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Can One σ^* -Antibonding Orbital Interact with Six Electrons of Lewis Bases? Analysis of a Multiply Interacting σ^* Orbital

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S Supporting Information

ABSTRACT: One empty orbital normally interacts with one lone pair of a Lewis base to form one dative bond, and we do not know any example where one antibonding orbital interacts with more than two lone pairs of Lewis bases. We wish to report here the first example which is beyond our aforementioned common knowledge of dative bonds. We synthesized heptacoordinate tris{(o-diphenylphosphino)phenyl}tin fluoride and found that three lone pairs of phosphine donors equivalently interact with the antibonding $\sigma^*(Sn-F)$ orbital of the Sn center. The nature of this "multiply interacting σ^* orbital" was theoretically elucidated by DFT calculations.

In general, one donor orbital interacts with one acceptor orbital to form one donor-acceptor bond. Compounds of heavier group 14 elements described as EX_4 (E = Si, Ge, Sn) are known to serve as Lewis acids because its $\sigma^*(E-X)$ orbital can interact with a lone pair of Lewis bases.¹⁻¹⁵ In such a compound, one $\sigma^*(E-X)$ orbital interacts with one lone pair of L to form one $L \rightarrow E$ dative bond, as mentioned above. For instance, silane and germane compounds containing three bidentate LX-type ligands have a heptacoordinate structure, as shown in type I in Scheme 1.⁵ In this structure, three dative $L \rightarrow E$ bonds (L = N; E =

Scheme 1. Reaction of EX_4 (E = Si, Ge, Sn) with Lewis Base(s) and Representative Coordination Patterns of Neutral Heptacoordinate Compounds of Group 14 Elements



Si, Ge) are formed at the position trans to the three covalent E-Xbonds, in which one lone pair of L interacts with one E–X σ^* antibonding orbital. In addition, heptacoordinate silane, germane, and stannane compounds with different types of chelating ligands, such as tetradentate XL₃-type ligands (type II in Scheme 1), have been reported. In this structure, the $L \rightarrow E$



dative bonds are formed at the position trans to the three E-X covalent bonds.¹¹⁻¹³ In this case also, one lone pair orbital interacts with one σ^* -antibonding orbital of the E–X bond in this type II compound.

However, there is no example where one $\sigma^*(E-X)$ orbital interacts with more than one lone pair, and the presence of such a "multiply interacting σ^* orbital" has not been reported yet, to the best of our knowledge. In this paper, we wish to report a novel structure for the heptacoordinate stannane complex, $\{o-(Ph_2P) C_6H_4$ $\{$ _3Sn(F) (1a), containing three (*o*-diphenylphosphino)phenyl moieties and a fluoride on the Sn atom. In 1a, one $\sigma^*(Sn-F)$ orbital interacts with three lone pair orbitals of three phosphines to form three donor-acceptor bonds.



The crystal structure of 1a was determined by X-ray diffraction (XRD) using a single crystal obtained from a saturated dichloromethane solution of 1a. The structure analysis showed that 1a has a C_3 -symmetrical structure with three equivalent interactions between the P atoms and the Sn center (Figure 1). The Sn–C bond distance is 2.141(5) Å, which is considered as a



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Figure 1. XRD structure of **1a** with thermal ellipsoids set at 40% probability. H atoms and phenyl groups, except the for ipso carbons, are omitted for clarity.

typical single Sn–C σ –bond.¹⁸ The sum of the three C–Sn–C angles is $358.23(7)^\circ$; therefore, three ipso carbons and the Sn atom are nearly in one plane. The Sn–P distance (3.3660(14) Å)is considerably longer than the sum of the covalent radii (2.46 Å)¹⁸ but significantly shorter than the sum of the van der Waals radii (4.20 Å),¹⁹ strongly indicating the presence of some bonding interactions between the P and Sn atoms. In addition, the Sn-P distance is only slightly longer than that of Bourrisou's compound bearing the same $\{(o-Ph_2P)C_6H_4\}$ Sn moiety (i.e., 3.125(4) Å in {(o-Ph₂P)C₆H₄}SnPh₂Cl), in which a dative P \rightarrow Sn interaction was well established.¹⁶ Further, the moderately longer Sn–F distance (1.985(5) Å) of 1a in comparison to that of Ar₃SnF $(1.961-1.972 \text{ Å})^{20,21}$ is consistent with the suggestion that the Sn-F bond is weakened by the presence of the Sn-P bonding interactions. On the basis of these geometrical features,²² it is concluded that three Sn-P bonds are formed by the interaction between the lone pairs of the phosphine moieties and the antibonding orbital of the Sn-F bond (Figure 2), which will be discussed below in detail.



