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Preliminary communication

Investigations on organoantimony compounds
VIII[★]. Geometric isomerism in hexacoordinate diphenyl- and 2,2'-biphenylyleneantimony(V) β-diketonates

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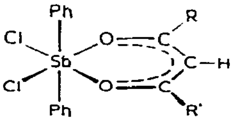
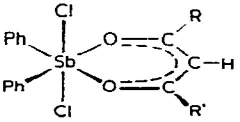
Until now, the existence of two isomers with structures (I) and (II) in solutions of $Ph_2SbCl_2(acac)$[1,2] appears to have been the only example of geometric isomerism in six-coordinate *organo*metallic complexes. We report here some preliminary information on the stereochemistry of some related diphenyl- and of 2,2'-biphenylyleneantimony(V) β-diketonate complexes[3].

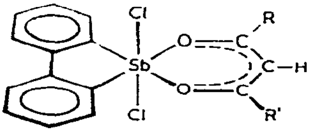
$Ph_2SbCl_2(dpm)$, $Ph_2SbCl_2(pac)$, $Ph_2SbCl_2(acac)$, (dpm = t-BuCOCHCO-t-Bu; pac = t-BuCOCHCOMe and acac = MeCOCHCOMe) and the corresponding 2,2'-biphenylyleneantimony complexes were obtained by the reaction of Ph_2SbCl_3 and 2,2'-biphenylylene$SbCl_3$[4] with the protonated ligand[★★]. Relevant PMR chemical shift data are shown in Table 1. The PMR spectrum of $Ph_2SbCl_2(dpm)$ in $CDCl_3$ shows two



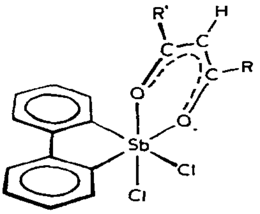
(I)



(II)



(III)



(IV)

[★] For Part VII see ref. 1.

[★★] Satisfactory analyses were obtained for all new compounds. All compounds are monomeric in benzene and they contain bidentate β-diketonate ligands as shown by IR spectroscopy.

TABLE 1

PMR CHEMICAL SHIFT DATA OF Ph_2SbCl_2X AND 2,2'-BIPHENYLYLENE$SbCl_2X$, (X = acac, dpm or pac), IN $CDCl_3$ AND C_6D_6 SOLUTIONS AT 25°

Compound	Isomer ratio		Chemical shifts, δ						
	I/II	III/IV	Isomer	Solvent $CDCl_3$			Solvent C_6D_6		
	in $CDCl_3$ (in C_6D_6)	in $CDCl_3$ (in C_6D_6)		CH	CH_3	t-Bu	CH	CH_3	t-Bu
Ph_2SbCl_2(acac)	3/1		I	5.38	2.02		4.57	1.37	
	(5/2)		II	5.83	2.17		5.05	1.47	
Ph_2SbCl_2(dpm)	5/4		I	5.64		1.11	5.45		0.89
	(2/3)		II	6.08		1.22	6.00		1.06
Ph_2SbCl_2(pac)	2/1		I	5.49	2.04	1.09	5.06	1.46	0.84
	(6/5)		II	5.94	2.20	1.20	5.56	1.56	0.98
2,2'-Biphenylylene$SbCl_2$(acac)		3/4	III	5.93	2.32		5.08	1.58	
		(3/5)	IV	5.77	2.34; 1.90		4.94	1.67; 1.08	
2,2'-Biphenylylene$SbCl_2$(dpm)		3/2	III	6.22		1.38	6.07		1.15
		(5/7)	IV	6.12		1.39; 0.94	6.01		1.24; 0.69
2,2'-Biphenylylene$SbCl_2$(pac)		3/2/1[a]	III	6.05	2.37	1.37	5.58	1.64	1.08
		(4/6/3)[a]	IVA	5.94	1.98	1.37	5.48	1.17	1.16
			IVB	5.90	2.38	0.89	5.47	1.73	0.60

[a] The isomer ratio III/IVA/IVB is given.

sets of signals of the t-Bu and the ring C—H protons of the dpm ligand, each with intensity ratio 18/1, indicating the presence of two isomers. As has been demonstrated in the elucidation of the two isomeric structures of Ph_2SbCl_2(acac) in solution[1], the 'high-field' set of signals belongs to the *trans*-diphenyl isomer (I) and the 'low-field' set to the *trans*-dichloro isomer (II) (R = R′ = t-Bu). Heating the chloroform solution for 1 min or leaving it at room temperature for 1 h results in the formation of an equilibrium mixture, with isomer ratio (I)/(II) ~ 5/4. A freshly prepared solution of Ph_2SbCl_2(dpm) in C_6D_6 shows only the presence of the *trans*-diphenyl isomer. Heating for 1—2 min at 80° or standing at room temperature for 24 h results in the formation of an equilibrium mixture with isomer ratio (I)/(II) ~ 2/3. Figure 1 illustrates the course of the isomerization process in each solvent.

