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Preliminary communication

Investigations on organoantimony compounds
XII*. Influence of stereochemistry on β-diketonate ligand exchange reactions in dichlorodiorganoantimony(V) β-diketonates. "*Cis*" and "*trans*" effects in octahedral main group organometallic complexes

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The stereochemistry of hexacoordinate dichlorodiorganoantimony(V) β-diketonates has been the subject of considerable recent interest. PMR spectroscopic studies have revealed that whereas in the crystalline state only one configuration is present, dichlorodiarylantimony(V) β-diketonates in solution isomerize to form an equilibrium mixture of two slowly interchanging geometrical isomers[2–4]. In order to obtain information concerning the nature of the isomerization process, we have studied ligand exchange reactions of the various isomeric β-diketonate complexes with free β-diketones.

The course of the ligand exchange process in the systems $Ph_2SbCl_2(Acac)$ + HDpm (dipivaloylmethane) and $Ph_2SbCl_2(Dpm)$ + HAcac (acetylacetone) in either chloroform or benzene solution has been followed by PMR spectroscopy. For dichlorodiphenylantimony β-diketonates in solution, the "high-field" set of β-diketonate ligand proton signals belongs to the *trans*-diphenyl isomer and the "low-field" set to the *trans*-dichloro *cis*-diphenyl isomer[2,3]. The results, illustrated in Fig. 1, clearly demonstrate that initially a fast ligand exchange process takes place exclusively between the *trans*-diphenyl isomer and the free ligand. Surprisingly, the *trans*-dichloro isomer appears to be inert. After a longer period, the occurrence of a much slower isomerization process leads to the formation of a mixture of isomers, as shown by a decrease of the amount of initially present *trans*-dichloro isomer and the appearance of the *trans*-dichloro isomer of the β-diketonate ligand exchanged product. The results, which are summarized in Scheme 1, clearly reveal the influence of the stereochemical position of the phenyl groups on the lability of the β-diketonate ligand. Our results suggest that a *trans*-position of the organic ligands in dichlorodiorganoantimony β-diketonates is accompanied by a weakened antimony β-diketonate ligand interaction, whereas a *cis*-position of the organic ligands stabilizes the antimony β-diketonate interaction to such an extent that ligand exchange does not occur.

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[*] For Part XI see ref. 1.

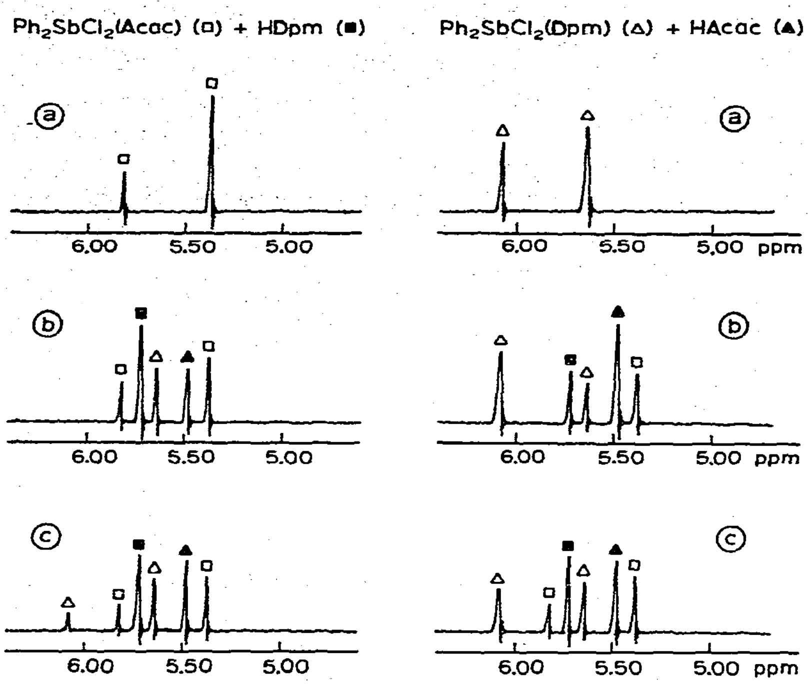
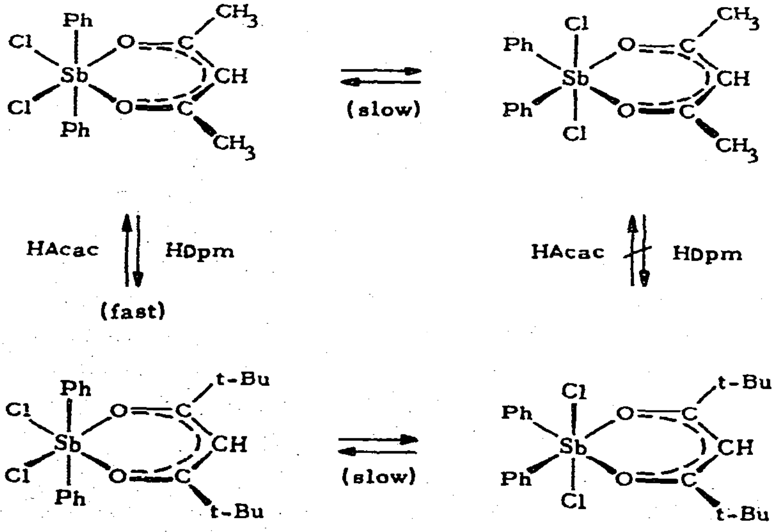


