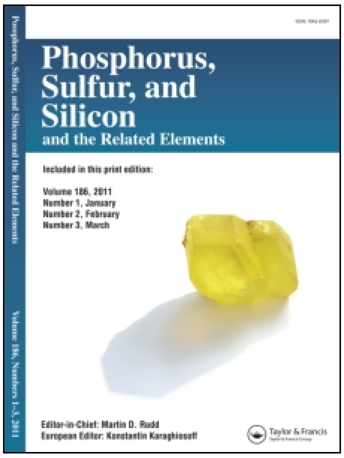

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Synthesis and Spectroscopic Characterization of Heterobimetallic $Bu_2Sn(IV)$ Complexes Derived from Some Chelating Ligands

Nandu Bala Sharma[a]; Anirudh Singh[a]; Ram C. Mehrotra[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

Phosphorus, Sulfur, and Silicon, 181:1527–1539, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500330877

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Nandu Bala Sharma
Anirudh Singh
Ram C. Mehrotra†
Department of Chemistry, University of Rajasthan, Jaipur, India

*The interaction of $Bu_2Sn(OPr^i)_2$ with a trifunctional tetradentate Schiff base (LH_3) (where $H_3L = HOC_6H_4CH{=}NCH_3C(CH_2OH)_2$) yields the precursor complex $Bu_2Sn(LH)$ **1**, which, on equimolar reactions with different metal alkoxides [$Al(OPr^i)_3$, $Bu_3Sn(OPr^i)$, $Ge(OEt)_4$]; $Al(Medea)(OPr^i)$ (where Medea = $CH_3N(CH_2CH_2O)_2$); and Me_3SiCl in the presence of Et_3N], affords, respectively, the complexes $Bu_2Sn(L)Al(OPr^i)_2$ **2**, $Bu_2Sn(L)Al(Medea)$ **3**, $Bu_2Sn(L)Bu_3Sn$ **4**, $Bu_2Sn(L)Ge(OEt)_3$ **5**, and $Bu_2Sn(L)SiMe_3$ **6**. The reactions of **2** with 2,5-dimethyl-2,5-hexanediol in a 1:1 ratio and with acetylacetone (acacH) in a 1:2 molar ratio afforded derivatives $Bu_2Sn(L)Al(OC(CH_3)_2CH_2CH_2C(CH_3)_2O)$ **7** and $Bu_2Sn(L)Al(acac)_2$ **8**, respectively. All of the derivatives **1–8** have been characterized by elemental analyses, molecular weight measurements, and spectroscopic [IR and NMR (^1H, ^{119}Sn, ^{29}Si, and ^{27}Al)] studies.*

Keywords Dibutyltin(IV) Schiff base complexes; heterobimetallic alkoxides; heterobiametallic derivatives; mixed ligand complexes

INTRODUCTION

The chemistry of homometallic derivatives derived from polyhydroxy multidentate ligands[1–7] has developed significantly during the last four decades. During this period, many new and interesting complexes

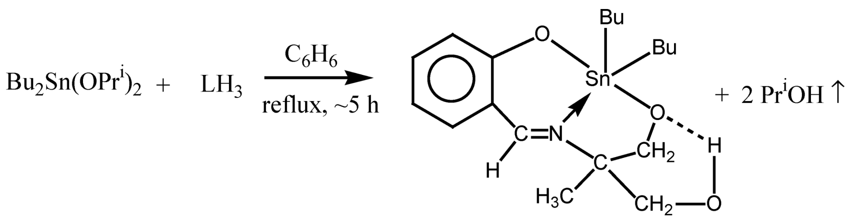
Received April 22, 2005; accepted August 1, 2005.
†Deceased.
Nandu Bala Sharma is grateful to the State Government of Rajasthan and the Department of Chemistry for a Fellowship under the Special Assistance Programme. Anirudh Singh (Emeritus Scientist) is grateful to the University Grant Commission, New Delhi, for financial support. We are grateful to the referee for helpful comments and suggestions. The authors are indebted to Mr. Suman Kumar Gupta for recording the NMR and microanalytical (C, H, and N) data.
Address correspondence to Anirudh Singh, University of Rajasthan, Department of Chemistry, Jaipur 32004, India. E-mail: anirudhsinghunivjpr@yahoo.co.in

with fascinating structural features and useful applications have been synthesized and characterized.

During the past few years, we have been successful in developing the chemistry of novel heterobimetallic alkoxide coordination compounds[8] derived from polyhydroxy alcohols such as glycols, di-, and triethanolamines. Prompted by the success with the previously discussed types of ligands, we report in this article the synthesis and spectroscopic characterization of different types of heterobimetallic organotin(IV) complexes derived from a trihydroxy tetradentate Schiff base $HOC_6H_4CH{=}NCH_3C(CH_2OH)_2$.

