Synthesis of the first examples of stable heterometallic isopropoxides of an organometallic RSn(IV) moiety

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Abstract

Five-, six-, and seven-coordinate volatile butyltin(IV) heterobimetallic derivatives, respectively of the types, $[BuSn\{(\mu-OPr^i)_2Al(OPr^i)_2\}Cl_2]$ (**1**), $[BuSn\{(\mu-OPr^i)_2Al(OPr^i)_2\}_2Cl]$ (**2**), and $BuSn\{(\mu-OPr^i)_2M(OPr^i)_{x-2}\}_3$ (**3**:M = Al ($x = 4$); **4**:M = Ga ($x = 4$); **5**:M = Nb ($x = 6$)) have been synthesized by the reactions of $BuSnCl_3$ with potassium tetraisopropoxoaluminate in 1:1, 1:2, and 1:3 molar ratios. Replacement reactions of chloride in (**1**) and (**2**) with appropriate alkoxometallate (tetraisopropoxoaluminate, tetraisopropoxogallate, or hexaisopropoxoniobate) ligands result in the formation of novel BuSn(IV) heterotri- and tetra-metallic derivatives. All of these derivatives have been characterized by elemental analyses, molecular weight measurements, and spectroscopic (IR, ^1H, ^{27}Al, and ^{119}Sn NMR) studies. Based on these studies, plausible structures for the new derivatives involving bidentate ligation of the alkoxometallate ligands have been suggested.
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1. Introduction

Chelating alkoxometallate ligands, like $Al(OPr^i)_4^-$, $Ga(OPr^i)_4^-$, and $Nb(OPr^i)_6^-$ for which bidentate ligating mode has been established by X-ray crystallographic studies [1–7], have been used extensively during the last two decades for the syntheses of novel classes of structurally interesting heterometallic derivatives (containing two, three, or four different species) of a large number of metals of the periodic table [8–12]. However, the investigations have been limited to non-organometallic moieties of transition or main group elements only.

Our pioneering work [2,8,9] on heterometallic alkoxide systems is now being extended for the first time to organometallic moieties; this paper describes results on butyltin(IV) heterometallic isopropoxide species.

The present study assumes special importance due to the volatility and solubility (in organic solvents) of the newly synthesized heterometallic isopropoxides of BuSn(IV), which should be excellent precursors for the synthesis of novel mixed metal oxide systems by MOCVD as well as sol–gel processes.

2. Results and discussion

During a detailed study [12] of alkyltin alkoxides, butyltin isopropoxide could be synthesized with some difficulty in only ∼55% yield by the 1:3 metathetic reaction of $BuSnCl_3$ with $NaOPr^i$; the over all reaction is rather slow after the first stage as indicated by the earlier
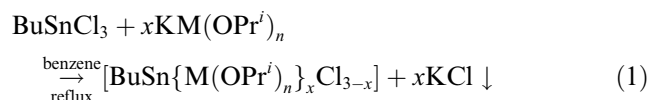
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findings of Davies et al. [13,14]. It may however, be mentioned that the reactions of alkyltin tris(dialkylamide), $RSn(NR'_2)_3$ with alcohols are comparatively more facile [15].

In this paper, we are reporting for the first time the synthesis of heterometallic isopropoxides of an alkylmetal (butyltin) moiety. It has been shown that the step-wise reactions of $BuSnCl_3$ with a variety of potassium isopropoxometallates (e.g., $KAl(OPr^i)_4$, $KGa(OPr^i)_4$, or $KNb(OPr^i)_6$) in 1:1, 1:2, and 1:3 molar ratios are quite facile, resulting in a number of novel heterometallic alkoxides and chloride alkoxides of butyltin moiety as indicated by the following general Eq. (1):

$$BuSnCl_3 + xKM(OPr^i)_n$$
$$\overset{\text{benzene}}{\underset{\text{reflux}}{\rightarrow}} [BuSn\{M(OPr^i)_n\}_x Cl_{3-x}] + xKCl \downarrow \qquad (1)$$

	M	n	x
(**1**)	Al	4	1
(**2**)	Al	4	2
(**3**)	Al	4	3
(**4**)	Ga	4	3
(**5**)	Nb	6	3

A noteworthy feature of the above reactions is that contrary to the difficulties [12–14] in the preparation of $BuSn(OPr^i)_3$, reactions of $BuSnCl_3$ with potassium isopropoxometallates are quite facile and on distillation under reduced pressure, the products can be isolated in quantitative (>80%) yields.

