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Some new organotin(IV), aluminium(III)-μ-oxoisopropoxides and their benzoylacetone derivatives

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Abstract

The first organotin(IV), aluminium(III)-μ-oxoisopropoxides of the type $[R_3SnOAl(O^iPr)_2]$ (R = Me or Ph) have been made by heating of trimethyl- or triphenyl-tin acetate with aluminium isopropoxide. The reactions of these μ-oxoisopropoxides with benzoylacetone in 1:1 and 1:2 molar ratios yielded the compounds of the type $[R_3SnOAl(O^iPr)(bzac)]$ and $[R_3SnOAl(bzac)_2]$ (where R = Me or Ph and bzac = deprotonated benzoylacetone), respectively.

Introduction

Metal alkoxides have recently attracted a great deal of attention as precursors for oxide ceramics, including the high temperature superconductor Ba_2CuO_7 [1,2], by CVD [3] or sol–gel [4] techniques. Bimetallic μ-oxoalkoxides of the type $[MO_2Al_2(OR)_4]$ (where M = Cr^{II}, Mn^{II}, Fe^{II}, Co^{II}, Zn^{II} and Mo^{II}; R = C_3H_7 or C_4H_9) have surprisingly high solubilities in common organic solvents (especially hydrocarbons), and are among the best catalysts for ring opening polymerisation reactions of the heterocyclic monomers such as lactones, oxiranes, thiiranes and epoxides [5–12]. Another important feature of bimetallic μ-oxoalkoxides with Fe, Cr and Mo as the central atom is their ability to bind molecular oxygen at room temperature [10,12]. We described previously [13,14] the synthesis of $[MgO_2Al_2(O^iPr)_4]$ and $[Me_2SiO_2Al_2(O^iPr)_4]$ containing a main group central metal atom. In this communication we report the synthesis of $[R_3SnOAl(O^iPr)_2]$, in which R = Me or Ph. In order to gain more information about their structure and solubilities and the effect of a chelating group on the stability, the benzoylacetone derivatives of these bimetallic μ-oxoisopropoxides have also been synthesised.

Experimental

Stringent precautions were taken to exclude moisture. The general technique and physical measurements were as described elsewhere [13,15]. Trimethyl-

Table 1

Analytical data

Compound	Found (Calc.) (%)		
	Sn	Al	O^{i}Pr
[$Me_3SnOAl(O^iPr)_2$]	36.5 (36.6)	8.1 (8.3)	36.2 (36.3)
[$Ph_3SnOAl(O^iPr)_2$]	23.2 (23.2)	5.2 (5.3)	23.1 (23.1)
[$Me_3SnOAl(O^iPr)(bzac)$]	27.7 (27.9)	6.3 (6.3)	-
[$Me_3SnOAl(bzac)_2$]	22.3 (22.5)	5.0 (5.1)	-
[$Ph_3SnOAl(O^iPr)(bzac)$]	19.2 (19.4)	4.3 (4.4)	-
[$Ph_3SnOAl(bzac)_2$]	16.5 (16.6)	3.6 (3.8)	-

and triphenyl-tin acetate were prepared by published methods [16]. ^{27}Al NMR and ^{119}Sn NMR spectra were recorded on a Bruker (FT) 400 MHz NMR spectrometer with $AlCl_3 \cdot 6H_2O$ and Ph_3SnBr as standards.

Preparation of bimetallic [Sn^{IV}, Al^{III}]-μ-oxoisopropoxide [$R_3SnOAl(O^iPr)_2$] (R = Me or Ph)

The bimetallic [Sn^{IV}, Al^{III}]-μ-oxoisopropoxides were prepared by heating of a mixture of R_3SnOAc (0.05 mol) (R = Me or Ph) and aluminium isopropoxide (0.05 mol) in toluene. The liberated isopropylacetate was fractionated out continuously from 80 °C to the boiling point of toluene (~ 110 °C). The excess of toluene was distilled off under reduced pressure to leave a pale yellow glassy solid (yield ~ 95%).

Reaction of [Sn^{IV}, Al^{III}]-μ-oxoisopropoxide with benzoylacetone in 1:1 molar ratio

A mixture of benzoylacetone (1.62 g) and $Me_3SnOAl(O^iPr)_2$ (2.67 g) in benzene (~ 60 ml) was refluxed for 4.5 h. The liberated isopropanol was collected at 73–78 °C as the binary isopropanol/benzene azeotrope, and was estimated oxidimetrically to check the completion of reaction. The excess of solvent was removed under reduced pressure and the pale yellow solid dried at 1 mmHg/60 °C (yield ~ 95%). Other derivatives were made from benzoylacetone and [$Me_3SnOAl(O^iPr)_2$] or [$Ph_3SnOAl(O^iPr)_2$] in various molar ratios.

