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SYNTHESIS, INFRARED SPECTRA AND THERMAL ANALYSIS OF SOME NEW SUBSTITUTED *ortho*-TRICHLOROSTANNYLBENZYLIDENEAMINE COMPOUNDS

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ABSTRACT

The novel substituted *o*-trichlorostannylbenzylideneamines *o*-$SnCl_3C_6H_4C(N\text{-}p\text{-}C_6H_4R)\text{-}COPh\ Cl_4C$ (R = H, Me, OMe or Br) complexes where synthesized and investigated in the solid state by infrared and thermal analysis

INTRODUCTION

Benzylideneaniline is isoelectronic with azobenzene and its *ortho*-metalation reactions are similar to those observed for azobenzene [1,2] The mode of coordination was first proposed by Cope and Siekman [3] for a series of palladium(II)-azobenzene derivatives

The first examples of *ortho*-metallation reactions in organotin chemistry were reported by Fitzsimmons et al in 1977 [4] These *o*-trihalogenostannylbenzylideneamines were prepared as solid etherates from the *N*-lithioketimine and tin halide in ether and spontaneously rearrange to form the *ortho*-metallated benzylamines These compounds can also be prepared from the tin(IV) halide and *N*-trimethylsilyl ketimine [4]

No other orthometallated complexes of tin(IV) with benzylideneamines as ligands have been reported

We report the synthesis and characterization of four new *ortho*-trichlorostannylbenzylideneamines obtained from the direct reaction of $SnCl_4$ with benzylideneamine derivatives The complexes isolated have been char-

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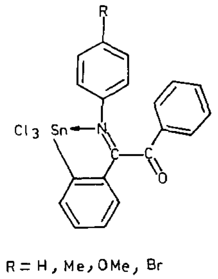

Fig 1 Structure of the complexes

acterized by elemental analysis, infrared spectroscopy and thermogravimetric and differential thermal analysis The relationship between spectroscopy and thermal properties with the different ligand substituents has also been studied (Fig 1)

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere Carbon tetrachloride was purified and dried by standard methods Tin tetrachloride was distilled under a nitrogen atmosphere in a Vigreux column The ligands, *N*-phenyl-benzoylbenzylideneamine (PBI), *N*-(1-phenylmethyl)-benzoyl-benzylideneamine (PMBI), *N*-(1-phenyl-methoxy)-benzoyl-1-benzylideneamine (PXBI) and *N*-(1-phenyl-bromo)-benzoyl-benzylideneamine (PBrBI) were kindly supplied by Drs J Plumet, C Escobar and R Alvarez-Osorio of the University Complutense of Madrid

Chemical analysis were carried out using standard methods Infrared spectra were measured on a Nicolet 5DX F T spectrophotometer in the range 4000–200 cm^{-1} Thermogravimetric measurements were obtained on a Mettler HE 20 thermobalance, with DTA accessory fitted The analytical constants were DTA range 20 μV, 0 33 kcal s^{-1}; TG range 20 mV, heating rate 5 °C min^{-1} record rate, 40 cm h^{-1}, thermocouple, Pt–(Pt–Rh 10%), sample mass 20 mg was placed on platinum crucibles located on top of the thermocouple

The instrument was calibrated employing indium (purity 99 99%) as standard The analyses were carried out in a dynamic air atmosphere with alumina (fine powder) as reference

Preparation of the complexes

The compounds were prepared by adding a solution of tin(IV) chloride (1 mmol) in CCl_4 dropwise to a solution of ligand (1 mmol) in the same solvent under stirring The solid precipitated was filtered, washed and dried in vacuum Analytical results (%) are reported below

$SnCl_3C_{20}H_{14}NO$ CCl_4 found C, 38 55, H, 2 26, N, 2 19 Calcd C, 38 03, H, 2 43, N, 2 11

$SnCl_3C_{21}H_{16}NO$ CCl_4 found C, 39 31, H, 2 95, N, 2 17 Calcd C, 38 95, H, 2 82, N, 2 06

$SnCl_3C_{21}H_{16}NO_2$ CCl_4 found C, 38 64, H, 2 87, N, 2 20 Calcd C, 38 05, H, 2 76, N, 2 02

