A NEW HETEROMETALLIC [AL^{III}-BU_2SN^{IV}-B^{III}]-M-OXOISOPROPOXIDE AND ITS DERIVATIVES WITH B- DIKETONES: SYNTHETIC, SPECTRAL AND ELEMENTAL STUDIES

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ABSTRACT

New heterometallic derivative [AlIII - Bu2SnIV - BIII] - μ – oxoisopropoxide has been prepared by the thermal condensation of compound Bu2SnIV- BIII - μ - oxoisopropoxyacetate (OAc) Bu2SnOB(OPri)2 with Al(OPri)3 in 1:1 molar ratio in xylene with continuous liberation of isopropyl acetate formed during the course of reaction. The Bu2SnIV - BIII - μ - oxoisopropoxyacetate was synthesized by reaction of tin diacetate with triisopropyl borate in 1:1 molar ratio in toluene. The reaction of μ-oxoisopropoxide with β- diketones (HL) in 1:1 and 1:2 molar ratios yielded Bu2SnO2AlB(OPri)3L, and Bu2SnO2AlB(OPri)2L2 respectively. (where L = acetylacetonate/ benzoylacetonate/p-bromo benzoylacetonate anion) respectively. The μ-oxoisopropoxide compound has been characterized by elemental and spectral (IR, 1H, 13C, 27Al, 119Sn, 11B NMR). The β-diketonates of [Bu2SnO2AlB(OPri)4] have been characterized by elemental, liberated isopropanol and spectral analysis (IR, 1H , 13C & 27Al NMR).

INTRODUCTION

The elucidation of structural features and reactivity patterns of polymetallic alkoxides has aroused deep scientific interest, because the complexes have been used as precursors for super or semi-conducting, ferroelectric, dielectric and even biocompatible oxide materials [1,2]. Further, the mixed metal oxides prepared from heterometallic-μ-oxoalkoxides [3-6] have been used for absorbing harmful chemicals [7] and gases such as SO_2, CCl_4, and decontaminating chemical warfare agents [8]. Recently, $MgAl_2O_4$ prepared from $[MgO_2Al_2(OPr^i)_4]_2$ have been used to destructively adsorb paraxon [diethyl-4-nitrophenol phosphate (DNPP)] [9]. In view of the solubility of metal alkoxides [10,11] and oxoalkoxides [12,13] in organic solvents, these materials are strongly preferred as precursors in sol- gel processes. In heterometallic-μ-oxoalkoxides M-O-M' linkage is present, which makes the M-O-M' bond strong and stable as compared to other precursors. Non-cleavage of the M-O-M' bond even upon hydrolysis followed by dehydration, makes homogenous oxides of high surface area mixed metal oxides nanoparticles. Therefore, these compounds are considered as especially suitable precursors over other precursors such as metal nitrate, acetate, monodispersed metal hydrous oxides, mainly due to the ease of their purification, solubility in organic solvents, volatility and their extremely facile hydrolizability. The rate of hydrolysis depends upon the nature of metal in terms of electrophilicity and ability to expand its coordination number [14]. The hydrolysis rates transition metal alkoxides (especially in the case of heterobimetallic alkoxides) are very high due to their highly electrophilic nature and their ability to expand its coordination number which complicates the problem by causing phase segregation.

To overcome this problem to provide modified precursor by replacing the alkoxide groups with other ligands for example acetylacetone, benzoylacetone which may undergo hydrolysis at slower rate, [15] structural features, solubilities and effect of chelating group on the stability of μ-oxo compounds, their β-diketones have also been synthesized. Systematic studies have been made on the catalytic application of bimetallic- μ-oxoalkoxides of transition metals reveals that these compounds rank among the best catalysts in ring opening polymerization of heterocyclic compounds like thiranes, oxiranes, epoxides and lactones [16-19]. It was observed that neither any alkoxide nor oxoalkoxides of Al-Bu_2Sn-B as a soluble heterometallic single source precursor have been reported so far.

The above features underline the importance and utility of μ-oxo compounds and its derivatives with β-diketones, so it was considered of interest to synthesis new heterometallic [$Bu_2SnO_2AlB(OPr^i)_4$] and its β-diketonates.

