140.37 (s), 127.94, 127.38, 126.75, (3d) (C_6H_5), 134.23 (d, C(3)), 119.25 (t, C(4)), 84.76 (d, C(1)), 75.42 (d, C(2)), 64.36 (t, OCH_2CH_3), 15.20 (q, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 62.896 MHz, signals of **57**) 140.37 (s), 127.94, 127.38, 126.75, (3d) (C_6H_5), 134.72 (d, C(3)), 118.90 (t, C(4)), 85.76 (d, C(1)), 76.56 (d, C(2)), 64.55 (t, OCH_2CH_3), 15.20 (q, OCH_2CH_3).

30. (3*S*,4*R*)-3-Ethoxy-1-tridecen-4-ol ((*R*)-58). Decanal (250 mg, 1.6 mmol) was brought to reaction with reagent (*R,R*)-**49** (1.3 equiv) as described above for benzaldehyde (**3** → (*R*)-**56** and (*R*)-**57**). Chromatography (80 g of silica gel, hexane/ether 3:1) afforded 0.283 g (73%) of a 97.3:2.7 mixture of (*R*)-**58** (92.4% ee) and (3*R*,4*R*)-3-ethoxy-1-tridecen-4-ol ((*R*)-**59**, 48% ee), as determined by GLC analysis (carrier 70 kPa, 170 °C, derivatized with *N*-isopropyl isocyanate): (3*R*,4*S*) isomer, (*S*)-**58** 3.7%, t_R = 31.81 min; (3*S*,4*R*) isomer, (*R*)-**58** 93.6%, t_R = 32.30 min; (3*S*,4*S*) isomer, (*S*)-**59** 0.7%, t_R = 34.50 min; (3*R*,4*R*) isomer, (*R*)-**59** 2.0%, t_R = 35.10 min; $[\alpha]_D$ = 26.6 (*c* = 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz) 5.72 (ddd, *J* = 17.5, 10.5, 8.0, H-C(2)), 5.26 (dd, *J* = 10.5, 1.5, H-C(1)), 5.19 (ddd, *J* = 17.5, 1.5, 1.0, H-C(1)), 3.61–3.49 (m, H-C(3), H-C(4)), 3.30, 3.52 (2dq, *J* = 9.5, 7.0, OCH_2CH_3), 2.05 (d, *J* = 4.0, O*H*), 1.12 (dd, *J* = 7.0, 7.0, OCH_2CH_3), 1.16–1.43 (m, 16 H), 0.81 (m, CH_3C(12)); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 134.90 (d, C(2)), 119.14 (t, C(1)), 84.10 (d, C(4)), 73.11 (d, C(3)), 63.94 (t, OCH_2CH_3), 22.65, 25.37, 29.27, 29.54, 29.63, 31.85, 32.13, (7t, C(5)–C(12)), 15.21 (q, OCH_2CH_3), 14.04 (q, C(13)).

31. (1*R*,2*S*)-2-(4′-Methoxyphenoxy)-1-phenyl-3-buten-1-ol ((*R*)-60). *sec*-Butyllithium in cyclohexane (2.5 mL, 1 M, 2.5 mmol) was added at −60 °C to a solution of 3-(4′-methoxyphenoxy)-1-propene (0.41 g, 2.5 mmol) in THF (20 mL). This reaction mixture was then transferred over 1 min via cannula to a solution of (*R,R*)-**15** (1.53 g, 2.5 mmol) in ether (40 mL, precooled to −74 °C, *exothermic reaction*). After stirring for 3 h, benzaldehyde (**3**, 0.16 g, 1.6 mmol) was added at −78 °C to the dark brown solution of (*R,R*)-**50**, and stirring was continued for an additional 3 h. Hydrolysis with 20 mL of aqueous 45% NH_4F solution and stirring for 12 h at room temperature, usual workup, and chromatography (80 g of silica gel, hexane/ether/CH_2Cl_2 5:1:1) afforded 0.403 g (93%) of (*R*)-**60**: $[\alpha]_D$ = −20.6 (*c* = 1.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz) 7.55–7.20 (m, C_6H_5), 6.87–6.70 (m, $OC_6H_4OCH_3$), 5.80 (ddd, *J* = 17.0, 10.0, 7.0, H-C(3)), 5.30 (dd, *J* = 10.0, 2.0, H-C(4)), 5.23 (dd, *J* = 17.0, 2.0, H-C(4)), 5.02 (dd, *J* = 4.0, 4.0, H-C(1)), 4.65 (dd, *J* = 7.0, 4,0, H-C(2)), 3.75 (s, OCH_3), 2.60 (d, *J* = 4.0, OH); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 154.38 and 151.37 (2s, OC_6H_4O), 139.81 (s, C_6H_5), 133.20 (d, C(3)), 128.04, 127.59, 127.21 (3d, C_6H_5), 119.6 (t, C(4)), 117.7 and 114.5 (2d, OC_6H_4O), 84.33 (d, C(1)), 75.36 (d, C(2)), 53.62 (q, CH_3O).

