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Synthesis of metallasiloxanes of group 13–15 and their application in catalysis†

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Received 30th May 2013,
Accepted 4th July 2013

DOI: 10.1039/c3dt51408k

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Herein we report on the synthesis, characterization and catalytic application of metallasiloxanes of group 13–15. Reactions of $R(Me)Si(OH)_2$ (R = $N(SiMe_3)$-2,6-$iPr_2C_6H_3$) (**A**) with $Bi(NEt_2)_3$, $Sb(NEt_2)_3$, $Ge[N(SiMe_3)_2]_2$ and $AlMe_3$ afforded $[R(Me)SiO_2BiNEt_2]_2$ (**1**), $[R(Me)SiO_2SbOSi(OH)(Me)R]_2$ (**2**), $[R(Me)SiO_2]_3(GeH)_2$ (**3**), and $[R(Me)SiO_2AlMe(THF)]_2$ (**4**), respectively. Reactions of $RSi(OH)_3$ (**B**) with $Bi(NEt_2)_3$ and $AlMe_3$ produced complexes $(RSiO_3Bi)_4$ (**5**) and $(RSiO_3)_2[AlMe(THF)]_3$ (**6**). Compounds **1–6** have been characterized by IR and NMR spectroscopy, single crystal X-ray structure and elemental analysis. Each of the compounds **1**, **2** and **4** features an eight-membered ring of composition $Si_2O_4Bi_2$, $Si_2O_4Sb_2$ and $Si_2O_4Al_2$, while **3** and **6** exhibit a bicyclic structure with the respective skeletons of $Si_3O_6Ge_2$ and $Si_2O_6Al_3$. Compound **5** has a cubic core of $Si_4O_{12}Bi_4$. Compounds **1–6** exhibit very good catalytic activity in the addition reaction of trimethylsilyl cyanide (TMSCN) with benzaldehyde. Compound **5** was found to be the best catalyst and its activity was probed in the reactions of TMSCN with a number of aldehydes and ketones.

Introduction

In recent years, metallasiloxanes derived from organic silanols have attracted considerable interest because they act as structural models for the naturally occurring metallasilicates, synthetic metal-containing zeolites,[1] and for the heterogeneous silica-supported transition metal catalysts.[2] Interestingly, some of the transition metal-containing siloxanes have been proved to act as catalysts for reactions such as alkene polymerization,[3] metathesis,[4] epoxidation,[5] hydroformylation,[6] and specified Diels–Alder reactions[7] with both homogeneous and heterogeneous applicability. So far, a considerable number of such siloxane complexes including main group elements and transition metals have been synthesized and structurally characterized.[8–10] However, investigations of the catalytic properties of these complexes are still scarce. Recently, we have shown the use of silanetriol $RSi(OH)_3$ (R = $N(SiMe_3)$-2,6-$iPr_2C_6H_3$)[11] as a precursor for the preparation of copper(I) siloxane, $[RSi(OCu)_3]_8$, which features a 56-membered core that resembles a metal-anchored silica-supported material. This compound exhibits good to excellent activity for catalyzing the homogeneous Ullmann–Goldberg-type C–N cross-coupling reaction of aryl or 2-thienyl bromides with heterocyclic nitrogen containing nucleophiles.[12] However, so far only a few $RSi(OH)_3$-derived main group metal compounds have been reported.[14] The use of $R(Me)Si(OH)_2$ for the synthesis of related siloxanes is much less reported although other organosilanediol-derived complexes have been documented.[15] Herein we report on the reactions of $R(Me)Si(OH)_2$[13] and $RSi(OH)_3$ to produce main group metallasiloxanes. A series of bismuth, antimony, germanium and aluminum siloxanes (**1–6**) exhibiting the ring and cage structures have been prepared and characterized. Furthermore, compounds **1–6** show good catalytic activity for the addition reaction of trimethylsilyl cyanide to aldehydes and ketones.

Results and discussion

Synthesis and spectroscopic characterization

The reaction of $R(Me)Si(OH)_2$ (**A**) with $Bi(NEt_2)_3$ in a molar ratio of 2 : 2 proceeded smoothly in toluene in a temperature range of −20 to 25 °C to afford $[R(Me)SiO_2BiNEt_2]_2$ (**1**). Under similar conditions, **A** reacted with $Sb(NEt_2)_3$ in a molar ratio of

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†Electronic supplementary information (ESI) available: Tables of crystal data and structure refinement of compounds **1–6**. Experimental procedures of the catalysis and the NMR (^1H, ^{13}C, and ^{29}Si) data of the catalytic reaction products. Additional experimental details and discussions. CCDC 941559–941564. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51408k

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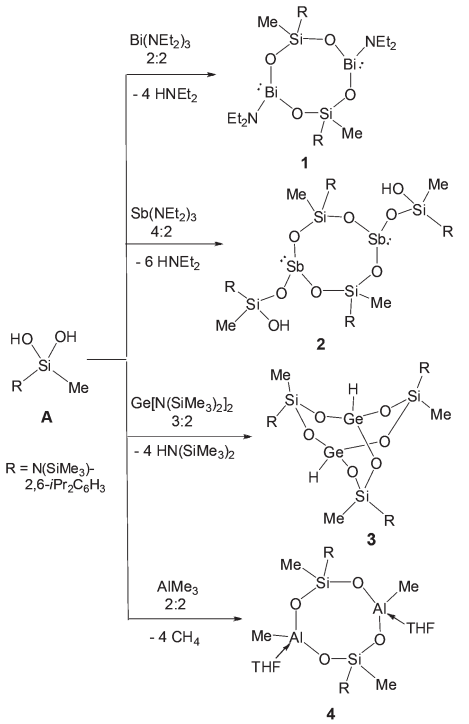

Scheme 1 Synthesis of compounds **1–4**.

