Heteroatom Chemistry
Volume 00, Number 0, 2012

Diorganotin(IV) Complexes of Polyaromatic Azo-Azomethine Ligand Derived from Salicylaldehyde and *ortho*-Aminophenol: Synthesis, Characterization, and Molecular Structures

Smita Basu,[1] Cheerfulman Masharing,[2] and Babulal Das[3]

[1]*Department of Chemistry, North Eastern Hill University, Shillong 793 022, India*

[2]*Department of Chemistry, Shillong College, Laitumkhrah, Shillong 793 003, India*

[3]*Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India*

Received 20 March 2012; revised 6 June 2012

ABSTRACT: *The diorganotin(IV) complexes of methyl 2-{4-hydroxy-3-[(2-hydroxy-phenylimino)-methyl]-phenylazo}-benzoate (H2L) were obtained by the reaction of* ortho*-aminophenol, R_2SnO (R = Me, ^nBu, or Ph) and methyl 2-[(E)-(3-formyl-4-hydroxy)diazenyl]benzoate ($H2PL^2$) in ethanol, which led to diorganotin(IV) compounds of composition $[Me_2SnL]_2$ (**1**), $^nBu_2SnL$ (**2**), and Ph_2SnL (**3**) in good yield. The ^1H, ^{13}C, and ^{119}Sn NMR, IR, the mass spectrometry along with elemental analyses allowed establishing the structure of ligand (H2L) and compounds **1**–**3**. In all the three cases, ^{119}Sn chemical shifts are indicators of five-coordinated Sn atoms in a solution state. The crystal structures of ligand H2L and complexes **1** and **2** were determined by a single crystal X-ray diffraction study. In the solid state, the ligand H2L exists as a keto-enamine tautomeric form. The molecular structure of complex **1** in the solid state shows a distorted octahedral geometry around a tin atom due to additional coordination with an oxygen atom from a neighboring molecule leading to a four-membered ring with Sn-O· · ·Sn-O intermolecular coordination, leading to a dimeric species. On the other hand, complex **2** is a monomer with trigonal bipyramidal geometry surrounding the tin atom.*
 Heteroatom Chem 00:1–9, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21037

Correspondence to: C. Masharing; e-mail: cmasharing@gmail.com.

Present Address of Smita Basu: Department of Organic Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland.

Contract grant sponsor: UGC (NERO), Guwahati, India.
Contract grant number: F.5-248/2009-10 (MRP/NERO).
Contract grant sponsor: RFSMS-UGC, New Delhi, India.
Contract grant number: F.42-2/Acad/UGC-SAP/Chem/2007-1113).

INTRODUCTION

The ever-increasing interest in the chemistry of organostannyl complexes has led to elaborate studies on their reactions with different Schiff base moieties [1–5]. The various applications of organotin(IV) compounds range from important and economical industrial catalysts [6] to an extensive array of biological activities [7] and hence are studied in view of their structural diversity and their possible biological applications [8].

A lot of literature is available on the coordination chemistry and mode of interaction of the tridentate *ONO* donor ligands containing amino acids and amino alcohols [9–18]. But a search of the

Cambridge Crystallographic Database (CCDB) [19] revealed not a single X-ray structure of diorganotin(IV) compounds with methyl, *n*-butyl, vinyl, or phenyl substituents attached to the tin atoms that have been constructed from azo-Schiff base ligand systems containing aromatic amino alcohols. The previously reported diorganotin(IV) compounds of amino alcohol Schiff base ligands were mainly monomeric [20–23] except the Sn-O···Sn-O or solvent···Sn coordination modes that were found in the di-*n*-butyltin(IV) derivatives [23–25]. These differences would be important for the biocidal activity and toxicity in the new tin prototype, which can be achieved through chemical substitution with electron-withdrawing or electron-releasing groups.

Thus, the recent interest lies in the molecular engineering of the substituted azo-Schiff base systems, which when coupled with diorganotin(IV) moieties, will result in dimeric aggregates with the Sn···O interaction, as a study reports very good *in vitro* cytotoxic activities with these kinds of ligand systems [26]. Hence, in this paper, we report the results of diorganotin(IV) work to the stable methyl 2-{4-hydroxy-3-[(2-hydroxyphenylimino)-methyl]-phenylazo}-benzoate (H2L) ligand system derived from *ortho*-aminophenol (Scheme 1). We also describe the simple synthesis, characterization, and detailed NMR study of the ligand H2L and its three new diorganotin(IV) complexes. Crystal and molecular structures of ligand H2L and two diorganotin(IV) complexes, i.e., $(Me_2SnL)_2$and $^nBu_2SnL$ have also been reported.

