

Subvalent germanium and tin complexes supported by a dianionic calixarene ligand: structural characterization of *exo* and *endo* isomers of [Bu^tcalix^(TMS)₂]₂Ge

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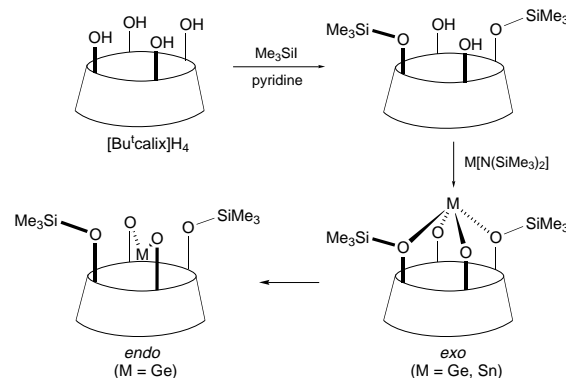
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The 1,3-bis(trimethylsilyl) ether of *p*-*tert*-butylcalix[4]arene, [Bu^tcalix^(TMS)₂]₂H₂, has been synthesized and used as a dianionic ligand for Ge and Sn; notably, the Ge complex [Bu^tcalix^(TMS)₂]₂Ge exhibits *exo/endo* isomerism, and provides the first calixarene system for which both isomers have been structurally characterized.

The calix[*n*]arenes are a class of ‘chalice-like’ macrocyclic molecules that have recently attracted widespread attention.¹ In particular, these molecules have been extensively studied as receptors for small organic molecules and simple cations.¹ By comparison, however, calix[*n*]arenes have been infrequently used as ancillary ligands for studying the chemistry of transition and main group metals.^{2,3} Moreover, for those situations where calix[*n*]arenes have been employed as supporting ligands, their application has been mainly restricted to the use of *p*-*tert*-butylcalix[4]arene in its tetraanionic form.[†] 1,3-Dialkyl ethers of calix[4]arenes, [calix^{R2}]₂H₂, on the other hand, offer the potential for providing dianionic macrocyclic ligands which may be considered as oxygen relatives of well known N-containing macrocycles, such as porphyrins, phthalocyanines and tetraazaannulenes. Despite such analogies, the application of 1,3-diethers of calix[4]arenes as ligands for main group metals has been limited to recent reports concerned with the 1,3-dimethyl ether of *p*-*tert*-butylcalix[4]arene.^{3a–c} Here, we report the synthesis of a more sterically demanding, 1,3-disubstituted calix[4]arene, namely bis(trimethylsilyl)-*p*-*tert*-butylcalix[4]arene, its use as a ligand for divalent Ge and Sn, and the first structural characterization of a pair of *exo* and *endo* isomers of a calix[*n*]arene derivative.

Our particular interest in the use of 1,3-dialkylcalix[4]arenes as O-donor macrocyclic ligands derives from recent studies concerned with Ge and Sn complexes supported by the octamethyldibenzotetraaza[14]annulene dianion, *e.g.* the subvalent and terminal chalcogenido complexes [η⁴-Me₈taa]M and [η⁴-Me₈taa]ME (M = Ge, Sn; E = S, Se, Te).^{4–6} In order to extend this chemistry, we sought to synthesize analogous complexes derived from related macrocycles which contain O (rather than N) donor functionalities. For this purpose, 1,3-dialkyl ether calix[4]arene derivatives incorporating bulky substituents (*e.g.* SiMe₃) appeared ideal. Although 1,3-diethers of *p*-*tert*-butylcalix[4]arene incorporating primary alkyl substituents have been synthesized previously by the reaction of the calix[4]arene with 2 equiv. of alkyl halides in the presence of a weak base,^{1c} the bis(trimethylsilyl) derivative [Bu^tcalix^(TMS)₂]₂H₂ could not be isolated using such procedures.^{‡8} Nevertheless, we have found that the reaction of *p*-*tert*-butylcalix[4]arene with Me₃SiH (2 equiv.) in the presence of pyridine (2 equiv.) affords a useful synthesis of [Bu^tcalix^(TMS)₂]₂H₂ (Scheme 1).