4 : 2 in *n*-hexane to afford $[R(Me)SiO_2SbOSi(OH)(Me)R]_2$ (**2**) (Scheme 1). From these results, it can be shown that compound **1** is formed under the elimination of four molecules of $HNEt_2$ leaving one NEt_2 group intact at each of the Bi atoms. Compound **2** may be generated by an intermediate $[R(Me)SiO_2SbNEt_2]_2$ in a similar way to that of **1**. Our attempts to isolate $[R(Me)SiO_2BiOSi(OH)(Me)R]_2$ or $[R(Me)SiO_2SbNEt_2]_2$ were not successful, but the stoichiometries given in Scheme 1 are important to achieve high yields of **1** and **2**.

Compounds **1** and **2** were isolated as light-yellow crystals with the respective yields of 81% and 65%, which are moisture-sensitive but stable under inert atmosphere (Ar or N_2). The ^{1}H NMR spectrum of **1** shows two quartet resonances (δ 4.21 and 4.07 ppm) for the methylene protons of the $BiNEt_2$ group and one triplet resonance (δ 1.17 ppm) for the methyl protons. This noticeable difference in the chemical shifts between the methylene and methyl protons is mainly attributed to the presence of a lone pair of electrons at the Bi center, which greatly affects the adjacent methylene proton resonances rather than the remote methyl ones. ^{1}H NMR measurement of **1** in C_6D_6 between 20 and 80 °C clearly shows the coalescence of methylene proton resonances. This implies a faster rotation of the two ethyl groups about the Bi–N bond at elevated temperatures. The two singlet resonances found at higher field (δ 0.29 and 0.42 ppm) are assigned for the $SiMe_3$ and O_2SiMe groups, respectively. The ^{29}Si NMR spectrum shows the silicon resonances for these two groups at δ 1.97 and −42.70 ppm. The latter value is typical of the resonance for oxygen bound silyl groups.[9] Compound **2** exhibits two distinguishable sets of ^{1}H NMR resonances for the bridged $R(Me)SiO_2$ moiety and the terminal RSiMe(OH)O group (for $R(Me)SiO_2$: δ 0.08 (Si*Me*$_3$), −0.10 (Si*Me*O_2), 4.84 (*Si*Me_3), −40.51 (*Si*MeO_2); for RSiMe(OH)O: δ 0.09 (Si*Me*$_3$), 0.23 (Si*Me*(OH)O), 7.02 (*Si*Me_3), −33.33 ppm (*Si*Me(OH)O)).[16] The SiOH proton resonance (RSiMe(O*H*)O) is not observed in the ^{1}H NMR spectrum of **2**. However, **2** exhibits in the IR spectrum an absorption band found at ν 3647 cm^{-1} that clearly indicates the SiOH stretching frequency.

The reaction of **A** with $Ge[N(SiMe_3)_2]_2$ in toluene (−20 to 25 °C) gave a germanium(IV) hydride siloxane $[R(Me)SiO_2]_3(GeH)_2$ (**3**) in 78% yield, whereas the corresponding reaction with $AlMe_3$ in THF produced $[R(Me)SiO_2AlMe(THF)]_2$ (**4**) (73% yield) (Scheme 1). The production of **3** involves the oxidation of Ge(II) to Ge(IV) and simultaneously the reduction of a proton of **A** to hydride. Similar compound $(RSiO_3GeH)_4$ has been reported in 2005 from the reaction of $RSi(OH)_3$ with $Ge[N(SiMe_3)_2]_2$.[17] Furthermore, the oxidative addition of an alcohol to an alkylgermanium(II) compound is also known.[18] The formation of **4** resembles that of **1**. However, CH_4 is eliminated instead of $HNEt_2$. The coordination of the THF at the Al center stabilizes **4** and the approach of a THF-free **4** in toluene or *n*-hexane was not successful. Moreover, heating **4** under vacuum to remove the coordinated THF resulted in the decomposition of **4**.

Compounds **3** and **4** are stable under an inert atmosphere (N_2 and Ar) but are moisture-sensitive. The ^{1}H NMR spectrum of **3** exhibits a singlet resonance (δ 6.24 ppm) for the GeH moiety and a characteristic stretching frequency (ν 2135 cm^{-1}) in the IR spectrum. These spectroscopic data are comparable to those found in $(RSiO_3GeH)_4$ (δ 5.83 ppm, ν_{GeH} 2211 and 2184 cm^{-1}),[17] $N(CH_2CH_2O)_3GeH$ (δ 5.77 ppm)[19a,b] and $Ar_2Ge(H)R$ (Ar = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$, R = CN, F, N_3, $(OH_2)(SO_3CF_3)$: δ 5.42–6.79 ppm, ν_{GeH} 2117–2146 cm^{-1}).[19c] In the ^{1}H NMR spectrum of **4**, two multiplets (δ 3.58 and 1.76 ppm) are assigned for the coordinated THF molecules. The AlMe methyl protons resonate at a higher field (δ −1.06 ppm) when compared with those of $SiMe_3$ (δ −0.02 ppm) and $SiMeO_2$ (δ 0.06 ppm). The ^{29}Si NMR spectrum of **4** displays two resonances (δ 0.75 and −52.26 ppm) for the $SiMe_3$ and $SiMeO_2$ groups, respectively.