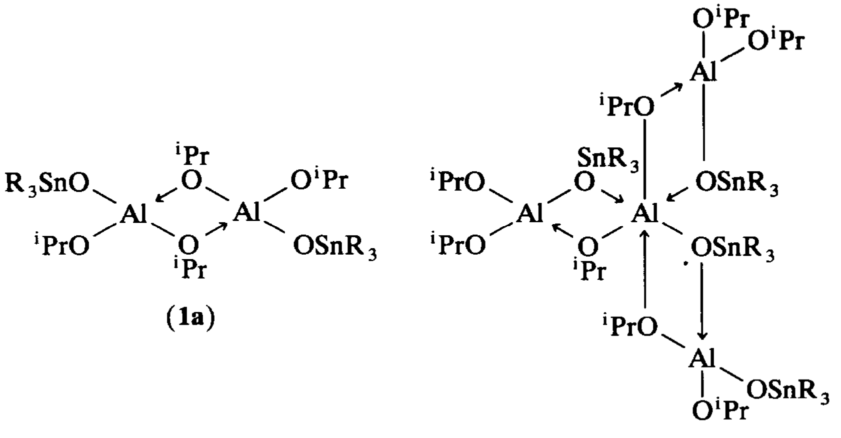
Analytical data for the compounds are given in Table 1.

Results and discussion

The reaction of trimethyl- and triphenyl-tin acetate with aluminium isopropoxide can be represented as follows:

$$R_3SnOAc + Al(O^iPr)_3 \xrightarrow[\text{reflux}]{\text{toluene}} [R_3SnOAl(O^iPr)_2] + {}^iPrOAc$$

R = Me or Ph



(1a)

(1b)

Fig. 1. $[R_3SnOAl(O^iPr)_2]$: (a) tetrahedrally surrounded aluminium; (b) octahedrally surrounded aluminium.

The bimetallic μ-oxoisopropoxides are pale yellow glassy solids, highly susceptible to hydrolysis and soluble in common organic solvents such as benzene, chloroform, ethanol, and acetone. Attempts to crystallise these derivatives from benzene/hexane or toluene/hexane mixtures were unsuccessful.

The IR spectra of the bimetallic $[Sn^{IV}, Al^{III}]$-μ-oxoisopropoxides show bands in the region 1375–1350, 1180–1165 and 1130–1100 cm^{-1} that can respectively be assigned to the *gem*-dimethyl portion of the isopropoxy group, the $\nu(C–O + O^iPr$ terminal) band, and the $\nu(C–O + O^iPr$ bridging) band [17]. The band at ~ 935 cm^{-1} was assigned to the $\nu(C–O)$ bridging [18] of the isopropoxy group. These bands clearly indicate that these bimetallic μ-oxoisopropoxides are associated molecules. Strong absorption bands at ~ 1580 cm^{-1} due to $\nu_{asym}(COO)$ and at ~ 1450 cm^{-1} due to $\nu_{sym}(COO)$ vibrations in the spectra of R_3SnOAc (R = Me or Ph) [19] are absent in the spectra of $[R_3SnOAl(O^iPr)_2]$, indicating the complete removal of the acetyl group.

The ^1H NMR spectrum of $[Ph_3SnOAl(O^iPr)_2]$ in $CDCl_3$ shows two doublet centred at δ 1.1 and δ 1.2 ppm, in the integration ratio 1:1, due to methyl protons of isopropoxy groups, indicating the presence of two types of isopropoxy groups (terminal and bridging). This suggests that the dimer (Fig. 1a) predominates over the tetramer (Fig. 1b), but the signals were not very sharp owing to the exchange between terminal and bridging isopropoxy groups. Broad multiplets centred at δ 4.1 ppm, δ 7.1–7.7 ppm were respectively assigned to the methine protons of the isopropoxy groups and the protons of the phenyl group of the Ph_3Sn moiety. In the case of $[Me_3SnOAl(O^iPr)_2]$ a broad peak centred at δ 0.8 ppm arising from overlap of signals of methyl protons of $(Me)_3Sn$ and isopropoxy groups was observed. This overlap of the signals from two types of protons is indicated by the proton integration ratio (~ 2:21) for the methine proton of the isopropoxy groups (~ 4.1 ppm) and methyl protons $(CH_3)_3Sn + 2(CH_3)_2CHO$.

