New heterosiloxanes of bivalent Group 14 elements and their reactions with $[Mo(CO)_6]$: crystal structures of $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ (M = Ge or Sn) and $[\{Sn(\mu\text{-}OBu^t)(OSiPh_3)\}_2Mo(CO)_5]$

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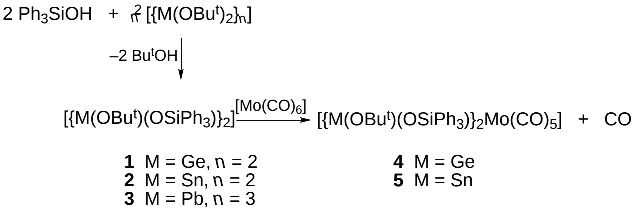
The protolysis of Ph_3SiOH with a toluene solution of $[\{M(OBu^t)_2\}_n]$ (M = Ge^{II} or Sn^{II}, $n = 2$; M = Pb^{II}, $n = 3$) in 1:1 molar ratio at room temperature *via* alcohol elimination facilitated the isolation of high yields of heteroleptic alkoxosiloxides of the type $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ (M = Ge^{II} **1**, Sn^{II} **2** or Pb^{II} **3**). Crystal structural analyses of compounds **1** and **2** revealed them to be isomorphous and isostructural. Both the dimeric structures feature a perfect planar M_2O_2 (M = Sn **1** or Ge **2**) core with a crystallographically imposed centre of inversion. Each metal atom is bound to two bridging *tert*-butoxide ligands and one terminal triphenylsiloxide ligand resulting in a trigonal-pyramidal co-ordination geometry around the metal atom. The stereochemical activity of the lone pair of electrons present on the metal atoms of **1** and **2** is demonstrated by their ability to form M−Mo bonds in $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2Mo(CO)_5]$ (M = Ge **4** or Sn **5**) on their reaction with an equimolar amount of $[Mo(CO)_6]$ in refluxing toluene *via* displacement of CO from the inner co-ordination sphere of $[Mo(CO)_6]$. The asymmetry in compound **5** was revealed by its crystal structure. The structure consists of a four-co-ordinate tin(II) centre, bearing an $Mo(CO)_5$ unit, linked *via* two bridging *tert*-butoxide groups to another Sn^{II} which exhibits (3 + 6) co-ordination with three normal Sn−O bonds and a weak tin(II)–arene (η^6) interaction originating from the orientation of a phenyl ring of the $OSiPh_3$ ligand such that the tin to ring centre distance is 3.58 Å. The identity of all the compounds in solution has been confirmed by multinuclear (^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb) NMR and IR spectra and elemental analyses.

Recent proposals in the field of material chemistry to use hybrid organic–inorganic materials as molecular precursors in the sol–gel process derive their current importance from the acclaimed utility of such compounds as suitable materials for optical and electrooptical applications and as promising precursors to metal oxides and silicates.[1,2] The disadvantages of a high frequency of oxide formation and increased reactivity of the metal centres in order to satisfy their co-ordination numbers leading to a high rate of hydrolysis of non-silicon metal alkoxides can be overcome by using compounds containing both alkoxo and siloxo groups. The hydrolytically stable Si−C bond and more reactive M−O bond will result in a differential susceptibility of the two groups to hydrolysis which is advantageous for obtaining homogeneous gels.

Although, neutral homoleptic siloxides of lanthanides,[3–5] Co^{II},[6] Groups 2,[7,8] 11,[9] 14[10–12] and 15[13,14] with a variety of structural features have been documented, there still exists a paucity in reports of heteroleptic metal siloxides containing both alkoxo and siloxo groups[15] and none in the sub-valent state has been reported. In view of the above, we describe herein the synthesis and characterization of mixed-ligand (alkoxo-siloxo) compounds of Sn^{II}, Ge^{II} and Pb^{II} and their chemical behaviour toward $[Mo(CO)_6]$ which yielded complexes containing M−Mo bonds. The solid-state structures of a few representative compounds are also reported.

Results and Discussion

tert-Butoxo triphenylsiloxides of composition $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ are easily accessible by deprotonation of the acidic OH group of triphenylsilanol with an equimolar quantity of $[\{M(OBu^t)_2\}_n]$ in toluene at room temperature (Scheme 1). The formation of the less acidic Bu^tOH in comparison to triphenylsilanol seems to be the driving force for the reaction. The Lewis basicity of the metal-centred nucleophiles **1** and **2** is exemplified by their reaction (Scheme 1) with $[Mo(CO)_6]$ in 1:1 stoichiometric ratio in refluxing toluene which afforded complexes $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2Mo(CO)_5]$ (M = Ge **4** or Sn **5**) in acceptable yields. However, the interaction of the lead analogue **3** with $[Mo(CO)_6]$ led to immediate precipitation of lead metal.



