

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

Tony Hascall,^a Arnold L. Rheingold,^b Iia Guzei^b and Gerard Parkin^{*a}

^a Department of Chemistry, Columbia University, New York, New York 10027, USA

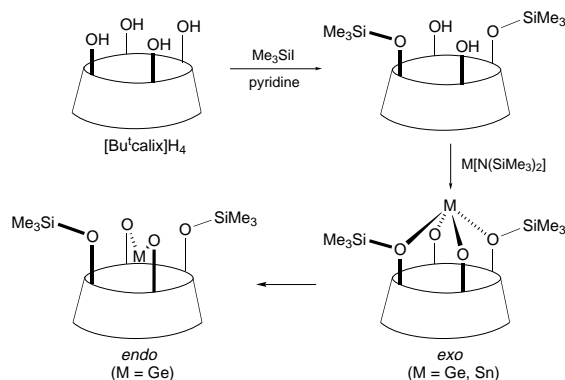
^b Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA

The 1,3-bis(trimethylsilyl) ether of *p*-*tert*-butylcalix[4]arene, [Bu^tcalix^(TMS)₂]H₂, has been synthesized and used as a dianionic ligand for Ge and Sn; notably, the Ge complex [Bu^tcalix^(TMS)₂]Ge 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}]H₂, 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]H₂ could not be isolated using such procedures.^{‡8} Nevertheless, we have found that the reaction of *p*-*tert*-butylcalix[4]arene with Me₃SiI (2 equiv.) in the presence of pyridine (2 equiv.) affords a useful synthesis of [Bu^tcalix^(TMS)₂]H₂ (Scheme 1).

Divalent Ge and Sn complexes [Bu^tcalix^(TMS)₂]M are readily obtained by the reaction of [Bu^tcalix^(TMS)₂]H₂ 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]Ge, 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}]AlH, 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}]AlH 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]Ge 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

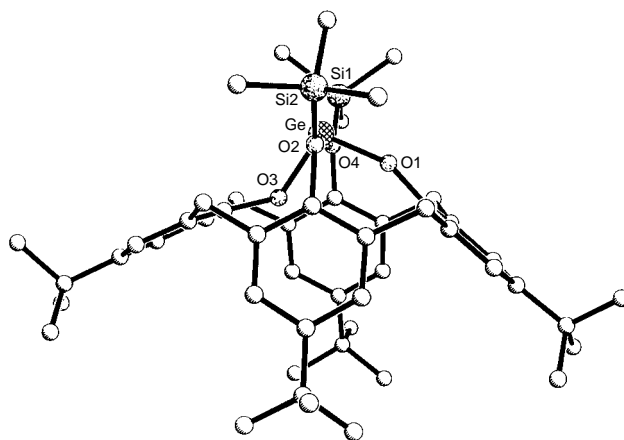
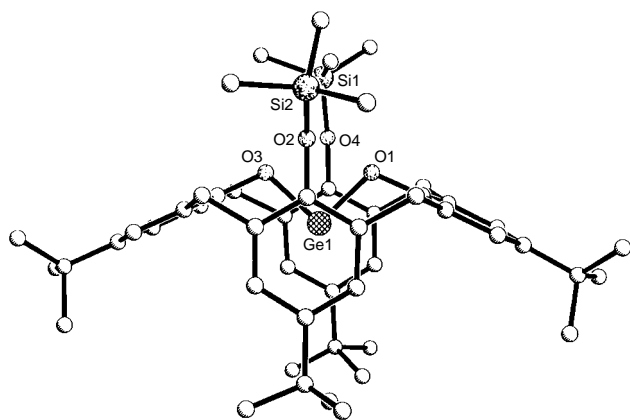


Fig. 1 The molecular structure of *exo*-[Bu^tcalix^(TMS)₂]Ge (the Sn analogue is similar)

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)₂Ge (Ar = C₆H₂MeBu_t₂) and (Bu_tCO)₂Ge.^{||} In contrast to the two-coordinate *endo* isomer, the *exo* isomer does exhibit interactions with the O atoms of the trimethylsilyloxy 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 trimethylsilyloxy 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)₂Ge 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)₂Ge derivatives, thereby suggesting that there is less strain for the *endo* isomer, so that it may be more thermodynamically favored.^{‡‡}

We thank the National Science Foundation (CHE 96-10497) for support of this research. G. P. is the recipient of a Presidential Faculty Fellowship Award (1992–1997).

Footnotes and References

* E-mail: parkin@chem.columbia.edu

† 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-(trimethylsilyloxy) ether derivative, but the product could not be isolated.^{7a} Tetrakis(trimethylsilyloxy)-*p*-*tert*-butylcalix[4]arene has, however, been obtained by the reaction of the calix[4]arene with N,O-tris(trimethylsilyloxy)-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)₂Ge (Ar = C₆H₂MeBu_t₂): (Ge–O) 1.802(8), 1.812(7) Å; O–Ge–O 92.0(4)°;^{9–a} (ii) (ArO)₂Sn (Ar = C₆H₂MeBu_t₂): (Sn–O) 1.995(4), 2.022(4) Å; O–Sn–O 88.8(2)°;^{9a} (iii) (Bu_tCO)₂Ge: (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 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. Gümürkçü, 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.

Received in Bloomington, IN, USA, 13th August 1997; 7/05937J