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Metal Ion-Aromatic Complexes. XIV. Structural Evidence for the $Sn_2Cl_2^{2+}$ Species in Ar · SnCl(AlCl$_4$)

Sir:

We report here the surprising and previously unknown dimer, $Sn_2Cl_2^{2+}$, in Ar · SnCl(AlCl$_4$) where Ar = C_6H_6 (I) or *p*-xylene (II). These complexes also include an axially symmetric aromatic–Sn(II) bond.

In an earlier communication[1] we reported the structure of $C_6H_6 \cdot Sn(AlCl_4)_2(C_6H_6)$ which consists of a pentagonal-bipyramidal Sn(II) entity (6Cl, 1C$_6$H$_6$) wherein the metal ion lies along the sixfold axis of the benzene ring. In this structure the second aromatic molecule is not coordinated to the metal but resides in a cleft in the Sn(AlCl$_4$)$_2$ chain. Very recently we have completed the crystal structure determination of $C_6H_6 \cdot Pb(AlCl_4)_2(C_6H_6)$[2] which is structurally similar to the analogous Sn compound.

For a variety of experimental reasons we have been unsuccessful in isolating crystalline aromatic Sn(II) complexes of the type Ar · Sn(AlCl$_4$)$_2$ under a wide variety of experimental conditions. However, we have succeeded in isolating interesting compounds of the type Ar · SnCl(AlCl$_4$) which contain a $Sn_2Cl_2^{2+}$ moiety. We report on two of these structures at this time.

Ar · SnCl(AlCl$_4$) was prepared by placing purified SnCl$_2$ (0.044 mol) and AlCl$_3$ (0.075 mol) in one arm of an "H" tube.[3] Dry, degassed aromatic was sublimed into the system and allowed to come to room temperature and then heated to ~50° for 1 hr. While the reaction was still warm it was filtered *in vacuo* and the excess solvent removed by immersion of one arm in a liquid nitrogen trap until crystals formed. The crystals could be repeatedly recrystallized from benzene.

Compounds I and II exhibited the following crystal data.

$C_6H_6 \cdot$SnCl(AlCl$_4$) (I): $P2_1/n$; $Z = 4$; $\rho_c = 2.02$ g cm^{-3}, $\rho_o = 2.1$ g cm^{-3}; $a = 19.624$ (6) Å, $b = 9.531$ (1) Å, $c = 7.099$ (1) Å; $\beta = 93.65$ (1)°; number of observations used in solution and refinement of structure = 2446; $\mu = 27.3$ cm^{-1}; crystal size 0.33 × 0.43 × 0.70 mm; transmission coefficient variation,[4] 0.47–0.50; $\lambda = 0.71068$ Å.

***p*-$C_8H_{10} \cdot$SnCl(AlCl$_4$) (II):** $I2/c$; $Z = 8$; $\rho_c = 1.86$ g cm^{-3}, $\rho_o \sim 1.7$ g cm^{-3}; $a = 18.970$ (7) Å, $b = 10.903$ (4) Å, $c = 15.470$ (4) Å; $\beta = 107.33$ (1)°; number of observations used in solution and refinement of structure = 2476; $\mu = 25.5$ cm^{-1}; crystal size 0.30 × 0.15 × 0.60 mm; transmission coefficient variation,[4] 0.47–0.71; $\lambda = 0.71068$ Å.

