

# Synthesis and structures of the group 1 metal/germanium cage complexes $[M(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$ ( $M = \text{Li, Na, K, Rb, Cs}$ ); periodic trends and alkali metal dependent arene bonding

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Received 11th February 2003, Accepted 10th March 2003

First published as an Advance Article on the web 25th March 2003

Reaction of three equivalents of the alkali salts of 2,6-diphenylphenoxide,  $[\text{MOC}_6\text{H}_3\text{Ph}_2\text{-2,6}]$  ( $M = \text{Li, Na, K, Rb, Cs}$ ) with  $\text{GeI}_2$  provides the corresponding cage complexes  $[M(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$ , all of which have been structurally characterized. These species contain a germanium(II) metal and an alkali metal connected by the oxygen atoms of the bridging aryloxy ligands. The two metal atoms are at the apices of a five-atom trigonal bipyramidal metal framework. The alkali cations are also bound to the carbon atoms of three of the 2,6-diphenyl substituents of the aryloxy ligands. The number of bonds to these arene rings is strongly dependent on the identity of the alkali metal. This results in high formal coordination numbers for the group 1 metals K, Rb and Cs. The germanium and alkali metal form similar bonds to all three aryloxy oxygens except in the case of the caesium compound. In this case some localization of bonding occurs with structural parameters more consistent with a caesium aryloxy adduct of a germanium(II) bis(aryloxy).

## Introduction

Cage and cluster compounds of the main group elements have recently attracted a great deal of interest.<sup>1,2</sup> These materials adopt a wide variety of structural motifs, and often contain bridging ligands, which serve to bring two or more metal or metalloidal atoms into close proximity with one another. These species can be comprised of one or more main-group elements, and the bridging ligands typically coordinate to the metal centers through chalcogenide or pnictide elements. Additionally, these materials can exist as discrete molecular frameworks, or exhibit extended polymeric structures.

The use of alkoxide and siloxide ligands in group 14 complexes has been the focus of many studies,<sup>3</sup> as the complexes prepared can potentially serve as molecular precursors for the synthesis of ceramics and/or superconducting materials.<sup>4-6</sup> A number of lead alkoxide and siloxide species have been reported, including  $[\text{Pb}(\text{O}^i\text{Pr})_2]_n$ ,<sup>7</sup>  $[\text{Pb}(\text{O}^t\text{Bu})_2]_3$ ,<sup>7,8</sup> and  $[\text{Pb}_7(\mu_3\text{-O})(\mu_4\text{-O})(\mu_3\text{-OSiMe}_3)_{10}]$ .<sup>9</sup> The isopropoxide derivative forms an infinite chain structure held together *via* bridging isopropoxide ligands, while the *tert*-butoxide derivative forms a trimeric structure containing lead(II) atoms in both six- and three-coordinate environments.<sup>7</sup> This species has been used for the preparation of  $[\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8]$ , which could potentially serve as a precursor for the formation of mixed group 4/14 metal oxide materials.<sup>8</sup> Several tin-containing species containing bridging alkoxide or siloxide ligands have also been prepared,<sup>10-23</sup> and germanium analogs, although less common, are also known.<sup>19,20,22</sup>

Compounds of the type  $[M(\mu\text{-OR})_3M']$ , where  $\mu\text{-OR}$  is a bridging alkoxy or siloxy group,  $M'$  is a group 14 metal, and  $M$  is a group 14 or other type of metal, share a common structural motif. These species typically adopt a trigonal bipyramidal framework comprised of five atoms—the two metal atoms and the three oxygen atoms of the bridging ligands. When  $M$  is a group 1 or group 2 metal, these species are considered to be “ate” complexes of the  $M(\text{OR})_3$  fragment, and the group 1 or 2 metal is typically encapsulated by the oxygen atoms of the bridging ligands. Examples include the group 14/group 2 complex  $[\text{Ge}(\mu\text{-O}^t\text{Bu})_3\text{Mg}(\mu\text{-O}^t\text{Bu})_3\text{Ge}]$ ,<sup>24</sup> the group 14/group 1 complex  $[\text{NaPb}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3]$  and  $[\text{KSn}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3]$ ,<sup>25</sup> and the group 13/group 14 complex

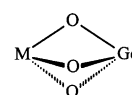
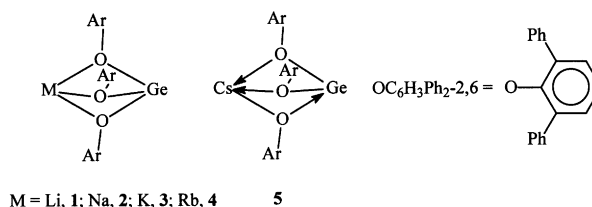
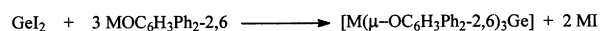
$[\text{Tl}(\text{O}^t\text{Bu})_3\text{Sn}]$ ,<sup>26</sup> which has been shown to form complexes with transition metal pentacarbonyl fragments.<sup>27</sup>

We have reported the synthesis and structure of the complex  $[\text{Li}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Sn}]$  ( $\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6} = 2,6\text{-diphenylphenoxide}$ ), which is a rare group 14 complex containing bridging aryloxy ligands and structurally resembles  $[\text{Ti}(\mu\text{-O}^t\text{Bu})_3\text{Sn}]$ .<sup>28</sup> As a continuation of our investigation into the chemistry of germanium(II) aryloxy<sup>29</sup> and binaphthoxide<sup>30</sup> complexes, we have obtained the series of group 1/germanium aryloxy cage compounds  $[M(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  ( $M = \text{Li, Na, K, Rb, Cs}$ ) and wish to report on aspects of their solid state structures. These compounds are of interest in that they allow an entire comparison of the effect of the alkali metal upon the solid state structure.

