STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIII, 1-2, 1998

^{1}H AND ^{13}C NMR SPECTROSCOPY AS A SUITABLE METHOD FOR THE CHARACTERIZATION OF PHENYLANTIMONY CHLORIDES

ANCA SILVESTRU, CRISTIAN SILVESTRU*

ABSTRACT. ^{1}H and ^{13}C NMR spectra have been recorded for $CDCl_3$ solutions of triphenylantimony, Ph_3Sb, phenylantimony(III) chlorides, Ph_2SbCl and $PhSbCl_2$, and phenylantimony(V) chlorides, Ph_3SbCl_2 and $Ph_2SbCl_3H_2O$, respectively, as well as for solutions containing mixtures of them. A possibility to establish the composition of mixtures containing the above mentioned compounds or to detect the impurities due to the synthetic methods usedd to prepare phenylantimony halides, using ^{1}H and ^{13}C NMR data, is presented.

INTRODUCTION

Phenylantimony(III) chlorides, $PhSbCl_2$ and $PhSbCl_3$, and phenylantimoniu(V) chlorides, Ph_3SbCl_2 and Ph_2SbCl_3, are useful to starting materials in syntheses of organoantimony compounds with different inorganic or organic ligands. The NMR studies in solution give a suitable method to identify them in mixtures, or to prove their purity. It has been reported before [1] about the possibilities to appreciate quantitatively the content of such compounds in reaction mixture using the ^{1}H NMR spectroscopy. Although the ^{1}H NMR spectra are very useful, in some cases, due to the presence of different phenyl groups bond to antimony and the proton – proton coupling phenomena, the overlap of signals is possible and the spectra appear very complicate. The ^{13}C NMR spectra seem to be more useful to characterize the phenylantimony chlorides and to identify the composition of reaction mixtures containing them, due to the clear separation between typical ^{13}C resonance signals for Ph_nSbCl_{3-n} derivatives. The ^{13}C NMR signals don't overlap each other and could be used certainly to identify the organoantimony impurities present in the phenylantimony chlorides used as starting materials in chemical synthesis.

EXPERIMENTAL

Triphenylantimony and all other starting materials were commercially available. $SbCl_3$ was freshly sublimed before use. ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on a VARIAN GEMINI 300 instrument operating at 299.5 and 75.4 MHz, respectively. The chemical shifts were referenced to the internal chloroform peak (d = 7.26 ppm and d = 77.0 ppm for ^{1}H and ^{13}C, respectively).

All the phenylantimony halides have been prepared according to literature methods. Ph_2SbCl and $PhSbCl_2$ obtained by redistribution reactions between

* *Faculty of Chemistry and Chemical Engineering, "Babe¿-Bolyai" University, 11 Arany Janos Str., 3400, Cluj-Napoca, Romania.*

Ph_3Sb and $SbCl_3$ in stoichiometric molar ratio in the absence of a solvent, were used without further purification [2]. The redistribution reaction between Ph_4Sn and $SbCl_5$ in CCl_4, followed by crystallisation from a 5N HCl solution led to $Ph_2SbCl_3.H_2O$ [3], while the oxidation reaction of Ph_3Sb with SO_2Cl_2 gave the corresponding triphenylantimony dichloride (recrystallized from CCl_4) [4].

All mixtures of phenylantimony compounds investigated by means of NMR spectroscopy were prepared directly in NMR tubes.

RESULTS AND DISCUSSIONS

1. Syntheses of $PhSbCl_2$, Ph_2SbCl, Ph_3SbCl_2 and $Ph_2SbCl_3.H_2O$

Phenylantimony(III) chlorides have been obtained by shaking for 24 hr reaction mixtures obtained from triphenylantimony and antimony(III) chloride, in stoichiometric ratio and in absence of solvent [2]:

