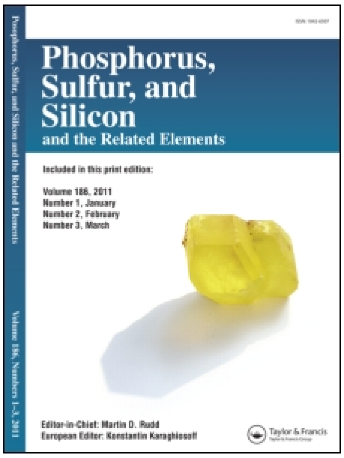

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Synthesis and Spectroscopic Characterization of New Homo- and Heterobimetallic Diorganotin(IV) Derivatives

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Synthesis and Spectroscopic Characterization of New Homo- and Heterobimetallic Diorganotin(IV) Derivatives

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The interaction in a 1:1 molar ratio of $Bu_2Sn(OPr^i)_2$ *with Schiff bases* $HOC_6H_4CH{=}NC_6H_3Me_2$*-2,6* (HL^1) *and* $HOC_{10}H_6CH{=}NC_6H_3Me_2$*-2,6*($HL^2$) *yields homometallic derivatives* $Bu_2Sn(\eta^2\text{-}L^1)(OPr^i)$ ***1*** *and* $Bu_2Sn(\eta^2\text{-}L^2)(OPr^i)$ ***2****, where deprotonated ligands* L^1 *and* L^2 *are bonded in a bidentate* (η^2) *fashion through O and N atoms. Complexes* ***1*** *and* ***2*** *react in an equimolar ratio with* $Al(OCHMeCH_2CMe_2O)(OCHMeCH_2CMe_2OH)$ ***A*** *or* $Al\{(OCH_2CH_2)_2(C_6H_5)N(OCH_2^{-}CH_2(C_6H_5)NCH_2CH_2OH)\}$ ***B*** *to afford heterobimetallic derivatives* ***3–6*** *incorporating five-coordinate tin and four-coordinate aluminium in* ***3*** *and* ***5*** *and five-coordinate both tin and aluminium in* ***4*** *and* ***6****. Furthermore, the reaction of* ***2*** *with* Ph_3SiOH *affords a heteronuclear derivative* ***7*** *having tin and silicon, respectively, in a five- and four-coordinate environment. All of these derivatives have been characterized by elemental analysis, spectroscopic (IR, NMR;* ^1H*,* ^{27}Al*,* ^{29}Si*, and* ^{119}Sn*) studies, and molecular weight determinations. The creation of new synthetic routes for heterometallic alkoxide coordination systems is an important goal, and investigations focused on this objective will ultimately increase our understanding of many aspects associated with the formation and stability of heterometallic coordination systems in general.*

Keywords Dibutyltin derivatives; heterobimetallic derivatives; mixed-ligand derivatives

Inspite of considerable development in the chemistry of heterometallic alkoxide and related systems[1–7] incorporating tin(IV), surprisingly organotin(IV) heterometallic systems are rare. Very recently we have been successful in the synthesis and spectroscopic characterization of novel heterometallic systems, such as $BuSn(OGO)_2Al(OPR^i)_2$,[8] $BuSn(L)M(OPr^i)_n$,[9] $Bu_2Sn(L)Al(OPr^i)_2$,[10a] and $BuSn(L)Ge(OET)_3$.[10b] Furthermore, a large number of tin(IV) and organotin(IV) derivatives

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of Schiff-bases and β-ketoamines with novel chemical, physical, and structural features are known, but heterometallic organotin(IV) derivatives featuring Schiff base moieties are limited[9–11] in number.

In view of more interesting results obtained during the last few years in our studies on novel types of heterometallic organotin(IV) derivatives,[8–11] we were encouraged to investigate the spectroscopic and some physical properties of the complexes formed by the reaction of $BuSn(\eta^2\text{-L})(OPr^i)$ (where $L = OC_6H_4CH{=}NC_6H_3Me\text{-}2,6$ and $OC_{10}H_6CH{=}NC_6H_3Me_2\text{-}2,6$) with an aluminium glycolate derivative containing one hydroxy group. We present here some results of such studies.

