Synthesis and crystal structure of a germanium(II) calix[6]arene containing unusual diamidosilyl ether groups

Anthony E. Wetherby Jr. [a], Arnold L. Rheingold [b], Christa L. Feasley [c], Charles S. Weinert [a,*]

[a] Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, USA
[b] Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093-0303, USA
[c] Department of Biochemistry and Molecular Biology, The Oklahoma Center for Medical Glycobiology, University of Oklahoma Health Science Center, Oklahoma City, OK 73104, USA

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ABSTRACT

The reaction of $Ge[N(SiMe_3)_2]_2$ with calix[6]arene furnishes a novel macrocyclic product having two divalent germanium atoms incorporated into a Ge_2NO rhombus which contains a μ_2-oxygen atom and a μ_2-NH_2 group. The crystal structure of the product indicates the presence of a conformationally rigid molecule where three of the six oxygen atoms of the calix[6]arene are bound to the germanium atoms while the remaining three have been converted into $-OSiMe_3$ or unusual $-OSi(H)(NH_2)_2$ groups. Spectral (^{1}H, ^{13}C, and ^{29}Si NMR) data in solution are consistent with the solid-state structure and indicate the germanium calix[6]arene retains its structure in solution.

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1. Introduction

Calix[n]arenes are an important class of macrocycles which contain four or more phenol moieties connected together by methylene bridges. These species have applications in the areas of catalysis, self-assembly, and molecular or ionic recognition, and can also serve as platforms for the support of multiple transition- or main group-metal centers [1–24], including silicon-[13,16,17,21], phosphorus- [10–15,18,20,22–24], and arsenic [19]. Variation of the number of phenolic subunits present in the molecule allows control over the cavity size in these systems, which in turn has a profound effect on their properties and reactivity. The presence or absence of conformational rigidity, which is typically influenced by the attachment of peripheral substituents to the para-positions (or upper rim) of the aromatic rings, is also important in this regard [2,6,7,25–27].

Calix[6]arenes have been confirmed to be more flexible than calix[4]- and calix[8]arenes bearing identical para-substituents by variable temperature NMR spectral studies [28,29]. Several oxygen-functionalized calix[6]arenes have been employed for the complexation of metal ions [30–43] and some bimetallic complexes containing group 2 or 4 metals [44–46] bound directly to the oxygen atoms have been prepared. The latter types of complexes are uncommon, presumably due to the high conformational mobility of the hexamers versus the related tetramers and octamers. We recently described the syntheses and structures of calix[4]- and calix[8]arene complexes containing two or four germanium(II) sites (respectively) bound to the oxygen atoms of the macrocycles which were prepared via the protonolysis reaction of $Ge[N(SiMe_3)_2]_2$ with the para-unsubstituted parent calixarenes [47]. The structures of these two compounds were similar in that the germanium atoms were incorporated into Ge_2O_2 rhombi each having one terminal and two bridging Ge–O attachments. The calix[8]arene species was also shown to undergo an oxidative addition reaction with $Fe_2(CO)_9$ resulting in an octa-iron compound containing four $GeFe_2$ triangles.

In light of these results, we attempted to prepare a similar complex by treatment of the para-unsubstituted calix[6]arene with three equivalents of $Ge[N(SiMe_3)_2]_2$, and we now wish to report the outcome of this investigation. Instead of forming a complexe containing a Ge_2O_2 rhombus as observed in reactions with calix[4]- and calix[8]arene, reaction of the germanium amide with the calix[6]arene substrate furnished a Ge_2NO rhombus which contains a bridging amide group and has the two germanium atoms bound to three of the six oxygen atoms present in the macrocycle. One of the remaining three oxygen atoms has been incorporated into a $-OSiMe_3$ moiety while the other two have been incorporated into structurally unprecedented $-OSi(H)(NH_2)_2$ groups.
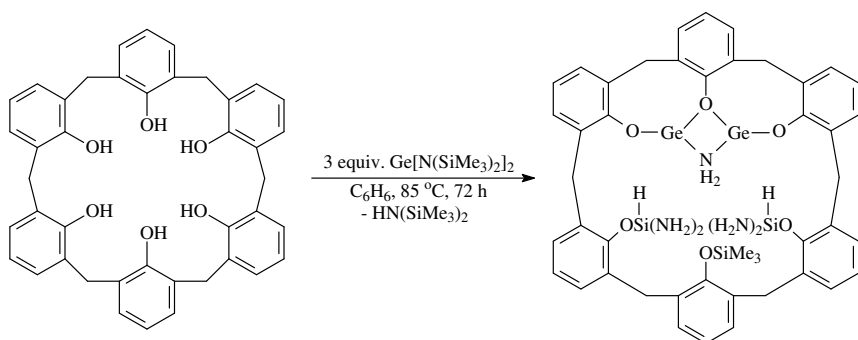
* Corresponding author. Tel.: +1 405 744 6543; fax: +1 405 744 6007.
E-mail address: weinert@chem.okstate.edu (C.S. Weinert).

2. Results and discussion

2.1. Synthesis and structure of compound *1*

Treatment of calix[6]arene with three equivalents of Ge[N-(SiMe$_3$)$_2$]$_2$ yielded complex **1** in 41% yield as shown in Eq. (1). The identity of **1** was ascertained by obtaining its X-ray crystal structure, and an ORTEP diagram of **1** is shown in Fig. 1 while selected bond distances and angles are collected in Table 1. Of the six phenolic oxygen atoms present in **1**, three are bound to the two Ge atoms in either a terminal or bridging fashion while the remaining three oxygen atoms have been incorporated into to either –OSiMe$_3$ or –OSi(H)(NH$_2$)$_2$ groups. We have previously observed the transformation of hydroxyl groups to trimethylsiloxy groups in the reactions of 3,3′-disubstituted binaphthols with metal(II) amides M[N(SiMe$_3$)$_2$]$_2$ (M = Be, Zn, Ge, Sn) [48]; however, the conversion of –OH groups to silylamides has not been previously described.

