electrophoresis (10% acrylamide gel containing 7 M urea) in the presence of a DNA molecular weight standard (GIBCO).

Fluorescence gel-shift analysis was carried out with an ABIPrism 377 DNA sequencing instrument (Perkin Elmer). The nucleotide sequence of the 5′-fluorescein-derivatized G18 oligonucleotide probe (NAPS) is 5′-fluorescein-GTA ATG GTC ATA GCT GTT-3′. In a typical experiment, 3 pmol of the hybrid component (3 μM stock solution in tris(hydroxymethyl)aminomethane (tris) buffer, pH 7.3, 150 mM NaCl) was mixed with 0.5 pmol of RNA **4** and 0.5 pmol of G18 probe and the mixture incubated for 30 min at 37 °C. If no temperature-sensitive components are present, the aggregation may also be carried out for 2 min at 50 °C. A volume of 1 μL of the mixture was applied to a nondenaturing 4% acrylamide gel, and electrophoresis was carried out at 750 V, 50 mA for 3.5 h at 20 °C. The fluorescence bands were analyzed with ABI Prism GeneScan 2.0.2 software (Perkin Elmer).

Amino-modified 1.4-nm gold clusters (20 nmol; Monoamino-Nanogold, Nanoprobes) in 100 μL of phosphate buffer were treated with 10 equiv of NHS-biotin (Pierce) for 60 min at room temperature and subsequently purified by chromatography on a Superdex Peptide FPLC column (Pharmacia). Coupling with **3** was performed by mixing typically 100 pmol of the DNA–STV hybrids with 2–8 molar equivalents of **7** followed by incubation for 60 min. The assembly was carried out by the addition of 100 pmol of RNA **4** and incubating the mixture for 60 min. In some cases, unlabeled aggregates **5** were prepared and purified by chromatography (Superdex-200, Pharmacia) and subsequently treated with **7**. The purified biometallic aggregates were concentrated by ultrafiltration (Centricon, Millipore) and quantified photometrically. To prepare aggregate **9**, **3a–e** were coupled with **7** and **3f** with biotinylated goat anti-mouse IgG (Dianova) in separate reactions prior to the addition of RNA. For TEM analysis, 400-mesh copper grids with a thin carbon coating (Plano) were coated with proteins (mouse or rabbit IgG or poly-D,L lysine, Boehringer-Mannheim, 1 mg mL^{-1} in phosphate-buffered NaCl solution). For immobilization, a 5-μL drop of the gold-labeled aggregates (1–10 nM) was deposited on the grids for 2 min. TEM analysis was carried out with a Philipps EM 420 instrument operating at 120 kV.

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Synthesis of an ansa-Zirconocene via a Novel S_4-Symmetric Spirobis(silastannaindacene) Compound**

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The utilization of chiral ansa-zirconocenes as catalysts for numerous reactions[1, 2] demands a diastereoselective synthetic access to these complexes.[3] One approach to this goal involves the diastereoselective reaction of $ZrCl_4$ with a silyl-bridged bis(cyclopentadienylstannyl) ligand unit[4, 5] or a substituted 8-sila-4-stannatetrahydroindacene, a cyclic stan-

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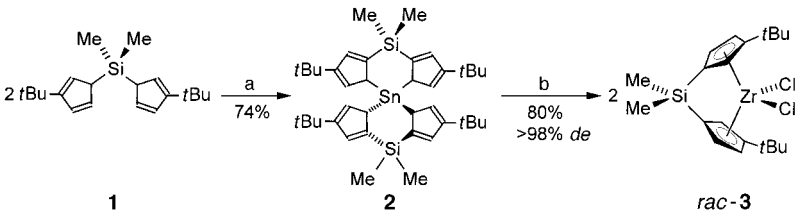
nylene ligand derivative.[6] A serious draw-back of these organotin-based zirconocene syntheses is the necessity to separate the *rac* and *meso* forms of the stannyl or stannylene intermediates, which are generally obtained with little or no diastereoselectivity.[4–6] To utilize the stereoselective transfer of Sn-bound cyclopentadienyl units to $ZrCl_4$[4–7] for a practicable ansa-zirconocene synthesis, we have searched for diastereoselective routes to cyclic silastannaindacene precursors and have found that this aim can be achieved in a straightforward manner with the tin amide $Sn(NMe_2)_4$ as a metalating agent.[8]

The reaction of $Sn(NMe_2)_4$ with two equivalents of the *tert*-butyl-substituted biscyclopentadienylsilane **1**,[9] present as a 1:1 mixture of its *rac* and *meso* isomers in diethyl ether, gave one product exclusively (Scheme 1): After removal of the solvent in vacuo and treatment of the residue with pentane, compound **2** was obtained as a yellow crystalline solid in 74% overall yield. Its identity was established as 2,2′,6,6′-tetra-*tert*-butyl-4,4′-spirobis(8-sila-4-stannatetrahydro-*s*-indacene) by NMR spectroscopy and X-ray diffractometry.[10, 11]

