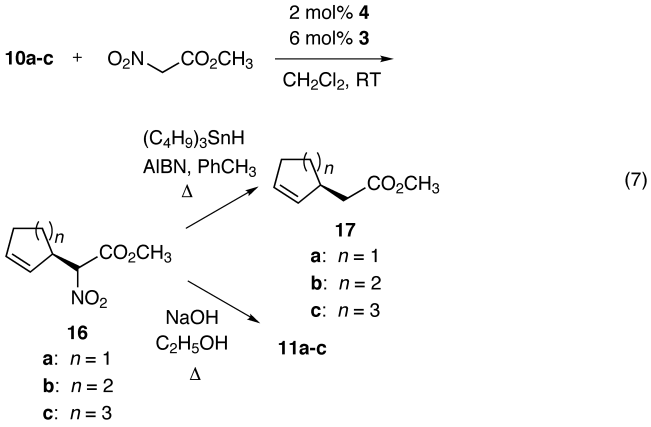
excellent results (**15a**[7], 74% yield, 97% *ee*; **15b**[7], 79% yield, 94% *ee*; **15c**[7], 50% yield, 96% *ee*).

The absolute configuration was established by correlation as depicted in Equation (7). Alkylation of the allyl carbonates **10a–c** using methyl nitroacetate proceeds with no added base to give the desired products (**16a**,[7] 80%; **16b**,[7], 93%; **16c**,[7], 87%). Radical denitronation[11] gave the known cycloalkenyl



(7)

acetates **17a–c**[10] thereby establishing the absolute configuration of **16a–c**. Alternatively, hydrolysis with concomitant decarboxylation gave the nitroalkenes (**11a**, 64% yield, 85% *ee*; **11b**, 65% yield, 95% *ee*; **11c**, 72% yield, >99% *ee*) thereby establishing their absolute configurations as depicted.

The utility of nitroalkanes as building blocks makes a significant step forward as a result of the ability to effect AAA reactions using cyclic allyl esters. It is clear that the nitroalkane significantly influences the catalyst. The significantly different reactivity between nitromethane and 2-nitropropane highlight this fact. A possible explanation suggests that the nitronate derived from nitromethane may serve as a competitive ligand to palladium. The lack of polyalkylation of nitromethane is noteworthy especially considering that the higher nitroalkanes are better nucleophiles and the reported significance of this problem in another system.[4] The current method provides a practical approach to these chiral nitroalkanes that enhances their utility as useful building blocks.

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Enantiomeric Self-Recognition: Cation-Templated Formation of Homochiral Isoguanosine Pentamers**

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Stereochemical information embedded within the building blocks of biopolymers is often translated into higher organization. Both the protein α-helix and the DNA duplex, structures that require homochiral chains, rely on such a hierarchy.[1] To illustrate the impact of stereochemistry in controlling the structure of noncovalent aggregates, we describe the enantiomeric self-recognition of the racemic 5′-*tert*-butyldimethylsilyl-2′-3′-di-*O*-isopropylidene-substituted isoguanosine, isoG **1**, to give homochiral, hydrogen-bonded pentamers.

Self-recognition is a process whereby a compound selectively associates with its own kind. Self-recognition relies on: 1) reversible processes[2] and 2) a subunit's "pre-disposition"[3] towards self-assembly. Stereochemistry can be crucial for self-recognition. Enantiomeric self-recognition in supramolecular systems has been achieved using metal ion coordination[4, 5] or hydrogen bonds.[6–8]

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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Our interest in self-recognition arose from studying isoG **1** and the guanosine derivative G **2** (see the Supporting Information and Figure 1).[9, 10] These nucleosides self-associate in the presence of cations,[11] with (D)-G **2** forming

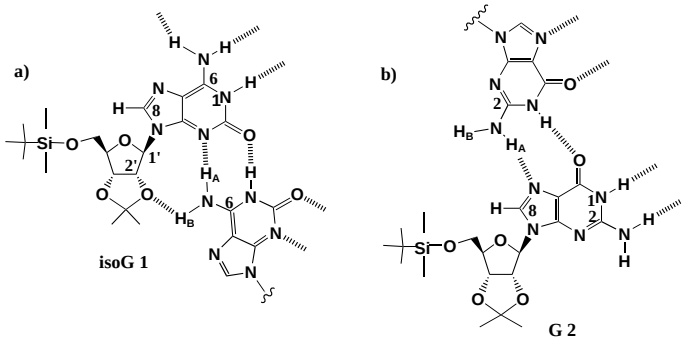


Figure 1. Hydrogen-bond geometry in a) an isoG **1**–isoG **1** basepair within an isoG pentamer and b) a G **2**–G **2** basepair within a G-quartet. The ribose O2′ atom in the isoG–isoG basepair hydrogen bonds with the neighboring amino proton N6-H_B. A G–G pair does not show such a sugar–base interaction.

