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Synthesis of bimetallic[Sn^{IV},Al^{III}]-μ-oxoisopropoxyacetate and -μ-oxoisopropoxide and their acetylacetone and benzoylacetone derivatives

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Abstract

Bimetallic [Sn^{IV},Al^{III}]-μ-oxoisopropoxyacetate [$Bu_2Sn(OAc)OAl(O^iPr)_2$] and bimetallic [Sn^{IV},Al^{III}]-μ-oxoisopropoxide [$Bu_2SnO_2Al_2(O^iPr)_4$] have been synthesized by thermal condensation of dibutyltin diacetate with aluminium isopropoxide in 1:1 and 1:2 molar ratio, respectively. Reactions of these compounds with acetylacetone and benzoylacetone in these molar ratios yielded compounds of the type [$Bu_2Sn(OAc)OAl(O^iPr)L$], [$Bu_2Sn(OAc)OAlL_2$], [$Bu_2SnO_2Al_2(O^iPr)_3L$] and [$Bu_2SnO_2Al_2(O^iPr)_2L_2$] (where L = acetylacetonate or benzoylacetonate anion). The μ-oxo compounds and their derivatives have been characterized by elemental analysis and spectroscopic techniques (IR, ^{1}H NMR, ^{13}C NMR, ^{27}Al NMR and ^{119}Sn NMR).

Key words: Tin; Aluminium; Alkoxide

1. Introduction

A large number of bimetallic-μ-oxoalkoxides of the general formula $(RO)_n$–M_1–O–M_2–O–M_1–$(OR)_n$, where $M_1 = Al^{III}$ ($n = 2$) or Ti^{IV} ($n = 3$) and M_2 is a bivalent transition metal [Cr^{II}, Mn^{III}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II} or Mo^{II}] and R = an alkyl group usually propyl or butyl, have been synthesized [1–3]. It has been reported that these bimetallic-μ-oxoalkoxides are among the best catalysts for polymerization of heterocyclic monomers such as lactones, oxiranes, thiiranes and epoxides [4–7]. Compounds with Fe, Cr and Mo as the central atom have been found to bind molecular oxygen rapidly at room temperature [6,8]. The bimetallic-μ-oxoalkoxides have surprisingly high solubilities in common organic solvents (especially hydrocarbons), and have been used as models for exploring the frontiers between heterogeneous and homogeneous catalysis [5].

Kapoor *et al.* [9–11] have reported the synthesis of some new bimetallic-μ-oxoalkoxides containing a Main Group metal atom Mg^{II}, Si^{IV} or Sn^{IV} in place of the transition metal. We report here the synthesis of two new bimetallic-μ-oxoalkoxides [$Bu_2Sn(OAc)OAl(O^iPr)_2$] and [$Bu_2SnO_2Al_2(O^iPr)_4$]. In order to gain more information about the structures of these bimetallic-μ-oxoalkoxides, we have also made their acetylacetone and benzoylacetone derivatives.

2. Experimental details

All manupulations were carried out in an inert atmosphere on a vacuum line by Schlenk techniques. Dibutyltin diacetate (Aldrich) was distilled (142°C/10 mm) prior to use. Aluminium isopropoxide was prepared by the reported method [12]. Metals and iso-

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propoxy determinations were carried out as described elsewhere [13,14]. IR spectra were recorded as Nujol mulls and as thin film on KBr plates in the range 4000–400 cm^{-1} on a Perkin-Elmer 842 grating spectrophotometer. The ^1H NMR spectra were recorded on a Perkin-Elmer R-32 90 MHz spectrometer. The ^{13}C, ^{27}Al and ^{119}Sn NMR were recorded on a Bruker 300 MHz instrument with TMS, $AlCl_3 \cdot 6H_2O$ and $(CH_3)_4Sn$ as standards, at RSIC Chandigath, IIT Bombay and IOC Faridabad.