Figure 2. Three P \rightarrow Sn interactions in **1a** between one $\sigma^*(Sn-F)$ orbital and one lone pair of each P atom.

Although the ¹¹⁹Sn{¹H} spectrum of 1a could not be obtained because of its poor solubility, the ³¹P{¹H} NMR spectrum at ambient temperature showed only one doublet at 1.8 ppm (² J_{P-F} = 28.3 Hz), and the ¹⁹F{¹H} NMR spectrum showed one quartet at -198.3 ppm (² J_{P-F} = 28.3 Hz) (Figure S1 in the Supporting Information). At -110 °C, one broad singlet was observed at 1.2 ppm ($w_{1/2}$ = 50.2 Hz) in the ³¹P{¹H} NMR spectrum, and a broad singlet ($w_{1/2}$ = 62.2 Hz) was observed at -207.7 ppm in the ¹⁹F{¹H} NMR spectrum. Although the origin of the signal broadening is still unclear, these spectral data may indicate, especially at low temperature, the presence of an equilibrium including other isomers, which is discussed in the Supporting Information (see page 22).

Compound 1a showed an unprecedented structure caused by the three P dative bonds to the $\sigma^*(Sn-F)$ orbital. To obtain insight into the role of the highly polar Sn–F bond, the XRD structure of $\{o - (Ph_2P)C_6H_4\}_3Sn(H)^{17}$ with a more covalent Sn–H bond was analyzed. The structure was named 2b, because it was found to have a heptacoordinate structure different from that of 1a. In 2b, although the three phosphines interact with the Sn, they are not located at the position trans to the Sn–H bond but at the positions trans to the ipso carbons of the phenylene moieties (Figure 3). The three Sn–C_{ipso} distances are



Figure 3. XRD structure of **2b** with thermal ellipsoids set at 40% probability. H atoms, except for a hydride, and phenyl groups, except for the ipso carbons, are omitted for clarity.

comparable (2.150(2), 2.150(2), and 2.152(2) Å), and the three C–Sn–C angles are similar, ranging from 103.09(7) to 108.04(7)°, indicating that **2b** has a pseudo- C_3 axis that contains the Sn–H bond. The Sn–P distances of **2b** (3.3257(10)–3.4141(9) Å) are considerably shorter than the sum of the van der Waals radii (4.20 Å), indicating the presence of the P \rightarrow Sn interactions. The reason for the difference of the phosphine positions from those for **1a** is attributed to the higher antibonding orbital energy of the Sn–H bond relative to that of the Sn–F bond, as discussed below for the DFT calculations.

The variable-temperature ${}^{31}P{}^{1}H$ NMR spectrum of **2b** supports that the structure determined by the XRD study is retained in a solution. A sharp singlet without spin-spin coupling was observed at -4.4 ppm at ambient temperature and the signal moved slightly to -5.4 ppm at -80 °C.