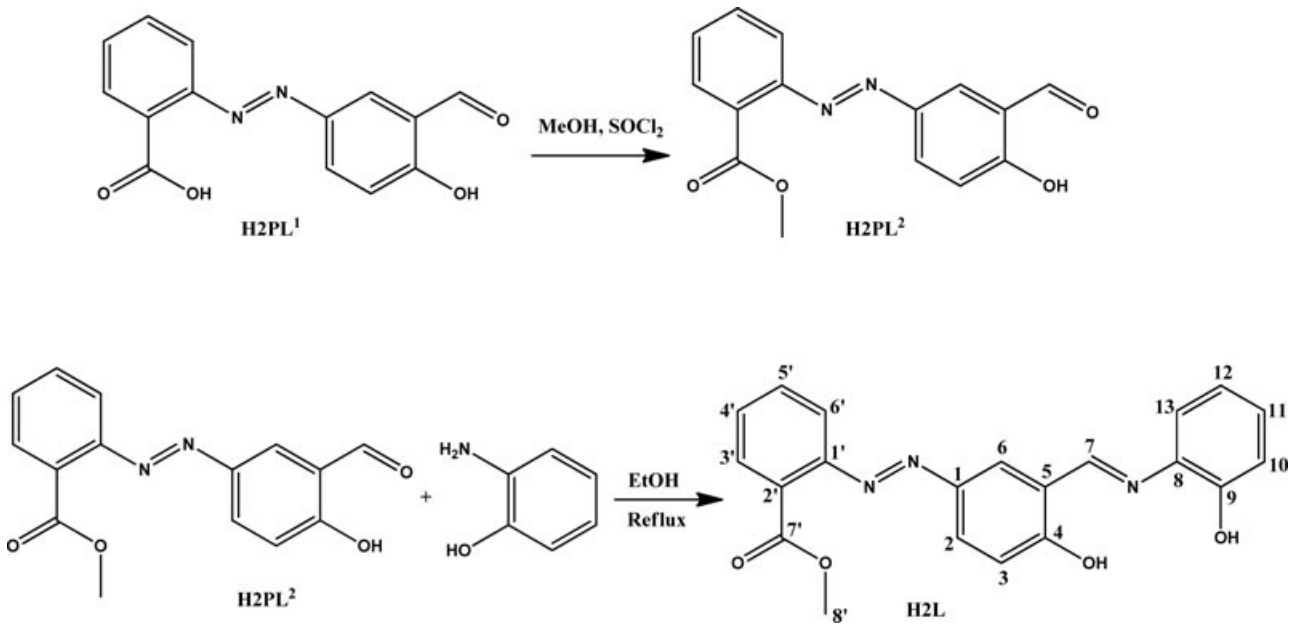
MATERIAL AND METHODS

Materials

Me_2SnCl_2 (Fluka), Ph_2SnO (Aldrich), $^nBu_2SnO$ (Lancaster), and *o*-aminophenol (Lobachemie) were used without further purification. The solvents used in the reactions were of AR grade and dried using standard procedures. Me_2SnO was prepared according to the literature method [27]. Salicylaldehyde (Lancaster) and the substituted anilines (reagent grade) were used without further purification. The preligands 2-[(*E*)-(3-formyl-4-hydroxy-phenyl)-1-diazenyl] benzoic acid ($H2PL^1$) and methyl 2-[(*E*)-(3-formyl-4-hydroxy-phenyl)diazenyl]benzoate ($H2PL^2$) were prepared according to literature methods [28,29].

Physical Measurements

Carbon, hydrogen, and nitrogen analyses were performed with a Perkin–Elmer 2400 series instrument. IR spectra in the range of 4000–400 cm^{-1} were obtained on a Perkin–Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr disks. The ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62, and 149.18 MHz. The ^1H, ^{13}C, and ^{119}Sn chemical shifts were referred to a Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm, and Me_4Sn set at 0.00 ppm, respectively. Mass spectra were obtained from a



SCHEME 1 Synthesis of the preligand $H2PL^2$ and ligand H2L.

Waters ZQ-4000 mass spectrometer by using the ESI method.

X-Ray Crystallography

Single crystals of ligand H2L, compounds **1** and **2** suitable for an X-ray crystal structure determination, were obtained from ethanol for ligand (H2L) and complex (**1**) and benzene–hexane mixture (v/v 1:4) for complex **2**, respectively, by slow evaporation of the solutions of the respective compounds. All measurements for the ligand H2L and complexes **1** and **2** were made on a Bruker Nonius SMART CCD diffractometer [30] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [31]. Refinement and all further calculations were carried out using SHELXS-97 [32]. Smart software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using saint software [33].

Synthesis of Ligand

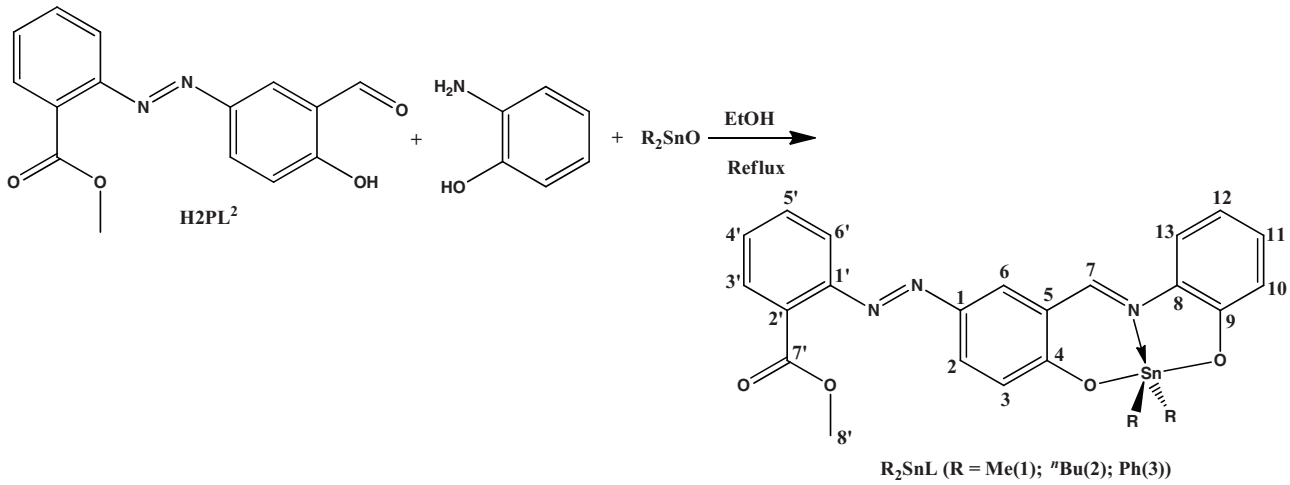
Preparation of Methyl 2-{4-Hydroxy-3-[(2-hydroxy-phenylimino)-methyl]-phenyl azo}-benzoate (H2L). Methyl 2-[(*E*)-(3-formyl-4-hydroxy-phenyl) diazenyl]benzoate H2PL[2] (0.50 g, 1.75 mmol) was dissolved in absolute ethanol (35 ml), and *ortho*-aminophenol (0.19 g, 1.74 mmol) in ethanol (10 ml) was added to it. The reaction mixture was refluxed for 5 h. The clear solution was filtered and reduced to one third of its initial solvent volume. The slow evaporation of the solution at room temperature afforded reddish crystals of H2L in 78% (0.51 g) yield; mp: 199–200°C. Anal. Calcd. for $C_{21}H_{17}N_3O_4$: C, 67.19; H, 4.56; N, 11.19. Found: C, 66.79; H, 4.05; N, 10.82. IR (KBr pellets, cm^{-1}): 3431 (ν_{NH}), 3052 (ν_{OH}), 1716 (ν_{COOMe}), 1620 ($\nu_{C=N}$). ^{1}H NMR (d_6-DMSO, δ_H) 13.12 [s, 1H, OH], 10.15 [s, 1H, OH]; 9.12 [s, 1H, H6], 7.98 [s, 1H, H7], 7.71 [d, (7.6 Hz) 1H, H2], 7.53 [d, (7.6 Hz), 2H, H3', and H10], 7.45 [m, 2H, H4', and H6'], 7.34 [m, 2H, H11, and H13], 6.98 [t, (6.4 Hz), 1H, H5'], 6.80 [d, (6.8 Hz), 1H, H3], 6.72 [t, (7.6 Hz) 1H, H12], 3.67 [s, 3H, H8'], ppm. ^{13}C NMR (d_6-DMSO, δ_C): 169.31 [C7'], 168.25 [C4], 160.15 [C7], 151.14 [C1'], 151.09 [C9], 143.92 [C1], 132.37 [C8], 132.09 [C5'], 131.55 [C11], 130.57 [C4'], 130.07 [C3'], 129.58 [C2] 129.16 [C6], 128.72 [C6'], 126.75 [C12], 120.23 [C10], 120.08 [C5], 119.33 [C2'], 118.42 [C3], 116.95 [C13], 52.75 [C8'] ppm. ESI-MS (*m/z*): 376.3 $[M]^{+1}$(25), 332.2 (20), 331.3 (100).