Table 1
Selected bond distances (Å) and angles (°) for compound 1 · 0.5 (C$_6$H$_6$)

Ge(1)–O(1)	1.860(3)	O(1)–Ge(1)–O(3)	91.4(1)
Ge(1)–O(3)	1.992(3)	O(1)–Ge(1)–N(5)	89.7(1)
Ge(1)–N(5)	2.011(4)	O(2)–Ge(2)–O(3)	91.6(1)
Ge(2)–O(2)	1.835(3)	O(2)–Ge(2)–N(5)	91.4(1)
Ge(2)–O(3)	1.993(3)	O(3)–Ge(1)–N(5)	77.1(1)
Ge(2)–N(5)	1.995(4)	O(3)–Ge(2)–N(5)	77.4(1)
Si(1)–O(6)	1.664(3)	Ge(1)–O(3)–Ge(2)	103.0(1)
Si(2)–O(5)[a]	1.696(5)	Ge(1)–N(5)–Ge(2)	102.3(2)
Si(2)–N(3)[a]	1.816(8)	O(5)–Si(2)–N(3)[a]	111.6(3)
Si(2)–N(4)[a]	1.715(8)	O(5)–Si(2)–N(4)[a]	108.2(3)
Si(3)–O(4)[a]	1.712(4)	N(3)–Si(2)–N(4)[a]	122.8(5)
Si(3)–N(1)[a]	1.700(8)	O(4)–Si(3)–N(1)[a]	112.4(4)
Si(3)–N(2)[a]	1.806(9)	O(4)–Si(3)–N(2)[a]	108.8(4)
		N(1)–Si(3)–N(2)[a]	119.6(4)

[a] The atoms Si(2) and Si(3) are disordered over two positions. The tabulated values are for the average of the two positions.

$$\text{(1)}$$

Compound **1** contains an unusual bridging –NH$_2$– group between the two germanium centers, and the structure of **1** can be compared to the two related calixarene complexes {calix[4]}Ge$_2$ (**2**) and {calix[8]}Ge$_4$ (**3**) [47] as well as the dimeric species [(C$_6$H$_3${C$_6$H$_3$Pr$^i_2$-2,6}$_2$-2,6)GeNH$_2$]$_2$ (**4**) which also contains bridging –NH$_2$– moieties [49]. Similar to the Ge$_2$O$_2$ rhombus in compound **2** the Ge$_2$NO rhombus adopts a planar geometry. The Ge(1)–O(3)–
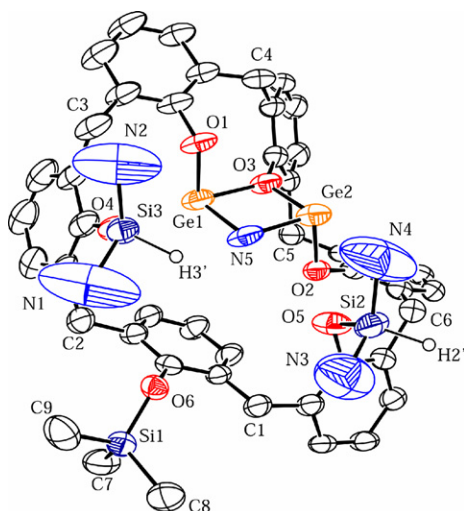
Fig. 1. ORTEP diagram of compound **1**. Thermal ellipsoids are drawn at 50% probability.

Ge(2) angle of 103.0(1)° is significantly more acute than the Ge–O$_{br}$–Ge angles in **2** and **3** which range from 106.1(1) to 107.89(6)° [47]. Furthermore, the Ge(1)–N(5)–Ge(2) angle measures 102.3(2)° which is more obtuse than the average Ge–N$_{br}$–Ge angles in **4** (100.0(1)°) [49]. The O(3)–Ge(1)–N(5) and O(3)–Ge(2)–N(5) angles average 77.3(1)° which are wider than the O$_{br}$–Ge–O$_{br}$ angles in **2** and **3** but more acute than the N$_{br}$–Ge–N$_{br}$ ligands angles in **4**. These structural differences can be attributed to the presence of two different types of bridging atoms in **1** and the internal angles in the Ge$_2$NO rhombus can be regarded as being intermediate between the Ge$_2$O$_2$ rhombi of **2** and **3** and the Ge$_2$N$_2$ rhombus of **4**.

The terminal Ge(1)–O(1) and Ge(2)–O(2) bond lengths in **1** are typical for germanium(II)–oxygen distances and are comparable to those in compounds **2** and **3** [47] as well as in other Ge(II) aryloxides [50–54]. The bridging Ge(1)–O(3) and Ge(2)–O(3) bond lengths in **1** are 1.992(3) and 1.993(3) Å (respectively) which fall between the average Ge–O$_{br}$ bond distances in **2** (1.988 Å) and **3** (2.000 Å) [47]. The bridging N atom is not symmetrically disposed between the two germanium atoms in **1** as indicated by the two Ge–N bond lengths measuring 2.011(4) and 1.995(4) Å. These distances are shorter than those found in the structure of **4** which has an average Ge–N distance of 2.013(3) Å [49]. The Ge–N distances in **1** are longer than those in germanium(II) compounds bearing ligands with terminal Ge–N bonds, including the well-known bulky bisamide Ge[N(SiMe$_3$)$_2$]$_2$ which has Ge–N bond lengths of 1.873(5) and 1.878(5) Å [55] and the bis(piperidinato) complex Ge[NC$_5$H$_6$Me$_4$-2,2,6,6]$_2$ which has distances of 1.87(1) and 1.90(1) Å [56]. However, the Ge–N distances in **1** are considerably shorter than those in divalent germanium compounds having dative N → Ge bonds including those in [Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)R] which measure 2.082(4) or 2.089(7) Å (R = Cl or CH(PPh$_2$)$_2$, respectively) [57]. These distances are also shorter than those in the divalent binhapthoxide complex

(*R*)-[Ge{O$_2$C$_{20}$H$_{10}$(SiMe$_2$Ph)$_2$-3, 3'}{NH$_3$}] (*d* Ge–N = 2.093(4) Å) which contains a coordinated NH$_3$ molecule [51] and also in [Ge{OCH(CF$_3$)$_2$}$_2${NH$_2$Ph}] (*d* Ge–N = 2.092(3) Å) which contains a coordinated aniline molecule [58].

The three remaining oxygen atoms in **1** are each attached to a silicon atom. One of these is incorporated into a –OSiMe$_3$ silyl ether group which arises from the transfer of the –SiMe$_3$ moiety from a –N(SiMe$_3$)$_2$ ligand in Ge[N(SiMe$_3$)$_2$]$_2$ to the phenolic oxygen atom [48]. The geometry of the silyl ether moiety is normal with an approximate tetrahedral environment at silicon and a typical Si–O bond distance of 1.664(3) Å. The Si–O–C$_{ipso}$ angle is 123.7(2)° and the –SiMe$_3$ group is directed outward from the central cavity of the molecule. The other two oxygen atoms have been incorporated into unusual –OSi(H)(NH$_2$)$_2$ groups. The silicon atoms in both groups are disordered over two positions (50% occupancy) which also results in each of the nitrogen atoms of the four attached –NH$_2$ groups also being disordered over two positions. The four nitrogen atoms were also disordered with very small positional differences over the two individual positions, and these were refined with a broad thermal parameter which resulted in the large ellipsoids present in the ORTEP plot of **1** (Fig. 1).