$SnCl_3C_{20}H_{13}NOBr$ CCl_4 found C, 34 56, H 2 23 N 1 84 Calcd C 33 95, H, 2 02, N, 1 80

RESULTS AND DISCUSSION

All the complexes are intensely coloured and are soluble in common organic solvents They appear to be air stable, but slowly decompose on standing at room temperature, and are best stored under N_2

The spectra of all the ligands show ν(C=N) at 1620 cm^{-1} and ν(C=O) at 1665 cm^{-1} (Table 1) A strong band at 1612 ± 10 cm^{-1} attributable to the ν(C=N) mode shows a consistent small negative shift in the spectra of the organotin(IV) complexes The ν(C=O) stretching band of benzylideneamine is shifted by 20–8 cm^{-1} towards the higher region in the spectra of the complexes This suggests that the C=O group of the bases are not involved in complexation and that nitrogen is coordinated to tin through its lone pair [5,6]

The presence of an *ortho*-substituted aromatic ring is shown in the infrared spectrum by extra bands (compared with the ligand) in the 800–700 and 1100 cm^{-1} region [5,7,8]

Two bands in the range 590–477 cm^{-1} present in the compounds but absent in the ligands are assigned to a ν(Sn–C) mode [9] A medium to strong intensity band occurs at 425–370 cm^{-1} in the region which has been associated with tin–nitrogen stretching frequencies in organotin oximates [10,11] There appears to be correlation between the electronic character of the substituent and the change in the azomethine stretching frequency Tin–chloride stretching modes for all four compounds are also assigned, in accordance with Harrison et al [9]

Thus, the complexes investigated seem to contain five-coordinated tin(IV) The geometry at tin would be distorted trigonal bipyramidal with the nitrogen and one chlorine atom occupying the axial position, whilst the carbon and the two remaining chlorine atoms are bonded at equatorial sites

The DTA curve (Fig 2) for the complex $SnCl_3C_{20}H_{13}NOBr$ CCl_4 shows well-defined peaks The first endothermic peak between 92 and 180 °C, corresponds on the TG curve to the loss of the one molecule of carbon tetrachloride of crystallization (calcd weight loss 20 75%, found 20 88%)

TABLE 1

Relevant infrared frequencies (cm^{-1}) of the ligands and their organotin complexes

	PBI	$SnCl_3C_{20}H_{14}NO\ CCl_4$	PMBI	$SnCl_3C_{21}H_{16}NO\ CCl_4$	PXBI	$SnCl_3C_{21}H_{16}NO_2\ CCl_4$	PBrBI	$SnCl_3C_{20}H_{13}NOBr\ CCl_4$
C=O	1664	1677	1660	1680	1669	1680	1671	1678
C=N	1620	1615	1615	1612	1624	1612	1630	1622
Sn–C		575		572		575		568
		484		493		514		477
Sn–N		370		401		424		376
Sn–Cl		347		351		350		353
		331		334		335		347
		307		306		309		335
CCl_4 793		805		807		810		807
784		785		790		800		786
762		770		760		790		765

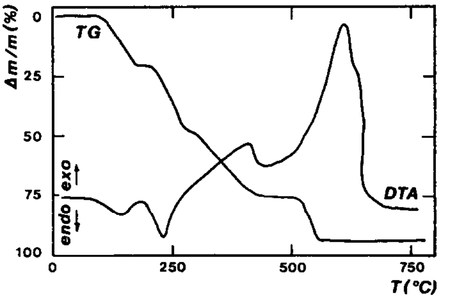

Fig 2 TG and DIA curves of $SnCl_3C_{20}H_{13}NOBr$ CCl_4

The residue is the complex $SnCl_3C_{20}H_{13}NOBr$ and the process can be fitted by the reaction

$$SnCl_3C_{20}H_{13}NOBr\ CCl_4 \rightarrow SnCl_3C_{20}H_{13}NOBr + CCl_4$$

The complex isolated ($SnCl_3C_{20}H_{13}NOBr$) has been identified by infrared spectroscopy and we did not observe the bands which can be attributed to carbon tetrachloride