Syntheses of Diorganotin(IV) Complexes

The general procedure for the preparation of complexes **1** to **3** is described below.

*Synthesis of 2-(12,12-Dimethyl-11,13-dioxa-5-aza-12-stanna-dibenzo{a, e}cyclononen-8-ylazo)-benzoic Methyl Ester [Me_2SnL]$_2$ (**1**).* To a reaction vessel, H2PL[2] (0.50 g, 1.75 mmol), *ortho*-aminophenol (0.19 g, 1.74 mmol), and di-methyltin(IV) oxide (0.28 g, 1.69 mmol) were added to 50-mL absolute ethanol and the resulting solution was maintained under reflux for 8 h. After the reaction was clear and completed, the solution was filtered and reduced to one third of its initial solvent volume. In this case, after some hours of cooling, orange-red crystals were obtained to give pure product of **1**. Yield: 52% (0.48 g); mp; 170–172°C. Anal. Calcd. for $C_{23}H_{21}N_3O_4Sn$: C, 52.91; H, 4.05; N, 8.05. Found: C, 52.63; H, 3.99; N, 7.98. IR (KBr pellets, cm^{-1}): 1720 (ν_{COOMe}), 1609 ($\nu_{C=N}$), 1479, 1385, 1267, 1151, 834, 748, 613 (ν_{Sn-C}), 510 (ν_{Sn-O}), 473 (ν_{Sn-N}). ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: 8.75 [s, 1H, H6], 8.01 [dd, (9.2, 2.0 Hz), 1H, H2], 7.93 [s, 1H, H7], 7.78 [d (8.0 Hz), 1H, H3'], 7.61–7.54 [m, 2H, H4', and H10], 7.45 [t, (6.4 Hz), 1H, H11], 7.38 [d (8.0 Hz) 1H, H6'], 7.20 [t, (8.0 Hz) 1H, H5'], 6.84 [dd, (8.8, 3.2 Hz), 2H, H13, and H3], 6.72 [t, (7.6 Hz), 1H, H12], 3.90 [s, 3H, H8']; Sn-Me skeleton (^2J (^{119}Sn–^{1}H) = 78.6 Hz): 0.83 [s, 6H], ppm. ^{13}C NMR ($CDCl_3$, δ_C): Ligand skeleton: 170.45 [C7'], 166.57 [C4], 160.10 [C7], 157.32 [C1'], 150.38 [C9], 142.60 [C1], 132.48 [C8], 130.44 [C5'], 129.51 [C11], 129.22 [C4'], 128.21 [C3'], 127.82 [C2] 127.73 [C6], 126.74 [C6'], 122.11 [C12], 117.48 [C10], 117.24 [C5], 115.61 [C2'], 115.45 [C3], 113.54 [C13], 50.91 [C8']; Sn-Me skeleton (^1J (^{119}Sn–^{13}C) = 632.4 Hz): −0.001 ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn} : −144.22, ppm. ESI-MS (*m/z*): 524.2 $[M]^{+2}$ (11), 475.6 (100).

*Synthesis of 2-(12,12-Dibutyl-11,13-dioxa-5-aza-12-stanna-dibenzo{a, e} cyclononen-8-ylazo)-benzoic Methyl Ester [$^nBu_2SnL$] (**2**).* Metallic brown crystals of **2** were obtained from a benzene–hexane mixture (v/v 1:4). Yield: 52%; mp; 96–98°C. Anal. Calcd. for $C_{29}H_{33}N_3O_4Sn$: C, 57.45; H, 5.49; N, 6.93. Found: C, 57.13; H, 5.12; N, 6.53%. IR (KBr pellets, cm^{-1}): 1724 (ν_{COOMe}), 1608 ($\nu_{C=N}$), 1479, 1389, 1267, 1152, 834 (ν_{Sn-C}), 511 (ν_{Sn-O}), 469 (ν_{Sn-N}). ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: 8.77 [s, 1H, H6], 8.01[dd, (8.8, 2.4 Hz), 1H, H2], 7.93 [s, 1H, H7], 7.79 [d, (7.6 Hz), 1H, H3'], 7.62–7.55 [m, 2H, H4', and H10], 7.44 [t, (7.2 Hz), 1H, H11], 7.38 [d, (8.0 Hz) 1H, H6'], 7.20 [t, (8.0 Hz) 1H, H5'], 6.84 [d, (9.6 Hz), 2H, H13, and H3], 6.71 [t, (7.6 Hz), 1H, H12], 3.91 [s, 3H, H8']; Sn-^{n}Bu skeleton: 2.69 [m, 1*], 1.52 [m, 2*], 1.33 [m,



SCHEME 2 Synthesis of diorganotin(IV) complexes (**1**–**3**).