The Si–N bond distances (when taking into consideration the distortion of the silicon atoms) are 1.816(8), 1.715(8), 1.700(8), and 1.806(9) Å while, the N–Si–N angles are 122.8(5) and 119.6(4)° at Si(2) and Si(3), respectively. Diaminosilyl ether groups similar to those attached to O(4) and O(5) in **1** have not been described previously and thus a direct comparison to other structurally characterized species is not possible. However, a few small molecules containing –NH$_2$ groups bound to silicon and having –NH$_2$ and –OH groups attached to the same silicon atom have been reported [59,60]. The structure of Mes$_2$Si(NH$_2$)$_2$ has Si–N distances of 1.713(2) and 1.717(2) Å and a N–Si–N angle of 106.89(5)° [59] while that of Bu$^t_2$Si(OH)NH$_2$ exhibits a Si–N distance of 1.746(4) Å [60].

The average of the four Si–N distances is 1.759(8) Å in **1** which is longer than the corresponding bond distance in Bu$^t_2$Si(OH)NH$_2$ [60] and can be attributed to the attachment of the –Si(H)(NH$_2$)$_2$ moieties in **1** to a phenolic oxygen atom. The two N–Si–N angles in **1** average 121.2(5)° which is significantly more obtuse than the N–Si–N angle in Mes$_2$Si(NH$_2$)$_2$ [59]. This structural difference is expected since the latter compound contains two sterically encumbering mesityl groups, while compound **1** instead has a proton and an oxygen atom bound to silicon.

2.2. NMR spectra of compound **1**

Spectroscopic (^{1}H, ^{13}C and ^{29}Si NMR) data in benzene-d_6 are consistent with the solid-state structure of **1**. Similar to compounds **2** and **3**, the conformational flexibility of **1** is restricted versus the calix[6]arene starting material due to the presence of the Ge$_2$NO rhombus and the relatively large –OSiMe$_3$ and –OSi(H)(NH$_2$)$_2$ groups. This renders the individual protons of the six methylene units in **1** magnetically non-equivalent, resulting in twelve distinct doublets in the ^{1}H NMR spectrum in the chemical shift range δ 3.1–4.8 ppm which are divided into two sets of six features. The downfield grouping of resonances correspond to the methylene protons directed inward toward the Ge$_2$NO rhombus while the upfield features are attributed to those directed away.

In the downfield grouping of resonances, the doublet at δ 4.74 (*J* = 13.2 Hz) ppm is assigned to the proton attached to C(5) which has two close contacts with O(2) and O(3) measuring 2.498 and 2.549 Å (respectively). The two sets of closely grouped doublets at δ 4.66 (*J* = 14.7 Hz) and 4.64 (*J* = 12.6 Hz) ppm correspond to the protons bound to C(4) and C(3) (respectively) due to their relative proximity to O(3) and O(1), and the features at δ 4.53 (*J* = 16.2 Hz) and 4.51 (*J* = 11.7 Hz) ppm are assigned to the protons attached to C(6) and C(2) (respectively) due to their proximity to

the silylated oxygen atoms O(4) and O(5). The remaining doublet at δ 4.34 (*J* = 13.5 Hz) ppm arises from the proton attached to C(1) which only has long (>2.6 Å) contacts with the neighboring oxygen atoms.

Assignments for the upfield group of six resonances are based on a COSY NMR experiment. The doublet at δ 3.53 (*J* = 16.2 Hz) ppm corresponds to the second proton bound to C(6), while the four closely spaced features at δ 3.32 (*J* = 13.2 Hz), 3.30 (*J* = 14.7 Hz), 3.24 (*J* = 13.5 Hz), 3.23 (*J* = 12.6 Hz) ppm arise from the remaining protons attached to C(5), C(4), C(1) and C(3) (respectively). The resonance at δ 3.19 (*J* = 11.7 Hz) ppm results from the second proton bound to C(2). Due to the rigidity in the Ge$_2$NO rhombus, the protons in the bridging –NH$_2$ group also are magnetically non-equivalent, appearing as two broad but clearly resolved doublets at δ 1.66 (*J* = 9.6 Hz) and 1.04 (*J* = 9.6 Hz) ppm. The two Si–*H* protons are also non-equivalent and appear as two singlets in the ^{1}H NMR spectrum at δ 6.34 and 6.32 ppm. The –Si(N*H*$_2$)$_2$ protons appear as two upfield singlets at δ 0.27 and 0.24 ppm while the protons of the –OSiMe$_3$ moiety appear as a singlet at δ 0.42 ppm. The ^{13}C NMR spectrum of **1** also is consistent with its solid-state structure and exhibits six distinct lines for the each of non-equivalent *ipso*- and *para*-carbon atoms as well as twelve lines for both the *ortho*- and *meta*-carbons. The six methylene groups result in six features between δ 31–35 ppm and there is only one resonance in the –SiR$_3$ region of the spectrum at δ 1.6 ppm corresponding to the carbon atoms of the –OSi(C*H$_3$*)$_3$ group.

The ^{29}Si{^{1}H} NMR spectrum of **1** contains three singlets at δ 21.63, 21.17, and 21.07 ppm, where the downfield resonance arises from the silicon atom in the –OSiMe$_3$ group and the two upfield resonances correspond to the silicon atoms in the two –Si(H)(NH$_2$)$_2$ groups. The chemical shift for the silyl ether feature is similar to that of C$_6$H$_5$OSiMe$_3$ which appears at δ 19.43 ppm [61]. The proton-coupled ^{29}Si NMR spectrum of **1** was also recorded, and the singlet at δ 21.63 in the ^{1}H-decoupled spectrum splits into a multiplet with eight of the ten expected lines being clearly discernable. This arises from the two-bond coupling between the silicon atom and the protons of the methyl groups, with a coupling constant of 6.43 Hz. The two features for the –Si(H)(NH$_2$)$_2$ groups are more complex due to the presence of both one-bond Si–H and three bond Si–NH$_2$ coupling. Each of these features are expected to appear as a doublet of quintets but their proximity resulted in overlap with one another such that the expected one-bond Si–H coupling could not be clearly observed.

