ORIGINAL ARTICLE

Selective inclusion of cesium ion in a cryptand-type Ti(IV) complex derived from a tripodal tris-2,3-dihydroxynaphthalene ligand

Simon Burk · Markus Albrecht · Kazuhisa Hiratani

Abstract A novel tripodand-type ligand (**L1**) having three 2,3-dihydroxynaphthalene end groups and a C_3 symmetric 1,3,5-tryimethylbenzene based backbone was prepared by the reaction of 1,3,5-tris(bromomethyl)-2,4,6-trimethyl-benzene with 3-(2-(hydroxymethyl)allyloxy)naphthalene-2-ol followed by triple Claisen rearrangement. A 1:1 titanium complex which acts as a metallo-cryptand is obtained by the reaction of ligand (**L1**) with Ti(IV)(=O)(acac)$_2$ in the presence of base. The formation of the me-tallo-cryptand strongly depends on templating effects by counter cations and it shows a high selectively for the encapsulation of cesium cations in its cavity.

Keywords Tripodand ligand · Claisen rearrangement · Catechol moiety · Metallo-supramolecular system · Ti(IV) complex · Inclusion of cations · Cesium selectivity

Introduction

During the last two decades, supramolecular coordination chemistry has developed based on molecular recognition and metal directed self-assembly processes [1]. In this context, the complexation of catechol-type ligands with various kinds of metal ions was used to obtain a broad scope of different supramolecular architectures [2]. Coordination gives rise to mononuclear as well as oligonuclear complexes with infinite polymeric (linear, two or three dimensional) or finite three dimensional molecular structures like metallo-cryptands [3], and metallo-macrocycles [4].

Tripodal ligands are of interest for different reasons. On the one hand, rigid ligands can be used to obtain container type coordination compounds with, e.g., tetrahedral geometry [5]. On the other hand, flexible ligands are able to coordinate only one metal ion. For example, enterobactin is a naturally occurring triscatechol-type sidereophore which binds iron(III) with extraordinary high affinity [6]. Although many kinds of artificial catechol-type ligands and their complexes have been reported so far, there is a need for simple synthetic approaches to new sophisticated ligands, which allow a systematic variation of the coordinating unit as well as of the spacer. Recently, Hiratani and coworkers developed a synthetic method to use isobutenyl ethers in a tandem Claisen rearrangement to simultaneously establish several new C–C-bonds [7]. Utilizing this reaction in a somewhat modified approach, a tripodal ligand with three catechol units has been prepared and its complexation with iron(III) has been studied [8]. In this paper, we report on a titanium(IV) coordination compound of a tripodal ligand posessing three 2,3-dihydroxynaphthyl groups. Additional coordination of an alkaline metal ion in the cap of the complex is crucial for its formation and a high selectivity for the binding of the cesium cation in comparison to the smaller homologs is found.