Reactions of heterobimetallic chloride–isopropoxide derivatives (**1**) and (**2**) with different potassium isopropoxometallates [e.g., $KNb(OPr^i)_6$ or $KGa(OPr^i)_4$] in benzene (Scheme 1) afford novel hetero(tri- and tetra-) metallic isopropoxides of butyltin(IV), all of which can be distilled without disproportionation.

All of these butyltin(IV) heterometallic isopropoxide derivatives are colourless, moisture sensitive, hydrocarbon soluble, volatile, non-crystalline solids or viscous liquids, and depict monomeric behaviour cryoscopically in benzene solution.

Heterometallic alkoxides have been shown [12] to be excellent precursors for the synthesis of mixed metal oxide ceramic materials [16]. The synthesis of heterometallic butyltin isopropoxide derivatives, therefore, opens up for the first time the possibilities of synthesizing interesting and useful ceramic materials involving butyltin species.
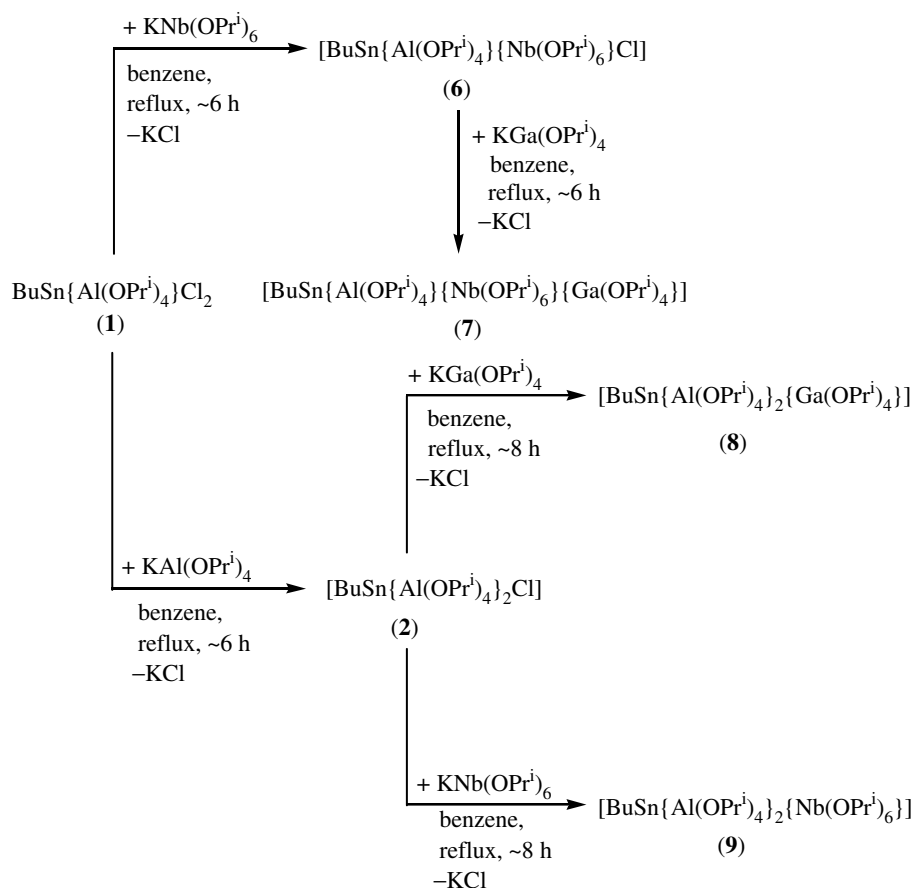
Scheme 1. Synthesis of hetero(tri-and tetra-) metallic isopropoxides of butyltin(IV).

The findings in this paper, therefore, open up a new direction for synthesis of other specific alkylmetal heterometallic species, as required for obtaining novel ceramic materials containing other organometallic moieties.

3. Spectroscopic studies

3.1. Infrared spectra

Infrared spectra of the new heterometallic isopropoxides have been recorded in the 200–4000 cm^{-1} region. All of these derivatives exhibit two bands in the 510–600 cm^{-1} region, which may be assigned to ν(Sn–C) [17,18] stretching frequencies. Similar to other organotin alkoxides and chlorides an absorption band have been observed near 665–670 cm^{-1}, which may assigned to (Sn–CH_2) rocking vibration arising from *trans* configuration [19]. The band observed at about 500 cm^{-1} may be associated with ν(Sn–O) (see Section 4) vibration.

