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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISAANCE

The Reactions of Mercurie Chloride With Diphenyltin Dichloride Complexes

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

The Reactions of Mercurie Chloride With Diphenyltin Dichloride Complexes

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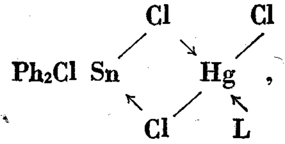
ABSTRACT

The reactions of solutions of mercuric chloride in organic solvents with diphenyltin dichloride complexes of the type, Ph_2SnCl_2, L; where L = bipyridyl, dimethyl-bipyridyl, o-phenanthroline, dimethyl-o-phenan-throline tripyridyl and pyridine-N-oxide were studied.

The products obtained were of the type, $HgCl_2$, nL where n = 1 or 3. Diphenyltin dichloride was recovered from the reaction mixture. This may be partly attributed to the stability of $HgCl_2$ complexes compared with that of the analogous complexes formed with diphenyltin dichloride, and partly to the labile nature of the ligand molecules.

When an ethanolic solution of mercuric chloride was added to the complex, Ph_2SnCl_2, Ph_3PO in the same solvent, phenyl mercuric chloride was readily obtained, PhHgCl as the first product. Because of the low accepting power of this compound, PhHgCl once it is formed no complex with Ph_3PO was obtained.

In no case a bridged complex of the type



$$\mathrm{Ph_2Cl\,Sn}\begin{array}{c}\mathrm{Cl}\\ \\ \mathrm{Cl}\end{array}\mathrm{Hg}\begin{array}{c}\mathrm{Cl}\\ \\ \mathrm{L}\end{array},$$

similar to that reported by Allison and Mann[1], was obtained.

In this connection we have found it interesting to prepare authentic samples of the $HgCl_2$, nL complex compounds, for the purpose of comparison, starting from mercuric chloride and the corresponding ligand in organic solvents. Attempted preparations of similar complexes starting from PhHgCl or Ph_2Hg, were unsuccessful.

Some physical properties of the formed complexes are reported.

INTRODUCTION

Allison and Mann[1] reported the reactions of some organic ligands with tin tetrachloride to give complex compounds of the type, $SnCl_4$, 2L. They stated that the alkylphosphine adducts, $SnCl_4$, $2R_3P$ give bridged derivatives of the composition, $(R_3P)_2SnCl_4$, $HgCl_2$, when treated with alcoholic solutions of mercuric chloride. The bridged compounds formed were found to be very stable.

In a previous paper[2] we reported the preparations and properties of some diphyltin dichloride complex compounds with oxygen and nitrogen donors of the type Ph_2SnCl_2,L. Attempted preparations of bridged compounds starting from the diphenyltin dichloride complexes and mercuric chloride were unsuccessful. On the other hand, mercuric chloride complexes were obtained.

A review by Deacon[3] gives a list of complex compounds of Hg(II) with halogen, carbon, nitrogen, phosphorus and sulphur as ligand atoms.

It is reported[4] that the affinity of Hg (II) for nitrogen ligands in aqueous solution exceeds that of transition metals. The characteristic coordination numbers and stereochemical arrangements for this ion are two-coordinate, linear and four-coordinate, tetrahedral[5]. Octahedral coordination is less common; other complexes in which Hg(II) has five-coordination number are also known[6] Tetrahedral complexes are given by such ligands, e.g. $HgCl_2$,$2Ph_3AsO$[5]. Carlin et al[7]. reported that although less sterically hindered donors such as pyridine-N-oxide react, more bulky oxides such as Ph_3PO do not. Lindqvist[8], on the bases of phase diagram studies, showed that there is a weak interaction between $HgCl_2$ and Ph_3PO to give $HgCl_2$, $2Ph_3PO$ at 128 °C. During the present work we obtained the adducts, $HgCl_2$, nPh_3PO, where n = 1 to 3.

EXPERIMENTAL

Chemicals used.– $HgCl_2$, Merck pro-analysis, was not further purified. PhHgCl was prepared following Nesmejanow[8], m.p. 249 °C, Ph_2Hg was prepared according to Pfeiffer and Truskier[9] and recrystallised from benzene, m.p. 125 °C. Ph_2SnCl_2 was prepared from tetraphenyltin (IV). Recrystallisation from $CHCl_3$/pet. ether, gave Ph_2SnCl_2, m.p. 42 °C.[10].

The organic ligands used were obtained as previously mentioned[2]. All solvents used were dried carefully by conventional methods.[11]

Infrared spectra were recorded on an infrared spectrophotometer Unicam SP 200G. Melting points were measured using a Unicam melting point apparatus.

