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Selective synthesis of conformationally restricted mono-cyclopentadienyl titanium(IV) complexes of *p*-^{t}Bu-calix[6]arene

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Reaction of *p*-^{t}Bu-calix[6]arene with potassium metal in methanol followed by [$TiCp_2Cl_2$] affords novel mononuclear and binuclear monocyclopentadienyl titanium(IV) complexes, both having the same inverted double cone conformation with a Cp in one of the cavities, in both complexes.

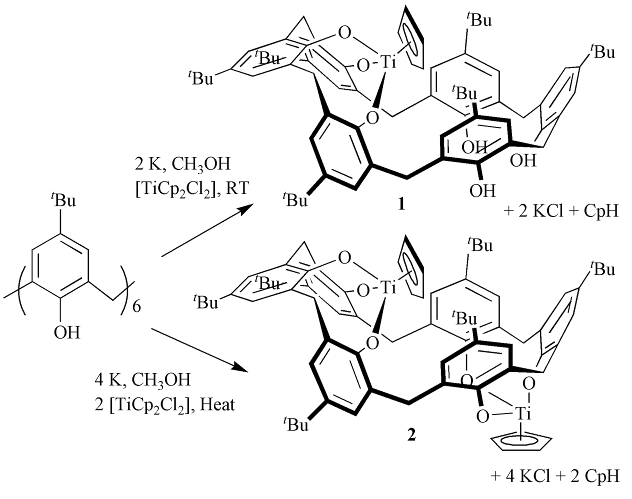
Calix[n]arenes are a family of macrocyclic molecules consisting of phenol units linked by methylene bridges in their ortho positions. For metal complexation, calix[n]arenes represent a unique type of flexible yet constrained polyalkoxide ligand.[1] Their conformational flexibility results in a variety of metal binding environments, and allows several metal centres to be accommodated simultaneously. Calix[4]arenes usually adopt the cone conformation when forming metal complexes, using a preorganised set of four pendant oxygen atoms for chelation. This generally forms molecular assemblies wherein the metal centres bridge two calix[4]arene molecules *via* phenolate complexation.[1] In contrast, the larger ring size and greater flexibility of calix[6]arene presents a more challenging and complex ligand system. The paucity of structurally authenticated calix[6]arene metal complexes[2] may reflect both the difficulty in arriving at synthetic methodologies that yield metal complexes, and probably also to difficulties in obtaining pure compounds, especially given the numerous binding sites available to the metal.

Considering that metal calix[6]arene complexation is likely to be dependent on the distribution of calix[6]arene conformers in solution, preorganisational energies, and accessible metal binding geometries, amongst other things, we rationalised that a way to control product outcomes would be through the use of a metal source that has limited stereochemical coordinative properties. Herein we report the use of [$TiCp_2Cl_2$] in the formation of two novel mono-nuclear and bi-nuclear monocyclopentadienyl complexes of *p*-^{t}Bu-calix[6]arene, ^{t}Bu-L[OH]$_6$, arising from cleavage of one cyclopentadienyl group from each metal.† The use of a cyclopentadienyl titanium source appears to offer protection against the formation of metallo-bridged species[1] and it directs reactivity specifically towards the inverted double cone conformation of the calix[6]arene. The new complexes, **1** and **2**, are prepared in high yield using simple synthetic procedures outlined in Scheme 1.

Selective synthesis of **1** involves slow addition of one equivalent of solid [$TiCp_2Cl_2$] to the solution formed on reaction of two equivalents of potassium with ^{t}Bu-L[OH]$_6$ in methanol. The gradual dissolution of [$TiCp_2Cl_2$] at room temperature was accompanied by precipitation of **1** as a yellow solid, and therefore completion of the reaction was signalled by the disappearance of [$TiCp_2Cl_2$]. Application of heat or the introduction of [$TiCp_2Cl_2$] as a solution in methanol produced a mixture of **1** and **2**. Complex **2** was prepared by treating the solution formed on reaction of four equivalents of potassium metal with ^{t}Bu-L[OH]$_6$ in methanol with two equivalents of [$TiCp_2Cl_2$] dissolved in methanol. Boiling the mixture for ~ 10 minutes resulted in the precipitation of **2**, as an orange solid.

The facile isolation of **1** and **2** is aided by their precipitation from methanol. Interestingly, similar attempts to prepare calix[4]arene–TiCp complexes from methanol were unsuccessful. For *p*-^{t}Bu-calix[4]arene cleavage of both cyclopentadienyl ligands occurs for a range of metal: calix[4]arene ratios. Success in preparing the monocyclopentadienyl titanium complexes of calix[6]arene possibly arises from the rapid formation and precipitation of the TiCp–calix[6]arene complexes from methanol, which protects the remaining Cp group from cleavage. Another aspect of the calix[6]arene, but not calix[4]arene, is possible kinetic protection of the first-formed monocyclopentadienyl complex by its binding in the cavity of the now inverted double cone conformation (see below). ^{t}Bu-L[OH]$_6$ itself crystallises in a double cone conformation[3] rather than the inverted double cone found in **1** and **2**. It is well documented that Cp groups are cleaved from titanocene reagents under basic conditions.[4] The rapid formation of **1** and **2** must occur through initial base induced cleavage of one Cp ligand from [$TiCp_2Cl_2$], followed by rapid complexation of the calix[6]arene in the inverted double cone conformation, which provides two sets of three pendant phenolato oxygen atoms for titanium chelation.