$$2\ Ph_3Sb + SbCl_3 \longrightarrow 3\ Ph_2SbCl$$

$$Ph_3Sb + 2\ SbCl_3 \longrightarrow 3\ Ph_2SbCl_2$$

These methods of synthesis afford the possibility to obtain mixtures of organoantimony compounds due to an equilibrium or other processes, *e.g.* oxidation to antimony(V). Therefore, phenylantimony(V) chlorides were also prepared. Diphenylantimony(V) trichloride was obtained by reacting tetraphenyltin and antimony pentachloride, and recrystallisation from a solution of 5N HCl affords its isolation as white crystals of $Ph_2SbCl_3.H_2O$ [3]:

$$Ph_4Sn + SbCl_5 \longrightarrow Ph_2SbCl_3 + Ph_2SnCl_2$$

Triphenylantimony(V) dichloride was prepared by oxidation of triphenylantimony with sulfuryl chloride [4]:

$$Ph_3Sb + SO_2Cl_2 \longrightarrow Ph_3SbCl_2 + SO_2$$

Since phenylantimony(III) chlorides are important starting materials for other organoantimony compounds, it is important to check their purity and a NMR spectroscopy is a very useful method for this purpose.

2. NMR spectra

^{1}H and ^{13}C NMR data recorded for the phenylantimony halides and Ph_3Sb are given in Tables 1 and 2.

As it was previously noted [1] the resonance signals of the *ortho*-protons of the discussed compounds are very useful to calculate the quantitative composition of a mixture or the purity of each phenylantimony compound, if they don't overlap with other signals. However, the proton NMR spectra for mixtures of organoantimony compounds containing phenyl groups are always complicated due to the proton-proton coupling phenomena.

The phenylantimony(III) chlorides, $PhSbCl_2$ and Ph_2SbCl are conveniently obtained by redistribution between Ph_3Sb and $SbCl_3$ in 1:2 and 2:1 molar ratio, respectively [2], but the use of this method might result in an impure product if the

reaction is not completed. The ^{1}H NMR spectrum for Ph_2SbCl (Fig. 1, a) presents a doublet of dublets at δ = 7.70 ppm (*ortho* – protons) and a multiplet signal at δ = 7.47 ppm (*meta* + *para* – protons). In additon, two groups of very low intensity signals, *i.e.* a doublet of doublets at δ = 8.32 ppm and a multiplet at δ = 7.60 ppm, are also present. According to the synthetic route, it was reasonable to suppose that these signals of low field (δ =8.32 ppm), but complicated very much the space at 7.3 -–7.5 ppm, where the signals due to the *meta* + *para* – protons in Ph_2SbCl and those due to the Ph_3Sb protons overlap each other (Fig. 1, b). This behavior suggests the low field resonance at δ = 8.32 ppm observed for the reaction product is due to an other phenylantimony compound.

As a consequence of the size and inductive effects of the substituents, in mixtures containing $PhSbCl_2$, Ph_2SbCl, Ph_3Sb, Ph_3SbCl_2 and Ph_2SbCl_3, the ^{13}C NMR signals do not overlap each other and it is easier to identify the composition of such reaction mixtures (Table 2).

The ^{13}C NMR spectrum of Ph_2SbCl (crude product) confirms the presence of an impurity, *i.e.* eight resonance signals (four of them of very low intensity) were observed, which could be assigned to two different phenyl groups in the mixture (Fig. 2, a, Table 2). The addition of the excess of Ph_3Sb resulted in four new signals, characteristic for the four nonequivalent carbon atoms of a new type of phenyl group (Fig. 2, b). None of the 12 signals overlap each other.

The comparison of the ^{13}C NMR spectra of Ph_2SbCl (crude product) and Ph_3SbCl_2 suggests the impurity to be this phenylantimony(V) chloride, probably formed in the reaction between Ph_3Sb and traces of HCl present in $SbCl_3$, although the later was freshly sublimed. This was confirmed by ^{1}H and ^{13}C NMR spectra. Indeed, the ^{13}Cresonance signals corresponding to the impurity increase in intensity when pure Ph_3SbCl_2 was added to the Ph_2SbCl (crude product) (Fig. 2, c).