EXPERIMENTAL

All manipulations have been carried out under anhydrous conditions [20] and the solvents and reagents used were purified and dried by standard methods [20]. The general technique and physical measurement were carried out as described elsewhere [6,21,22]. Tin diacetate [$Bu_2Sn(OAc)_2$] (Aldrich) and aluminium isopropoxide [$Al(OPr^i)_3$] (Aldrich) and triisopropyl borate $B(OPr^i)_3$ (Aldrich) were used as received. Acetyl acetone was dried prior to use. Benzoyl acetone (Hi-media) and p-bromobenzoyl acetone was used as received. The estimation of isopropoxy groups in the μ-oxoisopropoxide and isopropyl alcohol liberated in synthesis of β-diketonates of [$Bu_2SnO_2AlB(OPr^i)_4$] were carried out oxidimetrically [23]. Tin and aluminium were analyzed gravimetrically and boron was estimated volumetrically [22]. Further, spectral study of tin, aluminium and boron has also been carried out to find out their respective coordination number in order to elucidate the structure of μ-oxo compounds. The complex [$Bu_2SnO_2AlB(OPr^i)_4$] and its β-diketonates were decomposed in conc. HCl and extracted in dilute HCl, tin was precipitated as sulphide (pH 5-6), filtered and estimated as Bu2SnO_2 [22]. The H_2S was boiled off completely from the filtrate and aluminium was estimated as aluminium oxinate [22].

The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^{1}H, ^{13}C, ^{27}Al, ^{119}Sn and ^{11}B NMR spectra were recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer. TG study has been made on Diamond TG/DTA Perkin Elmer instrument and molecular weight data was determined by the cryoscopic method using a Beckman thermometer.

Synthesis of $[Bu_2SnO_2AlB(OPr^i)_4]$

The $[(OAc)Bu_2SnOB(OPr^i{}_2)]$ compound was synthesized by refluxing the $Bu_2Sn(OAc)_2$ and $B(OPr^i)_3$ in 1:1 molar ratio in toluene. The thermal condensation between $[(OAc)\ Bu_2SnOB(OPr^i{}_2)]$ (3.169 g, 9.811 mmol) and $Al(OPr^i)_3$ (2.004 g, 9.811 mmol) in xylene gives the $[Bu_2SnO_2AlB(OPr^i)_4]$. The contents were refluxed for about 8 h on a fractionating column and the isopropyl acetate formed during the reaction was distilled off continuously from 78 ^oC to boiling point of xylene [6,13] (139 ^oC). The solvent xylene was completely removed at (~70 ^oC /1mm) yielding a pale yellow solid. The product was redissolved in benzene and slow evaporation of benzene resulted in a pale yellow glassy solid. The μ-oxo compound was found to be soluble in common organic solvents such as $CHCl_3$, and C_6H_6, highly susceptible to hydrolysis and decomposed on heating (~210°C). [Yield: 96%]. Found: OPr^i, 21.36; Sn, 21.88; Al, 4.5; B, 1.88 for $[Bu_2SnO_2AlB(OPr^i)_4]$ Calcd: OPr^i, 22.26; Sn, 21.31; Al, 4.35; B, 1.59.

Reaction of [Bu2SnO2AlB(OPri)4] with acetylacetone (Hacac) in 1:1 molar ratio:

The compound $[Bu_2SnO_2AlB(OPr^i)_4]$ (0.478 g, 0.915 mmol) and acetylacetone (0.0915 g, 0.915 mmol) were refluxed in ~ 50 ml benzene in a flask connected to short distillation column on an oil bath for about 4 h. The isopropanol liberated at 72-78 ^oC was fractionated as the binary azeotrope of isoproponol-benzene [13]. The azeotrope was collected and checked for completion of the reaction. The excess of the solvent was then removed under reduced pressure (45 ^oC /1mm) yielding a yellowish brown solid. The preparations of other β-diketonates of $[Bu_2SnO_2AlB(OPr^i)_4]$ in different molar ratios were carried out by similar procedure and the analytical results have been summarized in Table-1.

RESULTS AND DISCUSSION

The preparation of the heterometallic-μ-oxoisopropoxide $[Bu_2SnO_2AlB(OPr^i)_4]$ follows the following reaction scheme:

$$(OAc)\ Bu_2SnOB(OPr^i{}_2)\ +\ Al(OPr^i)_3\ \xrightarrow[139\ ^oC]{\text{Refluxing xylene}}\ [Bu_2SnO_2AlB(OPr^i)_4]\ +\ Pr^iOAc$$

IR Spectra

The sharp band observed at ~ 1630 cm^{-1} due to C=O in IR spectrum of tin diacetate is absent in that of $[Bu_2SnO_2AlB(OPr^i)_4]$ indicating the complete removal of acetate groups in μ-oxo compound [24]. Instead, a band exhibited in the region ~1370-1340 cm^{-1} is assigned to *gem*-dimethyls of isopropoxy group. Similarly the bands observed at 1180-1160 and 1130- 1110 cm^{-1} have been assigned to the combination bands $\nu(C\text{-}O+OPr^i)$ of bridging and terminal isopropoxy group respectively. A band appearing at approximately 950 cm^{-1} is assigned to ν(C-O) stretching of bridging isopropoxy group [25,26]. A number of vibrations are observed in the region 700-400 cm^{-1} due to M-O stretching vibrations [27] in μ-oxo compound.