2.3. Analysis of compound **1** using mass spectrometry

The mass spectrum of compound **1** acquired using electrospray mass spectrometry (positive ion mode) exhibited a clear fragmentation pattern having nine well-defined peaks which are listed in Table 2. The proposed fragmentation pattern is illustrated in

Table 2
Electrospray mass spectrometry data for compound **1**

Ion	*m/z*	Formula	Relative intensity (%)
1a	988.5	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O$_3$Ge$_2$(NH$_2$){OSi(H)(NH$_2$)$_2$}$_2$OSiMe$_3$]H$^+$	n/a
1b	927.5	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O$_3$Ge$_2$(NH$_2$)OSi(H)(NH$_2$)$_2$OSiMe$_3$O]H$^+$	2
1c	898.5	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O$_3$Ge$_2$(NH$_2$)OSiH$_3$OSiMe$_3$OH]H$^+$	29
1d	826.4	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O$_3$Ge$_2$(NH$_2$)OSiH$_3$(OH)$_2$]H$^+$	72
1e	798.4	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O$_2$Ge$_2$(NH$_3$)(OH)$_4$]H$^+$	100
1f	754.4	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O$_2$Ge(NH$_2$)OSiH$_3$(OH)$_3$]H$^+$	8
1g	726.4	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$OGe(NH$_3$)(OH)$_5$]H$^+$	12
1h	682.4	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$O(NH$_2$)OSiH$_3$(OH)$_4$]H$^+$	16
1i	654.4	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$(NH$_3$)(OH)$_6$]H$^+$	28
1j	637.3	[(C$_6$H$_3$)$_6$(CH$_2$)$_6$(OH)$_6$]H$^+$	4

Scheme 1. Although the parent molecular ion at $m/z = 988.5$ was not observed a feature at $m/z = 927.5$ corresponding to the loss of one $-SiH(NH_2)_2$ fragment and monoprotonation of the remaining molecule was present in the spectrum. Subsequent fragmentations involve the loss of the $-SiMe_3$ group, the two germanium atoms, the oxygen atoms, and the bridging $-NH_2-$ group. The $-O$ and $-NH_2$ groups to which these fragments were bound appear to be protonated during the course of this process to yield $-OH$ or NH_3 groups (respectively). Ultimately, all of the substituents in compound **1** undergo fragmentation to produce the parent calix[6]arene in protonated form.

2.4. Pathway for the formation of compound **1**

The pathway for the formation of **1** is likely complex, but two key aspects for the generation of this species are evident. First, compound **1** contains twelve protons distributed among the single bridging $-NH_2-$ and the two $-Si(H)(NH_2)_2$ groups. Since calix[6]arene is the only proton source present in the reaction, all of these must originate from this starting material. Furthermore, 2 equiv. of calix[6]arene must be consumed for every one equiv. of **1** generated in the reaction since calix[6]arene contains only six phenolic protons. This dictates a maximum theoretical yield of 50% for **1** with the concomitant formation of one or more other products, and this postulate is further supported by the complete consumption of calix[6]arene in the reaction. Compound **1** has been isolated in a maximum of 41% during the course of these studies.

Second, the $-N(SiMe_3)_2$ ligands of $Ge[N(SiMe_3)_2]_2$ are the source of both the bridging $-NH_2-$ group and the $-Si(H)(NH_2)_2$ groups in **1**. We have recently demonstrated that $Ge[N(SiMe_3)_2]_2$ reacts with binaphthols via formation of an intermediate bearing a $-OGe[N-(SiMe_3)_2]$ moiety which subsequently transfers a $-SiMe_3$ fragment to the oxygen atom of one $-OH$ substituent of the binaphthol [48]. This results in generation of a $-OGe[NH(SiMe_3)]$ group and this process can occur a second time to yield a $-OGe[NH_2]$ moiety which could then serve as the source of the bridging amide in **1**. The $-Si(H)(NH_2)_2$ groups, however, must ultimately result from the demethylation of a $-SiMe_3$ group during the course of the reaction. The transfer of a methyl group to gallium in the reaction of $GaCl_3$ with $Li[N(SiMe_3)_2]$ has been reported [62], and similar methyl group migrations have been found upon treatment of $GaCl_3$ with $N(SiMe_3)_3$ [63] or $SiMe_4$ [64]. The germanium atoms present in **1** clearly are not methylated, but the generation of Me_4Ge or CH_4 might be expected to occur during the course of this reaction.
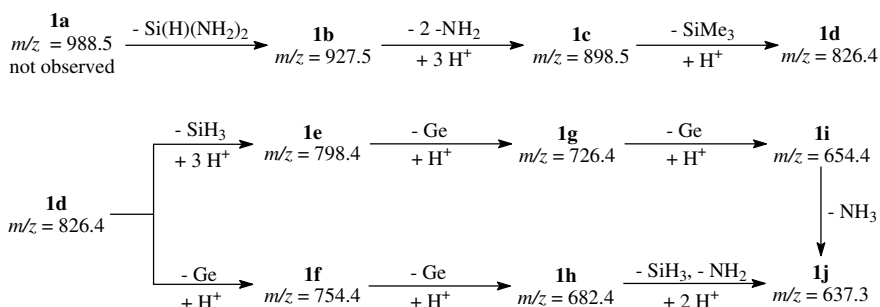
In order to probe the pathway for the formation of **1**, the progress of the reaction of one, two and three equivalents of $Ge[N-(SiMe_3)_2]_2$ with calix[6]arene was monitored over time using ^1H NMR spectroscopy in benzene-d_6 in three separate experiments. The methylene (δ 5.2–3.0 ppm) and alkylsilyl (δ 0.4–0.0 ppm) regions of these spectra contained diagnostic features which were compared over a reaction period of 120 h in each case. Upon