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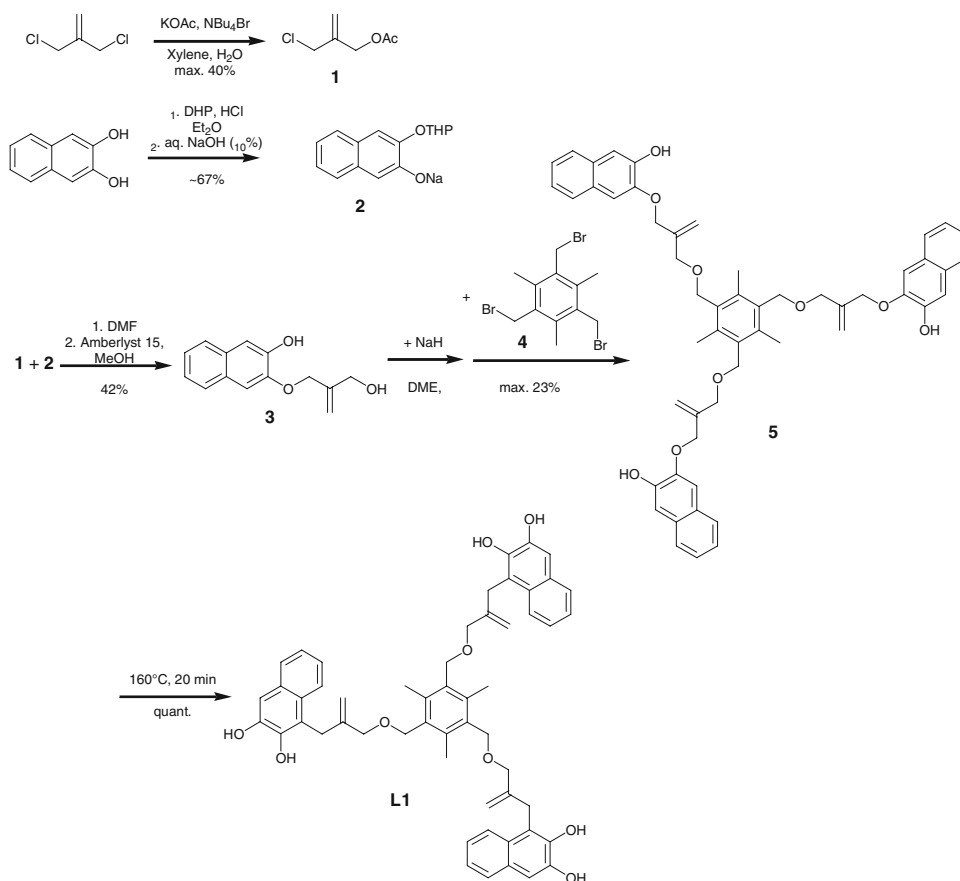52074 Aachen, Germany

Results and discussion

The tripodal tris(dihydroxynaphthyl) ligand **L1** was prepared in a reaction sequence as outlined in Scheme 1. As primary building blocks, the unsymmetrical isobutene derivative **1**[9] and the sodium salt of the THP-protected

Scheme 1 Synthesis of ligand **L1** by triple Claisen rearrangement

2,3-dihydroxynaphthalene $\mathbf{2}$[10] were obtained in standard reactions. Compound $\mathbf{3}$ was obtained in a Williamson ether synthesis by the reaction of $\mathbf{1}$ with $\mathbf{2}$. After deprotonation, $\mathbf{3}$ was triply connected to 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene $\mathbf{4}$ to afford the ligand precursor $\mathbf{5}$. Claisen rearrangement of $\mathbf{5}$ at elevated temperatures (no solvent, 160°C, 20 min.) resulted in the formation of ligand $\mathbf{L1}$ in quantitative yield. $\mathbf{L1}$ was characterized by standard techniques (NMR, ESI Mass, IR) and by elemental analysis (see experimental section).

In order to prepare titanium(IV) complexes of $\mathbf{L1}$, several experiments were performed. By mixing the ligand, titanium salt (TiOacac$_2$) and MOH (M = Na, Rb, Cs) in DMF, 1:1 titanium complexes $M_2[\mathbf{L1}Ti]$ were obtained in quantitative yields. This procedure failed in case of potassium hydroxide. Here only mixtures of complexes (with $K_2[\mathbf{L1}Ti]$ as a component) were formed (Scheme 2). Tetrabutyl ammonium hydroxide yielded only insoluble materials (probably oligomers or polymers). The described observations indicate that a strong templating effect by the counter cations, which are incorporated in the cap of the complex, is important for the specific formation of the 1:1 complexes [11]. Although only minor shift differences are observed by NMR, significant trends can be found. For example, the signal of the sp^2-methylene group (which is
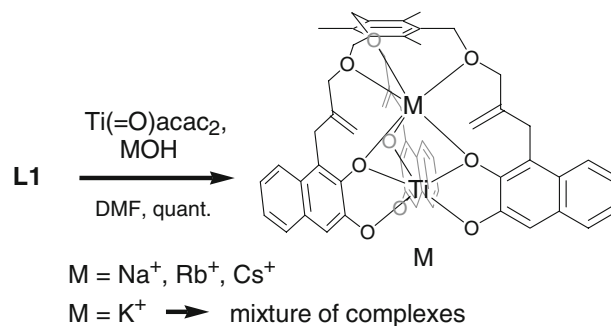
Scheme 2 Complexation of **L1** with Ti(IV) in the presence of alkaline hydroxide (MOH)