## Results and discussion

### Synthesis of compounds

The group 1 metal/germanium tris(aryloxy) cluster complexes  $[M(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  ( $M = \text{Li, 1; Na, 2; K, 3; Rb, 4; Cs, 5}$ ) were prepared *via* treatment of  $[\text{GeI}_2]$  with three equivalents of the corresponding alkali metal salt of 2,6-diphenylphenol, as shown in Scheme 1. Complex 1 was initially obtained



Scheme 1

**Table 1** Key structural parameters for  $[M(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]^a$ 

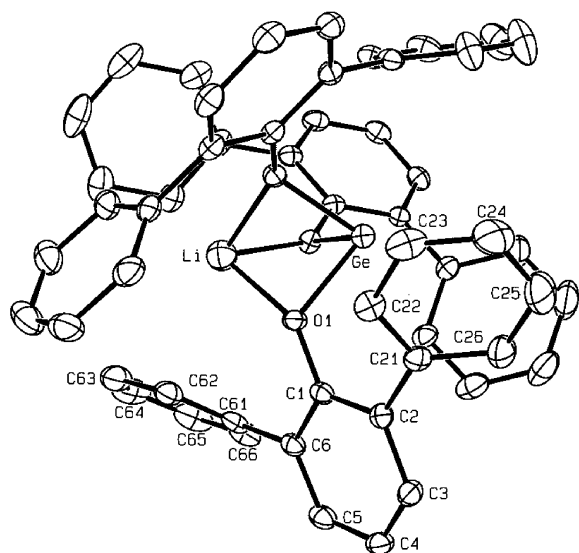
M = Compound	Li 1	Na 2	K 3		Rb 4	Cs 5
$r_{\text{metal}}/\text{\AA}$	1.57	1.91	2.35		2.50	2.72
$r_{\text{ion}}/\text{\AA}$	0.76	1.02	1.38		1.49	1.70
M–Ge/ $\text{\AA}$	2.624(7)	2.941(2)	3.407(1)	3.407(1)	3.6018(4)	3.849(1)
Ge–O/ $\text{\AA}$	1.958(1)	1.939(2)	1.933(3)	1.932(3)	1.930(2)	1.923(3)
			1.935(3)	1.938(3)	1.930(2)	1.960(3)
			1.929(3)	1.927(3)	1.940(2)	1.929(3)
M–O/ $\text{\AA}$	2.000(5)	2.306(2)	2.753(3)	2.769(3)	2.854(2)	3.236(3)
			2.684(3)	2.719(3)	2.932(2)	2.922(3)
			2.709(3)	2.653(3)	2.861(2)	3.219(3)
M–O–Ge/ $^\circ$	83.0(2)	87.25(6)	91.6(1)	91.1(1)	95.73(6)	92.97(9)
			93.6(1)	92.5(1)	93.27(7)	102.2(1)
			93.0(1)	94.8(1)	95.28(6)	93.39(1)
Ge–O–C/ $^\circ$	120.0(1)	119.7(1)	118.8(2)	121.0(2)	118.8(2)	134.4(3)
			125.5(2)	122.2(2)	125.4(2)	122.9(2)
			121.5(2)	119.3(2)	122.1(2)	137.3(2)
M–O–C/ $^\circ$	142.7(2)	139.3(1)	138.2(2)	139.1(2)	135.5(2)	109.6(2)
			134.1(2)	135.2(2)	136.8(2)	133.5(2)
			134.9(2)	135.6(2)	134.6(2)	107.5(2)
$\Sigma(\text{O–Ge–O})^\circ$	246	256	262	266	262	265
$\Sigma(\text{O–M–O})^\circ$	239	208	176	176	166	153

<sup>a</sup> Atomic and ionic radii are taken from ref. 59.

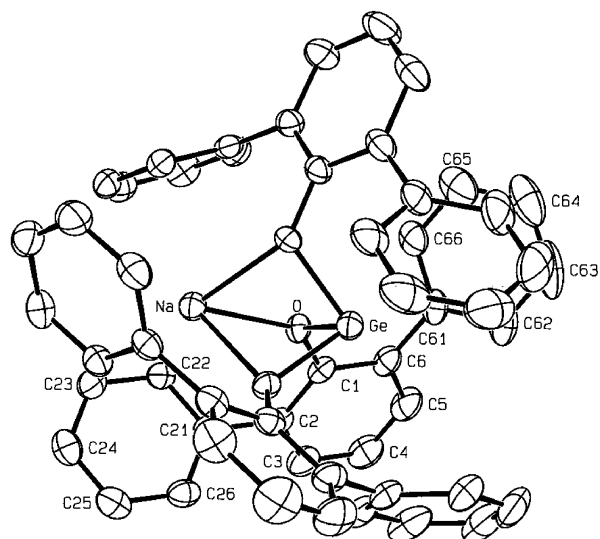
serendipitously in our efforts to prepare the aryloxy complex  $[\text{Ge}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$  from 2,6-diphenylphenol and  $[\text{Ge}(\text{N}\{\text{SiMe}_3\}_2)_2]$ .<sup>29</sup> When the starting bisamide was prepared according to the original literature procedure,<sup>31,32</sup> complex **1** was the only isolable product and no  $[\text{Ge}(\text{OAr})_2]$  was obtained. However, synthesis of  $[\text{Ge}(\text{N}\{\text{SiMe}_3\}_2)_2]$  by a more recently published method<sup>33</sup> produced the desired  $[\text{Ge}(\text{OAr})_2]$  compound in excellent yield. The Li/Ge complex **1** was undoubtedly produced due to an uncharacterized lithium complex generated in the attempted preparation of  $[\text{Ge}(\text{N}\{\text{SiMe}_3\}_2)_2]$ .

#### General structural considerations and periodic trends

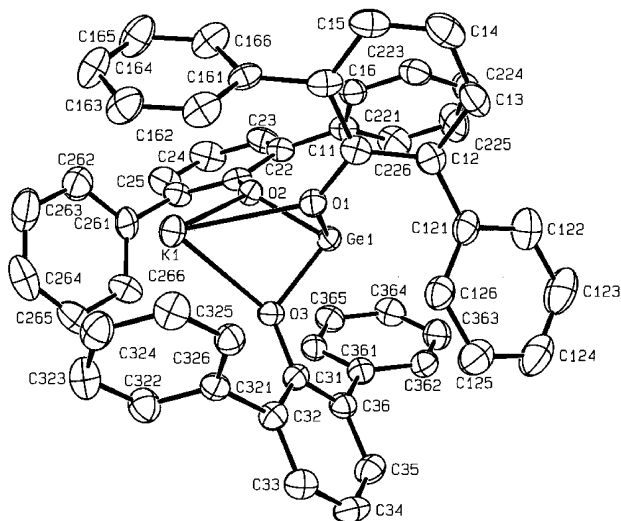
All five compounds were subjected to single crystal X-ray diffraction analysis. Selected structural parameters are compared in Table 1. In Tables 2–6 more explicit parameters are listed including close contacts between the alkali metal and *ortho*-phenyl ring carbon atoms. Complexes **1–5** each contain a five-atom cage comprised of the germanium atom, the alkali metal, and the three bridging oxygen atoms of the aryloxy ligands (Figs. 1–5). In each case, the alkali metal atom coordinated to



**Fig. 1** ORTEP diagram of  $[\text{Li}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  **1**. Thermal ellipsoids are drawn at 50% probability.