RESULTS AND DISCUSSION

A reaction in a 1:1 molar ratio of $Bu_2Sn(OPr^i)_2$ with Schiff bases HL^1 and HL^2 affords homometallic derivatives.

$$Bu_2Sn(OPr^i)_2 + HL^1 \text{ or } HL^2 \xrightarrow[\text{reflux}]{\text{benzene}}$$

$$Bu_2Sn(\eta^2\text{-}L^1)(OPr^i) \text{ or } Bu_2Sn(\eta^2\text{-}L^2)(OPr^i) + Pr^iOH\uparrow \qquad (1)$$

$$\mathbf{1}\text{: } L^1 = OC_6H_4CH{=}NC_6H_3Me_2\text{-}2{,}6$$

$$\mathbf{2}\text{: } L^2 = OC_{10}H_6CH{=}NC_6H_3Me_2\text{-}2{,}6$$

Homometallic derivatives **1** and **2** react in equimolar amounts with $Al(OCHMeCH_2CMe_2O)(OCHMeCH_2CMe_2OH)$ **A** (Eq. (2)) and $Al\{(OCH_2CH_2)_2\text{-}(C_6H_5)N(OCH_2CH_2(C_6H_5)NCH_2CH_2OH)\}$ **B** (Eq. (3)) to yield heterobimetallic derivatives **3–6**.

$$\mathbf{1/2} + \mathbf{A} \xrightarrow[\text{reflux}]{\text{benzene}} Bu_2Sn(\eta^2\text{-L})Al(OCHMeCH_2CMe_2O)_2 + Pr^iOH\uparrow \qquad (2)$$

$$\mathbf{3}\text{: } L = L^1, \quad \mathbf{4}\text{: } L = L^2$$

$$\mathbf{1/2} + \mathbf{B} \xrightarrow[\text{reflux}]{\text{benzene}} Bu_2Sn(\eta^2\text{-L})Al\{(OCH_2CH_2)_2NC_6H_5\}_2 + Pr^iOH\uparrow \qquad (3)$$

$$\mathbf{5}\text{: } L = L^1, \quad \mathbf{6}\text{: } L = L^2$$

A reaction of **2** with Ph_3SiOH produces a heteronuclear derivative containing five-coordinate tin(IV) and four-coordinate silicon(IV) in the same molecule.

$$\mathbf{2} + Ph_3SiOH \xrightarrow[\text{reflux}]{\text{benzene}} \underset{\mathbf{7}}{Bu_2Sn(L^2)Si(O)Ph_3} + Pr^iOH\uparrow \qquad (4)$$

All of the new derivatives **1–7** (Table I) are yellow semisolids soluble in typical organic solvents and monomeric (cryoscopically) in benzene solution.

TABLE I Analytical and Some Physical Data for Diorganotin(IV) Derivatives

Reactants[a] (g, mmol)		Liberated Pr^iOH found (Calcd.)	Product color and state[b] yield (g)	% Analysis found (Calcd.)					M. Wt. found (Calcd.)
				Sn	Al/Si	C	H	N	
$Bu_2Sn(OPr^i)_2$	L^1H	0.27	$Bu_2Sn(L^1)(OPr^i)$ **1**	22.90	—	60.98	8.18	2.11	530
(1.66, 4.72)	(1.07, 4.74)	(0.28)	(2.42)	(22.98)		(60.48)	(7.61)	(2.71)	(516)
$Bu_2Sn(OPr^i)_2$	L^2H	0.42	$Bu_2Sn(L^2)(OPr^i)$ **2**	20.81	—	64.95	7.06	2.41	574
(2.54, 7.23)	(1.99, 7.22)	(0.43)	(3.78)	(20.95)		(63.61)	(7.29)	(2.47)	(566)
1	Al (OGO)(OGOH)	0.31	$Bu_2Sn(L^1)Al(OGO)_2$ **3**	16.23	3.64	58.14	7.19	1.89	738
(2.73, 5.28)	(1.38, 5.30)	(0.32)	(3.78)	(16.56)	(3.76)	(58.65)	(7.87)	(1.95)	(717)
1	Al	0.31	$Bu_2Sn(L^1)Al(Phdea)_2$ **4**	14.00	3.18	61.18	6.90	4.90	860
(2.75, 5.32)	(Phdea)(PhdeaH)	(0.32)	(4.45)	(14.08)	(3.20)	(61.28)	(6.93)	(4.93)	(843)
	(2.06, 5.33)								
2	Al (OGO)(OGOH)	0.32	$Bu_2Sn(L^2)Al(OGO)_2$ **5**	15.01	3.10	61.27	7.59	1.70	790
(3.19, 5.63)	(1.47, 5.64)	(0.34)	(4.29)	(15.48)	(3.52)	(61.09)	(7.62)	(1.82)	(767)
2	Al	0.32	$Bu_2Sn(L^2)Al(Phdea)_2$ **6**	13.05	3.04	64.46	6.05	4.64	906
(3.16, 5.57)	(Phdea)(PhdeaH)	(0.33)	(4.95)	(13.29)	(3.02)	(63.22)	(6.77)	(4.70)	(893)
	(2.16, 5.58)								
2	Ph_3SiOH	0.34	$Bu_2Sn(L)OSiPh_3$ **7**	18.10		68.91	6.28	1.76	818
(3.31, 5.84)	(1.61, 5.82)	(0.35)	(4.55)	(18.86)		(68.99)	(6.31)	(1.78)	(783)