Divalent Ge and Sn complexes [Bu^tcalix^(TMS)₂]₂M are readily obtained by the reaction of [Bu^tcalix^(TMS)₂]₂H₂ with M[N(SiMe₃)₂]₂ (M = Ge, Sn) as illustrated in Scheme 1. Each of the products has been structurally characterized by X-ray diffraction, as shown in Fig. 1 and 2.[§] Interestingly, for the Ge



Scheme 1

system, the reaction yields sequentially two isomers, namely *exo*- and *endo*-[Bu^tcalix^(TMS)₂]₂Ge, which differ in the location of the Ge atom with respect to the calixarene cavity (Figs. 1 and 2).[¶] *Exo* and *endo* isomerism of this type has previously been suggested for the aluminium hydride complex [Bu^tcalix^{Me2}]₂AlH, for which the Al–H moiety may be directed into, or away from, the calixarene cavity.^{3b} However, only the structure of *exo*-[Bu^tcalix^{Me2}]₂AlH has been determined by X-ray diffraction, with the nature of the *endo* isomer having been inferred by NMR spectroscopy. The Ge complexes described here, therefore, constitute the first pair of *exo* and *endo* isomers to be structurally characterized.

The coordination geometries about Ge in *exo*- and *endo*-[Bu^tcalix^(TMS)₂]₂Ge are summarized in Table 1, from which it is evident that both complexes exhibit Ge–O bond lengths to the phenoxide moieties which are comparable to, but slightly shorter than, the sum of their covalent radii (1.96 Å).^{||} For the *endo* isomer, the Ge center is located *ca.* 3.5 Å from the O atoms of the trimethylsilylether groups, so that it is appropriately

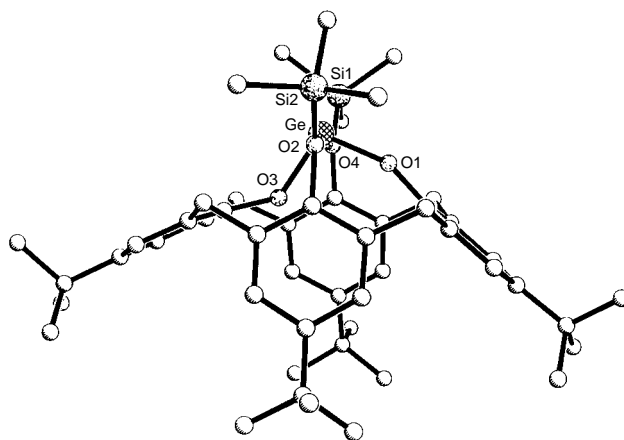
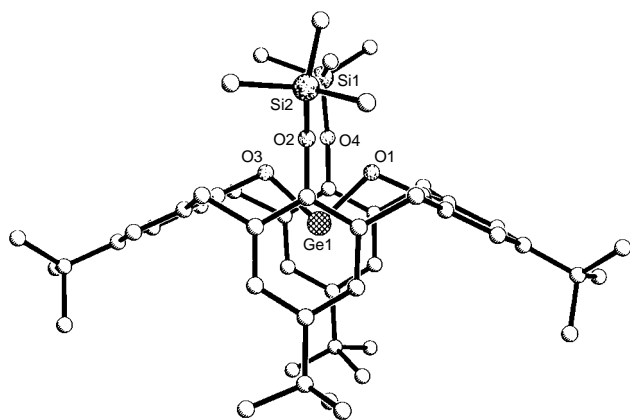


Fig. 1 The molecular structure of *exo*-[Bu^tcalix^(TMS)₂]₂Ge (the Sn analogue is similar)

Table 1 Metrical data for [Bu^tcalix^(TMS)₂]*M* (*M* = Ge, Sn)

	<i>d</i> (M–O ¹)/Å	<i>d</i> (M–O ³)/Å	<i>d</i> (M···O ²)/Å	<i>d</i> (M···O ⁴)/Å	O–M–O/ ^o
<i>exo</i> -[Bu ^t calix ^(TMS) ₂] <i>Ge</i>	1.765(6)	1.842(6)	2.421(5)	2.486(5)	100.2(3)
<i>endo</i> -[Bu ^t calix ^(TMS) ₂] <i>Ge</i>	1.841(5)	1.853(5)	3.460(5)	3.565(6)	92.81(22)
	1.840(5)	1.849(5)	3.454(6)	2.458(5)	92.02(23)
<i>exo</i> -[Bu ^t calix ^(TMS) ₂] <i>Sn</i>	1.956(7)	2.011(9)	2.521(6)	2.532(6)	96.3(4)