treatment of calix[6]arene with 3 equiv. of $Ge[N(SiMe_3)_2]_2$, a resonance for the formation of free $HN(SiMe_3)_2$ at δ 0.09 ppm was observed after 10 min at room temperature and $Ge[N(SiMe_3)_2]_2$ and a trace amount of calix[6]arene were still present in solution. After heating the sample at 85 °C for 1 h, the aromatic and methylene regions of the spectrum were complex but the appearance of peaks at δ 0.42, 0.29 and 0.25 ppm indicated that compound **1** was already present in solution. The absence of a resonance at δ 10.50 ppm attributable to the six phenolic protons also indicated all of the calix[6]arene had been consumed at this time.
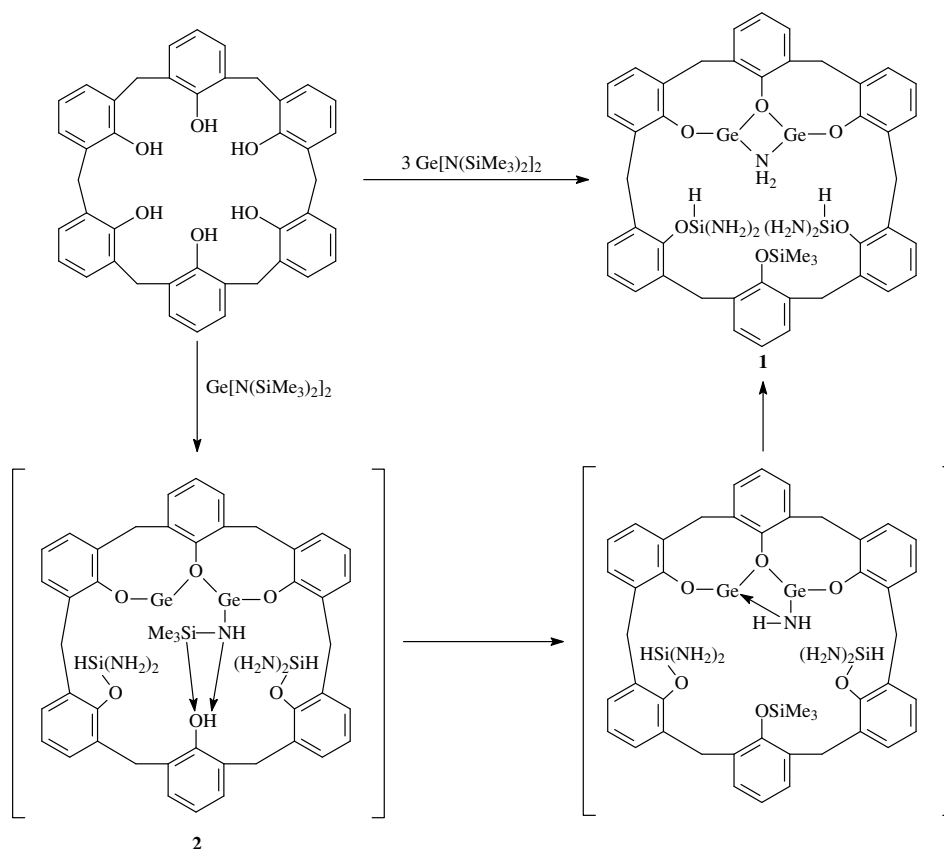
After heating the sample at 85 °C for a total of 6 h, the overall appearance of the spectrum had simplified and suggested that compound **1** was present in solution along with a second intermediate species. The methylene region of the spectrum contained 24 doublets divided into an upfield and downfield grouping of 12 features. Some overlap of these resonances was observed but four distinct peaks at δ 5.08 ($J = 15.0$ Hz), 4.43 ($J = 13.5$ Hz), 3.15 ($J = 12.3$ Hz), and 3.13 ($J = 12.9$ Hz) ppm were visible, which clearly are not attributable to **1** but arise from a second compound present in solution. Similarly, two additional peaks at δ 0.36 and 0.30 ppm in the alkylsilyl region were observed at this time as were two additional downfield singlets at δ 6.32 and 6.30 ppm arising from Si–H protons.

The presence of the four features at δ 6.32, 6.30, 0.36 and 0.30 ppm along with the structural rigidity apparent in the intermediate species suggest that all or part of the Ge_2NO rhombus and the two $-Si(H)(NH_2)_2$ groups are generated prior to silylation of the remaining hydroxyl group to generate the silyl ether moiety. Further evidence for this results from the presence of a broad singlet at δ 5.92 ppm which suggests the presence of a single hydroxyl group in the intermediate species. Similar ^1H NMR $-OH$ features were observed for the main group calixarenes {(OH)(calix[4]arene)P} (δ 5.4 ppm) [20], {(OH)(p-tert-butylcalix[4]arene)Si} (δ 4.59 ppm) [21], {(OH)(calix[4]arene)As} (δ 4.90 ppm) [19], and {(OH)(p-tert-butylcalix[4]arene)As} (δ 4.74 ppm) [19], all of which have a single unbound $-OH$ group and three oxygen atoms bound to the main group element. The resonance at δ 5.92 ppm had significantly reduced in intensity after heating the sample for a total of 48 h, as had the two features at δ 6.32 and 6.30 ppm and the upfield peaks at δ 0.36 and 0.30 ppm. We therefore postulate that the structure of the intermediate detected by ^1H NMR spectroscopy is that of **2** illustrated in Scheme 2, which undergoes an exchange of the $-SiMe_3$ group attached to the nitrogen with the remaining hydroxyl proton followed by closure of the Ge_2NO rhombus.

After heating the sample for an additional 12 h resonances corresponding only to **1**, free $HN(SiMe_3)_2$, and unreacted $Ge[N-(SiMe_3)_2]_2$ remained. The appearance of the spectrum remained unchanged with up to 120 h of heating at 85 °C. Nearly identical results were obtained when calix[6]arene was treated with 2 equiv. of $Ge[N(SiMe_3)_2]_2$ under the same reaction conditions except that $Ge[N(SiMe_3)_2]_2$ was absent after the reaction had gone

1a
$m/z = 988.5$
not observed
$\xrightarrow{\begin{array}{c} - Si(H)(NH_2)_2 \end{array}}$
1b
$m/z = 927.5$
$\xrightarrow{\begin{array}{c} - 2\ -NH_2 \\ + 3\ H^+ \end{array}}$
1c
$m/z = 898.5$
$\xrightarrow{\begin{array}{c} - SiMe_3 \\ + H^+ \end{array}}$
1d
$m/z = 826.4$

1d
$m/z = 826.4$

$\xrightarrow{\begin{array}{c} - SiH_3 \\ + 3\ H^+ \end{array}}$
1e
$m/z = 798.4$
$\xrightarrow{\begin{array}{c} - Ge \\ + H^+ \end{array}}$
1g
$m/z = 726.4$
$\xrightarrow{\begin{array}{c} - Ge \\ + H^+ \end{array}}$
1i
$m/z = 654.4$
$\xrightarrow{- NH_3}$

$\xrightarrow{\begin{array}{c} - Ge \\ + H^+ \end{array}}$
1f
$m/z = 754.4$
$\xrightarrow{\begin{array}{c} - Ge \\ + H^+ \end{array}}$
1h
$m/z = 682.4$
$\xrightarrow{\begin{array}{c} - SiH_3,\ - NH_2 \\ + 2\ H^+ \end{array}}$
1j
$m/z = 637.3$

Scheme 1.

Scheme 2.

to completion. The outcome of this process is consistent with the overall reaction stoichiometry since two germanium atoms are present in the framework of **1**. The ^{1}H NMR spectra of the reaction of calix[6]arene with 1 equiv. of Ge[N(SiMe$_3$)$_2$]$_2$ in benzene-d_6 indicated the formation of a complex mixture of species which included **1** and the intermediate **2** which remained present in solution even after heating the reaction mixture for 120 h.