Scheme 1

These air- and moisture-sensitive crystalline solids **1**–**5** are soluble in polar and hot aromatic solvents but insoluble in alkanes. Their molecular weights could not be determined cryoscopically due to insufficient solubility in cold benzene. They are non-volatile and attempted sublimations led to deposition of the corresponding metal(II) alkoxides (^{1}H NMR evidence) on the sublimation tube. Solvent-free crystals of **1** and **2** were grown by slowly cooling toluene–diethyl ether and a saturated hot toluene solution, respectively. A crystalline sample of **3** was obtained from a diethyl ether solution at −20 °C. The product shows rapid loss of crystallinity under a stream of nitrogen or upon application of a vacuum, presumably due to the loss of solvent molecules, and attempts to perform a structural analysis were not fruitful. Compound **2** could also be isolated by the reaction of $[(C_5H_5)Sn(\mu\text{-}OBu^t)_2Ge(OBu^t)]$[16] with an equivalent amount of Ph_3SiOH in toluene at room temperature followed by crystallization from CH_2Cl_2–hexane. To determine unambig-

Table 1 Selected metrical parameters (bond lengths in Å, angles in °) for compounds **1** and **2** with estimated standard deviations (e.s.d.s) in parentheses

	1 M = Ge	**2** M = Sn
M–O(2)	1.814(2)	1.949(5)
M–O(1)	1.966(2)	2.099(4)
M–O(1′)	1.967(2)	2.079(4)
O(1)–M′	1.967(2)	2.079(4)
O(2)–M–O(1)	94.86(10)	91.4(2)
O(2)–M–O(1′)	97.57(10)	95.3(2)
O(1)–M–O(1′)	74.72(10)	73.0(2)
Si–O(2)–M	150.2(2)	149.4(3)
M–O(1)–M′	105.28(10)	107.0(2)
O(2)–Si–C(5)	112.26(14)	109.5(3)
O(2)–Si–C(11)	109.31(14)	109.1(3)
O(2)–Si–C(17)	109.2(2)	112.3(3)

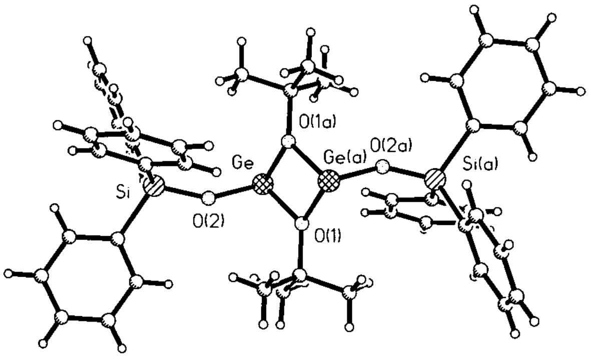


Fig. 1 Molecular structure of the centrosymmetric $[\{Ge(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ **1**. Atoms related to those shown by the crystallographic inversion of symmetry are designated with 'a'

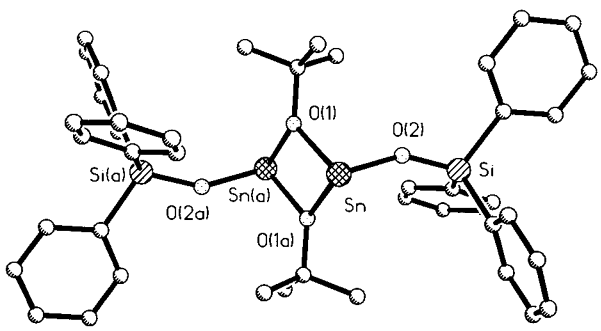


Fig. 2 Ball-and-stick drawing of the non-hydrogen atoms of $[\{Sn(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ **2**, showing selected atom labelling. Other details as in Fig. 1

uously the nuclearity of these compounds, X-ray crystallographic studies were undertaken on compounds **1**, **2** and **5**.

