exo and *endo* Isomerism of subvalent tin and germanium complexes derived from 1,3-diethers of *p-tert*-butylcalix[4]arene

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Abstract—A series of germanium and tin complexes of calix[4]arene diethers, namely [Calix$^{t\text{-}Bu}$(O)$_2$(OR)$_2$]M, has been prepared by the reaction of [Calix$^{t\text{-}Bu}$(OH)$_2$(OR)$_2$] with M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn; R = Me, CH$_2$Ph, CH$_2$C$_6$H$_4$Bu^t, SiPr$^i_3$). X-ray diffraction studies demonstrate that [Calix$^{t\text{-}Bu}$(O)$_2$(OR)$_2$]M exist as *exo* and *endo* isomers in which the metal is, respectively, located either outside or inside the calixarene cavity. The *exo* isomer is considered to be the kinetic product, whereas the *endo* isomer is thermodynamically more stable. The ability to access *endo*-[Calix$^{t\text{-}Bu}$(O)$_2$(OR)$_2$]M, however, depends critically on the nature of R and M.
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1. Introduction

Calix[4]arenes have found extensive use as ligands for both transition metals and main group metals.[1,2] In their tetraphenolic form, calix[4]arenes have the potential for serving as tetradentate tetraanionic X$_4$ ligands.[3] Modification of the calix[4]arene by selective alkylation of the phenolic groups, however, yields molecules that may serve in principle as tetradentate LX$_3$, L$_2$X$_2$, L$_3$X, and L$_4$ ligands,[4] thereby greatly expanding the versatility of calix[4]arenes in coordination chemistry. For example, dialkylation of two phenolic groups generates a molecule that may serve as an L$_2$X$_2$ ligand in its deprotonated form, akin to the nitrogen based porphyrins, phthalocyanines, and tetraazaannulene ligands.[5] In this paper, we describe the application of *p-tert*-butylcalix[4]arene diethers, [Calix$^{t\text{-}Bu}$(OH)$_2$(OR)$_2$], to the coordination chemistry of germanium and tin.

2. Results and discussion

We have previously reported the synthesis and structural characterization of the germanium and tin compounds [Calix$^{t\text{-}Bu}$(O)$_2$(OSiMe$_3$)$_2$]Ge and [Calix$^{t\text{-}Bu}$(O)$_2$(OSiMe$_3$)$_2$]Sn.[6] The most interesting aspect of this investigation was the discovery that the germanium derivative existed as both *exo*- and *endo*-isomers (which are differentiated according to whether the germanium is located outside or inside the calixarene cavity), whereas only the *exo* isomer was isolated for tin.[7] To extend our previous studies, we sought a series of [Calix$^{t\text{-}Bu}$(O)$_2$(OR)$_2$]M (M = Ge, Sn) derivatives with a variety of R substituents to evaluate whether *exo* and *endo*

isomerism is a more general phenomenon for this class of molecules. In this regard, while a selection of 1,3 (or distal) diethers, such as [Calix$^{t\text{-}Bu}$(OH)$_2$(OR)$_2$] (R = Me, Et, Pr^n, Pr^i, Bu^n, C$_3$H$_5$, CH$_2$Ph), have been synthesized by treatment of [Calix$^{t\text{-}Bu}$(OH)$_4$] with 2 equiv of RX (X = Hal, OSO$_2$Tol) in the presence of K$_2$CO$_3$,[8–10] development of the syntheses of bis(trialkylsilyl)ethers of *p-tert*-butylcalix[4]arene was not as straightforward as their alkyl analogs.

For example, an early attempt to silylate [Calix$^{t\text{-}Bu}$(OH)$_4$] using (Me$_3$Si)$_2$NH and Me$_3$SiCl in pyridine was reported to yield only recovered starting material.[11] Furthermore, treatment of [Calix$^{t\text{-}Bu}$(OH)$_4$] with Me$_3$SiCl and Li$_2$S afforded a crude product that appeared to be the bis(trimethylsilyl)ether, but attempts at purification resulted only in isolation of the starting material.[11] Despite these early difficulties, several procedures are now available for the synthesis of the bis(trimethylsilyl)ether, [Calix$^{t\text{-}Bu}$(OH)$_2$(OSiMe$_3$)$_2$]. In particular, Schmutzler reported that [Calix$^{t\text{-}Bu}$(OH)$_2$(OSiMe$_3$)$_2$] could, in fact, be obtained from the reaction of [Calix$^{t\text{-}Bu}$(OH)$_4$] with (Me$_3$Si)$_2$NH and catalytic Me$_3$SiCl.[12,13] On the other hand, Anwander reported that Me$_3$SiCl is not required to synthesize [Calix$^{t\text{-}Bu}$(OH)$_2$(OSiMe$_3$)$_2$] if the reaction is performed at high temperature in refluxing mesitylene.[5o] Anwander also described a synthesis of [Calix$^{t\text{-}Bu}$(OH)$_2$(OSiMe$_3$)$_2$] involving treatment of a mixture of [Calix$^{t\text{-}Bu}$(OH)$_4$] and Me$_3$SiCl with NaH,[5o] while we have reported that it may be obtained via treatment of [Calix$^{t\text{-}Bu}$(OH)$_4$] with 2 equiv of Me$_3$SiI and pyridine in acetonitrile.[6]