**Fig. 2** The molecular structure of *endo*-[Bu^tcalix^(TMS)₂]*Ge* (only one of the crystallographically independent molecules is shown)

considered to be two-coordinate, with the dianionic calixarene acting as a bidentate, rather than tetradentate, ligand. As such, the coordination environment offered by the dianionic calixarene provides a contrast with the tetracoordination provided by related macrocyclic derivatives, *e.g.* [η⁴-Me₈taa]*Ge*.⁴ The ability of the calixarene to sustain monomeric two-coordinate Ge^{II} centers is of interest since complexes with such coordination environments are uncommon; for example, only two two-coordinate Ge^{II} alkoxide complexes are listed in the Cambridge Structural Database (Version 5.13), namely (ArO)₂*Ge* (Ar = C₆H₂MeBu₂) and (Bu₃CO)₂*Ge*.^{||} In contrast to the two-coordinate *endo* isomer, the *exo* isomer does exhibit interactions with the O atoms of the trimethylsilylether groups (*ca.* 2.45 Å) that are shorter than the sum of their van der Waals radii (3.40 Å).^{||}

It is interesting to note that, despite the observation that the dative interaction between Ge and the trimethylsilyl ether groups is shorter for the *exo* isomer, the *endo* isomer is evidently the more thermodynamically stable, as judged by the observed *exo* to *endo* isomerization.^{**}†† Thus, the [O→Ge] dative interactions in the *exo* isomer are presumably weak and insufficient to compensate for other structural changes which accompany the isomerization. For example, one factor which favors the *endo* isomer being the more stable is concerned with the possibility that the calixarene conformation is such that it furnishes a more appropriate bite angle for Ge in the *endo* position than for Ge in the *exo* position (compare Figs. 1 and 2). Supporting this notion, the O–Ge–O bond angle for the *exo* isomer [100.2(3)°] is notably larger than is observed for simple (RO)₂*Ge* complexes (*ca.* 86–92°)^{||} which are not subject to the constraints of the macrocyclic configuration. In contrast, the *endo* isomer does exhibit a O–Ge–O bond angle (*ca.* 92.4°) that is comparable to the values for (RO)₂*Ge* derivatives, thereby suggesting that there is less strain for the *endo* isomer, so that it may be more thermodynamically favored.^{‡‡}

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Footnotes and References

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† For the use of neutral calixarene ligands, see ref. 3(f).

‡ Specifically, only recovered *p*-*tert*-butylcalix[4]arene was obtained from the reaction of (i) *p*-*tert*-butylcalix[4]arene with Me₃SiCl and (Me₃Si)₂NH, and (ii) *p*-*tert*-butylcalix[4]arene with Me₃SiCl and Li₂S. The latter reaction, however, did provide evidence for formation of the bis-(trimethylsilyl) ether derivative, but the product could not be isolated.^{7a} Tetrakis(trimethylsilyl)-*p*-*tert*-butylcalix[4]arene has, however, been obtained by the reaction of the calix[4]arene with N,O-tris(trimethylsilyl)-acetamide.^{7b}

§ **Crystallography.** *exo*-[Bu^tcalix^(TMS)₂]*Ge*·C₆H₅Me is monoclinic, *P*₂₁/*c* (no. 14), *a* = 23.275(3), *b* = 18.829(2), *c* = 13.245(1) Å, β = 105.059(7)°, *U* = 5605(1) Å³, *Z* = 4, *R* [*I* > 2σ(*I*)] = 0.0738. *endo*-[Bu^tcalix^(TMS)₂]*Ge* is monoclinic, *P*₂₁/*c* (no. 14), *a* = 28.2718(3), *b* = 18.4591(1), *c* = 20.5583(1) Å, β = 111.245(1)°, *U* = 9999.7(1) Å³, *Z* = 8, *R* [*I* > 2σ(*I*)] = 0.1027. *exo*-[Bu^tcalix^(TMS)₂]*Sn*·C₆H₆ is monoclinic, *P*₂₁/*c* (no. 14), *a* = 23.339(7), *b* = 18.684(4), *c* = 13.204(3) Å, β = 105.98(1)°, *U* = 5535(1) Å³, *Z* = 4, *R* [*I* > 2σ(*I*)] = 0.0744. CCDC 182/655.