RESULTS AND DISCUSSION

A reaction in a 1:1 molar ratio of $Bu_2Sn(OPr^i)_2$ with a trifunctional tetradentate Schiff base (LH_3) affords the precursor complex **1** (Eq. (1)):

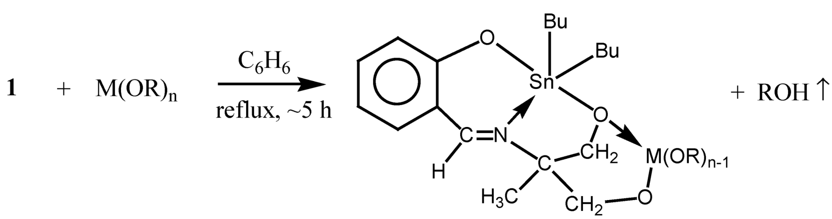


$L = OC_6H_4\,CH{=}NCH_3C(CH_2O)_2$

1

(1)

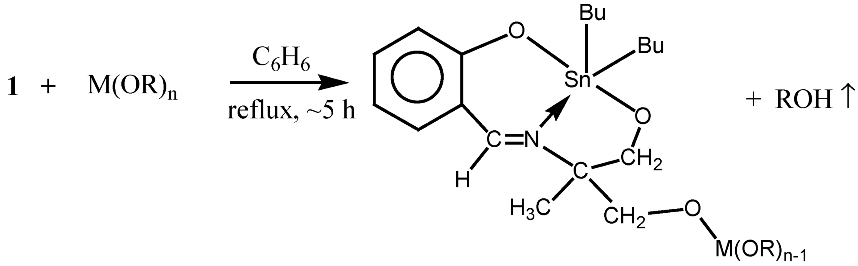
Interesting heterobimetallic dibutyltin(IV) complexes **2**, **3** (Eq. (2)), **4**, and **5** (Eq. (3)) have been prepared by the equimolar reactions of **1** with different metal alkoxides in benzene medium.



2, 3

	M	R	n
2:	Al	Pr^i	3
3:	Al(Medea)	Pr^i	1

(2)

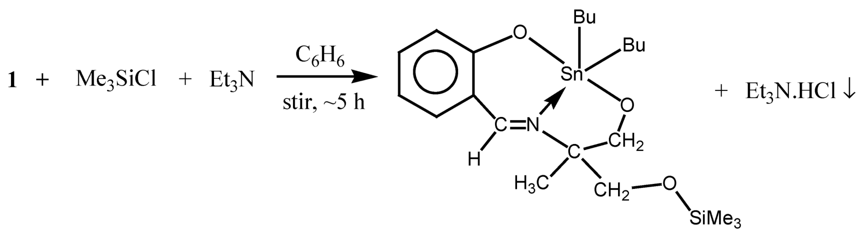


4, 5

	M	R	n
4:	Bu_3Sn	Pr^i	1
5:	Ge	Et	4

(3)

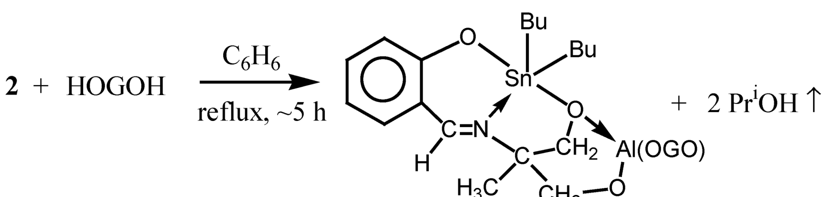
The interaction of **1** with Me_3SiCl in the presence of Et_3N as a proton acceptor yields **6** (Eq. (4)):



6

(4)

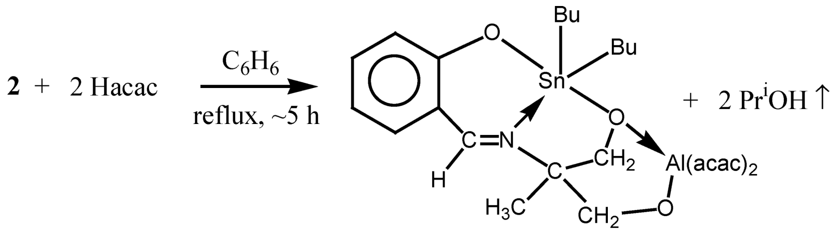
The reaction of **2** with 2,5-dimethyl-2,5-hexanediol or (Eq. (5)) acetylacetone (acacH) (Eq. (6)) yields the appropriate heterobimetallic compound **7** or **8**, respectively:



$G = C(CH_3)_2CH_2CH_2C(CH_3)_2$

7

(5)



8

(6)

All of the heterobimetallic derivatives **2–8** are moisture-sensitive solids or viscous liquids are and soluble in common organic solvents (e.g., benzene, toluene, carbon tetrachloride, dichloromethane, etc.). The cryoscopic molecular weight determinations (Table I) depict their monomeric nature.

Spectral Studies

Spectroscopic characterization of new derivatives (**2**)–(**8**) have been accomplished by IR and NMR (^{1}H, ^{27}Al, ^{29}Si, ^{119}Sn) spectral studies. IR[9–17] and NMR[18–39] spectral assignments, conclusions, and comparisons presented in the following pages are based on published data on related systems.

IR Spectra

Infrared spectra of organotin(IV) chelates derived from Schiff bases[3] provide valuable information regarding the structure of compounds in the solid state. In general either an increase or decrease in the frequency of a C=N stretching vibration,[13–17] which appears around 1630 ± 15 cm^{-1} in the spectra of free ligands by a few wave numbers, has been generally observed, and it has been inferred that ligands coordinate to the tin atom through the azomethine nitrogen atom.