The ^{27}Al NMR spectrum of $[Me_3SnOAl(O^iPr)_2]$ in $CDCl_3$ shows two signals at δ 64.1 ppm and δ 14.2 ppm (line width ~ 1600 Hz) that can be attributed to the equilibrium between tetrahedral and octahedral environments about the aluminium atom [20] (Fig. 1). The ^{119}Sn NMR spectrum of [$Me_3SnOAl(O^iPr)_2$] shows a sharp signal at low field (δ −156.0 ppm) indicating tetrahedrally surrounded tin [21]. The terminal R_3SnO in **1b** shows a slightly different ^{119}Sn peak from that of the bridging R_3SnO, suggesting that the dimer (**1a**) is the dominant form.

The reactions of bimetallic [Sn^{IV}, Al^{III}]-μ-oxoisopropoxide with benzoylacetone can be represented by the following equation:

$$[R_3SnOAl(O^iPr)_2] + n\ Hbzac \xrightarrow[\text{reflux}]{\text{benzene}} [R_3Sn(O^iPr)_{2-n}(bzac)_n] + n\,{}^iPrOH$$

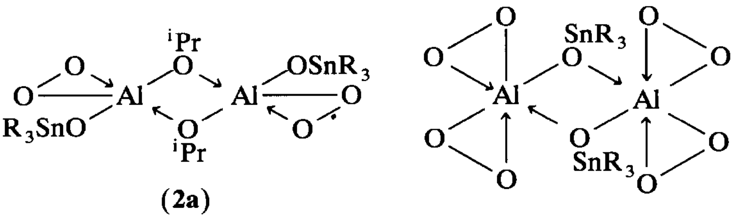
(where $n = 1$ or 2, R = Me or Ph and Hbzac = $C_6H_5COCH_2COCH_3$).

All these derivatives are pale yellow to yellow solids, soluble in common organic solvents such as chloroform, benzene and acetone, and susceptible to hydrolysis.

In the IR spectra of benzoylacetone derivatives the absence of broad band due to ν(O–H) (3000–2700 cm^{-1}) revealed that the benzoylacetone had been deprotonated in the μ-oxo complexes [22]. Strong bands at 1600 cm^{-1} and 1505 cm^{-1} due to ν_{sym}(C$\cdots$O) and ν_{sym}(C$\cdots$C) in the spectrum of benzoylacetone are respectively shifted by ~ 15 cm^{-1} to a lower wave number and to a higher wave number by ~ 10 cm^{-1} in the spectra of benzoylacetone derivatives of μ-oxo compounds. These shifts are in good agreement with the data obtained when benzoylacetone is symmetrically bonded to the metal through both of the carbonyl oxygens [22]. The IR spectra of 1:1 derivatives exhibit the usual absorptions due to bridging isopropoxy group, whereas, such bands are absent in the spectra of the 1:2 derivatives, indicating that the terminal isopropoxy group of dimeric [$R_3SnOAl(O^iPr)_2$] has been replaced by chelating benzoylacetone, giving pentacoordinate aluminium (Fig. 2a).

^{1}H NMR spectra of benzoylacetone derivatives of [$R_3SnOAl(O^iPr)_2$] show peaks at δ 7.1–7.6 ppm (multiplet), at δ ~ 6.3 ppm (singlet) and at δ ~ 2.1 ppm (singlet) due respectively to phenyl, methine, and methyl group protons of the benzoylacetone moiety. The methyl and methine protons of the isopropoxy groups of the 1:1 derivative resonate at their usual positions.

The ^{27}Al NMR spectrum of [$Ph_3SnOAl(bzac)_2$] shows a sharp peak at δ 0.12 ppm, indicating an octahedral environment about the aluminium atom [20] (Fig. 2b). The ^{119}Sn NMR spectrum of [$Me_3SnOAl(bzac)_2$] shows a peak at δ −156.2 ppm pointing to a tetrahedrally surrounded Sn atom in the benzoylacetone derivatives of [$R_3SnOAl(O^iPr)_2$] [21] and so indicating that the benzoylacetone does not coordinate to the Sn atom.



(2a)

(2b)

Fig. 2. (a) [$R_3SnOAl(O^iPr)(bzac)$]; (b) [$R_3SnOAl(bzac)_2$].

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