Solid-state structures of $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ (M = Ge 1 or Sn 2)

The dimeric nature of compounds **1** and **2** in the solid state was established by determinations of their crystal structures. As evident from the unit-cell parameters and atomic coordinates, **1** and **2** are isomorphous and crystallise in the triclinic space group $P\bar{1}$ with one molecule per unit cell. Figs. 1 and 2 show a perspective drawing of compounds **1** and **2**, respectively with atomic numbering scheme. Selected bond lengths and angles are listed in Table 1. Each structure consists of a discrete dimeric unit in which Ge (**1**) [Sn (**2**)] and bridging oxygen atoms form a strictly planar rhomboidal array. The dimers of **1** and **2** lie on a crystallographic centre of symmetry necessitating the presence of the observed perfect planar M_2O_2 ring and a mutually *trans* arrangement of the terminal ligands. The two crystallographically equivalent divalent metal atoms in each molecule are bridged by two *tert*-butoxide groups and terminally bound to one triphenylsiloxide moiety to complete a trigonal-pyramidal environment around each metal atom. Although the sum of the angles around M^{II} amounting to 267.1 (**1**) and 259.7° (**2**) supports the presence of a non-bonding lone pair of electrons, the acute endocyclic O–M–O angles at the three-co-ordinate M^{II} atom is consistent with a p^3 geometry. The rhombic M_2O_2 cores of compounds **1** and **2** are similar in terms of angles at the metal and oxygen atoms [O–M–O and M–O–M 74.72(10) and 105.28(10)° in **1** (M = Ge), 73.0(2) and 107.0(2)° in **2** (M = Sn)]. Within these rings the Ge–O bonds are symmetrical [1.967(2) and 1.966(2) Å] in **1** while the Sn–O bonds are slightly asymmetrical [2.099(4) and 2.079(4) Å] in **2**. As expected, the terminal M–O(2) bond distances of 1.814(2) Å in **1** and 1.949(5) Å in **2** are shorter than their corresponding bridging M–O distances and are also consistent with the lower co-ordination numbers at O(2) as compared to O(1). The bond lengths and angles at Sn^{II} and Ge^{II} are in accordance with other alkoxo-bridged compounds of Sn^{II} and Ge^{II}.[17,18] The geometry at the oxygen atoms of the bridged OBu^t group slightly deviates from planarity, as shown by the sums of their interbond angles {356.5° [O(1)] in compound **1** and 357.0° [O(1)] in **2**}.

The staggered conformation of the OBu^t groups and the orientation of the phenyl rings away from the M_2O_2 plane to prevent steric crowding are visible in Figs. 1 and 2. The phenyl rings on silicon adopt a propeller conformation and the angles at silicon (109 ± 3°) indicate it to be present at the centre of a tetrahedron. The terminal $OSiPh_3$ groups have symmetrical obtuse M–O–Si angles [150.2(2) (**1**), 149.4(3)° (**2**)]. The latter value is in the limit of the range observed in $Sn(OSiPh_3)_4$[11] where the terminal Sn–O–Si bond angles span 150–159°. The facial orientation of one of the phenyl rings of the $OSiPh_3$ group towards the OBu^t group results in nuclear shielding which is parallelled by a change in NMR parameters (see below). The Si–O (average 1.61 Å) and Si–C (average 1.87 Å) bond lengths do not show any special feature.

Solid-state structure of $[\{Sn(\mu\text{-}OBu^t)(OSiPh_3)\}_2Mo(CO)_5]$ 5

X-Ray crystallographic analysis of a single crystal of compound **5** revealed a nearly planar rhombus comprised of two Sn^{II} and two oxygen atoms of bridging OBu^t groups. The Sn(2) atom is ligated by three oxygen atoms and is also oriented towards an aryl ring of the $OSiPh_3$ ligand approximating the geometry about Sn(2) to a ψ trigonal bipyramid with the aryl ring centre and O(4) taking the axial positions and O(1), O(2) and the lone pair of non-bonding electrons of Sn(2) occupying the equatorial plane. The environments of Sn(1) and Mo resemble a distorted tetrahedron and octahedron, respectively (Fig. 3). Pertinent interatomic bond distances and angles are collected in Table 2. The co-ordination of the $Mo(CO)_5$ unit to only one of the tin atoms [Sn(1)] has an influence on the second metal centre and changes in the geometric parameters are observed: (*i*) loss of centrosymmetry in the Sn_2O_2 oxametallacycle; (*ii*) an increase in the endocyclic bond lengths at Sn(2) [Sn(2)–O(1) 2.164(2) and Sn(2)–O(2) 2.171(3) Å] by ≈0.08 Å compared to Sn(1) due to the withdrawal of the non-bonding lone pair of electrons present at the opposite tin [Sn(1)] by the pentacarbonylmolybdenum(0) acceptor; (*iii*) an increase in the coplanarity of bridging oxygens of the two *tert*-butoxy groups by ≈2° with reference to the precursor molecule **2** further accounting for the change in the conformation of the *tert*-butoxy groups to an eclipsed position from staggered in **2**; (*iv*) a new orientation of the $OSi(1)Ph_3$ group with respect to the plane of the Sn_2O_2 ring [O(3)–Sn(1)–O(1) 96.32(10), O(4)–Sn(2)–O(1) 92.42(10)°] and an increase in the Sn(1)–O(3)–Si(1) bond angle to 155.5(2) from 149.4(2)° [Sn(2)–O(4)–Si(2)].