Both methods reveal that compound **2** has an approximate S_4-symmetric structure.[12] As in other silastannaindacenes,[4, 6] the more electronegative Si atoms are bonded to the sp^2-hybridized cyclopentadienyl C atoms, while the Sn atom is bonded to the sp^3 C centers. Both of the central six-rings, which are joined at the Sn spiro center, assume a twist geometry—as required by the axial symmetry of the molecular structure (Figure 1). Remarkably, the two C_2-symmetric six-rings are of opposite configuration: While the two asymmetry centers in one of the six-rings are *R,R*-configured, those in the other six-ring have an *S,S* configuration. The preference for the *R,R,S,S* isomer over all the other diastereomers for complex **2**[13] appears to be a special case of the general phenomenon of chirality-directed self-assembly of organometallic and other coordination compounds: Other examples have also been found where S_4-symmetric assemblies with two chelating ligands of opposite configuration are more stable than species with two ligands of identical configuration, presumably because of reduced interligand repulsion.[14]



Scheme 1. Stereoselective formation of *rac*-**3** via the bicyclic tin compound (*R,R,S,S*)-**2**: a) $Sn(NMe_2)_4$, Et_2O, room temperature; b) $ZrCl_4$, toluene, room temperature.

When (*R,R,S,S*)-**2** is treated with two equivalents of $ZrCl_4$ in toluene, transmetalation to the ansa-zirconocene **3** occurs in approximately 12 h. This reaction leads exclusively to the racemic form of **3**,[9] which is obtained, after removal of $SnCl_4$ in vacuo, in around 80% isolated yield. This observation is in accord with the stereoselectivity established previously for Sn/Zr exchange reactions of this type.[4–7]

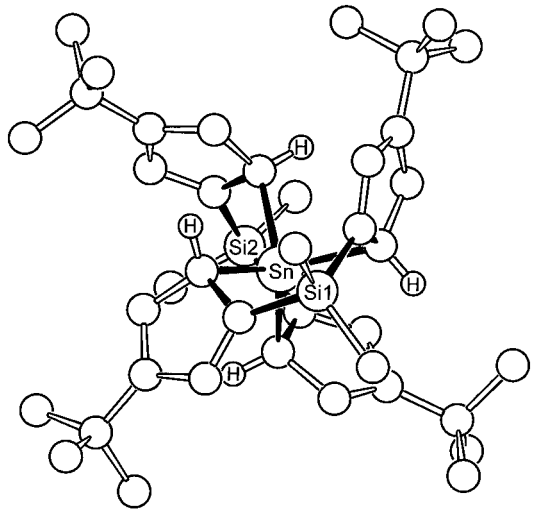


Figure 1. Idealized S_4-symmetric geometry of (*R,R,S,S*)-**2**.[12] Hydrogen atoms are only shown at stereogenic centers, the carbon atoms are unlabeled. The spiro-connected six-rings are represented by dark bonds.

Our results document that racemic ansa-zirconocenes can be obtained stereoselectively from a mixture of ligand diastereomers in a short sequence of smooth, high-yield reactions by the appropriate choice of reagents. Extensions of this methodology to other types of chiral ansa-metallocenes are presently under investigation.

Experimental Section

All manipulations were performed on argon/vacuum apparatus or in a glove box under nitrogen. Solvents were dried and distilled over sodium/benzophenone. $Me_2Si(3\text{-}tBuC_5H_4)_2$[9] and $Sn(NMe_2)_4$[8] were prepared according to literature methods. NMR spectra were recorded on Bruker AC250 and Bruker DRX600 spectrometers. ^1H NMR chemical shifts were determined by comparison with residual ^1H solvent peaks and reported relative to $\delta(Me_4Si) = 0$,.

Caution! Mixtures of tin amides with halogenated hydrocarbon solvents are potentially explosive.[15]

2: A solution of $Sn(NMe_2)_4$ (1.0 mL, 6 mmol) in Et_2O (50 mL) was added over 30 min to a solution of $Me_2Si(3\text{-}tBuC_5H_3)_2$ (3.3 g, 11 mmol)[9] in Et_2O (100 mL). The reaction mixture was stirred for 16 h. The solvent was reduced to 80 mL to remove the dimethylamine, and the mixture was stirred until the NMR signals of $Sn(NMe_2)_4$ were no longer observed. The solvent was removed and replaced by pentane (30 mL). A light-yellow precipitate was collected by filtration and washed with small amounts of cold pentane. The remaining mother liquor was reduced in volume and stored at $-30\,^\circ C$ to yield further precipitate. In total, 2.9 g (74%) of compound **2** were obtained. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 7.04$ (s, $^4J(H,Sn) = 17$ Hz, 4H, C_5-H), 6.12 (s, $^3J(H,Sn) = 9$ Hz, 4H, C_5-H), 3.50 (s, $^2J(H,Sn) = 103$ Hz, 4H, C_5-H), 1,23 (s, 36H, $C(CH_3)_3$), 0.37 (s, 12H, $SiCH_3$); ^{13}C NMR (broad-band decoupled, $CDCl_3$, 150 MHz, 25 °C): $\delta = 154.2$ (C_5, sp^2), 145.2 (C_5, sp^2), 137.4 (C_5, sp^2), 126.6 (C_5, sp^2), 58.9 (C_5, sp^3, $^1J(C,Sn) = 90$ Hz), 32.1 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), −2.2 ($SiCH_3$); ^{119}Sn NMR (broad-band decoupled, 223.6 MHz, $CDCl_3$, 25 °C, Me_4Sn): $\delta = -45.3$; elemental analysis calcd (%) for $C_{40}H_{60}Si_2Sn$: C 67.12, H 8.45; found: C 67.17, H 8.78.