G-quartets and (D)-isoG **1** giving pentamers.[12, 13] Crystal structure analyses[9, 10] showed that hydrogen-bonded macrocycles sandwich the cation diastereospecifically: G **2** forms the head-to-tail octamer $(G\,\mathbf{2})_8 \cdot K^+$, and isoG **1** forms the tail-to-tail decamer $(\text{isoG}\,\mathbf{1})_{10} \cdot Cs^+$.[14] Nucleobase–nucleobase hydrogen bonds and cation–dipole interactions stabilize these structures. The $[(D)\text{-isoG}\,\mathbf{1}]_{10} \cdot Cs^+$ decamer also has hydrogen bonds that link the 2′-oxygen atom of each sugar with its neighboring amine group (Figure 1).[10] As a result of this sugar–base hydrogen bond, each monomer within an isoG pentamer interacts directly with its neighbor's chiral sugar. In contrast, sugar–base hydrogen bonds do not occur in the G-quartet. Since the isoG O2′–NH6 sugar–base hydrogen bonds are only possible in a homochiral basepair, we considered isoG **1** to be an excellent candidate for enantiomeric self-recognition. Our question was simple: will racemic (D,L)-isoG **1** form homochiral pentamers in the presence of an achiral template? Herein, we report that it does.

To better appreciate the chiral sensing properties of isoG **1**, we first describe a guanosine system that does not display enantiomeric self-recognition. (D)-G **2** coordinates K^+ in the solid state and in solution to give a diastereomerically pure octamer, with G-quartets stacked in a head-to-tail arrangement.[15] Figures 2a and 2b show the isochronous ^{1}H NMR spectra for $[(D)\text{-G}\,\mathbf{2}]_8 \cdot K^+$ and $[(L)\text{-G}\,\mathbf{2}]_8 \cdot K^+$.[16] The enantiomeric $(G\,\mathbf{2})_8 \cdot K^+$ octamers both have two sets of resonances, one set for each unique G-quartet within the octamer. When equivalent amounts of the enantiomers were mixed in CD_3CN the resulting spectrum showed more than ten separate signals for each proton, which indicated a diastereomeric mixture (Figure 2c). Clearly, G **2** does not undergo enantiomeric self-recognition to give homochiral G-quartets, at least with a K^+ ion as the template. However, as described below, the isomeric isoG **1** is pre-disposed for self-recognition.

Preparation of (D)-isoG **1** has been described,[13a] and Scheme 1 outlines the synthesis of (L)-isoG **1**. The O6-

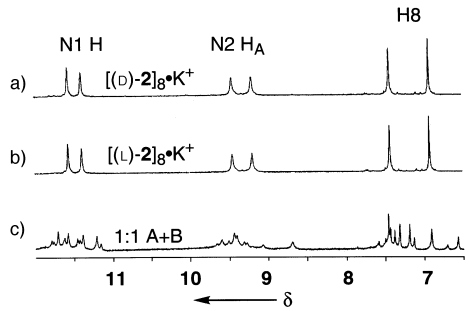
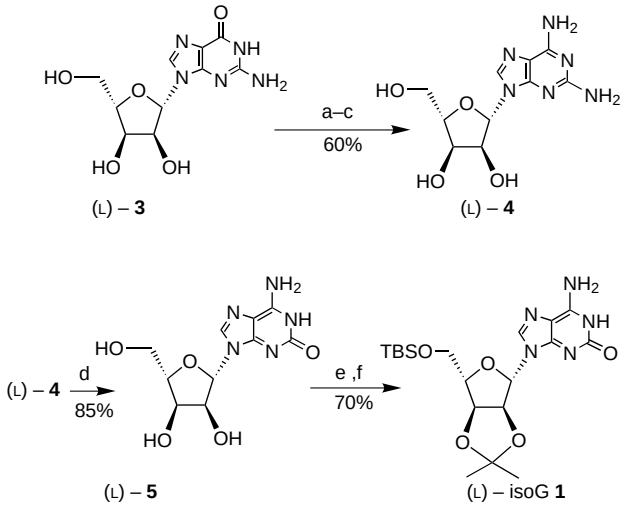


