

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

The First Butyltin(IV) Homo- and Heterobimetallic Diethanolaminates

Kanupriya Sharma^a; Nandu Bala Sharma^a; Anirudh Singh^a

^a Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Sharma, Kanupriya, Sharma, Nandu Bala and Singh, Anirudh(2006) 'The First Butyltin(IV) Homo- and Heterobimetallic Diethanolaminates', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 181: 12, 2735 – 2744

To link to this Article: DOI: 10.1080/10426500600864452

URL: <http://dx.doi.org/10.1080/10426500600864452>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The First Butyltin(IV) Homo- and Heterobimetallic Diethanolaminates

Kanupriya Sharma
Nandu Bala Sharma
Anirudh Singh

Department of Chemistry, University of Rajasthan, Jaipur, India

Equimolar reactions of $\text{BuSn}(\text{OPr}^i)_3$ with diethanolamines, $\text{RN}(\text{CH}_2\text{CH}_2\text{OH})_2$ (abbreviated as RdeaH_2 , where $\text{R} = \text{H}$ or Me), afford dimeric isopropoxo-bridged six-coordinate butyltin(IV) complexes $[\{\text{Bu}(\eta^3\text{-Rdea})\text{Sn}(\mu\text{-OPr}^i)\}_2]$ ($\text{R} = \text{H}$ (1), Me (2)). Interactions between $\text{BuSn}(\text{OPr}^i)_3$ and diethanolamines (RdeaH_2) in a 1:2 molar ratio yield monomeric derivatives of the type $[\text{BuSn}(\text{Rdea})(\text{RdeaH})]$ ($\text{R} = \text{H}$ (3), $\text{R} = \text{Me}$ (4)). These homometallic complexes on 1:1 reactions with an appropriate metal alkoxide form monomeric heterobimetallic complexes of the type $[\text{BuSn}(\text{Rdea})_2\{\text{M}(\text{OR}')_n\}]$ ($\text{R} = \text{H}$, $\text{M} = \text{Al}$, $\text{R}' = \text{Pr}^i$, $n = 2$ (5); $\text{R} = \text{H}$, $\text{M} = \text{Ti}$, $\text{R} = \text{Pr}^i$, $n = 3$ (6); $\text{R} = \text{H}$, $\text{M} = \text{Zr}$, $\text{R}' = \text{Pr}^i$, $n = 3$ (7); $\text{R} = \text{Me}$, $\text{M} = \text{Al}$, $\text{R}' = \text{Pr}^i$, $n = 2$ (8); $\text{R} = \text{Me}$, $\text{M} = \text{Ti}$, $\text{R}' = \text{Pr}^i$, $n = 3$ (9); $\text{R} = \text{Me}$, $\text{M} = \text{Ge}$, $\text{R}' = \text{Et}$, $n = 3$ (10)). The driving force behind this work was (i) to explore the utility of homometal complexes (1)–(4) in assembling a metal alkoxide fragment via a condensation reaction and (ii) to gain insights into the structures of new compounds by NMR spectral data. All of these derivatives have been characterized by elemental analysis, spectroscopic (IR, NMR; ^1H , ^{27}Al , and ^{119}Sn) studies, and molecular weight measurements. ^{119}Sn NMR spectral studies indicate that both the homometallic (3) and (4) and heterobimetallic (5)–(9) complexes exist in a solution in an equilibrium of six- and five-coordinated tin(IV) species.

Keywords Butyltin(IV) complexes; butyltin(IV) diethanolaminates; heterobimetallic diethanolaminates

Heterometallic alkoxides and related compounds are excellent “single-source” precursors to technologically important ceramic oxides via sol-gel and MOCVD processes^{1–6} as well as more recently to nanocrystal fabrication.⁷ To synthesise such precursors, a metathesis route

Received May 15, 2006; accepted June 6, 2006.

Nandu Bala Sharma is grateful to the CSIR, New Delhi, for a Senior Research Fellowship.

Address correspondence to Anirudh Singh, University of Rajasthan, Department of Chemistry, Jaipur, 302004 India. E-mail: anirudhsinghuvijpr@yahoo.co.in

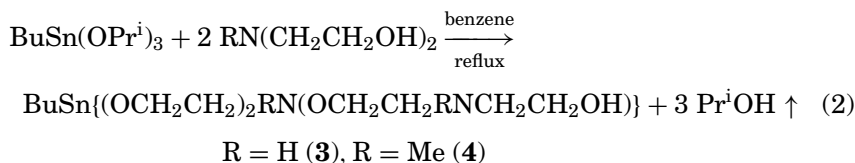
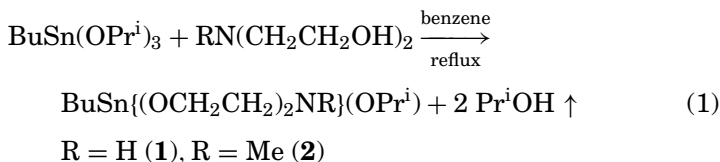
involving alkoxometallate ligands and metal chlorides has been widely employed.²⁻⁶