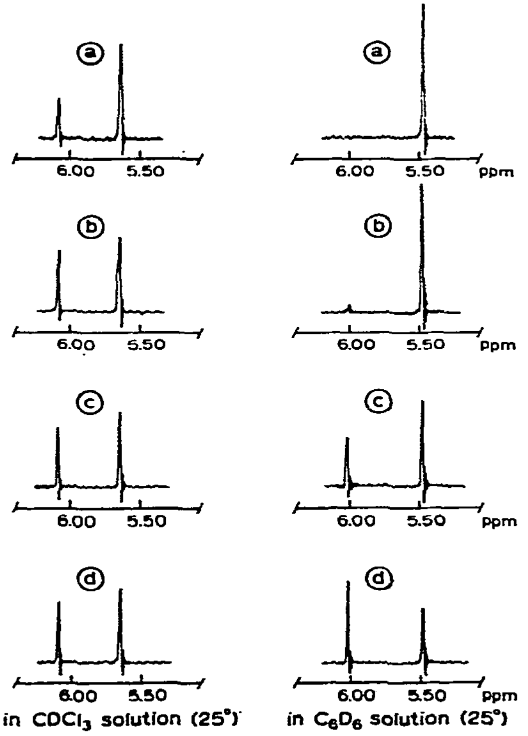


Fig. 1.—CH= PMR spectra of Ph_2SbCl_2(dpm) in $CDCl_3$ and C_6D_6 solution at 25°: (a) 10 min; (b) 1 h; (c) 8 h and (d) 24 h after dissolution.

Analogous results have been obtained for Ph_2SbCl_2(pac), where in $CDCl_3$ at 25° the equilibrium ratio of (I) and (II) (R = Me; R′= t-Bu), which is reached within 0.5 h, has a value of 2/1. A freshly prepared solution in C_6D_6 (25°) shows PMR signals due to configuration (I) only, equilibrium, (I)/(II) ~ 6/5, being reached in 5 h.

The exclusive presence of (I) in freshly prepared benzene solutions (25°) of Ph_2SbCl_2(dpm) and Ph_2SbCl_2(pac) may be taken to indicate that in the crystalline state both compounds adopt the *trans*-diphenyl structure (I). This is supported by the observation that the PMR spectrum of a freshly prepared benzene solution of Ph_2SbCl_2(acac), (for which configuration (I) in the solid state has been established by X-ray crystallography[5,6]) only shows the high-field signals of the *trans*-diphenyl isomer.

Although the presence of the *cis*-dichloro configuration (I) is precluded for steric reasons, the corresponding 2,2′-biphenylylene derivatives do display geometric isomerism. Configurations (III) and (IV) are easily assigned based on integration of PMR peak intensities and on the argument that the signal for the β-diketonate alkyl substituent located in the region above the 2,2′-biphenylylene group (R′ in IV) will appear at substantially higher field as a result of the diamagnetic anisotropy of the 2,2′-biphenylylene ring system.

In a freshly prepared C_6D_6 solution of 2,2′-biphenylylene$SbCl_2$(dpm) and 2,2′-biphenylylene$SbCl_2$(acac) only configuration (III) is present, indicating that both compounds adopt the *trans*-dichloro structure in the solid state. In benzene, and more rapidly in chloroform, an equilibrium mixture of (III) and (IV) is formed (*cf.* Table 1). In both solvents isomerization is extremely rapid at 80°.

Aged solutions of 2,2′-biphenylylene$SbCl_2$(pac) show three –CH=, three Me and three t-Bu proton signals, indicating the presence of three isomers in solution [(III), (IVA) (R′=Me and R=t-Bu) and (IVB) (R′=t-Bu and R=Me)] (*cf.* Table 1). The observation that a freshly prepared C_6D_6 solution shows only PMR signals due to configuration (III) may be taken as a proof that (III) represents the solid state structure.

For all organoantimony(V) β-diketonates studied the rate of isomerization increases rapidly with temperature, but the position of the equilibrium is rather insensitive to temperature changes. Isomerization always proceeds much faster in $CDCl_3$ than in C_6D_6 solution. Traces of acids such as the protonated form of the ligand or acetic acid enhance the isomerization rate. The PMR data indicate that specific solvation must be an important factor in determining the equilibrium ratios of (I) and (II) and of (III) and (IV).

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REFERENCES

1 H.A. Meinema, A. Mackor and J.G. Noltes, *J. Organometal. Chem.*, 37 (1972) 285.
2 N. Nishii, Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 703.
3 H.A. Meinema and J.G. Noltes, *Abstr. Vth Intern. Conf. Organometal. Chem. Moscow, Vol. I,* 1971, p. 197.
4 D. Hellwinkel and M. Bach, *J. Organometal. Chem.*, 17 (1969) 389.
5 J. Kroon, J.B. Hulscher and A.F. Peerdeman, *J. Organometal. Chem.*, 37 (1972) 297.
6 K.Onuma, Y. Kai and N. Kasai, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 143.