2.1. *Preparation of* $[Bu_2Sn(OAc)OAl(O^iPr)_2]$ *and* $[Bu_2SnO_2Al_2(O^iPr)_4]$

The bimetallic [Sn^{IV},Al^{III}]-μ-oxoisopropoxyacetate (**I**) and bimetallic [Sn^{IV},Al^{III}]-μ-oxoisopropoxide (**II**) were prepared by refluxing dibutyltin diacetate and aluminium isopropoxide in 1:1 and 1:2 molar ratios, respectively, in xylene for *ca.* 8 h under a fractionating column. The isopropyl acetate formed was continuously taken off from *ca.* 80°C up to the boiling point of xylene (*ca.* 139°C). The residual xylene was distilled off under reduced pressure. Compounds **I** and **II** were also prepared by heating a mixture of the reactants in the absence of solvent for *ca.* 6 h under reduced pressure and removing the isopropyl acetate periodically under reduced pressure. Yellowish glassy solids were obtained. The products were redissolved in benzene and the solutions filtered. Slow evaporation of the solution gave pale yellow solids (yield 95%).

I: Anal. Found: Sn, 25.9; Al, 5.6; O^iPr, 26.1. Calcd.: Sn, 26.2; Al, 5.9; O^iPr, 26.1%. **II**: Anal. Found: Sn, 20.6; Al, 9.3; O^iPr, 43.2. Calcd.: Sn, 21.4; Al, 9.7; O^iPr, 42.5%.

2.2. *Reaction of bimetallic-μ-oxoisopropoxyacetate with acetylacetone in 1:1 molar ratio*

A mixture of compound **I** (0.34 g, 0.74 mmol) and acetylacetone (0.07 g, 0.74 mmol) in benzene (*ca.* 50 ml) was refluxed for *ca.* 3 h. The generated isopropanol was distilled off azeotropically and its amount determined [14] in order to show when the reaction was complete. The excess solvent was removed under reduced pressure and the pale yellow solid dried at 40°C per 1 mm.

A similar procedure was used for other reactions of acetylacetone and benzoylacetone with **I** and **II** in various molar ratios. Details are given in Table 1 along with the analytical data.

3. Results and discussion

The reactions of dibutyltin diacetate and aluminium isopropoxide in molar ratios 1:1 and 1:2, respectively, can be represented as follows:

$$Bu_2Sn(OAc)_2 + Al(O^iPr)_3 \xrightarrow[\text{xylene}]{\text{reflux}} \underset{(\mathbf{I})}{Bu_2Sn(OAc)OAl(O^iPr)_2} + {}^iPrOAc$$

$$Bu_2Sn(OAc)_2 + 2Al(O^iPr)_3 \xrightarrow[\text{xylene}]{\text{reflux}} \underset{(\mathbf{II})}{Bu_2SnO_2Al_2(O^iPr)_4} + 2{}^iPrOAc$$

The above reaction involves stepwise replacement of the acetyl groups, as was confirmed by determining the amount of isopropyl acetate liberated during the progress of the reaction. Compounds **I** and **II** are pale