Furthermore, for trigonal bipyramidal diorganotin(IV) compounds, the observed spectral pattern provides valuable information[9g,10] regarding the placement of various groups within the coordination sphere of the tin atom.

The infrared spectra of the dibutyltin derivatives **1–8** exhibit structurally salient absorptions[9–11] (Table II) at 584 ± 2, $577 \pm 2 \nu$(Sn—C), 546 ± 1 ν(Sn—O), 1624 ± 1 ν(C=N), 1249 ± 1 ν(C—O) phenolic, 1062 ± 2 ν(C—O) alcoholic, and 452 ± 1 cm^{-1} ν(Sn $\leftarrow$ N). Absorptions characteristic of isopropoxy groups in the derivative **2** appear at 1140 and

TABLE I Preparative, Analytical, and Some Physical Data for Derivatives 1–8

Reactants (g, mmol)		Product state, yield[a](%)	Liberated Pr^iOH found (calc.)	% Analysis found (calc.) C	H	N	Sn/Ge/Si	Al	M.wt found (calc.)
1	$Al(OPr^i)_3$	$Bu_2Sn(L)\ Al(OPr^i)_2$ **2**	0.26	50.99	7.51	2.36	20.20	4.64	599
(1.97, 4.47)	(0.91, 4.45)	solid, 68	(0.26)	(51.33)	(7.58)	(2.39)	(20.31)	(4.62)	(584)
1	$Al(Medea)(OPr^i)$	$Bu_2Sn(L)Al$ (Medea) **3**	0.30	49.27	7.06	4.75	20.29	4.60	598
(2.26, 5.13)	(1.04, 5.11)	solid, 69	(0.30)	(49.37)	(7.08)	(4.80)	(20.34)	(4.62)	(583)
1	$Bu_3Sn\ (OPr^i)$	$Bu_2Sn(L)\ (Sn\ Bu_3)$ **4**	0.26	50.99	7.81	1.86	32.48	—	734
(2.03, 4.61)	(1.61, 4.61)	liquid, 98	(0.27)	51.01	(7.87)	(1.91)	(32.54)		(729)
1	$Ge(OEt)_4$	$Bu_2Sn(L)Ge(OEt)_3$ **5**	0.22	46.21	7.11	2.21	29.47		656
(2.14, 4.86)	(1.23, 4.86)	waxy solid, 78	(0.22)	(46.37)	(7.01)	(2.16)	(29.56)	—	(647)
			(EtOH)				(mixed oxide)		
1	Me_3SiCl	$Bu_2Sn(L)SiMe_3$ **6**	0.81	51.43	7.50	2.69	28.59		525
(2.61, 5.92)	(0.65, 5.98)	viscous liquid, 89	(0.81)	(51.52)	(7.67)	(2.73)	(28.64)		(512)
	ET_3N		$Et_3N.HCl$				(mixed oxide)	—	
	(0.60, 5.92)								
2	HOGOH[b]	$Bu_2Sn(L)\ Al(OGO)$ **7**	0.30	52.99	7.58	2.26	19.12	4.25	668
(1.48, 2.53)	(0.37, 2.53)	semisolid, 75	(0.31)	(53.13)	(7.59)	(2.29)	(19.44)	(4.42)	(610)
2	Hacac	$Bu_2Sn\ (L)\ Al(acac)_2$ **8**	0.24	52.39	6.51	2.06	17.65	4.08	680
(1.20, 2.05)	(0.41, 4.09)	semisolid, 61	(0.25)	(52.42)	(6.67)	(2.10)	(17.86)	(4.06)	(664)

[a]Yield refers to the purified product.
[b]$G = C(CH_3)_2CH_2CH_2C(CH_3)_2$.

TABLE II IR (cm^{-1}) and NMR (δ, ppm) Data for Heterobimetallic Derivatives **2–8**