Analyses for carbon, hydrogen and nitrogen were carried out in the microanalytical Unit El-Nasr Company Cairo. Thermogravimetric Analysis, TGA, was attempted using a Stanton thermogravimetric balance. The samples were transferred to weighed alumina crucibles fitted with stoppers. The crucibles were transferred to the silicapole in the centre of the furnace as quickly as possible. The thermo-balance is fitted with a linear temperature programme which could be arrested at any desired temperature. The decomposition of the samples, Ph_2SnCl_2 adducts, was studied over the range of the instrument, up to 800 °C.

The reactions of $HgCl_2$ with diphenyltin dichloride adducts:

Reaction of $HgCl_2$ with Ph_2SnCl_2,Ph_3PO complex; The addition of an ethanolic solution of $HgCl_2$ to a solution of Ph_2SnCl_2,Ph_3PO in the same solvent, in the mole ratio of 1:1, gave the first product proved by analysis and i.r. to be PhHgCl, m.p. 247–9 °C.

The second product obtained was Ph_3PO, m.p. 156–158 °C, and a third fumming residue presumably $PhSnCl_3$ was obtained. No bridged compound was formed.

In another experiment an ethanolic solution of $HgCl_2$ was added to a solution of Ph_2SnCl_2 in the same solvent, in the mole ratio of 1:1 and the first crop obtained recrystallised from 1,2-dichloroethane to give PhHgCl, and the second product was fumming liquid, presumably $PhSnCl_3$.

The complex compounds $HgCl_2,nPh_3PO$ where n = 1 to 3 were obtained by the addition of alcoholic solutions of $HgCl_2$ to the ligand in the same solvent using different stoichiometric ratio.

When solutions of $HgCl_2$ in the appropriate organic solvent (given in Table 1) were added to solutions of Ph_2SnCl_2, L (L = bipy., DM-bipy., o-phen., DM-o-phen., tripy., py. -N-oxide,) the complex compounds precipitated were proved to be $HgCl_2,nL$ (n = 1 tor 3) and Ph_2SnCl_2. was recovered. When dimethyl formamide (DMF) was used as a solvent the byproduct, $Ph_2SnCl_2,2DMF$ was obtained.

Authentic samples of the $HgCl_2$ complex compounds were prepared starting from $HgCl_2$ and the organic ligands.

Melting points, analytical data and solvents used during the reactions are given in Table 1.

Table (1)

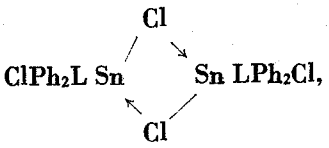
Compound	M.p. o:C	Required %			Formula	Found %			
		C	H	N/P		C	H	N/P	
1. $HgCl_2,Ph_3PO$	110	39.3	2.7	5.6	$C_{18}H_{15}Cl_2OPHg$	39.1	2.9	5.2	—
2. $HgCl_2,2Ph_3PO$	126	52.2	3.6	7.5	$C_{36}H_{30}Cl_2O_2P_2Hg$	51.8	3.2	7.1	—
3. a) $HgCl_2,3Ph_3PO$	172	58.6	4.1	8.4	$C_{54}H_{45}Cl_2O_2P_3Hg$	58.4	4.2	7.9	EtOH
b) PhHgCl*	247	23.0	1.6			23.1	1.6		xx
4. a) $HgCi_2$,o-phen.	250	31.9	1.8	6.2	$C_{12}H_8Cl_2N_2Hg$	32.1	2.0	5.7	DMF
b) Ph_2SnCl_2,2DMF**	145	44.1	4.9		$C_{18}H_{24}Cl_2N_2O_2Sn$	44.3	4.4		xx
5. $HgCl_2$,DM-phen.	251	35.0	2.5	5.8	$C_{14}H_{12}Cl_2N_2Hg$	34.7	2.8	5.3	Acetone
6. $HgCl_2$,bipy.	265	28.1	1.9	6.5	$C_{10}H_3Cl_2N_2Hg$	28.0	2.1	6.7	—
7. $HgCl_2$,3bipy.	> 250	48.7	3.3	11.3	$C_{30}H_{24}Cl_2N_6Hg$	48.8	3.6	10.8	$MeNO_2$
8. $HgCL_2$,DM-bipy.	> 250	31.6	2.6	6.1	$C_{12}H_{12}Cl_2N_2Hg$	31.8	2.7	5.8	Acetone
9. $HgCl_2$,2py.N Oxide	162	26.0	2.2	6.1	$C_{10}H_{10}Cl_2N_2O_2Hg$	26.3	2.0	5.7	$MeNO_2$
10. $HgCl_2$, tripy.	> 250	35.7	2.2	8.3	$C_{15}H_{11}Cl_2N_3Hg$	35.9	1.9	8.4	EtAc

* Solvent used in the displacement reaction.

