

Hierarchical self-assembly of metallo-dendrimers†‡

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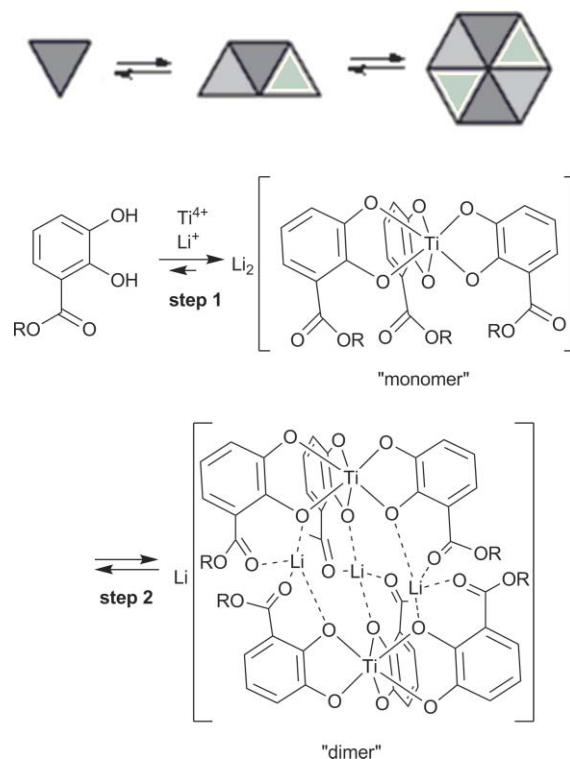
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2,3-Dihydroxybenzyl esters with Frechet-type dendritic branches as the alcohol component form, in a hierarchical self-assembly process, disk shaped dendrimers when titanium(IV) and lithium ions are added.

Dendrimers combine aesthetic appeal with a high potential for application. Since their first description in 1978¹ they have been an intensely investigated class of compounds. Many functionalities have been introduced in the periphery or in the interior of the dendrimers which enforced the development of new synthetic protocols in order to obtain the compounds in monodisperse form.² An elegant method to easily obtain the highly branched structures is self-assembly from relatively simple building blocks.³ Metal coordination has especially proved to be advantageous over weaker interactive forces.⁴

In preliminary studies, dendritic side chains were attached to simple ligands for mononuclear Werner-type metal complexes. Coordination of metal ions connected several of the ligands to form dendrimers.⁵ In more recent studies this was taken to a supramolecular level and oligotopic ligands which were decorated by dendritic side chains were assembled to form dendrimers with a metallosupramolecular aggregate as a central backbone.⁶

Here we describe a hierarchical approach in which first a dendritic Werner-type complex is formed and subsequently dimerizes to form a higher branched dendrimer. Therefore, Frechet-type dendritic moieties⁷ are connected to catechol units *via* an ester function in the 3-position of the ligand. Esters like this were recently shown to form triscatechol titanium(IV) complexes which in the presence of lithium cations are in equilibrium with dinuclear helicate-type⁸ titanium(IV) complexes.⁹ These possess three lithium cations as spacers (Scheme 1). Due to the stepwise formation of the compounds (step 1: formation of mononuclear metal complex, step 2: dimerization) the “dimer”-assembly can be described to be “hierarchical”.^{10,11} With corresponding ligands bearing dendritic substituents (**1a–c–H₂**) (Scheme 2) we expect



Scheme 1 Hierarchical assembly of lithium bridged dimeric helicate-type coordination compounds by initial complex formation (step 1) followed by dimerization (step 2).

to obtain mononuclear metallogendrimers [(**1a–c**),Ti]²⁻ which are able to “grow” (approximately doubling the molar weight) by formation of the dimer [Li₃(**1a–c**)₂Ti]²⁻. The synthesis of the ligands and formation of the complexes is the focus of this communication.

The preparation of the ligands **1a–c–H₂** follows a straightforward procedure. Reaction of 2,3-dihydroxybenzoic acid **2** with acetic anhydride results in the close to quantitative formation of the triacetyl derivative **3** as intermediate which is used without purification. The mixed anhydride part can easily be hydrolyzed with water (yield of **4**: 98% over two steps; crude product, which is used without further purification).¹² The protected ester ligands **6a–c** are made in an S_N-reaction with the benzylic bromides **5a–c**, which were already described by Frechet.⁷ Subsequently the acyl protecting groups are removed and the ligands **1a–c–H₂** are obtained (yield over two steps: 74% **a**, 66% **b**, 38% **c**).