3.2. ^1H NMR spectra

Assignments of ^1H NMR signals in the derivatives (**1**)–(**9**) are based on published/available data for isopropoxides of aluminium [20], gallium [21], monobutyltin(IV) [22], and niobium [23]; heterobimetallic isopropoxides of (i) niobium [24] with aluminium/gallium, and (ii) gallium/indium [25] with aluminium.
^1H NMR spectra of the new derivatives (see Section 4) exhibit a triplet in the δ 0.91–0.98 ppm region due to CH_3 protons of the butyltin moiety, which in a number of cases appear to be partially hidden within the signals due to isopropoxy methyl protons. The methylene protons (Sn(CH_2)$_3$CH$_3$) appear as a broad signal centred at δ 1.75 ± 0.12.

The isopropoxy methyl protons in (**1**) appear as two doublets centred at δ 1.14 and 1.33 for terminal and bridging isopropoxy groups, respectively; while signals due to methine protons appear as two overlapping septets (J = 5.65 Hz) in the range δ 3.99–4.85 in which 11 peaks can be distinguished.

The spectrum of (**2**) shows three doublets (J = 5.65 Hz) due to gem-dimethyl protons at δ 1.39 and 1.53 for bridging isopropoxy groups, whereas doublet (J = 5.65 Hz) due to terminal methyl isopropoxy protons appears at δ 1.25. The observed integrated intensity ratio 1:1 for bridging and terminal methyl proton signals is consistent with the structure depicted in Fig. 1. The methine protons have been observed as a complex multiplet in the range δ 3.87–5.00 arising from overlapping of two septets. The derivative (**3**) shows a spectral pattern similar to (**2**), the bridging isopropoxy methyl signals
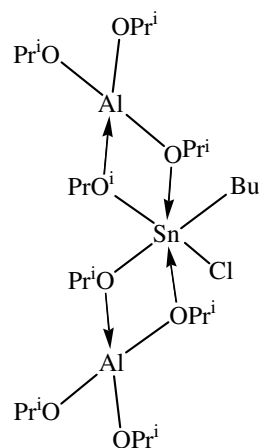

Fig. 1. Plausible structure for (**2**).

appearing at δ 1.31 and 1.48 and terminal ones at δ 1.14. The signals for methine protons of bridging and terminal isopropoxy groups appear as two overlapping septets (J = 5.65 Hz) in the δ 3.96–4.79 region, in which 10 peaks can be distinguished.

Surprisingly, the spectrum of (**4**) shows more complex nature of signals due to methyl isopropoxy protons, in which doublet (J = 5.65 Hz) for the terminal isopropoxy groups can be easily distinguished. The signal for methine protons appears at a broad peak in the δ 3.74–4.79 region.

The spectrum of (**5**), [BuSn{(μ-OPr^i)$_2$Nb(OPr^i)$_4$}$_3$], shows two doublets (J = 5.65 Hz) for terminal methyl isopropoxy groups at δ 1.24 and 1.33 in the 1:1 integrated intensity ratio consistent with the presence of two isopropoxy groups and both in axial and equatorial positions in an octahedral Nb(OPr^i)$_6$ moiety. The signal for bridging isopropoxy groups appears as a doublet (J = 5.65 Hz) at δ 1.39. The integrated intensity ratio of bridging and total terminal isopropoxy methyl protons appears to be 1:2, which is consistent with the proposed structural formulation. The signals for methine protons appear as septets (J = 5.65 Hz) at δ 4.70 and 4.18 in the integrated ratio 2:1, which shows that in this particular case signal for terminal methine protons are comparatively more deshielded in comparison to the bridging ones.

In the derivative (**6**), signals due to the methyl protons of the terminal isopropoxy groups attached to aluminium and niobium appear as doublets at δ 1.11 and 1.21, respectively, whereas a doublet for bridging isopropoxy groups (Nb(μ-OPr^i)$_2$BuSn(μ-OPr^i)$_2$Al) has been observed at δ 1.36. The two septets observed in the δ 3.96–4.46 (centred at δ 4.21) and δ 4.59–5.04 (centred at δ 4.82) range may be assigned on the basis of relative integrated intensity ratio to be due to bridging and terminal isopropoxy groups, respectively.

The heterotetrametallic derivative (**7**) shows four doublets for isopropoxy group methyl protons centred

at δ 1.10, 1.21; 1.29 and 1.37, assignable to terminally bonded isopropoxy groups to aluminium, niobium and gallium; bridging isopropoxy groups attached to niobium and gallium, and aluminium, respectively. Two broad signals in the δ 3.83–4.47 (centred at δ 4.15) and δ 4.60–5.13 (centred at δ 4.87) range are assignable to terminal and bridging methine protons, respectively.