We have now extended the latter method for the synthesis of bis(silyl) ethers with more sterically demanding substituents. Specifically, *tert*-butyldimethylsilyl and triisopropylsilyl
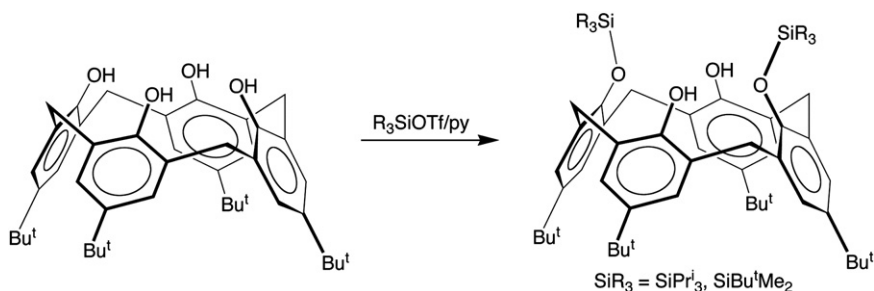
Scheme 1.

groups may be installed by treatment of [Calix$^{t\text{-Bu}}$(OH)$_4$] with the appropriate triflate, R$_3$SiOTf, in the presence of pyridine (Scheme 1).[14] The molecular structures of both [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$] and [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] have been determined by X-ray diffraction (Fig. 1), demonstrating that they adopt a distorted cone conformation analogous to that of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiMe$_3$)$_2$].[5o]

A series of mononuclear germanium and tin complexes [Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]M may be obtained via the reaction of [Calix$^{t\text{-Bu}}$(OH)$_2$(OR)$_2$] with M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn),[15] as illustrated in Scheme 2. The formation of these mononuclear compounds is in marked contrast to the dinuclear species, [Calix$^{t\text{-Bu}}$(O)$_4$]M$_2$, that are obtained from the corresponding reactions of [Calix$^{t\text{-Bu}}$(OH)$_4$] with M(NR$_2$)$_2$.[16] As such, the comparison between [Calix$^{t\text{-Bu}}$(OH)$_4$] and [Calix$^{t\text{-Bu}}$(OH)$_2$(OR)$_2$] provides a good example of how the coordination chemistry of the system may be modulated by functionalization of the calixarene oxygen atoms.

Our previous studies have demonstrated that the reaction of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiMe$_3$)$_2$] with Ge[N(SiMe$_3$)$_2$]$_2$ yields sequentially the *exo* and *endo* isomers of [Calix$^{t\text{-Bu}}$(O)$_2$(OSiMe$_3$)$_2$]Ge.[6] The more highly substituted calixarene [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] is also reactive towards Ge[N(SiMe$_3$)$_2$]$_2$, but more forcing conditions (120 °C) are required to effect the reaction and under these conditions the *endo* isomer of [Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Ge (Fig. 2) is

isolated; an intermediate has, nevertheless, been observed by ^{1}H NMR spectroscopy and is tentatively identified as the *exo* isomer. [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$] is even less reactive than is [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] towards Ge[N(SiMe$_3$)$_2$]$_2$, with no reaction being observed under comparable conditions. A possible explanation for the inertness of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$] is that the trialkylsilyl groups are oriented such that the Bu^t groups are located directly above the calixarene cavity (Fig. 1) and thereby could inhibit access of Ge[N(SiMe$_3$)$_2$]$_2$.

