

## SHORT COMMUNICATIONS

## Preparation of several sulfoxide complexes with Group IV organometallic compounds

Dimethyl sulfoxide (DMSO) complexes with Lewis acids were first reported by Cotton and Francis<sup>1</sup> who noted the high thermal stability of  $\text{SnCl}_4 \cdot 2\text{DMSO}$  which "can be sublimed without decomposition at 180°". More recently tetramethylene sulfoxide complexes with trimethyl- and triethyl-tin and -lead chloride have been investigated by Matwiyoff and Drago<sup>2</sup> followed by a preparation of DMSO complexes of diphenyllead dichloride and dibromide reported by Hills and Henry<sup>3</sup>.

We wish to report the preparation of several sulfoxide complexes with group IV organometallic compounds.

All organotin and lead halides listed in Table I can be prepared without hydrolysis in DMSO solution, DMSO-water mixtures, or organic solvents. Organosilicon and germanium halides appear to undergo hydrolysis or solvolysis in DMSO with

TABLE I  
ANALYSES

No.	Compound <sup>a</sup>	Analyses (calcd./found)				
		C	H	Cl	S	M <sup>b</sup>
1	$\text{SnCl}_4 \cdot 2\text{DMSO}^c$	11.53/11.05 12.4	2.90/2.76	34.03/33.72	15.39/15.82	28.48/28.83
2	$\text{PhSnCl}_3 \cdot 2\text{DMSO}$	26.20/26.69	3.74/3.75	23.20/23.16	13.99/14.12	25.89/26.02
3	$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{DMSO}$	38.43/38.52 38.6	4.43/4.54 4.5	14.18/13.93	12.82/13.05 13.4	23.74/23.52
4	$\text{Ph}_3\text{SnCl} \cdot 1\text{DMSO}$	51.81/52.12 51.4	4.57/4.59 4.6	7.65/7.65	6.92/6.94	25.60/25.36
5	$\text{MeSnCl}_3 \cdot 2\text{DMSO}$	15.15/14.78	3.81/3.70	26.84/25.62	16.18/15.85	29.95/28.53
6	$\text{Me}_2\text{SnCl}_2 \cdot 2\text{DMSO}$	19.17/19.29 19.5	4.83/4.78 4.9	18.86/18.81	17.06/16.82 17.2	31.57/31.43
7	$\text{Me}_3\text{SnCl} \cdot 1\text{DMSO}$	21.65/21.9 21.59	5.45/5.4 5.5	12.78/12.36 12.52	11.56/14.33 11.87	42.79/42.7 42.41
8	$\text{SnCl}_2 \cdot 1.5\text{DMSO}$	11.74/12.5	2.96/3.1	23.11	15.68/16.00	38.69
9	$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{TMSO}$	43.50/43.38 42.01	4.75/4.82 4.78	12.84/12.79 12.19	11.61/11.79 12.67	21.50/20.94 19.57
10	$\text{GeCl}_4 \cdot 2\text{DMSO}$	12.96/13.1 13.32	3.26/3.6 3.21	38.26/36.46	17.30/16.6 17.17	19.58/18.52
11	$\text{Ph}_2\text{PbCl}_2 \cdot 2\text{DMSO}^c$	32.65/32.87 32.6	3.77/3.03 3.5			

<sup>a</sup> DMSO =  $(\text{CH}_3)_2\text{SO}$ ; TMSO =  $(\text{CH}_3)_4\text{SO}$ . <sup>b</sup> M = metal (Sn, Ge, or Pb). <sup>c</sup> These data were measured in this laboratory for comparison.

formation of less well-defined oxide or hydroxide complexes. For organotin and lead halides octahedrally hexacoordinated structures seem to be the rule unless decreasing Lewis acid character or steric hindrance prohibits the formation of diadducts, as in the case of the triphenyltin chloride and trimethyltin chloride mono DMSO complexes.