¶ In contrast, for the Sn system, only the *exo* isomer has been isolated so far.

|| For comparison, the following metrical data have been reported for two-coordinate Ge and Sn alkoxide and aryloxy complexes: (i) (ArO)₂*Ge* (Ar = C₆H₂MeBu₂): (Ge–O) 1.802(8), 1.812(7) Å; O–Ge–O 92.0(4)°;^{9–a} (ii) (ArO)₂*Sn* (Ar = C₆H₂MeBu₂): (Sn–O) 1.995(4), 2.022(4) Å; O–Sn–O 88.8(2)°;^{9a} (iii) (Bu₃CO)₂*Ge*: (Ge–O) 1.896(6), 1.832(11) Å; O–Ge–O 85.9(4)°.^{9b}

** The conversion of *exo*-[Bu^tcalix^(TMS)₂]*Ge* to its *endo* isomer (*ca.* 95%) has been observed to occur over a 1 h at *ca.* 80 °C, as monitored by ¹H NMR spectroscopy.

†† The *endo* isomer of [Bu^tcalix^(Me)₂]*Al*H has also been reported to be more stable than its *exo* isomer. See ref. (3b).

‡‡ Other factors, such as the small conformational differences of the calixarene ligand, may also influence the stability of the *endo* with respect to *exo* isomer.

- (a) G. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, 1989; (b) *Calixarenes: A Versatile Class of Macrocyclic Compounds*, ed. J. Vincens and V. Böhmer, Kluwer, Dordrecht, 1991; (c) V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
- D. M. Roundhill, *Prog. Inorg. Chem.*, 1995, **43**, 533.
- For recent examples of the use of calix[*n*]arenes as ligands in main group metal chemistry, see: (a) M. G. Gardiner, S. M. Lawrence, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2491; (b) M. G. Gardiner, G. A. Koutsantonis, S. M. Lawrence, P. J. Nichols and C. L. Raston, *Chem. Commun.*, 1996, 2035; (c) J. L. Atwood, M. G. Gardiner, C. Jones, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2487; (d) J. L. Atwood, P. C. Junk, S. M. Lawrence and C. L. Raston, *Supramol. Chem.*, 1996, **7**, 15; (e) J. M. Smith and S. G. Bott, *Chem. Commun.*, 1996, 377; (f) S. G. Bott, A. W. Coleman and J. L. Atwood, *J. Incl. Phenom.*, 1987, **5**, 747.
- M. C. Kuchta and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1994, 1351.
- M. C. Kuchta and G. Parkin, *J. Am. Chem. Soc.*, 1994, **116**, 8372.
- M. C. Kuchta and G. Parkin, *Chem. Commun.*, 1996, 1669.
- (a) C. D. Gutsche, B. Dhawan, K. H. No and R. Muthukrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 3782; (b) C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No and L. J. Bauer, *Tetrahedron*, 1983, **39**, 409.
- For some other examples of O-silylated calixarenes see: (a) M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087; (b) X. Delaigue, M. W. Hosseini, A. De Cian, J. Fischer, E. Leize, S. Kieffer and A. Van Dorsselaer, *Tetrahedron Lett.*, 1993, **34**, 3285; (c) S. Shang, D. V. Khasnis, J. M. Burton, C. J. Santini, M. Fan, A. C. Small and M. Lattman, *Organometallics*, 1994, **13**, 5157; (d) M. Fan, H. Zhang and M. Lattman, *Organometallics*, 1996, **15**, 5216.
- (a) B. Cetinkaya, I. Gümrükcü, M. F. Lappert, J. L. Atwood, R. D. Rogers and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1980, **102**, 2088; (b) T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, S. J. Smith and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1985, 939.

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