Both structures crystallise in $P1$ with one calix[6]arene and covalently attached TiCp moieties as the asymmetric unit. Surprisingly the overall conformation of the calix[6]arene and disposition of the CpTi residing in one of the cavities is similar in each structure, Figures 1 and 2. It appears that the preorganisation of the calix[6]arene, upon binding of the first metal centre and binding of its Cp ligand in a cavity, orientates the other three phenolic oxygen centres for binding of the second TiCp, to give **2**. The distances between the three uncomplexed oxygen centres in **1** are consistent with intramolecular OH···O hydrogen bonding, O4···O5 and O5···O6 being 2.75, and 2.66 Å, respectively, although the imprecision of the data precluded location of hydrogen atoms. Correspond-



Scheme 1

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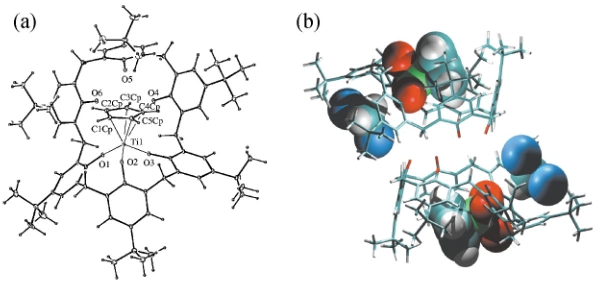

Fig. 1 Projections of **1** (a) ORTEP drawing. Selected interatomic distances (Å) and angles (°):Ti(1)–O(1, 2, 3) 1.816(3), 1.865(3), 1.815(3), Ti(1)–Cp 2.042(3), O(1)–Ti(1)–O(2, 3) 100.7(1), 107.3(1), O(2)–Ti(1)–O(3) 99.5(1), Cp–Ti(1)–O(1, 2, 3) 121.1(1), 109.5(1), 115.5(1). Cp is the centroid of the C_5H_5 ring. (b) Two molecules showing the snug fit of the Cp and CH_2Cl_2 in the cavities, with space filling for the metal centre and ligating atoms, and the solvent molecule.

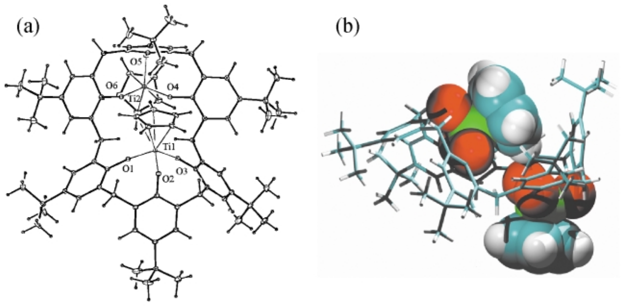

Fig. 2 Projections of **2** (a) ORTEP drawing. Selected interatomic distances (Å) and angles (°): Ti(1)–O(1, 2, 3), 1.806(2), 1.857(2), 1.814(2), Ti(1)–Cp 1.908(2), Ti(2)–O(3, 4, 5) 1.804(2), 1.854(2), 1.804(2), Ti(2)–Cp 2.035(2), O(1)–Ti(1)–O(2, 3) 99.2(1), 106.6(1), O(2)–Ti(1)–O(3) 100.7(1), O(4)–Ti(2)–O(5, 6) 99.9(1), 102.7(1), O(5)–Ti(2)–O(6) 103.3(1), Cp–Ti(1)–O(1, 2, 3, 4, 5, 6) 122.1(1), 109.2(1), 115.8(1), 117.2(1), 110.6(1), 120.7(1). Cp are the centroids of the C_5H_5 rings. (b) Space filling for the metal centres and ligating atoms.

ing O···O distances in complex **2** are 2.87, 2.80 Å, and the effect of binding the second metal centre is a diminution of the O4···O6 distance from 3.62 Å to 2.82 Å in consequence of the metal centre achieving symmetrical fourfold coordination (counting each Cp ligand as occupying one site). Complexation of the second metal centre results in little change to the pitch of the phenol planes relative to the plane of the three oxygen centres, changing from 29.2, 83.9, 57.1° to 30.8, 84.7, 33.7°. In **1** there appears to be some interplay between molecules through hydrogen bonding, the closest O···O distances being 2.73 Å, Figure 1(b).

For each compound **1** and **2**, the Cp ligand on Ti(1) reside in the calixarene cavity formed by three uncoordinated phenolic groups or three phenolate groups, respectively, Figures 1(b) and 2(b).[5] For **1** the cavity formed by the three phenolates attached to Ti(1) is filled by a dichloromethane solvate molecule, and the pitch angles of the planes of the three complexed phenyl groups are 43.9, 89.8, 28.7°, relative to the O plane. For **2** the corresponding pitch angles are 37.5, 86.9, 40.7°.