[a] Abbreviation: $L^1 = OC_6H_4CH{=}NC_6H_3Me_2\text{-}2,6$; $L^2 = OC_{10}H_6CH{=}NC_6H_3Me_2\text{-}2,6$; $G = CHMeCH_2CMe_2$; $Phdea = PhN(CH_2CH_2O)_2$.

[b] All are yellow semisolids.

Spectroscopic Studies

IR spectra[11–13] of homo- and heteronuclear derivatives **1–7** (Table II) exhibit (i) the absence of a broad absorption band due to the phenolic OH group of the Schiff base ligands; (ii) the ν(C=N) at ~1630 cm^{-1}, which is ~12 wavenumber lower than those observed in the parent ligands; (iii) phenolic ν(C-O) in the 1280–1290 cm^{-1} region; and (iv) bands at 585 ± 5, 557 ± 8, and 435 ± 5, which may be assigned to ν(Sn-C),[14] ν(Sn-O),[15] and ν(Sn $\leftarrow$ N),[16] respectively. Absorptions characteristic of isopropoxy groups in derivatives **1** and **2** appear in the 1175–1180 and 1159–1160 cm^{-1} regions. Bands due to a glycolate[17] moiety in derivatives **3** and **5** appear at 1350, 1370 $\nu(CMe_2)$, and 710–715 $\nu(CH_2)$. Absorptions due to a N-phenyldiethanolaminate[18] group in derivatives **4** and **6** appear at 1370 and 1375 ν(C-N). Aluminium–oxygen stretching vibrations in derivatives **3–6** appear at 620 ± 10 cm^{-1}.

The presence of the triphenylsilyl group in the derivative **7** is supported by the appearance of absorption bands at 1235 cm^{-1} due to the ν(Si-C) deformation and at 999, 825, and 750 arising from ν(Si-O), ρ_r(Si-C), and ν(Si-C), respectively.

The coordination of the azomethine nitrogen[9] atom to the tin(IV) center has been supported by the shifting of ν(C=N) to lower (~12 cm^{-1}) wavenumbers with respect to those observed (at 1638(HL^1)/1641(HL^2) cm^{-1}) in the free ligands. The appearance of new bands at 435 ± 5 are assignable[9] to Sn $\leftarrow$ N stretching frequencies.

^{1}H NMR Spectra

All the derivatives **1–7** show ^{1}H NMR signals (Table II) due to dibutyltin and Schiff-base moieties at (δ, ppm) 0.88–0.93 ($\mathbf{Me}(CH_2)_3Sn$), 1.29–1.31 ($MeC\mathbf{H}_2(CH_2)_2Sn$), 1.58–1.59 ($MeCH_2C\mathbf{H}_2CH_2Sn$), 1.61–1.64 ($Me(CH_2)_2C\mathbf{H}_2Sn$), 2.23–1.31 (**Me**), 6.43–8.00 (aromatic-**H**), and 8.34–9.12 (**H**C=N). Derivatives **1** and **2** show signals due to isopropoxy groups at δ 1.29–1.30 ($OCH\mathbf{Me}_2$) and 3.95–3.98 ($OC\mathbf{H}Me_2$).