NMR Spectra

^1H NMR

A sharp singlet observed at δ 2.1 ppm in the ^1H NMR spectrum of tin diacetate is found to be absent in the spectrum of $[Bu_2SnO_2AlB(OPr^i)_4]$ confirms the complete removal of acetate groups. ^1H NMR spectrum of $[Bu_2SnO_2AlB(OPr^i)_4]$ exhibits two doublet at δ 1.0 and 1.1 ppm assigning methyl protons of terminal and bridging isopropoxy groups [16,28]. A multiplet centered at δ 4.4 ppm is observed due to the methine proton of isopropoxy group in the μ-oxo compound [16].

^{13}C NMR

The ^{13}C NMR spectrum of $[Bu_2SnO_2AlB(OPr^i)_4]$ shows prominent peaks at δ 25.6, and 28.4 ppm assignable to the methyl carbon of non-bridging and bridging isopropoxy groups. The other peaks δ 62.6, and 67.9 ppm in the ^{13}C NMR spectrum are due to the different types of methine carbon of the isopropoxy groups [29].

^{27}Al NMR

The ^{27}Al NMR spectrum of $[Bu_2SnO_2AlB(OPr^i)_4]$ show a singlet at δ 62 ppm indicating tetrahedral environment about the Al atom and is surrounded by four oxygen atoms [30].

^{119}Bu2Sn NMR

The ^{119}Sn NMR spectrum of $[Bu_2SnO_2AlB(OPr^i)_4]$ exhibits a sharp signal at δ 489 ppm assignable to the tetracoordination about Sn(IV) attributed to the polymeric nature of μ-oxo compound [31].

^{11}B NMR

The ^{11}B NMR spectrum of the compound $[Bu_2SnO_2AlB(OPr^i)_4]$ display a signal at δ –3.23 ppm indicating a tetra-coordinated environment about B atom which is surrounded by four oxygen atoms [32].

Further reactions of $[Bu_2SnO_2AlB(OPr^i)_4]$ with β-diketones (HL) in various molar ratios have been performed in refluxing benzene yielded the compounds of the types $[Bu_2SnO_2AlB(OPr^i)_3L]$ and $[Bu_2SnO_2AlB(OPr^i)_2L_2]$ according to the following reaction scheme:

$$[Bu_2SnO_2AlB(OPr^i)_4] + nHL \xrightarrow{\text{Refluxing benzene}} [Bu_2SnO_2AlB(OPr^i)_{4-n}L_n] + nPr^iOH$$

(n= 1-2, L= acac/bzac/p-Brba)

The isopropanol liberated during the reaction collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction. It was observed that only two out of the four of isopropoxy groups of [$Bu_2SnO_2AlB(OPr^i)_4$] could be replaced by β-diketones. Futher replacement of isopropoxy groups could not be achieved even with an excess of ligand (β-diketones) and prolonged refluxing time (approx. 12 h). This indicates the substitution of only terminal isopropoxy groups not bridging.

IR Spectra

The spectra of 1:1 β-diketone derivatives of $Bu_2SnO_2AlB(OPr^i)_4$ show absorption bands in the region 1360-1340 cm^{-1}, 1165-1150 and 1115-1110 cm^{-1} are the characterstics of *gem*-dimethyl portion and combination bands ν(C-O+OPr^i) of the bridging and terminal isopropoxy group respectively. No peak is observed at 1115-1110 cm^{-1} in the 1:2 and 1:3 β-diketonates indicates the absence of terminal isopropoxy group. A band appeared at approximately 950 cm^{-1} is due to ν(C-O) stretching of bridging isopropoxy group. Similar spectra were recorded for 1:4 β-diketonates as found for 1:3 β-diketone derivatives. The IR spectrum of β-diketones [33] display strong bands at ~ 1600-1580 cm^{-1} and ~ 1520-1500 cm^{-1} due to ν_{sym}(C=O) and ν_{asym}(C=C) respectively along with a broad band at ~ 3100-2700 cm^{-1} due to enolic stretch. The absence of shift in C=O frequency and disappearance of broad band at 3100-2700 cm^{-1} in the β-diketonates of μ- oxoisopropoxide compound suggest that bonding takes place through both of the terminal oxygen of CO group. A number of vibrations are observed in the region 700-400 cm^{-1} due to M-O stretching vibrations in all β-diketonates.

