Titanocene dichloride route to a tetranuclear oxo-bridged monocyclopentadienyl titanium(IV) calix[4]arene complex

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Lithiation of p-^{t}Bu-calix[4]arene followed by reaction with titanocene dichloride affords a novel tetranuclear titanium(IV) monocyclopentadienyl complex, wherein a single calix[4]arene in a cone conformation provides O-phenoxy coordination to four titanium atoms, with additional μ-oxo bridging between titanium centres in an eight membered ring.

Metal complexation of calix[n]arenes has revealed their capacity to form multimetallated species through various coordination modes. In particular, the extensive exploration of calix[4]arene metal complexation chemistry has shown that, in the majority of complexes, calix[4]arene binds in the cone conformation.[1,2] Notable exceptions include the tetranuclear aluminium and gallium complexes.[3] In the cone conformation a preorganised set of four pendant oxygen atoms is available for metal chelation. This generally leads to the formation of molecular assemblies where the metal atoms bridge two calix[4]arene molecules *via* phenolate complexation.[1] Mono-calix[4]arene metal complexes have been made using partially *O*-alkylated derivatives.[4]

For titanium calix[4]arene complexes, reaction of under-ivatised calix[4]arenes with titanium sources such as $TiCl_4$[5] or $Ti(NMe_2)_4$[6] leads to the formation of dimeric titanium bridged complexes. The tendency of these titanium sources to form metallo-bridged dimers can be rationalised by the easy elimination of all four ligands from the titanium precursor by the acidic protons of the calix[4]arenes. In the light of these considerations, we sought a pathway to titanium calix[4]arene complexes with terminal titanium moieties, through the use of a titanium precursor containing less labile ligands.

Herein we report the use of titanocene dichloride, [$TiCp_2Cl_2$], in the synthesis of a novel tetranuclear titanium calix[4]arene complex **1**, equation 1, containing p-^{t}Bu-calix[4]arene.† The

(1)

complex represents the first structurally characterised titanium complex of an underivatised calix[4]arene where the titanium does not form metallo-bridges between calix[4]arenes. It is also, to our knowledge, the first phenolato bound cyclopentadienyl titanium calix[4]arene complex. Moreover, although there are numerous structurally characterised examples of two or more

calix[4]arenes binding several transition metal ions simultaneously,[1] the binding of four transition metal atoms by one calix[4]arene, as found in **1**, is unprecedented.

Complex **1** crystallises from toluene in the space group C2/c, with the molecules residing on C_2 symmetry axes, although the overall symmetry is C_{4v}, excluding the toluene molecule in the cavity (see below), Figure 1.‡ The phenoxide groups of the calix[4]arene are in the cone conformation, and each is coordinated to one titanium atom. Four μ-oxo groups link adjacent pairs of the four titanium atoms. Thus, at the base of the calix[4]arene, there is an eight membered ring of alternating titanium and oxygen centres. Similar ring structures have been reported previously, *e.g.* [{TiCl(μ-O)(η-C_5H_5)}$_4$].[7] Coordination around each Ti(IV) centre is completed by a perhapto-cyclopentadienyl ligand, and is a distorted tetrahedron, at least counting the hydrocarbyl group as occupying one coordination site. The presence of one cyclopentadienyl ligand on each titanium in **1** undoubtedly prevents the bridging coordination between different calix[4]arene molecules that is more commonly observed.[5,6] The symmetrical coordination of the four titanium atoms results in a highly symmetrical cone conformation for the calix[4]arene. This C_{4v} symmetry is reflected in the ^1H NMR spectrum, which contains one sharp signal for each of the sets of ^{t}Bu protons, the aromatic protons and the cyclopentadienyl protons. The oxo-groups presumably derive from adventitious water in the reaction mixture.
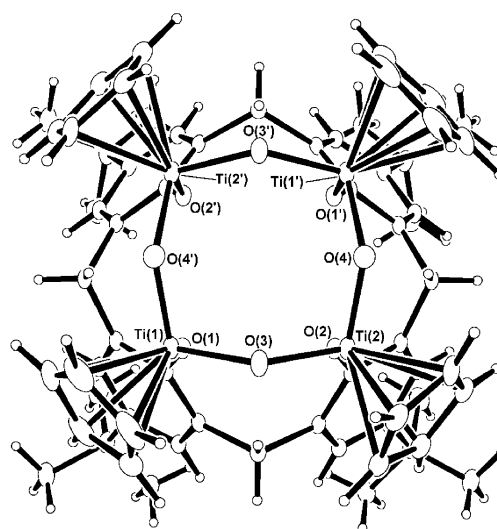