Compound	IR: ν(C=N)	IR: ν(C—O) Phenolic/Alcoholic	IR: ν(M—O)	IR: ν(Sn—C)	IR: ν(Sn—O)	IR: ν(Sn—N)	^{1}H	^{119}Sn	^{27}Al
2	1625	1248/1062	609 (M=Al)	584 578	547	453	0.95(t, 6H, Sn(CH$_2$)$_3$C**H**$_3$); 1.15–1.50(m, 27H, CC**H**$_3$ + Sn(C**H**$_2$)$_3$CH$_3$ + OCHC**H**$_3$); 3.80(s, 4H, C**H**$_2$O); 4.27(m, 2H, OC**H**CH$_3$); 6.62–7.40 (m, 4H, aromatic-**H**); 8.20(s, 1H, C**H**)	−169	53
3	1625	1250/1064	612 (M=Al)	586 577	546	452	0.90(t, 6H, Sn(CH$_2$)C**H**$_3$); 1.25–1.60(m, 15H, C**C**H$_3$ + Sn(C**H**$_2$)$_3$); 2.33(s, 3H, C**H**$_3$N); 2.60(t, 4H, NC**H**$_2$); 3.66(s,4H, C**H**$_2$O); 3.95(br, 4H, C**H**$_2$O(Medea)); 6.60–7.40(m, 4H, aromatic-**H**); 8.35(s, 1H, C**H**)	−175	14
4	1624	1250/1062	—	586 576	545	453	0.94(t, 15H, Sn(CH$_2$)$_3$C**H**$_3$); 1.26–1.73(m, 33H, CC**H**$_3$ + Sn(C**H**$_2$)$_3$CH$_3$); 3.66(s, 4H, C**H**$_2$O); 6.67–7.36(m, 4H, aromatic-**H**); 8.32(s, 1H, C**H**)	−192 (Bu$_2$Sn) −110 (Bu$_3$Sn)	
5	1625	1249/1062	798 (M=Ge)	585 578	547	452	0.96(t, 6H, Sn(CH$_2$)$_3$C**H**$_3$); 1.23(t, 9H, OCH$_2$C**H**$_3$); 1.25–1.62(m, 15H, CC**H**$_3$ + Sn(C**H**$_2$)$_3$CH$_3$); 3.72(s, 4H, C**H**$_2$O); 4.0(m, 6H,OC**H**$_2$CH$_3$); 6.91–7.38(m, 4H, aromatic-**H**); 8.34(s, 1H, C**H**)	−195	—
6	1624	1250/1063	672 (M=Si)	583 576	546	453	0.10(s, 3H, SiC**H**$_3$); 0.90(t, 6H, Sn(CH$_2$)$_3$C**H**$_3$); 1.25–1.60(m, 15H, CC**H**$_3$ + Sn(C**H**$_2$)$_3$CH$_3$); 3.65(s, 4H, C**H**$_2$O); 6.65–7.40(m, 4H, aromatic-**H**); 8.35(s, 1H, C**H**)	−190	—
7	1625	1250/1062	609 (M=Al)	584 575	546	453	0.87(t, 6H, Sn(CH$_2$)$_3$C**H**$_3$); 1.26(s, 12H, (C**H**$_3$)$_2$); 1.36–1.62(m, 19H, CC**H**$_3$ + Sn(C**H**$_2$)$_3$CH$_3$ + C**H**$_2$); 3.51(s, 4H, C**H**$_2$O); 6.65–7.36(m, 4H, aromatic-**H**); 8.10(s, 1H, C**H**)	−178	52
8	1624	1249/1063	610 (M=Al)	583 577	545	453	0.90(t, 6H, Sn(CH$_2$)$_3$C**H**$_3$); 1.25–1.60(m, CC**H**$_3$ + Sn(C**H**$_2$)$_3$CH$_3$); 1.95(s, 12H, C**H**$_3$CO); 3.70(s, 4H, C**H**$_2$O); 5.55(s, 2H, C**H**CO); 6.67–7.50(m, 4H, aromatic-**H**); 8.25(s, 1H, C**H**)	−165	7

1109 cm^{-1}. Derivatives **2**, **4**, **5**, **6**, **7**, and **8** exhibit absorptions characteristic of heterometal-oxygen stretching vibrations at 609 ν(Al—O), 798 ν(Ge—O), 612 ν(Al—O), 844 ν(Si—O), 609 ν(Al—O), and 611 ν(Al—O) cm^{-1}, respectively. The appearance of two absorptions associated with Sn—C and only one for Sn-O stretching vibrations is consistent with the trigonal bipyramidal geometry[9g,10] in which two n-butyl groups and a donor nitrogen atom are occupying equatorial positions, whereas two oxygens are in axial sites.

The presence of the trimethylsilyl group in the derivative (**6**) is supported by the appearance of a strong absorption at 1248 cm^{-1} due to the $\nu(Si{-}CH_3)$ deformation and at 844, 750 arising from ν(Si—C) stretching vibrations.[12]

The coordination of the azomethine nitrogen atom to the tin(IV) center has been supported by shifting ν(C=N) to lower ($\sim$15 cm^{-1}) wave numbers[11,16] with respect to that observed (1640 cm^{-1}) in the free ligand. The appearance of new bands at 452 ± 1 are assignable to Sn $\leftarrow$ N stretching frequencies.[11,34]

^{1}H NMR

The compound **1** shows a sharp signal for the hydroxy proton ($CH_2O\mathbf{H}$) at δ3.52 along with the signals due to the dibutyltin(IV) moiety at δ0.87 ($Sn(CH_2)_3C\mathbf{H}_3$), 1.25–1.58 ($CC\mathbf{H}_3$ + $Sn(CH_2)_3C\mathbf{H}_3$), 6.53–7.24 (aromatic-**H**), and 8.21 (**H**C=N). ^{1}H NMR spectra (Table II) of **2–8** exhibit signals at δ 0.87–0.96 ($Sn(CH_2)_3C\mathbf{H}_3$), 1.15–1.73 ($CC\mathbf{H}_3$ + $Sn(C\mathbf{H}_2)_3CH_3$), 3.51–3.80 ($C\mathbf{H}_2O$), 6.60–7.50 (aromatic-**H**), and 8.10–8.35 (**H**C=N). Derivative **3** shows signals characteristic of deprotonated *N*-methyldiethanolamine at δ2.33 ($C\mathbf{H}_3N$), 2.60 ($NC\mathbf{H}_2$), and 3.95 ($C\mathbf{H}_2O$). Additional signals for glycolate moiety in **7** and the acetylacetonate group in **8** have been observed, respectively, at δ1.26 $(C\mathbf{H}_3)_2$, 1.36–1.62 ($C\mathbf{H}_2$), 1.95 ($C\mathbf{H}_3CO$), and 5.55 (C**H**CO). Signals for isopropoxy in **2** and ethoxy groups in **5** appear, respectively, at δ 1.15, 4.27, 1.23, 4.00.

