Inorg. Chem. **1994,** *33,* 411–414

Articles

Syntheses and Molecular Structures of the Dialkylaluminum and -gallium Stannoxides $[R_2M(\mu\text{-}OSnPh_3)]_2$

Shahid U. Ghazi, Rajesh Kumar, Mary Jane Heeg, and John P. Oliver*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received August 4, 1993[⊗]

The reaction of trialkylaluminum derivatives, R_3Al (R = Me, Et, *i*-Bu), and trimethylgallium with the distannoxane $(Ph_3Sn)_2O$ yields $R_2MOSnPh_3$ (M = Al, R = Me (**1a**); Et (**1b**), *i*-Bu (**1c**); M = Ga, R = Me (**2**)) and the corresponding organotin compound, $RSnPh_3$. Attempts to disrupt the Al–O bridge bonds of $[R_2Al(\mu\text{-}OSnPh_3)]_n$ (R = Me (**1a**), Et (**1b**)) and form stable adducts with diethyl ether failed, but 4-picoline gives a 1:1 complex. The resulting derivatives have been characterized by ^1H and ^{13}C NMR spectroscopy. The structure of **1a** was determined by single-crystal X-ray diffraction techniques and was found to be in the triclinic space group $P\bar{1}$ with cell constants $a = 9.076(1)$ Å, $b = 9.733(2)$ Å, $c = 13.084(3)$ Å, $\alpha = 71.03(2)°$, $\beta = 74.22(1)°$, $\gamma = 65.05(1)°$, and $Z = 1$. The structure was refined to a final $R = 2.6\%$ ($R_w = 3.9\%$) based on 3185 ($I > 2.5\sigma(I)$) observed reflections. The molecule exists as a dimer, $(Me_2AlOSnPh_3)_2$, with Al–O bond distances of 1.84 Å and Sn–O bond distances of 1.98 Å. Both aluminum and tin centers in the dimer are in a pseudotetrahedral environment.

Introduction

The structures of organoaluminum alkoxides/aryloxides, $R_{3-n}Al(OR')_n$ ($n = 1$–3), have been studied extensively.[1,2] Their chemistry, especially their wide use in regio- and stereoselective organic syntheses, is well established.[3–5] The analogous organoaluminum silanoxides, $R_{3-n}Al(OSiR'_3)_n$, are also known, and their inorganic materials such as aluminosilicates and -zeolites find applications as ion exchangers, catalysts, catalyst supports, and molecular sieves.[6–13] However, the chemistry of the related organoaluminum stannoxides is essentially unknown. The use of trialkylaluminum compounds to alkylate the organotin oxides to give asymmetrical tetraorganotin derivatives was reported in a patent, but no attempt was made to isolate the mixed aluminum stannoxide derivative.[14] A study has been reported of the adduct $[(t\text{-}BuN)_3Sn_4\text{-}\mu_3\text{-}O]\cdot AlMe_3$ where the trialkylaluminum is bound to the μ_3-oxide.[15] In another study, Nomura[16] has explored the reaction of indium alkyl derivatives with Bu_2SnO and reported the formation of indiostannoxides. In this paper, we report the synthesis and characterization of heterometallic complexes, $R_2MOSnPh_3$, formed by the reaction of the distannoxane $(Ph_3Sn)_2O$ with trialkylaluminum derivatives and trimethylgallium. Such bimetallic systems may serve as molecular models to provide specific information on unique modes of bonding and substrate activation of their material counterparts since they are amenable to precise characterization using a variety of structural determination methods. In this study, we have included the crystal and molecular structure of the organoaluminum stannoxide $[Me_2Al(\mu\text{-}OSnPh_3)]_2$.