During the last few years, we have been involved in developing a new synthetic approach aiming at obtaining heterometallic alkoxide coordination complexes by using homometal complexes containing at least one hydroxy group as a reactive centre to bind different metal and organometal fragments. Accomplishments in this direction have been summarized in a review article.⁸ Furthermore, recently this synthetic strategy has resulted in a number of interesting publications.^{9,10}

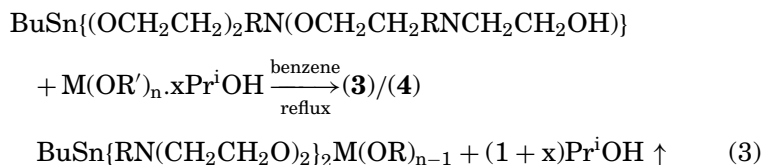
Surprisingly, heterometallic derivatives of butyltin(IV) derived from diethanolamine and N-substituted diethanolamines to the best of our knowledge are unknown. In this article, we report for the first time the synthesis and properties of homo- and heterobimetallic derivatives of butyltin(IV) based on diethanolamine ligands.

RESULTS AND DISCUSSION

Reactions of $\text{BuSn}(\text{OPr}^i)_3$ with $\text{RN}(\text{CH}_2\text{CH}_2\text{OH})_2$ in 1:1 and 1:2 molar ratios in benzene afford soluble derivatives according to Eqs. (1) and (2), respectively.



Equimolar reactions of (3) and (4) with different metal alkoxides in benzene yield hydrocarbon soluble complexes (5)–(10) according to Equation (3).



R = H, R' = Al, R' = Prⁱ, n = 3, x = 0 (**5**); R = H, M = Ti, R' = Prⁱ, n = 4, n = 0 (**6**); R = H, M = Zr, R' = Prⁱ, n = 4, x = 1 (**7**); R = Me, M = Al, R' = Prⁱ, n = 3, x = 0 (**8**); R = Me, M = Ti, R' = Prⁱ, n = 4, x = 0 (**9**); R = Me, M = Ge, R' = Et, n = 4, x = 0 (**10**).

All of the derivatives (**1**)–(**10**) (Table I) are moisture sensitive, viscous liquids or solids, and soluble in common organic solvents. Molecular weight determinations (cryoscopically/ebullioscopically) in benzene solution show that all these derivatives are monomeric in nature.

Spectral Studies

Homometallic derivatives (**1**) and (**4**) show infrared absorptions (Table II) characteristic of the diethanolamine⁹ and butyltin^{10a} moieties at 3387 ± 3 ν(OH), 2938, 2861 ν(CH), 2915, 2907 ν(NH), 1446 ν(CH₂), 1084–1038 ν(C–O), 592–589 ν(Sn–C), 520–575 ν(Sn–O) and 453–422 cm^{−1} ν(Sn←N). As expected, heterobimetallic derivatives (**5**)–(**10**) (Table II) do not show a band due to the OH group. Absorptions due to diethanolamine and isopropoxy groups in derivatives (**5**)–(**10**) are observed in the expected regions (Table II). Absorptions due to M–O (M = Al, Ti, Ge or Zr) bands⁶ are observed in the region 810–563 cm^{−1}. The medium to weak intensity bands¹⁰ due to ν(Sn–C), ν(Sn–O), and ν(Sn←N) appear at 592–565, 540–575, and 460–410 cm^{−1} regions, respectively.

¹H NMR spectra of the precursor derivatives (**3**) and (**4**) exhibit signals characteristic of a butyl group¹¹ attached to tin atom at δ 0.88–0.89 (Me(CH₂)₃Sn) and 1.28–1.79 (Me(CH₂)₃Sn) along with signals due to the diethanolamine moieties¹² at 2.68, 2.65 (Me), 2.83 ± 0.19 (NCH₂), 3.87 ± 1 (OCH₂), and a broad peak at δ 4.46 arising from the overlapping of NH and OH proton signals. The low-field shifting (~0.16 ppm) in the positions of signals for OH and NH groups indicate the involvement of these groups in bonding with the metal centre.