^{29}Si NMR

The spectrum of the derivative (**6**) shows a ^{29}Si NMR signal at δ88 ppm, which is consistent with a four-coordinate silicon atom.[12,18–20]

^{119}Sn NMR

^{119}Sn NMR spectroscopy has proven to be a powerful technique for obtaining information about the coordination status of tin atoms.[21–37] ^{119}Sn chemical shifts in organotin(IV) compounds have been found to be influenced by several factors,[26–28] such as the coordination number, identity of the donor atoms in the coordination sphere, nature of "R" groups on tin, structural feature of the chelating ligand as well as the aggregation of the concerned compound. In view of this, at present, their interpretation is limited to an essentially qualitative level.[29] ^{119}Sn resonances for five-coordinate organotin(IV) compounds are generally located between −90–236 ppm.

^{119}Sn NMR chemical shifts in trigonal bipyramidal diorganotin(IV) compounds appear to depend not only on the coordination number but also on the identity of the donor atom in the coordination sphere,[21–37] in addition to the dependence on concentration of the solution[27] as well as on the nature of alkyl or aryl group attached to the tin atom.[27–37] For example, diorganotin(IV) glycolates incorporating pentacoordinate tin[22,23,27,30] exhibit ^{119}Sn chemical shifts in the −120–190 ppm region and corresponding acyclic alkoxides, such as $Bu_2Sn(OMe)_2$, which is known to associate into a dimer containing pentacoordinate tin[22] that shows a $\delta(^{119}Sn)$ signal of −165 ppm. Interestingly, 2,2-di-tert-butyl-1,3,2-dioxastannolane[27] which is dimeric involving five-coordinate tin, exhibits a ^{119}Sn chemical shift at $\delta - 225$. Furthermore, the five-coordinate tin in dimethyltin(IV) salicylaldiehyde thiosemicarbazonate[28] shows a ^{119}Sn signal at $\delta{-}104.7$. This difference is probably due to the sulfur atom having a lower shielding effect on the tin nuclei than the oxygen atom. Further, it is interesting to note that the diphenyltin(IV) derivative[28] shows a ^{119}Sn signal ($\delta - 235.4$) at a higher field than in an analogous dimethyltin compound, in spite of the greater electron-withdrawing capability of the phenyl group.

A comparison of ^{119}Sn chemical shifts of **1**($\delta - 191$), **2**($\delta - 169$), **3**($\delta - 192$), **4**($\delta - 195$), **5**($\delta - 175$), **6**($\delta - 190$), **7**($\delta - 178$) and **8**($\delta - 165$) with those of analogous compounds, such as diorganotin(IV)diethanolaminates[33]($\delta - 113$), $Bu^t_2Sn(OCH_2CH_2)_2NR$[24] (R=H, $\delta - 210$; R=Me, $\delta - 205$) and diorganotin(IV) n-arylsalicylaldiminates[34]($\delta - 137 \pm 6, -170 \pm 2$), which form a discrete, five-coordinate, R_2SnNO_2 monomeric unit, reveals a close relationship in their structural features. The appearance of two signals in cases of latter derivatives[34] has been interpreted in terms of isomeric forms resulting from azomethine nitrogen occupying either an equatorial or axial position. Similar behavior is also supported by the observation of two sets of ^{119}Sn NMR chemical shifts ($\delta - 198.5, -219.9; -203.2, -221.7; -220.4; -238.8; -190.8, -239.4$) in tetraorganodistannoxanes $[\{R_2Sn(ON{=}C(Me)Py)\}_2O]_2$ (R=Bu^n, Et) whose structures have been crystallographically[35] determined. Two other types of X-ray crystallographically established dimeric distannoxanes, $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}OCH_3)_2O]_2$ and $[(n\text{-}Bu_2SnO_2(C_6H_4\text{-}O\text{-}Cl)_2O]_2$, with tin in a five-coordinate state[36] generated by two n-butyl groups; three oxygen atoms also exhibit a pair of signals at $\delta - 212.9$, and -213.4; -203.6, and -201.2, respectively. The appearance of a pair of ^{119}Sn signals appears to be characteristic of a dimeric structure for the trigonal bipyramidal diorganotin(IV) compounds.[36]

In view of the previously discussed description, it may be concluded that all the new derivatives **1–8** are monomeric species in which trigonal bipyramidal geometry around a tin atom is generated by two alkyl groups, a nitrogen atom in the equatorial positions, and two oxygen atoms in axial sites.

A perusal of the ^{119}Sn chemical shifts reported in Table II for **1–8** indicates that a heterometal fragment appears to have some influence on the tin center in these compounds. Although it is difficult to pinpoint factors responsible for subtle variations in the ^{119}Sn chemical shifts of the new derivatives, the group electronegativity of the heterometal fragment along with its Lewis acidity/ability to achieve higher coordination state may be playing a key role.