**Fig. 2** ORTEP diagram of  $[\text{Na}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  **2**. Thermal ellipsoids are drawn at 50% probability.



**Fig. 3** ORTEP diagram of  $[\text{K}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  **3** (molecule 1). Thermal ellipsoids are drawn at 50% probability.

**Table 2** Selected bond lengths (Å) and angles (°) for [Li(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] (1)

Ge–O(1)	1.958(1)	Li–C(62)	2.720(4)
Li–O(1)	2.000(5)		
O(1)–Ge–O(1)	81.89(6)	Ge–O(1)–Li	83.0(2)
O(1)–Li–C(62)	77.30(6)	O(1)–Li–C(62)	109.44(7)
O(1)–Li–C(62)	153.1(1)	C(62)–Li–C(62)	97.3(2)

**Table 3** Selected bond lengths (Å) and angles (°) for [Na(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] (2)

Ge–O	1.939(2)	Na–C(22)	2.742(3)
Na–O	2.306(2)	Na–C(23)	3.100(3)
O–Ge–O	85.43(7)	O–Na–O	69.55(8)
Ge–O–Na	87.25(6)		

**Table 4** Selected bond lengths (Å) and angles (°) for [K(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] (3)

Molecule 1		Molecule 2	
Ge(1)–O(1)	1.933(3)	Ge(2)–O(4)	1.932(3)
Ge(1)–O(2)	1.935(3)	Ge(2)–O(5)	1.938(3)
Ge(1)–O(3)	1.929(3)	Ge(2)–O(6)	1.927(3)
K(1)–O(1)	2.753(3)	K(2)–O(4)	2.769(3)
K(1)–O(2)	2.684(3)	K(2)–O(5)	2.719(3)
K(1)–O(3)	2.709(3)	K(2)–O(6)	2.653(3)
K(1)–C(161)	3.376(4)	K(2)–C(461)	3.415(4)
K(1)–C(162)	3.085(4)	K(2)–C(462)	3.097(4)
K(1)–C(163)	3.166(5)	K(2)–C(463)	3.219(4)
K(1)–C(261)	3.171(4)	K(2)–C(521)	3.206(4)
K(1)–C(262)	3.281(5)	K(2)–C(522)	3.202(4)
K(1)–C(263)	3.388(5)	K(2)–C(523)	3.222(4)
K(1)–C(264)	3.374(5)	K(2)–C(524)	3.207(4)
K(1)–C(265)	3.259(5)	K(2)–C(525)	3.187(4)
K(1)–C(266)	3.135(4)	K(2)–C(526)	3.177(4)
K(1)–C(321)	3.250(4)	K(2)–C(621)	3.232(4)
K(1)–C(326)	3.190(4)	K(2)–C(622)	3.249(4)
K(1)–C(325)	3.347(4)	K(2)–C(623)	3.380(4)
O(1)–Ge(1)–O(2)	87.6(1)	O(5)–Ge(2)–O(6)	86.5(1)
O(2)–Ge(1)–O(3)	87.2(1)	O(4)–Ge(2)–O(6)	87.2(1)
O(1)–Ge(1)–O(3)	86.7(1)	O(4)–Ge(2)–O(5)	87.5(1)
O(1)–K(1)–O(2)	58.97(8)	O(4)–K(2)–O(5)	58.37(8)
O(2)–K(1)–O(3)	59.21(8)	O(5)–K(2)–O(6)	59.07(8)
O(1)–K(1)–O(3)	58.10(8)	O(4)–K(2)–O(6)	58.75(8)
K(1)–Ge(1)–O(1)	53.86(8)	K(2)–Ge(2)–O(4)	54.34(8)
K(1)–Ge(1)–O(2)	51.83(8)	K(2)–Ge(2)–O(5)	52.88(7)
K(1)–Ge(1)–O(3)	52.56(8)	K(2)–Ge(2)–O(6)	50.90(8)

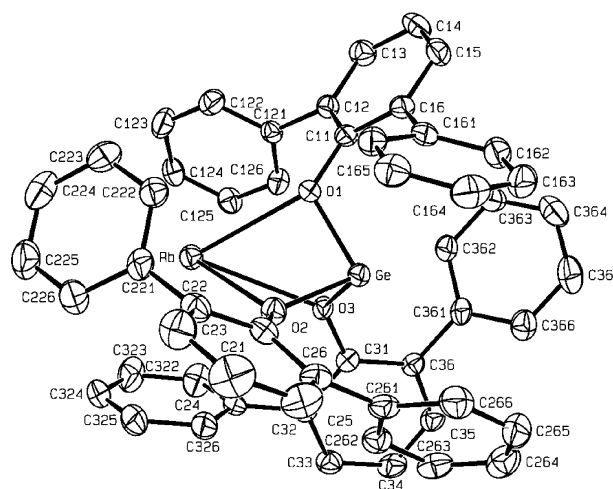
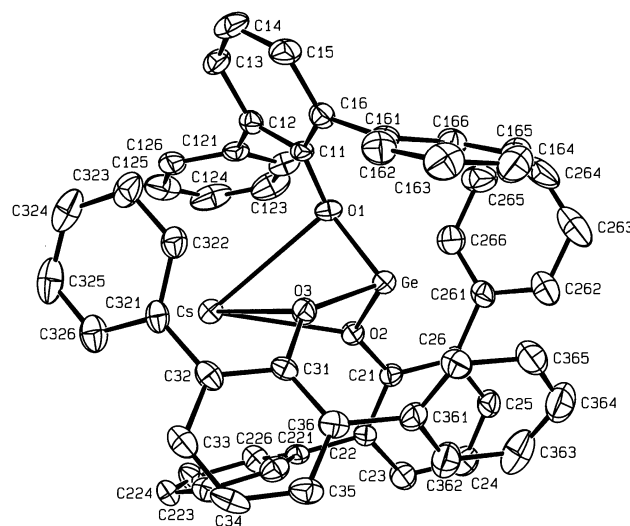
**Table 5** Selected bond lengths (Å) and angles (°) for [Rb(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] (4)