The ^{13}C NMR spectra were also used to prove their utility to establish undoubtfully the composition of mixtures of phenylantimony compounds. Thus, ($PhSbCl_2$ + Ph_3Sb), ($PhSbCl_2$ + Ph_2SbCl) and ($PhSbCl_2$ + Ph_2SbCl +Ph_3Sb), as well as ($PhSbCl_2$ + Ph_3Sb) mixtures were prepared and their spectra show that in each case the resonances are very well separated and can be easily assigned to a particular phenylantimony compound. Even when four components are present in the mixture, *i.e.* $PhSbCl_2$ + Ph_2SbCl + Ph_3Sb + Ph_3SbCl_2, the sixteen expected ^{13}C resonances are not overlapped.

In case of the triphenylantimony(V) dichloride, the ^{1}H NMR spectra are not very suggestive. If the compound contains some Ph_3Sb, and this is possible taking into account the syntheses method, in the ^{1}H NMR spectra three groups of multiplets signals are present (Table 1). The signal at the lowest field corresponds to the *ortho* – protons in Ph_3SbCl_2 (greater deshielding), while the signal at the highest field corresponds to the overlap of the signals given by the *ortho* – protons in Ph_3Sb and those given by the *meta* and *para* – protons in Ph_3Sb (the lowest deshielding).