A small endothermic peak is observed in the region 203–282 °C The weight loss recorded up to the end of this endothermic process is 33 33% and can be attributed to the initial decomposition of the ligand *N*-(1-phenyl-bromo)-benzoyl-benzylideneamine, the rupture of the tin–carbon bond and the probable formation of $|SnCl_3C_6H_4NBr|$ as intermediate (calcd weight loss 32 82%) This decomposition has been also observed in other complexes with similar ligands [12] However, this intermediate could not be isolated since the decomposition of the compound continues slowly above 425 °C This decomposition shows on the DTA curve a shallow exothermic peak The mass loss accompanying this exothermic transition corresponds on the TG curve to 51 99% This loss is probably due to the formation of the intermediate corresponding to the formula $[SnCl_3]$ which is simultaneously decomposed to tin oxydichloride, $SnOCl_2$ (calcd weight loss 52 08%)

The process may be schematized as follows

$$2\,|SnCl_3C_6H_4NBr| + 16O_2 \rightarrow Br_2 + 4H_2O + 12CO_2 + 2NO_2 + [SnCl_3]$$

$$2\,|SnCl_3| + O_2 \rightarrow 2SnOCl_2 + Cl_2$$

Between 425 and 506 °C, the TG curve shows that tin oxydichloride is relatively stable Beyond this temperature decomposition sets in abruptly and the TG curve descends linearly up to 651 °C In this range of temperatures, the DTA curve has a large exothermic peak which corresponds to the formation of tin dioxide However, the loss weight observed on the TG curve is greater than expected (calcd weight loss 34 52%, found 78 26%), according to the reaction

$$2SnOCl_2 + O_2 \rightarrow 2SnO_2 + 2Cl_2$$

TABLE 2

Thermal data

Compound	Temperature (° C)	Mass loss (%)		Process	Identified compound
		Cacld	Found		
$\|SnCl_3C_{20}H_{14}NO\ CCl_4\|$	94–178	23 22	23 08	Endo	$\|SnCl_3C_{20}H_{14}NO\|$
	196–332	37 90	37 86	Endo	$\|SnCl_3C_6H_4N\|$
	381–560	40 01	40 23	Exo	$SnOCl_2$
	574–700	34 52	65 38	Exo	SnO_2
$\|SnCl_3C_{21}H_{16}NO\ CCl_4\|$	114–198	22 74	22 50	Endo	$\|SnCl_3C_{21}H_{16}NO\|$
	206–267	36 89	37 10	Endo	$\|SnCl_3C_7H_7N\|$
	366–552	42 55	42 31	Exo	$SnOCl_2$
	578–664	34 52	77 78	Exo	SnO_2
$\|SnCl_3C_{21}H_{16}NO_2\ CCl_4\|$	82–175	22 22	22 22	Endo	$\|SnCl_3C_{21}lH_{16}NO_2\|$
	209–286	35 79	35 71	Endo	$\|SnCl_3C_7H_7NO\|$
	305–483	45 21	45 70	Exo	$SnOCl_2$
	512–628	34 52	86 36	Exo	SnO_2
$\|SnCl_3C_{20}H_{13}NOBr\ CCl_4\|$	92–180	20 75	20 88	Endo	$\|SnCl_3C_{20}H_{13}NOBr\|$
	203–282	32 82	33 33	Endo	$\|SnCl_3C_6H_4NBr\|$
	282–425	51 99	52 08	Exo	$SnOCl_2$
	506–651	34 52	78 26	Exo	SnO_2

This difference is due to the unquantitative oxidation by the volatilization of $SnOCl_2$ in agreement with the results of Duval [13]

The DTA and TG curves of the other complexes $SnCl_3C_{20}H_{14}NO\ \ CCl_4$, $SnCl_3C_{21}H_{16}NO \cdot CCl_4$ and $SnCl_3C_{21}H_{16}NO_2 \cdot CCl_4$ are analogous to those first studied for $SnCl_3C_{20}H_{13}NOBr\ \ CCl_4$ The results obtained are given in Table 2

If we compare the endothermic process of the rupture of the tin–carbon σ-bond for the four complexes studied in this paper, we observe that the initiation temperature is lower for $SnCl_3C_{20}H_{14}NO\ \ CCl_4$ (196 °C) and higher for $SnCl_3C_{21}H_{16}NO_2 \cdot CCl_4$ (209 °C) The greater thermal stability can be attributed to a tin–carbon σ-bond which is stronger in this complex than in the others

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