In addition to silyl ether derivatives, the reactivity of alkylated calixarenes towards Ge[N(SiMe$_3$)$_2$]$_2$ has also been investigated. Thus, analogous to [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiMe$_3$)$_2$], the methyl ether derivative [Calix$^{t\text{-Bu}}$(OH)$_2$(OMe)$_2$] reacts with Ge[N(SiMe$_3$)$_2$]$_2$ to yield the *exo* isomer of [Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge (Fig. 3). However, in contrast to *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiMe$_3$)$_2$]Ge, the methyl ether derivative *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge does not convert readily to the *endo* isomer,[17] but rather requires forcing conditions (130 °C for 18 h). This observation is markedly different to the corresponding reaction between the benzyl ether derivative [Calix$^{t\text{-Bu}}$(OH)$_2$(OCH$_2$Ph)$_2$] and Ge[N(SiMe$_3$)$_2$]$_2$ which yields the *endo* isomer of [Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Ge (Fig. 2) at 80 °C; the presumed *exo* isomer is only observed as an intermediate by ^{1}H NMR spectroscopy. Thus, compared to a methyl group, the benzyl substituent greatly facilitates *exo* to *endo* isomerism.
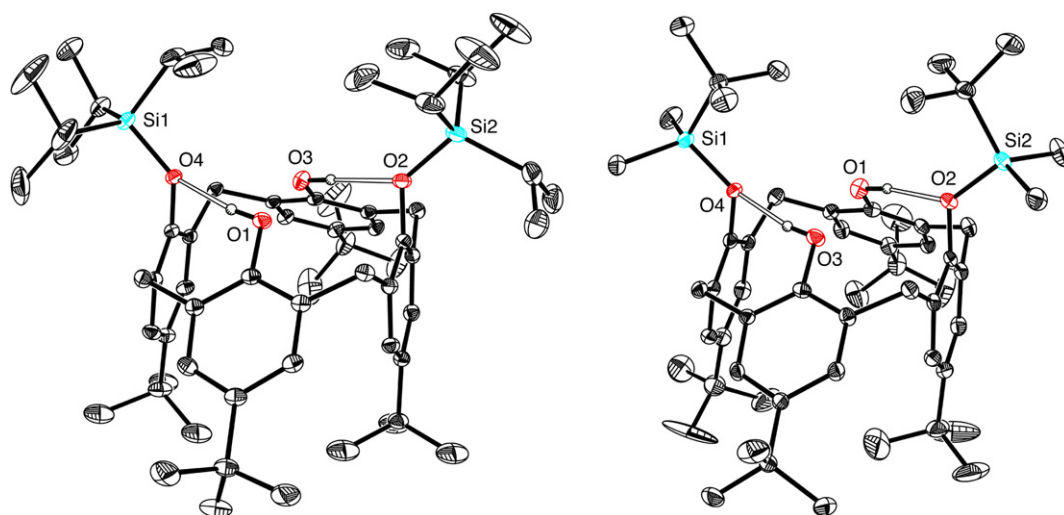
Figure 1. Molecular structures of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] (left) and [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$] (right).