isochronic in the complexes but not in the ligand) is detected at lower field for the small sodium (5.03 ppm) compared to the bigger rubidium (5.00 ppm) and cesium (4.97 ppm). An opposite shifting occurs for one of the sp^3-methylene moieties (Na: 3.80 ppm, Rb: 3.90 ppm, Cs: 4.06 ppm).

The unspecific complex formation in the presence of potassium hyrdroxide is assigned to a special size effect of the cavity of $[\mathbf{L1}Ti]^{2-}$. The sodium cation is relatively small and for an efficient coordination the cavity has to shrink and form a folded complex (Scheme 3, left). On the contrary, rubidium and cesium ions are bigger in size and
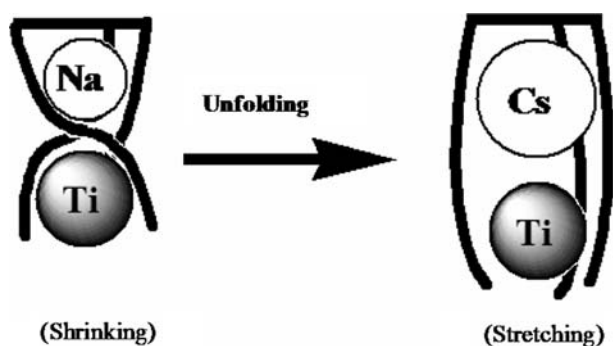
Scheme 3 Postulated formation of compressed (left) and expanded complexes (right) depending upon the size of the encapsulated alkaline metal ion

probably lead to a strongly unfolded ("stretched") complex (Scheme 3, right). Potassium is intermediate in size and presumably does neither support the compressed nor the expanded conformation of the coordinated ligand.

In competition experiments, preferred binding of cesium as a counter ion was found. The cavity which is formed in the 1:1 complex $[\mathbf{L1}Ti]^{2-}$ can include Rb^+, Cs^+ and Na^+ as counter cations. The small sodium cations can be easily exchanged by addition of either rubidium or cesium salts to a solution of $Na_2[\mathbf{L1}Ti]$. This exchange was followed by NMR spectroscopy and ESI Mass spectrometry (see experimental section).

Furthermore, rubidium can be exchanged by cesium but not by sodium. Thus, the cesium complex $Cs_2[\mathbf{L1}Ti]$ proved to be the most stable and no exchange took place in the presence of an excess of sodium or rubidium cations (Scheme 4).

In order to confirm the stoichiometry of the alkaline cation binding, a Job's Plot was measured for the addition of cesium carbonate to a solution of $Na_2[\mathbf{L1}Ti]$ in DMSO-d_6. From this result, we conclude the binding of cesium to $[\mathbf{L1}Ti]^{2-}$ in a 1:1 fashion. This is due to the ability of the titanium complex $[\mathbf{L1}Ti]^{2-}$ to take up one metal cation in its interior, while the second cation is not an integral part of the complex structure but solely acts as a "counterion" (Fig. 1).