In respect to the Cp centroid, the O–Ti–Cp bonds angles in **1** and **2** range from 109–122° and the Ti–Cp bond lengths are 1.91 and 2.04 Å. In comparison, the only other structurally authenticated cyclopentadienyl titanium(IV) tris-aryloxide ($CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_3$)[6] has bond angles in the range 113–156° and a Ti–Cp bond distance of 2.1 Å .

Overall, we show that mono-cyclopentadienyltitanium(IV) complexes of *p*-^{t}Bu-calix[6]arene are readily accessible in high yields. This approach lends itself to the synthesis of complexes using other metallocenes, and with higher calixarenes, particularly, the readily available calix[8]arenes, and also to calixarenes bearing other hydrocarbyl groups in place of ^{t}Bu, for example benzyl and phenyl. Moreover, the open cavity in complex **1** is poised for binding large globular type molecules, assuming the dichloromethane can be displaced.

Notes and references

† *Syntheses:*. **1** To a suspension of ^{t}Bu-L[OH]$_6$ (1.0 g, 1.03 mmol) in methanol (50 ml) was added potassium metal (0.09 g, 2.3 mmol). The mixture was stirred affording a clear pale yellow solution on complete consumption of the potassium. Solid [$TiCp_2Cl_2$] (0.26 g, 1.04 mmol) was then added affording an orange precipitate which was collected after most of the [$TiCp_2Cl_2$] had been consumed. Yield 1.0 g, 90%. **2** To a solution formed by reacting potassium metal (0.18 g, 4.60 mmol) with ^{t}Bu-L[OH]$_6$ (1.0 g, 1.03 mmol) in methanol (50 ml), was added a solution of [$TiCp_2Cl_2$] (0.52 g, 2.09 mmol) in methanol (50 ml). The mixture was refluxed (~ 10 min), whereupon an orange solid precipitated. Yield 1.1 g, 90%. Crystals of **1** and **2** suitable for X-ray structure determination were grown by mixing a dichloromethane solution with acetonitrile.^{1}H NMR ($CDCl_3$, 300 MHz, 298 K):**1** δ 7.24 (d, 2 H, J = 3 Hz aryl), 7.14 (d, 2 H, J = 3 Hz, aryl), 6.94, (s, 2 H, aryl), 6.92 (d, 12 H, J = 3 Hz, aryl), 6.90 (s, 2 H, aryl), 6.31 (d, 2 H, J = 3 Hz, aryl), 5.38 (s, 5 H, Cp), 4.34 (d, 2 H, J = 15 Hz, CH_2), 4.14 (d, 2 H, J = 15 Hz, CH_2), 3.99 (d, 2 H, J = 15 Hz, CH_2), 3.60 (d, 2 H, J = 15 Hz, CH_2), 3.40 (d, 2 H, J = 15 Hz, CH_2), 3.25 (d, 2 H, J = 15 Hz, CH_2), 1.27 (s, 18 H, ^{t}Bu), 1.18 (s, 18 H, ^{t}Bu), 1.12 (s, 9 H, ^{t}Bu), 0.84 (s, 9 H, ^{t}Bu). **2** 7.15 (d, 4 H, J = 3 Hz, aryl), 6.82 (s, 4 H, aryl), 6.62 (d, 4 H, J = 3 Hz, aryl), 6.07 (s, 10 H, Cp), 5.30 (s, 2 H, CH_2Cl_2), 4.24 (d, 4 H, J = 12 Hz, CH_2), 3.74 (s, 4 H, CH_2), 3.28 (d, 4 H, J = 12 Hz, CH_2), 1.23 (s, 36 H, ^{t}Bu), 3.08 (s, 18 H, ^{t}Bu). *X-ray crystal data*: **1** was collected at 150(2) K on a Bruker-AXS SMART 1000 CCD diffractometer. **2** was collected at 150(2)K on an Enraf-Nonius Kappa CCD diffractometer. Both structures were solved by direct methods (SIR92) and refined with a full matrix least-squares refinement on F (RAELS). **1** $C_{71}H_{83}O_6Ti.CH_2Cl_2$, M = 1165.3, triclinic, a = 13.871(8), b = 16.411(9), c = 16.474(9) Å, α = 81.76(1), β = 69.15(1), γ = 89.29(1)°, U = 3465(3) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ(Mo–K$_\alpha$) = 0.244 mm^{-1}, 33488 reflections measured, 15811 unique (R_{int} = 0.050). The final R = 0.116, and wR = 0.180 (observed data). **2** $C_{76}H_{88}O_6Ti_2.CH_2Cl_2$, M = 1278.3, triclinic, a = 13.034(1), b = 16.744(2), c = 19.276(2) Å, α = 66.479(4), β = 86.395(1), γ = 68.356(5)°, U = 3568(2) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ(Mo–K$_\alpha$) = 0.344 mm^{-1}, 76059 reflections measured, 16318 unique (R_{int} = 0.051). The final R = 0.087, and wR = 0.132 (observed data).‡

‡ CCDC 202723 and 202724. See http://www.rsc.org/suppdata/cc/b3/b301075a/ for crystallographic data in .cif or other electronic format.

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