Table 2 Selected bond distances (Å) and angles (°) for compound **5** with e.s.d.s in parentheses

Sn(1)–O(3)	1.968(2)	Sn(1)–O(1)	2.083(2)
Sn(1)–O(2)	2.088(3)	Sn(1)–Mo	2.7449(6)
Sn(2)–O(4)	2.000(3)	Sn(2)–O(1)	2.164(2)
Sn(2)–O(2)	2.171(3)	Mo–C(49A)	1.933(11)
Mo–C(48)	2.012(3)	Mo–C(49B)	2.009(10)
Mo–C(46)	2.018(7)	Mo–C(47)	2.044(5)
Mo–C(45)	2.046(5)		
O(3)–Sn(1)–O(1)	96.32(10)	O(3)–Sn(1)–O(2)	94.91(10)
O(1)–Sn(1)–O(2)	74.80(9)	O(3)–Sn(1)–Mo	112.90(8)
O(1)–Sn(1)–Mo	132.20(6)	O(2)–Sn(1)–Mo	134.78(7)
O(4)–Sn(2)–O(1)	92.42(10)	O(4)–Sn(2)–O(2)	90.75(10)
O(1)–Sn(2)–O(2)	71.51(8)	C(49A)–Mo–C(48)	78.2(4)
C(48)–Mo–C(49B)	98.4(4)	C(49A)–Mo–C(46)	99.0(4)
C(48)–Mo–C(46)	177.1(2)	C(49B)–Mo–C(46)	78.7(3)
C(49A)–Mo–C(47)	85.6(3)	C(48)–Mo–C(47)	91.4(2)
C(49B)–Mo–C(47)	90.6(3)	C(46)–Mo–C(47)	89.0(2)
C(49A)–Mo–C(45)	92.1(3)	C(48)–Mo–C(45)	86.4(2)
C(49B)–Mo–C(45)	87.9(3)	C(46)–Mo–C(45)	93.1(2)
C(47)–Mo–C(45)	177.1(2)	C(49A)–Mo–Sn(1)	169.3(4)
C(48)–Mo–Sn(1)	95.0(2)	C(49B)–Mo–Sn(1)	166.3(3)
C(46)–Mo–Sn(1)	87.8(2)	C(47)–Mo–Sn(1)	86.33(12)
C(45)–Mo–Sn(1)	95.73(12)	O(3)–Si(1)–C(9)	109.2(2)
O(3)–Si(1)–C(15)	112.62(14)	O(3)–Si(1)–C(21)	108.6(2)
O(4)–Si(2)–C(33)	108.3(2)	O(4)–Si(2)–C(27)	110.2(2)
O(4)–Si(2)–C(39)	109.4(2)	Sn(1)–O(1)–Sn(2)	106.88(9)
Sn(1)–O(2)–Sn(2)	106.41(10)	Si(1)–O(3)–Sn(1)	155.5(2)
Si(2)–O(4)–Sn(2)	149.4(2)		

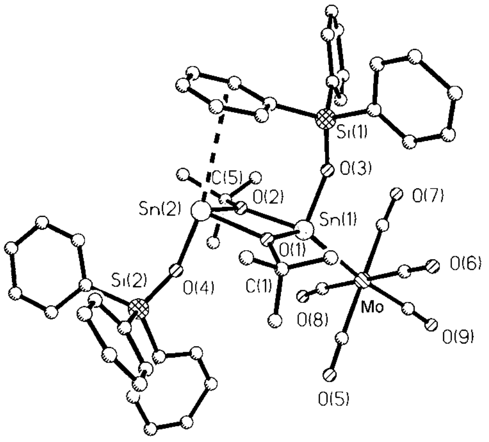


Fig. 3 Ball-and-stick representation of the molecular structure of $[\{Sn(\mu\text{-}OBu^t)(OSiPh_3)\}_2Mo(CO)_5]$ **5**, showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity. The dotted line shows the tin(II)–arene (centre of the ring) interaction

