

**Preliminary communication**

---

***Cis-* and *trans*-influences in octahedral complexes of methyltin trihalides and tin tetrahalides with tertiary phosphines \***

**O.A. Reutov, V.S. Petrosyan, N.S. Yashina and E.I. Gefel**

*Department of Chemistry, Moscow State University, Moscow 119 899 (U.S.S.R.)*

(Received August 18th, 1987)

**Abstract**

By analysis of  ${}^1J({}^{119}\text{Sn}-{}^{31}\text{P})$  coupling constants for complexes of methyltin trihalides and tin tetrahalides with mono- and bi-dentate tertiary phosphines, it is proposed that strengthening of the Sn–P bonds occurs when the phosphine is situated in a *trans*-position to the most electron-donating substituent, and it is accompanied by a concomitant weakening of the *cis*-Sn–P bond.

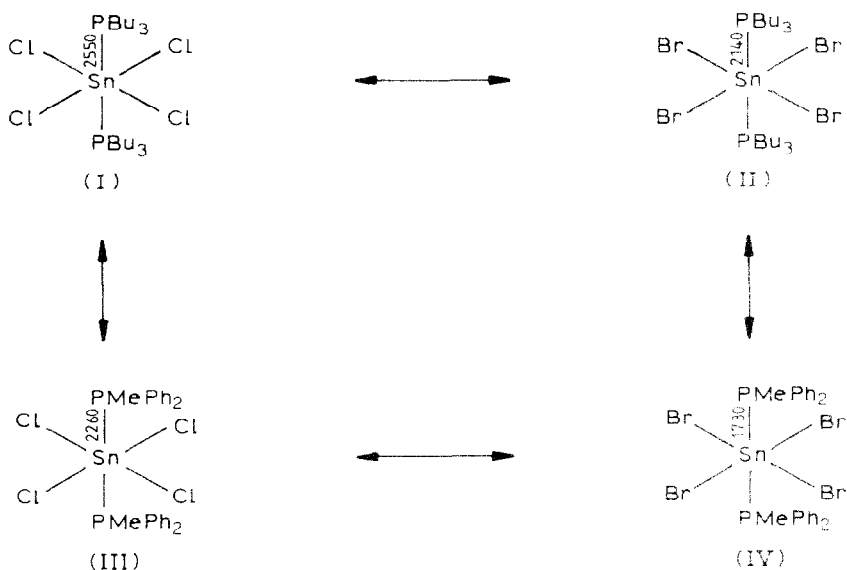
---

We have reported earlier [1,2] the results of our systematic studies of fifty coordination compounds of tin tetrahalides and methyltin trihalides with various mono- and bi-dentate phosphines by means of  ${}^{119}\text{Sn}$  and  ${}^{31}\text{P}$  NMR spectroscopy. In this paper, we analyse the  ${}^1J({}^{119}\text{Sn}-{}^{31}\text{P})$  spin–spin coupling constants for those complexes of tin tetrahalides and methyltin trihalides with tertiary phosphines in which the *cis*- and *trans*-influences demonstrated earlier for coordination compounds of tin(IV) with other types of ligands by means of X-ray analysis [3,4]) could be observed and separated with confidence.

Analysis of  ${}^1J({}^{119}\text{Sn}-{}^{31}\text{P})$  coupling constants for complexes of tin tetrahalides with monodentate tertiary phosphines (structures I–IV) demonstrates that substitution of chlorine atoms in I and III by bromine atoms (II and IV) lowers the  ${}^1J({}^{119}\text{Sn}-{}^{31}\text{P})$  values. These changes are due to the *cis*-influences of the halogens, lowering the *s*-character of hybrid orbitals and the covalency of tin–phosphorus bonds, which is consistent with data and conclusions for coordination compounds of mercury with phosphines [5]. In spite of the fact that additional experimental data are needed, we propose that higher  ${}^1J({}^{119}\text{Sn}-{}^{31}\text{P})$  values are indicative of shorter lengths and higher strengths of the tin–phosphorus bonds. The higher  ${}^1J({}^{119}\text{Sn}-{}^{31}\text{P})$  values for complexes I and II in comparison with complexes III and

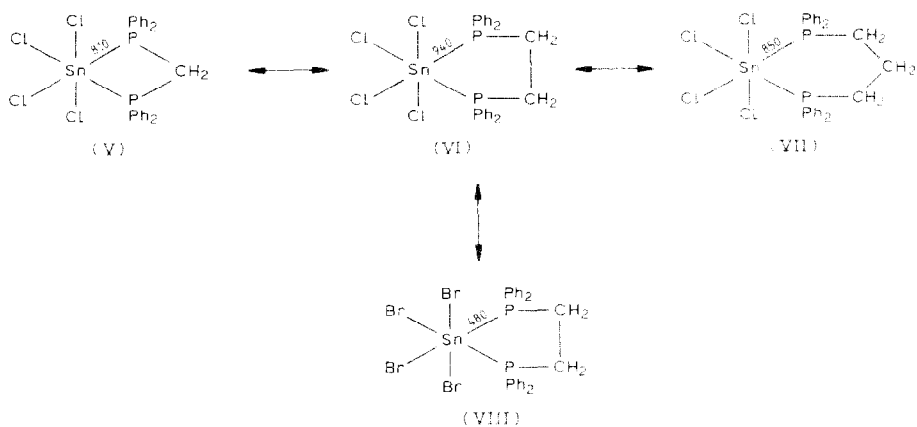
---

\* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.



