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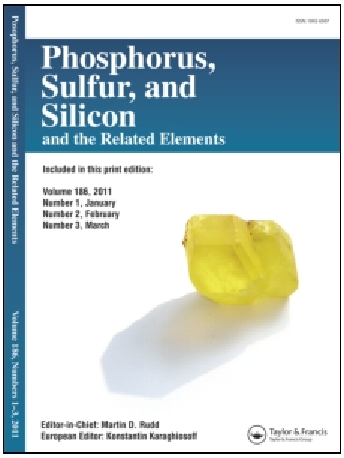

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Organoantimony Derivatives of Organophosphorus Ligands Containing Inorganic Chelate Rings

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Organoantimony complexes of the type $PhSbCl_{2-x}L_x$ and Me_3SbL_2($L = [(OPPh_2)(XPPh_2)N]^-$, X = O, S; x = 1,2) were prepared and investigated by means of IR and multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy. The PhSb(Cl)L compounds exhibited a redistribution process to give $PhSbL_2$ and $PhSbCl_2$. The molecular structures of $PhSb[(SPPh_2)_2N]_2$ and $Me_3Sb[(OPPh_2)(SPPh_2)N]_2$ were established by single crystal X-ray diffractometry.

Keywords: dichalcogenoimidodiphosphinato ligands; organo-Sb(III) and -Sb(V) complexes

INTRODUCTION

Antimony complexes of 1,1-dichalcogenophosphorus ligands exhibit a large variety of structural patterns[1]. By contrast, few organoSb(V) compounds containing $[(XPR_2)(YPR'_2)N]^-$ ligands (X, Y = O, S, Se; R, R' = alkyl, aryl, alkoxy, aroxy), *i.e.* Ph_2SbCl_2L,[2] have been investigated only in recent years.

Here we report on the synthesis and spectroscopic characterization of several compounds of the type $PhSbCl_{2-x}L_x$ and Me_3SbL_2 ($L = [(OPPh_2)(XPPh_2)N]^-$, X = O, S; x = 1,2), as well as the molecular structure of $PhSb[(SPPh_2)_2N]_2$ and $Me_3Sb[(OPPh_2)(SPPh_2)N]_2$ derivatives.

RESULTS AND DISCUSSION

The organo-Sb(III) and -Sb(V) were prepared by metathesis reactions (Table 1):

$$PhSbCl_2 + x\,ML \longrightarrow PhSbCl_{2-x}L_x + x\,MCl$$

$$Me_3SbCl_2 + 2\,ML \longrightarrow Me_3SbL_2 + 2\,MCl$$

The strong infrared absorptions observed for all organoantimony complexes in the regions 1240-1210, 1180-1010 and 610-530 cm^{-1} were assigned to $\nu_{as}(P_2N)$, $\nu(PO)$, and $\nu(PS)$ stretching vibrations, respectively. The absence of a strong absorption at *ca.* 900 cm^{-1} due to $\nu_{as}(P_2NH)$, is indicative of the presence of the ligand in its deprotonated form.

The magnitude of the ^{31}P chemical shifts are consistent with a monometallic biconnective and monoconnective coordination pattern of the phosphorus ligand for compounds **1-4** and **5-6**, respectively.

A redistribution process of **1** to give **3** and $PhSbCl_2$ occurred during attempts to grow crystals for X-ray studies. The crystal of $PhSb[(SPPh_2)_2N]_2$ contains discrete molecules. The ligand unit is

Table 1. Synthesis and NMR data for organo-Sb derivatives.

Compounds	Yield (%)	$\delta(^{31}P)$ (ppm)	
		*P*S	*P*O
$PhSbCl[(SPPh_2)_2N]$,[a] 1	90	37.3s,br	
$PhSbCl[(OPPh_2)(SPPh_2)N]$,[b] 2	86	33.4s	27.6s
$PhSb[(SPPh_2)_2N]_2$,[b] 3	77	37.6s	
$PhSb[(OPPh_2)(SPPh_2)N]_2$,[b] 4	78	35.5s,br	23.2s,br
$Me_3Sb[(OPPh_2)_2N]_2$,[a] 5	73		14.5s, 21.1s
$Me_3Sb[(OPPh_2)(SPPh_2)N]_2$,[b] 6	94	40.1s $^1J_{PC}$ 107.6 Hz	16.8s $^1J_{PC}$ 139.9 Hz

[a] Using the Na salt of the ligand; [b] Using the K salt of the ligand;
[c] Abbreviations: s = singlet, br = broad; [c] $^1J_{PC}$ 107.6 Hz; [d] $^1J_{PC}$ 139.9 Hz.

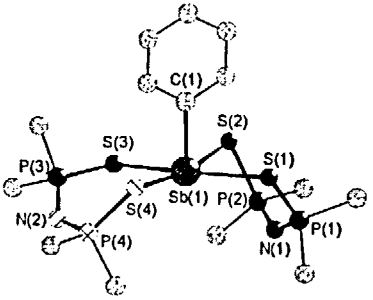

Figure 1. View of the structure of $PhSb[(SPPh_2)_2N]_2$ (for clarity only *ipso* carbons on phosphorus atoms are shown.).

asymmetric coordinated through both sulfur atoms (Sb-S 2.666/2.778 and 2.690/2.810 Å, respectively) (Fig. 1), resulting in a spiro-bicyclic system. The coordination geometry at the metal atom is distorted square pyramidal [S-Sb-S (*trans*) 169.5, 170.2°, S-Sb-C (range) 83.8-96.2°].

The molecular structure of $Me_3Sb[(OPPh_2)(SPPh_2)N]_2$ was also established by X-ray diffractometry (Fig. 1). The asymmetric monothioimidodiphosphinato ligands are monodentate, being connected to the metal atom only through the oxygen atoms (Sb-O 2.38/2.116 Å). The resulting coordination geometry is trigonal bipyramidal, with a planar SbC_3 moiety and the oxygen atoms in axial positions [C-Sb-C (range) 119.5-120.2°, O-Sb-O 173.2°].

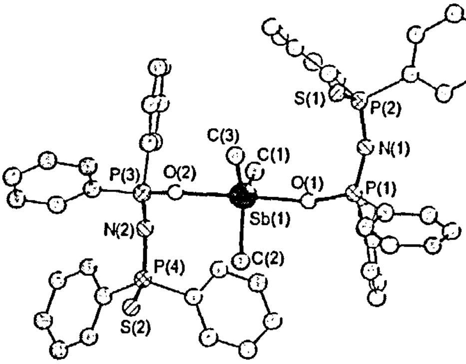

Figure 2. View of the structure of $Me_3Sb[(OPPh_2)(SPPh_2)N]_2$.

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