For the synthesis of the metallasiloxanes with three-dimensional structures aminosiloxanetriols are used as building blocks.[8a,b] The aminosiloxanetriol $RSi(OH)_3$ (**B**) was utilized for the preparation of germanium $(RSiO_3GeH)_4$[17] and antimony $(RSiO_3Sb)_4$[20] complexes. A bismuth compound of composition $(RSiO_3)_8Bi_{12}(\mu_3\text{-}O)_4Cl_4(THF)_8$ was obtained by refluxing $RSi(OH)_3$ with $Bi(NMe_2)_3/Bi(NMe_2)_2Cl$.[20] Herein, we report on the reaction of $RSi(OH)_3$ with $Bi(NEt_2)_3$ in toluene to yield compound $(RSiO_3Bi)_4$ (**5**) under elimination of $HNEt_2$ (Scheme 2). Although a series of alumosiloxane derivatives have been reported, we tried the reaction of **B** with $AlMe_3$ in a molar ratio of 2 : 3. As a result, a bicyclic compound $(RSiO_3)_2[AlMe(THF)]_3$ was obtained (**6**, Scheme 2). **6** exhibits a unique structure among the known ring- $[R(HO)SiO_2Al\mathit{t}Bu(THF)]_2$,[14a] cube- $(R'SiO_3AlS)$ (R′ = $N(SiMe_3)$-2,4,6-$Me_3C_6H_2$, $N(SiMe_3)$-2,6-$Me_2C_6H_3$, $N(SiMe_3)$-2,6-$Et_2C_6H_3$, $N(SiMe_3)$-2,6-$iPr_2C_6H_3$,

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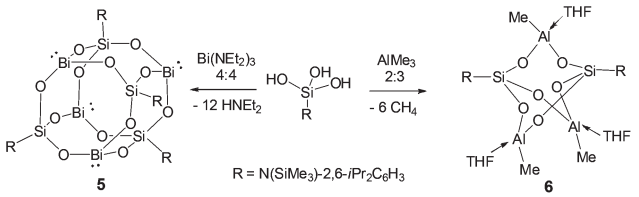

Scheme 2 Synthesis of compounds **5** and **6**.

$CCo_3(CO)$;[9] S = 1,4-dioxane, THF, $N(CH_2CH_2)_3N$),[6,11,16,21] and drum-like $(R''SiO_3)_2AltBu(AltBu_2)$ (R'' = $N(SiMe_3)$-2,4,6-$Me_3C_6H_2$, $N(SiMe_3)$-2,6-$Me_2C_6H_3$, $N(SiMe_3)$-2,6-$iPr_2C_6H_3$)[14a,16a] compounds so far isolated.

Compounds **5** and **6** were isolated as colorless crystalline solids in 90% and 89% yield, respectively. Compound **6** is moisture-sensitive, while **5** is more stable in open air without decomposition within one day. The ^{1}H NMR spectrum of **5** exhibits one septet and two doublets typical of the isopropyl methine and methyl protons at R (δ 3.90 (C*H*Me$_2$), 1.36 and 1.28 ppm (CH*Me*$_2$)) as well as one singlet (δ 0.35 ppm (Si*Me*$_3$)). The ^{29}Si NMR spectrum shows two resonances (δ 2.42 and −79.12 ppm) corresponding to the $SiMe_3$ and SiO_3 groups, respectively. In compound **6**, the resonance of methyl protons of AlMe is observed at higher field (δ −1.03 ppm) when compared with that of the $SiMe_3$ (δ −0.09 ppm). The ^{29}Si NMR spectrum of **6** displays two resonances (δ 0.99 and −79.96 ppm) for the $SiMe_3$ and SiO_3 groups.

Single crystal X-ray structures of 1–6

X-ray quality single-crystals of **1** and **4–6** were obtained by crystallization at low temperature (−20 °C), where **5** co-crystallized with one molecule of toluene and half a molecule of *n*-hexane and **6** with one molecule of THF. The crystals of **2** and **3** were obtained by slow evaporation under an inert atmosphere (Ar). The structural analyses unambiguously confirm that compounds **1**, **2** and **4** each feature a cyclic structure with a metal-anchored eight-membered ring core of $Si_2O_4M_2$ (M = Bi, **1**; Sb, **2**; Al, **4**). Compounds **3** and **6** adopt a bicyclic structure with the respective skeleton cores of $Si_3O_6Ge_2$ and $Si_2O_6Al_3$, whereas compound **5** has a cage structure with a cubic core of $Si_4O_{12}Bi_4$. The crystal structures of **1**, **3**, **5** and **6** are shown in Fig. 1–4, respectively. The single crystal structure plots of **2** and **4** are added to the ESI.†

The cores of **1–6** show the silicon atom in a tetrahedral geometry, while in **1**, **2** and **5** the Bi and Sb atoms are three-coordinate with the sum of the peripheral angles of 275.8(4)° in **1**, 282.01(9)° in **2** and of 278.8(3)–305.3(3)° in **5**. These angles are close to 270°, which suggests that each Bi or Sb center adopts a trigonal-pyramidal geometry with a lone pair of electrons in the apex.[22] It is interesting to note that the distances between the metal center and the adjacent aryl ring from the R group or the co-crystallized toluene molecule (M···arene$_{centroid}$) are found of 3.321 Å (for aryl group at R) in **1**, 3.312 Å (for aryl group at R) in **2**, and 3.225–3.273 Å (for aryl group at R and toluene) in **5**. These distances are comparable to those found in $[(Ph_2tBuSiO)_3Bi]_2$ (3.340 Å)[23a] and $[(2\text{-Cl-}C_6H_4CH_2)_3Bi]_2$ (3.659 Å),[23b] suggesting the presence of the bismuth(III) and antimony(III)···arene π-interactions that have been extensively documented in the literature.[24] In the structures of **4** and **6**, each Al center is four-coordinate in a distorted tetrahedral geometry. These structures fit well to the Loewenstein rule, one of the fundamental principles applicable to the structures of

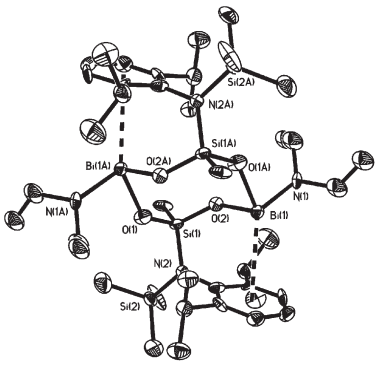

Fig. 1 Thermal ellipsoid (50%) drawing of **1**. The H atoms are omitted for clarity. Bi···arene$_{centroid}$: 3.321 Å.