Fig. 1. –CH = PMR spectra of mixtures of Ph_2SbCl_2Acac □ + HDpm ■, and of Ph_2SbCl_2Dpm △ + HAcac ▲ in $CDCl_3$ solution at 25°: (a) equilibrium mixture of the two isomers of either Ph_2SbCl_2Acac or Ph_2SbCl_2Dpm; (b) 10 min after addition of HDpm or HAcac; (c) after 1 h.

Scheme 1



In order to further explore this apparent influence of stereochemistry of the complex on the occurrence of ligand exchange, we have investigated β-diketonate ligand exchange reactions with $Me_2SbCl_2(Acac)$, which is known to possess exclusively the *trans*-dimethyl configuration[2,5], and with 2,2'-biphenylylene-$SbCl_2$ β-diketonates, which are forced into a *cis*-diaryl configuration[3].

Upon addition of dipivaloylmethane (HDpm) to a solution of $Me_2SbCl_2(Acac)$ in $CDCl_3$, β-diketonate ligand exchange occurs instantaneously, resulting in the formation of an equilibrium mixture of $Me_2SbCl_2(Acac)$, $Me_2SbCl_2(Dpm)$, HAcac and HDpm. The reaction has been followed by PMR spectroscopy. (Chemical shift data in $CDCl_3$ (25°) are for $Me_2SbCl_2(Acac)$, δ(CH) 5.65; $\delta(C{-}CH_3)$ 2.20; $\delta(Sb{-}CH_3)$ 2.40 ppm and for $Me_2SbCl_2(Dpm)$, δ(CH) 5.96; δ(t-Bu) 1.18 and $\delta(Sb{-}CH_3)$ 2.32 ppm).

2,2'-Biphenylylene-$SbCl_2$-β-diketonates are present in solution as two slowly interchanging geometrical isomers. In freshly prepared solutions solely the *trans*-dichloro isomer is present which at room temperature slowly isomerizes to an equilibrium mixture of *trans*- and *cis*-dichloro isomers[3]. As shown in Fig. 2 for the system 2,2'-biphenylylene-$SbCl_2(Dpm)$ + HAcac in $CDCl_3$ isomerization normally proceeds in the presence of free β-diketone ligand. Significantly, neither of the two isomers undergoes ligand exchange. The results of a series of experiments are shown in Scheme 2.