¹¹⁹Sn NMR spectroscopy with a spread of ¹¹⁹Sn chemical shifts of about 1000 ppm has proven to be a powerful technique for the unequivocal determination of the coordination number of tin in organotin(IV) complexes.¹³ ¹¹⁹Sn NMR signals for butyltin(IV) complexes are found in the region δ −389–451 for (five) coordinated tin atoms,^{11a,14} and for six-coordinated tin in butyltin(IV) complexes,¹⁵ signals are observed in the region δ −521–542. In this context, it is worth mentioning that the observed ¹¹⁹Sn chemical shifts are found to depend¹⁶ on the (i) coordination number, (ii) identity of the donor atoms in the coordination sphere, (iii) nature of 'R' group(s) attached to tin, (iv) structural feature of chelating ligand, and (v) state of aggregation of the concerned compound. Keeping all the previously discussed factors in mind, one can

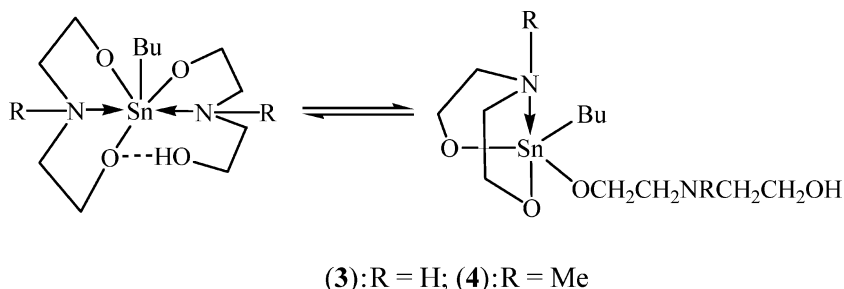
TABLE I Preparative, Analytical, and Some Physical Data for Compounds (1)–(10)

Reactants (g,mmol)	Product ^a Empirical Formula Yield ^b (g, %)	Liberated Pr ⁺ OH/EtN. Found (Calcd.)	% Analysis Found (Calcd.)					M.Wt.Found (Calcd.)
			C	H	N	Al/Ti/Nb/Zr	Sn	
BuSn(OPr ⁱ) ₃ (1.74, 4.94)	HdeaH ₂ (0.52, 4.94)	BuSn(Hdea)(OPr ⁱ) ⁽¹⁾ C ₁₁ H ₃₅ NO ₃ Sn (1.58, 95)	0.57 (0.59)	7.44 (7.45)	4.30 (4.14)	—	34.89 (35.11)	689 (338)
BuSn(OPr ⁱ) ₃ (3.78, 10.70)	MedeaH ₂ (1.28, 10.74)	BuSn(Medea)(OPr ⁱ) ⁽²⁾ C ₁₂ H ₃₇ NO ₃ Sn (3.76, 99)	1.28 (1.28)	7.54 (7.73)	3.95 (3.97)	—	33.60 (33.71)	728 (352)
BuSn(OPr ⁱ) ₃ (2.42, 6.85)	HdeaH ₂ (1.44, 13.70)	BuSn(Hdea)(HdeaH) ⁽³⁾ C ₁₂ H ₃₉ N ₂ O ₄ Sn (2.60, 99)	1.23 (1.24)	7.34 (7.36)	7.11 (7.31)	—	30.61 (30.98)	410 (383)
BuSn(OPr ⁱ) ₃ (1.36, 3.85)	MedeaH ₂ (0.92, 7.72)	BuSn(Medea)(MedeaH) ⁽⁴⁾ C ₁₄ H ₃₉ N ₂ O ₄ Sn (1.58, 99)	1.58 (1.58)	7.82 (7.84)	6.78 (6.81)	—	28.68 (28.86)	435 (411)
(3) (1.96, 5.11)	Al(OPr ⁱ) ₃	BuSn(Hdea) ₂ Al(OPr ⁱ) ₂ ⁽⁵⁾ C ₁₈ H ₄₁ AlN ₂ O ₆ Sn (2.69, 99)	0.28 (0.31)	7.81 (7.84)	5.17 (5.31)	5.10 (5.12)	22.83 (22.51)	540 (527)
(3) (2.23, 5.82)	Ti(OPr ⁱ) ₄ (1.65, 5.81)	BuSn(Hdea) ₂ Ti(OPr ⁱ) ₃ ⁽⁶⁾ C ₂₁ H ₄₈ N ₂ O ₇ SnTi (3.36, 95)	0.34 (0.35)	7.91 (7.96)	4.42 (4.61)	27.64 (27.42)	635 (607)	635 (607)
(3) (1.70, 4.43)	Zr(OPr ⁱ) ₄ ·Pr ⁺ OH (1.71, 4.41)	BuSn(Hdea) ₂ Zr(OPr ⁱ) ₃ ⁽⁷⁾ C ₂₁ H ₄₈ N ₂ O ₇ SnZr (2.84, 98)	0.53 (0.53)	7.40 (7.43)	4.12 (4.31)	14.19 (14.02)	18.26 (18.24)	685 (650)
(4) (1.58, 3.84)	Al(OPr ⁱ) ₃ (0.78, 3.81)	BuSn(Medea) ₂ Al(OPr ⁱ) ₂ ⁽⁸⁾ C ₂₀ H ₄₅ AlN ₂ O ₆ Sn (1.95, 91)	0.23 (0.23)	8.14 (8.16)	4.99 (5.04)	4.84 (4.86)	21.01 (21.37)	570 (555)
(4) (1.00, 2.43)	Ti(OPr ⁱ) ₄ (0.69, 2.42)	BuSn(Medea) ₂ Ti(OPr ⁱ) ₃ ⁽⁹⁾ C ₂₃ H ₅₂ N ₂ O ₇ SnTi (1.50, 97)	0.14 (0.15)	8.10 (8.16)	4.19 (4.40)	26.10 (26.22)	670 (635)	670 (635)
(4) (3.12, 7.58)	Ge(OEt) ₄ (1.92, 7.59)	BuSn(Medea) ₂ Ge(OEt) ₃ ⁽¹⁰⁾ C ₂₀ H ₄₆ GeN ₂ O ₇ Sn (4.51, 96)	0.34 (0.35)	7.45 (7.50)	4.42 (4.53)	30.49	30.95 (30.95)	640 (618)