Experimental Section

General Experimental Procedures. All solvents were purified and dried by standard techniques.[17] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and calcium sulfate. Aluminum alkyls (Aldrich: Me_3Al, 2 M solution in toluene; Et_3Al, 1.9 M solution in toluene; $(i\text{-}Bu)_3Al$, 1 M solution in toluene), bis(triphenyltin) oxide (Aldrich), and 4-methylpyridine (4-picoline) (Aldrich) were used as received. All of the glassware used in the synthetic work was oven-dried. The compounds are both oxygen and water sensitive, so standard Schlenk line techniques were employed. ^1H and ^{13}C NMR spectra were recorded either on a General Electric QE-300 NMR or on a GN-300 NMR spectrometer. The chemical shifts were referenced to the residual proton line from benzene-d_6 ($\delta = 7.15$ ppm for ^1H; $\delta = 128.0$ ppm for ^{13}C). The reported J_{SnH} values are an average of ^{117}Sn and ^{119}Sn coupling constants. The resolution in most cases did not permit assignment of individual coupling constants.

Preparation of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (1a). Bis(triphenyltin) oxide (1.0 g, 1.40 mmol) was stirred in pentane (ca. 60 mL), and Me_3Al (0.70 mL, 1.40 mmol) was added over a period of 5 min. The reaction mixture was stirred for 24 h, during which time a white precipitate appeared. This precipitate was isolated and washed with 10–15 mL of very cold pentane and dried under vacuum. The solid was identified from its ^1H and ^{13}C NMR spectra as $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (**1a**): yield 60%; mp 300 °C dec. Anal. Calc for $C_{20}H_{21}AlOSn$: C, 56.78; H, 5.00. Found: C, 55.26; H, 5.09. ^1H NMR (C_6D_6; δ, ppm): 7.04–7.71 (m, 15H, $^3J_{SnH} = 59$ Hz, Ph), −0.58 (s, 6H, Al*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 136.6, 130.4, 128.9 (Ph); −6.3 (Al*Me*). Mass spectral data (EI mode): peaks at *m/e* 351, 289, 197, 120, 78 corresponding to fragments $Ph_3Sn^{\cdot+}$, $Ph_2SnO^{\cdot+}$, $PhSn^{\cdot+}$, $Sn^{\cdot+}$, $C_6H_5^{\cdot+}$.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1993.

(1) Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH Publishers: New York, 1993; pp 167–195.

(2) Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *8*, 827.

(3) Maruoka, K.; Concepcion, A. B.; Murase, N.; Oishi, M.; Hirayama, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 3943.

(4) Maruoka, K.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1992**, *114*, 1089.

(5) Corey, E. J.; Sarshar, S.; Bordner, J. *J. Am. Chem. Soc.* **1992**, *114*, 7938.

(6) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288.

(7) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638.

(8) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *Polyhedron* **1993**, *12*, 591.

(9) Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137.

(10) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Can. J. Chem.* **1992**, *70*, 771.

(11) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Chem. Mater.* **1992**, *4*, 167.

(12) Terry, K. W.; Ganzel, P. K.; Tilley, T. D. *Chem. Mater.* **1992**, *4*, 1290.

(13) Mulhaupt, R.; Calabrese, J.; Ittel, S. D. *Organometallics* **1991**, *10*, 3403.

(14) Mangham, J. R. *Chem. Abstr.* **1963**, *59*, 6440, U.S. Patent No. 3,095,433.

(15) Veith, M.; Recktenwald, O. *Z. Naturforsch.* **1981**, *36B*, 144.

(16) Nomura, R.; Fujii, S.; Matsuda, H. *Inorg. Chem.* **1990**, *29*, 4586.

(17) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986.

0020-1669/94/1333-0411$04.50/0

1a was also synthesized in diethyl ether solvent. In this case, a clear solution resulted during 24 h of stirring the reaction mixture. The product was crystallized by freezing the solution in liquid nitrogen and then warming to –20 °C. The crystals were isolated at dry ice/acetone bath temperature, washed with diethyl ether, and dried under vacuum. The ^{1}H NMR spectrum of this product was identical to that of **1a** and showed that no ether was retained.