R	*exo*	*endo*
SiMe$_3$	Ge & Sn	Ge
SiPr$^i_3$		Ge & Sn
Me	Ge & Sn	
CH$_2$Ph	Sn	Ge
CH$_2$C$_6$H$_4$Bu^t	Sn	
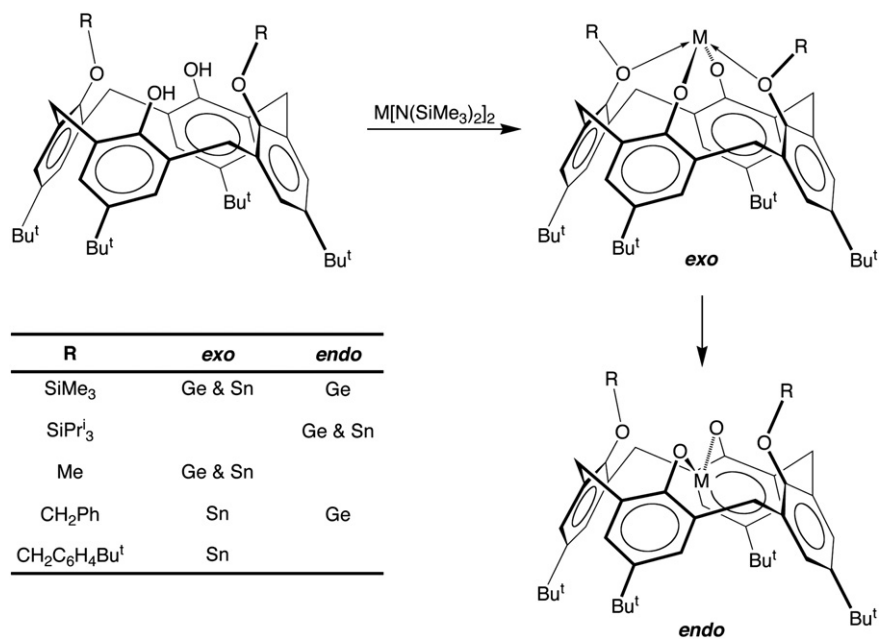
Scheme 2.
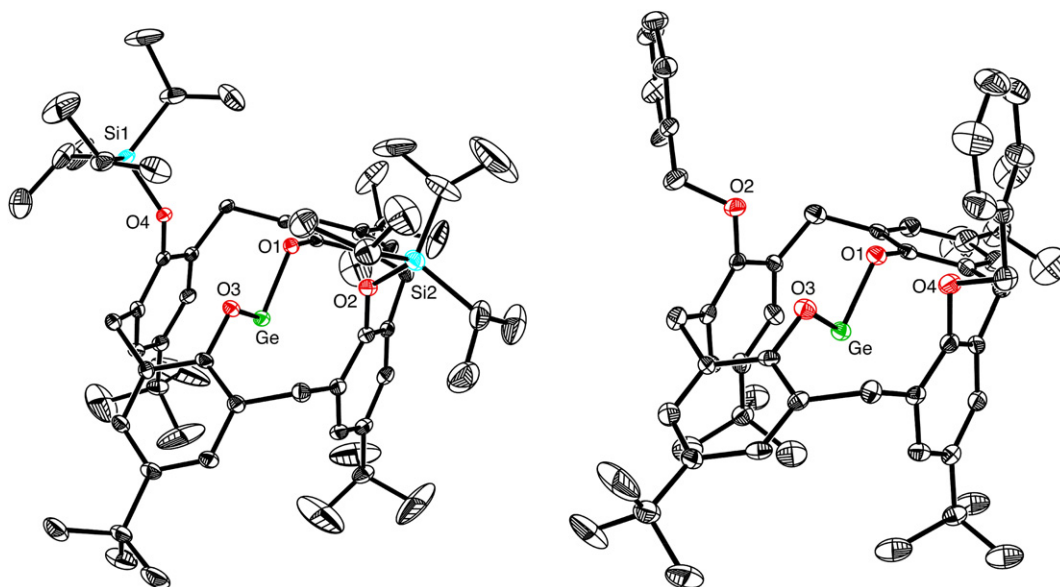
Figure 2. Molecular structures of *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Ge (left) and *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Ge (right).
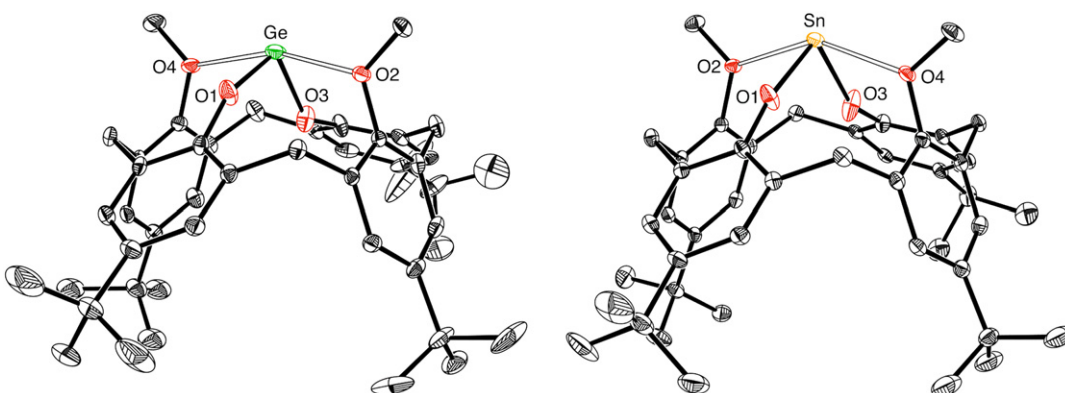
Figure 3. Molecular structures of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge (left) and *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Sn (right).
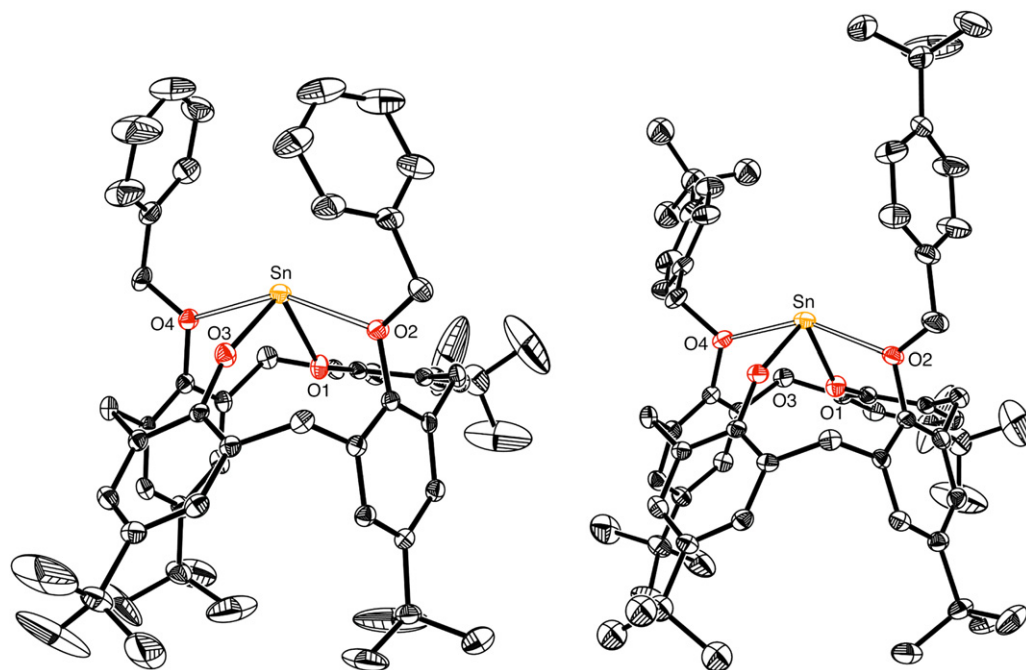
Figure 4. Molecular structures of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Sn (left) and *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$C$_6$H$_4$Bu^t)$_2$]Sn (right).

