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NOTE

PREPARATION AND STRUCTURE OF SOME COMPLEXES DERIVED FROM AN ORGANOTIN BASE

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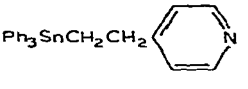
INTRODUCTION

Recently, Reifenberg and Considine showed that tetrakis(2-cyanoethyl)tin can function as a Lewis base and, with stannic chloride and bromide, the 1/1 adducts $SnX_4 \cdot Sn(CH_2CH_2CN)_4$ are formed[1]. The shift in the $\nu(C{\equiv}N)$ band of tetrakis(2-cyanoethyl)tin on complex formation indicates that coordination probably occurs from nitrogen to tin but the structure is uncertain and it is remarkable that only a single $\nu(C{\equiv}N)$ frequency was observed.

Triphenyltin azide gives a solid product with stannic chloride and this was assumed to have a 1/1 stoichiometry by analogy with other Group IVB organometallic azides. Infrared evidence was obtained for interaction in solution between triphenyltin azide and boron tribromide and between trimethyltin azide and stannic chloride[2].

RESULTS

We now report some experiments using triphenyl[2-(4-pyridyl)ethyl]tin (I) as a Lewis base. Compound I was prepared by the addition of triphenyltin hydride to 4-vinylpyridine by the method of Noltes and van der Kerk[3]. Attempts to make II by a corresponding reaction with diphenyltin dihydride were unsuccessful, the 4-vinylpyridine catalysing the decomposition of the dihydride to diphenyltin.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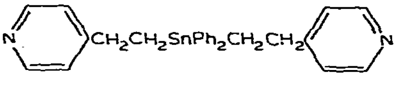
II

Details of the adducts formed from I and some metallic and organotin chlorides are shown in Table 1. The preparation of these adducts was straightforward except that cupric chloride underwent reduction and the only adduct isolated was CuCl · L. Two forms of the zinc chloride adduct were isolated, the low-melting form was converted to the high-melting form on heating. No adduct was obtained with

TABLE 1

COMPOSITIONS AND MELTING POINTS OF THE ADDUCTS

Compound[a]	M.p. (°C)	Formula	Analysis, found (calcd.) (%)			
			C	H	Cl	N
$ZnCl_2 \cdot 2L$[b]	64	$C_{50}H_{46}Cl_2N_2Sn_2Zn$	57.1	4.3	6.7	2.6
$ZnCl_2 \cdot 2L$[c]	159–162		57.5	4.5	6.7	2.8
			(57.3)	(4.4)	(6.8)	(2.7)
$CoCl_2 \cdot 4L$[b]	150–152	$C_{100}H_{92}Cl_2CoN_4Sn_4$	61.3	5.0	3.7	3.1
			(61.4)	(4.7)	(3.6)	(2.9)
$NiCl_2 \cdot 4L$[b]	184–185 dec.	$C_{100}H_{92}Cl_2N_4NiSn_4$	61.6	4.5	3.8	3.2
			(61.4)	(4.7)	(3.6)	(2.9)
$CuCl \cdot L$	106 dec.	$C_{25}H_{23}ClCuNSn$	54.2	4.6	1.2[e]	2.55
			(54.1)	(4.2)	(6.4)	(2.5)
$Ph_2SnCl_2 \cdot 2L$[c]	175–178	$C_{62}H_{56}Cl_2N_2Sn_3$	59.4	4.8	5.6	2.4
			(59.3)	(4.5)	(5.6)	(2.2)
$Ph_3SnCl \cdot L$[d]	166–168	$C_{43}H_{38}ClNSn_2$	61.2	4.7	4.3	1.9
			(61.35)	(4.6)	(4.2)	(1.7)

[a] L = triphenyl[2-(4-pyridyl)ethyl]tin. [b] Recrystallised from ethanol. [c] Recrystallised from a mixture of benzene and light petroleum (b.p. 60–80°). [d] Recrystallised from light petroleum (b.p. 60–80°). [e] We are unable to account for the low chlorine analysis: the analysis for copper was satisfactory.

mercuric chloride, instead phenyl–tin cleavage occurred and phenylmercuric chloride was isolated.

The solid-state infrared spectra of the complexes were measured and some assignments are recorded in Table 2.