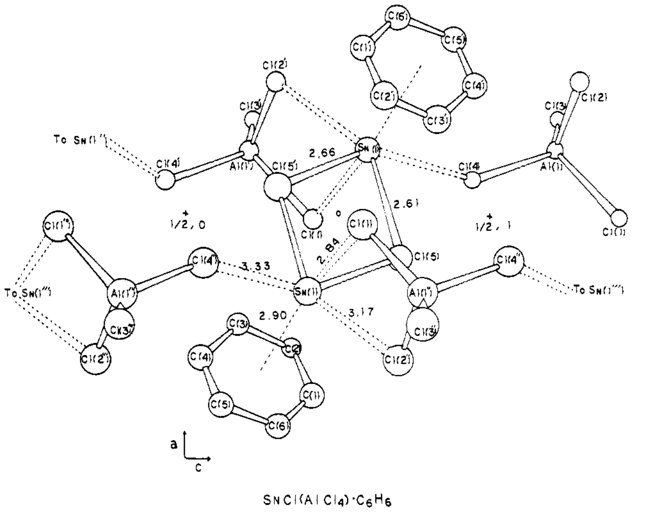

Figure 1. Perspective view of the structure of $C_6H_6 \cdot$SnCl(AlCl$_4$) down the *b* axis. The $Sn_2Cl_2^{2+}$ dimer is composed of atoms Sn(1), Cl(5), Cl(5′), and Sn(1′). The Sn(AlCl$_4$)$^+$ chain goes from Sn(1′′′) at the lower far left through Sn(1) to Sn(1′′′) at the far right. Esd's for interatomic distances are Sn–Cl ±0.005 Å, Al–Cl ±0.007 Å, and Sn–C ±0.02 Å. The angle between the normal to the ring and Sn center of the ring is 7 ± 1°.

Single crystal intensity data were collected on a Picker automated diffractometer by standard techniques.[5] The structures were solved by standard heavy atom techniques and refined by full-matrix least squares.[5] I refined to a final conventional *R* of 0.070 and II to a final *R* of 0.049. Although the crystals of I and II are not isomorphous, the structures are quite similar in spite of the differing steric requirements of the aromatic moieties. The most prominent and unexpected feature of the structures is the presence of the lozenge-shaped dimer (Figure 1) with Sn–Cl distances of ~2.6 Å. These structures are the first reports of such species which may be formally considered as $Sn_2Cl_2^{2+}$ units. The coordination polyhedron of each Sn is completed by three longer Sn–Cl interactions ranging from 2.8 to 3.3 Å and an axially symmetric Sn–aromatic bond to produce a distorted octahedron (5Cl, 1C$_6$H$_6$) (Figure 2). One might ask the question whether the dimer is indeed the structural building block as we maintain, since the Sn–Cl distances vary between 2.61 and 3.33 Å in these two structures. We reason as follows. (1) In I the Sn–Cl lozenge distances are 2.61 and 2.66 Å with the next shortest distance at 2.84 Å (Sn–Cl axial), and in II the lozenge Sn–Cl distances are 2.62 and 2.68 Å with the next shortest Sn–Cl distance at 2.92 Å. Hence, the Sn–Cl distances within the dimer are always the shortest, and the next shortest Sn–Cl distance is at least 0.18 Å longer. Furthermore, the next shortest distances are associated with chlorine atoms bound to AlCl$_4^-$ units and are expected to be weaker. (2) These 2.61–2.68-Å bridging Sn–Cl distances are essentially

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(3) R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.*, 88, 1877 (1966).

(4) Absorption corrections were made with a local variation of program GONO9 originally written by W. C. Hamilton, Brookhaven National Laboratory, Upton, N. Y.

(5) For data collection methods, weighting scheme, computer programs, and source of scattering factors, see R. L. Girling and E. L. Amma, *Inorg. Chem.*, 10, 335 (1971). Data for I and II were collected on a Picker card-controlled diffractometer. Listings of structure factors, coordinates, and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-2135. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

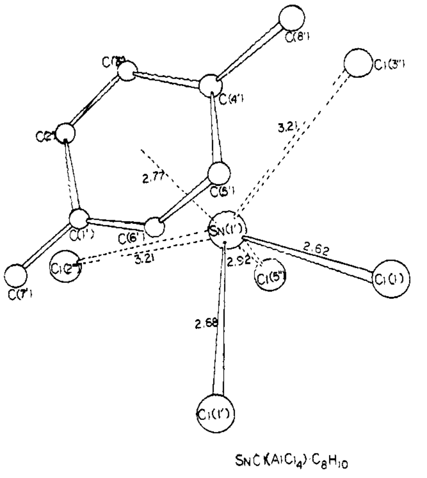

Figure 2. View of the structure of *p*-xylene·SnCl(AlCl$_4$) showing the immediate environment about Sn(II) including the axially symmetric Sn–Ar interaction. Esd's are all approximately three-quarters of those in Figure 1. The angle between the normal to the ring and the Sn center of the ring is 8 ± 1°. For both compounds the rings are planar well within experimental error.