3*], 0.85 [t, 4*], ppm. ^{13}C NMR ($CDCl_3$, δ_C): Ligand skeleton: 172.70 [C7'], 168.11 [C4], 161.31 [C7], 159.59 [C1'], 151.96 [C9], 143.97 [C1], 134.10 [C8], 131.94 [C5'], 131.37 [C11], 130.62 [C4'], 129.71 [C3'], 129.20 [C2] 129.15 [C6], 128.20 [C6'], 123.59 [C12], 118.98 [C10], 118.80 [C5], 117.25 [C2'], 116.68 [C3], 114.98 [C13], 52.38 [C8']; Sn-^{n}Bu skeleton: 26.97 [C-2*], 26.62 [C-3*], 22.42 [C-1*], 13.59 [C-4*], ppm. ^{119}Sn NMR (CDCl3) δ_{Sn} : −183.40, ppm. ESI-MS (*m/z*): 606.3 $[M]^{+1}$ (18), 475.6 (100).

*Synthesis of 2-(12, 12- Diphenyl-11, 13-dioxa-5-aza-12-stanna-dibenzo{a, e} Cyclononen-8-ylazo)-benzoic Methyl Ester [Ph_2SnL] (**3**).* Dark red crystals of **3** were obtained from ethanol. Yield: 67%; mp; 186–188°C. Anal. Calcd. for $C_{33}H_{25}N_3O_4Sn$: C, 61.33; H, 3.90; N, 6.50. Found: C, 60.97; H, 3.66; N, 6.23. IR (KBr pellets, cm^{-1}): 1718 (ν_{COOMe}), 1608 ($\nu_{C=N}$), 1477, 1382, 1300, 1150, 837 (ν_{Sn-C}), 523 (ν_{Sn-O}), 449 (ν_{Sn-N}). ^{1}H NMR ($CDCl_3$, δ_H): Ligand skeleton: 8.76 [s, 1H, H6], 8.11 [dd, (9.2, 2.0 Hz), 1H, H2], 7.93 [s, 1H, H7], 7.78 [d (7.2 Hz), 1H, H3'], 7.59–7.52 [m, 1H, H4'c, and H10], 7.38 [m, 1H, H11], 7.23 [t, (8.0 Hz) 1H, H5'], 7.17 [d, (9.2 Hz) 2H, H13, and H3], 7.13 [d, (8.0 Hz), 1H, H6'], 6.72 [t, (7.6 Hz), 1H, H12], 3.90 [s, 3H, H8']; Sn-Ph skeleton: 7.94 [m, 4H, H-2*], 7.46–7.34 [m, 6H, H-3*, and H-4*] ppm. ^{13}C NMR ($CDCl_3$, δ_C): Ligand skeleton: 172.37 [C7'], 168.10 [C4], 161.18 [C7], 158.98 [C1'], 151.90 [C9], 144.36 [C1], 136.53 [C8], 131.98 [C5'], 130.88 [C11], 130.86 [C4'], 130.60 [C3'], 128.25 [C2], 123.89 [C6], 128.25 [C6'], 123.89 [C12], 119.23 [C10], 119.00 [C5], 117.38 [C2'], 117.28 [C3], 114.93 [C13], 52.44 [C8']; Sn-Ph skeleton: 139.17 [C-1*], 134.11 [C-2*], 128.88 [C-4*], 128.44 [C-3*], ppm. ^{119}Sn NMR (CDCl3) δ_{Sn} : −326.92, ppm. ESI-MS (*m/z*): 647.4 $[M]^{+1}$ (9), 475.7 (15) 160.0 (100).

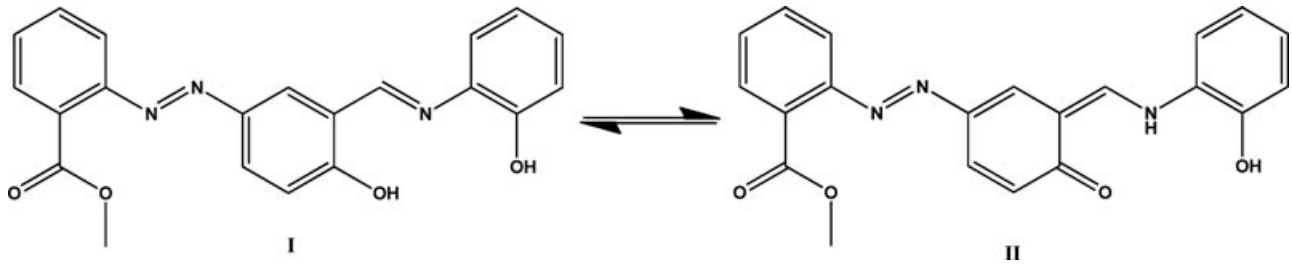
RESULTS AND DISCUSSION

Synthetic Aspect

The preligand 2-[(*E*)-(3-formyl-4-hydroxy-phenyl)-1-diazenyl]benzoic acid (H2PL^1) was prepared according to the literature method by a diazo-coupling reaction between the appropriate aniline and salicylaldehyde, in alkaline medium under cold conditions [28]. The preligand H2PL^2 was further prepared by methylation of 2-[(*E*)-(3-formyl-4-hydroxy-phenyl)-1-diazenyl] benzoic acid (H2PL^1) in the presence of a catalytic amount of $SOCl_2$ [29]. On the other hand, H2L was prepared by condensation of H2PL^2 with *ortho*-aminophenol in ethanol at reflux temperature. The preparation of diorganotin(IV) complexes of type R_2SnL followed the procedure involving 1:1:1 stoichiometric addition of *ortho*-aminophenol, diorganotin(IV) oxides, R_2SnO (R = Me, ^{n}Bu, Ph), and H2PL^2 to ethanol. The details of the synthesis are presented in the Experimental section, and methods of preparation are described in Scheme 2. All the complexes **1**–**3** could be isolated by fractional crystallization with high purity and moderate yield. The complexes are crystalline in nature, stable in air, and soluble in all common organic solvents. ^{1}H, ^{13}C, ^{119}Sn NMR, IR, elemental analyses, mass spectrometry, and single crystal X-ray crystallography accomplished the structural elucidation of ligand H2L and complexes 1–3.