Preparation of $Et_2AlOSnPh_3$ (1b). Bis(triphenyltin) oxide (3.0 g, 4.19 mmol) dissolved in pentane (ca. 60 mL) was reacted with Et_3Al (2.21 mL, 4.19 mmol) according to the procedure given for **1a**. This solid was identified from its ^{1}H and ^{13}C NMR spectra as $Et_2AlOSnPh_3$ (**1b**): yield 60%; mp >300 °C. ^{1}H NMR (C_6D_6; δ, ppm): 7.09–7.78 (m, 15H, $^3J_{SnH}$ = 56 Hz, Ph), 1.02 (t, 6H, J_{HH} = 8 Hz, $AlCH_2Me$), 0.04 (q, 4H, J_{HH} = 8 Hz, $AlCH_2Me$). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 137.2, 130.7, 129.3 (Ph); 9.4 ($AlCH_2Me$); 3.2 ($AlCH_2Me$).

Preparation of $(i\text{-}Bu)_2AlOSnPh_3$ (1c). Bis(triphenyltin) oxide (2.0 g, 2.80 mmol) dissolved in pentane (ca. 60 mL) was reacted with $(i\text{-}Bu)_3Al$ (2.80 mL, 2.80 mmol) according to the procedure given for **1a**. The solid was identified as $(i\text{-}Bu)_2AlOSnPh_3$ (**1c**) from its ^{1}H and ^{13}C NMR spectra: yield >90%; mp 165 °C dec. The filtrate from the above reaction deposited white solid upon cooling to –20 °C overnight. The secondary product was identified as $(i\text{-}Bu)SnPh_3$, (**1c′**): mp 70 °C. NMR Data for **1c** are as follows. ^{1}H NMR (C_6D_6; δ, ppm): 7.14–7.80 (m, 15H, $^3J_{SnH}$ = 57 Hz, Ph), 0.08 (d, J_{HH} = 7 Hz, 4H, $AlCH_2CHMe_2$), 1.70 (m, J_{HH} = 7 Hz, 2H, $AlCH_2CHMe_2$), 0.85 (d, J_{HH} = 6 Hz, 12H, $AlCH_2CHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 137.5, 130.7, 129.2 (Ph); 24.8 ($AlCH_2CHMe_2$); 26.2 ($AlCH_2CHMe_2$); 28.8 ($AlCH_2CHMe_2$). NMR data for **1c′** are as follows. ^{1}H NMR (C_6D_6; δ, ppm): 7.14–7.80 (m, $^3J_{SnH}$ = 46 Hz, Ph), 1.44 (d, J_{HH} = 8 Hz, $^3J_{SnH}$ = 56 Hz, 2H, $AlCH_2CHMe_2$), 1.99 (m, J_{HH} = 7 Hz, 1H, $AlCH_2CHMe_2$), 0.93 (d, J_{HH} = 7 Hz, 6H, $AlCH_2CHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 139.9, 137.4, 129.0, 128.8 (Ph); 22.9 ($AlCH_2CHMe_2$); 27.1 ($AlCH_2CHMe_2$); 26.8 ($AlCH_2CHMe_2$). Mass spectral data (EI mode): peaks at *m/e* 351, 275, 197, 119, 78, 57 corresponding to fragments $Ph_3Sn^{\cdot+}$, $Ph_2Sn^{\cdot+}$, $PhSn^{\cdot+}$, $Sn^{\cdot+}$, $Ph^{\cdot+}$, $C_4H_9^{\cdot+}$.