The short, long, short Sn–Mo–C–O bond-distance sequence of the carbonyl group *trans* to the Sn–Mo bond reflects a strong p_π–d_π co-ordination of Mo to Sn. The Sn(1)–Mo bond distance of 2.7449(6) Å in compound **5** is slightly longer than normal indicating a weaker bonding between the two metals. The strong back bonding from Mo to C(49) is supported by the shorter *trans* Mo–C(9) (average 1.96 Å) and longer C(49)–O(49) (average 1.18 Å) bond distances than to the *cis* CO groups (averages: Mo–C 2.03, C–O 1.15 Å). Similar trends in bond lengths are observed in the crystal structures of $[Tl(\mu\text{-}OBu^t)_3Sn\text{–}Mo(CO)_5]$ and $[(OC)_5Mo\text{–}In(\mu\text{-}OBu^t)_3Sn\text{–}Mo(CO)_5]$.[19] The phenyl rings of the $OSiPh_3$ groups are twisted relative to each other as observed in **1** and **2**. One lies just over the Sn(2) centre and the long distance of 3.58 Å between the centroid of the phenyl ring and Sn(2) is however shorter than the sum of van der Waals radii of 4.0 Å[20] indicating a weak interaction. This value is comparable to that observed in ionic tin(II) compounds of the type $[Sn(RH)Cl][AlCl_4]$ (RH = benzene, toluene, xylene or mesitylene)[20] (2.90–3.39 Å) when the tin in cationic form is neglected and is considered to be covalently bonded. Also, a closer look at the terminal Sn–O bond lengths of **5** shows that the long Sn(2)–O(4) bond distance of 2.000(3) Å as compared to Sn(1)–O(3) [1.968(2) Å] is not consistent with the lower co-ordination number at Sn(2) (if co-ordination of the arene ring is not considered). Further, in the absence of a tin(II)–arene interaction, the terminal Sn(2)–O(4) bond distance is expected to be comparable with the Sn–O(2) distances in the precursor molecule **2.** However, a considerable lengthening [2.000(3) Å in **5** against 1.949(5) Å in **2**] supports an effective interaction of the π-electronic cloud of the phenyl ring with the Sn^{II} atom. The Si–C (average 1.87 Å) and Si–O (1.60 Å) bond lengths are typical of their types.

Spectroscopic properties

NMR. At ambient temperatures, $CDCl_3$ solutions of compounds **1**–**3** exhibit only one set of signals for the *tert*-butoxy and phenyl groups in the ^1H and ^{13}C NMR spectra, indicating high symmetry in solution along with the presence of monosubstituted phenyl rings. The 1:1 stoichiometry of the *tert*-butoxide to siloxide is confirmed by integration of ^1H NMR spectra. A relatively upfield shift of ≈0.30 ppm for the bridging *tert*-butoxy groups with reference to $[\{M(OBu^t)_2\}_n]$, (δ 1.44) is evidence in support of the influence of the phenyl ring currents. Although single resonances for the OBu^t groups are observed in the ^1H and ^{13}C NMR spectra of compounds **4** and **5**, the ^{13}C NMR spectra of the phenyl region show two sets of the expected four-peak pattern indicating two different types of environment for the phenyl rings. The carbonyl groups in the ^{13}C NMR spectrum of **5** are observed as three resonances at δ 210.1, 205.5 and 204.9 in the intensity ratio 1:3:1, presumably due to a restricted motion of the carbonyl groups.

Silicon-29 NMR spectroscopy has recently been proved to be a suitable tool for solution dynamics and in describing the shape of co-ordination polyhedra around silicon for a large number of metal siloxides.[4] The ^{29}Si NMR spectra of compounds **1** and **2** give single sharp resonances at δ −22.09 and −22.95, respectively corresponding to the presence of terminal siloxides. However, the appearance of two distinct singlets each in the ^{29}Si and ^{207}Pb NMR spectra of **3** at δ −21.14, −13.49 and +800.04, 880.95, respectively, in an integrated ratio of *ca.* 1:2 shows the compound to be stereochemically rigid with the possibility of *cis* and *trans* conformers in solution. An associative–dissociative equilibrium for **3** in solution can be discounted as the difference in the two chemical shift values in the ^{207}Pb NMR spectrum is less (keeping in mind the wide chemical shift dispersion) than would occur upon a change in the co-ordination number of lead. The presence of two magnetically inequivalent $OSiPh_3$ groups in compounds **4** and **5** is consistent with the observation of two signals each in the ^{29}Si spectra.