In the course of these studies, no conclusive evidence for the formation of Me$_4$Ge or CH$_4$ was found which exhibit similar ^{1}H NMR resonances at δ 0.14 and 0.15 ppm in benzene-d_6. However, identification of calix[6]arene as the source of all of the protons in the two –Si(H)(NH$_2$)$_2$ groups and in the bridging –NH$_2$– group was confirmed by the reaction of three equiv. of Ge[N(SiMe$_3$)$_2$]$_2$ with calix[6]arene-d_6 which contained six deuterated hydroxyl groups. The ^{1}H NMR spectrum of the resulting product contained only a single line at δ 0.42 ppm arising from the –OSiMe$_3$ moiety as well as a feature corresponding to unreacted germanium amide.

3. Conclusions

In conclusion, the reactivity of calix[6]arene with Ge[N-(SiMe$_3$)$_2$]$_2$ differs considerably from that found in reactions involving calix[4]arene and calix[8]arene. Instead of forming complexes containing Ge$_2$O$_2$ rhombi, the germanium calix[6]arene complex **1** contains a central Ge$_2$NO rhombus incorporating three of the six oxygen atoms of the macrocycle. The remaining three oxygen atoms have been converted to two –OSi(H)(NH$_2$)$_2$ moieties and one –OSiMe$_3$ group. The pathway for the formation of **1** is likely complex, but involves the consumption of two equivalents of calix[6]arene for each equivalent of **1** produced in the reaction.

4. Experimental

All manipulations were carried out using standard Schlenk, syringe, and glovebox techniques [65]. Calix[6]arene was purchased from Alfa Aesar and Ge[N(SiMe$_3$)$_2$]$_2$ was synthesized according to the published procedure [66–68]. Solvents were dried using a Glass Contour Solvent Purification System. One and two-dimensional ^{1}H NMR spectra were recorded at 400 MHz on a Varian Unity INOVA 400 spectrometer and referenced to residual protio solvent. For the ^{1}H NMR assignments in **1**, the numbering scheme of the carbon atoms corresponds to the crystal structure of **1**, *i.e.* –C(5)H_2– refers to a proton bound to C(5). ^{13}C NMR spectra were recorded at a frequency of 100.6 MHz on a Varian Unity INOVA 400 and referenced to the solvent while ^{29}Si NMR were acquired using a Varian Unity INOVA 600 operating at 119.2 MHz and were referenced to external SiMe$_4$. Mass spectra were acquired using a Bruker Agilent 1100 LC/MSD System in acetonitrile solvent. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN).

4.1. Synthesis of compound **1**

To a solution of calix[6]arene (0.458 g, 0.719 mmol) in benzene (10 mL) was added a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.852 g, 2.17 mmol) in benzene (4 mL). The mixture was sealed in a Schlenk tube and heated at 85 °C for 72 h. The solvent was removed *in vacuo* to yield a white solid which was recrystallized from hot benzene (5 mL) to yield **1** as colorless crystals which were washed with hexane (3 × 5 mL) and dried *in vacuo*. Yield: 0.292 g (41%). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.29–6.75 (m, 18H, aromatics), 6.34 (s, 1H, –Si(*H*)(NH$_2$)$_2$), 6.32 (s, 1H, –Si(*H*)(NH$_2$)$_2$), 4.74 (d, *J* = 13.2 Hz, 1H –C(5)*H*$_2$–), 4.66 (d, *J* = 14.7 Hz, 1H, –C(4)*H*$_2$–), 4.64 (d, *J* = 12.6 Hz, 1H, –C(3)*H*$_2$–), 4.53 (d, *J* = 16.2 Hz, 1H, –C(6)*H*$_2$–), 4.51

(d, J = 11.7 Hz, 1H, –C(2)H_2–), 4.34 (d, J = 13.5 Hz, 1H, –C(1)H_2–), 3.53 (d, J = 16.2 Hz, 1H, –C(6)H_2–), 3.32 (d, J = 13.2 Hz, 1H, – C(5)H_2–), 3.30 (d, J = 14.7 Hz, 1H, –C(4)H_2–), 3.24 (d, J = 13.5 Hz, 1H, –C(1)H_2–), 3.23 (d, J = 12.6 Hz, 1H, –C(3)H_2–), 3.19 (d, J = 11.7 Hz, 1H, -C(2)H_2–), 1.66 (br d, J = 9.6 Hz, 1H, –NH_2–), 1.04 (br d, J = 9.6 Hz, 1H, –NH_2–), 0.42 (s, 9H, –OSi(CH_3)$_3$), 0.27 (s, 4H, –Si(H)(NH_2)$_2$), 0.24 (s, 4H, –Si(H)(NH_2)$_2$) ppm. ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 156.1, 154.4, 152.0, 151.6, 151.1, 150.8 (*ipso*-C), 136.8, 136.6, 136.4, 136.1, 135.9, 135.2, 134.5, 133.3, 132.8, 132.6, 132.1, 132.0 (*meta*-C), 131.0, 130.8, 130.7, 130.5, 130.4, 130.3, 129.8, 129.7, 129.4, 129.3, 129.1, 128.8 (*ortho*-C), 123.6, 122.7, 122.3, 122.2, 120.9, 120.8 (*para*-C), 34.2, 34.0, 33.9, 33.4, 33.1, 31.1 (–CH_2–), 1.6 (-OSi(CH_3)$_3$) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 21.63, 21.17, and 21.07 ppm. IR (Nujol): 3348, 3266, 3255, 2720, 2664, 2288, 1916, 1859, 1807, 1713, 1661, 1589 cm^{-1}. *Anal.* Calc. for C$_{45}$H$_{51}$Ge$_2$N$_5$O$_6$Si$_3$: C, 54.74; H, 5.21. Found: 54.15; H, 5.41%.

4.2. NMR scale reaction of calix[6]arene with 3 equiv. Ge[N(SiMe$_3$)$_2$]$_2$

A solution of calix[6]arene (0.050 g, 0.078 mmol) in benzene-d_6 (0.25 mL) was treated with a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.093 g, 0.24 mmol) in benzene-d_6 (0.25 mL) in a screw-cap NMR tube.

4.3. NMR scale reaction of calix[6]arene with 2 equiv. Ge[N(SiMe$_3$)$_2$]$_2$

A solution of calix[6]arene (0.050 g, 0.078 mmol) in benzene-d_6 (0.25 mL) was treated with a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.062 g, 0.16 mmol) in benzene-d_6 (0.25 mL) in a screw-cap NMR tube.

4.4. NMR scale reaction of calix[6]arene with 1 equiv. Ge[N(SiMe$_3$)$_2$]$_2$

A solution of calix[6]arene (0.050 g, 0.078 mmol) in benzene-d_6 (0.25 mL) was treated with a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.031 g, 0.079 mmol) in benzene-d_6 (0.25 mL) in a screw-cap NMR tube.