Similarly, (2,2'-methylenediphenylene)antimonydichloro β-diketonates, which in solution occur only in the *trans*-dichloro configuration[6] fail to undergo ligand exchange. Our results suggest that the presence of the organic ligand in *trans*-positions is a

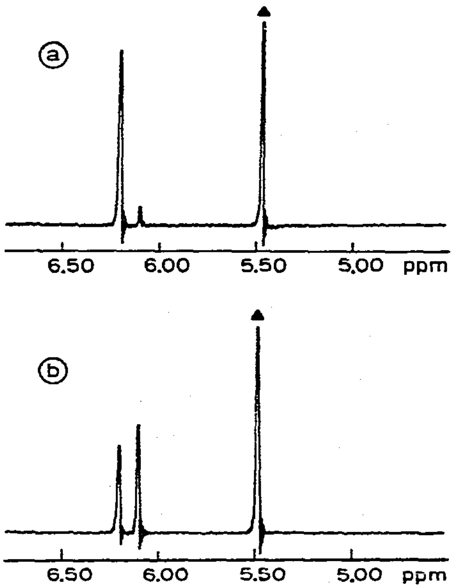
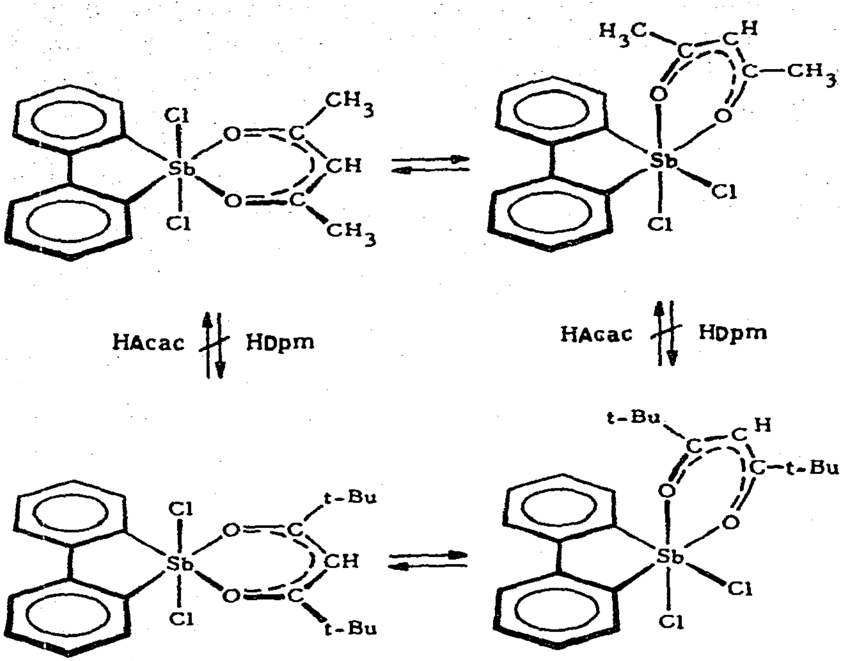


Fig. 2. –CH = PMR spectra of 2,2'-biphenylylene-$SbCl_2$Dpm + HAcac ▲ in $CDCl_3$ solution (25°): (a) 10 min after dissolution, (b) 2 min at 65°.

Scheme 2



prerequisite for ligand exchange to take place.