Derivatives **3** and **5** show signals characteristic of a glycolate moiety in the δ 1.21–1.25 (C**Me**), 1.27–1.30 (CH**Me**), 1.55–1.56 ($C\mathbf{H}_2$), and 4.21–4.25 (C**H**Me) ppm regions. Signals for the deprotonated N-phenyldiethanolaminate group in derivatives **4** and **6** appear in the δ 3.51–3.57 ($NC\mathbf{H}_2$), 3.91–3.95 ($OC\mathbf{H}_2$), and 6.43–8.08 ($C_6\mathbf{H}_5$) ppm regions.

^{119}Sn NMR Spectra

The observed ^{119}Sn NMR signals (Table II) for **1–7** in the δ $-172 - -190$ ppm region support five-coordinate[19] tin in these derivatives (Figures 1a and 1b).

TABLE II IR (cm^{-1}) and NMR (δ, ppm) Spectral Data for Dioganotin(IV) Derivatives

Compound	IR	^{1}H	$^{27}Al/^{29}Si$	^{119}Sn
1	1630 $\nu(C{=}N)$, 1280 ν(C-O)phenolic, 1180, 1159 $\nu(OPr^{i})$, 580 ν(Sn-C), 560 ν(Sn-O), 430 $\nu(Sn \leftarrow N)$	0.91 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.29 (d, 6H, $OCH\mathbf{Me}_2$); 1.31 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.59 (m, 4H, $MeCH_2C\mathbf{H}_2CH_2Sn$); 1.64 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.23 (s, 6H, **Me**); 6.60–7.39 (m, 7H, aromatic-**H**); 8.67 (s, 1H, $\mathbf{H}C{=}N$)	—	−190
2	1632 $\nu(C{=}N)$, 1290 ν(C-O)phenolic, 1175, 1160 $\nu(OPr^{i})$, 580 ν(Sn-C), 550 ν(Sn-O), 437 $\nu(Sn \leftarrow N)$	0.93 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.29 (d, 6H, $OCH\mathbf{Me}_2$); 1.32 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.58 (m, 4H, $MeCH_2C\mathbf{H}_2CH_2Sn$); 1.61 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.29 (s, 6H, **Me**); 6.90–7.45 (m, 9H, aromatic-**H**); 9.12 (s, 1H, $\mathbf{H}C{=}N$)	—	−186
3	1630 $\nu(C{=}N)$, 1350 $\nu(CMe_2)$, 1280 ν(C-O)phenolic, 710 $\nu(CH_2)$, 610 ν(Al-O), 585 ν(Sn-C), 560 ν(Sn-O), 440 $\nu(Sn \leftarrow N)$	0.91 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.22 (s, 12H, $C\mathbf{Me}$); 1.27 (s, 6H, $CH\mathbf{Me}$); 1.30 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.55 (d, 4H, $C\mathbf{H}_2$); 1.64 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.24 (s, 6H, **Me**); 4.23 (m, 2H, $C\mathbf{H}Me$); 6.95–7.36 (m, 7H, aromatic-**H**); 8.34 (s, 1H, $\mathbf{H}C{=}N$)	41	−185
4	1631 $\nu(C{=}N)$, 1370 ν(C-N), 1280 ν(C-O)phenolic, 612 ν(Al-O), 585 ν(Sn-C), 560 ν(Sn-O), 437 $\nu(Sn \leftarrow N)$	0.91 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.31 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.59 (m, 4H, $MeCH_2C\mathbf{H}_2CH_2Sn$); 1.64 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.20 (s, 6H, **Me**); 3.51 (t, 4H, $NC\mathbf{H}_2$); 3.95 (t, 4H, OCH_2); 6.43–7.48 (m, 12H, aromatic-**H**); 8.34 (s, 1H, $\mathbf{H}C{=}N$)	13	−190
5	1632 $\nu(C{=}N)$, 1370 $\nu(CMe_2)$, 1285 ν(C-O)phenolic, 715 $\nu(CH_2)$, 616 ν(Al-O), 590 ν(Sn-C), 562 ν(Sn-O), 435 $\nu(Sn \leftarrow N)$	0.91 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.20 (s, 12H, $C\mathbf{Me}$); 1.30 (s, 6H, $CH\mathbf{Me}$); 1.32 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.56 (d, 4H, $C\mathbf{H}_2$); 1.62 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.30 (s, 6H, **Me**); 4.25 (m, 2H, $C\mathbf{H}Me$); 7.00–8.10 (m, 7H, aromatic-**H**); 9.13 (s, 1H, $\mathbf{H}C{=}N$)	41	−184
6	1633 $\nu(C{=}N)$, 1375 ν(C-N), 1281 ν(C-O)phenolic, 613 ν(Al-O), 580 ν(Sn-C), 560 ν(Sn-O), 440 $\nu(Sn \leftarrow N)$	0.91 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.31 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.58 (m, 4H, $MeCH_2C\mathbf{H}_2CH_2Sn$); 1.63 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.30 (s, 6H, **Me**); 3.57 (t, 4H, $NC\mathbf{H}_2$); 3.91 (t, 4H, OCH_2); 6.63–7.86 (m, 14H, aromatic-**H**); 9.13 (s, 1H, $\mathbf{H}C{=}N$)	14	−172
7	1632 $\nu(C{=}N)$, 1285 ν(C-O)phenolic, 1235 ν(Sn-C), 999 ν(Si-O), 825 ν(Si-C), 750 ν(Si-C), 585 ν(Sn-C), 560 ν(Sn-O), 440 $\nu(Sn \leftarrow N)$	0.82 (t, 6H, $\mathbf{Me}(CH_2)_3Sn$); 1.29 (m, 4H, $MeC\mathbf{H}_2(CH_2)_2Sn$); 1.58 (m, 4H, $MeCH_2C\mathbf{H}_2CH_2Sn$); 1.63 (t, 4H, $Me(CH_2)_2C\mathbf{H}_2Sn$); 2.30 (s, 6H, **Me**); 7.01–8.00 (m, 24H, aromatic-**H**); 9.12 (s, 1H, $\mathbf{H}C{=}N$)	16	−185