Reaction of three equivalents of ligand **1–H₂** with one equivalent of Ti(O)(acac)₂ (or Ga(acac)₃) in the presence of one (or 1.5) equivalent of lithium carbonate results in the formation of compounds with the general formula “Li₂[(**1a–c**)₃Ti]” or “Li₃[(**1a,b**)₃Ga]”. For comparison purposes, the potassium salt “K₂[(**1b**)₃Ti]” was

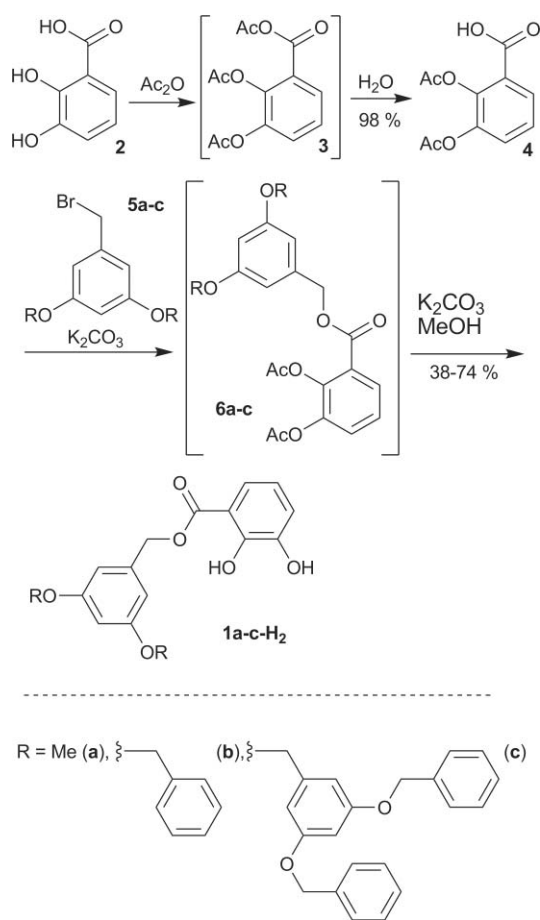
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‡ Crystal data for Li₃(C₁₆H₁₄O₆)₆Ti₂ · Li(C₃H₇NO)₄ · C₄H₁₀O, *M* = 2303.70, triclinic, space group *P*1̄ (No. 2), *a* = 12.7987(7), *b* = 16.9382(7), *c* = 27.3122(10) Å, α = 101.847(2), β = 199.370(2), γ = 93.316(4)°, *V* = 5633.3(4) Å³, *D_c* = 1.358 g cm⁻³, μ = 1.957 mm⁻¹, *Z* = 2, λ = 1.54178 Å, *T* = 223(2) K, 73756 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å⁻¹, 19708 independent (*R_{int}* = 0.090), and 14984 observed reflections [*I* ≥ 2σ(*I*)], 1463 refined parameters, *R* = 0.081, *wR*² = 0.240. CCDC 775940.



Scheme 2 Preparation of catechol ligands bearing Fréchet-type dendritic ester side chains.

prepared. Results with the gallium(III) ions are similar to those with titanium(IV) and therefore only the latter are discussed in here.

Characterization of the complexes was done by ¹H NMR spectroscopy. Using this technique, the methylene protons at the ester act as spectroscopic probes. *e.g.* for the corresponding ethyl ester the methylene signal of the monomeric titanium complex appears in methanol-d₄ at $\delta = 3.11$ ppm (t) and is shifted and split in the dimer into two signals at $\delta = 2.72$ and 2.12 (m each).¹⁰ They are observed in the free ligands (in CDCl₃) as a singlet at $\delta = 5.29$ (**1a**-H₂), 5.21 (**1b**-H₂) or 5.28 (**1c**-H₂). From earlier studies, it is known that upon metal coordination those signals are sensitive to the formation of the monomeric or dimeric complexes. In the monomer they appear as singlets due to a fast inversion of configuration at the metal complex unit. This is locked in the dimer and the protons show diastereotopic behaviour leading to the observation of two doublets.¹³

Exclusively the monomeric titanium complex K₂[(**1b**)₃Ti] is formed with potassium cations as counterions. This is confirmed by the observation of only one singlet for the corresponding CH₂-group (in CD₃OD/CDCl₃ 1 : 2; a solvent mixture has to be used due to the low solubility in more polar solvents) at $\delta = 5.05$.

For the lithium complexes “Li₂[(**1a,b**)₃Ti]” diastereotopic behaviour is observed. The doublets of the ester CH₂ group appear at $\delta = 4.37$ and 3.92 ($J = 12.6$ Hz) for [Li₃(**1a**)₆Ti₂]⁻ (CD₃OD) and at

$\delta = 4.35$ and 3.87 ($J = 11.4$ Hz) for [Li₃(**1b**)₆Ti₂]⁻ (CD₃OD/CDCl₃ 1 : 2). The upfield shift, as well as the splitting of the signal, indicates the presence of the dimeric helicate-type dendrimers in solution. Signals of a corresponding monomer are not observed or are only present in traces. For “Li₂[(**1c**)₃Ti]”, NMR analytics were problematic. Due to the low polarity of the compound it is only soluble in non-polar solvents like 1 : 4 CD₃OD/CDCl₃. In this mixture broad resonances are observed, which might be due to aggregation of the dendrimers under the chosen conditions.¹⁴ Nevertheless, broad resonances at $\delta = 4.31$ and 3.82 indicate the dimeric complex formed.