With respect to the corresponding tin system, the *exo* isomer has been isolated and structurally characterized for [Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Sn, [Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Sn, [Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$C$_6$H$_4$Bu^t)$_2$]Sn,[18] and [Calix$^{t\text{-Bu}}$(O)$_2$(OSiMe$_3$)$_2$]Sn[6] (Scheme 2 and Figs. 3 and 4). It is, therefore, evident that isolation of the *exo* isomer is experimentally more facile for tin than for the germanium system. Indeed, only one tin complex with an *endo* geometry has so far been structurally characterized, namely *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn (Fig. 5). The synthesis of *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn

is, nevertheless, significant because it demonstrates that it is indeed possible to isolate *endo* isomers for tin. The fact that [Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]Sn is more commonly isolated as the *exo* isomer may be a consequence of the larger size of tin, which inhibits facile transfer through the [O$_4$] plane and access to the *endo* isomer.[19]

Selected metrical data for the various [Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]M (M = Ge, Sn) derivatives are summarized in Table 1. While the data clearly indicate that the secondary M···O distances for the *exo* and *endo* isomers are significantly different, detailed comparisons of the primary M–O bond lengths are not warranted due to a poorly resolved disorder pertaining to the M(OAr)$_2$ fragment of the *exo* isomers; such disorder may result in an apparent shortening of the M–OAr bond lengths.[20]

Finally, consideration should also be given to the possibility that the bonding to the metal in the two-coordinate *endo* isomers could be supplemented by interactions with the aromatic rings. In this regard, both germanium and tin may be viewed to exhibit an η^3-interaction with two *trans* arene rings with distances (≈ 3 Å) that are comparable to the values that have been reported for other arene complexes of these metals.[21] While these distances are considerably longer than the sum of the covalent radii, it is nevertheless evident that weak metal–arene interactions of this type could contribute to the stability of the *endo* isomers.

3. Conclusion

In summary, a series of germanium and tin complexes of calix[4]arene diethers, namely [Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]M, has been prepared by the reaction of [Calix$^{t\text{-Bu}}$(OH)$_2$(OR)$_2$] with M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn). [Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]M
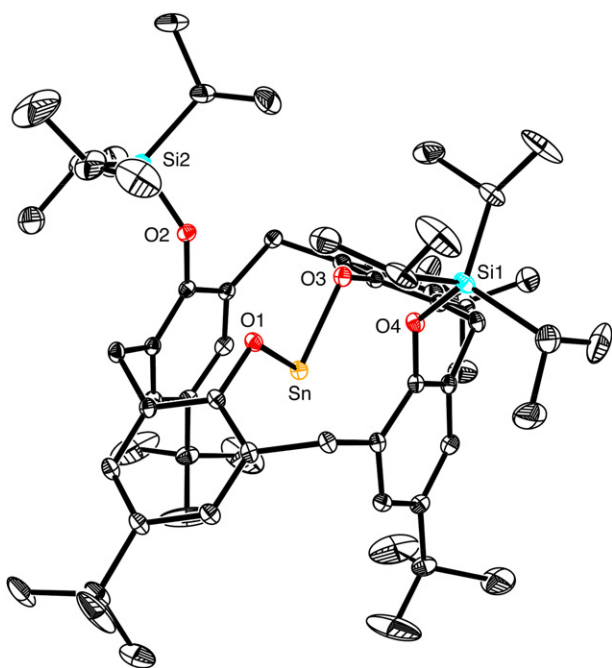
Figure 5. Molecular structure of *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn.

Table 1. Metrical data for [Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]Ge (M = Ge, Sn)[a]

	d(M–O$_1$)/Å	d(M–O$_3$)/Å	d(M⋯O$_2$)/Å	d(M⋯O$_4$)/Å	O–M–O/°
exo-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge	1.757(4)	1.888(4)	2.320(3)	2.411(3)	98.8(2)
exo-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiMe$_3$)$_2$]Ge[b]	1.765(6)	1.842(6)	2.421(5)	2.486(5)	100.2(3)
exo-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Sn	1.978(3)	2.006(3)	2.417(3)	2.465(3)	95.9(2)
exo-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Sn	2.035(4)	2.020(4)	2.553(4)	2.542(4)	95.5(2)
exo-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$C$_6$H$_4$Bu^t)$_2$]Sn	2.025(4)	2.027(4)	2.524(4)	2.422(4)	96.3(2)
exo-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiMe$_3$)$_2$]Sn[b]	1.956(7)	2.011(9)	2.521(6)	2.532(6)	96.3(4)
endo-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Ge	1.835(5)	1.824(5)	3.568(5)	3.486(5)	92.4(2)
endo-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiMe$_3$)$_2$]Ge[b]	1.841(5)	1.853(5)	3.460(5)	3.565(6)	92.8(2)
	1.840(5)	1.849(5)	3.454(6)	3.458(5)	92.0(2)
endo-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Ge	1.868(2)	1.860(2)	3.468(3)	3.387(2)	94.5(1)
endo-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn	2.067(2)	2.070(2)	3.542(2)	3.460(2)	89.4(1)

[a] O$_1$ and O$_3$ are the aryloxide oxygen atoms; O$_2$ and O$_4$ are the ether oxygen atoms.
[b] Data taken from Ref. 6.

exist as *exo* and *endo* isomers, of which the former is considered to be the kinetic product while the latter is the thermodynamic product. The ability to access the thermodynamically more stable *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OR)$_2$]M isomer, however, depends critically on the nature of both the metal and the ether substituents.