TABLE 1. Analytical data

S.No.	Compound g (mmol)	Ligand g (mmol) [a]	Molar ratio	Refluxing time (h)	Product	Anal. found (calcd.)		
						^iPrO (g)	Sn (%)	Al (%)
1	$[(Bu)_2Sn(OAc)OAl(O^iPr)_2]$ 0.34 (0.74)	Hacac 0.07 (0.74)	1:1	3	$[(Bu)_2Sn(OAc)OAl(O^iPr)(acac)]$	0.04 (0.04)	23.3 (24.1)	5.0 (5.4)
2	$[(Bu)_2Sn(OAc)OAl(O^iPr)_2]$ 0.41 (0.90)	Hacac 0.18 (1.80)	1:2	6	$[(Bu)_2Sn(OAc)OAl(acac)_2]$	0.10 (0.11)	22.1 (22.3)	4.8 (5.0)
3	$[(Bu)_2Sn(OAc)OAl(O^iPr)_2]$ 0.25 (0.56)	Hbzac 0.09 (0.56)	1:1	3	$[(Bu)_2Sn(OAc)OAl(O^iPr)(bzac)]$	0.03 (0.03)	21.3 (21.4)	4.7 (4.8)
4	$[(Bu)_2Sn(OAc)OAl(O^iPr)_2]$ 0.28 (0.61)	Hbzac 0.2 (1.22)	1:2	6	$[(Bu)_2Sn(OAc)OAl(bzac)_2]$	0.07 (0.07)	17.8 (18.0)	3.8 (4.1)
5	$[(Bu)_2SnO_2Al_2(O^iPr)_4]$ 0.48 (0.87)	Hacac 0.09 (0.87)	1:1	4	$[(Bu)_2SnO_2Al_2(O^iPr)_3(acac)]$	0.05 (0.05)	19.7 (19.9)	9.2 (9.1)
6	$[(Bu)_2SnO_2Al_2(O^iPr)_4]$ 0.41 (0.74)	Hacac 0.15 (1.47)	1:2	8	$[(Bu)_2SnO_2Al_2(O^iPr)_2(acac)_2]$	0.09 (0.09)	18.2 (18.7)	8.7 (8.5)
7	$[(Bu)_2SnO_2Al_2(O^iPr)_4]$ 0.51 (0.92)	Hbzac 0.15 (0.92)	1:1	4	$[(Bu)_2SnO_2Al_2(O^iPr)_3(bzac)]$	0.05 (0.05)	17.6 (18.1)	8.3 (8.2)
8	$[(Bu)_2SnO_2Al_2(O^iPr)_4]$ 0.45 (0.81)	Hbzac 0.26 (1.62)	1:2	8	$[(Bu)_2SnO_2Al_2(O^iPr)_2(bzac)_2]$	0.1 (0.1)	15.3 (15.6)	7.2 (7.1)

[a] Hacac, acetylacetone; Hbzac, benzoylacetone.

TABLE 2

S.No.	Compound	^{1}H NMR data [a]					^{13}C NMR data						^{27}Al NMR data	^{119}Sn NMR data
		$-CH_3(O^iPr)$ $-CH_2$ (Bu) $-CH_3$(Bu)	-CH (O^iPr)	$-CH_3$ ligand/ acetyl	-CH ligand	$-C_6H_5$ ligand	$-CH_3$ (O^iPr)	-CH (O^iPr)	$\geq Sn-CH_2-CH_2-CH_2-CH_3$ 4 3 2 1	>C=O acetyl/ ligand	$-CH_3$ acetyl/ ligand	$-C_6H_5$ ligand	-Al<	>Sn-
1	$Bu_2Sn(OAc)OAl(O^iPr)_2$	0.8–1.2bm	4.1m	2.1s	–	–	27.6, 27.8	62.6 62.8	25.4(C1), 25.3(C2) 23.9(C3), 13.6(C4)	146.0	13.6	–	40.0 64.1	–
2	$Bu_2SnO_2Al_2(O^iPr)_4$	0.8–1.2bm	4.1m	–	–	–	27.6, 27.8, 28.2	62.6 62.8 64.2	25.4(C1), 25.3(C2) 23.9(C3), 13.6(C4)	–	13.6	–	64.2	75.3
3	$Bu_2Sn(OAc)OAl(O^iPr)(acac)$	0.8–1.1bm	4.1m	2.1bs	5.5s	–	27.8	62.8	25.4(C1), 25.2(C2) 23.9(C3), 13.6(C4)	146.1	13.6	–	1.8	74.9
4	$Bu_2Sn(OAc)OAl(acac)_2$	0.9–1.2bm	–	2.0bs	5.5s	–	–	–	25.4(C1), 25.3(C2) 23.8(C3), 13.7(C4)	146.3	13.7	–	1.8	74.9
5	$Bu_2Sn(OAc)OAl(O^iPr)(bzac)$	0.8–1.1bm	4.1m	2.1bs	6.2s	7.2– 7.8	27.7	62.7	25.6(C1), 25.4(C2) 23.9(C3), 13.6(C4)	146.2	13.6	128.4–145.1	1.7	75.6
6	$Bu_2Sn(OAc)OAl(bzac)_2$	0.9–1.2bm	–	2.1bs	6.2s	7.2– 7.7	–	–	25.6(C1), 25.4(C2) 23.8(C3), 13.6(C4)	146.2	13.6	129 –145.1	1.8	75.7
7	$Bu_2SnO_2Al_2(O^iPr)_3(acac)$	0.8–1.1bm	3.9m	1.9s	5.4s	–	27.6, 27.7, 28.2	62.6, 62.7, 64.2	25.4(C1), 25.3(C2) 23.9(C3), 13.7(C4)	146.0	13.7	–	1.8 65.4	74.8
8	$Bu_2SnO_2Al_2(O^iPr)_2(acac)_2$	0.8–1.2bm	4.1m	1.9s	5.3s	–	27.8, 28.3	62.7, 64.2	25.4(C1), 25.3(C2) 23.8(C3), 13.7(C4)	146.3	13.7	–	1.8 65.3	74.9
9	$Bu_2SnO_2Al_2(O^iPr)_3(bzac)$	0.8–1.2bm	4.1m	2.0s	6.1s	7.2– 7.8	27.6, 27.8, 28.2	62.6, 62.8, 64.2	25.6(C1), 25.4(C2) 23.8(C3), 13.6(C4)	146.2	13.6	130.5–145.3	1.8 65.4	75.3
10	$Bu_2SnO_2Al_2(O^iPr)_2(bzac)_2$	0.8–1.2bm	4.0m	2.0s	6.2s	7.2– 7.7	27.8, 28.2	62.8, 64.1	25.6(C1), 25.3(C2) 23.9(C3), 13.6(C4)	146.2	13.6	130.7–145.3	1.8 65.4	75.4