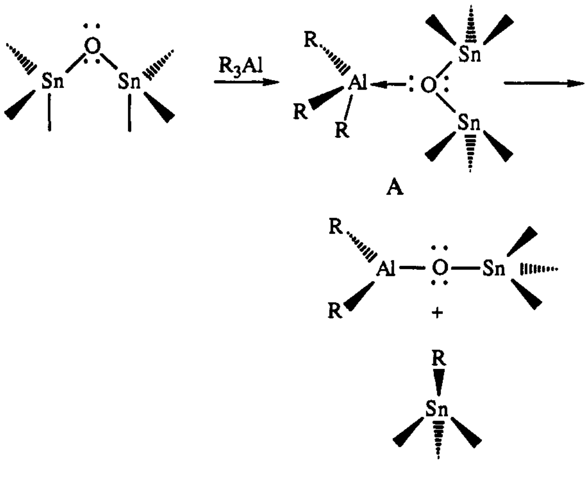
Preparation of $Me_2GaOSnPh_3$ (2). Bis(triphenyltin) oxide (1.0 g, 1.40 mmol) dissolved in pentane (ca. 60 mL) was reacted with Me_3Ga (0.14 mL, 1.40 mmol) according to the procedure given for **1a**. This solid was identified from its ^{1}H and ^{13}C NMR spectra as $Me_2GaOSnPh_3$ (**2**): yield 50%. ^{1}H NMR (C_6D_6; δ, ppm): 7.00–7.59 (m, 15H, $^3J_{SnH}$ = 56 Hz, Ph), –0.23 (s, 6H, $GaMe$). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 138.5, 136.6, 129.8, 128.7 (Ph); –1.66 ($GaMe$).

Attempted Synthesis of 1:1 Addition Compounds. The synthesis of $R_2(Ph_3SnO)Al$ addition complexes was attempted by preparation of **1a** and **1b** with addition of the base before final workup. When diethyl ether was added, it was readily removed under vacuum. When 4-picoline was added to **1b**, a white solid was obtained from its –20 °C recrystallization from pentane: mp 200 °C dec. The product was identified as $Et_2(Ph_3SnO)Al{\cdot}4\text{-picoline}$ by ^{1}H NMR spectral data (C_6D_6; δ, ppm): –0.06 (q, 4H, $AlCH_2CH_3$), 0.91 (t, 6H, $AlCH_2CH_3$), 8.35 (d, 2H, CH (4-picoline)), 6.44 (d, 2H, CH (4-picoline)), 7.47–7.68 (m, 15H, $^3J_{SnH}$ = 57 Hz, Ph), 1.65 (s, 3H, 4-CH_3 (4-picoline)). The ^{1}H NMR spectrum of authentic 4-picoline showed resonances at 8.36 (d, 2H), 6.98 (d, 2H), and 2.23 ppm (s, 3H, CH_3).

X-ray Structure Determination of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (1a). Crystals of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (**1a**) were grown from diethyl ether at –20 °C. A crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube in a drybox; the tube was plugged with grease, removed from the drybox, flame-sealed, mounted on a goniometer head, and placed on a Nicolet $P2_1$ diffractometer for data collection. Crystal structure parameters are presented in Table 1. The crystal of **1a** was found to be triclinic. Lattice constants were verified by axial photographs. **1a** was assigned to the space group $P\bar{1}$ (No. 2), which was later confirmed by successful refinement of the structure. Data reduction and calculations were carried out using the SHELXTL program.[18] Direct-methods routines produced acceptable solutions for the structures, yielding positions for some of the non-hydrogen atoms, while other atoms were located during subsequent refinement. Full-matrix least-squares refinement was carried out using SHELX-76.[19] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, oxygen, tin, and aluminum atoms were used. No correction for secondary extinction was made.[20] Phenyl carbon atoms were refined as rigid bodies with C–C = 1.395 Å and C–C–C = 120°. In **1a**, hydrogen atomic positions were observed or calculated, riding on the carbon atoms to which they were bound. Additional cycles of refinement of the data led to a convergence with R = 2.6% (R_w = 3.9%) for **1a**. The atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms of **1a** are presented in Table 2.