4. Experimental

4.1. General considerations

All manipulations were performed using a combination of glove box and Schlenk techniques.[22] Solvents were purified by standard procedures. All commercially available reagents were used as received without any further purification. [Calix$^{t\text{-Bu}}$(OH)$_4$],[23] [Calix$^{t\text{-Bu}}$(OH)$_2$(OMe)$_2$],[9h] [Calix$^{t\text{-Bu}}$(OH)$_2$(OCH$_2$Ph)$_2$],[9h] Ge[N(SiMe$_3$)$_2$]$_2$,[15] and Sn-[N(SiMe$_3$)$_2$]$_2$[15] were synthesized by the literature methods.

IR spectra were recorded as KBr pellets on a Perkin–Elmer Paragon 1000 FTIR Spectrometer and are reported in cm^{-1}. Carbon, hydrogen, and nitrogen elemental analyses were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. ^{1}H NMR spectra were recorded on Varian VXR-200, VXR-300, and Bruker Avance DPX 300, DRX 300, and DMX 500 spectrometers. ^{13}C spectra were recorded on Varian VXR-300 and Bruker Avance DRX 300 spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million relative to SiMe$_4$ (δ 0) and were referenced internally to the residual protio solvent (δ 7.15 for C$_6$D$_5$H and 7.26 for CHCl$_3$) and the ^{13}C resonance of the solvent (δ 128.0 for C$_6$D$_6$ and 77.0 for CDCl$_3$). ^{119}Sn spectra were recorded on a Bruker Avance DRX 300 spectrometer and are reported relative to SnMe$_4$ (δ 0) using SnMe$_4$ as an external standard. Tables of NMR spectroscopic data are provided in the Supplementary data.

X-ray diffraction data were collected on a Siemens P4 diffractometer or a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.10).[24] Tables of crystallographic data are provided in the Supplementary data and CIF files for [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] (CCDC #647927), [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$] (CCDC #647921), *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Ge (CCDC #647926), *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn (CCDC #647922), *exo*-[Calix$^{t\text{-Bu}}$-(O)$_2$(OMe)$_2$]Ge·C$_6$H$_6$ (CCDC #647928), *exo*-[Calix$^{t\text{-Bu}}$-(O)$_2$(OMe)$_2$]Sn·C$_6$H$_6$ (CCDC #647925), *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$-(OCH$_2$Ph)$_2$]Ge (CCDC #647929), *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$-Ph)$_2$]Sn (CCDC #647924), and *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$C$_6$-H$_4$Bu^t)$_2$]Sn·C$_7$H$_8$ (CCDC #647923) have been deposited at the Cambridge Crystallographic Data Centre.

4.2. Synthesis of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$]

A suspension of [Calix$^{t\text{-Bu}}$(OH)$_4$]·toluene (1.30 g, 1.75 mmol) in CH$_3$CN (25 mL) in a glass ampule was treated with pyridine (0.3 mL, 3.7 mmol) and then Bu^{t}Me$_2$–SiOTf (0.9 mL, 3.9 mmol). The mixture was heated for 1 day at 90 °C and allowed to cool to room temperature, thereby depositing a white precipitate. The mixture was filtered and the precipitate was washed with CH$_3$CN (30 mL) and dried in vacuo to give [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiBu^{t}Me$_2$)$_2$] as a white solid (1.18 g, 77%). IR data (KBr, cm^{-1}): 3470 (w, br) [$\nu_{\text{O-H}}$], 3175 (w, br) [$\nu_{\text{O-H}}$], 2961 (s), 2862 (w), 1484 (m), 1393 (w), 1363 (w), 1305 (w), 1256 (m), 1201 (m), 1125 (w), 921 (m), 875 (m), 844 (m), 812 (w), 782 (m), 731 (w), 697 (w), 628 (w), 553 (w). Anal. Calcd for C$_{56}$H$_{84}$O$_4$Si$_2$: C, 76.7%; H, 9.6.%. Found: C, 76.7%; H, 9.7%.

4.3. Synthesis of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$]

A suspension of [Calix$^{t\text{-Bu}}$(OH)$_4$]·toluene (4.34 g, 6.69 mmol) in CH$_3$CN (40 mL) in a glass ampule was treated with pyridine (1.1 mL, 13.6 mmol) and then Pr$^i_3$SiOTf (4.0 mL, 14.9 mmol). The mixture was heated at 90 °C overnight and then allowed to cool to room temperature, thereby depositing a white precipitate. The mixture was filtered and the precipitate was washed with CH$_3$CN (20 mL) and dried in vacuo to give [Calix$^{t\text{-Bu}}$(OH)$_2$-(OSiPr$^i_3$)$_2$] as a white solid (5.28 g, 82%). IR data (KBr, cm^{-1}): 3185 (w, br) [$\nu_{\text{O-H}}$], 2962 (s), 2869 (m), 1482 (s), 1363 (w), 1302 (w), 1248 (w), 1201 (m), 1125 (w), 1017 (w), 921 (w), 886 (m), 819 (w), 776 (w), 684 (m), 656 (w), 520 (w). Anal. Calcd for C$_{62}$H$_{96}$O$_4$Si$_2$: C, 77.4%; H, 10.1%. Found: C, 77.5%; H, 10.0%.