Heterotrimetallic derivative (8) also shows four doublets for gem-dimethyl protons centred at δ 1.10 (terminally bonded isopropoxy groups both to niobium and gallium), 1.29 (bridged isopropoxy groups of niobium and gallium), 1.37 (bridged isopropoxy groups of aluminium). The methine protons signal appears as a complex multiplet in the δ 3.96–4.94 range.

The three doublets observed for the derivative (9) at δ 1.11, 1.23, and 1.37 may be assigned to four isopropoxy groups terminally bonded to aluminium, six isopropoxy groups four of which are terminally bonded to niobium and two of them are bridging isopropoxy groups attached to aluminium, four bridged isopropoxy groups two of which are bonded to aluminium and the other two to niobium.

The methine proton signals appear as a complex multiplet in the δ 3.90–4.53 (centred at δ 4.22) and δ 4.67–5.17 (centred at δ 4.92) range for terminal and bridging isopropoxy groups, respectively.

It is noteworthy that the ^{1}H NMR spectra of the new derivatives generally follow the pattern exhibited by the tetrameric aluminium isopropoxide, $[Al\{(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_3]$ [20] and $[In\{(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_3]$ [25], which depicts essentially three types of methyl doublets, the high field doublet is assigned to the terminal isopropoxy groups, whereas the bridging isopropoxy groups give rise to two almost equal doublets. The splitting of these low field doublets has been ascribed by Shiner and coworkers [20] to steric factors, whereas Worrall and coworkers [26] ascribed it to the asymmetric bridging oxygen.

3.3. ^{27}Al NMR spectra

The ^{27}Al NMR spectra of (1), (2), (3), (6), (7), (8), and (9) (see Section 4) show signals at δ 83, 55, 80, 65, 74, 60, and 62 ppm, respectively, which are consistent with the structures shown in Figs. 1–3 with tetra-coordinate [27] aluminium.
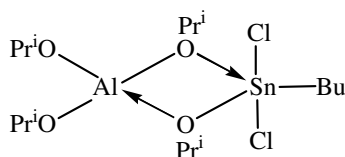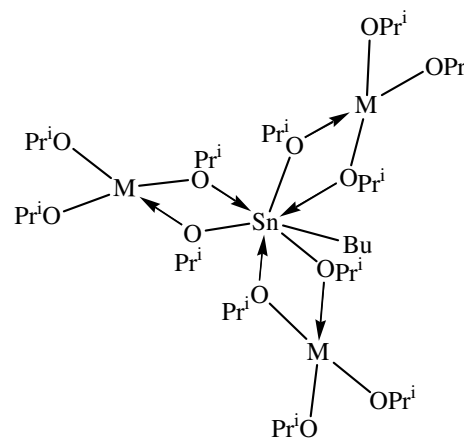

Fig. 3. Plausible structure for the derivatives (3) (M = Al) and (4) (M = Ga).

3.4. ^{119}Sn NMR spectra

The derivative (1) exhibits one sharp ^{119}Sn NMR signal at δ −316 ppm, consistent with penta-coordinated tin(IV) [28] as shown in Fig. 2.

Six-coordinated nature (Fig. 1) of tin [29] in derivatives (2) and (6) is supported by the appearance of signals at δ −417 and −418 ppm, respectively.

The derivatives (3), (4), (5), (7), (8), and (9) exhibit signals at δ −517, −499, −509, −517, −517, and −517 ppm, respectively, consistent with structure (Fig. 3) involving seven-coordinated tin [30].

It would not be out of place to mention that repeated efforts for structural elucidation by X-ray crystallographic method have not been successful so far due to non-crystalline and/or viscous liquid nature of these new compounds. However (^{119}Sn, ^{27}Al, and ^{1}H) NMR spectroscopic data along with X-ray crystallographically established bidentate ligating mode of tetraalkoxoaluminate and hexaalkoxoniobate [12], support strongly the structures depicted in Figs. 1–3.