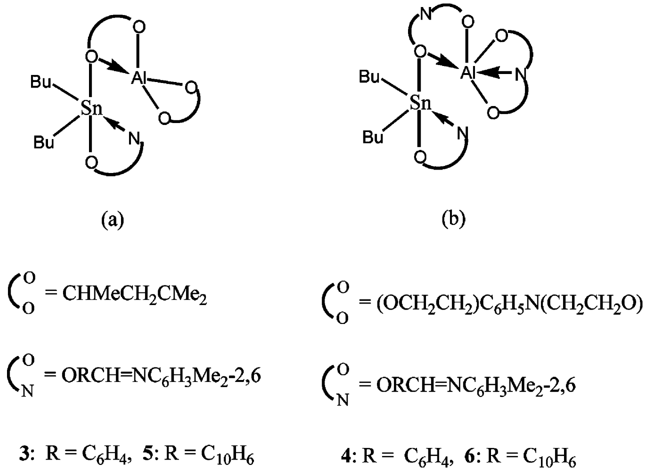

FIGURE 1 Plausible structures of (a) **3**, **5** and (b) **4, 6**.

^{29}Si NMR Spectra

The spectrum of derivative **7** shows an ^{29}Si NMR signal at δ 16 ppm, which is consistent with the four-coordinate[20] silicon atom.

^{27}Al NMR Spectra

The observed ^{27}Al NMR signals (Table II) at δ 41 ppm for derivatives **3** and **5** support four-coordinate[21] aluminium (Figure 1a). Signals at δ 13 and δ14 ppm, respectively, for derivatives **4** and **6** are consistent with five-coordinate[22] aluminium (Figure 1b).

Herein we have shown that the chelating ligand metal complexes **1** and **2** are a versatile scaffold for the construction of novel heterobimetallic coordination complexes incorporating an organotin(IV) moiety and an aluminium complex or an organosilicon fragment. Furthermore, for these complexes one can foresee promising application as single-source precursors to binary tin/aluminium and tin/silicon oxides via sol-gel process.