^{27}Al NMR Spectra

The observed ^{27}Al NMR signals at $\delta 53$ and 52 ppm, respectively, for **2** and **7** support for four-coordinate[38a,39] aluminium. Derivatives **3** and **8** exhibit signals at δ 14 and 7 ppm, respectively, which are consistent with five- and six-coordinate aluminium.[38b,39]

EXPERIMENTAL

Rigorous precautions were taken to exclude moisture from the glassware, reactants, and solvents. Solvents (benzene, *n*-hexane, isopropyl alcohol, ethyl alcohol, and dichloromethane) were dried and purified by the literature methods.[40] Isopropoxides of dibutyltin,[41] tributyltin,[42] aluminium,[43] and germanium ethoxide[44] were prepared by the published procedures. 2,5-dimethyl-2,5-hexanediol[45] and *N*-methyldiethanolamine[15] were dried and purified by the methods reported in the literature. A Schiff base (LH_3) was prepared by the equimolar condensation of salicylaldehyde and 2-amino-2-methyl-1,3-propanediol in benzene, followed by recrystallization from EtOH, and it was and analyzed for its nitrogen content 6.69% (Calc. 6.69%); ^1H NMR (δ, ppm): 1.30 (s, 3H, C**H**$_3$); 1.56 (s, 2H, CH$_2$O**H**); 3.83 (s, 4H, C**H**$_2$); 6.89–7.33 (m, 4H, aromatic-**H**); 8.10 (s, 1H, C**H**); 13.70 (br, 1H, phenolic-O**H**). Aluminium was determined as an oxinate.[46] The total content of germanium and tin or silicon and tin in the same compound was determined as a mixed oxide.[46] Alcohols in the azeotrope were determined by an oxidimetric method.[47–49]

IR (4000–400 cm^{-1}) spectra were recorded on Magna 550 spectrophotometer using CsI optics. The ^{1}H (89.55 MHz), ^{27}Al (23.29 MHz), ^{119}Sn (33.35 MHz), and ^{29}Si (17.55 MHz) NMR were recorded in $CDCl_3$ and benzene solutions on a JEOL FX 90 Q and JEOL AL300 NMR spectrometers using tetramethylsilane (TMS) as an internal reference. Carbon, hydrogen, and nitrogen analyses were recorded on a Perkin-Elmer Series II CHNS/O analyzer-2400. Molecular weights were determined cryoscopically in benzene solutions.

The Synthesis of $Bu_2Sn(OC_6H_4CH{=}NCH_3C(CH_2O)(CH_2OH))$ 1

To a benzene (~40 mL) solution of $Bu_2Sn(OPr^i)_2$ (5.68 g, 16.17 mmol) was added $HOC_6H_4CH{=}NCH_3C(CH_2OH)_2$ (3.38 g, 16.15 mmol) was added, and the resulting brown solution was refluxed under a fractionating column with the continuous removal of the liberated azeotropically isopropyl alcohol (1.94 g) with benzene until the distillate showed a negligible presence of isopropyl alcohol. After completion of the reaction, refluxing was stopped, and volatiles from the solution were removed under reduced pressure to obtain brown semisolid of 7.05 g (99%), which, on recrystallization from *n*-hexane at −20°C, gave an analytically pure product **1** as a brown semisolid in a 5.55 g (78%) yield. IR (Nujol): 1625ν(C=N), 1249 ν(C—O) phenolic, 1062 ν(C—O) aliphatic, 585, 578 ν(Sn—C), 546 ν(Sn—O), and 453 $\nu(Sn \leftarrow N)$ cm^{-1}. ^{1}H NMR ($CDCl_3$)δ0.87 (t, 6H, $Sn(CH_2)_3C\mathbf{H}_3$); 1.25–1.58 (m, 16H, $CC\mathbf{H}_3$ + $Sn(C\mathbf{H}_2)_3CH_3$ + $CH_2O\mathbf{H}$); 3.52 (s, 4H, $C\mathbf{H}_2O$); 6.53–7.24 (m, 4H, aromatic-**H**); 8.21 (s, 1H, C**H**). ^{119}Sn NMR ($CDCl_3$) : $\delta - 191$ ppm. Anal. calc.: C, 51.80; H, 7.09; N, 3.18; Sn, 26.96%; mol. wt., 440. Found: C, 52.16; H, 7.27; N, 3.03; Sn, 26.89%; mol. wt., 557.

The Synthesis of Heterobimetallic Complexes

$Bu_2Sn(OC_6H_4CH{=}NCH_3C(CH_2O)_2)Al(OPr^i)_2$ 2

The benzene (~50 ml) solution of **1** (1.97 g, 4.47 mmol) and $Al(OPr^i)_3$ (0.91 g, 4.45 mmol) was refluxed with continuous removal of the liberated isopropyl alcohol until the required amount (0.26 g) of isopropyl alcohol was collected in the distillate. After completion of the reaction, refluxing was stopped, and volatiles from the solution were removed under reduced pressure to obtain a brown solid, which, on recrystallization from a 1:2 mixture of *n*-hexane and dichloromethane at −20°C, gave the analytically pure product **2** as a brown solid in a 1.78 g (68%) yield.