Fig. 1 Job's plot of host $[Ti(\mathbf{L1})Na]Na$ with Cs_2CO_3. The vertical axis is the $[Ti(\mathbf{L1})Cs]^-$ concentration (mM) calculated from the induced shifts in the ^{1}H-NMR (500 MHz). (The deviation of the shift of the 1:1 complex from the expected curve is due to the limit of the experimental technique)

In additional, preliminary experiments we checked the ability of $[\mathbf{L1}Ti]^{2-}$ to bind a series of other cations. By ESI MS, complexes with bound lanthanum(III) and lead(II) in the complexes could be detected but no significant change of the ^{1}H-NMR was observed. On the other hand, n-tetrabutylammonium, silver (I) and barium (II) are not appropriate to be included as a guest (no inclusion was detected by ESI MS as well as NMR). The factors of ion size and valency of metal ions could play an important role for incorporation of ions into the cavity of $[\mathbf{L1}Ti]^{2-}$. Based on these results a selectivity series could be suggested as follows (brackets indicate the observation of mixtures of oligomeric complexes):

$$\left[Ba^{2+}, Ag^+, NBu_4^+\right] < Pb^{2+}, La^{3+} < \left[K^+\right]$$
$$< Na^+ < Rb^+ << Cs^+.$$
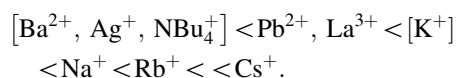
This rather preliminary interpretation is based on our ESI MS and NMR experiments and gives an outlook on future work to be done with modified ligands and using templating metal cations with different coordination geometries, charges and sizes.

Scheme 4 Selectivity of cation binding in the cavity of $[\mathbf{L1}Ti]^{2-}$

$[MTi\mathbf{L1}]^-$
M = Na, Rb

Cs_2CO_3

M_2CO_3

$[CsTi\mathbf{L1}]^-$

Conclusion

The newly prepared tripodal ligand **L1** with three 2,3-dihydroxynaphthyl units reacts with titanium(IV) ions to give rise to the metallo-cryptands in quantitative yields only if appropriate templating cations are present. The formed metallo-cryptand encapsulates the templating metal ions depending on the size and the valency of the guests. The selectivity for the cesium ion is superior compared to the other alkaline metal, silver, and lanthanum ions, which is assigned to the size of this cation. This shows that adjustment of the ligand size is a way to rationally approach the selective binding of various guest species. In this context the tandem Claisen rearrangement or modified versions thereoff in the vicinity of different C_3-symmetric platforms seems to be an appropriate synthetic tool for the easy preparation of a valuable set of ligands in the future.

Experimental section

General information

All experiments were carried out using oven dried glassware. All solvent were used as purchased. ^{1}H-NMR spectra (500 MHz) were recorded on a Varian NMR System 500 spectrometer, with chemical shift values being reported in ppm relative to residual chloroform or DMSO as an internal standard unless otherwise stated. All coupling constants are reported in Hertz (Hz). Mass spectra were recorded using a Waters 2690 Separations Module ESI mass spectrometer. IR spectra were recorded using a JASCO FT-IR 430.

Column chromatography was carried out using Merck silica gel 60. Merck aluminium packed plates precoated with silica gel 60 (UV254) were used for thin-layer chromatography and were visualised by UV.

3-(Tetrahydro-2*H*-pyrane-2-yloxy)-2-naphthol sodium salt was prepared by the reaction of 2,3-dihydroxynaphthalene with 3,4-dihydro-2H-pyran followed by the treatment with aqueous sodium hydroxide [10].

Procedure for the synthesis of the tripodal ligand (**L1**)

2-(Chloromethyl)allylacetate (1)

3-Chloro-2-(chloromethyl)prop-1-ene (22.1 g, 0.177 mol) was dissolved in 30 ml of xylene and added to a stirred solution of potassium acetate (17.6 g, 0.179 mol) and tetrabutylammonium bromide (1.70 g, 0.005 mol) in 30 ml of water. Then the reaction mixture was heated to reflux for 2 h and 15 min. The organic phase was separated and the aqueous phase was extracted three times with ether. The organic phases were combined, dried and concentrated under reduced pressure. Further purification was achieved by vacuum distillation (70°C/1 mmHg). The product was obtained as colorless liquid (10.8 g, 0.072 mol, 40%).