** Compounds obtained as by-products.

No complex compounds were obtained from the reactions of PhHgCl or Ph_2Hg with the above mentioned ligands.

DISCUSSION

It has been shown by Mann and Purdie[12] that alkylphosphine complexes of the type $[(R_3P)_2PdCl_2]$ when heated in a vacuum distil unchanged, whereas the analogous arsine complexes $[(R_3As)_2PdCl_2]$ when similarly treated lose half their arsine content with the formation of the bridged derivatives $[(R_3As)_2(PdCl_2)_2]$. The bridged derivatives in both series were readily obtained, by boiling the unbridged compounds in alcoholic solution with ammonium palladochloride. We have investigated the application of both these methods to the preparation of a bridged tin(IV) compound of the type  $\mathrm{ClPh_2L\,Sn\overset{Cl}{\underset{Cl}{\rightleftarrows}}Sn\,LPh_2Cl}$, in which two 6-covalent octahedra are bridged through two chlorine atoms, but without success, The complexes Ph_2SnCl_2,L when heated at atmospheric pressure and high temperatures decompose, but no indication of the formation of a bridged derivative could be obtained.

Alternatively, the complexes Ph_2SnCl_2,L, where L = bipy., DM-bipy., o-phen., DM-o-phen., tripy, and py. N-oxide were treated with one equivalent of mercuric chloride in organic solutions, but the required bridged derivatives could not be prepared. Complexes of the type $HgCl_2$, nL were obtained and Ph_2SnCl_2 was recovered from the reaction solution.

Similar result was obtained when the complex, Bu_2SnCl_2, bipy[13,14]. was treated with mercuric chloride in acetone, where $HgCl_2$, bipy. was immediately precipitated, and Bu_2SnCl_2 was recovered. This is in contrast to the behaviour of tetrachlorobis (tripropylphosphine) $SnCl_4$, $2pr_3P$, which is reported to react with mercuric chloride to form a halogen bridged dinuclear complex.

Infrared studies showed that in the $HgCl_2$, $3Ph_3PO$ complex compound, the phosphoryl stretching frequency appeared at 1150 cm^{-1} and 1130 cm^{-1}. This when compaired with the P=0 absorption band in the pure ligand at 1190 cm^{-}(15), indicates that donation is through the oxygen atom[16].

The shift for the $HgCl_2$, $3Ph_3PO$ complex is almost identical to those found for the transition metal complexes[17], but is much smaller than the shifts reported for the complexes MCl_5,Ph_3PO, M = Pa, Nb and Ta[18].

The infrared spectra of the $HgCl_2$ complex compounds with nitrogen ligands show multiple splitting in the region 1400–1600 cm^{-1}. In[19] the case of the complex with py. N oxide the N-O stretching frequency at 1180 cm^{-1} in the pure ligand shifts to 1190 cm^{1-} on complex formation and this is attributed [20] to coordination through the nitrogen atom.

Thermal decomposition studies for the Ph_2SnCl_2 complex compounds reported here showed that they decompose on heating between 20 and 800 °C as given in Table 2. The molecular weights of the intermediate compounds are calculated from the graphs (Fig. 1–4). The final products, after heating up to 800 °C are either Sn or SnO_2or the compound volatalized.

Table 2. Thermal Decomposition of Some Diphenyltin dichloride Complexes.

Temp. (°C)	Mobs.	Formula		Mcal.
1. Ph_2SnCl_2,Ph_3PO				
25 – 170	622.73	Ph_2SnCl_2,Ph_3PO		622.73
200 – 240	608	Ph_2SnCl_2,Ph_3P	(A)	606.73
300 – 800	——	Volatile		
2. Ph_2SnCl_2,o-Phen., H_2O				
25 – 100	542.04	Ph_2SnCl_2, o-phen., H_2O		542.04
200 – 240	522	Ph_2SnCl_2, o-phen.	(D)	524.04
430 – 500	189.7	$SnCl_2$	(E)	189.8
560 – 800	151	SnO_2	(F)	150.8
3. Ph_2SnCl_2, DM-o-phen., H_2O				
25 – 100	550	Ph_2SnCl_2, (DM-o-phen.)	(G)	552.09
320 – 475	340	Ph_2SnCl_2,	(H)	343.8
580 – 800	120	Sn		118.7
4. Ph_2SnCl_2, bipy.				
25 – 180	500	Ph_3SnCl_3, bipy.		500
280 – 325	120	Sn	(I)	118.7
5. Ph_2SnCl_2, DM-bipy.				
25 – 200	528.04	Ph_2SnCl_2, DM-bipy.		528.049
220 – 245	496.3	Ph_2SnCl_2, bipy.	(J)	500
280 – 350	116	Sn		118.7
500	——	Volatile		——
6. Ph_2SnCl_2, py. N oxide				
25 – 160	438.91	Ph_2SnCl_2, py. N oxide		438.91
200 – 250	342.34	Ph_2SnCl_2	(L)	343.81
340 – 400	118	Sn	(M)	118.7