Spectroscopic Characterization

Diagonistically important infrared absorption frequencies for the carboxylate antisymmetric (ν_{COOMe}) stretching vibration of the ligand H2L are given in the Experimental section. The assignment of the symmetric ($\nu_{OCO\ sym}$) stretching vibration band could



SCHEME 3 Tautomeric equilibrium: enol-imine (I) and Keto-enamine (II) in H2L.

not be made owing to the complex pattern of the spectra. The solid-state IR spectra of the free ligand H2L display a medium intensity band at around 3431 cm^{-1}, which has been assigned to a ν_{NH} vibration. These data are consistent in accordance with our earlier report [18] and show that the ligand H2L exists in enol-imine(I) and keto-enamine(II) tautomeric forms, as shown in Scheme 3. The tautomeric form II was found to be predominant in the solid state, where the phenolic proton of the central aromatic ring moved to the nearby imine N-atom (see Fig. 1 for crystal structure). The assignment of the band is based on comparison with the spectra of the previously reported free ligand $H2PL^1$ and $H2PL^2$. The antisymmetric (ν_{COOMe}) stretching vibration for the uncomplexed ligands has been detected around 1725 and 1716 cm^{-1} for $H2PL^2$ and H2L, respectively. The IR spectra of the complexes **1**–**3** showed diagnostically important bands for the ν_{COOMe} fragment at 1720 cm^{-1} and $\nu_{C=N\,asym}$at 1608 cm^{-1}. The IR band due to ν_{OH} around 3000 cm^{-1} in the free ligand H2L disappears completely upon complexation in accordance with earlier reports [34,35].

The mass spectrometry of all compounds was recorded employing the ESI-MS technique, showing in all cases the expected molecular ions, which resulted to be the base peak. The main pattern evidences the initial loss of a methyl, butyl, or phenyl moiety from the respective compounds.

The ^1H and ^{13}C NMR data of H2L and complexes **1**–**3** are given in the Experimental section. The ^1H and ^{13}C NMR signals were assigned by the use of homonuclear-correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC), heteronuclear multiple bond connectivities (HMBC), and distortionless enhancement by polarization transfer (DEPT) experiments. The conclusions drawn from the ligands ($H2PL^2$ and H2L) assignments were then subsequently extrapolated to complexes, especially **1**–**3**, owing to their data similarity, and it was also possible to detect all protons and carbon signals for compounds **1**–**3**.

The ^1H NMR integration values (see the Experimental section) were consistent with the formulation of products. The ^{13}C NMR spectra of the ligand and Sn-R skeletons displayed the expected carbon signals in all cases; also the assignment of the phenyltin

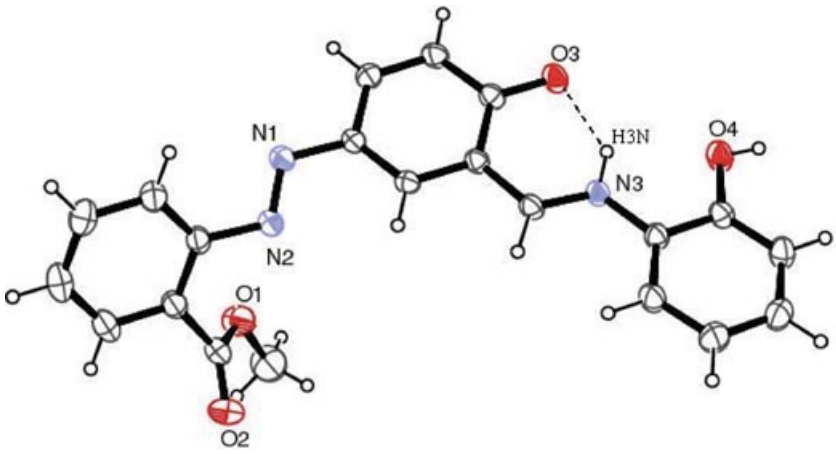


FIGURE 1 Molecular structure of H2L showing the atom-labeling scheme at the 30% probability level; N–H· · ·O intramolecular hydrogen bonds are drawn as dashed lines.

moiety is straightforward from the multiplicity patterns, resonance intensities, and also by comparing their $^{n}J(^{13}C–^{119/117}Sn)$ values. The ^{1}H NMR spectra of the ligand H2L shows two singlets due to two different hydroxyl groups. However, upon complex formation, the singlet disappears due to Sn-O bonding.

The ^{119}Sn NMR chemical shifts of the diorganotin(IV) complexes (**1**–**3**) obtained in a noncoordinating ($CDCl_3$) solvent are listed in the Experimental section. The dimethyltin(IV) complex (**1**) in $CDCl_3$ exhibits a single sharp ^{119}Sn resonance at −144.22 ppm; the dibutyltin(IV) complex (**2**) at −183.4 ppm, whereas, in the diphenyltin(IV) complexes (**3**) at −326.9 ppm. The chemical shift data for complexes **1**–**3** in $CDCl_3$ suggest that in noncoordinating solvents all species are monomeric, with pentacoordinated tin atoms bound to two oxygen atoms, one nitrogen atom, and two alkyl or aryl groups, since all chemical shifts appear in the typical range for a trigonal bipyramidal (TBP) geometry [36]. Thus ^{119}Sn NMR shift for complex **1** indicates that the dimer, revealed in the crystal structure (Fig. 2), is not retained in solution state.

X-Ray Crystallography

Crystals of methyl 2-{4-hydroxy-3-[(2-hydroxyphenylimino)-methyl]-phenyl azo}-benzoate (H2L) and diorganotin(IV) complexes **1** and **2** suitable for X-ray crystal structure determination were obtained from ethanol for ligand H2L and complex **1**, and benzene–hexane mixture (v/v 1:4) for complex **2** by slow evaporation of the solvent at room temperature. The results of the X-ray crystallographic studies were fully consistent with the other spectroscopic evidence presented above. The data collection and refinement parameters for ligand H2L and complexes **1** and **2** are given in Table 1. The selected geometric and H bond parameters for H2L are collected in Tables 2 and 3, respectively, whereas that of complexes **1** and **2** are given in Table 4. The structures of ligand H2L and complexes **1** and **2** are discussed in sequel.

The ligand H2L consist of a three-ring system, which assumes an extended *E*-conformation both around the −N=N− and −C=N− linkage with both outer ring displaying a slightly twisted conformation (Fig. 1) with respect to the central aromatic ring. The twisting around the −N=N− is more prominent compared to the twisting around the −C=N− linkages. This is also reflected in the dihedral angle between the aromatic rings of 59.61(9)° formed between the C3–C8 and C9–C10 aromatic rings in −N=N− linkage, which is further reflected in the N1–N2–C9–C10 and, in particular, the N2–N1–C8–C3 torsion angles of 158.5(2)° and 154.9(2)°, respectively. Similarly, in the case of −C=N− linkage, a dihedral angle of 60.18(8)° is observed between the C12–C14 and C16–C17 aromatic rings with torsion angles of 177.9(2)° and 171(2)° in C14–C13–C15–N3 and C15–N3–C16–C17, respectively. The hydrogen atom of the hydroxyl group from the central aromatic ring is found to migrate to the nearby nitrogen atom of the −C=N− bond which results in an intramolecular N3–H···O3 hydrogen bond.