4. Experimental

All syntheses and manipulations were carried out under strictly anhydrous conditions. All apparatus were oven dried (∼150 °C) and were allowed to cool to room temperature in moisture free atmosphere prior to use. Solvents such as benzene (BDH) and isopropyl alcohol (Qualigenes, India) were made anhydrous by the methods described in literature [31] and freshly distilled prior to use. Butyltin trichloride (Aldrich) was distilled (b.p. 93°/10 mm) before use. Isopropoxides of aluminium [32], gallium [33], and niobium [34] were prepared by the literature procedures. Aluminium and gallium were estimated as their oxinates [35], while

Fig. 2. Plausible structure for (1).

niobium and tin were estimated as their oxides [35]. The isopropoxy content in the compounds was determined by the oxidimetric method [36] using 1 N $K_2Cr_2O_7$ solution in 12.5% H_2SO_4. Molecular weights were determined cryoscopically in benzene (0.28–0.61 M) solutions.

The ^1H (89.55 MHz, $CDCl_3$) NMR spectra were recorded at ambient temperatures on a JEOL FX-90Q FT NMR spectrometer using TMS as an internal reference. ^{119}Sn (33.35 MHz) and ^{27}Al (23.79 MHz) NMR spectra were recorded at room temperature in benzene solutions using tetramethyltin and aqueous solution of aluminium nitrate as external references, respectively. IR(4000–200 cm^{-1}) spectra were recorded as Nujol mulls on a Nicolet magna 550 spectrophotometer using CsI optics.

4.1. Preparation of heterometallic isopropoxides of butyltin(IV)

4.1.1. [BuSn{(μ-OPr^i)$_2$Al(OPr^i)$_2$}Cl$_2$] (1)

A benzene (~20 ml) solution of freshly prepared KAl(OPr^i)$_4$, by the reaction of K (0.59 g, 15.09 mgatom) with Al(OPr^i)$_3$ (3.08 g, 15.07 mmol) in dry isopropyl alcohol (~5 ml) and benzene (~20 ml), was added slowly to a prestirred benzene (~20 ml) solution of BuSnCl$_3$ (4.26 g, 15.06 mmol). The resulting reaction mixture was heated under reflux for ~5 h. The precipitated KCl (1.12 g, 15.06 mmol) was removed by filtration. Removal of volatiles from the filtrate under reduced pressure gave the title compound as a colourless semisolid (7.71 g, 82%), which was distilled under reduced pressure at 128 °C/0.2 mm to obtain analytically pure product: 6.86 g, 89%. IR (Nujol):1175 s, 1125 s [ν(OPr^i)], 1050 m [ν(C–O), terminal], 937 m [ν(C–O), bridging], 675 m, 650 m [ν(Al–O)], 580 m [ν(Sn–C)], 510 m [ν(Sn–C)], 500 m [ν(Sn–O)], 319 m [ν(Sn–Cl)] cm^{-1}. NMR: ^1H (CDCl$_3$) δ 0.98 (t (J = 5.65 Hz), 3H, CH$_3$(BuSn)), 1.87 (br, 6H, Sn(CH$_2$)$_3$CH$_3$), 1.14, 1.33 (d (J = 5.65 Hz), 24H, terminal/bridging OCHMe$_2$), 4.42 (septet (J = 5.65 Hz), 4H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 83 ppm. ^{119}Sn(C$_6$H$_6$): −316 ppm. Anal. (Found: Al, 5.30; Cl, 13.50; Sn, 23.20; OPr^i, 45.99; C, 37.55; H, 7.30; mol. weight, 521. C$_{16}$H$_{37}$AlCl$_2$O$_4$Sn (510) Calc.: Al, 5.29; Cl, 13.89; Sn, 23.26; OPr^i, 46.33; C, 37.63; H, 7.31%).

[BuSn{(μ-OPr^i)$_2$Al(OPr^i)$_2$}$_2$Cl] (2), [BuSn{(μ-OPr^i)$_2$Al(OPr^i)$_2$}$_3$] (3), [BuSn{(μ-OPr^i)$_2$Ga(OPr^i)$_2$}$_3$] (4), and [BuSn{(μ-OPr^i)$_2$Nb(OPr^i)$_4$}$_3$] (5) were also prepared by similar reaction using appropriate reactants in desired molar ratios as indicated below:

(2): BuSnCl$_3$ [3.33 g, 11.80 mmol], K [0.93 g, 23.79 mgatom] and Al(OPr^i)$_3$ [4.86 g, 23.78 mmol]. B.p. 132 °C/0.15 mm. Yield: 8.10 g, 93%, colourless semisolid. IR (Nujol): 1170s, 1125s [ν(OPr^i)], 1050s [ν(C–O), termi-

nal], 925s [ν(C–O), bridging], 685s, 680s [ν(Al–O)], 585m [ν$_{as}$(Sn–C)], 510m, [ν$_s$(Sn–C)], 495s [ν(Sn–O)], 375m [ν(Sn–Cl)] cm^{-1}. NMR: ^1H (CDCl$_3$) δ 0.91 (t (J = 5.65 Hz), 3H, CH$_3$(BuSn)), 1.85, 1.65 (br, 6H, Sn(CH$_2$)$_3$CH$_3$), 1.25, 1.39, 1.53 (d (J = 5.65 Hz), 48H, terminal/bridging OCHMe$_2$), 4.44 (septet (J = 5.65 Hz), 8H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 55 ppm. ^{119}Sn(C$_6$H$_6$): −417 ppm. Anal. (Found: Al, 7.32; Cl, 4.80; Sn, 16.01; OPr^i, 63.98; C, 45.50; H, 8.68; mol. weight, 742. C$_{28}$H$_{65}$Al$_2$ClO$_8$Sn (738) Calc.: Al, 7.31; Cl, 4.80; Sn, 16.08; OPr^i, 64.40; C, 45.52; H, 8.87%).

(3): BuSnCl$_3$ [1.96 g, 6.94 mmol], K [0.82, 20.97 mgatom], and Al(OPr^i)$_3$ [4.26 g, 20.86 mmol]. B.p. 138 °C/0.1 mm. Yield: 5.56 g, 83%, colourless semisolid. IR (Nujol): 1165m, 1120m [ν(OPr^i)], 1075m [ν(C–O), terminal], 925m [ν(C–O), bridging], 685m, 680m [ν(Al–O)], 590m [ν$_{as}$(Sn–C)], 510m [ν$_s$(Sn–C)], 500m [ν(Sn–O)], cm^{-1}. NMR: ^1H (CDCl$_3$) δ 0.91 (t (J = 5.65 Hz), 3H, CH$_3$(BuSn)), 1.70 (br, 6H, Sn(CH$_2$)CH$_3$), 1.14, 1.31, 1.48 (d (J = 5.65 Hz), 72H, terminal/bridging OCHMe$_2$), 4.38 (septet (J = 5.65 Hz), 12H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 80 ppm. ^{119}Sn(C$_6$H$_6$): −517 ppm. Anal. (Found: Al, 8.39; Sn, 12.07; OPr^i, 72.90; C, 49.69; H, 9.40; mol. weight, 986. C$_{40}$H$_{93}$Al$_3$O$_{12}$Sn (966) Calc.: Al, 8.38; Sn, 12.28; OPr^i, 73.40; C, 49.68; H, 9.70%).

(4): BuSnCl$_3$ [1.56 g, 5.52 mmol], K [0.65 g, 16.62 mgatom], and Ga(OPr^i)$_3$ [4.11 g, 16.64 mmol]. B.p. 146° − 147 °C/0.4 mm. Yield: 5.37 g, 89%, colourless viscous liquid. IR (Nujol): 1175s, 1125s [ν(OPr^i)], 1025m [ν(C–O), terminal], 950m [ν(C–O), bridging], 625s, 615s [ν(Ga–O)], 580m [ν$_{as}$(Sn–C)], 510m [ν$_s$(Sn–C)], 500s [ν(Sn–O)] cm^{-1}. NMR: ^1H (CDCl$_3$) δ 0.92 (t (J = 5.65 Hz), 3H, CH$_3$(BuSn)), 1.65 (br, 6H, Sn(CH$_2$)$_3$CH$_3$), 1.17, 1.33 (d (J = 5.65 Hz), 72H, terminal/bridging OCHMe$_2$), 4.27 (septet (J = 5.65 Hz), 12H, terminal/bridging OCHMe$_2$). ^{119}Sn(C$_6$H$_6$): −499 ppm. Anal. (Found: Ga, 19.09; Sn, 10.25; OPr^i, 64.06; C, 43.31; H, 8.43; mol. weight, 1099. C$_{40}$H$_{93}$Ga$_3$O$_{12}$Sn (1094) Calc.: Ga, 19.11; Sn, 10.87; OPr^i, 64.81; C, 43.87; H, 8.56%).