MATERIALS AND METHODS

Adequate precautions were taken to exclude moisture during reactions and storage of reactants/products. Solvents[23] (benzene, isopropyl alcohol, *n*-hexane, and dichloromethane), glycol,[8] and N-phenyldiethanolamine[18] were purified and dried by the literature procedures. Isopropoxides of dibutyltin(IV)[24] and aluminium[25] were prepared by the literature methods. Schiff-bases,[26] $Al(OCHMeCH_2CMe_2O)$ $(OCHMeCH_2CMe_2OH)$,[17] and $Al\{(OCH_2CH_2)_2(C_6H_5)N(OCH_2CH_2(C_6H_5)NCH_2\text{-}CH_2OH)\}$[27] were prepared by the methods already reported in the literature. Aluminium was determined as oxinate.[28] Tin and silicon were determined as their oxides.[28] Isopropyl alcohol in the azeotrope was determined oxidimetrically.[29] Molecular weights were determined cryoscopically in benzene solution. ^1H, ^{27}Al, ^{29}Si, and ^{119}Sn NMR were recorded in $CDCl_3$ on a JEOL FTAL 300 MHz NMR spectrometer. IR spectra (4000–400 cm^{-1}) were recorded as Nujol mulls on a Nicolet Magna 550 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin Elmer 2400-II CHNS/O analyzer.

The Preparation of $Bu_2Sn(OC_6H_4CH{=}NC_6H_3Me_2\text{-}2,6)(OPr^i)$ 1

To a benzene (∼60 mL) solution of $Bu_2Sn(OPr^i)_2$ (1.66 g, 4.72 mmol) was added $HOC_6H_4CH{=}NC_6H_3Me_2\text{-}2,6$ (1.07 g, 4.74 mmol), and the resulting yellow solution was refluxed under a fractionating column with continuous removal of the liberated isopropyl alcohol. When the required amount (0.28 g) of alcohol was collected in the azeotrope and further distillate showed a negligible presence of an oxidizable species, the refluxing was stopped, and the reaction mixture was allowed to cool to r.t. The volatile components from the solution were removed under reduced pressure to obtain a yellow semisolid. Recrystallization from *n*-hexane at −20°C gave an analytically pure title compound (2.42 g, 99%) as a yellow semisolid. Analytical data are summarized in Table I.

Compound **2** was prepared by a procedure similar to that already described for **1**. Preparative and analytical data are listed in Table I.

The Preparation of $Bu_2Sn(OC_6H_4CH{=}NC_6H_3Me_2\text{-}2,6)Al(OCHMeCH_2CMe_2O)_2$ 3

A benzene solution (∼50 mL) containing **1** (2.73 g, 5.28 mmol) and $Al(OCHMeCH_2CMe_2O)(OCHMeCH_2CMe_2OH)$ (1.38 g, 5.30 mmol) was refluxed with continuous removal of the liberated isopropyl alcohol azeotropically untill the distillate required amount (0.32 g) of isopropyl alcohol was collected. After completion of the reaction was evident by the absence of an oxidizable material in the distillate collected thereafter, refluxing was stopped, and volatiles from the solution were removed under reduced pressure to obtain a yellow semisolid. Recrystallization from the 1:2 mixture of *n*-hexane and dichloromethane at

−20°C gave analytically pure product **3** as a yellow semisolid (3.78 g, 99%).

Compounds **4–6** were prepared by a procedure similar to **3**. Further details are summarized in Table I.

The Preparation of $Bu_2Sn(OC_{10}H_6CH{=}NC_6H_3Me_2\text{-}2,6)OSiPh_3$ 7

To a benzene (∼45 mL) solution of $Bu_2Sn(OC_{10}H_6CH{=}NC_6H_3Me_2$-2,6)($OPr^i$) (3.31 g, 5.84 mmol), Ph_3SiOH (1.61 g, 5.82 mmol) was added, and the resulting yellow solution was refluxed under a fractionating column with continuous removal of the liberated isopropyl alcohol (0.34 g). When the distillate showed negligible presence of isopropyl alcohol, the 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 semisolid. Recrystallization from a (1:2) mixture of *n*-hexane and dichloromethane at −20°C gave analytical pure product **7** as a yellow semisolid (4.45 g, 99%). Analytical details are summarized in Table I.

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