Figure 2. A region of the ^{1}H NMR spectra in CD_3CN at −40 °C for a) $[(D)\text{-G}\,\mathbf{2}]_8 \cdot K^+PF_6^-$; b) $[(L)\text{-G}\,\mathbf{2}]_8 \cdot K^+PF_6^-$, and c) a 1:1 mixture of $[(D)\text{-G}\,\mathbf{2}]_8 \cdot K^+PF_6^-$ and $[(L)\text{-G}\,\mathbf{2}]_8 \cdot K^+PF_6^-$ (the spectrum was identical 10 min and 24 h after mixing).



Scheme 1. a) Trifluoroacetic acid anhydride, pyridine; b) pentafluorophenol, pyridine; c) NH_3/H_2O, 55 °C; d) $NaNO_2$, HOAc, 50 °C; e) 2,2-dimethoxypropane, *para*-toluene-4-sulfonic acid; f) *tert*-butyldimethylsilyl chloride, imidazole.

activation of (L)-G **3**,[16] followed by aminolysis gave (L)-2,6-diaminopurine **4**.[17] Diazotization of (L)-**4**,[18] followed by modification of the hydroxyl groups of (L)-**5** gave the enantiomeric (L)-isoG **1**. This nucleoside and $CsPh_4B$ crystallized from CH_3CN to give $[(L)\text{-}\mathbf{1}]_{10} \cdot Cs^+Ph_4B^-$. Optical rotations and CD spectra for the all-L decamer and the all-D decamer were of opposite sign and the same magnitude.[19]

A ^{1}H NMR experiment provided the first indication for the stereoselective self-recognition of racemic isoG **1**. Figures 3a and 3b show the ^{1}H NMR spectra for the all-D and all-L isoG decamers in CD_3CN. Mixing equimolar solutions of these enantiomers gave a simple spectrum, with two species present in a 4:1 ratio (Figure 3c). The minor signals were identical to those observed for the all-L and all-D decamers. The major set of signals, which were different from those for the enantiomeric decamers, indicated that a new diastereomer predominates when (D,L)-isoG **1** binds a Cs^+ ion under thermodynamic conditions.

An X-ray crystal structure analysis confirmed that (D,L)-(isoG **1**) undergoes enantiomeric self-recognition.[20] The *meso* decamer $[(D)\text{-isoG}\,\mathbf{1}]_5 \cdot Cs^+ \cdot [(L)\text{-isoG}\,\mathbf{1}]_5Ph_4B^-$ has one pentamer composed of only (D)-isoG **1** and the other

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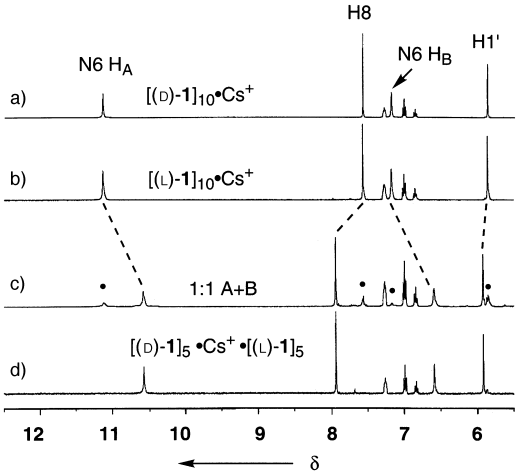

Figure 3. A region of the ^{1}H NMR spectra for a) [(D)-isoG **1**]$_{10}\cdot Cs^+Ph_4B^-$; b) [(L)-isoG **1**]$_{10}\cdot Cs^+Ph_4B^-$; c) a 1:1 mixture of [(D)-isoG **1**]$_{10}\cdot Cs^+Ph_4B^-$ and [(D)-isoG **1**]$_{10}\cdot Cs^+Ph_4B^-$ (after 24 h); d) *meso* decamer, [(D)-isoG **1**]$_5\cdot Cs^+\cdot$[(L)-isoG **1**]$_5Ph_4B^-$ (immediately after dissolving crystals). Spectra were recorded in CD_3CN at 25 °C after dissolving crystallized complexes.

pentamer made up of (L)-isoG **1** (Figure 4). Both homochiral pentamers have the key O2′–NH6 sugar–base hydrogen bonds between neighbors (mean $d_{N6HB\cdots O2'} = 2.83$ Å, mean $\theta_{N6HB\cdots O2'} = 136°$). Apparently, the five sugar–base hydrogen bonds within an (isoG **1**)$_5$ pentamer help overcome the entropic demands associated with enantiomeric self-sorting.