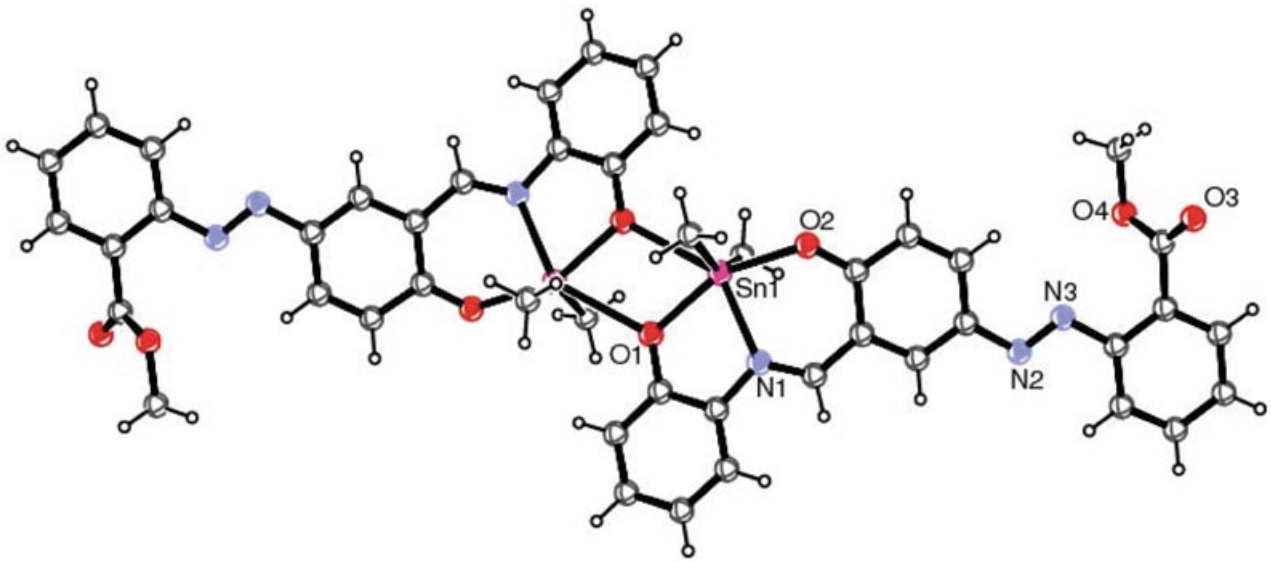


FIGURE 2 Molecular structure of $[Me_2SnL]_2$ (**1**) at the 30% probability level.

TABLE 1 Crystallographic Data and Structure Refinement Parameters for H2L and Complexes **1** and **2**

	H2L	***1***	***2***
Empirical formula	$C_{21}H_{17}N_3O_4$	$C_{23}H_{21}N_3O_4Sn$	$C_{29}H_{33}N_3O_4Sn$
Formula weight	375.38	522.12	606.27
Crystal size (mm)	0.32 × 0.20 × 0.12	0.45 × 0.24 × 0.15	0.35 × 0.25 × 0.14
Crystal shape	Block	Tablet	Prism
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*c*	$P2\bar{1}/c$
a (Å)	12.7560(6)	17.2319(9)	15.5979(9)
b (Å)	8.5812(4)	7.5305(3)	19.6927(11)
c (Å)	20.5720(10)	18.1171(9)	9.0285(5)
α (°)	90	90	90
β (°)	125.499(3)	105.181(3)	91.359(3)
γ (°)	90	90	90
V (Å^3)	1833.29(15)	2268.92(19)	2772.5(3)
Z	4	4	4
D_x (g cm^{-3})	1.360	1.528	1.452
μ (mm^{-1})	0.096	1.159	0.960
Scan range (°)	$1.96 < \theta < 28.33$	$2.90 < \theta < 28.36$	$1.31 < \theta < 28.54$
Reflections measured	21125	15201	42279
Independent reflections; R_{int}	4492; 0.0741	5434; 0.0675	6802; 0.1081
Number of parameters	263	284	338
Number of restraints	0	0	0
R(*F*) ($I > 2\sigma(I)$ reflns.)	0.0422, *w*R$_2$ 0.1022	0.0384,*w*R$_2$ 0.0907	0.0367,*w*R$_2$ 0.0711
R indices [$I > 2\sigma(I)$]	0.1134, *w*R$_2$ 0.1305	0.0471,*w*R$_2$0.0949	0.0784,*w*R$_2$0.0772
GOF (F^2)	0.964	0.985	0.968
max, min $\Delta\rho$ (e/Å^{-3})	0.132, −0.161	1.429, −1.312	0.678, −0.599

TABLE 2 Selected Bond Lengths and Angles for H2L

Bond Lengths (Å)		*Bond Angles (°)*	
O(3)–C(12)	1.292(2)	N(2)–N(1)–C(8)	113.61(15)
O(4)–C(17)	1.357(2)	N(1)–N(2)–C(9)	114.62(15)
O(4)–H(4)	0.8200	C(15)–N(3)–C(16)	126.90(16)
N(1)–C(8)	1.429(2)	N(3)–C(15)–C(13)	123.04(17)
N(2)–C(9)	1.413(2)	C(15)–N(3)–H(3)	115.9(12)
N(3)–C(15)	1.301(2)	C(16)–N(3)–H(3)	117.2(12)
N(3)–H(3N)	0.929(19)		

TABLE 3 Hydrogen Bond Parameter (Å and °) for H2L

Bond Lengths (Å)				Bond Angles (°)
D–H···A	D–H	D–H···A	D···A	< D–H···A,
N3-H···O3	0.82	1.85(18)	2.60(2)	134

Figure 1 clearly indicates that the keto-enamine form predominates in the solid state. The hydroxyl group of the phenolic aromatic ring forms the intermolecular interaction O4-H···O3 with a centrosymmetric mate.