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.36 (s, 1H, CH$_{alkene}$), 5.29 (s, 1H, CH$_{alkene}$), 4.70 (s, 2H, CH$_2$), 4.12 (s, 2H, CH$_2$), 2.10 (s, 3H, CH$_3$).

3-(2-(Hydroxymethyl)allyloxy)naphthalene-2-ol (3)

2-(2-(Chloromethyl)allylacetate (1.27 g, 8.6 mmol, 1.3 eq) and sodium 3-(tetrahydro-2*H*-pyrane-2-yloxy))-2-naphtholate (1.75 g, 6.6 mol) were dissolved in DMF. After 20 h of stirring at 60°C, the solvent was evaporated. The crude brownish oily residue was used in the deprotection without further purification steps.

The oily residue was dissolved in methanol and Amberlyst 15 (0.5 g) was added. After stirring under reflux overnight the mixture was cooled and filtrated. Solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO$_2$, CHCl$_3$/EtOAc 5:1) to yield a colorless oil (0.64 g, 2.8 mmol, 42%).

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.65 (m, 2H, CH$_{arom}$), 7.26–7.34 (m, 3H, CH$_{arom}$), 7.20 (s, 1H, CH$_{arom}$), 6.15 (s, 1H, OH), 5.38 (s, 1H, CH$_{alkene}$), 5.35 (s, 1H, CH$_{alkene}$), 4.81 (s, 2H, CH$_2$), 4.34 (d, J^3 = 5.5 Hz, 2H, CH$_2$), 1.67 (brs, J^3 = 5.5 Hz, 1H, OH).

IR (KBr): ν_{max}/(cm^{-1}) = 3415, 2360, 2342, 1511, 1483, 1459, 1261, 1216, 1166, 1111, 1010, 857, 747.

Negative ESI (CH$_3$CN): m/z = 229.2 [M-H]$^-$.

C$_{14}$H$_{14}$O$_3$ · H$_2$O: calc.: C 67.73, H 6.50; found: C 67.34, H 6.75.

1,3,5-Trimethyl-2,4,6-tris(2-(2-hydroxynaphthyl-3-oxymethyl)-1-propenyl-3-oxymethyl)benzene (5)

3-(2-(Hydroxymethyl)allyloxy)naphthalene-2-ol (0.64 g, 2.8 mmol) was dissolved in 15 ml of dried and degassed DME and was cooled to 0°C. Then NaH (0.27 g, 6.2 mmol, 2.2 eq) was added. The suspension was stirred for 20 min at 0°C and then heated to room temperature. After additional 10 min stirring, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.37 g, 0.9 mmol, 0.33 eq) was added and the mixture was stirred for 1 h at room temperature. After the reaction was complete, the suspension was quenched by addition of 10 ml NH$_4$Cl-solution (5%). After separation of the phases, the aqueous phase was extracted several times with chloroform. All organic phases were combined, dried over anhydrous MgSO$_4$ and concentrated under reduced pressure. Further purification was performed by column chromatography (SiO$_2$, gradient from pure chloroform to 40 vol% ethylacetate). The product was obtained as brownish oil (0.18 g, 0.22 mmol, 23%).

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.61 (m, 6H, CH$_{arom}$), 6.28 (m, 6H, CH$_{arom}$), 7.21 (s, 3H, CH$_{arom}$), 7.11 (s, 3H, CH$_{arom}$), 6.16 (s, 3H, OH), 5.31 (s, 3H, CH$_{alkene}$), 5.30 (s, 3H, CH$_{alkene}$), 4.69 (s, 6H, CH$_2$), 4.50 (s, 6H, CH$_2$), 4.11 (s, 6H, CH$_2$), 2.37 (s, 9H, CH$_3$).

Positive ESI (CH$_3$CN): m/z = 870.0 [M+Na]$^+$.

IR (KBr): ν_{max}/(cm^{-1}) = 3434, 3073, 2922, 2360, 2342, 1467.6, 1452, 1382, 1354, 1255, 1190, 1088, 1039, 913, 863, 837, 777, 746.