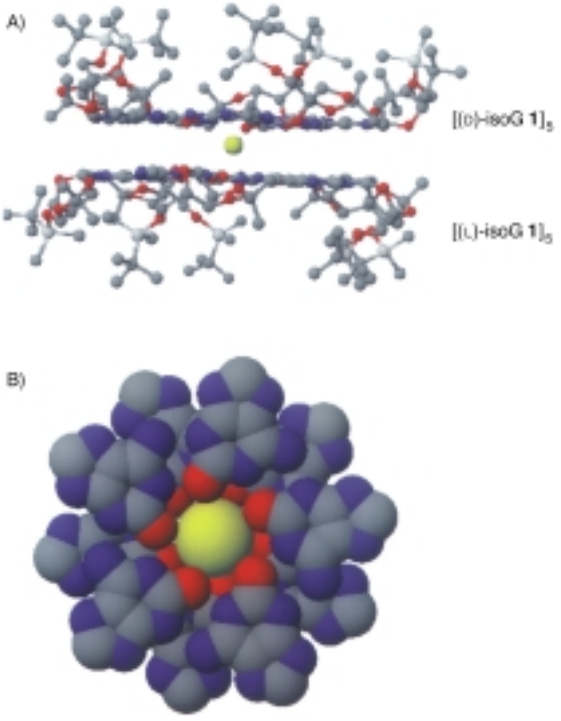

Figure 4. A) A side view of the X-ray crystal structure of the *meso* decamer [(D)-isoG **1**]$_5\cdot Cs^+\cdot$[(L)-isoG **1**]$_5Ph_4B^-$. The Ph_4B^- ion, located above [(D)-**1**]$_5$, is removed for clarity. This view shows the stacking of the two homochiral isoG pentamers ($d = 3.26$ Å between planes) around the Cs^+ ion. B) A top view with the sugar molecules and H atoms removed for clarity; Cs^+: yellow; oxygen: red; nitrogen: blue; and carbon: gray. The encapsulated Cs^+ ion is bound to 10 oxygen atoms, with a mean $d_{Cs-O} =$ 3.41 Å.

The decacoordinate Cs^+ ion ($d_{Cs-O} = 3.29-3.67$ Å) is sandwiched by the two homochiral pentamers. As expected, dissolving crystals of the *meso* decamer [(D)-isoG **1**]$_5\cdot Cs^+\cdot$[(L)-isoG **1**]$_5Ph_4B^-$ in CD_3CN gave ^{1}H NMR chemical shifts identical to those for the major diastereomer observed in the mixing experiment (Figure 3d). The system achieved thermodynamic equilibrium within 30 minutes in CD_3CN to give a spectrum similar to that in Figure 3c.

IsoG **1**, upon coordinating a Cs^+ ion, uses sugar–base hydrogen bonds to transmit stereochemical information from one nucleoside to its neighbor. The result is a homochiral pentamer (isoG **1**)$_5$. Decamer formation, achieved by stacking two homochiral pentamers around a Cs^+ ion, is also diastereoselective; a *meso* isomer exists in the solid state and predominates in solution. Importantly, it is the achiral Cs^+ ion that enables enantiomeric self-recognition of isoG **1**. Experiments with other alkali cations, Li^+, Na^+, K^+, or Rb^+, have not provided convincing evidence for enantiomeric self-recognition. In a broader context, this work illustrates that the appropriate ligand and template (isoG **1** and Cs^+) may provide homochiral aggregates, while related ligand and template combinations (G **2** and K^+) yield diastereomeric libraries.[23] In addition, nucleosides such as isoG **1** may be ideal models for exploring the origins of biomolecular homochirality.[24]