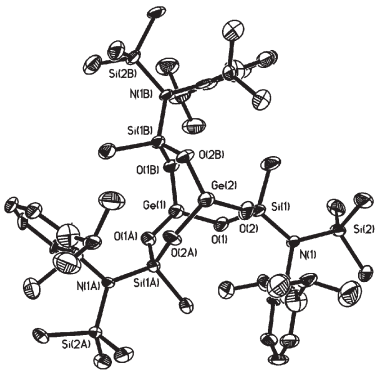

Fig. 2 Thermal ellipsoid (30%) drawing of **3**. The GeH hydrogen atom is not able to be located by difference Fourier synthesis and other hydrogen atoms are omitted for clarity.

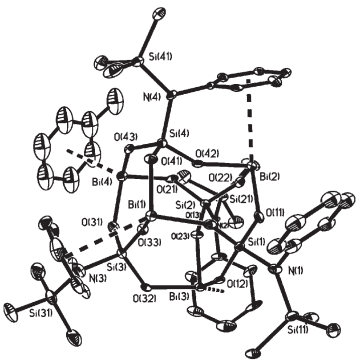

Fig. 3 Thermal ellipsoid (30%) drawing of **5**. The iPr groups of the *N*-aryl substituents and H atoms are omitted for clarity. Bi···arene$_{centroid}$: 3.225, 3.252, and 3.273 Å (for aryl at R); 3.227 Å (for toluene).

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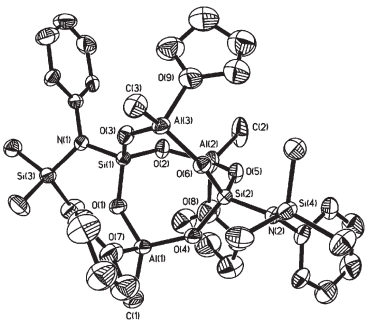


Fig. 4 Thermal ellipsoid (50%) drawing of **6**. The iPr groups of the *N*-aryl substituents and H atoms are omitted for clarity.

aluminosilicate solids, which states that the Si and Al geometric tetrahedrons must be linked by one oxygen bridge.[25,26] In the structure of **3**, the H atom at the Ge center could not be located from difference Fourier synthesis. Nevertheless, the presence of the GeH functionality has been unambiguously evidenced by IR and NMR spectroscopy. In addition, the geometric features with respect to the Ge–O bond lengths (1.717(6)–1.738(7) Å) and the sum of the O–Ge–O angles (328.5(3)–331.5(4)°) are comparable to those found in $(RSiO_3GeH)_4$ (Ge-O, 1.737(1)–1.742(1) Å; the sum of the O–Ge–O angles ranges from 326.66(7) to 326.85(7)°).[17] These data indicate that the Ge center in **3** exhibits actually a tetrahedral geometry containing an H atom.

It is worth to mention that the eight-membered $Si_2O_4M_2$ ring can be considered as a basic building block for constituting the cyclic cores of **1**, **2**, and **4**, as well as the bicyclic cores of **3** and **6**, and the cubic core of **5**. A lateral projecting view of the ring system is given in the ESI.†

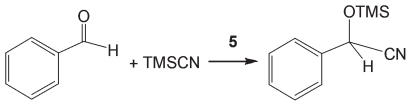
Catalytic studies

The addition reactions of trimethylsilyl cyanide (TMSCN) to aldehyde or ketone to form cyanohydrin trimethylsilyl ethers (*O*-trimethylsilyl cyanohydrins) were first reported in 1973 by Evans and Lidy.[27] This type of reaction can be catalyzed by a variety of Lewis acids and bases as well as nucleophiles. Group 13–15 metal halides and alkoxides have been used as the Lewis acid catalysts for this reaction.[28] Silanols are electron-withdrawing ligands[29] and in combination with group 13–15 metals an increase in acidity is discovered.[30,31] However, there is no report on using metallasiloxanes as catalysts for the addition reaction of TMSCN to aldehydes or ketones. Herein, we report on metallasiloxanes **1–6** as effective catalysts for this reaction.

The reaction of TMSCN with benzaldehyde was carried out in the presence of **1–6** (1 mol%, based on benzaldehyde) at ambient temperature under solvent-free condition. The complete results of compounds **1–6** as catalysts are given in the ESI.† Herein, we selected the catalytic property of compound **5** for various aldehydes and ketones.

The reactions of TMSCN with benzaldehyde catalyzed by **5** with reduced loadings were carried out (Table 1). The results indicate that the reaction can also be completed to give an almost quantitative yield of product within 5 min even with 0.10 mol% loading. When the loading is reduced to 0.05 mol%, the reaction is completed in 15 min. When **5** is reduced to 0.01 mol%, a significantly lower yield of the product (10%) is given in 24 h. This reaction does not proceed with a loading of 0.003 mol% or less even by running for two days. Nonetheless, when compared with other compounds mentioned above, **5** can be regarded as a superior catalyst. We continued to test its catalytic property for the reactions of TMSCN with other aldehydes and ketones and such results are shown in Table 2.