The chemical shift value of δ −225.79 in the ^{119}Sn NMR spectrum of compound **2** is in the region characteristic of three-co-ordinate tin(II).[21] The resonance at δ −263.32 in the spectrum of **5** also indicates the presence of three-co-ordinate Sn^{II} and the relatively upfield chemical shift of δ −24.13 is consistent with co-ordination of the $Mo(CO)_5$ unit to the second Sn^{II} atom.

IR. The IR spectra of all the compounds recorded as $CDCl_3$ solutions show intense absorption bands corresponding to aromatic ν(CH) and ν(OSi) modes near 3070, 3050 and 1080 and 950 cm^{-1}, respectively. Overtone patterns between 1959 and 1824 cm^{-1} are also observed for the monosubstituted aromatics. No high-frequency ν(OH) bands are found. The aliphatic ν(C–H) and bridging ν(C–O) stretching frequencies are assigned near 2930 and 1115 cm^{-1}, respectively. Additionally, compounds **4** and **5** exhibited an intense and a broad absorption band corresponding to the A_1 [2065 (**4**), 2077 cm^{-1} (**5**)] and A_1 + E modes [1965 (**4**), 1959 cm^{-1} (**5**)] of carbonyl stretching of an $Mo(CO)_5L$ (L = ligand) system[19] having local C_{4v} symmetry.

Table 3 Crystallographic data, data-collection and refinement parameters for compounds **1**, **2** and **5**

	1	**2**	**5**
Formula	$C_{44}H_{48}Ge_2O_4Si_2$	$C_{44}H_{48}O_4Si_2Sn_2$	$C_{49}H_{48}MoO_9Si_2Sn_2$
M	842.18	934.38	1170.37
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	9.055(12)	9.056(7)	19.797(4)
b/Å	9.647(13)	9.658(8)	17.894(4)
c/Å	13.62(2)	13.712(10)	14.781(3)
α/°	98.62(11)	98.49(6)	90
β/°	100.39(11)	100.10(6)	94.51(3)
γ/°	110.91(10)	109.74(6)	90
U/Å^3	1063(2)	1083.4(14)	5220(2)
Z	1	1	4
Crystal size/mm	0.5 × 0.4 × 0.35	0.5 × 0.4 × 0.1	0.3 × 0.28 × 0.2
D_c/Mg m^{-3}	1.308	1.432	1.489
F(000)	436	472	2336
θ scan range/°	1.56–22.50	1.55–22.50	2.28–24.16
Reflections collected	2786	2843	32 923
Independent reflections	2786	2843	8234
Observed reflections	2668	2531	7363
Final R indices [$I > 2\sigma(I)$]	0.0331	0.0590	0.0322
(all data)	0.0349	0.0652	0.0369
Goodness of fit	1.154	1.315	1.026
Largest difference peak and hole/e Å^{-3}	0.723, −0.470	0.991, −1.917	0.512, −0.755

All these spectral data are consistent with the formulations of the compounds and the solid-state structures of **1**, **2** and **5**.

Conclusion

This study illustrates that monosubstitution of the *tert*-butoxide ligand of $[\{M(OBu^t)_2\}_n]$ (M = Sn or Ge, $n = 2$; M = Pb, $n = 3$) by a triphenylsiloxide ligand can be used as an effective method in the synthesis of mixed-ligand compounds $[\{M(\mu\text{-}OBu^t)(OSiPh_3)\}_2]$ containing both ancillary alkoxide and siloxide ligands. The preferential bridging nature of alkoxides over siloxides as observed in the structures of these compounds reinforces the expected weak basicity of siloxides, although bridging of each has been observed in a large number of corresponding homoleptic compounds. This newly isolated class of mixed-ligand dimers functions as soft ligands and undergoes selective co-ordination of pentacarbonylmolybdenum(0) to only one of the metal(II) (Sn^{II} or Ge^{II}) centres of the dimeric unit to form a bimetallic heterosiloxane cluster containing an M−Mo bond. These heterosiloxanes seem relevant to the growing interest in M−O−Si systems which have been used in the preparation of mixed-metal solid-state materials and polymetallic siloxide aggregates. Further, metal siloxides are often obtained as solvent adducts which lead to a high percentage of carbonaceous impurity in ceramic processing and the solvent-free state of these new heterosiloxanes may be advantageous in sol–gel processing.