C$_{54}$H$_{54}$O$_9$ · 4H$_2$O: calc.: C 70.57, H 6.80; found: C 70.31, H 6.54.

1,3,5-Trimethyl-2,4,6-tris(2-(2,3-dihydroxynaphthyl-1-methyl)-1-propenyl-3-oxymethyl)benzene (L1)

1,3,5-Trimethyl-2,4,6-tris(2-(2-hydroxynaphthyl-3-oxymethyl)-1-propenyl-3-oxymethyl)benzene (5) (0.18 g, 0.22 mmol) is heated to 160°C for 20 min. The product was obtained as an amorphous brownish solid (0.18 g, 0.22 mmol, quant).

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 8.12 (s, 3H, OH), 7.85 (m, 3H, CH$_{arom}$), 7.63 (m, 3H, CH$_{arom}$), 7.30 (m, 6H, CH$_{arom}$), 7.16 (s, 3H, CH$_{arom}$), 6.69 (s, 3H, OH), 5.42 (s, 3H, CH$_{alkene}$), 5.26 (s, 3H, CH$_{alkene}$), 4.73 (s, 6H, CH$_2$), 4.08 (s, 6H, CH$_2$), 3.93 (s, 6H, CH$_2$), 2.51 (s, 9H, CH$_3$).

IR (KBr): ν_{max}/(cm^{-1}) = 3436, 2922, 2360, 2342, 1511, 1482, 1461, 1451, 1413, 1379, 1260, 1167, 1111, 1090, 922, 858, 746, 669, 652.

Positive ESI (CH$_3$CN): m/z = 869.9 [M+Na]$^+$; negative ESI (CH$_3$CN): m/z = 846.2 [M−H]$^-$.

C$_{54}$H$_{54}$O$_9$ · H$_2$O: calc.: C 74.98, H 6.53; found: C 75.10, H 6.58.

Synthesis of the complexes

General procedure

1,3,5-Trimethyl-2,4,6-tris(2-(2,3-dihydroxynaphthyl-1-methyl)-1-propenyl-3-oxymethyl)benzene (L1) (25 mg, 0.03 mmol), titanoylacetonylacetonate (7.7 mg, 0.03 mmol) and MOH (0.06 mmol) were combined in anhydrous DMF and stirred overnight. After the removal of DMF a red orange solid was obtained (M = Na, Rb, Cs).

Na[NaTi(L1)]

Yield: 0.035 g, 0.03 mmol, quant.

^{1}H-NMR (500 MHz, DMSO): δ = 7.61 (d, ^3J = 8.5 Hz, 3H, CH$_{arom}$), 7.27 (d, ^3J = 8.5 Hz, 3H, CH$_{arom}$), 6.90 (m, 6H, CH$_{arom}$), 6.14 (s, 3H, CH$_{arom}$), 5.03 (m, 6H, CH$_{alkene}$), 4.79 (s, 6H, CH$_2$), 3.80 (s, 6H, CH$_2$), 3.1–3.5 (s, 6H, CH$_2$, hidden under the water signal), 2.2–2.6 (s, 9H, CH$_3$, hidden under DMSO).

IR (KBr): ν_{max}/(cm^{-1}) = 3427, 2924, 2360, 2342, 1659, 1631, 1597, 1511, 1444, 1350, 1281, 1261, 1171, 1093, 105, 986, 863, 779, 745, 668, 651, 573.

Negative ESI (DMF/CH$_3$CN): m/z = 890.0 [Ti(L1)H]$^-$, 895.2 [Ti(L1)Li]$^-$, 912.1 [Ti(L1)Na]$^-$, 927.8 [M(L1)K]$^-$.

C$_{54}$H$_{48}$O$_9$TiNa$_2$ · H$_2$O · 3 DMF: calc. C 64.56, H 6.11, N 3.59; found: C 64.40, H 6.45, N 3.34.

Rb[RbTi(L1)]

Yield: 0.036 g, 0.03 mmol, quant.