Table 1 Addition reaction of TMSCN to benzaldehyde catalyzed by **5** with different loadings[a]



5[b] (mol%)	Reaction time	Yield[d] (%)
1.00	5 min	≥99
0.75	5 min	≥99
0.40	5 min	≥99
0.10	5 min	≥99
0.05	15 min	≥99
0.01[c]	24 h	10
0.003[c]	24–48 h	Trace
0	24–48 h	0

[a] Benzaldehyde, 2 mmol; TMSCN, 3 mmol; at ambient temperature. [b] Based on benzaldehyde. [c] The amount was exacted by using diluted toluene solution of **5**. [d] Yield was obtained according to thin-layer chromatographic (TLC) and ^{1}H NMR spectral analysis.

It is generally considered that using a Lewis acidic catalyst the reaction usually undergoes a preliminary coordinative interaction between the catalytic metal center and the carbonyl oxygen atom of the substrate followed by a nucleophilic attack of the cyanide to the carbonyl carbon atom.[28,32] The results in Table 2 indicate that the reactions involving the *ortho*-substituted aryl aldehydes and double-substituted ketones show relatively lower activities, meanwhile 2-thiophenecarboxaldehyde appears to have a better reactivity than 2-furaldehyde. Accordingly, it is reasoned that the steric and/or electronic properties of the substitutes at the carbonyl functionality of the aldehyde and ketone substrates may have a great influence on the interaction between the metal center and the carbonyl oxygen atom and thereby on the catalytic activity (see Scheme S1 in ESI†).

Conclusion

In summary, we have prepared and structurally characterized a series of 13–15 group metallasiloxanes **1–6** derived from aminosiloxanediol and aminosiloxanetriol. Compounds **1**, **2**, and **4** are forming a cyclic structure with an eight-membered ring core of $Si_2O_4Bi_2$, $Si_2O_4Sb_2$, and $Si_2O_4Al_2$, respectively. Compound **3** and **6** exhibit a bicyclic structure with the skeletons of $Si_3O_6Ge_2$ and of $Si_2O_6Al_3$, whereas in **5** a cubic cage structure of $Si_4O_{12}Bi_4$ is found. The $Si_2O_4M_2$ (M = Bi, Sb, Ge, Al) rings in **1–6** adopt different conformations. Metallasiloxanes **1–6** have been explored for the first time to show excellent activities for the addition reaction of TMSCN to benzaldehyde, exhibiting

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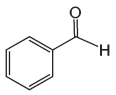
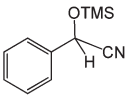
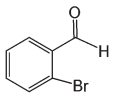
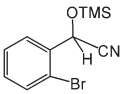
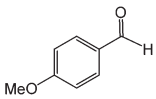
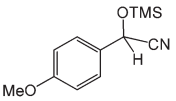
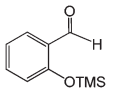
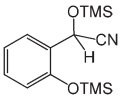
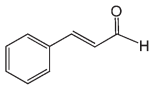
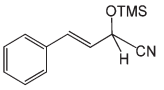
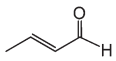
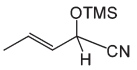
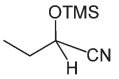
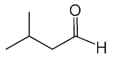
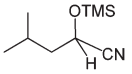
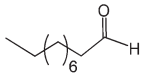
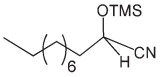
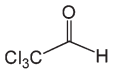
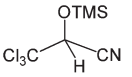
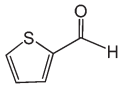
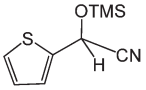
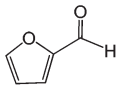
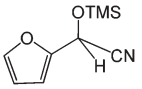
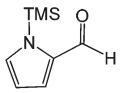
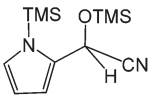
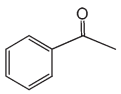
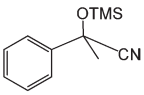
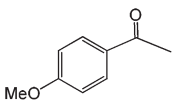
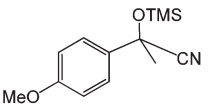
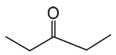
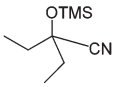
Table 2 Addition reactions of TMSCN to aldehyde or ketone catalyzed by **5**[a]

Aldehyde or ketone	Product	Reaction time (min)	Yield[b] (%)
		5	≥99 (96)
		5	92 (89)
		5	≥99 (96)
		5	≥88 (80)
		5	≥99 (96)
		5	≥99 (96)
		5	≥99 (95)
		5	≥99 (95)
		5	≥99 (96)
		5	≥99 (95)
		5	≥99 (94)
		5	82 (77)
		120[c]	20 (13)
		88[d]	≥99 (96)
		120[d]	74 (68)
		120[d]	85 (80)

[a] Aldehyde or ketone, 2 mmol; TMSCN, 3 mmol; **5**, 0.002 mmol; at ambient temperature. [b] Yield was obtained according to thin-layer chromatographic (TLC) and ^{1}H NMR spectral analysis. The value in the bracket is the isolated yield. [c] This reaction must be run for a long time to give the result. [d] The reaction of TMSCN with the ketone required a long time to give optimal results.

the advantages by the good solubility in the reaction system as well as by the significantly low loadings over more conventional catalytic systems (see ESI†). This is due to the increased Lewis acidity of these compounds containing a highly electron-withdrawing environment at the metal centers.[29–31] The bismuth(III) siloxane **5** is still effective in this reaction with a loading as low as 0.05 mol%. Moreover, this compound was further tested to catalyze the reaction of TMSCN with a variety of other aldehydes and ketones. The detailed investigations on the use of the other metallasiloxanes for catalyzing this kind of reactions as well as for other organic transformations will be published in due course.