rac-**3**: A solution of **2** (0.62 g, 0.85 mmol) in toluene (250 mL) was added dropwise to a well-stirred suspension of $ZrCl_4$ (0.4 g, 1.7 mmol) in toluene (200 mL), and the reaction mixture stirred for 16 h. The toluene was removed in vacuo, the residue was taken up in pentane, and any insoluble impurities were removed by filtration. The pentane and $SnCl_4$ were removed in vacuo to give 0.64 g (80%) of pure *rac*-**3** as a yellow residue. ^1H

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NMR (C_6D_6, 250 MHz, 25 °C, see ref. [9]): $\delta = 6.72$ (m, 2H), 5.67 (m, 4H), 1.39 (s, 18H), 0.19 (s, 6H).

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[10] The ^1H and ^{13}C NMR spectra of **2** in $CDCl_3$ are in accord with the expected S_4 symmetry: The number of signals observed is only one fourth of that expected for an unsymmetrical molecule (see Experimental Section). The signal assigned to the H atom at C1 exhibits a large $^1H - ^{117/119}Sn$ coupling of 103 Hz (see ref. [6a]).

[11] Colorless monoclinic prisms of **2** ($C_4H_{60}Si_2Sn \cdot 0.5\,O(C_2H_5)_2$) were obtained by crystallization from diethyl ether at 4 °C. Further details on the crystal structure investigation of **2** may be obtained from the Fachinformtionszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-380134.

[12] The molecular geometry of **2** in the solid state is distorted from the idealized S_4 symmetry represented in Figure 1 in that the Si(1) – Sn axis deviates from the Sn – Si(2) axis by 18°. This distortion might be caused by packing effects related to the cocrystallization of a diethyl ether molecule.

[13] Compound **2** is thermally stable; even after several days in solution there were no indications of any rearrangement having occurred.

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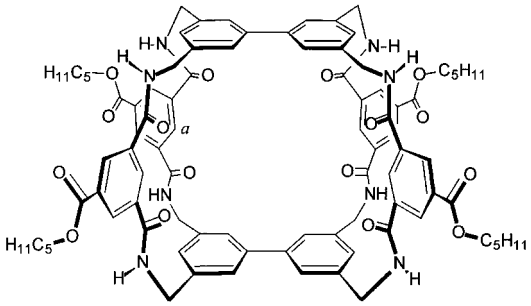
A Tricyclic Polyamide Receptor for Carbohydrates in Organic Media**

Anthony P. Davis* and Richard S. Wareham

Carbohydrates are important[1] but especially challenging substrates for supramolecular chemistry. Their structures are complex, yet lack (in the general case) individual features, such as ionic or strongly hydrophobic units, able to partake in strong and specific noncovalent interactions.[2] The problem intensifies in hydroxylic solvents, where a receptor must distinguish its target from a large excess of similarly functionalized competitors. With the exception of boron-based systems which operate through covalent bond formation,[3] there are still no effective synthetic receptors for carbohydrates in aqueous solution.[4] Of the many published systems for operation in organic media,[5, 6] only a few can tolerate significant quantities of hydroxylic cosolvents.[6]

We now report a new carbohydrate receptor **1**, which shows unusual levels of affinity and selectivity in chloroform, and remains effective even in the presence of 8% CD_3OH. The design of **1** was inspired by carbohydrate-binding proteins,



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which commonly place aromatic surfaces against patches of carbohydrate CH groups while accepting the hydroxyl groups into networks of hydrogen bonds.[1d, 7] The intended target of **1**, the β-D-glucopyranosyl unit **2**, possesses axial CH groups and equatorially directed hydroxyl groups (Figure 1). The

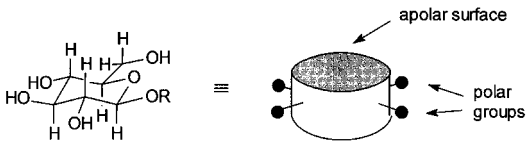

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Figure 1. Target molecule of the receptor **1** with axial hydrophobic and equatorial polar groups.

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