[a] bm, broad multiplet; m, multiplet; s, singlet; bs, broad singlet; acac, acetylacetonate; bzac, benzoylacetonate.

yellow solids, highly susceptible to hydrolysis, and soluble in common organic solvents such as C_6H_6, $CHCl_3$, CCl_4 etc.

The reactions of **I** and **II** with acetylacetone and benzoylacetone can be represented as follows:

$$Bu_2Sn(OAc)OAl(O^iPr)_2 + nHL \xrightarrow[\text{reflux}]{\text{benzene}} \underset{\textbf{(I)}}{Bu_2Sn(OAc)OAl(O^iPr)_{2-n}L_n} + n\,^iPrOH$$

$$Bu_2SnO_2Al_2(O^iPr)_4 + nHL \xrightarrow[\text{reflux}]{\text{benzene}} \underset{\textbf{(II)}}{Bu_2SnO_2Al_2(O^iPr)_{4-n}L_n} + n\,^iPrOH$$

where $n = 1$ or 2, L = acac or bzac.

All the derivatives are pale yellow solids, soluble in common organic solvents such as $CHCl_3$ and C_6H_6, and susceptible to hydrolysis. The fact that further isopropoxy groups are not displaced even with an excess of the ligand and increase in the reflux time indicates that two types of isopropoxy groups are present, *viz.* bridging and terminal. Bridging isopropoxy groups are not usually displaced [10,15].

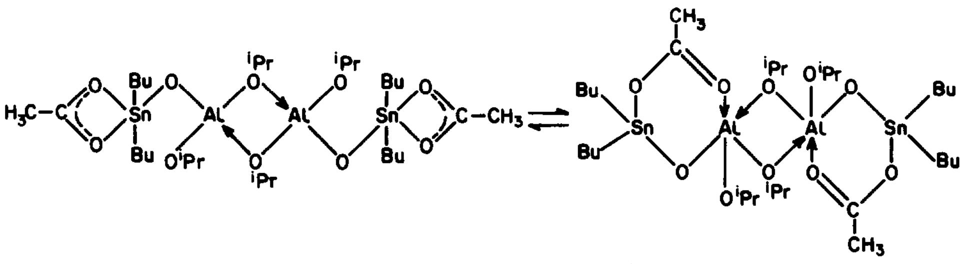
The IR spectra of I and II show bands at *ca.* 1150 cm^{-1} and *ca.* 1100 cm^{-1} which may be assigned to ν(C–O + ^{i}PrO) terminal and ν(C–O + ^{i}PrO) bridging groups, respectively [16]. The band appearing at approximately 950 cm^{-1} is due to the ν(C$\equiv$O) band of the bridging isopropoxy group [16]. Strong bands present at *ca.* 1610 cm^{-1} and 1420 cm^{-1} in the IR spectrum of dibutyltin diacetate due to (C$\equiv$O) asym stretching and COO^- sym. stretching [17] are also observed in the IR spectrum of I, which indicates the partial replacement of the acetyl group. However, the spectrum of **II** does not show a band at these positions, confirming the complete removal of the acetyl group. A number of bands observed in the region 600–400 cm^{-1} are due to metal–oxygen bonds. Thus the IR spectra of these compounds clearly suggest that they are made up of associated molecules. This association results from the tendency of the aluminium atom to increase its coordination number by inter- and intramolecular metal–oxygen bonding, as observed in the case of simple alkoxides.