Experimental section

Materials and methods

All syntheses and manipulations were carried out using a Schlenk line or in an argon-filled MBraun glovebox (typically oxygen and moisture were controlled at less than 1.2 ppm). Toluene, *n*-hexane, and tetrahydrofuran were predried over sodium wires and then refluxed with sodium/potassium benzophenone under N_2 prior to use. Benzene-d_6 was degassed and dried over sodium/potassium alloy, and $CDCl_3$ and CD_2Cl_2 were degassed and dried over CaH_2. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker Avance II 400 and 500 MHz spectrometers. Melting points of compounds were measured in sealed glass tubes using Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Companies and used as received. $R(Me)Si(OH)_2$,[13] $RSi(OH)_3$[11] (R = $N(SiMe_3)$-2,6-$iPr_2C_6H_3$), $Bi(NEt_2)_3$,[33] $Sb(NEt_2)_3$,[34] and $Ge[N(SiMe_3)_2]_2$[35] were prepared according to published procedures.

$[R(Me)SiO_2BiNEt_2]_2$ (1)

A solution of $Bi(NEt_2)_3$ (0.14 g, 0.33 mmol) in toluene (10 mL) was added to a solution of $R(Me)Si(OH)_2$ (0.11 g, 0.33 mmol) in toluene (20 mL) at −20 °C. The mixture was warmed to room temperature and stirred for 12 h. After workup, all volatiles were removed under reduced pressure and the residue was extracted with *n*-hexane (10 mL). The extract was stored at −20 °C for two days to obtain light-yellow crystals of **1**. Yield: 0.16 g (80%). Mp 209 °C (dec). ^{1}H NMR (C_6D_6, 400 MHz, 298 K, ppm): δ 7.06–6.90 (m, 6 H, C_6H_3), 4.21 (q, 4 H, $^3J_{HH}$ = 6.8 Hz), 4.07 (q, 4 H, $^3J_{HH}$ = 6.8 Hz) (NCH_2CH_3), 3.96 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz), 3.72 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz) ($CHMe_2$), 1.46 (d, 6 H, $^3J_{HH}$ = 6.8 Hz), 1.41 (d, 6 H, $^3J_{HH}$ = 6.8 Hz), 1.33 (d, 6 H, $^3J_{HH}$ = 6.8 Hz), 1.22 (d, 6 H, $^3J_{HH}$ = 6.8 Hz) ($CHMe_2$), 1.17 (t, 12 H, $^3J_{HH}$ = 6.8 Hz, NCH_2CH_3), 0.42 (s, 6 H, $SiMeO_2$), 0.29 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 298 K, ppm): δ 147.6, 144.6, 139.8, 125.5, 124.2, 123.3 (C_6H_3), 28.5, 28.0, 25.4, 24.8, 23.8 ($CHMe_2$ and CH_2CH_3), 2.0 ($SiMeO_2$), 0.8 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 99 MHz, 298 K, ppm): δ 1.97 ($SiMe_3$), −42.70 ($SiMeO_2$). Anal. calcd for $C_{40}H_{78}Bi_2N_4O_4Si_4$ (M_r = 1209.37): C, 39.73; H, 6.50; N, 4.63. Found: C, 39.84; H, 6.62; N, 4.52.

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[R(Me)SiO$_2$SbOSi(OH)(Me)R]$_2$ (2)

A solution of Sb(NEt$_2$)$_3$ (0.10 g, 0.33 mmol) in *n*-hexane (10 mL) was added to a solution of R(Me)Si(OH)$_2$ (0.21 g, 0.66 mmol) in *n*-hexane (20 mL) at −20 °C. The mixture was warmed to room temperature and stirred for 12 h. After workup, a small amount of precipitate was filtered off, and the filtrate was kept under Ar atmosphere at ambient temperature, allowing for slow evaporation. Light-yellow crystals of **2** were formed after 5 days. Yield: 0.12 g (62%). Mp: 219 °C (dec). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 298 K, ppm): δ 7.09–7.03 (m, 12 H, C$_6$*H*$_3$), 3.64–3.47 (m, 8 H, C*H*Me$_2$), 1.27–1.13 (m, 48 H, CH*Me*$_2$), 0.23 (s, 3 H, Si*Me*(OH)O), 0.09 (s, 9 H, Si*Me*$_3$ of R in RSiMe(OH)O), 0.08 (s, 9 H, Si*Me*$_3$ of R in RSiMeO$_2$), −0.03 (s, 3 H, Si*Me*O$_2$). The SiOH proton resonance was not observed. ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz, 298 K, ppm): δ 147.5, 147.4, 147.3, 141.1, 140.9, 124.7, 124.6, 124.1, 124.0, 123.9, 123.8, 123.9 (*C*$_6$H$_3$), 27.6, 27.4, 27.3, 26.1, 25.4, 25.2, 25.3, 24.7, 24.6, 24.5, 24.3 (*C*HMe$_2$), 2.1 (Si*Me*$_3$ of R in RSiMe(OH)O), 2.0 (Si*Me*$_3$ of R in RSiMeO$_2$), 0.74 (Si*Me*(OH)O), 0.16 (Si*Me*O$_2$). ^{29}Si NMR (CD$_2$Cl$_2$, 99 MHz, 298 K, ppm): δ 7.02 (*Si*Me$_3$ of R in RSiMe(OH)O), 4.84 (*Si*Me$_3$ of R in RSiMeO$_2$), −33.33 (*Si*Me(OH)O), −40.51 (*Si*MeO$_2$). IR (Nujol mull, cm^{-1}): ν 3647 (SiOH). Anal. calcd for C$_{64}$H$_{118}$N$_4$O$_8$Sb$_2$Si$_8$ (M_r = 1539.85): C, 49.92; H, 7.72; N, 3.64. Found: C, 50.12; H, 7.83; N, 3.49.