(5): BuSnCl$_3$ [1.32 g, 4.67 mmol], K [0.55 g, 14.07 mgatom] and Nb(OPr^i)$_6$ [5.44 g, 14.00 mmol]. B.p. 128° − 130 °C/0.15 mm. Yield: 6.25 g, 88%, colourless semisolid. IR (Nujol): 1175s, 1125s [ν(OPr^i)], 1000s [ν(C–O), terminal], 950m [ν(C–O), bridging], 580s[ν(Nb–O)], 575m [ν$_{as}$(Sn–C)], 520m [ν$_s$(Sn–C)], 495s [ν(Sn–O)] cm^{-1}. NMR: ^1H (CDCl$_3$) δ 0.90 (t (J = 5.65 Hz), 3H, CH$_3$(BuSn)), 1.75 (br, 6H, Sn(CH$_2$)$_3$CH$_3$), 1.24, 1.33, 1.39 (d (J = 5.65 Hz), 108H, terminal/bridging OCHMe$_2$), 4.18/4.70 (septet (J = 5.65 Hz), 18H, terminal/bridging CHMe$_2$). ^{119}Sn(C$_6$H$_6$): −509 ppm. Anal. (Found: Nb + Sn, 25.99; OPr^i, 69.87; C, 45.85; H, 8.63; mol. weight, 1560. C$_{58}$H$_{135}$Nb$_3$O$_{18}$Sn (1518) Calc.: Nb + Sn, 26.16; OPr^i, 70.06; C, 45.84; H, 8.96%).

4.2. [BuSn{(μ-OPr^i)$_2$Al(OPr^i)$_2$}{(μ-OPr^i)$_2$Nb(O-Pr^i)$_4$}Cl] (6)

Reaction of (1) with one equivalent of KNb(OPr^i)$_6$ [prepared from the reaction of K (0.23 g, 5.84 mgatom) with Nb(OPr^i)$_5$ (2.27 g, 5.84 mmol) in dry isopropyl alcohol (∼5 ml) and benzene (∼25 ml)] in benzene after usual work-up affords the title derivative, which was distilled at 158° − 160 °C/0.2 mm to obtain analytically pure compound as a colourless viscous liquid. Yield: 4.90 g, 91%. IR (Nujol): 1175s, 1125s [ν(OPr^i)], 1000s [ν(C–O), terminal], 950s [ν(C–O), bridging], 685s, 680s [ν(Al–O)], 580s, 575s [ν(Nb–O)], 580m [ν$_{as}$(Sn–C)], 510m [ν$_s$(Sn–C)], 500s [ν(Sn–O)], 375m [ν(Sn–Cl)] cm^{-1}. NMR: ^{1}H (CDCl$_3$) δ 0.92 (t ($J = 5.65$ Hz), 3H, CH_3(BuSn)), 1.68 (br, 6H, Sn(CH_2)$_3$CH$_3$), 1.11, 1.21, 1.36 (d ($J = 5.65$ Hz), 60H, terminal/bridging OCHMe_2), 4.21/4.82 (septet ($J = 5.65$ Hz), 10H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 65 ppm. ^{119}Sn(C$_6$H$_6$): −418 ppm. Anal. (Found: Al, 2.95; Cl, 3.80; Nb + Sn, 22.90; OPr^i, 63.98; C, 44.17; H, 8.59; mol. weight, 935. C$_{34}$H$_{79}$AlClNbO$_{10}$Sn (922) Calc.: Al, 2.92; Cl, 3.84; Nb + Sn, 22.92; OPr^i, 64.07; C, 44.24; H, 8.63%).

4.3. [BuSn{(μ-OPr^i)$_2$Al(OPr^i)$_2$}{(μ-OPr^i)$_2$Nb(OPr^i)$_4$}-{(μ-OPr^i)$_2$Ga(OPr^i)$_2$}] (7)

Reaction of (6) with one equivalent of KGa(OPr^i)$_4$ [prepared by the method as described in the preparation of KAl(OPr^i)$_4$] in benzene after usual work-up, results in the title derivative, which was distilled at 182° − 185 °C/0.3 mm to yield analytically pure compound as a colourless viscous liquid. Yield: 2.17 g, 89%. IR (Nujol): 1150m, 1125m [ν(OPr^i)], 1025m [ν(C–O), terminal], 955m [ν(C–O), bridging], 685m, 670m [ν(Al–O)], 625m, 615m [ν(Ga–O)], 590m, 585m [ν(Nb–O)], 600m [ν$_{as}$(Sn–C)], 510m [ν$_s$(Sn–C)], 500m [ν(Sn–O)], cm^{-1}. NMR: ^{1}H (CDCl$_3$) δ 0.92 (t ($J = 5.65$ Hz), 3H, CH$_3$ (BuSn)), 1.70 (br, 6H, Sn(CH_2)$_3$CH$_3$), 1.10, 1.21, 1.29, 1.37 (d ($J = 5.65$ Hz), 84H, terminal/bridging OCHMe$_2$), 4.15/4.87 (septet ($J = 5.65$ Hz), 14H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 74 ppm. ^{119}Sn(C$_6$H$_6$): −517 ppm. Anal. (Found: Al + Ga, 8.10; Nb + Sn, 17.18; OPr^i, 68.98; C, 46.28; H, 8.82; mol. weight, 1205. C$_{46}$H$_{107}$AlGaNbO$_{14}$Sn (1192) Calc.: Al + Ga, 8.10; Nb + Sn, 17.73; OPr^i, 69.35; C, 46.27; H, 8.82%).