32. (1*R*,2*S*)-2-(4-Methoxyphenoxy)-1-phenyl-1-(trimethylsiloxy)-3-butene ((*R*)-66). Trimethylsilyl triflate (0.5 mL, 2.76 mmol) was added dropwise at −74 °C to a solution of (*R*)-**60** (0.57 g, 2.11 mmol) in CH_2Cl_2 (20 mL). After the mixture was stirred for 5 min, Et_3N (0.32 mL, 2.31 mmol) was added, and stirring was continued for 30 min at −74 °C and for another 30 min at 0 °C. Evaporation of solvent and chromatography (60 g of silica gel, hexane/ether 5:1) afforded 0.654 g (90.5%) of (*R*)-**66**: ^1H NMR ($CDCl_3$, 250 MHz) 7.06–7.34 (m, C_6H_5), 6.50–6.70 (m, $OC_6H_4OCH_3$), 5.88 (ddd, *J* = 17.0, 10.0, 6.0, H-C(3)), 5.15 (dd, *J* = 10.0, 2.0, H-C(4)), 5.06 (dd, *J* = 17.0, 2.0, H-C(4)), 4.79 (d, *J* = 5.5, H-C(1)), 4.65 (dd, *J* = 6.0, 5.5, H-C(2)), 3.61 (s, OCH_3), 0.1 (s, $Si(CH_3)_3$).

33. (1*R*,2*S*)-1-Phenyl-3-butene-1,2-diol ((*R*)-67). To a solution of (*R*)-**66** (0.14 g, 0.41 mmol) in CH_3CN/H_2O (4:1, 13 mL) was added cerammonium nitrate (0.56 g, 1.02 mmol) at 0 °C in portions. The reaction mixture was stirred for 30 min, diluted with ether (20 mL), and extracted twice with saturated aqueous NH_4F solution (25 mL) and twice with H_2O (20 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated. Evaporation of the solvent and chromatography (60 g of silica gel, ether/CH_2Cl_2 5:1) afforded 54.7 mg (81.4%) of (*R*)-**67**, one isomer according to GLC analysis (carrier 80 kPa, 190 °C, derivatized with *N*-isopropyl isocyanate): (1*S*,2*R*) isomer, (*S*)-**67** not detected, t_R = 55.47 min (reference obtained from analogous reaction sequence, omitting transmetalation with (*R,R*)-**15**); (1*R*,2*S*) isomer, (*R*)-**67** 100%, t_R = 56.19 min; (1*RS*,2*RS*) diastereomer not detected, t_R = 69.2 and 71.7 min (reference obtained from analogous reaction sequence, omitting transmetalation with (*R,R*)-**15**); ^1H NMR ($CDCl_3$, 250 MHz) 7.25–7.40 (m, C_6H_5), 5.82 (ddd, *J* = 17.0, 10.0, 6.0, H-C(3)), 5.28 (ddd, *J* = 17.0, 2.0, 2.0, H-C(4)), 5.21 (dd, *J* = 10.0, 2.0, H-C(4)), 4.75 (m, H-C(1)), 4.30 (m, H-C(2)), 2.65 and 2.28 (2bs, OH).

34. (4*S*,5*R*)-4-Ethenyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (68). A few crystals of pyridinium *p*-toluenesulfonate were added to a solution of (*R*)-**67** (38 mg, 0.23 mmol) in acetone (4 mL) and 2,2-dimethoxypropane (4 mL). After the reaction was stirred for 24 h, volatiles were evaporated. Chromatography (60 g of silica gel, hexane/ether 5:1) afforded 40 mg (84%) of **68**: ^1H NMR ($CDCl_3$, 500 MHz) 7.23–7.35 (m, C_6H_5), 5.29 (ddd, *J* = 17.0, 10.0, 7.0, C*H*=CH_2), 5.29 (d, *J* = 7.0, H-C(5)), 5.18 (d, *J* = 17.0, 2.0) and 4.98 (dd, *J* = 10.0, 2.0) (CH=C-H_2), 4.81 (dd, *J* = 7.0, 7.0, H-C(4)), 1.64 and 1.45 (2s, $(CH_3)_2C(2)$) (NOE's of around 3% are observed between the CH_3 group at δ = *1.45* ppm and both H-C(4) (δ = 4.81 ppm) and H-C(5) (δ = 5.29 ppm), but *no* NOE's are observed from the other CH_3 group at δ = 1.64 ppm); ^{13}C NMR ($CDCl_3$, 62.9 MHz) 137.48 (s, C_6H_5), 134.98 (d, *C*H=CH_2); 126.92, 127.68, 128.12 (3d, C_6H_5), 117.99 (t, CH=CH_2), 108.91 (s, C(2)), 80.76 and 80.25 (2d, C(4), C(5)), 27.39 and 25.03 (2q, $(CH_3)_2C(2)$).