[R(Me)SiO$_2$]$_3$(GeH)$_2$ (3)

A solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.12 g, 0.30 mmol) in toluene (10 mL) was added to a solution of R(Me)Si(OH)$_2$ (0.15 g, 0.45 mmol) in toluene (15 mL) at −20 °C. The mixture was warmed to room temperature and stirred for 12 h. After workup, all volatiles were removed under reduced pressure and the residue was extracted with *n*-hexane (15 mL). The *n*-hexane extract was kept under Ar atmosphere at ambient temperature, allowing for slow evaporation. Colorless crystals of **3** were formed after 3 days. Yield: 0.13 g (78%). Mp: 226 °C (dec). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K, ppm): δ 7.04–7.00 (m, 9 H, C$_6$*H*$_3$), 6.24 (s, 2 H, Ge*H*), 3.73 (sept, 6 H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 1.27 (d, 18 H, $^3J_{HH}$ = 7.0 Hz), 1.21 (d, 18 H, $^3J_{HH}$ = 7.0 Hz) (CH*Me*$_2$), 0.30 (s, 9 H) (Si*Me*O$_2$), 0.2 (s, 27 H, Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$, 125 MHz, 298 K, ppm): δ 147.7, 139.8, 125.7, 124.6 (C$_6$*H*$_3$), 30.2, 27.8, 25.5, 25.3 (*C*HMe$_2$), 2.83 (Si*Me*O$_2$), 1.35 (Si*Me*$_3$). ^{29}Si NMR (C$_6$D$_6$, 99 MHz, 298 K, ppm): δ 6.52 (*Si*Me$_3$), −30.92 (*Si*MeO$_2$). IR (Nujol mull, cm^{-1}): ν 2135 (GeH). Anal. calcd for C$_{48}$H$_{89}$Ge$_2$N$_3$O$_6$Si$_6$ (M_r = 1118.03): C, 51.57; H, 8.02; N, 3.76. Found: C, 51.36; H, 8.11; N, 3.52.

[R(Me)SiO$_2$AlMe(THF)]$_2$ (4)

AlMe$_3$ (0.5 mL, 0.5 mmol, 1 M solution in *n*-hexane) was added to a solution of R(Me)Si(OH)$_2$ (0.16 g, 0.50 mmol) in THF (50 mL) at −20 °C. During the addition, the CH$_4$ gas evolution was observed. The mixture was warmed to room temperature and stirred for 12 h. After workup, all volatiles were removed under reduced pressure and the residue was extracted with *n*-hexane–THF (5 mL, 4 : 1) solvent mixture. The extract was stored at −20 °C within 3 days to give colorless crystals of **4**. Yield: 0.16 g (73%). Mp: 257 °C (dec). ^{1}H NMR (CDCl$_3$, 500 MHz, 298 K, ppm): δ 7.00–6.90 (m, 6 H, C$_6$*H*$_3$), 3.77 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz), 3.62 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz) (C*H*Me$_2$), 3.58 (m, 8 H, OC*H*$_2$CH$_2$), 1.76 (m, 8 H, OCH$_2$C*H*$_2$), 1.19 (d, $^3J_{HH}$ = 7.0 Hz), 1.18 (d, $^3J_{HH}$ = 7.0 Hz), 1.14 (d, $^3J_{HH}$ = 7.0 Hz) (24 H, CH*Me*$_2$), 0.06 (s, 6 H, Si*Me*O$_2$), −0.02 (s, 18 H, Si*Me*$_3$), −1.06 (s, 6 H, Al*Me*). ^{13}C NMR (CDCl$_3$, 125 MHz, 298 K, ppm): δ 148.4, 147.6, 144.9, 122.6 (C$_6$*H*$_3$), 69.9 (O*C*H$_2$CH$_2$), 25.1 (OCH$_2$*C*H$_2$), 31.6, 27.5, 26.4, 25.3, 23.8, 22.6 (*C*HMe$_2$), 2.0 (Si*Me*$_3$), 1.0 (Si*Me*O$_2$), −14.4 (Al*Me*). ^{29}Si NMR (CDCl$_3$, 99 MHz, 298 K, ppm): δ 0.75 (*Si*Me$_3$), −52.26 (*Si*MeO$_2$). Anal. calcd for C$_{42}$H$_{80}$Al$_2$N$_2$O$_6$Si$_4$ (M_r = 875.40): C, 57.63; H, 9.21; N, 3.20. Found: C, 57.52; H, 9.12; N, 3.13.