A 1:1 complex was observed for phenyltin trichloride, which is irregular and can only be obtained under controlled conditions and with an excess of phenyltin trichloride being present. Melting points and the fact that most complexes can be recrystallized from organic solvents show the remarkable stability of these complexes. However, complicated systems are formed in solution and at the melting point of most of these compounds which are presently being investigated using differential thermal analysis, mass spectrometric thermal analysis and mass spectrometry as well as infrared spectroscopy in solution. The results will be reported at a later date.

A lowering of the S-O stretching frequency was observed for the infrared spectra of all halide compounds which indicates that oxygen and not sulfur is the donor atom<sup>4</sup> (See Table 2.)

TABLE 2  
INFRARED SPECTRA AND MELTING POINTS

Compound	$\nu(\text{S-O})$ ( $\text{cm}^{-1}$ )	$\Delta\nu(\text{S-O})$ ( $\text{cm}^{-1}$ )	M.p. ( $^{\circ}\text{C}$ )
$\text{SnCl}_4 \cdot 2\text{DMSO}$	(919 sh) 907 s	(-134) -146	287
$\text{PhSnCl}_3 \cdot 2\text{DMSO}$	911 s	-142	152
$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{DMSO}$	948 s	-105	135
$\text{Ph}_3\text{SnCl} \cdot 1\text{DMSO}$	954 m	-99	112
$\text{MeSnCl}_3 \cdot 2\text{DMSO}$	928 s	-127	175
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{DMSO}$	944 s	-109	113
$\text{Me}_3\text{SnCl} \cdot 1\text{DMSO}$	958 m	-95	49
$\text{Ph}_2\text{PbCl}_2 \cdot 2\text{DMSO}$	945 s	-108	171
$\text{GeCl}_4 \cdot 2\text{DMSO}$	894 sb	-159	135
$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{TMSO}$	950 s	-103	136

s = strong; m = medium; sh = shoulder.

Possible correlations between spectroscopic or thermal data and electro-negativity or Lewis acidity have been discussed<sup>5-8</sup>. In this connection it is interesting to note the relative positions of the observed S-O stretching frequencies and melting point elevations. Detailed investigations of these effects are in progress.

Solution spectra obtained for a variety of complexes in DMSO and chloroform indicated complete dissociation into DMSO and the organometallic compound.

### Experimental

In general, the preparation of all compounds was carried out by dissolving the Lewis acid in neat DMSO, if necessary by heating to approximately 100°. In most cases the complex started to crystallize upon cooling. However, to increase the yield, water or alcohol can be used as a precipitation agent. Some complexes can be recrystallized from benzene or other organic solvents where solubility factors permit.

All preparations were air-dried by suction. Individual procedures are summarized in Table 3.