^{1}H-NMR (500 MHz, DMSO): δ = 7.52 (d, ^3J = 7.5 Hz, 3H, CH$_{arom}$), 7.32 (d, ^3J = 8.5 Hz, 3H, CH$_{arom}$), 6.92 (m, 6H, CH$_{arom}$), 6.21 (s, 3H, CH$_{arom}$), 5.00 (bs, 6H, CH$_{alkene}$), 4.77 (s, 6H, CH$_2$), 3.90 (bs, 6H, CH$_2$), 3.1–3.5 (s, 6H, CH$_2$, hidden under the water signal), 2.2–2.6 (s, 9H, CH$_3$, hidden under DMSO).

IR (KBr): ν_{max}/(cm^{-1}) = 3438, 2921, 2360, 2342, 1659, 1441, 1384, 1256, 1201, 1169, 1093, 1052, 984, 860, 742, 653, 571.

Negative ESI (DMF/CH$_3$CN): m/z = 889.9 [Ti(L1)H]$^-$, 911.5 [Ti(L1)Na]$^-$, 928.1 [Ti(L1)K]$^-$, 973.2 [Ti(L1)Rb]$^-$.

C$_{54}$H$_{48}$O$_9$TiRb$_2$ · 2H$_2$O · 1.5 DMF: calc. C 57.77, H 5.48, N 2.74; found: C 57.66, H 5.61, N 2.26.

Cs[CsTi(L1)]

Yield: 0.048 g, 0.03 mmol, quant.

^{1}H-NMR (500 MHz, DMSO): δ = 7.35 (m, 6H, CH$_{arom}$), 6.94 (m, 6H, CH$_{arom}$), 6.30 (s, 3H, CH$_{arom}$), 4.97 (bs, 6H, CH$_{alkene}$), 4.78 (s, 6H, CH$_2$), 4.06 (bs, 6H, CH$_2$), 3.1–3.5 (s, 6H, CH$_2$, hidden under the water signal), 2.2–2.6 (s, 9H, CH$_3$, hidden under DMSO).

IR (KBr): ν_{max}/(cm^{-1}) = 3437, 2924, 2360, 2342, 1658, 1641, 1630, 1441, 1383, 1259, 1052, 669, 652, 567.

Negative ESI: m/z = 1021.4 [Ti(L1)Cs]$^-$.

C$_{54}$H$_{48}$O$_9$TiCs$_2$ · 12H$_2$O · 3 DMF: calc.: C 47.59, H 5.90, N 2.64; found: C 47.61, H 6.07, N 2.64.

ESI -competition-experiments

A sample of Na[NaTi(L1)] was dissolved in DMF/acetonitril and some salts (cations) were added. After 4 h, an ESI was measured to analyze the formed species.

1. Addition of Pb(OAc)$_2$ Negative ESI: m/z = 889.7 [Ti(L1)H]$^-$, 912.2 [Ti(L1)Na]$^-$, 928.2 [Ti(L1)K]$^-$, 973.7 [Ti(L1)Rb]$^-$, 1131.9 [Ti(L1)PbCl]$^-$.
2. Addition of CsOAc or Cs$_2$CO$_3$ Negative ESI: m/z = 1022.2 [Ti(L1)Cs]$^-$.
3. Addition of Rb$_2$CO$_3$ Negative ESI: m/z = 973.2 [Ti(L1)Rb]$^-$.
4. Addition of La(OAc)$_3$ Positive ESI: m/z = 1027.0 [Ti(L1)La]$^+$.

Job's plot

Two solutions of the host [Ti(**L1**)Na]Na (concentration 0.056 mol/l) in DMSO-d_6 and Cs_2CO_3 (concentration 0.056 mol/l) in DMSO-d_6 were prepared and used in the experiments. The concentration of [Ti(**L1**)Cs]$^-$ was measured via ^{1}H-NMR against the sodium salt of dimethyl-*tert*-butylsiliciumsulfoxide as internal standard.

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