Results and Discussion

Reaction of R_3M with $(Ph_3Sn)_2O$ To Give $R_2MOSnPh_3$ (M = Al, R = Me (1a), Et (1b), *i*-Bu (1c); M = Ga, R = Me (2)). In the solid state, the distannoxane $(Ph_3Sn)_2O$ has a bent structure with a Sn–O–Sn angle of 137.3°, and therefore in this linkage $p\pi(O)$–$d\pi(Sn)$ bonding should be minimal.[21] As a consequence, the bridging oxygen atoms of the bent stannoxanes may be more basic and form adducts with Lewis acids. In order to explore this possibility of basicity/reactivity, we attempted the reaction of bis(triphenyltin) oxide, $(Ph_3Sn)_2O$, with trialkylaluminum derivatives, R_3Al (R = Me, Et, *i*-Bu), and trimethylgallium as shown in eq 1. The reaction presumably proceeds through a two-step sequence. The first stage is the formation of the 1:1 adduct, **A**, which decomposes rapidly by the migration of the alkyl group from the aluminum center to the tin atom to yield the final product. We have not been able to isolate the addition compound, but Veith[15] has obtained a stable 1:1 adduct, $(\mu_3\text{-}t\text{-}BuN)_3Sn_4(\mu_3\text{-}O){\cdot}AlMe_3$. Furthermore, in related studies on the interaction of trialkylaluminum derivatives with siloxanes, adducts of the type presented in eq 1 have been observed in solution by NMR and proposed as reaction intermediates.[13] The reaction of Bu_3In with diorganotin oxides, a mechanism involving ligand transfer, is similar to that proposed here.[16]



(1)

The $R_2AlOSnPh_3$ complexes are isolated as colorless solids which decompose rapidly on contact with air and moisture. They are moderately soluble in pentane, benzene, and toluene.

Cleavage of the dimer by addition of a Lewis base was also studied via the reaction shown in eq 2. Diethyl ether was unable to shift the equilibrium to the right whereas 4-picoline yielded an isolable addition product. These findings are consistent with the order of the donor strength (N > P ≥ O > S > Se > Te) of the ligand Me_nE for trimethylaluminum.[2]

Crystal Structure of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (1a). The molecular structure of **1a** is shown in Figure 1. Selected bond distances and bond angles are presented in Table 3. The molecule has a center of inversion requiring the Al_2O_2 unit to be rigorously planar. The gross features of the molecular structure are similar to related organoaluminum alkyl- and aryloxides. Each aluminum atom

---

(18) Sheldrick, G. M. SHELXTL. University of Gottingen, Germany, 1978.

(19) Sheldrick, G. M. SHELX-76. University Chemical Laboratory, Cambridge, England, 1976.

(20) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. (present distributor D. Reidel, Dordrecht, The Netherlands).

(21) Lockhart, T. P.; Puff, H.; Schuh, W.; Reuter, H.; Mitchell, T. N. *J. Organomet. Chem.* **1989**, *366*, 61.

Table 1. Experimental Parameters for the X-ray Diffraction Study of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (**1a**)

formula	$C_{40}H_{42}Al_2O_2Sn_2$
M_r	846.118
crystal prepn	recrystallized from diethyl ether at −20 °C
crystal color	colorless
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
cell constants obtained from 25 high-angle reflections with $2\theta > 20°$	
a	9.076(1) Å
b	9.733(2) Å
c	13.084(3) Å
α	71.03(2)°
β	74.22(1)°
γ	65.05(1)°
V	978.6 (.4) Å^3
d(calc)	1.436 g cm^{-3}
Z	1 (dimer)
radiation type	Mo K$\bar{\alpha}$, λ = 0.710 73 Å, graphite monochromator
temp	22 °C
type of data collection	$\theta/2\theta$ scan
2θ scan range	6–50°
hkl ranges	$+h,\pm k,\pm l$
scan rate	variable, 3–25°/min
scan width	1 0° above K$\bar{\alpha}$, 1.0° below K$\bar{\alpha}$
background/scan ratio	0.5
std reflns	3 measured per every 97 reflections
dev from the std	Max dev less than 2%
no. of data collected	3785
no. of unique data	3436
no. of obs reflns	3185 (with $I \geq 2.5\sigma(I)$)
linear abs coeff (μ)	13.54 cm^{-1}
F(000)	424 e
abs cor	ψ scan
no. of params refined	172
obs/param ratio	18.5/1
R $(=\sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert)$	2.6%
R_w $(=[\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$; $w = (\sigma_{F^2} + 0.0001F^2)^{-1})$	3.9%
maxshift/esd	0.001σ
max/min residual electron density	+0.35/−0.69 e/Å^3