NMR spectra

^{1}H NMR

^{1}H NMR spectra of all the β-diketone derivatives of [$Bu_2SnO_2AlB(OPr^i)_4$] show broad multiplet centered between δ 0.8–1.2 ppm due to the intermixing of methyl protons of isopropoxy groups. A broad multiplet centered at δ 4.0-4.2 is due to the methine proton of isopropoxy groups in the spectra of all derivatives. All the β-diketone derivatives of μ-oxoisopropoxide compound show singlet at δ 2.1 ppm and ~ δ 5.8 ppm due to methyl and methine proton of the ligand moiety respectively. Further, the peaks observed in the region δ 7.0–7.7 ppm in benzoylacetone derivative of [$Bu_2SnO_2AlB(OPr^i)_4$] are due to the phenyl ring protons.

^{13}C NMR

The ^{13}C NMR spectra of 1:1 β-diketone derivatives of μ-oxoisopropoxide compound show two prominent peaks between δ 26.4 – 27.7 ppm and δ 27.9 – 28.4 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups. The two peaks observed at δ 62.6 – 62.8 ppm and δ 63.1 – 63.4 ppm assignable to the methine carbons of isopropoxy groups in the derivatives. Two single peak are observed at ~ δ 26.1 and about ~ δ 62.4 ppm in 1:2 and 1:3 derivatives due to the methyl and methine carbon of terminal isopropoxy group. Two peaks observed in the range δ 190.2 – 181.7 ppm and δ 98.4 – 92.3 ppm are due to carbonyl carbon and methine carbon of ligand moiety in all the β-diketone derivatives of μ-oxoisopropoxide compound. The peaks observed at 127.1, 126.4, 125.3 and 136.7 ppm are due to ortho, meta, para and substituted carbon of the phenyl ring respectively in the spectra of benzoylacetone derivative of μ-oxoisopropoxide compound. Further, the spectra of p-bromobenzoylacetone derivatives of μ-oxoisopropoxide show the shifting of the para carbon peak from 125.3 to ~ 131 ppm due to the bromo group substituted at para position.

^{27}Al NMR Spectra

The 1:1 β-diketone derivatives spectra show the presence of tetrahedral and octahedral enviorment about aluminium atom. But the spectra of 1:2 and 1:3 β-diketone derivatives of μ-oxoisopropoxide indicate that the aluminium atom is surrounded octahedrally by oxygen atoms in these compounds [34].

The aforesaid spectral, and elemental analysis suggest the following tentative structures of [$Bu_2SnO_2AlB(OPr^i)_4$], and its β-diketone derivatives of the type [$Bu_2SnO_2AlB(OPr^i)_3(L)$], [$Bu_2SnO_2AlB(OPr^i)_2(L)_2$] are given as below (Fig. 1).