The molecule of **1** consists of centrosymmetric dimers of the basic Me_2SnL moiety (Fig. 2), where the two Sn atoms are linked by two asymmetric Sn–O···Sn–O bridges involving hydroxyl O atom of the aminophenol ligand. It has a distorted octahedral (DOC) geometry around the tin atoms [20–22]. The *O,N,O*-tridentate ligand is in a mer orientation to the tin octahedron. The methyl substituents are trans to each other, allowing the intramolecular coordination of the O1 with tin to build a dimeric species. The dimeric assembly occurs via the formation of a Sn_2O_2 four-membered ring [24, 25]. The O···Sn bonding occurs with the oxygen atom at the five-membered ring. The crystal structure of **2** (Fig. 3) reveals a TBP geometry surrounding the tin atom. The *O,N,O*-tridentate ligand places its two oxygen donating atoms in the axial positions, and the nitrogen atom occupies one equatorial position.

Compound $[Me_2SnL]_2$ (**1**) and $^nBu_2SnL$ (**2**) crystallizes in the monoclinic *P*2(1)/*c* space group. The N(1)–Sn(1) bond distance for **1** is 2.20 and 2.22 Å for **2**. The Sn(1)–O(1) bond distance for **1** and **2** are 2.12 and 2.11 Å, whereas, Sn(1)–O(2) bond distance for **1** and **2** are 2.19 and 2.16 Å, respectively. The bond angles between carbon and tin atoms (C–Sn–C) are

TABLE 4 Selected Bond Lengths and Angles for Complexes **1** and **2**

Complex 1		*Complex 2*	
	Bond lengths (Å)		
O(1)–Sn(1)	2.1227(19)	O(1)–Sn(1)	2.1126(18)
O(2)–Sn(1)	2.191(2)	O(2)–Sn(1)	2.1652(19)
N(1)–Sn(1)	2.209(2)	N(1)–Sn(1)	2.222(2)
C(22)–Sn(1)	2.093(3)	C(22)–Sn(1)	2.121(3)
C(23)–Sn(1)	2.096(3)	C(26)–Sn(1)	2.104(3)
C(9)–O(2)	1.289(3)	C(1)–O(1)	1.337(3)
C(1)–O(1)	1.337(3)	C(9)–O(2)	1.298(3)
	Bond angles (°)		
O(1)–Sn(1)–C(22)	97.85(12)	O(1)–Sn(1)–C(26)	94.56(10)
O(1)–Sn(1)–C(23)	99.91(12)	O(1)–Sn(1)–C(22)	101.42(11)
C(22)–Sn(1)–C(23)	145.65(15)	C(26)–Sn(1)–C(22)	142.65(13)
O(1)–Sn(1)–O(2)	155.02(8)	O(1)–Sn(1)–O(2)	156.41(8)
C(22)–Sn(1)–O(2)	85.02(12)	C(26)–Sn(1)–O(2)	87.09(10)
C(23)–Sn(1)–O(2)	90.92(13)	C(22)–Sn(1)–O(2)	91.11(11)
O(1)–Sn(1)–N(1)	75.47(7)	O(1)–Sn(1)–N(1)	76.13(8)
C(22)–Sn(1)–N(1)	110.05(13)	O(2)–Sn(1)–N(1)	81.76(8)
C(23)–Sn(1)–N(1)	102.78(11)	C(26)–Sn(1)–N(1)	114.48(10)
O(2)–Sn(1)–N(1)	80.22(8)	C(22)–Sn(1)–N(1)	102.11(11)

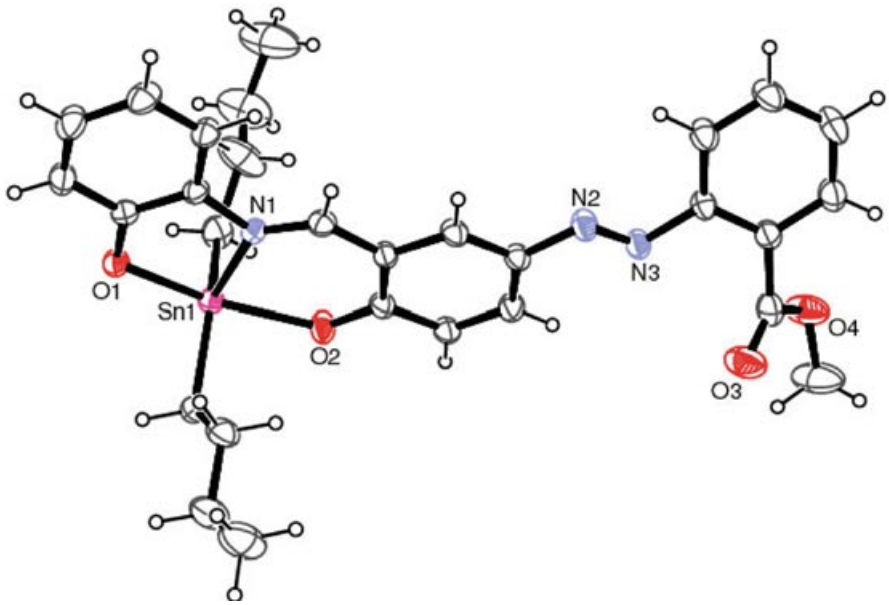


FIGURE 3 Molecular structure of $^{n}Bu_2SnL$(**2**) at the 30% probability level.

145.65° for **1** and 142.65° for **2**, indicating DOC geometry around **1** and TBP geometry surrounding tin atom around **2.**

CONCLUSIONS

This article reports the preparation and crystal structures of three novel diorganotin(IV) complexes of composition R_2SnL (where R = Me (**1**), ^{n}Bu (**2**), or Ph (**3**) and L = methyl 2-{4-hydroxy-3-[(2-hydroxyphenylimino)-methyl]-phenylazo}-benzoate), which were carried out through a one-step procedure leading to crystalline pure substances in good yield. This is also the first reported diorganotin(IV) complexes containing azo-Schiff ligand systems obtained by the condensation of methyl 2-[(*E*)-(3-formyl-4-hydroxyphenyl)diazenyl]benzoate with *ortho*-aminophenol. It is intended to employ this new ligand system to other diorganotin(IV) starting material. This will open a prospective gateway in application of these

complexes in cancer chemotherapy as both diorganotin(IV) complexes, and amino alcohols were found to be as potential candidates as anti-cancer drugs.