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (**1a**)

atom	x	y	z	U_{eq},[a] Å^2
Sn1	0.32366(3)	0.39063(3)	0.24284(2)	0.0393(1)
Al1	0.6482(1)	0.4290(1)	0.03466(9)	0.0467(5)
O1	0.4301(3)	0.4754(3)	0.0961(2)	0.044(1)
C1	0.7500(6)	0.5526(7)	0.0623(4)	0.075(3)
C2	0.7675(6)	0.2033(5)	0.0547(4)	0.079(2)
C3	0.0990(2)	0.5736(3)	0.2770(2)	0.044(1)
C4	−0.0133(2)	0.6457(3)	0.2035(2)	0.060(2)
C5	−0.1628(2)	0.7638)3)	0.2274(2)	0.079(2)
C6	−0.1999(2)	0.8098(3)	0.3247(2)	0.084(3)
C7	−0.0875(2)	0.7378(3)	0.3981(2)	0.085(3)
C8	0.0619(2)	0.6197(3)	0.3743(2)	0.062(2)
C9	0.4942(3)	0.3337(3)	0.3467(2)	0.043(1)
C10	0.5611(3)	0.4416(3)	0.3417(2)	0.060(2)
C11	0.6722(3)	0.4042(3)	0.4111(2)	0.073(3)
C12	0.7164(3)	0.2589(3)	0.4855(2)	0.069(2)
C13	0.6495(3)	0.1511(3)	0.4905(2)	0.076(2)
C14	0.5384(3)	0.1885(3)	0.4211(2)	0.059(2)
C15	0.2751(3)	0.2015(3)	0.2324(2)	0.047(2)
C16	0.1165(3)	0.2004(3)	0.2728(2)	0.063(2)
C17	0.0759(3)	0.0824(3)	0.2632(2)	0.081(3)
C18	0.1940(3)	−0.0345(3)	0.2132(2)	0.088(3)
C19	0.3526(3)	−0.0335(3)	0.1728(2)	0.096(3)
C20	0.3931(3)	0.0845(3)	0.1824(2)	0.073(2)

[a] $U_{eq} = {}^1/_3\sum i\sum_j U_{ij} a_i^* \cdot a_j^* \bar{a}_i \cdot \bar{a}_j$.

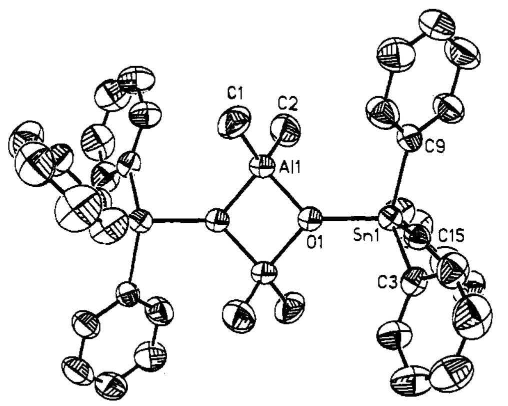
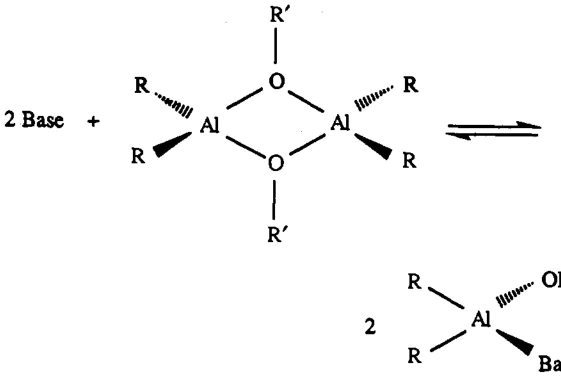


Figure 1. ORTEP diagram (50% thermal ellipsoids) of $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (**1a**), showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Me_2Al(\mu\text{-}OSnPh_3)]_2$ (**1a**)