4.5. Synthesis of calix[6]arene-d_6

To a solution of calix[6]arene (0.300 g, 0.471 mmol) in diethyl ether (30 mL) was added a solution of 2.5 M Bu^{n}Li in hexanes (1.51 mL, 3.78 mmol) at −78 °C. The reaction mixture was allowed to come to room temperature and was stirred for 4 h. The reaction mixture was quenched with D$_2$O (5 mL) at −78 °C via cannula from a sure-seal bottle. The organic layer was separated and dried over anhydrous MgSO$_4$ and the solvent was removed *in vacuo* to yield calix[6]arene-d_6 (0.221 g, 72%). The ^{1}H NMR spectrum of the product recorded in benzene-d_6 did not exhibit an –OH resonance.

4.6. NMR scale reaction of calix[6]arene-d_6 with 3 equiv. Ge[N(SiMe$_3$)$_2$]$_2$

To a solution of calix[6]arene-d_6 (0.057 g, 0.088 mmol) in benzene-d_6 (0.35 mL) was added a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.107 g, 0.272 mmol) in benzene-d_6 (0.30 mL). The reaction mixture was heated in an oil bath for 48 h and the ^{1}H NMR spectrum was recorded.

4.7. X-ray crystal structure of 1 · 0.5(C$_6$H$_6$)

Diffraction intensity data were collected with a Siemens P4/CCD diffractometer. Absorption corrections were applied for all data by SADABS. The structures were solved using direct methods, completed by Fourier syntheses, and refined by full-matrix least squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. Contributions from the benzene solvent molecule were removed using SQUEEZE. All software and sources of scattering factors are contained in the SHEXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI). ORTEP diagrams were drawn using the ORTEP3 program (L.J. Farrugia, Glasgow).

Crystallographic data for **1 · 0.5(C$_6$H$_6$)**: Crystal size: 0 × 0.22 × 0.17 mm. Crystal color and habit: colorless block. Empirical formula: C$_{48}$H$_{54}$Ge$_2$N$_5$O$_6$Si$_3$. Formula weight: 1026.42. Wavlength: 0.71073 Å. Temperature: 100(2) K. Crystal system: triclinic. Space group: $P\bar{1}$. Unit cell dimensions: a = 13.199(2) Å, b = 14.774(2) Å; c = 16.569(4) Å; α = 105.373(4)°; β = 102.641(4)°; γ = 115.225(3)°. Volume = 2606.5(9) Å^3. Z = 2. D_{calc} = 1.309 g/cm^3. Absorption coefficient = 1.274 mm^{-1}. $F(000)$ = 1064. θ-Range for data collection = 1.67–25.00°. Index ranges: $-14 \leqslant h \leqslant -15$; $-15 \leqslant k \leqslant 17$; $-19 \leqslant l \leqslant 19$. Reflections collected = 15 228. Independent reflections = 9124 (R_{int} = 0.0295). Completeness to θ = 99.2% (θ = 25.00°). Absorption correction = multi-scan. Refinement method = full-matrix least-squares on F^2. Data/restraints/parameters = 9124/0/584. Goodness-of-fit on F^2 = 1.014. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0581; wR_2 = 0.1414. R indices (all data): R_1 = 0.0884; wR_2 = 0.1580. Largest difference in peak and hole = 0.512 and −0.547 e Å^{-3}.

Acknowledgement

Appendix A. Supplementary data

CCDC 669869 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.02.027.

References

[1] F. Hof, S.L. Craig, C. Nuckolls, J. Rebek Jr., Angew. Chem., Int. Ed. Engl. 41 (2002) 1488.
[2] Z. Asfari, V. Böhmer, J. Harrowfield, J. Vincens, Calixarenes 2001, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.
[3] A.F.D. de Namor, R.M. Cleverley, M.L. Zapata-Ormachea, Chem. Rev. 98 (1998) 2495.
[4] J. Vincens, V. Böhmer, Calixarenes, A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991.
[5] A. Pochini, R. Ungaro, in: F. Vögtle (Ed.), Comprehensive Supramolecular Chemistry, Pergamon Press, New York, 1996.
[6] V. Böhmer, Angew. Chem., Int. Ed. Engl. 34 (1995) 713.
[7] C.D. Gutsche, Calixarenes Revisited, Royal Society of Chemistry, Cambridge, 1998.
[8] D.M. Redkevich, Angew. Chem., Int. Ed. Engl. 43 (2004) 558.
[9] M. Lattman, in: R.A. Kemp (Ed.), Modern Aspects of Main Group Chemistry, ACS Symposium Series, 2006, pp. 237–251.
[10] M. Fan, H. Zhang, M. Lattman, Inorg. Chem. 45 (2006) 6490.
[11] P. Sood, M. Koutha, M. Fan, Y. Klichko, H. Zhang, M. Lattman, Inorg. Chem. 43 (2004) 2975.
[12] M. Fan, H. Zhang, M. Lattman, Phosphorus, Sulfur, Silicon Relat. Elem. 177 (2002) 1549.
[13] M. Fan, I.V. Shevchenko, R.H. Voorhies, S.F. Eckert, H. Zhang, M. Lattman, Inorg. Chem. 39 (2000) 4704.
[14] M. Fan, H. Zhang, M. Lattman, Phosphorus, Sulfur, Silicon Relat. Elem. 144–146 (1999) 257.
[15] M. Fan, H. Zhang, M. Lattman, Chem. Commun. (1998) 99.
[16] M. Fan, H. Zhang, M. Lattman, Organometallics 15 (1996) 5216.
[17] P. Sood, H. Zhang, M. Lattman, Organometallics 21 (2002) 4442.
[18] I.V. Shevchenko, H. Zhang, M. Lattman, Inorg. Chem. 34 (1995) 5405.
[19] S. Shang, D.V. Khasnis, H. Zhang, A.C. Small, M. Fan, M. Lattman, Inorg. Chem. 34 (1995) 3610.
[20] D.V. Khasnis, J.M. Burton, J.D. McNeil, C.J. Santini, H. Zhang, M. Lattman, Inorg. Chem. 33 (1994) 2657.
[21] S. Shang, D.V. Khasnis, J.M. Burton, C.J. Santini, M. Fan, A.C. Small, M. Lattman, Organometallics 13 (1994) 5157.