4.4. Synthesis of [Calix$^{t\text{-Bu}}$(OH)$_2$(OCH$_2$C$_6$H$_4$Bu^t)$_2$]

A suspension of [Calix$^{t\text{-Bu}}$(OH)$_4$]·toluene (2.02 g, 2.73 mmol) and K$_2$CO$_3$ (0.50 g, 3.6 mmol) in CH$_3$CN

(10 mL) and *p-tert*-butylbenzyl bromide (1.0 mL, 5.4 mmol) was added. The mixture was refluxed under nitrogen overnight. After this period, the volatile components were removed in vacuo and the residue was extracted into Et_2O (20 mL). The mixture was filtered and the solvent removed from the ether extract in vacuo to give [Calix$^{t\text{-Bu}}$(OH)$_2$-(OCH$_2$C$_6$H$_4$Bu^t)$_2$] as a white solid (1.95 g, 76%). IR data (KBr, cm^{-1}): 3424 (br) [$\nu_{O–H}$], 2962 (s), 2906 (m), 2868 (m), 1511 (w), 1485 (s), 1461 (m), 1413 (w), 1393 (w), 1363 (m), 1301 (w), 1269 (w), 1195 (m), 1123 (w), 1108 (w), 1015 (w), 980 (w), 945 (w), 872 (w), 818 (w). Anal. Calcd for C$_{66}$H$_{84}$O$_4$: C, 84.2%; H, 9.0%. Found: C, 83.7%; H, 8.4%.

4.5. Synthesis of *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Ge

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] (0.31 g, 0.32 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (0.14 g, 0.36 mmol) in toluene (5 mL) was heated at 120 °C for 3 days; after this period, additional Ge[N(SiMe$_3$)$_2$]$_2$ (50 mg) was added and the mixture was stirred for another day at 120 °C. The volatile components were removed in vacuo and the residue obtained was extracted into pentane (10 mL). The mixture was filtered and the solvent was removed from the filtrate in vacuo to give *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Ge as an off-white solid (0.12 g 35%). IR data (KBr, cm^{-1}): 2957 (s), 2923 (s), 2866 (s), 1461 (s), 1390 (w), 1363 (w), 1304 (m), 1260 (w), 1195 (m), 1109 (w), 1074 (w), 1015 (w), 996 (w), 925 (m), 886 (m), 823 (w), 788 (w), 770 (w), 740 (w), 684 (w), 655 (w), 622 (w), 550 (w), 514 (w). Anal. Calcd for C$_{62}$H$_{94}$O$_4$Si$_2$Ge: C, 72.1%; H, 9.2%. Found: C, 72.3%, H, 8.7%.

4.6. Synthesis of *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OSiPr$^i_3$)$_2$] (0.40 g, 0.46 mmol) and Sn[N(SiMe$_3$)$_2$]$_2$ (0.19 g, 0.43 mmol) in toluene (5 mL) was stirred overnight at 120 °C. After this period, the volatile components were removed in vacuo and the residue was extracted into pentane (20 mL). The mixture was filtered and the solvent was removed from the filtrate in vacuo to yield *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OSiPr$^i_3$)$_2$]Sn as an off-white solid (0.21 g 49%). IR data (KBr, cm^{-1}): 2962 (s), 2868 (m), 1459 (s), 1364 (w), 1308 (m), 1252 (m), 1204 (m), 1110 (w), 1016 (w), 921 (m), 886 (m), 824 (w), 792 (w), 770 (w), 741 (w), 684 (m), 656 (w), 520 (w). Anal. Calcd for C$_{62}$H$_{94}$O$_4$Si$_2$Sn: C, 69.1%; H, 8.8%. Found: C, 68.5%; H, 8.8%.

4.7. Synthesis of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OMe)$_2$] (0.21 g, 0.31 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (0.14 g, 0.36 mmol) in benzene (5 mL) was heated at 80 °C for 3 h. After this period, the volatile components were removed in vacuo and the residue obtained was dissolved in pentane (10 mL). The mixture was filtered and the solvent was removed from the filtrate in vacuo to give *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge as a white solid (0.11 g, 47%). IR data (KBr, cm^{-1}): 2961 (s), 1601 (w), 1482 (s), 1461 (s), 1392 (w), 1362 (w), 1304 (m), 1249 (m), 1201 (s), 1122 (w), 1102 (w), 1011 (m), 922 (w), 871 (w), 838 (w), 774 (w), 535 (w). Anal. Calcd for C$_{46}$H$_{58}$O$_4$Ge: C, 73.9%; H, 7.8%. Found: C, 73.0%; H, 8.2%.