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[20] Crystal data for $[(D)\text{-isoG } \mathbf{1}]_5 \cdot Cs^+ \cdot [(L)\text{-isoG } \mathbf{1}]_5Ph_4B^-$: $[(C_{19}H_{31}N_5O_{5}Si)_{10} \cdot Cs] \cdot B(C_6H_5)_4 \cdot 14\,NCCH_3$, $M_r = 5402.66$, crystal dimensions $0.724 \times 0.268 \times 0.192$ mm^3, monoclinic, space group $P2_1$, $a = 18.844(2)$, $b = 35.984(4)$, $c = 22.193(3)$ Å, $\beta = 92.027(5)^\circ$, $V = 15{,}039(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.193$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.239$ mm^{-1}. Data were collected on a Bruker SMART 1000 CCD diffractometer at 193(2) K. The structure was determined by direct methods.[21] Refinement, using the SHELXL program,[22] was done to convergence on F^2 with $R(F) = 0.0907$ % and $wR(F^2) = 0.1936$ % for 39328 independent reflections. More information can be obtained from the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144859. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Synthesis and Characterization of Iron Silasesquioxane Phosphane Complexes**

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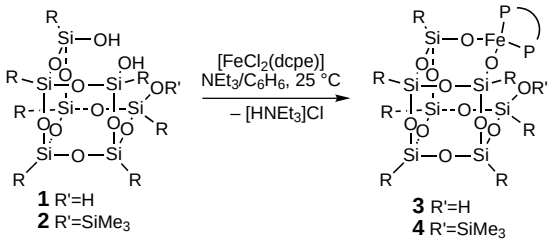
Iron centers supported on inorganic silicate matrices have been shown to be very active for the catalytic reduction of nitrogen oxides (NO_x)[1] and the selective oxidation of hydrocarbons using nitrous oxide. In the latter case, a purported iron – oxo species supported on an inorganic zeolite matrix has been shown to insert rapidly and cleanly into the C–H bonds of methane and benzene in the presence of N_2O as the oxidant.[2] In our studies of the catalytic chemistry of framework and extra-framework (ion-exchanged) metal-ion substituted zeolites we are interested in the development of soluble analogues of these iron silicates. Thus we have focused our attention on the synthesis and characterization of iron complexes of polyhedral silasesquioxanes (POSSs). Herein, we report the first structurally characterized iron – silasesquioxane complexes substituted into the silicate framework; the Fe centers are protected from oligomerization by a phosphane ligand. We have also delineated a reaction pathway that removes a phosphane ligand from a Fe^{III} – POSS complex to form a dimeric μ-oxo diiron complex. These compounds are of interest as homogeneous models for the heterogeneous iron zeolite catalysts.

Feher and co-workers have elegantly demonstrated that incompletely condensed polyhedral silasesquioxanes can serve as homogeneous models for both silica surfaces and zeolites, which is possible because of their flexible Si–O frameworks and defined cagelike structures.[3] A number of metal – silasesquioxane complexes have been synthesized and characterized as models of heterogeneous catalysts. For example, titanium – silasesquioxane complexes can efficiently catalyze the liquid-phase epoxidation of olefins,[4] thereby modeling the reactivity of heterogeneous titanasilicate (for example TS-1[5]) catalysts. Analogously, soluble iron – silicate compounds might model the heterogeneous iron – zeolite catalysts; however, no Fe – POSS complexes have been reported. Reactions of simple iron salts with POSS and similar analogues lead to mixtures that have been difficult to characterize,[6] although dimeric POSS complexes have been reported for several other metals.[3b] Our approach to making molecular Fe – POSS complexes has centered on protecting iron centers from oligomerization by the use of simple phosphane ligands. This approach is similar to that used by Lugmair and Tilley to synthesize the soluble monomeric iron silicate $[Fe\{OSi(OtBu)_3\}_3] \cdot THF$ in which the steric bulk of the organosilicate ligand is used to prevent oligomerization.[7]

We have employed both the incompletely condensed POSS **1** and its trimethylsilyl mono-protected analogue **2** to support iron centers. Reactions of the iron(II) precursor $[FeCl_2(dcpe)]$ (dcpe = bis(dicyclohexylphosphanyl)ethane) with **1** or **2** in the presence of triethylamine in benzene afforded the iron(II)-(dcpe) – silasesquioxane compounds **3** and **4**, respectively (Scheme 1), which were isolated in high yield as colorless crystals. The iron(III) analogue **5** was prepared and isolated in a similar manner from the reaction of $[FeCl_3(PCy_3)]$ (Cy = cyclohexyl) and **1** (Scheme 2, top). Complexes **3** – **5** are paramagnetic and give broad signals in the NMR spectra.



1 R'=H
2 R'=SiMe$_3$
3 R'=H
4 R'=SiMe$_3$

Scheme 1. Synthesis of the mono iron compounds, R = *c*-C_5H_9.

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