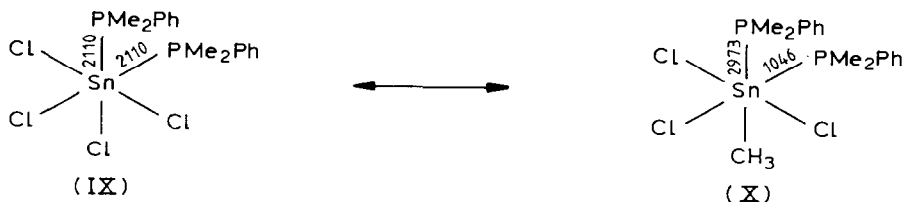
IV (in which the electron-donating ability of the phosphines is lower), in our opinion, provides additional evidence in favour of this assumption.

Analogous trends in the  $^1J(^{119}\text{Sn}-^{31}\text{P})$  coupling constants for complexes of tin tetrahalides with bidentate tertiary phosphines (structures V–VIII) are observed, however, geometrical factors have to be considered for these more strained octahedral complexes.

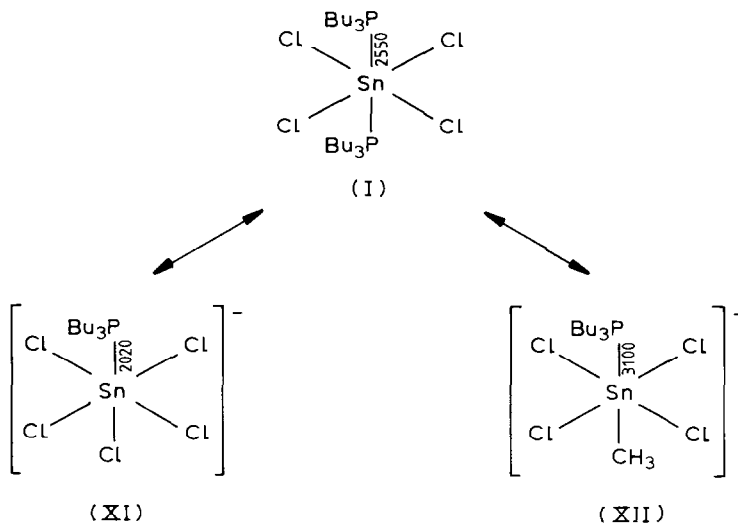


On going from the tin tetrahalide complexes to the coordination compounds of methyltin trihalides, one can also see manifestations of *cis*- and *trans*-influences. For example, substitution of one chlorine atom in complex IX by a methyl group (in X) brings a substantial increase in the  $^1J(^{119}\text{Sn}-^{31}\text{P}_{\text{trans}})$  value and a large decrease in  $^1J(^{119}\text{Sn}-^{31}\text{P}_{\text{cis}})$ . These changes can be explained in terms of *trans*-strengthening and *cis*-weakening of the tin–phosphorus bonds. In so doing, it is evident that the

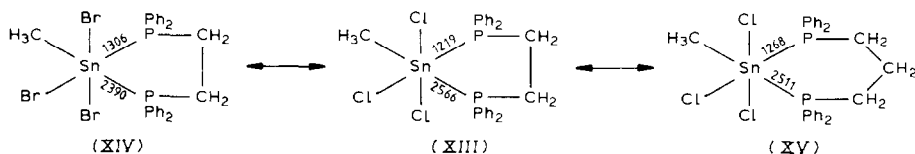
*cis*-weakening can even exceed the *trans*-strengthening.



Substitution of one phosphine in I by chlorine (XI) leads to a decrease in  $^1J(^{119}\text{Sn}\text{--}^{31}\text{P})$ , whereas appropriate substitution by an electron-donating methyl group (XII) gives an inversion in  $^1J(^{119}\text{Sn}\text{--}^{31}\text{P})$ .



In the case of coordination compounds of methyltin trihalides with bidentate phosphines, the geometrical factors play a more important role than for the corresponding complexes of tin tetrahalides. For example,  $^1J(^{119}\text{Sn}\text{--}^{31}\text{P})$  values for the *trans*-Sn-P bonds (in relation to the CH<sub>3</sub> group) in XIII-XV are always substantially higher than for the *cis*-bonds. Moreover  $^1J(^{119}\text{Sn}\text{--}^{31}\text{P})$  coupling constants for XIII and XIV exceed the spin-spin coupling values for the analogous complexes of tin tetrahalides (cf. VI and VIII).



Thus, analysis of  $^1J(^{119}\text{Sn}\text{--}^{31}\text{P})$  coupling constants for the octahedral complexes of methyltin trihalides and tin tetrahalides with mono- and bi-dentate tertiary phosphines suggests that, in these coordination compounds, the substitution of one ligand by a more electronegative one brings about *trans*-strengthening and *cis*-weakening of bonds, if there are no substantial distortions of the octahedral structures of the complexes.

**References**

- 1 N.S. Yashina, E.I. Gefel, V.S. Petrosyan and O.A. Reutov, Dokl. Akad. Nauk SSSR, 281 (1985) 1387; 283 (1985) 654; Koord. khim., 11 (1985) 1639; Vestn. Mosk. Univ., ser. khim., 26 (1985) 90.
- 2 V.S. Petrosyan, N.S. Yashina and E.I. Gefel, Silicon, Germanium, Tin and Lead Compounds, 9 (1986) 213.
- 3 L.A. Aslanov, V.M. Ionov, W.M. Attia, A.B. Permin and V.S. Petrosyan, J. Organomet. Chem., 144 (1978) 39.
- 4 O.A. Reutov, L.A. Aslanov, V.S. Petrosyan, V.I. Nefedov and Yu.A. Buslaev, Koord. Khim., 8 (1982) 1161.
- 5 H.B. Burgi, R.W. Kunz and P.S. Pregosin, Inorg. Chem., 19 (1980) 3707.