Abbreviations: Hdea = HN(CH₂CH₂O)₂, HdeaH = HN(CH₂CH₂O)(CH₂CH₂OH), Medea = MeN(CH₂CH₂O)₂, MedeaH = MeN(CH₂CH₂O)(CH₂CH₂OH)
^aAll are yellow. Derivatives (1), (3), (5), (6), and (8) are solids, whereas (2), (4), (7), (9), and (10) are viscous liquids.
^bYield refers to the purified product (see the Experimental section).

TABLE II IR (cm⁻¹) and NMR (δ, ppm) Spectral Data for Compounds (1)–(10)

Compound	IR	¹ H	²⁷ Al	¹¹⁹ Sn
(1)	2940 ν(NH); 1190, 1140 ν(OP ⁺); 1050, 1010 ν(C–O); 565 ν(Sn–O), 426 ν(Sn←N)	0.83(t, 3H, Me (CH ₂) ₃ Sn); 1.17(s, 6H, OCHMe ₂); 1.61 (m, 6H, Me (CH ₂) ₃ Sn); 2.64(br, 4H, NCH ₂); 3.20(br, 4H, OCH ₂); 3.80 (br, 1H, NH); 4.15(Sept., 1H, OCHMe ₂)	—	–540
(2)	2938, 2868 ν(CH); 1449, ν(CH ₂) deformation, 1160, 1120 ν(OP ⁺), 1080, 1031 ν(C–O), 580 ν(Sn–C); 510 ν(Sn–O); 450 ν(Sn←N)	0.88(t, 3H, Me (CH ₂) ₃ Sn); 1.14(d, 6H, OCHMe ₂); 1.26(m, 2H, Me (CH ₂) ₂ CH ₂ Sn); 1.66(m, 2H, Me (CH ₂) ₂ CH ₂ Sn); 1.75(t, 2H, Me (CH ₂) ₂ CH ₂ Sn); 2.66(s, 3H, Me); 2.84(t, 4H, NCH ₂); 3.85 (m, 4H, OCH ₂); 4.01 (m, 1H, OCHMe ₂)	—	–537
(3)	3390 ν(OH); 2915, 2907 ν(NH); 1085 ν(C–O); 589 ν(Sn–C); 520 ν(Sn–O); 422 ν(Sn←N)	0.88(t, 3H, Me (CH ₂) ₃ Sn); 1.42(m, 6H, Me (CH ₂) ₂ CH ₂ Sn); 3.02 (br, 8H, NCH ₂); 3.88(br, 8H, OCH ₂); 4.46 (br, 3H, NH + OH)	—	–542 –389
(4)	3384 ν(OH); 2938, 2861 ν(CH); 1446 ν(CH ₂) deformation, 1084, 1038 ν(C–O), 592 ν(Sn–C), 515 ν(Sn–O), 453 ν(Sn←N)	0.89(t, 3H, Me (CH ₂) ₃ Sn); 1.28(m, 2H, Me (CH ₂) ₂ CH ₂ Sn); 1.69 (m, 2H, Me (CH ₂) ₂ CH ₂ Sn); 1.79(t, 2H, Me (CH ₂) ₂ CH ₂ Sn); 2.68, 2.65 (s, 6H, Me); 2.86(m, 8H, NCH ₂); 3.86(m, 9H, OCH ₂ + OH)	—	–543 –451
(5)	2914 ν(NH); 1183, 1110 ν(OP ⁺); 1085, 1040 ν(C–O) 686 ν(Al–O), 571 ν(Sn–O), 525 ν(Sn–O), 410 ν(Sn←N)	0.86(t, 3H, Me (CH ₂) ₃ Sn); 1.16(d, 12H, OCHMe ₂); 1.55 (m, 6H, Me (CH ₂) ₃ Sn); 2.53 (b, 8H, NCH ₂); 3.08(br, 8H, OCH ₂); 3.67 (br, 2H, NH); 4.24(m, 2H, OCHMe ₂)	28	–521 –526 –386 –388