REFERENCES

1. *J. Livage, New. J. Chem.,* ***25,*** *1* ***(2001).***
2. *R.J.P.Corriu; Angew.Chem., Int. Ed.,* ***39,*** *1377* ***(2000)****; R.J.P.Corriu; New J.Chem.,* ***25,*** *2* ***(2001)****; R.J.P.Corriu; Angew. Chem., Int. Ed.,* ***40,*** *2853* ***(2001).***
3. *P.N. Kapoor, A.K.Bhagi, R.S.Mulukutla, K.Klabunde; ‘Dekker Encyclopedia of Nanoscience and Nanotechnology’, Marcel Deker, Inc.; NewYork, 2007* ***(2004).***
4. *P.N.Kapoor, H.K.Sharma, A.K.Bhagi, M.Sharma; J.Ind.Chem.Soc.,* ***81,*** *273* ***(2004).***
5. *P.N.Kapoor, D.Heroux, R.S.Mulukutla, V.Zaikovskii, K.J.Klabunde; J.Mater.Chem.,* ***13,*** *410(2003).*
6. *H.K.Sharma, Rajesh Kumar; Indian J.chem.,* ***47A,*** *854* ***(2008).***
7. *C.L.Carnes, P.N.Kapoor, K.J.Klabunde, J.Bonevich; Chem.Mater.,* ***14****, 2922* ***(2002).***
8. *G.W.Wagner, L.R.Procell, R.J.O'Connor, S.Munavalli, C.L.Carnes, P.N.Kapoor, K.J. Klabunde; J.Am.Chem.Soc.,* ***123,*** *1636* ***(2001).***
9. *G.M.Medine, V.Zaikovskii, K.J.Klabunde; J.Mater.Chem.* ***14,*** *757* ***(2004).***
10. *M.Bhagat, A.Singh, R.C.Mehrotra; Synth.React.Inorg.Metal-org.Chem.,* ***28,*** *997* ***(1998).***
11. *R.C.Mehrotra, A.Singh, M.Bhagat, J.Godhwani; J.Sol-gel.Sci.&Tech.,* ***13,*** *45* ***(1998).***
12. *H.K.Sharma and P.N.Kapoor; Indian J.chem.,* ***43A,*** *556* ***(2004).***
13. *M.Sharma, A.K.Bhagi, Priti, R.Kansal, R.Kumar, P.N.Kapoor; Indian J.Chem.,* ***44A,*** *1* ***(2005).***
14. *D.R.Rolison, B.Dunn; J.Mater.Chem.,* ***11,*** *963* ***(2001).***

15. *F.Ribot, P.Toledano, C.Sanchez; Chem.Mater.,* ***3,*** *759* ***(1991).***

16. *T.Ouhadi, A.Hamitou, R.Jerome, Ph.Teyssie; Macromolecules,* ***9,*** *927* ***(1976).***

17. *L.Hocks, J.P.Bioul, P.Durbut, A.Hamitou, J.L.Marbehant, T.Ouhadi, Ch.Stevens, Ph.Teyssie; J.Mol.Catal.,* ***3,*** *135* ***(1977).***

18. *Ph.Teyssie, J.P.Bioul, P.Conde, J. Druet, J.Heuschen, R.Jerome; Am.Chem.Soc.,Symp.Ser.,286, 97 (1985).*

19. *J.Heuschen, R.Jerome, Ph.Teyssie; Macromolecules,* ***14,*** *242* ***(1981).***

20. *D.D.Perrin, W.L.F.Armarego, D.R. Perrin; ‘Purification of Laboratory Chemicals’, 2nd Edn., Pergamon Press; New York,* ***(1980).***

21. *R.Ramchandran, B.Singh , A.K.Narula, P.K.Gupta, R.N. Kapoor; Polyhedron* ***4,*** *1007* ***(1985).***

22. *A.I.Vogel, ‘A Text Book of Quantitative analysis’, Longman; London,* ***(1989).***

23. *D.C.Bradley, F.M.A.Halim, W. Wardlaw; J.Chem.Soc., 3450* ***(1950).***

24. *A.K.Sawyer, ‘Organotin Compounds, Vol-I, Marcel Deckker’, INC; New York,* ***(1971).***

25. *C.T.Lynch, K.S.Masdiyanni, J.S.Smith, W.J.Grawford, Anal.Chem.,* ***36,*** *2332* ***(1964).***

26. *V.A.Koznov, N.I.Kuzlova, N.Ya.Turova, Yu.S. Nekrasov; Zh.Neorg.Khim.,* ***24,*** *1526* ***(1979).***

27. *K.Nakamoto, ‘Infrared and Raman Spectra of Inorganic and Coordination Compounds’, John Wiley and Sons; New York,* ***(1986).***

28. *Sonika, A.K.Narula, O.P.Vermani, H.K.Sharma; J.Org.Chem.,* ***470,*** *67* ***(1994).***

29. *E.Brcitmair, W.Voelter; ‘^{13}C NMR spectroscopy (High Resolution Methods and Application in Organic Chemistry and Biochemistry)’, VCH; New York,* ***(1990).***

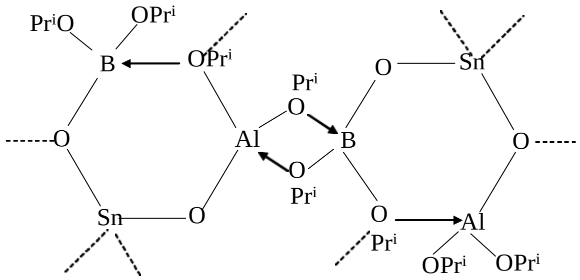
30. *D.Mueller, Hoebbel, W.GesBu2Sner; Chem.Phys.Lett.,* ***84,*** *2.* ***(1981)***