To better understand these compounds, **1a** and **2b** were investigated by density functional theory (DFT) with the M06 functional²³ (see page 9 in the Supporting Information for computational details). The optimized structures of **1a** and **2b** (Figure 4a,d) agree with the experimental structures (Table S5 in the Supporting Information). For better comparison, we also optimized **1b** and **2a** with structures similar to those of **2b** and **1a**, respectively (Figure 4b,c). As shown in Figure 4, **1a** is more stable than **1b**, while **2b** is more stable than **2a**. These relative stabilities are consistent with the experimental results; {o-(Ph₂P)C₆H₄}₃Sn(F) has the **1a** structure and {o-(Ph₂P)-C₆H₄}₃Sn(H) has the **2b** structure. The charge-transfer (CT) stabilization energy was analyzed by the second-order



Figure 4. Optimized structures of the Sn compounds 1 and 2 with forms a and b at the M06 level of theory: (a) 1a; (b) 1b; (c) 2a; (d) 2b. Hydrogen atoms and phenyl groups (except ipso carbons) are omitted for clarity. The Gibbs energy is provided below the compound as a relative value.

perturbation with the natural bond orbitals (NBOs). In 1a, the lone pair of phosphine LP(P) interacts with the outside part of the $\sigma^*(Sn-F)$ molecular orbital (MO), as shown in Figure 5a,



Figure 5. Intramolecular charge-transfer interactions of the lone pair of the phosphine with the σ antibonding MOs of Sn–F and Sn–C bonds: (a) **1a** and **2a**; (b) **1b** and **2b**.

because the phosphine is located trans to the F atom. This interaction corresponds to the LP(P)– $\sigma^*(Sn-F)$ CT, and its stabilization energy in 1a was estimated as follows: 7.54 (P = P1), 8.11 (P = P2), 7.84 kcal/mol (P = P3). In 1b, the LP(P) interacts with Sn sp³ orbital, which forms the LP(P)– $\sigma^*(Sn-C)$ CT, as shown in Figure 4b. The stabilization energy was estimated to be 2.76 (P = P1), 2.78 (P = P2), 2.76 kcal/mol (P = P3). The sum of the LP(P)– $\sigma^*(Sn-C)$ stabilization energies is considerably smaller than that of LP(P)– $\sigma^*(Sn-F)$ in 1a by 15.19 kcal/mol.

It should be concluded that the larger stabilization energy due to the LP(P)- $\sigma^*(Sn-F)$ interaction in **1a** in comparison to that due to the LP(P)- $\sigma^*(Sn-C)$ interaction in **1b** is responsible for the greater stability of **1a** in comparison to that of **1b**, which arises from the differences in energy and space between the $\sigma^*(Sn-F)$ and the $\sigma^*(Sn-H)$ antibonding orbitals (vide infra).

The next question is why 2a is less stable than 2b, unlike the case for 1a. The LP(P)– $\sigma^*(Sn-C)$ interaction energy in 2b (11.09 kcal/mol) is much larger than the LP(P)– $\sigma^*(Sn-H)$ interaction energy in 2a (6.16 kcal/mol). Apparently, the LP(P)– $\sigma^*(Sn-C)$ stabilization energy is responsible for the greater stability of 2b in comparison to that of 2a. Because the LP(P)– $\sigma^*(Sn-H)$ stabilization energy (6.16 kcal/mol) in 2a is intrinsically much smaller than that of the LP(P)– $\sigma^*(Sn-F)$ interaction (23.49 kcal/mol) in 1a, the LP(P)– $\sigma^*(Sn-H)$ interaction does not contribute to the stabilization of 2a (see pages 11–21 in the Supporting Information for details).

The above discussion leads to the conclusion that the $LP(P)-\sigma^*(Sn-F)$ interaction plays an important role in providing the new heptacoordinate hypercoordinate structure of **1a**. Another factor in the formation of the unprecedented geometry **a** is the electrostatic interaction, which is discussed in the Supporting Information (see page 27). To elucidate the reason why $\{o-(Ph_2P)C_6H_4\}_3Sn(F)$ has such a new structure, **1a**, but $\{o-(Ph_2P)C_6H_4\}_3Sn(H)$ does not, we evaluated the $\sigma^*(Sn-F)$ MO energy in **1a** and $\sigma^*(Sn-H)$ MO energy in **2a**, because

LP(P)– $\sigma^*(Sn-X)$ CT (X = F, H) significantly depends on the $\sigma^*(Sn-X)$ MO energy.