35. (1*R*,2*S*)-1-Phenyl-2-(trimethylsilyl)-3-buten-1-ol ((*R*)-61). To a solution of KO(*t*-Bu) (0.20 g, 1.8 mmol, freshly sublimed) in THF (10 mL) was added slowly allyltrimethylsilane (0.29 mL, 1.8 mmol) dissolved in THF (5 mL) at 0 °C. The reaction mixture was cooled to −74 °C,

and a solution of *n*-butyllithium (1.13 mL, 1.6 M in hexane, 1.8 mmol) was added dropwise (exothermic reaction). After stirring for 1 h at −74 °C, the mixture was transferred via cannula to a solution of (*R*,*R*)-**15** (1.225 g, 2.0 mmol) in 50 mL of ether, precooled to −74 °C. Stirring at −74 °C was continued for 2.5 h, and benzaldehyde (**3**, 0.16 g, 1.6 mmol) was added to the dark brown solution of (*R*,*R*)-**51**. After stirring for 3 h at −74 °C, the reaction was worked up as usual. Chromatography (80 g of silica gel, hexane/ether/CH_2Cl_2 5:1:1) afforded 0.24 g (68%) of (*R*)-**61** ($[\alpha]_D$ = −46.43 (*c* = 2.8, $CHCl_3$)), ≥95% ee, according to GLC analysis (carrier 50 kPa, 140 °C, derivatization with *N*-isopropyl isocyanate): (1*R*,2*S*) isomer, (*R*)-**61** t_R = 19.3 min; (1*S*,2*R*) isomer, (*S*)-**61** t_R = 19.6 min (obtained with (*R*)-**61** in a reaction using $Cp(2\text{-}PrO)_2TiCl$ **42** for transmetalation, not detected); ≥95% de as the (1*RS*,2*RS*) diastereomer (syn) was not detected by ^1H and ^{13}C NMR; ^1H NMR ($CDCl_3$, 400 MHz) 7.23–7.35 (m, C_6H_6), 5.86 (ddd, *J* = 17.0, 10.0, 10.0, H-C(3)), 5.11 (dd, *J* = 10.0, 2.0, H-C(4)), 5.02 (dd, *J* = 17.0, 2.0, H-C(4)), 4.79 (dd, *J* = 8.5, 2.0, H-C(1)), 2.20 (d, *J* = 2.0, OH), 2.08 (dd, *J* = 10.0, 8.5, H-C(2)), −0.21 (s, $Si(CH_3)_3$); ^1H NMR (CCl_4, 250 MHz) 7.23–7.35 (m, C_6H_6), 5.73 (ddd, *J* = 17.0, 10.5, 10.5, H-C(3)), 4.87 (dd, *J* = 10.5, 2.0, H-C(4)), 4.73 (dd, *J* = 17.0, 2.0, H-C(4)), 4.70 (dd, *J* = 6.5, 2.0, H-C(1)), 1.64 (d, *J* = 2.0, OH), 1.90 (dd, *J* = 10.5, 6.5, H-C(2)), −0.21 (s, $Si(CH_3)_3$).