31. *T.T.Nguyen, N.Ogwuru, G.Eng, App.Org.Chem.,* ***14,*** *345* ***(2000).***

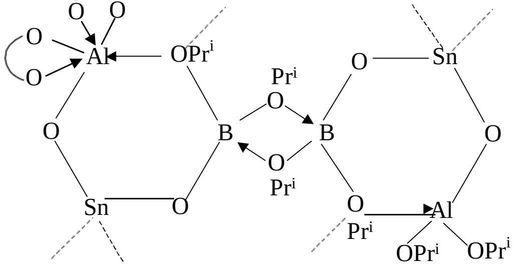
32. M.S.Mayadeo; J.Ind.Chem.Soc., ***11,*** *502* ***(1967).***

33. *L.Thomas, W.Henderson, G.A.Bowmaker, J.M.Seakins, R.P.Cooney; J.Mater.Chem.,* ***7(8),*** *1553* ***(1997).***

34. *V.J.Shiner, Jr.D.Whittaker, V.F.Fernandes; J.Am.Chem.Soc.,* ***85,*** 23 **(1963)**



$[Bu_2SnO_2AlB(OPr^i)_4]$



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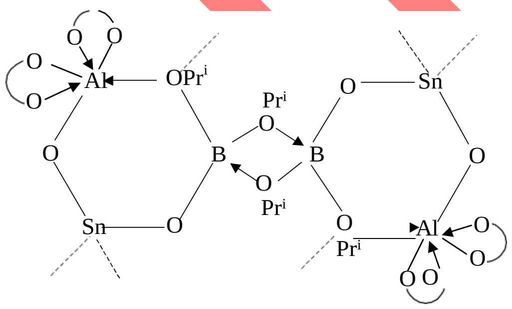

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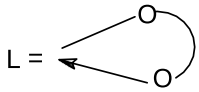

Fig. 1

Table 1 : Analytical data

S.No.	Compound g (mmol)	Ligand g(mmol)	Molar ratio	Refluxing time (hrs.)	Product g (%)	HOPr^i g	Anal. Calcd. (found) Sn (%)	Al (%)	B (%)
1.	$[Bu_2SnO_2AlB(OPr^i)_4]$ 0.478 (0.915)	Hacac 0.0915 (0.915)	1:1	4	$[Bu_2SnO_2AlB(OPr^i)_3(acac)]$ 0.448(72.9)	0.055 (0.53)	21.59 (21.62)	4.80 (5.72)	1.74 (2.1)
2.	$[Bu_2SnO_2AlB(OPr^i)_4]$ 0.524 (1.002)	Hacac 0.200 (2.00)	1:2	5	$[Bu_2SnO_2AlB(OPr^i)_2(acac)_2]$ 0.543 (78.5)	0.120 (0.12)	19.56 (19.58)	4.34 (4.37)	1.68 (1.58)
3.	$[Bu_2SnO_2AlB(OPr^i)_4]$ 0.534 (1.023)	Hbzac 0.166 (1.023)	1:1	3	$[Bu_2SnO_2AlB(OPr^i)_3(bzac)]$ 0.578 (79.6)	0.061 (0.059)	18.57 (18.61)	4.12 (4.08)	1.60 (1.63)
4.	$[Bu_2SnO_2AlB(OPr^i)_4]$ 0.539 (1.08)	Hbzac 0.350 (2.16)	1:2	5	$[Bu_2SnO_2AlB(OPr^i)_2(bzac)_2]$ 0.735 (84.8)	0.130 (0.128)	14.90 (14.86)	3.28 (3.30)	1.58 (1.52)
5.	$[Bu_2SnO_2AlB(OPr^i)_4]$ 0.524 (1.007)	Hp-Brba 0.243 (1.007)	1:1	4	$[Bu_2SnO_2AlB(OPr^i)_3(p\text{-}Brba)]$ 0.654 (83.9)	0.06 (0.059)	16.63 (16.67)	3.45 (3.48)	1.61 (1.66)
6.	$[Bu_2SnO_2AlB(OPr^i)_4]$ 0.534 (1.02)	Hp-Brba 0.492 (2.04)	1:2	6	$[Bu_2SnO_2AlB(OPr^i)_2(p\text{-}Brba)_2]$ 0.842(85.8)	0.12 (0.12)	13.11 (13.16)	2.42 (2.44)	1.28 (1.28)