Here, the $\sigma^*(Sn-X)$ MO energies in Ph₃SnX were calculated at the same level of theory, where the geometries were taken to be the same as those in **1a** and **2a** but the PPh₂ moieties were replaced by H atoms to avoid the effect of the phosphine lone pair on the $\sigma^*(Sn-X)$ MO energy. The $\sigma^*(Sn-H)$ MO energy (2.50 eV) was calculated to be much higher than the $\sigma^*(Sn-F)$ MO energy (-1.39 eV) (Figure S7 in the Supporting Information). Because of the lower $\sigma^*(Sn-F)$ MO energy, the LP(P)- $\sigma^*(Sn-F)$ CT is stronger than the LP(P)- $\sigma^*(Sn-H)$ CT. Also, the $\sigma^*(Sn-F)$ MO expands more toward the phosphine than does the $\sigma^*(Sn-H)$ MO, probably because the 5p orbital of Sn more contributes to the $\sigma^*(Sn-F)$ MO than to the $\sigma^*(Sn-H)$ MO. Remember that the covalency is greater in the Sn-H bond than in the Sn-F bond; see Figure S7 for the features of these MOs.

The $\sigma^*(\text{Sn}-\text{F})$ MO (-0.89 eV) in 1a is more unstable than that in Ph₃Sn(F) (-1.39 eV). Consistent with this result, the lone pair orbital energies of the phosphine moieties are lower in 1a (-5.93, -5.98, and -6.53 eV; Figure S5 (Supporting Information)) than those in { $(o-\text{Ph}_2\text{P})C_6\text{H}_5$ }, (-5.60, -5.66, and -6.15 eV; Figure S9 (Supporting Information)), in which the SnF moiety of 1a was removed and three H atoms were introduced instead of the SnF moiety (see pages 12 and 21 in the Supporting Information). All of the results indicate that the LP(P)- $\sigma^*(\text{Sn}-\text{F})$ interaction destabilizes the $\sigma^*(\text{Sn}-\text{F})$ MO and stabilizes the LP(P) MOs in 1a, which strongly supports the presence of an LP(P)- $\sigma^*(\text{Sn}-\text{F})$ CT interaction.

In summary, we report the first example of a "multiply interacting σ^* orbital": the three phosphine donors in 1a equivalently coordinate to the Sn center at the position trans to the Sn-F bond. This unusual bonding situation involving five atoms would be considered as a five-center-eight-electron bond. In contrast to the case for 1a, the hydride analogue, 2b, has a different heptacoordinate structure, in which all the phosphine atoms occupy the positions trans to the ipso carbons of the phenylene moieties and cis to the hydride ligand. The DFT calculations rationalize why 1a adopts the new structure. Strong $P \rightarrow Sn CT$ interactions are formed in 1a because of the presence of the $\sigma^*(Sn-F)$ MO at a low energy level; therefore, the three phosphine donors interact with the Sn center at the position trans to the Sn-F bond. On the other hand, in the hydride analogue, the $\sigma^*(Sn-H)$ MO exists at a high energy level because of the strong Sn-H covalent bonding. Therefore, the lone pairs of phosphine can not strongly interact with the $\sigma^*(Sn-H)$ MO but alternatively interact with the $\sigma^*(Sn-C)$ MO. The energy level of the $\sigma^*(Sn-X)$ MO is responsible for the presence of the "multiply interacting σ^* orbital".

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF and xyz files giving experimental details, spectroscopic characterization data, X-ray crystallographic data, and details of the quantum calculations. This material is available free of charge via the Internet at http://pubs. acs.org.

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Notes

The authors declare no competing financial interest.

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(22) One may expect that the high electronegativity (EN) of fluorine is responsible for wide C–Sn–C angles because it concentrates p character in the Sn–F bond (Bent's rule). However, the structural analysis of $\{o-(t-Bu)C_6H_4)\}_3Sn(F)$ using DFT calculations indicates that the formation of the isomer bearing wide C–Sn–C angles is difficult without the presence of CT interactions (see page 24 in the Supporting Information).

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