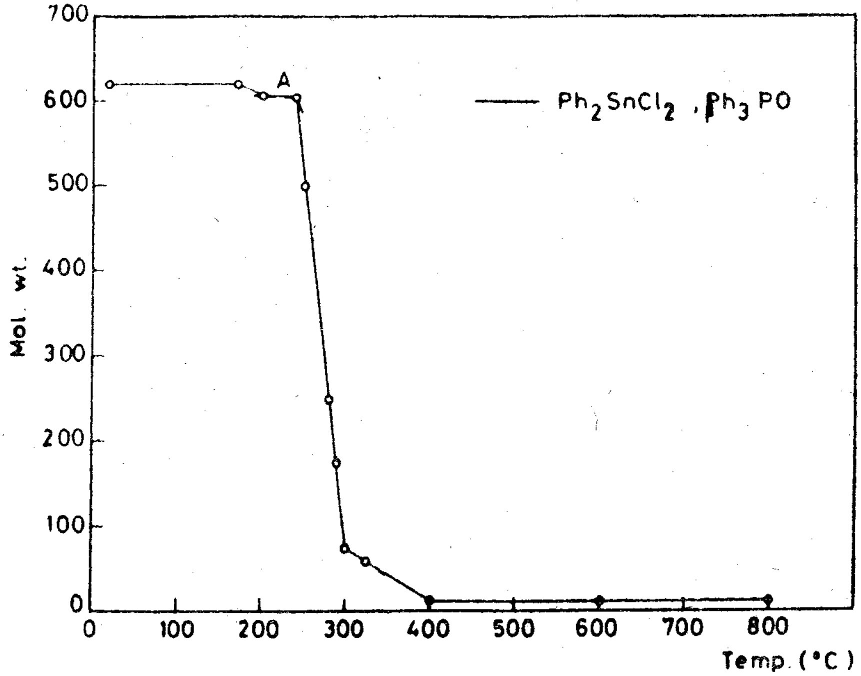

Mol. wt.
Temp. (°C)
A
Ph2SnCl2 , Ph3 PO
0
100
200
300
400
500
600
700
800

Fig. (1)

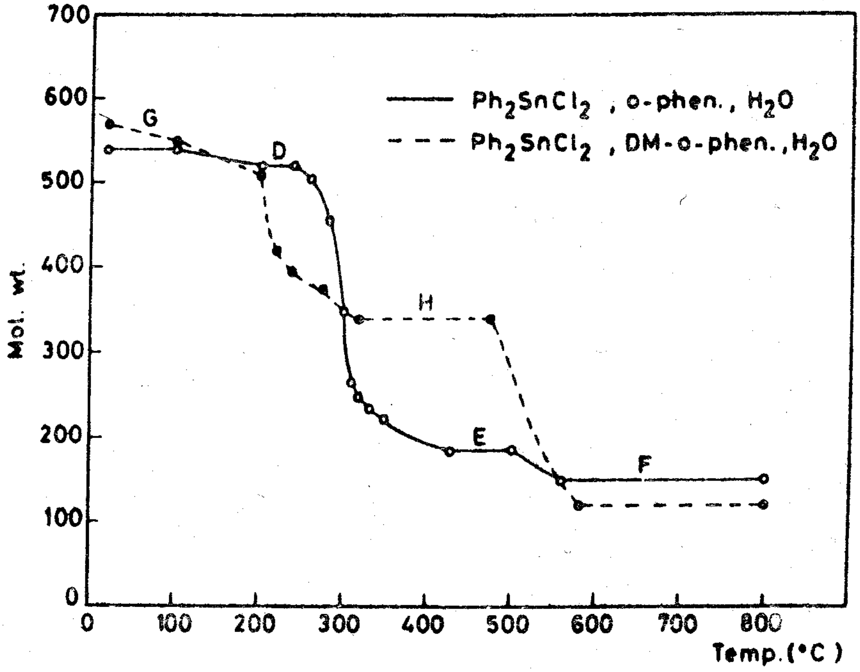

Mol. wt.
Temp. (°C)
G
D
H
E
F
Ph2SnCl2 , o-phen., H2O
Ph2SnCl2 , DM-o-phen., H2O
0
100
200
300
400
500
600
700
800