	Distances		
Sn1–O1	1.984(4)	Al1···Al1′	2.711(2)
Sn1–C3	2.118(2)	O1···O1′	2.480(6)
Sn1–C9	2.117(3)	Al1–O1	1.840(3)
Sn1–C15	2.117(4)	Al1–C1	1.958(8)
Sn1···Al1	3.473(1)	Al1–C2	1.960(7)
	Angles		
Sn1–O1–Al1	131.3(2)	Al1–O1–Al1′	95.1(2)
O1–Sn1–C3	105.9(1)	O1–Al1–C2	111.5(2)
O1–Sn1–C9	103.8(1)	Cl–Al1–C2	118.6(3)
O1–Sn1–C15	107.7(2)	C3–Sn1–C9	113.0(1)
O1–Al1–C1	113.7(2)	C3–Sn1–C15	109.7(1)
O1–Al1–O1′	84.9(1)	C9–Sn1–C15	115.9(1)



(2)

has a quasitetrahedral geometry. The oxygen atom is trigonal, and the Al–O bond distance is similar to those found in other dimeric four-coordinate aluminum alkyl- and aryloxides and shorter than the Al–O distances observed in ether adducts.[2] Furthermore, the average Al–C bond distance and the exocyclic C–Al–C angle are also in the normal ranges for such complexes. However, the most significant difference between **1a** and other dimeric organoaluminum alkyl- and aryloxides lies in the structure of the Al_2O_2 ring. A number of structural parameters such as O···O and Al···Al distances and endocyclic O–Al–O and Al–O–Al angles can be used to describe the structure of the Al_2O_2 ring. These parameters for **1a** and several other dimeric organoaluminum alkyl- and aryloxides are presented in Table 4. These data reveal that the Al···Al separation of 2.711 Å in **1a** is substantially shorter than those in organoaluminum silanoxides and alkyl- and aryloxides, and it approaches the separation observed for an Al–Al single bond but does not imply a direct Al–Al bond. The short Al···Al distance in **1a** also has direct effect on O–Al–O and Al–O–Al angles in the Al_2O_2 ring since the Al–O bond distance remains nearly constant at 1.86 Å in all Al–O–Al bridged compounds. In **1a**, the Al–O–Al angle of 95.1° is 3–7° smaller while the O–Al–O angle of 84.9° is 3–7° larger than the corresponding angles found in other related compounds. The O···O distance of 2.480 Å in **1a** is significantly longer than those in $[Me_2Al(\mu\text{-}OC_6F_5)]_2$ and other alkoxides, and the view

Table 4. Comparison of the Average Selected Bond Distances (Å) and Bond Angles (deg) for $[R_2Al(\mu\text{-}OMR)]_2$

compd	Al···Al	Al–O	Al–O–Al	O–Al–O
$\{[(Me_3Si)_2CH]_2Al\text{–}Al[CH(SiMe_3)_2]_2\}^-[Li(tmeda)_2]^+$ [a]	2.530			
$[(Me_3Si)_2CH]_2Al\text{–}Al[CH(SiMe_3)_2]_2$ [b]	2.660			
$(2,4,6\text{-}Pr_3C_6H_2)_2Al\text{–}Al(2,4,6\text{–}Pr_3C_6H_2)_2$ [c]	2.660			
$[(2,4,6\text{-}Pr_3C_6H_2)_2Al\text{–}Al(2,4,6\text{-}Pr_3C_6H_2)]_2^-$ [c]	2.470			
$[Me_2Al(\mu\text{-}OSnPh_3)]_2$ [d]	2.711	1.840	95.1	84.9
$\{Me_2Al[\mu\text{-}OSi(C_6H_5)Me_2]\}_2$ [e]	2.760	1.854	96.3	83.7
$\{Me_2Al[\mu\text{-}OSi(O\text{-}t\text{-}Bu)_3]\}_2$ [f]	2.774	1.865	96.1	81.8
$[Me_2Al(\mu\text{-}OC_6F_5)]_2$ [g]	2.951	1.895	102.3	77.7
$[Me_2Al(\mu\text{-}O\text{-}menthyl\text{-}l)]_2$ [h]	2.807	1.841	99.4	80.6
$[Me_2Al(\mu\text{-}O\text{-}t\text{-}Bu)]_2$ [i]	2.820	1.864	98.1	81.9
$[Me_2Al(\mu\text{-}OC_6H_3\text{-}2\text{-}allyl\text{-}6\text{-}Me)]_2$ [j]	2.866	1.861	100.8	79.2
$[(i\text{-}Bu)_2Al(\mu\text{-}OC_6H_3\text{-}2,6\text{-}Me_2)]_2$ [k]	2.899	1.873	101.5	78.5
$[Me_2Al(\mu\text{-}OCH_2C_6H_2\text{-}2,4,6\text{-}(t\text{-}Bu)_3)]_2$ [l]	2.840	1.850	100.2	79.5