(6)	2915 ν(NH); 1171, 1135 ν(OP ⁺); 1064, 1030 ν(C–O); 578 ν(Sn–C), 557 ν(Ti–O), 515 ν(Sn–O), 415 ν(Sn←N)	0.82(t, 3H, Me (CH ₂) ₃ Sn); 1.22(d, 18H, OCHMe ₂); 1.58 (m, 6H, Me (CH ₂) ₃ Sn); 2.61(br, 8H, NCH ₂); 3.18 (br, 8H, OCH ₂); 3.72 (br, 2H, NH); 4.27(m, 3H, OCHMe ₂)	—	–523 –527 –386 –382
(7)	2908 ν(NH); 1171, 1124 ν(OP ⁺); 1065, 1025 ν(C–O); 590 ν(Zn–C), 585 ν(Sn–C), 520 ν(Sn–O), 416 ν(Sn←N)	0.85(t, 3H, Me (CH ₂) ₃ Sn); 1.20(d, 18H, OCHMe ₂); 1.58 (m, 6H, Me (CH ₂) ₃ Sn); 2.59(br, 8H, NCH ₂); 3.12 (br, 8H, OCH ₂); 3.89 (br, 2H, NH); 4.26(m, 3H, OCHMe ₂)	—	–524 –528 –386 –383
(8)	2900, 2870 ν(CH); 1446 ν(CH ₂) deformation; 1100, 1070 ν(OP ⁺); 1040, 1000 ν(C–O), 610 ν(Al–O), 565 ν(Sn–C), 520 ν(Sn–O); 460 ν(Sn←N)	0.87(t, 3H, Me (CH ₂) ₃ Sn); 1.24(d, 12H, OCHMe ₂); 1.40 (m, 6H, Me (CH ₂) ₃ Sn); 2.62(s, 6H, Me); 2.86 (t, 8H, NCH ₂); 3.88(m, 8H, OCH ₂); 4.33 (m, 2H, OCHMe ₂)	25	–534 –538 –415 –426
(9)	2910, 2870 ν(CH); 1440 ν(CH ₂) deformation; 1120, 1090 ν(OP ⁺); 1030, 1000 ν(C–O), 583 ν(Sn–C), 563 ν(Ti–O), 530 ν(Sn–O); 460 ν(Sn←N)	0.87(t, 3H, Me (CH ₂) ₃ Sn); 1.23(d, 18H, OCHMe ₂); 1.42 (m, 6H, Me (CH ₂) ₃ Sn); 2.40(s, 6H, Me); 2.57 (t, 8H, NCH ₂); 3.84(m, 8H, OCH ₂); 3.94 (m, 3H, OCHMe ₂)	—	–536 –539 –415 –426
(10)	2940, 2890 ν(CH); 1448 ν(CH ₂) deformation; 1081 ν(C–O), 810 ν(Ge–O), 575 ν(Sn–O), 540 ν(Sn–O); 460 ν(Sn←N)	0.87(t, 3H, Me (CH ₂) ₃ Sn); 1.24(d, 9H, CH ₂ Me); 1.43 (m, 6H, Me (CH ₂) ₃ Sn); 2.51(s, 6H, Me); 2.58 (t, 8H, NCH ₂); 2.86(t, 8H, OCH ₂); 3.94 (m, 6H, CH ₂ Me)	—	–536 –540 –415 –426

**FIGURE 1**

arrive at a useful conclusion regarding the coordination geometry of the tin centre in organotin(IV) compounds. Derivatives **(3)** and **(4)** exhibit two ^{119}Sn signals at δ -542 and -389 and -543 and 451 , respectively. The presence of two signals in each of them indicates the occurrence of an equilibrium between six- and five-coordinated organotin(IV) species (Figure 1).