Ge–O(1)	1.930(2)	Ge–O(2)	1.930(2)
Ge–O(3)	1.940(2)	Rb–O(1)	2.854(2)
Rb–O(2)	2.932(2)	Rb–O(3)	2.861(2)
Rb–C(121)	3.364(3)	Rb–C(122)	3.469(3)
Rb–C(123)	3.583(3)	Rb–C(124)	3.587(3)
Rb–C(125)	3.469(3)	Rb–C(126)	3.349(3)
Rb–C(221)	3.438(3)	Rb–C(222)	3.198(3)
Rb–C(223)	3.274(3)	Rb–C(224)	3.558(3)
Rb–C(321)	3.319(3)	Rb–C(322)	3.314(3)
Rb–C(323)	3.364(3)	Rb–C(324)	3.424(3)
Rb–C(325)	3.417(3)	Rb–C(326)	3.363(3)
O(1)–Ge–O(2)	87.99(8)	O(1)–Ge–O(3)	86.72(8)
O(2)–Ge–O(3)	87.42(8)	Ge–O(1)–Rb	95.73(6)
Ge–O(2)–Rb	93.27(7)	Ge–O(3)–Rb	95.28(6)
O(1)–Rb–O(2)	55.20(5)	O(1)–Rb–O(3)	55.42(5)
O(2)–Rb–O(3)	54.97(5)		

three oxygen atoms of a pyramidalized germanium tris(aryl-oxide). The remaining lone pair of electrons on germanium is presumably located pointing away from the three Ge–O bonds.

**Table 6** Selected bond lengths (Å) and angles (°) for [Cs(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] (5)

Ge–O(1)	1.923(3)	Ge–O(2)	1.960(3)
Ge–O(3)	1.929(3)	Cs–O(1)	3.236(3)
Cs–O(2)	2.922(3)	Cs–O(3)	3.219(3)
Cs–C(121)	3.408(4)	Cs–C(122)	3.821(5)
Cs–C(125)	3.775(4)	Cs–C(126)	3.381(4)
Cs–C(221)	3.512(4)	Cs–C(222)	3.455(4)
Cs–C(223)	3.625(4)	Cs–C(224)	3.804(4)
Cs–C(225)	3.847(4)	Cs–C(226)	3.707(4)
Cs–C(321)	3.440(4)	Cs–C(322)	3.754(4)
Cs–C(325)	3.798(4)	Cs–C(326)	3.472(4)
O(1)–Ge–O(2)	86.2(1)	O(1)–Ge–O(3)	87.2(1)
O(2)–Ge–O(3)	91.9(1)	Ge–O(1)–Cs	92.97(9)
Ge–O(2)–Cs	102.2(1)	Ge–O(3)–Cs	93.39(1)
O(1)–Cs–O(2)	50.76(7)	O(1)–Cs–O(3)	48.60(7)
O(2)–Cs–O(3)	53.88(7)		

**Fig. 4** ORTEP diagram of [Rb(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] 4. Thermal ellipsoids are drawn at 50% probability.**Fig. 5** ORTEP diagram of [Cs(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Ge] 5. Thermal ellipsoids are drawn at 50% probability.

No direct, intramolecular alkali metal–germanium interaction occurs. Furthermore, the steric bulk of the 2,6-diphenylphenoxide ligands prohibits any extensive oligomerization through intermolecular Ge–M bonding. This type of bonding has precedence, however. The complex [Ti(μ-O<sup>t</sup>Bu)<sub>3</sub>Sn] was shown to form complexes of the type [(CO)<sub>5</sub>M–Sn(μ-O<sup>t</sup>Bu)<sub>3</sub>Ti] (M = Cr, Mo) upon thermal or photolytic reaction with M(CO)<sub>6</sub>,<sup>27</sup> and the trimeric complexes

$[M(\mu\text{-O}^t\text{Bu})_3\text{Pb}(\mu\text{-O}^t\text{Bu})_3M]$  ( $M = \text{Ge}, \text{Sn}$ ) were also found to form complexes with the  $[\text{Fe}(\text{CO})_4]$  fragment by thermal reaction with  $[\text{Fe}_2(\text{CO})_9]$ .<sup>34</sup> We recently reported the structure of the silver(I)/germanium complex  $[\text{Ag}(\mu\text{-OC}_6\text{HPh}_4\text{-2,3,5,6})_3\text{Ge}(\text{AgOSO}_2\text{CF}_3)]$ ,<sup>30</sup> in which the germanium lone pair interacts with the silver atom of the  $\text{AgOSO}_2\text{CF}_3$  fragment.<sup>30,35</sup> The lack of oligomerization in **1–5** is presumably a consequence of steric factors and/or the stabilization of the formally three coordinate group 1 metals by interactions with the *ortho*-phenyl rings of the bridging aryloxy ligands. The nature of this interaction depends strongly on the identity of the group 1 metal (*vide infra*).

The structures of **1–5** consist of a five-atom cage containing the germanium atom, the three  $\mu$ -oxygen atoms, and the group 1 metal. The structure of the framework approaches trigonal bipyramidal in all cases. It can be seen (Table 1) that the M–Ge distance increases gradually as one moves down the group 1 metals. The M–Ge distance correlates extremely well with both the ionic and metallic radii for the alkali metals (Table 1, Fig. 6).

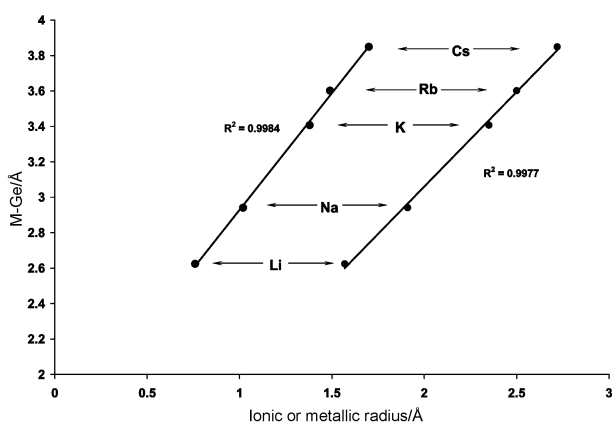


Fig. 6 Plots showing correlation of M–Ge distances (Å) in  $[\text{M}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  **1–5** and ionic and metallic radii for the group 1 metals  $M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ .

However, there is a significant difference in the structure of the caesium cluster **5** compared to the other four (Fig. 5). In compounds **1–4** the Ge–O distances span the very narrow range of 1.927(3)–1.958(1) Å. These distances are slightly longer than the Ge–O distances of 1.822(1) and 1.817(1) Å reported for  $[\text{Ge}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$ .<sup>29</sup> The M–O distances increase with metal atomic number, but within each cluster are very similar. In the lithium and sodium compounds **1** and **2** there is a crystallographic three-fold axis of symmetry so that all three sets of parameters are identical (Figs. 1 and 2). For potassium compound **3** there are two independent molecules within the unit cell. However, the six non-equivalent K–O distances are very similar and an ORTEP plot of molecule 1 is shown in Fig. 3. One of the Rb–O distances in **4** (Fig. 4) is slightly longer than the other two; although in this compound the three Ge–O distances are essentially the same. Within compounds **1–4** the M–O–Ge angle increases upon moving down the group, paralleling the M–Ge distance. The Ge–O–Ar angles in **1–4** are in the narrow range of 118–125°. In  $[\text{Ge}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2]$  the Ge–O–Ar angles are found to be very similar, 117°.<sup>29</sup> In contrast there is definite localization of the bonding in caesium compound **5** (Table 1, Fig. 5). Specifically it can be seen that there is one short Cs–O distance of 2.922(3) Å and two longer distances of 3.219(3) and 3.236(3) Å. The corresponding distances to germanium are 1.960(3) Å, and short 1.923(3), 1.929(3) Å. This localization is consistent with a formulation in this case of a caesium aryloxy adduct of a germanium(II) aryloxy as shown in Scheme 1. Another important difference between **5** and its lighter congeners lies in the Ge–O–Ar angles (Tables 1 and 6). The two aryloxides with the shortest Ge–O distances have relatively large Ge–O–Ar angles of 134 and 137° compared

to 123° for the other aryloxy bridge. We believe these large angles are present in order to accommodate the arene–Cs interactions present within this cluster.

### Arene–alkali metal interactions

Compounds **1–5** contain a pyramidalized alkali metal with the three (O–M–O) angles summing to values of between 293 and 153° on moving down the group from Li to Cs. Hence in all five compounds the alkali metal atom is formally extremely electron deficient with a large, vacant site of electrophilicity. This open cavity is occupied in all cases by three *ortho*-phenyl rings, one each from each of the bridging 2,6-diphenylphenoxide ligands. The extent of arene–M interaction depends strongly on the size of the group 1 metal. The lithium atom in **1** exhibits a close contact with one *ortho*-carbon atoms of one *ortho*-phenyl ring of each aryloxy ligand. The arene–Li interactions are highlighted in Fig. 7. The Li–C(62) distance is 2.720(4) Å, which is close to the upper limit for an electrostatic interaction between a Li atoms and  $\pi$ -electron cloud of an aromatic ring.<sup>36–38</sup> Dimeric base-free phenyllithium was reported to have intermolecular Li–C<sub>aromatic</sub> contacts ranging from 2.40(1) to 2.86(1) Å.<sup>39</sup> The lithium thiolate complex  $(\text{LiSC}_6\text{H}_2\text{Ph}_3\text{-2,4,6})_4\text{C}_7\text{H}_8$  exhibits intramolecular Li–C contacts up to 2.73(2) Å in length,<sup>40</sup> and the gallium/lithium  $\mu$ -iodo complex  $[\text{Li}(\text{THF})_4][\text{GaI}(\text{SiPh}_3)_3]$  has two Li–C intermolecular contacts of 2.630(1) and 2.854(9) Å.<sup>41</sup> Based on the available structural data, only the Li–C(62) interaction is significant. The other lithium–carbon distances range from 3.185(4) Å for Li–C(61) to 4.443(4) Å for Li–C(65). The structure of the isomorphous and isostructural tin congener,  $[\text{Li}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Sn}]$  **6**, has been reported and closely resembles that of **1**.<sup>28</sup> This species exhibits a  $\pi$ -interaction between the Li atom and the same (*ortho*) carbon atom of the 2,6-phenyl rings of the ligands.

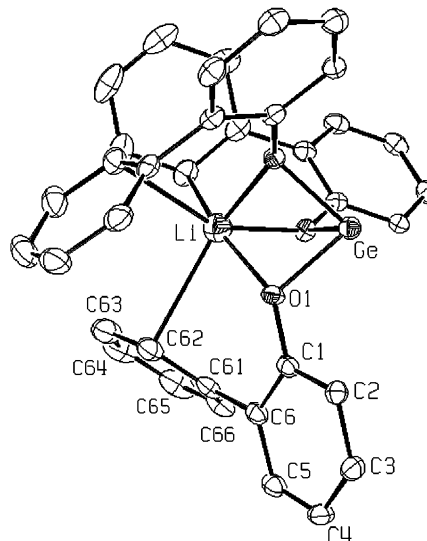
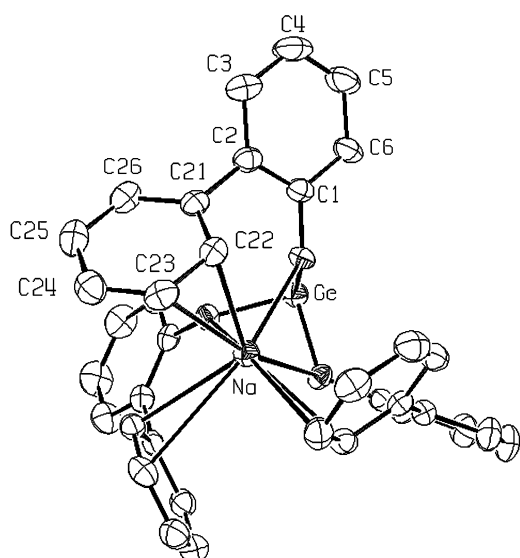


Fig. 7 Diagram illustrating the coordination environment about lithium in  $[\text{Li}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  **1**.