Fig. (2)

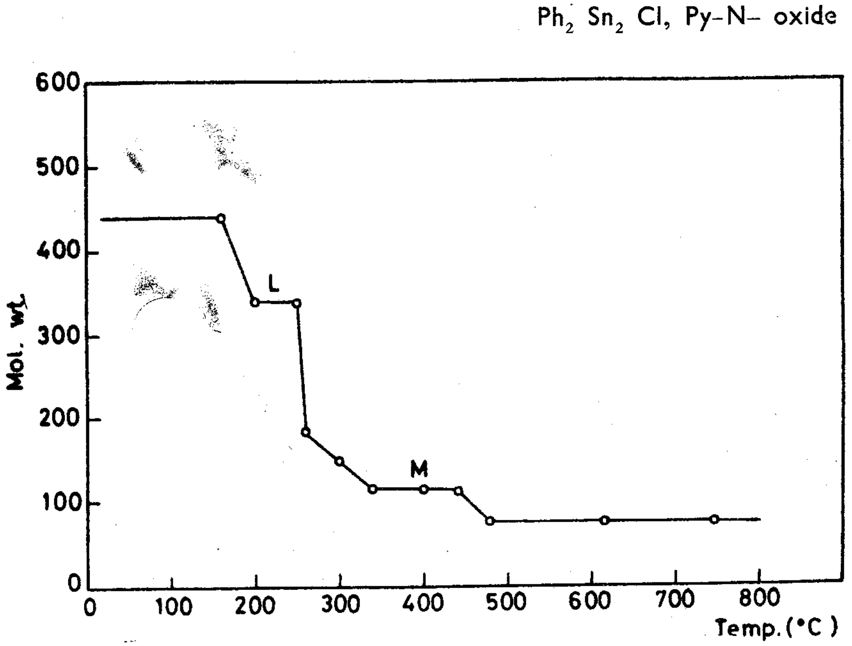

Ph$_2$ Sn$_2$ Cl, Py-N- oxide
600
500
400
300
200
100
0
Mol. wt.
L
M
0
100
200
300
400
500
600
700
800
Temp. (°C)

Fig. (3)

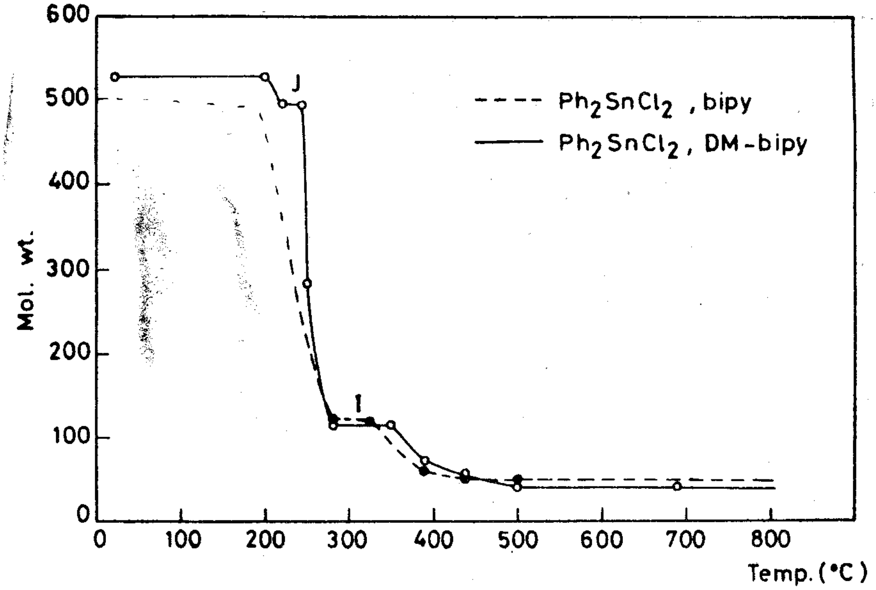

600
500
400
300
200
100
0
Mol. wt.
J
I
Ph$_2$SnCl$_2$, bipy
Ph$_2$SnCl$_2$, DM-bipy
0
100
200
300
400
500
600
700
800
Temp. (°C)

Fig. (4)

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