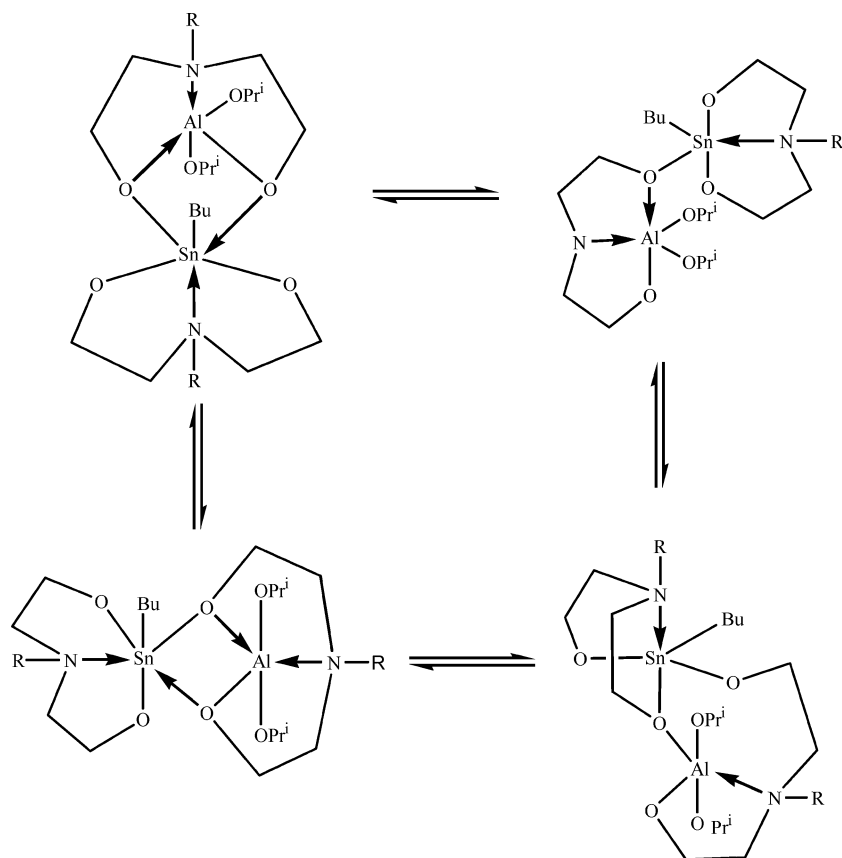
Heterometallic derivatives **(5)**–**(10)** exhibit ^1H NMR resonances characteristic of (i) diethanolamine groups¹² at δ 2.40–2.62 (**Me**), 2.53–2.86 (NCH_2), 3.08–3.88 (OCH_2), and 3.67–3.89 (**NH**); (ii) isopropoxy groups^{6,10} at δ 1.16–1.24 (doublet) and δ 3.94–4.33 (multiplet) due to methyl and methine protons, respectively; and (iii) a butyltin group¹¹ appears in the δ 0.82–0.87 (**Me**(CH_2)Sn) and 1.55–1.58 (**Me**(CH_2)Sn) regions.

Each of the **(5)**–**(10)** show two ^{119}Sn NMR signals in each of the δ -521 – -540 and -382 – -426 regions, indicating that in solution (i), the tin(IV) centre is present both in six- and five-coordinated geometries, and (ii) the appearance of a set of two signals in both of these regions may be due to the variation (especially in the axial positions) in the connectivity of the ligand donor sites around the central butyltin(IV) centre. These observations are tentatively interpretable in terms of an equilibrium shown in Figure 2.

In spite of repeated efforts, X-ray crystal structures of some of these derivatives could not be determined so far. However, ^1H , ^{27}Al , and ^{119}Sn NMR spectra have been quite helpful in arriving at plausible structures, such as shown in Figures 1 and 2 for all the derivatives.

EXPERIMENTAL

All reactions and manipulations were conducted under extreme anhydrous conditions, using oven-dried glassware fitted with interchangeable quickfit joints. Analytical-grade solvents were made anhydrous by

**FIGURE 2**

literature methods.¹⁷ Diethanolamines were purified and dried by the procedures described in the literature.^{12d} Alkoxides of aluminium,¹⁸ germanium,⁶ butyltin(IV),¹⁹ titanium,²⁰ and zirconium⁶ were prepared by literature methods. Aluminium was determined as oxinate.²¹ Zirconium, tin, titanium, and germanium were determined as their oxides.²¹ Isopropyl/ethyl alcohol in azeotrope was determined oxidimetrically.²² Molecular weights were determined cryoscopically in benzene solution. Nitrogen was determined by Kjeldahl's method.

IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded as Nujol mulls using CsI optics on a Nicolet Magna-550 spectrophotometer. ^1H , ^{27}Al , and ^{119}Sn NMR spectra were recorded on JEOL AL 300 FT NMR and JEOL FX 90Q NMR spectrometers. Carbon and hydrogen analyses were performed on a Perkin Elmer 2400-II CHNS/O analyzer.

The Synthesis of Homometallic Butyltin(IV) Diethanolamate Derivatives

BuSn{(OCH₂CH₂)₂NH}(OPrⁱ) (1)

The reaction mixture containing BuSn(OPrⁱ)₃ (1.74 g, 4.94 mmol) and HN(CH₂CH₂OH)₂ (0.52 g, 4.94 mmol) in benzene (~50 mL) was refluxed for 6 h. Liberated isopropyl alcohol during this period was fractionated out azeotropically and determined periodically to monitor progress and completion of the reaction. On completion of the reaction (as was evident by the amount of isopropyl alcohol collected), the reaction was stopped, and the volatiles from the solution were removed under reduced pressure to obtain a yellow solid compound, which was purified by recrystallization from a (2:1) mixture of dichloromethane and *n*-hexane at -20°C. Yield 1.58 (95%).

A similar procedure was employed for the synthesis of (2)–(4); the preparative details and analytical data are listed in Table I.

The Synthesis of Heterobimetallic Butyltin(IV) Diethanolamate Derivatives

BuSn{(OCH₂CH₂)₂NH}₂Al(OPrⁱ)₂(5)

A benzene solution (~60 mL) containing (3) (1.96 g, 5.11 mmol) and Al(OPrⁱ)₃ (1.04 g, 5.09 mmol) was refluxed under a fractionating column with continuous removal of the liberated isopropyl alcohol, which was determined periodically to monitor completion of the reaction. When the distillate showed negligible presence of isopropyl alcohol, refluxing was stopped, and the reaction mixture was allowed to cool to r.t. The solvent was removed under reduced pressure to obtain a yellow solid, which was dissolved in dichloromethane and precipitated by the addition of an excess of *n*-hexane to obtain after the usual workup the analytically pure product (5) as a yellow solid in a 2.69-g (99%) yield.

Derivatives (6)–(10) were prepared in an analogous manner. Preparative and analytical details are listed in Table I.

CONCLUSIONS

Homometal complexes (1)–(4) synthesized by the 1:1 and 1:2 molar reactions of BuSn(OPrⁱ)₃ with diethanolamines RN(CH₂CH₂OH)₂ (R=H, Me) have provided the opportunity to assemble a metal alkoxide fragment via a condensation reaction and the formation of novel complexes (5)–(10). ¹¹⁹Sn NMR spectral studies have been quite successful in indicating the presence of different (five- and six-coordinated) species in solution