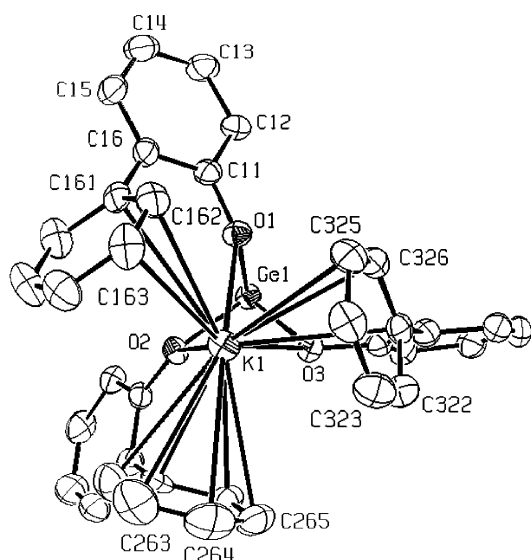
The sodium complex  $[\text{Na}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}]$  **2** crystallizes in the cubic space group  $Pa\bar{3}$ . As for **1**, a crystallographic  $C_3$  axis passes through both the Na and Ge atoms rendering all three aryloxy ligands equivalent. Compound **2** also exhibits interactions between the sodium atom and the  $\pi$ -electron cloud of the *ortho*-phenyl rings (Fig. 8). The typical range for Na–C contacts for the carbon atoms of arene or cyclopentadienyl rings is 2.6–3.0 Å,<sup>42</sup> and the Na–C(21), Na–C(22) and Na–C(23) distances of 3.204(3), 2.742(3) and 3.100(3) Å, respectively, represent close contacts. As with **1** the strongest interaction is again with the *ortho*-carbons. A series of thiolate complexes  $[\text{MSC}_6\text{H}_3\text{Trip}_2\text{-2,6}]_2$  ( $M = \text{La}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}; \text{Trip} = 2,4,6\text{-tri}$



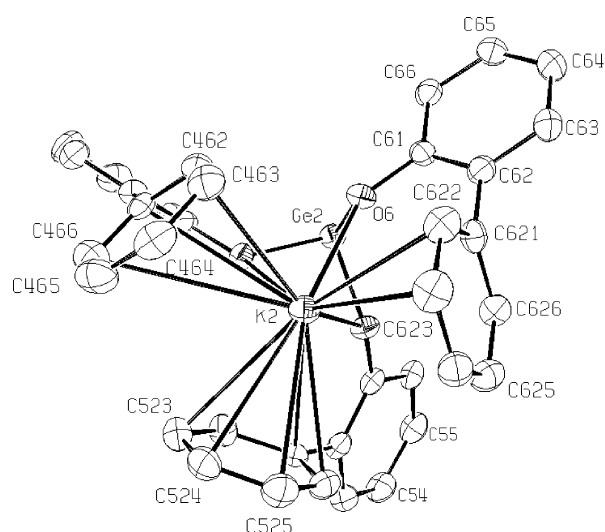
**Fig. 8** Diagram illustrating the coordination environment about sodium in  $[\text{Na}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}] \mathbf{2}$ .

isopropylphenyl) has been prepared and structurally characterized, and the Na–C distances in the sodium derivative  $[\text{NaS-C}_6\text{H}_3\text{Trip}_2\text{-2,6}]_2 \cdot 0.5 \text{C}_7\text{H}_8$  range from 2.839(5) to 3.266(5) Å.<sup>40</sup> The complex  $\text{NaC}(\text{SiMe}_2\text{Ph})_3$  also exhibits such interactions, ranging from 2.80(1) to 3.39(2) Å.<sup>43</sup> The other sodium–carbon distances in **2** vary from 3.807(3) to 4.146(3) Å, which are too long to be considered bonding interactions.

The potassium analog  $[\text{K}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}] \mathbf{3}$ , is of lower symmetry in the solid state, crystallizing in the orthorhombic space group  $Pca2_1$ . Compound **3** contains two unique molecules in the unit cell and the ORTEP diagram for molecule 1 is shown in Fig. 3 and the environment about the each of the potassium atoms is illustrated in Figs. 9 and 10. The potassium ions in complex **3** interact with the  $\pi$ -electron clouds of the *ortho*-phenyl rings to a larger extent than for **1** and **2**. In molecule 1, the K atom is bound in two different fashions to the three *ortho*-phenyl rings. The approximate range of distances for K–C bonding is 3.1–3.3 Å.<sup>42</sup> However, longer K–C distances have been reported for bonds between a potassium cation and an arene ring. For example, the coordinated toluene molecules in  $[\text{K}(\text{[18]crown-6})_3][\text{C}_{60}(\text{C}_6\text{H}_5\text{CH}_3)_2]$  were reported to bind as  $\eta^3$  ligands, with K–C bond lengths ranging from 3.230(8) to 3.517(5) Å,<sup>44</sup> and the complex  $\text{KS}(\text{C}_6\text{H}_3\text{Trip}_2\text{-2,6})_2$  exhibits



**Fig. 9** Diagram illustrating the coordination environment about potassium in molecule 1 of  $[\text{K}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}] \mathbf{3}$ .

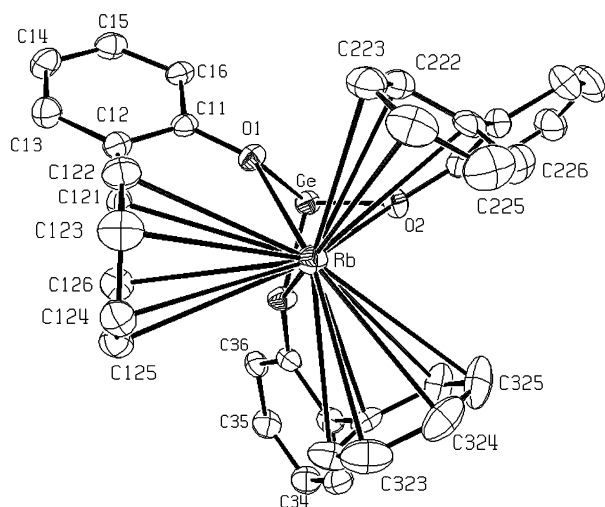


**Fig. 10** Diagram illustrating the coordination environment about potassium in molecule 2 of  $[\text{K}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}] \mathbf{3}$ .

intramolecular K–C contacts ranging from 3.279(5) to 3.564(5) Å.<sup>40</sup>

The ring encompassing C(161) to C(166) contains three K–C contacts that roughly fall into the 3.1–3.3 Å range, and thus coordinates to the K atom in an  $\eta^3$  fashion, as does the ring containing C(361)–C(366). The other proximal phenyl ring containing C(261)–C(266) is coordinated in what can be considered an  $\eta^6$  fashion. The potassium atom of molecule 2 is in a similar environment. The phenyl ring containing C(461)–C(466) coordinates in an  $\eta^2$  fashion, as the K–C(461) contact of 3.415(4) Å is slightly too long for bonding to occur. The ring containing C(521)–C(526) coordinates in an  $\eta^6$  bonding mode, and the ring containing C(621)–C(666) is coordinated in an  $\eta^4$  bonding mode. Thus, both discrete molecules of **3** contain formally very highly-coordinated potassium metal centers.