4.4. [BuSn{(μ-OPr^i)$_2$Al(OPr^i)$_2$}$_2${(μ-OPr^i)$_2$Ga(O-Pr^i)$_2$}] (8) and [BuSn{Al(OPr^i)$_4$}$_2${Nb(OPr^i)$_6$}] (9)

Reaction of (2) with one equivalent of KGa(OPr^i)$_4$ [prepared by the reaction of K (0.15 g, 3.83 mgatom) with Ga(OPr^i)$_3$ (0.96 g, 3.88 mmol) in dry isopropyl alcohol (∼5 ml) and benzene (∼20 ml)] in benzene after usual work-up affords the title derivative, which was distilled at 142 − 143 °C/0.2 mm to obtain analytically pure

compound as a colourless viscous liquid. Yield: 3.17 g, 82%. IR (Nujol): 1150m, 1125m [ν(OPr^i)], 1056s [ν(C–O), terminal], 950s [ν(C–O), bridging], 675s, 650s [ν(Al–O)], 625s, 620s [ν(Ga–O)], 590m [ν$_{as}$(Sn–C)], 520s [ν$_s$(Sn–C)], 495s [ν(Sn–O)] cm^{-1}. NMR: ^{1}H (CDCl$_3$) δ 0.95 (t ($J = 5.65$), 3H, CH_3(BuSn)), 1.71 (br ($J = 5.65$), 6H, Sn(CH_2)$_3$CH$_3$), 1.10, 1.29, 1.37 (d ($J = 5.65$ Hz), 72H, terminal/bridging OCHMe_2), 4.45 (septet ($J = 5.65$ Hz), 12H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 60 ppm. ^{119}Sn(C$_6$H$_6$): −517 ppm. Anal. (Found: Al + Ga, 12.24; Sn, 11.21; OPr^i, 69.99; C, 47.59; H, 9.26; mol. weight, 1019. C$_{40}$H$_{93}$Al$_2$GaO$_{12}$Sn (1009) Calc.: Al + Ga, 12.26; Sn, 11.77; OPr^i, 70.29; C, 47.58; H, 9.29%).

Adopting a similar procedure, reaction of (2) with KNb(OPr^i)$_6$ in 1:1 molar ratio afforded [BuSn{Al(O-Pr^i)$_4$]$_2$ {Nb(OPr^i)$_6$] (9). K [0.13 g, 3.32 mgatom], and Nb(OPr^i)$_5$ [1.28 g, 3.29 mmol]. B.p. 145° − 148 °C/0.15 mm. Yield: 3.38 g, 89%, colourless viscous liquid. IR (Nujol): 1150m, 1125m [ν(OPr^i)], 1050m [ν(C–O), terminal], 940m [ν(C–O), bridging], 675m, 625m [ν(Al–O)], 585m, 580m, [ν(Nb–O)], 590m [ν$_{as}$(Sn–C)], 510m [ν$_s$(Sn–C)], 500m [ν(Sn–O)], cm^{-1}. NMR: ^{1}H (CDCl$_3$) δ 0.92 (t ($J = 5.65$ Hz), 3H, CH_3(BuSn)), 1.72 (br ($J = 5.65$ Hz), 6H, Sn(CH_2)$_3$CH$_3$) 1.11, 1.23, 1.37 (d ($J = 5.65$ Hz), 84H, terminal/bridging OCHMe_2), 4.22/4.92 (septet ($J = 5.65$ Hz), 14H, terminal/bridging CHMe$_2$). ^{27}Al(C$_6$H$_6$): 62 ppm. ^{119}Sn(C$_6$H$_6$): −517 ppm. Anal. (Found: Sn + Nb, 18.39; Al, 4.70; OPr^i, 71.61; C, 48.01; H, 9.12; mol. weight, 1160. C$_{46}$H$_{107}$Al$_2$NbO$_{14}$Sn (1150) Calc.: Sn + Nb, 18.39; Al, 4.69; OPr^i, 71.93; C, 47.99; H, 9.37%).

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