REFERENCES

- [1] L. G. Hubert-Pfalzgraf, *New J. Chem.*, **11**, 663 (1987).
- [2] D. C. Bradley, *Chem. Rev.*, **89**, 1317 (1989).
- [3] K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, **90**, 969 (1990).
- [4] C. D. Chandler, C. Roger, and M. J. Hampden-Smith, *Chem. Rev.*, **93**, 1205 (1993).
- [5] R. C. Mehrotra and A. Singh, *Prog. Inorg. Chem.*, **46**, 239 (1997).
- [6] D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals* (Academic Press, London, 2001).
- [7] (a) T. J. Boyle, T. M. Alam, C. J. Tafoya, E. R. Mechenbier, and J. W. Ziller, *Inorg. Chem.*, **38**, 2422 (1999); (b) T. J. Boyle, T. M. Alam, D. Dimos, G. J. Moore, C. D. Buchheit, H. N. Al-Shareef, E. R. Mechenbier, and B. R. Bear, *Chem. Mater.* **9**, 3187 (1997); (c) T. J. Boyle, P. Clem, M. A. Rodriguez, B. Tuttle, and M. Heagy, *J. Sol. Gel. Sci., Technol.*, **16**, 47 (1999); (d) T. J. Boyle, J. J. Gallegos, D. M. Pedrotty, E. R. Mechenbier, and B. L. Scott, *J. Coord. Chem.*, **47**, 155 (1999); (e) T. J. Boyle, M. A. Rodriguez, D. Ingersoll, T. J. Headley, S. D. Bunge, D. M. Pedrotty, S. M. De Angeli, S. C. Vick, and H. Fan, *Chem. Mater.*, **15**, 3903 (2003).
- [8] A. Singh and R. C. Mehrotra, *Coord. Chem. Rev.*, **248**, 101 (2004).
- [9] M. Sharma, A. Singh, and R. C. Mehrotra, *Polyhedron*, **19**, 77 (2000).
- [10] (a) N. B. Sharma, A. Singh, and R. C. Mehrotra, *J. Chem. Res.*, 450 (2004); (b) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Main Group Met. Chem.*, **27**, 211 (2004); (c) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Main Group Met. Chem.*, **27**, 193 (2004); (d) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Main Group Met. Chem.*, **28**, 159 (2005); (e) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Transition Met. Chem.*, **30**, 845 (2005); (f) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Phosphorus, Sulfur and Silicon* (2006).
- [11] (a) S. Mishra, M. Goyal, and A. Singh, *Main Group Met. Chem.*, **25**, 437 (2002); (b) N. B. Sharma, A. Singh, and R. C. Mehrotra, *J. Organomet. Chem.*, **690**, 69 (2005).
- [12] (a) M. Sharma, A. Singh, and R. C. Mehrotra, *Polyhedron*, **18**, 77 (2002); (b) R. S. Ghadwal, R. C. Mehrotra, and A. Singh, *J. Chem. Res.*, 352 (2005); (c) R. S. Ghadwal, R. C. Mehrotra, and A. Singh, *Indian J. Chem.*, **44A**, 2439 (2005); (d) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Transition Met. Chem.*, **30**, 103 (2005).
- [13] (a) M. Pereyre, J.-P. Quintard, and A. Rahm, *Pure Appl. Chem.*, **54**, 29 (1982); (b) P. G. Harrison, In ed. P. G. Harrison, *Chemistry of Tin*, pp. 60–117 (Blackie, Glasgow, 1989); (c) B. Wrackmeyer, *Annu. Rep. NMR Spectroscopy*, **16**, 73 (1985).
- [14] (a) A. Jain, S. Saxena, and A. K. Rai, *Main Group Met. Chem.*, **16**, 223 (1993); (b) M. Biesemans, R. Willem, S. Bamoun, P. Geerlings, E. R. T. Tiekink, P. Jaumier, M. Lahcini, and B. Jousseume, *Organometallics*, **17**, 90 (1998); (c) B. Wrackmeyer, In ed. M. Gielen, R. Willem, and B. Wrackmeyer, *Physical Organometallic Chemistry, Advanced Applications of NMR to Organometallic Chemistry*, pp. 87–122 (John Wiley, Chichester, 1996) and references cited therein.
- [15] (a) J. Otera, A. Kusaba, T. Hinoishi, and Y. Kawasaki, *J. Organomet. Chem.*, **228**, 223 (1982); (b) G. G. Lobbia, F. Bonati, P. Cecchi, A. Lorenzotti, and C. Pettinari, *J. Organomet. Chem.*, **403**, 317 (1991); (c) G. G. Lobbia, S. Calogero, B. Bavio, and P. Cecchi, *J. Organomet. Chem.*, **440**, 27, (1992); (d) S. Mishra, M. Goyal, and A. Singh, *Main Group Met. Chem.*, **25**, 437 (2002).
- [16] (a) R. K. Harris, J. D. Kennedy, and W. Mc. Farlane, In ed. R. K. Harris and B. E. Mann, *NMR and the Periodic Table* (Academic Press, London, pp. 342, 1978); (b) J. S. Casas, A. Sánchez, J. Sordo, A. Vázquez-López, E. E. Castellano, J. Zukerman-Schpector, M. C. Rodríguez-Argüelles, and U. Russo, *Inorg. Chim.*

- Acta.*, **216**, 169, 1994; (c) T. B. Grindley and R. Thangarasa, *J. Am. Chem. Soc.*, **112**, 1364 (1990) and references cited therein.
- [17] W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., (Butterworth/Heinemann, Oxford, 1996).
- [18] L. M. Brown and K. S. Mazdiyasni, *Inorg. Chem.*, **9**, 2783 (1970).
- [19] D. P. Gaur, G. Srivastava, and R. C. Mehrotra, *J. Organomet. Chem.*, **63**, 221 (1973).
- [20] J. Nelle's, *Brit. Patent*, 1939, 512452; *Chem. Abstr.*, **34**, 3764 (1940).
- [21] J. Bassett, R. C. Denney, G. H. Jeffery, and J. Mendham, *Vogel's A Text Book of Quantitative Inorganic Analysis*, 5th ed. (Longman, London, 1989).
- [22] (a) C. Adams and J. R. Nichollas, *Analyst*, **50**, 2 (1929); (b) D. C. Bradley, F. M. A. Halim, and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950); (c) R. C. Mehrotra, *J. Indian Chem. Soc.*, **30**, 583 (1953).