Compounds **3, 4**, and **5** were prepared by the procedure similar to **2**. Preparative and analytical details are given in Table I.

$Bu_2Sn(OC_6H_4CH{=}NCH_3C(CH_2O)_2)SiMe_3$ 6

The benzene solution (~15 mL) containing Me_3SiCl (0.65 g, 5.98 mmol) and Et_3N (0.60 g, 5.92 mmol) was added to a solution of **1** (2.61 g, 5.92 mmol) in benzene (~25 mL). The reaction mixture was stirred at r.t. for ~4 h. After removal of the precipitated $Et_3N.HCl$ (0.81 g), volatiles from the solution were removed under reduced pressure to yield **6** (2.98 g). The product was dissolved in a 2:1 mixture of dichlromethane and *n*-hexane and kept at $-20°C$ for several days, but no crystallization took place. The solvent was then removed under reduced pressure to obtain the title compound as a viscous liquid in a 2.69 g (89%) yield. Further details are given in Table I.

$(Bu_2Sn(OC_6H_4CH{=}NCH_3C(CH_2O)_2Al(OC(CH_3)_2CH_2CH_2C(CH_3)_2O)$ 7

The brown benzene (~45 mL) solution of **2** (1.48 g, 2.53 mmol) and $HOC(CH_3)_2CH_2CH_2C(CH_3)_2OH$ (0.37 g, 2.53 mmol) was refluxed for ~4 h with the continuous azeotropic removal of isopropyl alcohol (0.30 g). When the distillate showed the negligible presence of an oxidizable species, volatile components from the solution were removed under reduced pressure to obtain a brown semisolid (1.54 g), which, on recrystallization from a 1:2 mixture of *n*-hexane and dichloromethane at $-20°C$, gave the analytically pure product **7** as a brown semisolid 1.15 g (75%).

Compound **8** was prepared as a brown semisolid in 1.34 g (98%) by a procedure similar to that described for **7**. Analytical details are summarized in Table I.

REFERENCES

[1] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Prog. Inorg. Chem.*, **7,** 83 (1966).
[2] S. Yamada, *Coord. Chem. Rev.*, **1,** 415 (1966).
[3] R. C. Mehrotra, G. Srivastava, and B. S. Saraswat, *Revs. Si, Ge, Sn, Pb Compounds*, **6,** 171 (1982).
[4] J. C. G. Bunzli and D. Wessner, *Coord., Chem. Rev.*, **60,** 191 (1984).
[5] D. E. Fenton and P. A. Vigato, *Chem. Soc. Rev.*, **17,** 69 (1988).
[6] M. Nath and S. Goyal, *Main Group Met. Chem.*, **19,** 75 (1996).
[7] S. Yamada, *Coord. Chem. Rev.*, **192,** 537 (1999).
[8] A. Singh and R. C. Mehrotra, *Coord. Chem. Rev.*, **248,** 101 (2004).
[9] (a) R. A. Cummins and J. V. Evans, *Spectrochim Acta*, **21,** 1016 (1965); (b) R. A. Cummins, *Aust. J. Chem.*, **18,** 985 (1965); (c) T. Tanaka, *Organomet. Chem. Rev.* (A), **5,** 1 (1970); (d) F. K. Butcher, W. Gerrard, E. F. Mooney, R. G. Rees, and H. A. Willis, *Spectrochim Acta*, **20,** 5, (1964); (e) J. Lorberth and M. R. Kula, *Chem. Ber.*, **97,** 3444