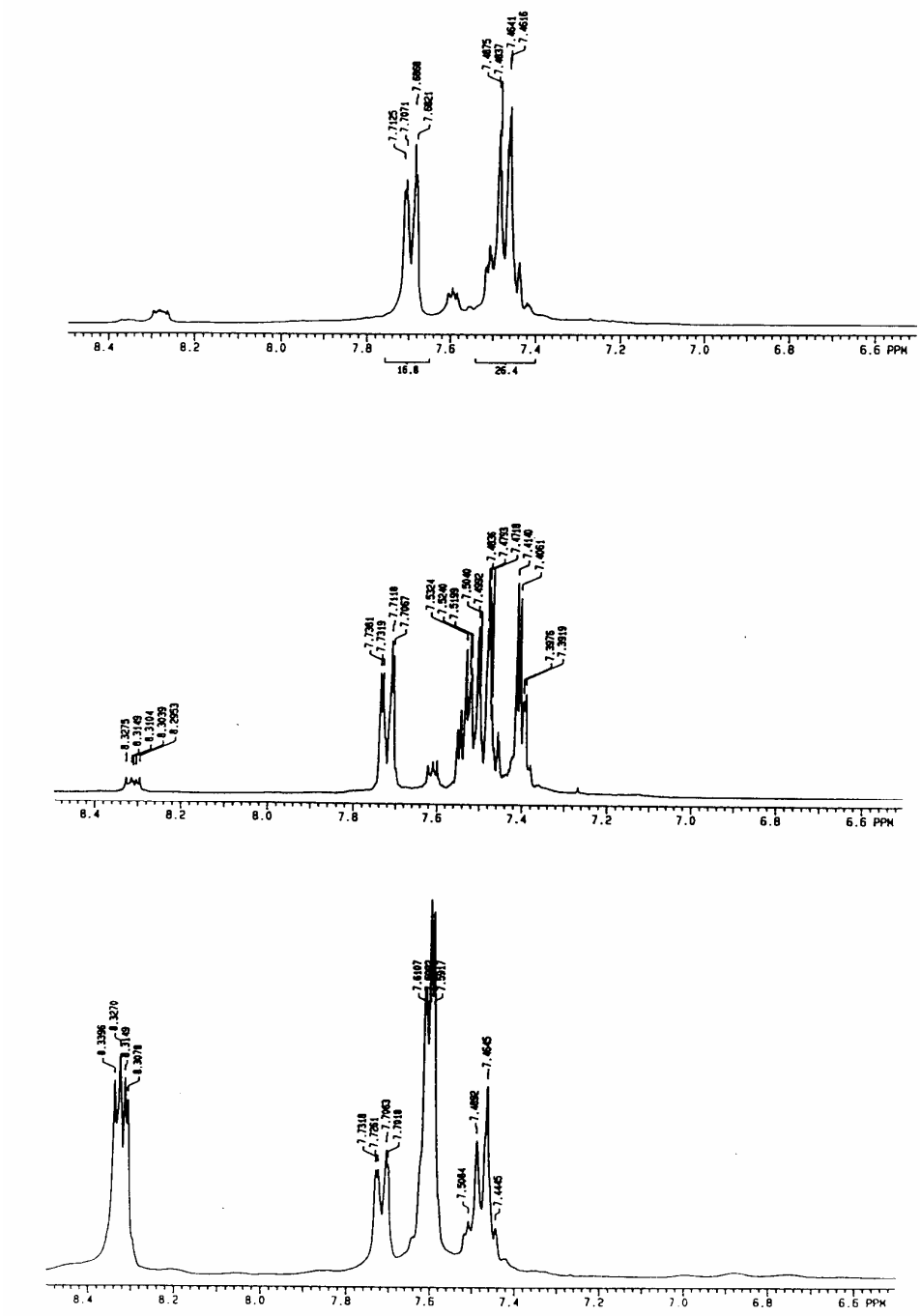

Figure 1. ^{1}H – NMR spectra for (a) Ph_2SbCl, (b) $Ph_2SbCl + Ph_3Sb$ and (c) $Ph_2SbCl + Ph_3SbCl_2$

Table 1.

^{1}H NMR data (δ, ppm and J, Hz) for phenylantimony(III)- and phenylantimony(V) chlorides, Ph_3Sb and mixtures of these compounds

Compound / mixture	**Chemical shifts (δ, ppm) and coupling constants proton – proton ($^{n}J_{HH}$, Hz)**	
	H - *ortho*	H – *meta* + *para*
Ph_2SbCl (Ph_3SbCl_2 as impurity)	[8.28dd ($^{3}J_{HH}$ = 7.1; $^{4}J_{HH}$ = 3.8)] 7.70dd ($^{3}J_{HH}$ = 7.6; $^{4}J_{HH}$ = 1.5)	[7.60m] (Ph_3SbCl_2) 7.47m (Ph_2SbCl)
Ph_3Sb	7.55dd ($^{3}J_{HH}$ = 6.5; $^{4}J_{HH}$ = 3.0)	7.41m
(Ph_2SbCl + Ph_3Sb) (also Ph_3SbCl_2 as impurity)	[8.31dd ($^{3}J_{HH}$ = 7.1; $^{4}J_{HH}$ = 3.8)] 7.72dd ($^{3}J_{HH}$ = 7.7; $^{4}J_{HH}$ = 1.7) 7.50m[a]	[7.61m] (Ph_3SbCl_2) (Ph_2SbCl) 7.44m (Ph_3Sb)
(Ph_2SbCl + Ph_3SbCl_2 + Ph_3Sb)	8.38dd ($^{3}J_{HH}$ = 6.4; $^{4}J_{HH}$ = 2.9) 7.76dd ($^{3}J_{HH}$ = 7.2; $^{4}J_{HH}$ = 1.2) 7.54m[b]	(Ph_3SbCl_2) (Ph_2SbCl)
(Ph_2SbCl + Ph_3SbCl_2)	8.32dd ($^{3}J_{HH}$ = 6.6; $^{4}J_{HH}$ = 3.0) 7.72dd ($^{3}J_{HH}$ = 7.5; $^{4}J_{HH}$ = 1.5)	7.60m (Ph_3SbCl_2) (Ph_2SbCl) 7.48m (Ph_3Sb)
Ph_3SbCl_2	8.27dd ($^{3}J_{HH}$ = 6.6; $^{4}J_{HH}$ = 3.0)	7.57m
$PhSbCl_2$	7.87d ($^{3}J_{HH}$ = 7.7)	7.59dd[c] (*meta*) 7.51t[d] (*para*)
($PhSbCl_2$ + Ph_3Sb)	7.93d ($^{3}J_{HH}$ = 6.9) 7.63m[e]	(Ph_3SbCl_2) 7.46m (Ph_3Sb)
($PhSbCl_2$ + Ph_2SbCl + Ph_3Sb) (also Ph_3SbCl_2 as impurity)	[8.36dd ($^{3}J_{HH}$ = 6.6; $^{4}J_{HH}$ = 3.0)] 7.93d($^{3}J_{HH}$ = 6.8) 7.79dd ($^{3}J_{HH}$ = 7.2; $^{4}J_{HH}$ = 1.4) 7.56m[f]	(Ph_3SbCl_2) ($PhSbCl_2$) (Ph_2SbCl)
($PhSbCl_2$ + Ph_2SbCl) (also Ph_3SbCl_2 as impurity)	[8.24dd ($^{3}J_{HH}$ = 6.6; $^{4}J_{HH}$ = 3.0)] 7.88d($^{3}J_{HH}$ = 6.8) 7.70dd ($^{3}J_{HH}$ = 7.4; $^{4}J_{HH}$ = 1.6) 7.54m[g]	(Ph_3SbCl_2) ($PhSbCl_2$) (Ph_2SbCl)
$Ph_2SbCl_3.H_2O$[h]	8.32dd ($^{3}J_{HH}$ = 6.4; $^{4}J_{HH}$ = 3.1)	7.63m
(Ph_3SbCl_2 + Ph_2Sb)	8.38dd ($^{3}J_{HH}$ = 7.1; $^{4}J_{HH}$ = 2.3) 7.61m[i]	(Ph_3SbCl_2) 7.44m (Ph_2SbCl)