Fig. 1 Molecular projection of complex **1**. Selected interatomic distances (Å) and angles (°): Ti(1)–O(1, 3, 4′) 1.8209(14), 1.8159(14), 1.8160(16), Ti(2)–O(2, 3, 4) 1.8224(14), 1.8164(14), 1.8165(16), Cp–Ti(1, 2), 2.059, 2.062, O(1)–Ti(1)–O(3, 4′) 102.57(6), 102.02(7), O(3)–Ti(1)–O(4′) 105.17(8), O(2)–Ti(2)–O(3, 4) 102.52(6), 102.07(7), O(3)–Ti(2)–O(4) 104.92(8). Cp–Ti(1)–O(1, 3, 4), 115.51, 115.68, 114.223, Cp–Ti(2)–O(2, 3, 4) 114.79, 115.04, 115.76. Cp are the centroids of the C_5H_5 rings.

The extended structure shows two interesting features: (i) Molecules of **1** stack into columns such that two of them shroud a molecule of toluene, and thus **1** is acting as a novel divergent receptor, Figure 2. (ii) The columns in (i) are packed side-by-side into layers, and these layers are separated by layers of toluene molecules, Figure 3.

Complex **1** was prepared by the addition of two equivalents of ^{n}BuLi to p-^{t}Bu-calix[4]arene in toluene followed by the addition of a deficit of [TiCp$_2$Cl$_2$] in THF/toluene, as outlined in equation 1. Despite the modest yield based on calix[4]arene, the method is reproducible. Surprisingly, attempts to add the logically suggested four equivalents of TiCp$_2$Cl$_2$ to fully alkali metallated calix[4]arene gave a poorer yield of **1**. The formation of **1** requires some base in solution to cleave one Cp group from each metal centre, however the cleavage of the second Cp group must not occur before coordination. Amongst many unsuccessful attempts to improve the yield, we tried sterically hindered bases, thinking to attenuate the rate of Cp cleavage. Since the reaction in equation 1 redeposits substantial calix[4]arene starting material, we speculate that calix[4]arene itself may act as the base required to mediate the formation of **1**. Other efforts to improve the yield using alternative titanium metallocene sources such as [CpTiCl$_3$] and [CpTiCl$_2$OMe] were unsuccessful, as were experiments where the identity or ratio of the alkali metal was varied. Furthermore, we were not able to obtain any calix[4]arene-TiCp$_2$ complexes where both Cp ligands remained intact. This finding is not surprising considering reports that the formation of TiCp$_2$-bis-alkoxides is complicated and often results in products where one Cp ligand is cleaved.[8] Our present results concur with our other recent findings that p-^{t}Bu-calix[6]arene reacts with [TiCp$_2$Cl$_2$] to give either mono- or bi-nuclear monocyclopentadienyl titanium(IV) complexes.[9]

The lack of reactivity of [TiCp$_2$Cl$_2$] with alkali-metallated forms of calix[4]arene could be ascribed to the low Lewis acidity of the titanium centre in [TiCp$_2$Cl$_2$] coupled with the low nucleophilicity of the alkali-metallated calix[4]arene intermediates. Reactions of cyclopentadienyl transition metal sources with calix[4]arenes have been previously reported,[7] however this has been through the use of considerably stronger Lewis acids such as [CpTaCl$_4$].[10] Although it is not clear how **1** forms, it is probably reliant on the partial hydrolysis of [TiCp$_2$Cl$_2$] to form an intermediate that is a stronger Lewis acid.