The ^{1}H NMR spectra of **I** and **II** (Table 2) show peaks between δ 0.8–1.2 that are due to intermixing of the terminal and bridging methyl protons of the isopropoxy groups along with the butyl group. The multiplet centered at δ 4.1 is due to the methine protons of the isopropoxy groups. The ratio of the integral of the signal from the methine proton of isopropoxy group to that from the methyl proton of the acetate group in compound **I** is consistent with the replacement of only one acetyl group.

The ^{13}C NMR spectra of **I** and **II** (Table 2) show two prominent peaks, at δ 27.6 and 27.8, assignable to the methyl carbon of terminal and intermolecularly bridged isopropoxy moiety. Two signals at δ 62.6 and δ 62.8 can be assigned to the two different types of methine carbons of the isopropoxy groups [18]. The spectrum of compound **II** shows two additional peaks at δ 28.2 and 64.2 due to methyl and methine carbons of the isopropoxy group, suggesting the presence of a third type of isopropoxy group. The other peaks at δ 25.4, δ 25.3, δ 23.9 and δ 13.6 are assignable to C-1, C-2, C-3, and C-4 ($>Sn-\underset{4}{C}H_2-\underset{3}{C}H_2-\underset{2}{C}H_2-\underset{1}{C}H_3$) of the butyl group [19]. The weak signal observed at δ 146 in case of **I** is due to carbon of the carbonyl group [19]. However, the signal due to methyl protons was observed at δ 13.7 along with that of the methylene carbon (C-4) of the butyl group. The upfield shift is probably due to the electropositive nature of the Sn atom.

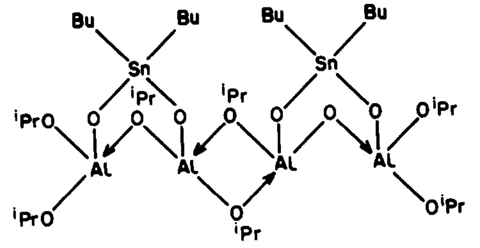
The ^{27}Al NMR spectrum of **II** (Table 2) shows a signal at δ 64.2 that can be attributed to the tetrahedral environment about the aluminium atom [20] (Fig. 2). The ^{27}Al NMR spectrum of **I** shows a fairly sharp peak at δ 64.1, and a broad peak centered at δ 40 that is probably due to an equilibrium between tetra- and penta-coordinated Al-environments in the solution [20] (Fig. 1(a, b)).

The ^{119}Sn NMR spectrum (Table 2) of **II** shows a sharp signal at δ 75 that can be attributed to the tetracoordinated Sn atom [21] (Fig. 2).



(a) $Bu_2Sn(OAc)OAl(O^iPr)_2$ (b)

Fig. 1.

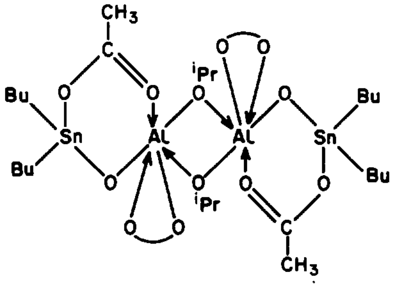


$Bu_2SnO_2Al_2(O^iPr)_4$

Fig. 2.