[a](Ph_2SbCl – *meta* + *para*, Ph_3Sb – *ortho*); [b]Ph_2SbCl – *meta* + *para*, Ph_3SbCl_2 – *meta* + *para*, Ph_3Sb – *ortho* + *meta* + *para*; [c3]J_{HH} = 7.1; [d3]J_{HH} = 6.9; [e]($PhSbCl_2$ - *meta* + *para*, Ph_3Sb – *ortho*); [f] Ph_2SbCl – *meta* + *para*, $PhSbCl_2$ - *meta* + *para*, Ph_3Sb – *ortho* + *meta* + *para*, Ph_3SbCl_2 – *meta* + *para*; [g]Ph_2SbCl – *meta* + *para*, $PhSbCl_2$ - *meta* + *para*, Ph_3SbCl_2 – *meta* + *para*; [h]The signal due to the protons in water molecule appears at δ = 2.18 ppm (singlet); [1] Ph_3Sb – *ortho*, Ph_3SbCl_2 – *meta* + *para*.

The central signal is due to the overlap of the signals given by the *ortho* – protons in Ph_3Sb and those given by the *meta* and *para* – protons in Ph_3SbCl_2. In the ^{13}C NMR spectra of the same mixture it is easier to distinguish the two components because the signals are very well separated (Figure 3).

