quency (991 cm^{-1}) is also within the given range (948–1109 cm^{-1}[15]).

The fact that the ^{51}V NMR spectrum of **2** reveals an increase in shielding for the solution state (C_6D_6, 78.86 MHz: −240.9 ppm relative to external $OVCl_3$) versus the solid state (MAS 78.86 MHz: −205.5 ppm) may be taken to suggest that the $V{-}N_{ax}$ bond is stronger in the solution state, in conformity with the relatively strong rigidity of the metallatrane frameworks of **2** (and **3**) found in solution. Interestingly, the $^{13}C\{^1H\}$ spectrum[15] of **2** reveals clearly resolved V–C couplings (rarely observed[17]) for which the 7.2-Hz two-bond coupling involving C2 is the largest. The properties of **2** and **3** as CVD agents and the applicability of transmetalation reaction 1 to other transition metals as well as other ligand systems are currently under investigation.

Acknowledgment. We thank the AFOSR, the NSF, and the Deutsche Forschungsgemeinschaft (postdoctoral scholarship for W.P.) for financial support and Dr. Victor Young of the Iowa State Molecular Structure Laboratory for the crystal structure determination of **2**. We are grateful to the W. R. Grace Company for a research sample of tren.

Supplementary Material Available: Tables of complete crystal structure data, bond lengths and angles, and positional and anisotropic thermal parameters (5 pages); a listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Enantioselective Catalytic Isomerization of an Unfunctionalized Achiral Alkene

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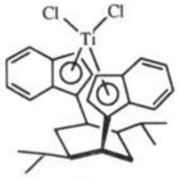
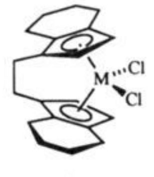
Asymmetric catalytic reactions using functionalized substrates such as the epoxidation of allylic alcohols[1] or hydrogenation of dehydroalanines[2] have had spectacular successes over the past decade, yet the development of catalysts for asymmetric reactions involving relatively unfunctionalized substrates remains an important challenge. Although catalysts have been reported for the highly enantioselective double-bond isomerization of allylic amines,[3] similar success using an isolated double bond have not been reported. We report here the development of the new chiral bis(indenyl)titanium catalyst **1** containing a chiral bridging group and its application in the first highly enantioselective isomerization of an isolated double bond.



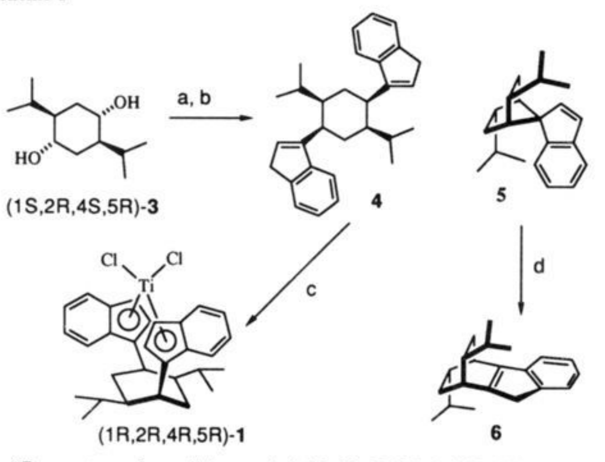
1



2

Chiral *ansa*-bis(indenyl)metal complexes are emerging as an important class of catalysts for asymmetric hydrogenation[4a] and stereoregular polymerizations[4b] and as a reagent for the asymmetric synthesis of allylic amines.[4c] The most common complexes of this type are the ethylene-bridged *ansa*-bis(tetrahydroindenyl)zirconium and -titanium dichlorides **2** prepared from the 1,2-ethylenebis(1-indenyl) ligand by Brintzinger.[5] Since the two faces of each indenyl ligand are enantiotopic in the ethylene-bridged ligand, metalation generally produced a mixture of meso and *dl* isomers from which the desired C_2-symmetric complex had to be separated and resolved. In an effort to simplify the synthesis of enantiomerically enriched bis(indenyl)metal complexes, we have developed *ansa*-bis(indenyl)metal complexes containing chiral, enantiomerically pure bridging groups.[6] By introducing chirality

Scheme I^a



^{a}Reagents and conditions: (a) MsCl, Et_3N, 0 °C; (b) indenyllithium, Et_2O, 0–23 °C, 12 h (60% of **4**); (c) (i) *n*-butyllithium, THF −78 to 0 °C, 0.5 h, 23 °C, 0.5 h; (ii) $TiCl_3$, −78 to 65 °C, 12 h; (iii) 6 N HCl, $CHCl_3$, air, −78 to 23 °C, 2 h; (d) 280 °C, 24 h.

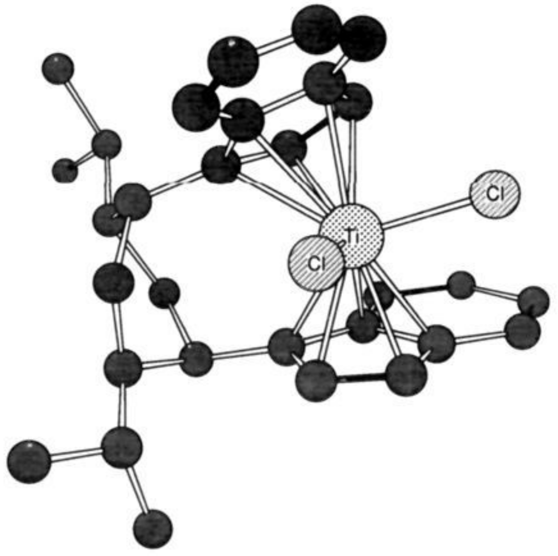


Figure 1. Solid-state structure of **1** determined by X-ray diffraction.