DISCUSSION

The positions of the tin–phenyl stretching vibrations of the triphenyltin group present in the ligand agree well with those assigned for other triphenyltin compounds[4]. The spectra of the two zinc chloride adducts are very similar and it is considered that these are two crystalline forms of the same compound in which zinc is in a tetrahedral environment. There is good agreement between the positions of the ν(Zn–Cl) bands

TABLE 2

INFRARED ASSIGNMENTS OF THE COMPLEXES[a]

Adduct	ν(M–Cl)	ν_{as}(Sn–Ph) (ligand)	ν_s(Sn–Ph) (ligand)
$ZnCl_2 \cdot 2L$ (m.p. 64°)	337–329; 298	263	244
$ZnCl_2 \cdot 2L$ (m.p. 159–162°)	336; 298, 291 sh	269–255	249–242
$NiCl_2 \cdot 4L$	228	260	245, 241
$CoCl_2 \cdot 4L$	234–< 204	270–254	242
$Ph_2SnCl_2 \cdot 2L$[b]	234	267	245
$Ph_3SnCl \cdot L$[c]	279–255		244–240

[a] Absorption frequencies are in cm^{-1}, all absorptions were of strong intensity. [b] Additional bands due to the Ph_2SnCl_2 residue are ν_{as}(Sn–Ph) 287 cm^{-1} and ν_s(Sn–Ph) 227 cm^{-1}. [c] Only one additional ν(Sn–Ph) band due to the Ph_3SnCl residue could be assigned at 233–226 cm^{-1}, the second band is either absent or masked.

in Table 2 and those of $ZnCl_2 \cdot 2$ Py (329, 296 cm^{-1})[5] which is known to be tetrahedral[6].

It is probable that the pale green $NiCl_2 \cdot 4$ L and purple $CoCl_2 \cdot 4$ L complexes have octahedral configurations with equatorial nitrogen and *trans* chlorine atoms since $NiCl_2 \cdot 4$ Py and $CoCl_2 \cdot 4$ Py have this configuration[7] and $NiCl_2 \cdot 4$ L shows the expected single band at 228 cm^{-1} to be compared with the corresponding band[5] in $NiCl_2 \cdot 4$ Py at 246 cm^{-1}. Assignment of the ν(Co–Cl) band in $CoCl_2 \cdot 4$ L is less certain since there is strong background absorption in this region.

The interpretation of the spectrum of $Ph_2SnCl_2 \cdot 2$ L is complicated by the presence of two types of tin–phenyl bands; however the two ν(Sn–Ph) bands of the ligand Ph_3Sn group can be assigned with confidence. Also, there is little doubt that the phenyl groups of the Ph_2Sn residue are *cis* since two ν(Sn–Ph) bands can be identified (Table 2, footnote b), which are in excellent agreement with those of the corresponding group in $Ph_2SnCl_2 \cdot 4,4'$-Bipy[8] which occur as 287 and 222 cm^{-1}. Although only one ν(Sn–Cl) band is shown in Table 2 a second, masked, band could be present so that it is not known whether the chlorine atoms in $Ph_2SnCl_2 \cdot 2$ L are *cis* or *trans*.

As expected triphenyltin chloride forms a 1/1 complex but the spectrum of this compound is difficult to interpret due to overlapping bands and no stereochemical conclusions can be drawn.

The spectrum of $CuCl \cdot L$ showed unresolved strong intensity absorption in the range 275 cm^{-1} to the limit of the instrument at 204 cm^{-1} and no assignments were possible.

EXPERIMENTAL

Infrared spectra were recorded with the compounds as Nujol mulls using a Grubb–Parsons Spectromaster spectrometer.

Preparation of the adducts

A solution containing a slight excess of the ligand in hot ethanol was added to a solution of the metal chloride in the same solvent, the complex was obtained on cooling or on concentration of the solution (in the preparation of the copper complex 2 equivs. of ligand were used). For the preparation of the diphenyltin dichloride and triphenyltin chloride adducts the solvent was light petroleum (b.p. 60–80°). The yields varied from 73–97%, details of melting points, analyses and recrystallisation solvents are given in Table 1.

Reaction between triphenyl[2-(4-pyridyl)ethyl]tin and mercuric chloride

A solution of the ligand (0.416 g) in hot ethanol (7.5 ml) was added to a solution of mercuric chloride (0.125 g) in ethanol (2.0 ml). On cooling white phenylmercuric chloride was obtained (0.157 g) which, after crystallisation from ethanol, had m.p. 243–250°. (Found: C, 23.2; H, 1.9. C_6H_5ClHg calcd.: C, 23.0; H, 1.6%.)

ACKNOWLEDGEMENT

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