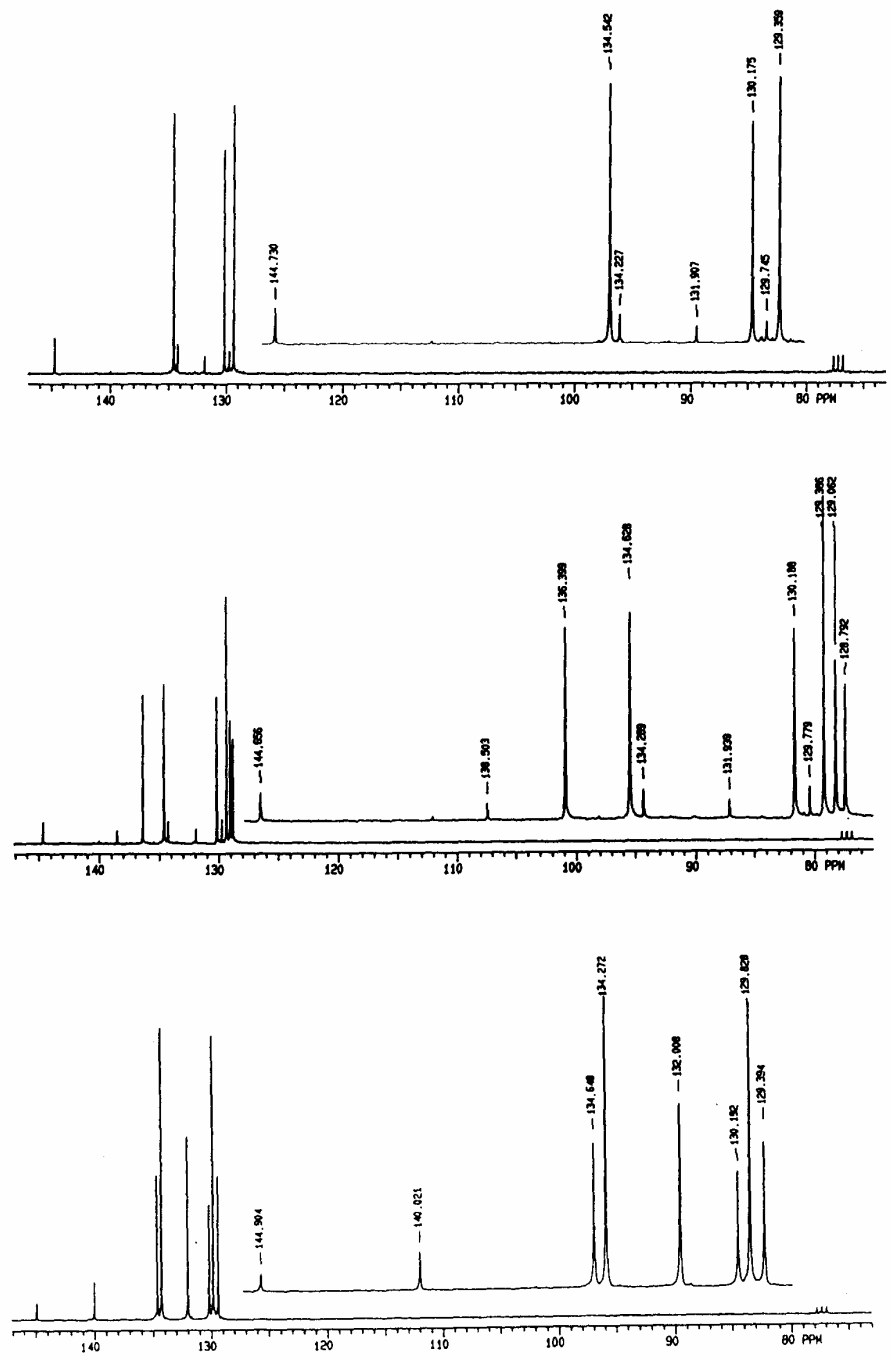

Figure 2. ^{13}C – NMR spectra for (a) Ph_2SbCl, (b) $Ph_2SbCl + Ph_3Sb$ and (c) $Ph_2SbCl + Ph_3SbCl_2$