36. (3*S*,4*R*)-3-(Trimethylsilyl)-1-tridecen-4-ol ((*R*)-62). Reaction of decanal (285 mg, 1.825 mmol) with (*R*,*R*)-**51** as described above for benzaldehyde (**3** → **61**) afforded 0.34 g (69%) of (*R*)-**62**, purified by chromatography (80 g of silica gel, hexane/ether/CH_2Cl_2 5:1, $[\alpha]_D$ = 1.40 (*c* = 3.5, $CHCl_3$)), ≥95% ee, as determined by ^1H NMR (addition of (*S*)-2,2,2-trifluoro-1-(9′-anthryl)ethanol (TFAE)[51]): (3*S*,4*R*) isomer, (*R*)-**62** δ H_{cis}-C(1) = 4.94; (3*R*,4*S*) isomer, (*S*)-**62** δ H_{cis}-C(1) = 4.91 ppm (not observed, racemic **62** was produced using $Cp(2\text{-}PrO)_2TiCl$ **42** for transmetalation); ^1H NMR ($CDCl_3$, 400 MHz) 5.80 (ddd, *J* = 17.0, 10.5, 10.5, H-C(2)), 5.04 (dd, *J* = 10.5, 2.5, H-C(1)), 4.93 (dd, *J* = 17.0, 2.0, H-C(1)), 3.79 (m, H-C(4)), 1.68 (dd, *J* = 10.5, 5.5, H-C(3)), 1.46 (d, *J* = 4.5, OH), 1.34–1.21 (m, 16 H), 0.83 (t, *J* = 6.75, CH_3), 0.04 (s, $Si(CH_3)_3$).

Supplementary Material Available: Tables of crystal structure data, positional parameters, displacement parameters, bond distances, and bond angles (8 pages); tables of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

Gas-Phase Electron-Transfer Reactions between Selected Molecular Anions and Halogenated Methanes

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Abstract: The products and rate constants for the thermal gas-phase reactions of eight halogenated methanes (RX), including CCl_4, $CFCl_3$, CF_2Cl_2, $CHCl_3$, CH_3I, CCl_3Br, CF_2Br_2, and CH_2Br_2, with selected molecular anions (A^-), including azulene(−), nitrobenzene(−), and several substituted nitrobenzenes(−), are reported. The electron affinities of the donor molecules (A) range from 16 kcal mol^{-1} for azulene to 46 kcal mol^{-1} for *p*-dinitrobenzene. CCl_4, CCl_3Br, and CF_2Br_2 react rapidly with several A^- to form halide ions (X^-) and clustered halide ions ($A{\cdot}X^-$). No molecular ions of the type RX^- are observed as reaction products. For these three halomethanes, a continuous decrease in the reaction rate constants with increased electron affinity of A is observed. The other five halomethanes react either with none of the molecular anions or only with Az^-. The products and rates of these reactions are shown to be consistent with an electron-transfer mechanism in which the clustered halide ion, $A{\cdot}X^-$, rather than X^-, is first formed in a two-part reaction sequence. The low reactivities of $CFCl_3$, CF_2Cl_2, $CHCl_3$, CH_3I, and CH_2Br_2 with the molecular anions can be explained in terms of unfavorable polarizabilities and unfavorable dipole-moment-induced orientations for these molecules in the transition states of the proposed mechanism.

Introduction

Several classes of compounds have been shown to react rapidly with either thermal electrons or electron donors to form stable negative ions in the gas phase. In these studies, a diversity of mechanistic behaviors for electron-capture (EC) and electron-transfer (ET) processes have been revealed.[1-5] For EC reactions,[1] several classes of compounds (nitroaromatics and perfluorinated alkanes, for example) have been shown to undergo EC by the resonance electron capture (REC) mechanism, shown as reaction 1 in which an excited intermediate, A^{-*}, has a sufficiently long

$$e + A \rightleftharpoons A^{-*} \rightarrow A^- \qquad (1)$$

lifetime that it is collisionally stabilized in a bath gas of moderately high pressure. Several other classes of compounds (chlorinated, brominated, and iodinated alkanes, for example) have been found to undergo thermal EC by the dissociative electron capture (DEC) mechanism, reaction 2, in which an excited intermediate, RX^{-*},

$$e + RX \rightarrow RX^{-*} \rightarrow R + X^- \qquad (2)$$

has a very short lifetime against dissociation relative to the time required for stabilizing collisions with a bath gas. Even though some halogenated alkane molecules, RX, are known to have positive electron affinities (EA), molecular anions, RX^-, have never been observed as stable reaction products in their EC reactions.

The formation of molecular anions A^- by resonance electron transfer (RET) from donor molecular anions B^-, as shown in reaction 3, have been extensively studied[2,3,5] for compounds A and

$$B^- + A \rightleftharpoons B + A^- \qquad (3)$$

B of the type that tend to form stable molecular anions upon exposure to thermal electrons by REC (reaction 1). It has been noted that most RET reactions (those of substituted aromatic compounds, substituted benzo-, naphtho-, and anthroquinones, and tetracyanoethylene, for example) occur at near collision frequency as long as the reaction is exothermic by a few kilocalories

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0002-7863/92/1514-2336$03.00/0