Experimental

Materials and physical measurements

All manipulations with reagents, the syntheses and spectroscopic measurements were carried out under anaerobic and anhydrous conditions in a dinitrogen atmosphere. Toluene, hexane and diethyl ether were distilled from sodium–benzophenone immediately before use. The compounds Ph_3SiOH and $[Mo(CO)_6]$ were obtained commercially (Aldrich). The *tert*-butoxides of Sn^{II}, Ge^{II} and Pb^{II} were synthesized by literature methods.[17] The NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC-200 spectrometer (^1H, 200.13; ^{13}C, 50.3; ^{29}Si, 39.7; ^{119}Sn, 74.6; ^{207}Pb, 41.8 MHz), ^1H and ^{13}C referenced internally to the residual $CDCl_3$ undeuteriated solvent, ^{29}Si, ^{119}Sn and ^{207}Pb externally to $SiMe_4$, $SnMe_4$ and $Pb(NO_3)_2$, respectively. An inverse-gated decoupling routine was used to record the ^{29}Si NMR spectra and an acquisition time of 4–6 h was necessary to obtain acceptable spectra. The IR spectra were obtained on a Bio-Rad FTS-165 spectrophotometer. Carbon and hydrogen combustion analyses were obtained by using a LECO CHN 900 elemental analyser. The contents of Sn and Pb were estimated by standard analytical procedures.[22]

Syntheses

Compound 1. In a typical experiment, Ph_3SiOH (0.79 g, 2.85 mmol) and $[\{Ge(OBu^t)_2\}_2]$ (0.63 g, 2.87 mmol) were dissolved in toluene (15 cm^3). The colourless solution was stirred overnight at room temperature. After the removal of solvent under reduced pressure the resulting white powder was redissolved in hot toluene. Slow cooling over 24 h to 0 °C gave prismatic colourless crystals suitable for X-ray diffraction studies. Yield 1.01 g, 83.4% (Found: C, 62.7; H, 5.7. Calc. for $C_{44}H_{48}Ge_2O_4Si_2$: C, 62.75; H, 5.75%). NMR (296 K, $CDCl_3$): ^1H, δ 7.73–7.69, 7.38–7.31 (br m, 15 H, Ph) and 1.14 (s, 9 H, OBu^t); ^{13}C, δ 138.2 (*ipso*), 135.4 (*ortho*), 129.4 (*para*), 127.7 (*meta*) (Ph), 78.1 (OBu^t) and 31.8 (OBu^t); ^{29}Si, δ −22.09. IR ($CDCl_3$, cm^{-1}): no ν(OH); ν(CH) 3070, 3050, 2955 and 2926; aromatic overtones at 1960, 1895 and 1826; other bands at 1115, 1086, 965, 700, 608 and 515.

Compounds **2** and **3** were prepared analogously. Colourless crystals of **2** were obtained by cooling a toluene–diethyl ether (1 : 1) solution at 0 °C for 24 h. Yield 0.8 g, 77.6% (Found: C, 56.4; H, 5.15; Sn, 25.2. Calc. for $C_{44}H_{48}O_4Si_2Sn_2$: C, 56.55; H, 5.15; Sn, 25.4%). NMR (296 K, $CDCl_3$): ^1H, δ 7.67–7.63, 7.34–7.30 (br m, 15 H, Ph) and 1.16 (s, 9 H, OBu^t); ^{13}C, δ 139.7 (*ipso*), 135.3 (*ortho*), 129.1 (*para*), 127.6 (*meta*) (Ph), 76.09 (OBu^t) and 33.7 (OBu^t, $^3J = 10$ Hz); ^{29}Si, δ −22.95; ^{119}Sn, δ −225.79. IR ($CDCl_3$, cm^{-1}): no ν(OH); ν(CH) 3070, 3050, 2958 and 2928; aromatic overtones at 1958, 1875 and 1826; other bands at 1114, 1080, 962, 735, 610 and 515.