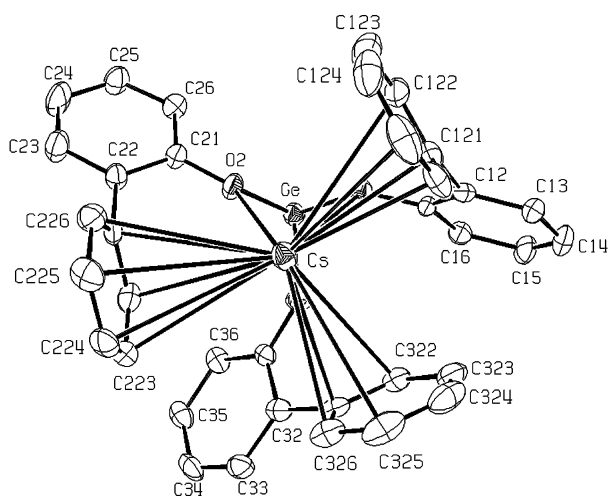
An ORTEP diagram for the rubidium-containing species  $[\text{Rb}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}] \mathbf{4}$  is shown in Fig. 4, selected bond distances and angles are collected in Table 5, and the coordination environment about the rubidium atom is illustrated in Fig. 11. Like the potassium compound **3**, the rubidium center is in a high coordination environment in **4**, as it exhibits a total of 16 interactions to the carbon atoms of the *ortho*-phenyl rings. The majority of complexes containing arene rings coordinated to rubidium exhibit Rb–C contacts of 3.1–3.6 Å,<sup>42</sup> and the two Rb–C contacts between Rb–C(225) and Rb–C(226) have distances of 3.761(3) and 3.716(3) Å, which are longer than typical



**Fig. 11** Diagram illustrating the coordination environment about rubidium in  $[\text{Rb}(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3\text{Ge}] \mathbf{4}$ .

reported values.<sup>40,43,45–48</sup> Thus, the two phenyl rings attached to C(12) and C(32) are both coordinated to Rb in an  $\eta^6$  fashion, while the remaining phenyl ring attached to C(22) is closer to an  $\eta^4$  bonding mode. Highly coordinated rubidium metal centers are not uncommon, and examples include  $\text{RbC}(\text{SiMe}_2\text{Ph})_3$ ,<sup>43</sup>  $[\text{Ph}_3\text{CRb}\cdot\text{PMDTA}]_n$ ,<sup>48</sup> and the selenolate complex  $[\text{RbSeC}_6\text{H}_3\text{-Trip}_{2-2,6}]$  (Trip =  $\text{C}_6\text{H}_2\text{Pr}_{3-2,4,6}$ ).<sup>47</sup>

The structure of the  $[\text{CsO}_3\text{Ge}]$  core in the caesium complex  $[\text{Cs}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$  **5** was shown to be significantly different than those in complexes **1–4**. An ORTEP diagram of **5** is shown in Fig. 5, and the coordination environment about the caesium atom is shown in Fig. 12. Selected bond distances and angles are listed in Table 6. Examination of the Cs–C interactions present in **5** show the phenyl ring attached to C(22) is coordinated to the caesium metal center though all six carbon atoms. The C(22) atom is attached to O(2), which exhibits the shortest Cs–O contact of 2.922(3) Å. The other two proximal phenyl rings, which contain the atoms C(121)–C(126) and C(321)–C(326), are both coordinated to the Cs metal center in an  $\eta^4$  fashion. The non-bonded distances for the four uncoordinated carbon atoms range from 4.077(4) to 4.173(4) Å, which are outside the typical range, 3.3–3.8 Å, of bonding contacts.<sup>42</sup> In the complex  $[(\text{C}_6\text{H}_3)_3\text{CsC}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2]_2$ , the benzene solvate molecules coordinate to the Cs metal center in  $\eta^4$ ,  $\eta^2$  and  $\eta^1$  bonding modes and exhibit Cs–C contacts in the range of 3.5–3.7 Å.<sup>49</sup>



**Fig. 12** Diagram illustrating the coordination environment about caesium in  $[\text{Cs}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$  **5**.

## Conclusions

The entire series of germanium/group 1 cage complexes  $[\text{M}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$  (M = Li **1**, Na **2**, K **3**, Rb **4**, Cs **5**) have been prepared from the corresponding aryloxy salt and germanium(II) iodide. The species adopt a common structural motif in which the group 1 metal is encapsulated by the three oxygen atoms of the 2,6-diphenylphenoxide ligands. In the complexes **1–4**, the alkali metal atom, the germanium atom, and the three oxygen atoms form a trigonal bipyramidal cage, and these four species are approximately isostructural. In the case of the caesium complex **5**, the structure of this fragment more closely resembles a  $\text{CsOAr}$  adduct of a germanium(II) aryloxy. Complexes **1–5** all exhibit interactions between the alkali metal cation and the  $\pi$ -electron cloud of the *ortho*-phenyl rings of the aryloxy ligands. The number of these interactions increases with increasing size of the alkali cation.

## Experimental

All manipulations were carried out using standard syringe, Schlenk, and glovebox techniques.<sup>50</sup> The compounds 2,6-di-

phenylphenol,<sup>51</sup>  $\text{MOC}_6\text{H}_3\text{Ph}_{2-2,6}$ ,<sup>52</sup> and  $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ <sup>33</sup> were prepared according to literature procedures or slight variations thereof. Germanium(II) iodide was purchased from Aldrich and used as received.

### Preparation of $[\text{Li}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$ (**1**)

Germanium(II) iodide (0.44 g, 1.7 mmol) was suspended in benzene (10 mL). To this was added  $\text{LiOC}_6\text{H}_3\text{Ph}_{2-2,6}$  (0.18 g, 0.55 mmol) in benzene (5 mL). The suspension was stirred for 12 h, then filtered through Celite to yield a yellow solution. The volatiles were removed *in vacuo*, resulting in a white solid which was recrystallized from hot benzene (5 mL) to give 0.16 g (34%) of **1** as colorless crystals. Anal. Calc. for  $\text{C}_{54}\text{H}_{39}\text{GeLiO}_3$ : C, 79.54; H, 5.07. Found: C, 79.19; H, 5.07%.