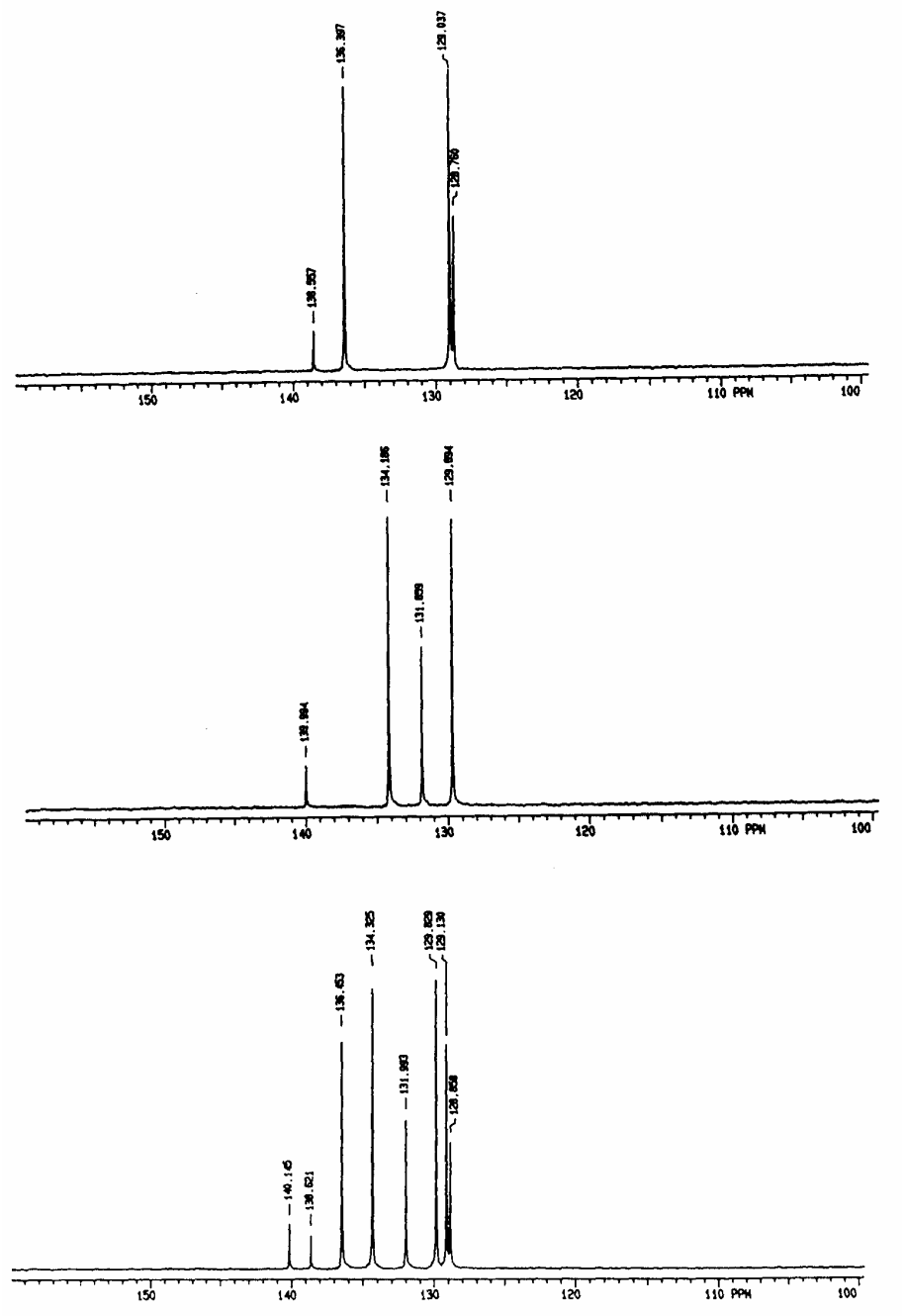

Figure 3. ^{13}C – NMR spectra for (a) Ph_3Sb, (b) Ph_3SbCl_2 and (c) Ph_3Sb + Ph_3SbCl_2

ACKNOWLEDGEMENTS

This work was supported by the Roumanian Academy. The financial support provided by OLTCHIM S.A. (C.Roibu – General Manager) for the service of the Varian NMR equipment ("Babes – Bolyai" University) is also greatly acknowledged.

REFERENCES

1. G.Alonzo, H.J.Breunig, M.Denker,K.H.Ebert, W.Offermann, *J.Organomet.Chem.*, 522 (1996), 237.
2. M.Nunn, D.B.Sowerby, D.M.Wesolek, *J.Organomet.Chem.*, 251 (1983), C45.
3. I.Haiduc, C.Silvestru, *Inorg. Synth.*, 23 (1985), 194.
4. A.J.Banister, L.F.Moore, *J.Chem.Soc.A,* (1968), 1137.