the same length as the shortest Sn–Cl distance found in anhydrous stannous chloride[6] (2.66 Å). Anhydrous stannous chloride may be described as pyramidal Sn(II) forming a chlorine-bridged chain structure. In addition, the Sn–Cl distances in $SnCl_2 \cdot 2H_2O$[7] are 2.59 Å while those in the $SnCl_3^-$ ion are 2.63 and 2.54 Å.[8] (3) The Sn–Cl distances in $C_6H_6 \cdot Sn(AlCl_4)_2(C_6H_6)$[1] are all 2.77 Å or greater. As a consequence, we feel that the 2.61–2.68-Å distance represents a more substantial Sn–Cl bond than any other in the Ar·SnCl(AlCl$_4$) structures and is an important structural feature of these compounds.

The phase diagram of the $SnCl_2 \cdot AlCl_3$[9] system indicates a compound of the composition SnCl(AlCl$_4$). It may well be that the $Sn_2Cl_2^{2+}$ unit is a structural feature of this compound also.

It is to be noted that the Sn–aromatic interaction is essentially axially symmetric and along with $C_6H_6 \cdot Sn(AlCl_4)_2(C_6H_6)$ represents the only known cases of axially symmetric complexes between post-transition metal ions and aromatic moieties.

The overall crystal structure might be described as made up of $(SnAlCl_4)_n$ chains (Figure 1) in which the $AlCl_4^-$ tetrahedra are bonded together by Sn–Cl bonds, Sn–Cl(1), Cl(2''), Cl(4'''). These chains are in turn interconnected *via* the formation of the dimers mentioned above.

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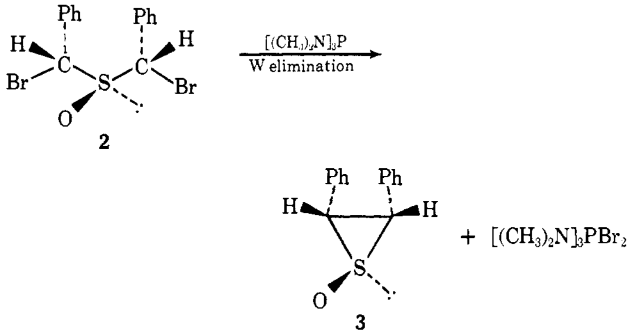
Stereochemistry of 1,3 Eliminations from Dibromo Sulfoxides

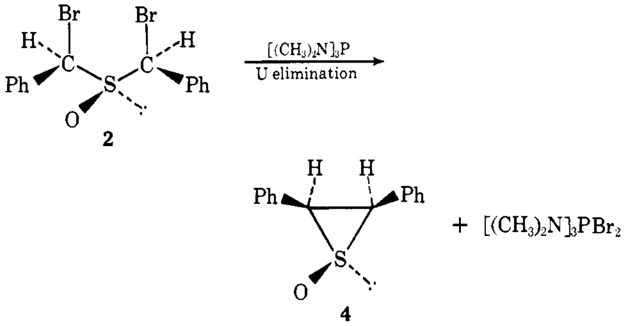
Sir:

In general, the 1,3-elimination reactions[1] studied to date have exhibited preferences for W eliminations (inversion at each center)[2–7] and exo sickle eliminations (retention at the carbon atom bearing the electrofugal group and inversion at the carbon bearing the nucleofugal group).[8–10] In the cases of the W eliminations, the systems studied were either rigid polycyclic systems in which the groups were held in the W conformations[4,6,7] or acyclic systems in which the stereochemical results could have been interpreted as being U eliminations[1] (retention at each center) rather than W eliminations. We wish to report a W-1,3 debromination of the dibromo sulfoxides **1** and **2** with hexamethylphosphorictriamide, $(Me_2N)_3P$, wherein the U elimination can be excluded.

Loss of bromine from *meso*-**2** with double inversion would give the *cis,anti*-episulfoxide **3**, while loss with double retention would result in the formation of the *cis,syn*-episulfoxide **4**.



2 → **3**



2 → **4**

The sulfoxides **1** and **2** were synthesized in a manner analogous to that reported earlier for **1**.[11] Bromination (Br_2–CCl_4) of dibenzyl sulfide followed by oxidation of the crude bis(α-bromobenzyl) sulfide in methylene chloride at 0° with 1 equiv of *m*-chloroperbenzoic acid

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