(RSiO$_3$Bi)$_4$ (5)

A solution of Bi(NEt$_2$)$_3$ (0.21 g, 0.50 mmol) in toluene (10 mL) was added to a solution of RSi(OH)$_3$ (0.16 g, 0.50 mmol) in toluene (10 mL) at −20 °C. The mixture was warmed to room temperature and stirred for 12 h. After workup, all volatiles were removed under reduced pressure and the residue was extracted with *n*-hexane (15 mL). The *n*-hexane filtrate was evaporated to dryness to give **5** as colorless crystalline solid. Yield: 0.24 g (90%). Mp: 310 °C (dec). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K, ppm): δ 7.13–6.84 (m, 12 H, C$_6$*H*$_3$), 3.90 (sept, 8 H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 1.36 (d, 24 H, $^3J_{HH}$ = 7.0 Hz), 1.28 (d, 24 H, $^3J_{HH}$ = 7.0 Hz) (CH*Me*$_2$), 0.35 (s, 36 H, Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$, 125 MHz, 298 K, ppm): δ 148.9, 145.3, 137.9, 129.3, 128.6, 125.7, 124.7, 124.3 (*C*$_6$H$_3$), 27.6, 26.8, 25.5 (*C*HMe$_2$), 2.7 (Si*Me*$_3$). ^{29}Si NMR (C$_6$D$_6$, 99 MHz, 298 K, ppm): δ 2.42 (*Si*Me$_3$), −79.12 (*Si*O$_3$). Anal. calcd for C$_{60}$H$_{104}$Bi$_4$N$_4$O$_{12}$Si$_8$ (M_r = 2134.09): C, 33.77; H, 4.91; N, 2.63. Found: C, 33.54; H, 4.86; N, 2.52. X-ray quality single crystals of **5**·toluene·0.5*n*-hexane were obtained from recrystallization in a solvent mixture (toluene–*n*-hexane = 1 mL/4 mL) at −20 °C.

(RSiO$_3$)$_2$[AlMe(THF)]$_3$ (6)

AlMe$_3$ (1.5 mL, 1.5 mmol, 1 M solution in *n*-hexane) was added to a solution of RSi(OH)$_3$ (0.33 g, 1.0 mmol) in THF (20 mL) at −20 °C. During the addition, the CH$_4$ gas evolution was observed. The mixture was warmed to room temperature and stirred for 12 h. After workup, all volatiles were removed under reduced pressure and the residue was extracted with *n*-hexane. The *n*-hexane extract was evaporated to dryness to give a colorless crystalline solid of **6**. Yield: 0.44 g (89%). Mp: 239 °C (dec). ^{1}H NMR (CDCl$_3$, 500 MHz, 298 K, ppm): δ 7.01–6.92 (m, 6 H, C$_6$*H*$_3$), 4.00 (m, 12 H, OC*H*$_2$CH$_2$), 3.87 (sept, 4 H, $^3J_{HH}$ = 6.5 Hz, C*H*Me$_2$), 1.94 (m, 12 H, OCH$_2$C*H*$_2$), 1.22 (d, 12 H, $^3J_{HH}$ = 6.5 Hz), 1.15 (d, 12 H, $^3J_{HH}$ = 6.5 Hz) (CH*Me*$_2$), 0.09 (s, 18 H, Si*Me*$_3$), −1.03 (s, 9 H, Al*Me*). ^{13}C NMR (CDCl$_3$, 125 MHz, 298 K, ppm): δ 148.2, 143.2, 122.8, 122.6 (*C*$_6$H$_3$), 70.2 (O*C*H$_2$CH$_2$), 25.1 (OCH$_2$*C*H$_2$), 31.6, 27.4, 25.6, 24.8, 23.8, 22.6 (*C*HMe$_2$), 2.2 (Si*Me*$_3$), −13.6 (br, Al*Me*). ^{29}Si NMR (CDCl$_3$, 99 MHz, 298 K, ppm): δ 0.99 (*Si*Me$_3$), −79.96 (*Si*O$_3$). Anal. calcd for C$_{45}$H$_{85}$Al$_3$N$_2$O$_9$Si$_4$ (M_r = 991.45): C, 54.51; H, 8.64; N, 2.83. Found: C, 54.35; H, 8.56; N, 2.75. X-ray quality single crystals of **6**·THF were formed by recrystallization from a solvent mixture (THF–*n*-hexane = 9 mL, 1 : 8) at −20 °C.

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X-ray crystallographic analyses of complexes 1–6

Crystallographic data for compounds **1–3**, **5**·toluene·0.5*n*-hexane, and **6**·0.75THF were collected on an Oxford Gemini S Ultra system and the data for **4** was obtained on a Rigaku R-Axis Spider IP. In all cases graphite-monochromatic Mo-K_α radiation (λ = 0.71073 Å) was used. Absorption corrections were applied using the spherical harmonics program (multiscan type). All the structures were solved by direct methods (SHELXS-96)[36] and refined against F^2 using SHELXL-97 program.[37] In general, the non-hydrogen atoms were located from the difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. In **1**, the two ethyl groups of the $BiNEt_2$ functionality were both disordered and treated in a splitting mode. In **3**, three one-third target molecules were located. Due to the quality of the crystals, the hydrogen atom at the Ge center could not be located from different Fourier synthesis. Besides, one of the $iPr_2C_6H_3$ groups and one of the $SiMe_3$ substituents were disordered and treated in a splitting mode. The non-hydrogen atoms of Ge(5), Ge(6), C(16), C(17A), and C(34) and the atoms of the disordered $iPr_2C_6H_3$ group were refined isotropically due to instability upon anisotropic refinement. The residual electron density of this structure thus appears high. In **5**·toluene·0.5*n*-hexane, the toluene solvent molecule was disordered and treated in a splitting mode. The carbon atoms from the half molecule of *n*-hexane were refined isotropically due to the significant vibration. In **6**·0.75THF, the carbon atoms of the non-coordinated THF molecules were refined isotropically because of the significant vibration. Cell parameters, data collection, and structure solution and refinement are given in Tables S1 and S2 in the ESI.†

Acknowledgements

This work was supported by the 973 Program (2012CB821704), the National Nature Science Foundation of China (91027014 and 20972129), and the National Key Lab Foundation for PCOSS (20923004) and the Innovative Research Team Program (IRT1036).

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