The present results are the first example of the influence of geometric configuration on ligand stabilization in octahedral main group organometallic complexes. In a recent communication Tobias[7] discussed the various factors involved in so-called "*cis*" and "*trans*" effects in square planar and octahedral metal complexes. However, at that time examples of d^{10} metal complexes of the type R_2MX_4 in which the groups R occupy *cis*-positions were not available. *Trans*- and *cis*-diorganodichloroantimony β-diketonates present an excellent model for studying the influence of metal-orbital hybridization on the strength of metal—ligand interaction. If it is assumed that ultimate *d* orbitals do not contribute to the antimony—ligand bonding in a major way we propose, in accordance with the model described by Tobias[7], that for *trans*-diphenyl Ph_2SbCl_2 β-diketonates two *sp*-hybridized orbitals of antimony are used for bonding of the phenyl groups. The two chlorine and two oxygen atoms in the equatorial plane are bound to antimony by σ orbitals of these atoms and the remaining two 5*p* orbitals of antimony, forming three-center four-electron bonds. In the *cis*-diphenyl *trans*-dichloro isomer we propose the two phenyl groups to be bound to antimony either by two 5*p* orbitals or by two sp^2 orbitals of antimony. The bonds to the β-diketonate ligand are then formed by three-center four-electron bonds using σ orbitals of oxygen and an antimony 5*s* or sp^2 orbital, whereas the two chlorine atoms are bound to antimony by a three-center four-electron bond involving an antimony 5*p* orbital.

While these models are extreme descriptions of the bonding, they are useful in pointing out that upon isomerization from *trans*-diphenyl to *cis*-diphenyl *trans*-dichloro Ph_2SbCl_2 β-diketonates the *s*-character in the antimony β-diketonate bonding increases, which might account for a stronger metal—ligand interaction in the latter isomers.

Various processes may be envisaged for the isomerization of dichlorodiaryl-antimony(V) β-diketonates such as (a) dissociation of a chloride anion to give a five coordinate intermediate, (b) complete dissociation of the β-diketonate ligand, (c) rupture of one Sb—O bond to give a five coordinate intermediate possessing a monodentate β-diketonate ligand, and (d) a twist mechanism involving isomerization without antimony—ligand bond breaking.

Chloride anion separation is very unlikely, as isomerizations occur even in the non-polar solvent benzene. Complete dissociation of the β-diketonate ligand may be ruled out since for the *cis*-diphenyl *trans*-dichloro isomers of Ph_2SbCl_2 β-diketonates and for the two isomeric forms of 2,2′-biphenylylene-$SbCl_2$ β-diketonates ligand exchange with free β-diketones does not occur under conditions where the isomerization process proceeds. A choice between a single Sb—O bond rupture mechanism and a twist mechanism cannot be made on the basis of presently available data. Our results indicate that if an Sb—O bond rupture is involved in the isomerization process, the reactivity of the intermediate pentacoordinate species depends very much on the mutual positions of the aryl groups. It is expected that the pentacoordinate species arising from the *trans*-dichloro isomers are thermodynamically more stable than their counterparts from the *trans*-diphenyl isomers, since the most covalently bonded groups are in equatorial positions[8]. In the hexacoordinated species the *trans*-diphenyl isomers are more stable[2,3]. Obviously, in the presence of free β-diketone, Sb—O bond rupture in *trans*-diphenyl Ph_2SbCl_2-β-diketonates results in a rapid ligand exchange process (*cf.* ref. 9) rather than isomerization, whereas Sb—O bond rupture for *cis*-diaryl isomers results either in isomerization or in recombination of the Sb—O bond.

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REFERENCES

1 F. Di Bianca, E. Rivarola, A.L. Spek, H.A. Meinema and J.G. Noltes, *J. Organometal. Chem.*, in the press.
2 H.A. Meinema, A. Mackor and J.G. Noltes, *J. Organometal. Chem.*, 37 (1972) 285.
3 H.A. Meinema and J.G. Noltes, *J. Organometal. Chem.*, 37 (1972) C31.
4 N. Nishii and R. Okawara, *J. Organometal. Chem.*, 38 (1972) 335.
5 R. Okawara, Y. Matsumura and N. Nishii, *Proc. IVth Int. Conf. Organometal. Chem., Bristol*, (1969) Z8.
6 H.A. Meinema and J.G. Noltes, unpublished results.
7 R.S. Tobias, *Inorg. Chem.*, 9 (1970) 1296.
8 E.L. Muetterties and R.A. Schunn, *Quart. Rev.*, 20 (1966) 245.
9 G.E. Glass and R.S. Tobias, *J. Organometal. Chem.*, 15 (1968) 481.