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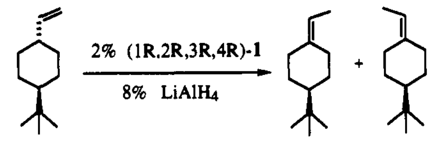
Table I. Asymmetric Alkene Migration Catalyzed by **1**[a]



7 *S*-**8** *R*-**8**

entry	temp (°C)	time (h)	yield	% ee[b] of (*S*)-**8**
1	180	2	100	44
2	180	12	100	14
3	80	12	100	65
4	80	24	100	55
5	50	17	100	74[c]
6	23	120	100	76
7	23	67	24[d]	80

[a] Reaction procedure: (1*R*,2*R*,4*R*,5*R*)-**1** (5.1 mg, 0.010 mmol) and $LiAlH_4$ (Fluka 97%, 1.6 mg, 0.04 mmol) in mesitylene (0.3 mL) were heated in an ampule at 164 °C for 30 min and then cooled to 23 °C. *trans*-**7** in *n*-decane as internal standard (0.2 mL, 0.5 mmol) was added and the sealed ampule heated at the indicated temperature for the indicated time. [b] Determined by chiral gas chromatography (50 m CP-cyclodex β-236, 80 °C isothermal, 15 psi, R_f (*R*)-**8** 77.02 min, (*S*)-**8** 77.74 min). [c] $[\alpha]^{23}_D$ +11.5° (*c* 3.01, 27:1 mesitylene/decane) indicates formation of the *S* isomer, ref 11. [d] *trans*-**7** recovered in 76% yield.

in the bridging group, we convert the previously enantiotopic faces of the indenyl ligands into diastereotopic faces and can theoretically favor the formation of a single stereoisomer of a single diastereomeric bis(indenyl)metal complex, eliminating the need for separating and resolving the complex.

The facile preparation of bis(indenyl)titanium complex **1** from the known (1*S*,2*R*,4*S*,5*R*)-2,5-diisopropylcyclohexane-1,4-diol (**3**)[7] is shown in Scheme I. Addition of indenyllithium to the bis(methanesulfonate) ester of diol **3** yielded either the spiro-annulated indene **5** or the desired bis(indene) **4**, depending on the reaction conditions. Addition of indenyllithium in THF to the dimesylate of **3** in the presence of HMPA gave almost exclusively the spiro product **5**, which could be thermally converted[7,9] to the novel fused indene **6**. Carrying out the displacement in Et_2O gave a 60% yield of the desired C_2-symmetric bis(indene) (1*R*,2*R*,4*R*,5*R*)-**4** as a mixture of double-bond isomers. Addition of the *n*-butyllithium-generated dianion of bis(indene) **4** to $TiCl_3$ followed by oxidation with HCl/air in $CHCl_3$ gave an 80% yield of a single isomer of *ansa*-bis(indenyl)titanium dichloride **1**. The solid-state structure of this complex was determined by X-ray diffraction of a suitable single crystal and is shown in Figure 1.[8] We rationalize the very high yield of a *single* isomer of metallocene **1** as being due to the highly preferred placement of the indenyl moieties away from the isopropyl groups on the bridging cyclohexane ring.

The catalytic isomerization of achiral alkenes using prereduced achiral titanocene dichlorides has been developed previously and is postulated to occur via an (η^1-allyl)- or (η^3-allyl)titanium hydride intermediate.[10] In order to study an asymmetric version of this isomerization, we chose to examine the conversion of the achiral meso *trans*-4-*tert*-butyl-1-vinylcyclohexane (**7**), a molecule devoid of any functionality other than the single vinyl group, into the chiral axially dissymmetric ethylidenecyclohexane **8**. In our case, we reduced our precatalyst, *ansa*-bis(indenyl)titanium dichloride (1*R*,2*R*,4*R*,5*R*)-**1**, with $LiAlH_4$ and then introduced 50 equiv of *trans*-**7** at various temperatures. As shown in Table I, the chiral alkene product (*S*)-**8** was formed in up to 80% enantiomeric excess in generally quantitative yield. The rate of the reaction and the enantiomeric purity of the product are strongly dependent on the reaction temperature. The lower enantiomeric purity obtained at the higher temperatures is apparently due to racemization by equilibration of the product, a process which should be enhanced with longer reaction times (as evident from entries 1–4). Isolated, enantiomerically enriched **8** was resubjected to the reaction conditions at 50 °C, affording a slightly diminished enantiomeric purity of **8** (74 to 71% ee after 24 h), which indicates probable slow equilibration of the ethylidenecyclohexane at this lower temperature. Further studies on the origin of enantioselectivity, the scope, and the mechanism of this unique asymmetric isomerization of an unfunctionalized alkene are in progress.

Acknowledgment. We thank the National Institutes of Health for support (GM-42735A).

Supplementary Material Available: Tables of bond lengths and angles, crystallographic data, and thermal and positional parameters for **1** (12 pages); listings of *h*, *k*, *l*, F_o, F_c, and $\sigma(F_o)$ for **1** (17 pages). Ordering information is given on any current masthead page.

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Electron Transfer to Triplet C_{60}

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The recent isolation of fullerenes such as C_{60} and C_{70} has led to several studies of the reactivity and physical properties of their excited states.[1-10] We recently reported that triplet C_{60} ($^3C_{60}$)

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