We have prepared a remarkable tetranuclear calix[4]arene complex, the calixarene being effectively a cluster builder under the conditions and reagents employed. The structure has implications in host–guest chemistry, potentially as a divergent receptor, and as a model for the binding of calix[4]arenes to metal oxide surfaces.
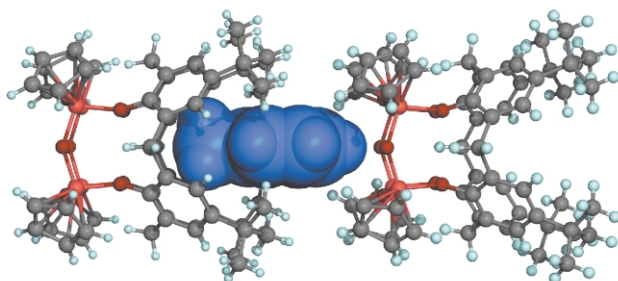

Fig. 2 Columnar stacking of **1**.
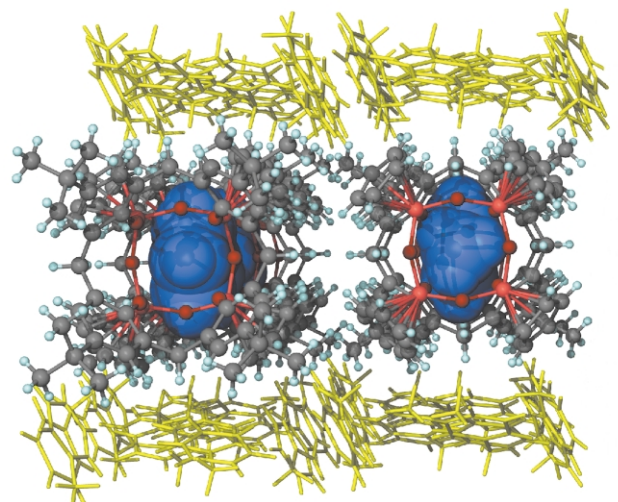
Fig. 3 Extended structure of **1**, showing the layering arrangement of the columns and toluene molecules.

Notes and references

1 S. Steyer, C. Jeunesse, D. Armspach, D. Matt, J. Harrowfield, C. Floriani and R. Floriani-Morro, *Calixarenes* 2001 (Eds.: Z. Asfari, V. Bohmer, J. Harrowfield, and J. Vicens), Kluwer, Dordrecht, 2001, Chapters 28 & 29, p. 513–560; C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93–136.
2 J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1992, 1349–1351.
3 J. L. Atwood, M. G. Gardiner, C. Jones, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2487–2489.
4 A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, N. Re, Chiesi-A. Villa and C. Rizzoli, *Inorg. Chim. Acta*, 1998, **270**, 298–311and references therein.
5 W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw and V. C. Gibson, *Dalton Trans.*, 1998, 3037–3039.
6 M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087–8091.
7 A. C. Skapski, P. G. H. Troughton and H. H. Sutherland, *Chem. Commun.*, 1968, **22**, 1418–19.
8 M. Bottrill, P. D. Gavens, J. W. Kelland and J. McMeeking, *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, and E. W. Abel), Pergamon Press, 1982, 33.
9 A. J. Petrella, N. K. Roberts, D. C. Craig, C. L. Raston and R. N. Lamb, *Chem. Commun.*, 2003, 1014.
10 J. A. Acho, H. L. Doerrer and S. J. Lippard, *Inorg. Chem.*, 1995, **34**(10), 2542–56.