4.8. Conversion of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge to *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge

A solution of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Ge (90 mg) in toluene (5 mL) was heated at 130 °C for 18 h. After this period, the volatile components were removed in vacuo and solid obtained was washed with pentane (5 mL) and dried in vacuo. ^{1}H NMR spectroscopy revealed the clean formation of a new product, tentatively identified as *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$-(OMe)$_2$]Ge on the basis of ^{1}H NMR spectroscopy (C$_6$D$_6$): δ 0.90 [s, 2Bu^t], 1.39 [s, Bu^t], 3.24 [d, $J_{H–H}$ = 14, 4H, CH_2], 3.49 [s, 2OCH_3], 4.61 [d, $J_{H–H}$ = 14, 4H, CH_2]; δ 6.99 [s, 4H, calix aromatic H]; 7.29 [s, 4H, calix aromatic H].

4.9. Synthesis of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Sn

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OMe)$_2$] (0.31 g, 0.46 mmol) and Sn[N(SiMe$_3$)$_2$]$_2$ (0.21 g, 0.48 mmol) in pentane (20 mL) was stirred overnight at room temperature, resulting in the formation of a white precipitate, which was isolated by filtration, washed with pentane (2×20 mL) and dried in vacuo to give *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OMe)$_2$]Sn as a white solid (0.17 g, 47%). IR data (KBr, cm^{-1}): 2959 (s), 1601 (w), 1481 (s), 1461 (s), 1392 (w), 1361 (w), 1308 (m), 1210 (m), 1122 (w), 1098 (w), 1006 (m), 920 (w), 870 (w), 839 (w), 779 (w), 531 (w).

4.10. Synthesis of *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Ge

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OCH$_2$Ph)$_2$] (0.41 g, 0.49 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (0.22 g, 0.56 mmol) was stirred in benzene (5 mL) at 80 °C overnight. After this period, the volatile components were removed in vacuo. The resulting solid washed with pentane (5 mL) and dried in vacuo to give *endo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Ge as a white solid (0.26 g, 58%). IR Data (KBr, cm^{-1}): 2959 (s), 2868 (m), 1597 (w), 1464 (s), 1364 (m), 1294 (m), 1243 (m), 1199 (s), 1107 (m), 983 (m), 918 (m), 874 (m), 824 (m), 784 (m), 744 (m), 697 (m), 640 (w), 557 (m), 436 (w). Anal. Calcd for C$_{58}$H$_{66}$O$_4$Ge: C, 77.4%; H, 7.4%. Found: C, 77.4%; H, 7.7%.

4.11. Synthesis of *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Sn

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OCH$_2$Ph)$_2$] (0.50 g, 0.60 mmol) and Sn[N(SiMe$_3$)$_2$]$_2$ (0.30 g, 0.68 mmol) was stirred in pentane (15 mL) for 2 h, resulting in the formation of a white precipitate. The solid was isolated by filtration, washed with pentane (15 mL), and dried in vacuo to give *exo*-[Calix$^{t\text{-Bu}}$(O)$_2$(OCH$_2$Ph)$_2$]Sn as a white solid (0.38 g, 67%). IR Data (KBr, cm^{-1}): 3032 (w), 2957 (s), 2870 (m), 1601 (w), 1477 (s), 1427 (w), 1932 (w), 1363 (m), 1305 (m), 1259 (m), 1209 (s), 1173 (m), 1123 (m), 1097 (w), 981 (m), 944 (w), 919 (w), 870 (w), 837 (m), 780 (w), 761 (m), 718 (w), 695 (w), 638 (w), 596 (w), 549 (w), 531 (w), 498 (w). Anal. Calcd for C$_{58}$H$_{66}$O$_4$Sn: C, 73.7%; H, 7.0%. Found: C, 73.7%; H, 7.2%.

4.12. Synthesis of *exo*-[Calix$^{t\text{-Bu}}$(OH)$_2$-(OCH$_2$C$_6$H$_4$Bu^t)$_2$]Sn

A mixture of [Calix$^{t\text{-Bu}}$(OH)$_2$(OCH$_2$C$_6$H$_4$Bu^t)$_2$] (0.12 g, 0.13 mmol) and Sn[N(SiMe$_3$)$_2$]$_2$ (0.06 g, 0.14 mmol) in

pentane (3 mL) was stirred for 2.5 h, resulting in the formation of a white precipitate. The mixture was filtered and the precipitate was dried in vacuo to give *exo*-[Calix$^{t\text{-Bu}}$-(OH)$_2$(OCH$_2$C$_6$H$_4$Bu^t)$_2$]Sn as a white solid (50 mg, 39%). IR data (KBr, cm^{-1}): 2960 (s), 2869 (w), 1478 (s), 1461 (s), 1423 (w), 1364 (w), 1309 (m), 1270 (w), 1211 (m), 1123 (w), 985 (m), 943 (w), 921 (w), 872 (w), 839 (w), 823 (w), 781 (w). Anal. Calcd for C$_{66}$H$_{82}$O$_4$Sn: C, 74.9%; H, 7.8%. Found: C, 75.2%; H, 8.0%.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.127.

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