TABLE 3  
 PREPARATIONS

Reagents	Solvents	Precipitating agents	Yield	Recrystallized from	Compounds formed
$\text{SnCl}_4 + \text{DMSO}$	DMSO	$\text{EtOH}^a$	90%	Benzene	$\text{SnCl}_4 \cdot 2\text{DMSO}$
$\text{Ph}_3\text{SnCl}_3 + \text{DMSO}$	DMSO	$\text{H}_2\text{O}^a$	95	Benzene	$\text{Ph}_3\text{SnCl}_3 \cdot 2\text{DMSO}$
	$\text{DMSO}/\text{C}_6\text{H}_6$				
$\text{Ph}_2\text{SnCl}_2 + \text{DMSO}$	DMSO	...	80	Benzene	$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{DMSO}$
		$\text{EtOH}$	98	Benzene	$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{DMSO}$
$\text{Ph}_3\text{SnCl} + \text{DMSO}$	DMSO	$\text{H}_2\text{O}^a$	91	Benzene	$\text{Ph}_3\text{SnCl} \cdot 3\text{DMSO}$
$\text{Ph}_4\text{Sn} + \text{DMSO}$	DMSO	...	...	...	Starting material
$\text{Me}_3\text{SnCl}_2 + \text{DMSO} + \text{SnCl}_4$	DMSO	$\text{C}_6\text{H}_6, \text{EtOH}$	> 80	$\text{DMSO} + \text{EtOH}, \text{C}_6\text{H}_6$	$\text{MeSnCl}_3 \cdot 2\text{DMSO}$
$\text{Me}_3\text{SnCl}_2 + \text{DMSO}$	DMSO	Ether <sup>d</sup>	> 64		$\text{Me}_3\text{SnCl}_2 \cdot 2\text{DMSO}$
$\text{Me}_3\text{SnCl} + \text{DMSO}$	DMSO	...	94		$\text{Me}_3\text{SnCl} \cdot 1\text{DMSO}$
$\text{SnCl}_4 + \text{DMSO}$	DMSO	Ether	85		$\text{SnCl}_4 \cdot 1.5\text{DMSO}$
$\text{Ph}_2\text{SnCl}_2 + \text{TMSO}$	TMSO	...	95		$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{TMSO}$
$\text{GeCl}_4 + \text{DMSO}$	DMSO	...	89		$\text{GeCl}_4 \cdot 2\text{DMSO}$
$\text{Ph}_3\text{PbCl}_2 + \text{DMSO}$	DMSO	$\text{H}_2\text{O}^a$	87		$\text{Ph}_3\text{PbCl}_2 \cdot 2\text{DMSO}$

<sup>a</sup> Optional.

Melting points were obtained both from a Fisher-Johns instrument and on a DuPont 900 Differential Thermal Analyzer.

Infrared spectra were recorded as Nujol mulls on a Baird infrared recording spectrophotometer Model 4-55 and on a Perkin-Elmer 337 grating infrared spectrophotometer, calibrated with polystyrene film.

Elemental analyses were carried out by Dr. CAROL K. FITZ, Needham Heights, Massachusetts and Galbraith Laboratories, Inc., Knoxville, Tennessee.

*Eastern Research Laboratory, The Dow Chemical Company,  
Wayland, Massachusetts (U.S.A.)*

H. G. LANGER  
A. H. BLUT

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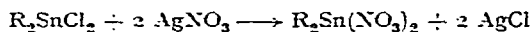
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### Preparation of dialkyltin dinitrates

Trialkyltin nitrates<sup>1</sup> have been prepared by the interaction of the appropriate trialkyltin halide with alcoholic silver nitrate solution. The preparation of dimethyltin dinitrate from tetramethyltin and liquid dinitrogen tetroxide<sup>2</sup>, and also from dimethyltin oxide and nitric acid<sup>3</sup> has recently been reported. The preparation of diethyltin dinitrate<sup>4</sup> is claimed in the early literature.

We now report the preparations of dimethyltin dinitrate and the previously unreported di-*n*-propyltin and di-*n*-butyltin dinitrates by the silver nitrate method.



The 1,10-phenanthroline complexes of the di-*n*-propyltin and di-*n*-butyltin dinitrates have been prepared.

The dialkyltin dinitrates are very deliquescent compounds which are soluble in polar organic solvents. The nitrates undergo decomposition with the liberation of oxides of nitrogen at room temperature even when stored in a sealed tube, but they can be stored at low temperature ( $-18^\circ$ ) without appreciable decomposition.

The 1,10-phenanthroline complexes, on the other hand, are perfectly stable at room temperature and are non-deliquescent.

The NMR and IR spectra of these compounds are being studied.

### Experimental

*Di-n-propyltin dinitrate\**. Silver nitrate (36.90 g, 2.0 mol.) in a Soxhlet thimble was extracted for several hours by dry methanol (200 ml) in which di-*n*-propyltin dichloride (30.0 g, 1.0 mol.) was dissolved. The precipitated silver chloride (31.4 g, ~ 100%) was removed by filtration. Evaporation of the filtrate at 20°/0.1 mm, fol-