SUPPLEMENTARY MATERIAL

CCDC-864863 (H2L), 864864 (**1**), and 864865 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

ACKNOWLEDGMENT

We thank the NMR facility at Indian Institute of Science, Bangalore, India, for providing NMR spectra.

REFERENCES

[1] Gielen, M. Coord Chem Rev 1996, 151, 41–51.
[2] Yamada, S. Coord Chem Rev 1966, 1, 415–437.
[3] Sacconi, L. Coord Chem Rev 1966, 1, 126–132.
[4] Collinson, S. R.; Fenton, D. E. Coord Chem Rev 1996, 148, 19–40.
[5] Nath, M.; Saini, P. K. Dalton Trans. 2011, 40, 7077–7121 and the references therein.
[6] Davies, A. G.; Gielen, M.; Pannell, K. H,; Tiekink, E. R. T. (Eds.). Tin Chemistry Fundamentals, Frontiers and Applications; Wiley, Chichester, UK, 2008; ch. 4, pp. 413–719.
[7] Rossen, K.; Steven, A.; Sager, J.; Reamer, R. A.; Askin, D.; Volante, R. P.; Reider, P. J. Tetrahedron Lett 1995, 36, 6419–6422.
[8] Manju, Kishore, D.; Kumar, D. J. Coord Chem 2011, 12, 2130–2156.
[9] Cashion, J. D.; Bomazetis, G.; James, B. D. J Organomet Chem 1980, 185, 433–441.
[10] Hynes, M. J.; O'Dowd, M. J Chem Soc, Dalton Trans 1987, 563–566.
[11] Arena, G.; Gianguzza, A.; Pellerito, L.; Musumeci, S,; Purello, R.; Rizzarelli, E. J Chem Soc, Dalton Trans 1990, 2603–2608.
[12] Buzas, N. N.; Gajda, T.; Kuzmann, E.; Vertes, A.; Burger, K. Main Group Met Chem 1995, 11, 641–649.
[13] Arena, G.; Cali, R.; Contino, A.; Musumeci, A.; Musumeci, S.; Purello, R. Inorg Chim Acta 1995, 237, 187–191.
[14] Beltrán, H. I.; Damian-Zea, C.; Ortega, S. H.; Camacho, A. N.; Apan, M. T. R. J. Inorg Biochem 2007, 101, 1070–1085.
[15] Reyes, H.; Santillan, R.; Ochoa, M. E.; Romero, M.; Farfán, N. J Mexican Chem Soc 2007, 51, 39–44.
[16] Zamudio-Rivera, L. S.; George-Tellez, R.; Lopez-Mendoza, G.; Morales-Pacheco, A.; Flores, E.; Höpfl, H.; Barba, V.; Fernandez, F. J.; Cabirol, N.; Beltrán, H. I. Inorg Chem 2005, 44, 5370–5378.
[17] Gomez, E.; Ordoñez, G. C.; Apan, T. R. Chem Pharma Bull 2006, 54, 54–57.
[18] Basu, S.; Gupta, G.; Das, B.; Rao, K. M. J Organomet Chem 2010, 695, 2098–2104.
[19] http://www.ccdc.cam.ac.uk.
[20] Narula, S. P.; Bharadwaj, S. K.; Sharda, Y.; Day, R. O.; Howe, L.; Holmes, R. R. Organometallics 1992, 11, 2206–2211.
[21] Dakternieks, D.; Jurkschat, K.; van Dreumel, S.; Tiekink, E. R. T. Inorg Chem 1997, 36, 2023–2029.
[22] Dakternieks, D.; Basu Baul, T. S.; Dutta, S.; Tiekink, E. R. T. Organometallics 1998, 17, 3058–3062.
[23] Narula, S. P.; Kaur, S.; Shankar, R.; Verma, S.; Venugopalan, P.; Sharma, S. K.; Chada, R. K. Inorg Chem 1999, 38, 4777–4783.
[24] (a) Reyes, H.; Garcia, C.; Farfan, N.; Santillan, R.; Lacroix, P. G.; Lepetit, C.; Nakatani, K. J Oragnomet Chem 2004, 689, 2303–2310; (b) Farfán, N.; Mancilla, T.; Santillan, R.; Gutierrez, A.; Zamudio-Rivera, L. S.; Beltrán, H. I. J Organomet Chem 2004, 689, 3481–3491.
[25] Beltrán, H. I.; Zamudio-Rivera, L. S.; Mancilla, T.; Santillan, R.; Farfan, N. Chem Eur J 2003, 9, 2291–2306.
[26] Basu Baul T. S. (2008). Patent under process.
[27] (a) Ingham, R. K.; Rosenberg, S. O.; Gilman, H. Chem Rev 1960, 60, 459–539; (b) Rochow, E. G.; Seyferth, D. J Am Chem Soc 1953, 75, 2877–2878.
[28] Basu Baul, T. S.; Pyke, S. M.; Sharma, K. K.; Tiekink, E. R. T. Main Group Met Chem 1996, 19, 807–814.
[29] Basu Baul,.S.; Basu, S.; Tiekink, E. R. T. Acta Cryst E 2007, 63, o3358.
[30] SMART-NT, Data Reduction Software, version 5.0. Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1999.
[31] G M SHELXL 97, Program for the solution of crystal structure; University of Göttingen, Göttingen, Germany, 1997.
[32] 12 G M SHELXL 97, Program for the refinement of crystal structure; University of Göttingen, Germany, 1997.
[33] *SAINT-NT, Data Reduction Software, version 5.0,* Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1999.
[34] Basu Baul, T. S.; Dhar, S.; Kharbani, N.; Pyke, S. M.; Butcher, R.; Smith, F. E. Main Group Met Chem 1999, 22, 413–421.
[35] Basu Baul, T. S.; Dhar, S.; Pyke, S. M.; Tiekink, E. R. T.; Rivarola, E.; Butcher, R.; Smith, F. E. J Organomet Chem 2001, 633, 7–17.
[36] Holeček, J.; Nádvornik, M.; Handlíř, K.; Lyčka, A. J Organomet Chem 1986, 315, 299–308.