[22] D.V. Khasnis, J.M. Burton, J.D. McNeil, H. Zhang, M. Lattman, Phosphorus, Sulfur, Silicon Relat. Elem. 75 (1993) 253.
[23] D.V. Khasnis, J.M. Burton, M. Lattman, H. Zhang, J. Chem. Soc., Chem. Commun. (1991) 562.
[24] D.V. Khasnis, M. Lattman, C.D. Gutsche, J. Am. Chem. Soc. 112 (1990) 9422.
[25] J.O. Magrans, A.M. Rincón, F. Cuevas, J. López-Prados, P.M. Nieto, M. Pons, P. Prados, J. de Mendoza, J. Org. Chem. 63 (1998) 1079.
[26] S. Kanamathareddy, C.D. Gutsche, J. Org. Chem. 57 (1992) 3160.
[27] S. Shinkai, Tetrahedron 49 (1993) 8933.
[28] C.D. Gutsche, L.J. Bauer, J. Am. Chem. Soc. 107 (1985) 6052.
[29] J.C. Iglesias-Sánchez, B. Souto, C.J. Pastor, J. de Mendoza, P. Prados, J. Org. Chem. 70 (2005) 10400.
[30] G. Izzet, M.-N. Rager, O. Reinaud, Dalton Trans. (2007) 771.
[31] U. Darbost, O. Sénèque, Y. Li, G. Bertho, J. Marrot, M.-N. Rager, O. Reinaud, I. Jabin, Chem. Eur. J. 13 (2007) 2078.
[32] B. Boulet, C. Bouvier-Capely, C. Cossonnet, G. Cote, Solvent Extr. Ion Exc. 24 (2006) 319.
[33] J.P.W. Eggert, J.M. Harrowfield, U. Lüning, B.W. Skelton, A.H. White, Polyhedron 25 (2006) 910.
[34] Y. Obora, Y.K. Liu, S. Kubouchi, M. Tokunaga, Y. Tsuji, Eur. J. Inorg. Chem. (2006) 222.
[35] G. Izzet, H. Akdas, N. Hucher, M. Giorgi, T. Prange, O. Reinaud, Inorg. Chem. 45 (2006) 1069.
[36] O. Sénèque, M.-N. Rager, M. Giorgi, T. Prange, A. Tomas, O. Reinaud, J. Am. Chem. Soc. 127 (2005) 14833.
[37] Y. Obora, Y.K. Liu, L.H. Jiang, K. Takenaka, M. Tokunaga, Y. Tsuji, Organometallics 24 (2005) 4.
[38] K. Belhamel, T.K.D. Nguyen, M. Benamor, R. Ludwig, Eur. J. Inorg. Chem. (2003) 4110.
[39] R. Souane, V. Hubscher, Z. Asfari, F. Arnaud, J. Vicens, Tetrahedron Lett. 44 (2003) 9061.
[40] O. Sénèque, Y. Rondelez, L. Le Clainche, C. Inisan, M.-N. Rager, M. Giorgi, O. Reinaud, Eur. J. Inorg. Chem. (2001) 2597.
[41] F. Loffler, U. Luning, G. Gohar, New J. Chem. 24 (2000) 935.
[42] Y. Rondelez, O. Sénèque, M.-N. Rager, A.F. Duprat, O. Reinaud, Chem. Eur. J. 6 (2000) 4218.
[43] O. Sénèque, M.-N. Rager, M. Giorgi, O. Reinaud, J. Am. Chem. Soc. 122 (2000) 6183.
[44] A.J. Petrella, N.K. Roberts, D.C. Craig, C.L. Raston, R.N. Lamb, Chem. Commun. (2003) 2288.
[45] A.J. Petrella, D.C. Craig, R.N. Lamb, C.L. Raston, N.K. Roberts, Dalton Trans. (2004) 327.
[46] A.J. Petrella, N.K. Roberts, D.C. Craig, C.L. Raston, R.N. Lamb, Chem. Commun. (2003) 1014.
[47] A.E. Wetherby Jr., L.R. Goeller, A.G. DiPasquale, A.L. Rheingold, C.S. Weinert, Inorg. Chem. 46 (2007) 7579.
[48] A.E. Wetherby Jr., L.R. Goeller, A.G. DiPasquale, A.L. Rheingold, C.S. Weinert, Inorg. Chem. 47 (2008) 2162.
[49] C. Stanciu, S.S. Hino, M. Stender, A.F. Richards, M.M. Olmstead, P.P. Power, Inorg. Chem. 44 (2005) 2774.
[50] C.S. Weinert, A.E. Fenwick, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2003) 1795.
[51] C.S. Weinert, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2002) 2948.
[52] T. Hascall, A.L. Rheingold, I. Guzei, G. Parkin, Chem. Commun. (1998) 101.
[53] B.G. McBurnett, A.H. Cowley, Chem. Commun. (1999) 17.
[54] B. Çetinkaya, I. Gümrükçü, M.F. Lappert, J.L. Atwood, R.D. Rogers, M.J. Zaworotko, J. Am. Chem. Soc. 102 (1980) 2088.
[55] R.W. Chorley, P.B. Hitchcock, M.F. Lappert, W.P. Leung, P.P. Power, M.M. Olmstead, Inorg. Chim. Acta 198–200 (1992) 203.
[56] M.F. Lappert, M.J. Slade, J.L. Atwood, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1980) 621.
[57] S. Benet, C.J. Cardin, D.J. Cardin, S.P. Constantine, P. Heath, H. Rashid, S. Teixeira, J.H. Thorpe, A.K. Todd, Organometallics 18 (1999) 389.
[58] S. Suh, D.M. Hoffman, Inorg. Chem. 35 (1996) 6164.
[59] K. Ruhland-Senge, R.A. Bartlett, M.M. Olmstead, P.P. Power, Angew. Chem., Int. Ed. Engl. 32 (1993) 425.
[60] C. Reiche, S. Kliem, U. Klingebiel, M. Noltemeyer, C. Voit, R. Herbst-Immer, S. Schmatz, J. Organomet. Chem. 667 (2003) 24.
[61] J. Schraml, M. Kvicalova, V. Blechta, J. Cermak, Mag. Res. Chem. 35 (1997) 659.
[62] B. Luo, V.G. Young Jr., W.L. Gladfelter, J. Organomet. Chem. 649 (2002) 268.
[63] C.J. Carmalt, J.D. Mileham, A.J.P. White, D.J. Williams, J.W. Steed, Inorg. Chem. 40 (2001) 6035.
[64] H. Schmidbaur, W. Findeiss, Angew. Chem., Int. Ed. Engl. 3 (1964) 696.
[65] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air Sensitive Comounds, John Wiley and Sons, New York, 1986.
[66] D.H. Harris, M.F. Lappert, J. Chem. Soc., Chem. Commun. (1974) 895.
[67] M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Rivière, M. Rivière-Baudet, J. Chem. Soc., Dalton Trans. (1977) 2004.
[68] Q. Zhu, K.L. Ford, E.J. Roskamp, Heteroatom Chem. 3 (1992) 647.