Negative ESI FT-ICR MS showed the characteristic peak of [K(**1b**)₃Ti]⁻ at $m/z = 1450$ for the potassium salt. In the case of the corresponding lithium compounds only the dimers were observed as [Li₃(**1a**)₆Ti₂]⁻ ($m/z = 1929$) and [Li₃(**1b**)₆Ti₂]⁻ ($m/z = 2843$). No peaks for the monomers were detected. However, isolation of the dimer peak [Li₃(**1a**)₆Ti₂]⁻ at $m/z = 1929$ in the gas phase followed by a CID (collision induced decay) experiment generated the monomer [Li(**1a**)₃Ti]⁻, which was observed at $m/z = 961$. The dimer of “Li₂[(**1c**)₃Ti]” could not be detected, probably due to its high mass ($m/z > 5000$).

In addition to the solution studies we crystallized the compounds in order to get X-ray structure analyses.[†] We were able to obtain crystals of Li[Li₃(**1a**)₆Ti₂] as well as of Li[Li₃(**1b**)₆Ti₂]. Only the former resulted in a structure of sufficient quality for X-ray analysis. The preliminary structure of the latter reveals only fragments of the complex which, however, indicate a high level of structural similarity to the smaller analogue possessing the lithium-bridged dimeric unit.

The central helicate-part of Li[Li₃(**1a**)₆Ti₂] shows an overall structure as illustrated for the dimer in Scheme 1. Two tris(catechol)titanium(IV) units are formed, which each additionally coordinate through the salicylate units to three lithium cations. A distorted tetrahedral geometry is found at the alkali metal cations. The titanium cations are separated by Ti–Ti = 5.553(1) Å. One of them is located above, the other below the plane defined by the three lithium ions (Li–Li = 3.497(9), 3.516(10), 3.542(9) Å). Therefore the positive charge of the five cations is concentrated in a relatively small volume of space. However, this charge is compensated by six dianionic catecholato ligands which surround the cluster of cations. The representations of the molecular structure in the crystal (Fig. 1) show the attachment of the ester substituents at the waist of the central “helicate cylinder”. Due to the proximity of the esters to the lithium cations, the substituents are all more or less lying within the plane of the three lithium cations. The dendrimer is not globular, but rather disc shaped. This is decorated by the dendritic side chains on its periphery. From the X-ray structure it is understood that, upon dimerization of the complex units, the size of the dendrimers (monomer *versus* dimer) does not change significantly, while the density increases.¹⁵ This is schematically represented in Fig. 1, bottom.

Thus, the formation of monomeric (“syn”) complexes with three catecholates leads to a triangular coordination compound with the dendritic groups arranged in one plane. Two of such units dimerize in a head to head fashion but twisted by 45° so that the substituents of the two units are able to interlock. Hereby the size of the system is not significantly altered. The substituents of the first unit are filling up the gap between those of the second one.

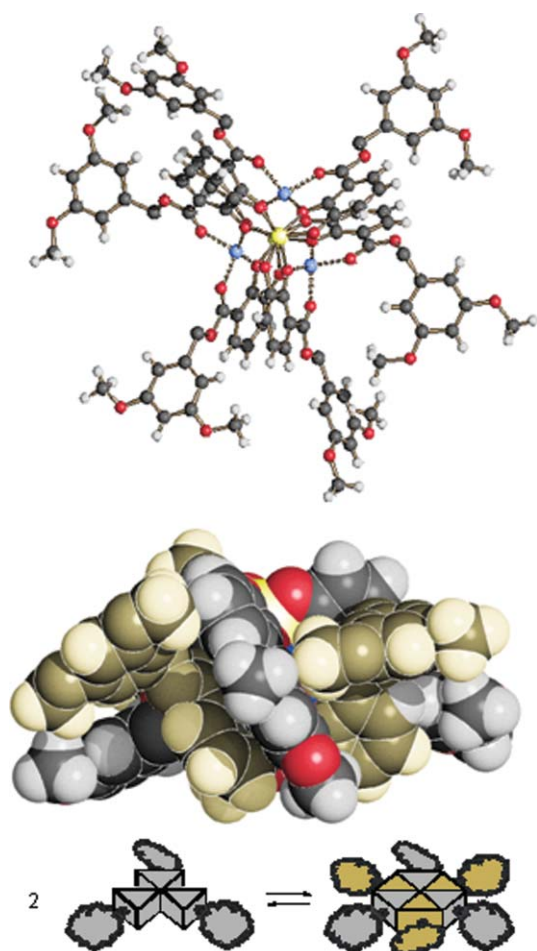


Fig. 1 Representation of the dimeric complex $[Li_3(1a)_6Ti_2]$ in the solid state (view down the Ti–Ti axis in ball-and-stick and side view in space filling representation). In the space filling model the ligands of the two monomeric units are shown in different colours (grey and ochre) and schematic representation of the “volume” of the monomeric *versus* the dimeric compounds (bottom).

In summary, we have presented a simple way to obtain highly branched dendrimers with a bistitanium(IV)-trislithium core. The compounds are derived by simple synthesis of dendritic catecholate esters followed by complexation of three such derivatives to titanium(IV). Lithium coordination leads to the formation of dimeric, very dense, disc shaped dendrimers.

Acknowledgements

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