### Preparation of $[\text{Na}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$ (**2**)

Compound **2** was prepared using 0.25 g (0.76 mmol) of  $\text{GeI}_2$  and 0.66 g (2.5 mmol) of  $\text{NaOC}_6\text{H}_3\text{Ph}_{2-2,6}$  by the same procedure used for the synthesis of **1**. Yield: 0.46 g (73%). Anal. Calc. for  $\text{C}_{54}\text{H}_{39}\text{GeNaO}_3$ : C, 78.00; H, 4.73. Found: C, 78.15; H, 4.98%.

### Preparation of $[\text{K}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$ (**3**)

A suspension of  $\text{KOC}_6\text{H}_3\text{Ph}_{2-2,6}$  (0.20 g, 0.70 mmol) in benzene (10 mL) was added to a suspension of  $\text{GeI}_2$  (0.071 g, 0.22 mmol) in benzene (10 mL). The reaction mixture was gently heated to reflux, allowed to cool, and then was stirred for 15 h at room temperature, resulting in a yellow suspension. The volatiles were removed *in vacuo* and benzene (10 mL) was added to the resulting yellow solid. The mixture was heated to reflux, shaken and filtered while still warm. The filtrate was reserved and the remaining yellow solid was again extracted by an identical procedure. The filtrates were combined and the benzene was removed *in vacuo*. To the resulting white powder was added a 1 : 1 mixture of benzene–hexane (10 mL). The suspension was heated until all solids dissolved; slow cooling yielded colorless crystals of **3**. Yield: 0.060 g (33%). Anal. Calc. for  $\text{C}_{54}\text{H}_{39}\text{GeKO}_3$ : C, 76.52; H, 4.64. Found: C, 76.37; H, 4.83%.

### Preparation of $[\text{Rb}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$ (**4**)

A suspension of  $\text{RbOC}_6\text{H}_3\text{Ph}_{2-2,6}$  (0.76 g, 2.3 mmol) in benzene (20 mL) was added to a suspension of  $\text{GeI}_2$  (0.25 g, 0.77 mmol) in benzene (10 mL). The mixture was gently heated to reflux, allowed to cool, and was stirred for 48 h, resulting in a pink precipitate. The solid was isolated by filtration, washed with benzene ( $3 \times 5$  mL) and hexane ( $3 \times 5$  mL) and dried *in vacuo*. The desired product was obtained by a method analogous to that used for **3** to yield 0.47 g (69%) of **4** as colorless crystals. Anal. Calc. for  $\text{C}_{54}\text{H}_{39}\text{GeO}_3\text{Rb}\cdot\text{C}_6\text{H}_6$ : C, 74.13; H, 4.67. Found: C, 73.92; H, 4.74%.

### Preparation of $[\text{Cs}(\mu\text{-OC}_6\text{H}_3\text{Ph}_{2-2,6})_3\text{Ge}]$ (**5**)

A suspension of  $\text{CsOC}_6\text{H}_3\text{Ph}_{2-2,6}$  (0.63 g, 1.7 mmol) in benzene (25 mL) was added to a suspension of  $\text{GeI}_2$  (0.17 g, 0.52 mmol) in benzene (25 mL). The reaction mixture was stirred for 48 h, resulting in a deep purple precipitate. The solvent was removed *in vacuo* and the solid was extracted with hot benzene ( $4 \times 20$  mL). Removal of the solvent yielded a white powder which was recrystallized from a hot solution of 2 : 1 benzene/hexane (15 mL), yielding 0.22 g (45%) of **5** as colorless crystals. Anal. Calc. for  $\text{C}_{54}\text{H}_{39}\text{CsGeO}_3$ : C, 68.90; H, 4.18. Found: C, 68.05; H, 4.24%.

### X-Ray data collection and reduction

Crystal data and data collection parameters are contained in **Table 7**. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen.

**Table 7** Crystallographic data for compounds 1–5

	1·C <sub>6</sub> H <sub>6</sub>	2·0.5C <sub>6</sub> H <sub>6</sub>	3·C <sub>6</sub> H <sub>6</sub>	4·C <sub>6</sub> H <sub>6</sub>	5
Formula	C <sub>60</sub> H <sub>45</sub> GeLiO <sub>3</sub>	C <sub>57</sub> H <sub>42</sub> GeNaO <sub>3</sub>	C <sub>60</sub> H <sub>45</sub> GeKO <sub>3</sub>	C <sub>60</sub> H <sub>45</sub> GeO <sub>3</sub> Rb	C <sub>54</sub> H <sub>39</sub> CsGeO <sub>3</sub>
Space group	R3̄ (no. 146)	Pa3̄ (no. 205)	Pca2 <sub>1</sub> (no. 29)	P2 <sub>1</sub> /c (no. 14)	C2/c (no. 15)
a/Å	15.7846(6)	20.7127(3)	17.7319(3)	15.6217(3)	38.6426(9)
b/Å	15.7846(6)	20.7127(3)	16.987332)	17.1706(4)	10.7401(2)
c/Å	15.839(2)	20.7127(3)	31.0061(5)	17.7554(4)	21.2400(4)
a/°	90	90	90	90	90
β/°	90	90	90	100.662(1)	108.184(1)
γ/°	120	90	90	90	90
V/Å <sup>3</sup>	3417.7(7)	8886.1(2)	9339.6(3)	4680.4(2)	8374.9(3)
Z	3	8	8	4	8
D <sub>c</sub> /g cm <sup>-3</sup>	1.302	1.301	1.317	1.379	1.493
T/K	150	150	150	150	150
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073
R	0.031	0.046	0.038	0.037	0.047
R <sub>w</sub>	0.061	0.113	0.078	0.077	0.103

Preliminary examination and final data collection were performed with Mo-Kα radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.<sup>53</sup> An empirical absorption correction using SCALEPACK was applied.<sup>54</sup> Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.<sup>55</sup> The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least squares where the function minimized was  $\sum w(|F_o|^2 - |F_c|^2)^2$  and the weight  $w$  is defined as  $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Scattering factors were taken from the "International Tables for Crystallography".<sup>56</sup> Refinement was performed on a Alpha-Server 2100 using SHELX-97.<sup>57</sup> Crystallographic drawings were done using programs ORTEP.<sup>58</sup>

CCDC reference numbers 203281 (1), 203290 (2), 203292 (3), 203289 (4) and 203293 (5).

See <http://www.rsc.org/suppdata/dt/b3/b301623d/> for crystallographic data in CIF or other electronic format.

## Acknowledgements

This work was supported by a grant from the National Science Foundation (Grant CHE-0078405).

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