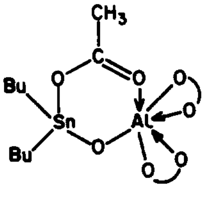
The IR spectra of the β-diketones display strong bands at *ca.* 1600 cm^{-1} and *ca.* 1510 cm^{-1} due to $\nu_{sym}(C{=}O)$ and $\nu_{asym}(C{=}C)$ respectively, and a broad band at 3000–2700 cm^{-1} due to enolic O–H. The absence of a shift in the carbonyl frequency and disappearance of the broad O–H band in the β-diketonates of **I** and **II** suggest that bonding takes place through both of the terminal oxygens of the carbonyl groups [22]. The IR spectra of these derivatives thus show that β-diketones behave as monobasic bidentate ligands. The IR spectra of 1:2 β-diketonates of **I** show the absence of the isopropoxy group, whereas those of the 1:1 derivatives indicate the presence of bridging isopropoxy groups only. The IR spectra of 1:1 β-diketonates of **II** indicate the presence of three types of isopropoxy groups, as observed in the parent compound, whereas in the 1:2 derivatives no bands due to terminal isopropoxy group are observed. In case of the benzoylacetonates, the bands due to phenyl group are observed at their usual positions.

The ^1H NMR spectra of the derivatives show singlets at δ 2.1 and δ 5.6–6.2 that are due to methyl and methine protons, respectively, of the ligand moiety of acetylacetonates and benzoylacetonates. The benzoyl derivatives also show multiplets at δ 7.2–7.8 due to phenyl ring protons of the benzoylacetone moiety. In the μ-oxoisopropoxyacetate derivatives, a broad peak centered at δ 2.1 is due to the mixing of the methyl protons of the acetate and the ligand. The other peaks appear at their usual positions.



$Bu_2Sn(OAc)OAl(O^iPr)L$

Fig. 3.

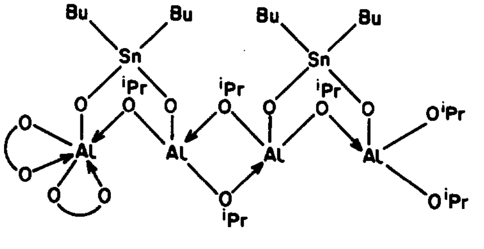


$Bu_2Sn(OAc)OAlL_2$

Fig. 4.

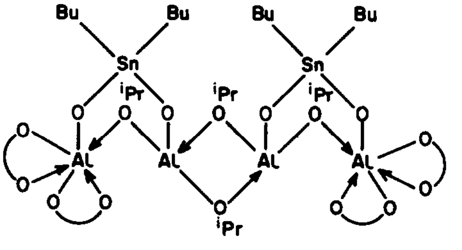
The ^{13}C NMR spectra of 1:2 derivatives of **I** indicate the absence of the isopropoxy group whereas those of the 1:1 derivatives indicate the probable presence of bridging isopropoxy group. The ^{13}C NMR spectra of 1:1 β-diketonates of **II** indicate three types of isopropoxy groups as observed in the parent compound, whereas 1:2 derivatives show no peaks due to terminal isopropoxy group. In the case of benzoylacetonates, the peaks due to the phenyl group are observed at their usual position.

The ^{27}Al NMR spectra of the derivatives of **I** show a signal at δ 1.8 that can be attributed to the hexa-coordinated Al-atom. The spectra of the derivatives of **II** show signals at δ 65.4 and δ 1.8 that can be attributed to the tetrahedral and octahedral environment about



$Bu_2SnO_2Al_2(O^iPr)_3L$

Fig. 5.



$Bu_2SnO_2Al_2(O^iPr)_2L_2$

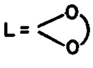


Fig. 6.

the Al-atom [21]. This is probably due to replacement of both of the isopropoxy groups from the same Al-atom. Since the 5-coordination at Al produced by the replacement of the first isopropoxy group is relatively unstable compared with the tetrahedral and octahedral coordination, the second isopropoxy group is then displaced from the same Al-atom.

The ^{119}Sn NMR spectra of the derivatives suggest that the Sn-atom is tetra-coordinated.

On the basis of the above results, the structures shown in Figs. 3–6 can tentatively be assigned to the various derivatives.

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