(1964); (f) J. Mendelsohn, A. Marchand, and J. Valade, *J. Organomet. Chem.*, **6,** 25 (1968); (g) J. P. Clark, and C. J. Wilkins, *J. Chem. Soc.* (A), 871 (1966).
[10] K. Nakamoto, In pp. 73–135. *Characterization of Organometallic Compounds*, M. Tsutsui, Ed., pp. 73–135 (Interscience Publishers, London/New York, 1969).
[11] M. Nath, C. L. Sharma, and N. Sharma, *Synth. React. Inorg. Met.-Org. Chem.*, **21,** 807 (1991).
[12] M. Goyal, S. Mishra, and A. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **31,** 1705 (2001) and references cited therein.
[13] V. P. Sokalov, V. A. Kogan, O. A. Osipov, and M. I. Rumyantseva, *J. Gen. Chem. USSR*, **38,** 2404 (1968).
[14] (a) T. N. Srivastava and A. K. S. Chauhan, *J. Inorg. Nucl. Chem.*, **39,** 371 (1977); (b) T. N. Srivastava and A. K. S. Chauhan, *Synth. React. Inorg. Met.-Org. Chem.*, **7,** 373 (1977); (c) T. N. Srivastava, A. K. S. Chauhan, and V. K. Awasthi, *Ind. J. Chem.*, **15A,** 1023 (1977).
[15] R. S. Ghadwal, A. Singh, and R. C. Mehrotra, *Transition Met. Chem.*, **29,** 419 (2004).
[16] (a) P. Teyssie and J. J. Charette, *Spectrochim Acta*, **19,** 1407 (1963); (b) G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, **34,** 3369 (1972); (c) J. E. Kovacic, *Spectrochim Acta*, **23A,** 183(1967).
[17] L. V. Orlova, A. D. Garnovskii, O. A. Osipov, and O. A. Raevskii, *J. Gen. Chem. USSR*, **37,** 1704 (1967).
[18] M. Goyal, S. Mishra, and A. Singh, *Phosphorus, Sulfur, and Silicon*, **175,** 143 (2001).
[19] E. A. Williams, In *The Chemistry of Organic Silicon Compounds*, S. Patai and Z. Rapport, Eds., pp. 520 (Wiley, Chichester, 1989).
[20] B. Wrackmeyer, In *Physical Organometallic Chemistry, Advanced Application of NMR to Organometallic Chemistry*, M. Gielen, R. Willem, and B. Wrackmeyer, Eds., p. 87 (John Wiley, Chichester, 1996).
[21] N. B. Sharma, A. Singh, and R. C. Mehrotra, *Main Group Met. Chem.*, **27,** 211 (2004) and references cited therein.
[22] P. J. Smith, R. F. M. White, and L. Smith, *J. Organomet. Chem.*, **40,** 341 (1972).
[23] C. Luchinat and S. Roelens, *J. Am. Chem. Soc.*, **108,** 4873 (1986).
[24] K. Jurkschat, C. Mügge, A. Tzschach, A. Zschunke, M. E. Larin, V. A. Pestunovich, and M. G. Voronkov, *J. Organomet. Chem.*, **139,** 279 (1977).
[25] B. Wrackmeyer, *Ann. Rep. NMR Spectrosc.*, **16,** 73 (1985).
[26] R. K. Harris, J. D. Kennedy, and W. McFarlane, in *NMR and the Periodic Table*, R. K. Harris and B. E. Mann Eds., p. 342 (Academic Press, London, 1978).
[27] T. B. Grindley and R. Thangarasa, *J. Am. Chem. Soc.*, **112,** 1364 (1990) and references cited herein.
[28] J. S. Casas, A. Sánchez, J. Sordo, A. Vázquez-López, E. E. Castellano, J. Zukerman-Schpector, M. C. Rodriguez-Argüelles, and U. Russo, *Inorg. Chem. Acta*, **216,** 169 (1994).
[29] R. Hani and R. A. Geanangel, *Coord. Chem. Rev.*, **44,** 239 (1982).
[30] J. Otera, *J. Organomet Chem.*, **221,** 57 (1981).
[31] J. C. Pommier and J. Valade, *J. Organomet. Chem.*, **12,** 433 (1968).
[32] P. J. Smith and A. P. Tupciauska, *Ann. Rep. NMR Spectrosc.*, **8,** 29 (1978).
[33] K. Sharma, M. Sharma, A. Singh, and R. C. Mehrotra, *Main Group Met. Chem.*, **26,** 131 (2003).
[34] S. Mishra, M. Goyal, and A. Singh, *Main Group Met. Chem.*, **25,** 437 (2002).
[35] V. Sharma, R. K. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. B. Hursthouse, and M. E. Light, *J. Organomet. Chem.*, **651,** 98 (2002).
[36] S. P. Narula, S. Kaur, R. Shankar, S. K. Bharadwaj, and R. K. Chadha, *J. Organomet. Chem.*, **506,** 181 (1996).

[37] R. G. Swisher and R. R. Holmes, *Organometallic*, **3,** 365 (1984).
[38] (a) N. B. Sharma, A. Singh, and R. C. Mehrotra, *J. Organomet. Chem.*, **690,** 96 (2005); (b) N. B. Sharma, A. Singh, and R. C. Mehrotra, *Main Group Met. Chem.*, **27,** 191 (2004).
[39] O. Kriz, B. Casensky, A. Lyccka, J. Fusek, and S. Hermanek, *J. Magn. Res.*, **60,** 375 (1984).
[40] D. D. Perrin, W. I. F. Aramarego, and D. R. Perrin, Eds., *Purification of Laboratory Chemicals*, 3rd ed. (Pergamon Press, Oxford, U.K., 1986).
[41] R. C. Mehrotra and B. P. Bachlas, *J. Oraganomet. Chem.*, **22,** 121 (1970).
[42] (a) D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals* (Academic Press, London, 2001); (b) D. P. Gaur, G. Srivastava, and R. C. Mehrotra, *J. Organomet. Chem.*, **63,** 221 (1973).
[43] L. M. Brown and K. S. Mazdiyasni, *Inorg. Chem.*, **9,** 2783 (1970).
[44] D. C. Bradley, L. J. Kay, and W. Wardlaw, *J. Chem. Soc.*, 4916 (1956).
[45] N. B. Sharma, A. Singh, and R. C. Mehrotra, *J. Chem. Res.*, 450 (2004).
[46] A. I. Vogel, *A Text Book of Quantitative Chemical Analysis*, 5th ed. (Longman, London, 1989).
[47] C. Adams and J. R. Nichollas, *Analyst*, **50,** 2 (1929).
[48] D. C. Bradley, F. M. A. Halim, and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950).
[49] R. C. Mehrotra, *J. Indian Chem. Soc.*, **30,** 585 (1953).