Compound **3** was purified by cooling its diethyl ether solution at −20 °C upon which ivory crystals precipitated. Yield 1.1 g, 72% (Found: C, 47.35; H, 4.3; Pb, 37.0. Calc. for $C_{44}H_{48}O_4Pb_2Si_2$: C, 47.45; H, 4.35; Pb, 37.2%). NMR (296 K, $CDCl_3$): ^1H, δ 7.71–7.48, 7.42–7.04 (br m, 15 H, Ph) and 1.13 (br s, 9 H, OBu^t); ^{13}C, δ 140.1 (*ipso*), 135.3 (*ortho*), 129.2 (*para*), 127.8 (*meta*) (Ph), 71.6 (OBu^t) and 35.9 (OBu^t); ^{29}Si, δ −21.14 and −13.49; ^{207}Pb, δ 880.95 and 800.04. IR ($CDCl_3$, cm^{-1}): no ν(OH); ν(CH) 3067, 3050, 2954 and 2928; aromatic overtones at 1959, 1890 and 1824; other bands at 1186, 1080, 958, 732, 610 and 522.

Compounds 4 and 5. As both compounds were prepared by the same procedure, only the experimental details of **5** are given. To a toluene solution of **2** (0.53 g, 1.13 mmol) was added $[Mo(CO)_6]$ (0.30 g, 1.13 mmol). Warming the reaction mixture to reflux for 72 h yielded a yellow solution. The solvent was then removed *in vacuo* and the residue treated with hexane–diethyl ether (1 : 1). Subsequent storage at room temperature for 48 h produced yellow crystals of **5** (0.8 g, 68.3%) (Found: C, 49.85; H, 4.05; Sn, 20.2. Calc. for $C_{49}H_{48}MoO_9Si_2Sn_2$: C, 50.3; H, 4.15; Sn, 20.3%). NMR (296 K, $CDCl_3$): ^{1}H, δ 7.58–7.47, 7.22–7.20 (br m, 30 H, Ph), 1.12 (s, 18 H, OBu^t); ^{13}C, δ 210.1, 205.5, 204.9 (CO), 138.9, 138.4 (*ipso*), 135.4, 135.2 (*ortho*), 129.5, 129.4 (*para*), 127.8 (*meta*) (Ph), 78.7 (OBu^t) and 33.3 (OBu^t); ^{29}Si, δ −21.71 and −20.75; ^{119}Sn, δ −263.32 ($^2J = 92$) and −24.13 ($^1J = 73$ Hz). IR ($CDCl_3$, cm^{-1}): no ν(OH); ν(CH) 3070, 3053, 2975 and 2928; ν(CO) 2077s and 1959 (vbr); other bands at 1114, 1082, 979, 880, 741, 584 and 513.

Compound **4** was purified from a toluene–hexane solution as a light brown solid. Yield 0.8 g, 52% (Found: C, 54.45; H, 4.4. Calc. for $C_{49}H_{48}Ge_2MoO_9Si_2$: C, 54.6; H, 4.5%). NMR (296 K, $CDCl_3$): ^{1}H, δ 7.41–7.34, 7.22–7.09 (br m, 30 H, Ph) and 1.05 (s, 18 H, OBu^t); ^{13}C, δ 219.1, 215.2, 214.3 (CO); 138.8, 138.4 (*ipso*), 135.5, 135.3 (*ortho*), 129.7, 129.2 (*para*), 127.7 (*meta*) (Ph), 78.2 (OBu^t) and 31.6 (OBu^t); ^{29}Si, δ −21.82 and −20.52. IR ($CDCl_3$, cm^{-1}): no ν(OH); ν(CH) 3070, 3052, 2978 and 2935; ν(CO) 2065s and 1965 (vbr); other bands at 1115, 1085, 975, 874, 732, 582 and 532.

Crystallography

All X-ray experiments were carried out at room temperature on a Siemens Stoe AED 2 diffractometer (compounds **1** and **2**) or a Stoe IPDS image-plate system (**5**) equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) operating in the ω–θ mode (in the case of **1** and **2**) or *via* image plate (**3**). The general procedure was as follows. A suitable crystal was selected from the bulk sample, mounted under N_2 in a random orientation in a quartz capillary, flame sealed and then transferred to the goniometer head of the diffractometer. The unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three standard reflections were chosen as intensity standards and measured every 90 min of X-ray exposure time (in the case of **1** and **2**) while in the case of **5** 50–200 control reflections were observed. Data were corrected for Lorentz-polarization effects and absorption (empirical, **1**; numerical, **5**); no absorption correction was made in the case of **2**. The structures were solved by direct methods[23] (SHELXS 86) and refined[24] by full-matrix least squares on F^2 (SHELXL 93) using anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were treated as idealized contributions. The carbon [C(49)] and the oxygen [O(9)] atoms of a carbonyl group of compound **5** were found to be disordered (Table 2). Details of the structural solution and refinement for compounds **1**, **2** and **5** are shown in Table 3.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/390.

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