[a] Pluta, C.; Pörschke, K.-R., Krüger, C.; Hildenbrand, K. *Angew. Chem., Int. Ed. Engl.* **1993**, **32**, 388. [b] Uhl, W. *Z. Naturforsch.* **1988**, *43b*, 1113. [c] Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983. [d] Present work. [e] Reference 9. [f] Reference 12. [g] Hendershot, D. G.; Kumar, R.; Barber, M.; Oliver, J. P. *Organometallics* **1991**, *10*, 1917. [h] Sierra, M. L.; Kumar, R.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1992**, *11*, 206. [i] Haaland, S.; Stokkeland, O. *J. Organomet. Chem.* **1975**, *94*, 345 (determined in the gas phase by electron diffraction). [j] Kumar, R.; Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 484. [k] Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A.; Angermund, K.; Betz. P.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1991**, *411*, 37. [l] Cetinkaya, B.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *Polyhedron* **1990**, *9*, 239.

along O–O axis shows that the phenyl groups in $SnPh_3$ moieties are staggered, thus minimizing steric interactions. The view along the Al–Al axis shows that the two $SnPh_3$ groups are *trans* to each other, as required by the inversion symmetry of the space group. The two tin atoms are placed above and below the plane of the $Al(\mu\text{-}O)_2Al$ ring with an O–O–Sn angle of 5.9°. Finally, as expected for a tetrahedral aluminum geometry, the methyl groups attached to an aluminum center are placed above and below the $Al(\mu\text{-}O)_2Al$ plane.

The Sn–O bond distance of 1.984 Å is similar to distances found for two- or three-coordinate bridging oxygen atoms in linear and polycyclic organostannoxanes. The Sn–C bond distances range from 2.117 to 2.118 Å and are comparable to such distances found in triorganotin compounds.[21]

NMR Studies. The ^1H and ^{13}C NMR spectral data for the complexes $R_2AlOSnPh_3$ (R = Me (**1a**), Et (**1b**), *i*-Bu (**1c**)) and $Me_2GaOSnPh_3$ (**2**) are presented in the Experimental Section. In the ^1H NMR spectrum of $R_2MOSnPh_3$, the presence of a sharp upfield resonance for the α-protons of the alkyl group attached to the group 13 element, along with the resonances associated with the $\text{–}OSnPh_3$ group in the appropriate ratio, provides good evidence for the $\text{–}MR_2$ coordination at the stannoxy oxygen. Furthermore, the ortho protons of the phenyl groups of the $\text{–}OSnPh_3$ moiety show relatively sharp ^{117}Sn ($I = {}^1/_2$, 7.61%) and ^{119}Sn ($I = {}^1/_2$, 8.58%) satellites with characteristic $^3J_{^{117,119}SnH}$ values in the range 46–59 Hz for the groups coordinated to Sn(IV). Interestingly, no $^4J_{^{117,119}SnH}$ coupling of the tin atom to the α-protons of the R_2M (M = Al or Ga) moiety was observed. The ^{13}C spectra of the $R_2MOSnPh_3$ compounds also confirm the presence of various organic groups in these complexes.

Supplementary Material Available: Listings of complete bond distances and bond angles, anisotropic thermal parameters for the heavy atoms, hydrogen atom positional parameters, and torsion angles (4 pages). Ordering information is given on any current masthead page.