Tin Pincer Complexes

DOI: 10.1002/anie.201406283

A Bis-Sulfonyl O,C,O Aryl Pincer Ligand and its Tin(II) Complex: Synthesis, Structural Studies, and DFT Calculations**

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Abstract: *The efficiency of the deprotonated aryl bis-sulfone [2,6-{(p-tolyl)SO_2}$_2$$C_6H_3$]$^-$ as an O,C,O-coordinating pincer-type ligand was described. The bis-sulfone precursor was synthesized using a straightforward palladium-catalyzed cross-coupling reaction. As a result of directed ortho metalation (DoM) through sulfonyl groups, a selective lithiation of the aryl group was achieved and the corresponding carbanion was isolated and its structure determined by single-crystal X-ray diffraction analysis. A heteroleptic tin(II) complex has been prepared by a nucleophilic substitution reaction. Crystallographic analysis and DFT calculations indicate that the bis-sulfonyl moiety acts as a new O,C,O-coordinating pincer-type ligand with intramolecular S=O coordination to a tin(II) center. The cis form with the two nonbonded oxygen atoms of the sulfonyl groups on the same side is preferentially obtained.*

The chemistry of pincer ligands has been a continuously expanding area of research since their first report in 1976.[1] The main utilization of pincer ligands has been for the stabilization of transition-metal compounds and metal complexes of this type have found widespread use in catalysis and in various physical applications.[2] However, the use of Group 14 elements in this field has been less developed, despite the fact that organotin(IV) compounds bearing pincer ligands were synthesized at almost the same time.[3] Since then, a surge of interest has occurred thanks to the ability of these ligands to stabilize reactive species with low-valent tin centers.[4] In these compounds, the divalent center is stabilized by the coordination of the peripheral donor groups and by the rigid structure of the aryl group linked to the metal center. The stereoelectronic properties of these E,C,E pincer systems can be modified by changing the structure of the ligand backbone. This includes changes in the *ortho* substituents (including the length and the nature of the spacer between the C_{ipso} atom and the donor atom) and also in the nature of the donor atoms and the substituents in the backbone. In the series of reported tin compounds, *ortho* substituents have been mainly limited to amino-[4b,5] or alkoxymethylene[4f,6] moieties (Figure 1, A and B), or imino[4e] or phosphonate[4c,d,7] groups (C and D).

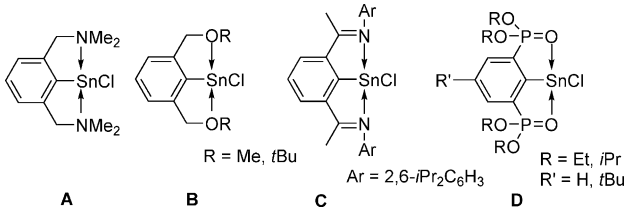

Figure 1. Examples of reported chlorostannylene pincer complexes.

Although S,C,S pincer ligands with soft S-donor sites have been widely used in pincer-based transition-metal chemistry,[2c] there is no example using low-valent Group 14 elements. Additionally, stabilization of a metallylene moiety by a sulfonyl group remains, to our knowledge, totally unexplored. With this in mind, the purpose of this study is to report an alternative approach employing a bis-sulfonyl aryl pincer ligand which will combine the donating ability of the pincer-type ligand and the steric bulk of the sulfonyl group. In this paper, we report the synthesis of a new monoanionic O,C,O pincer ligand [2,6-{(*p*-tolyl)SO_2}$_2$$C_6H_3$]$^-$ and its application in the synthesis of a heteroleptic stannylene complex. Structural investigations and DFT calculations were performed to gain further insight into the chelation mode of this pincer ligand.

We have developed a straightforward synthesis of the bis-sulfone ligand **1**[8,9] using a palladium-catalyzed cross-coupling reaction between 1,3-diiodobenzene and sodium *p*-toluenesulfinate (Scheme 1).[10]

The molecular structure of **1** was determined by single-crystal X-ray diffraction. Interestingly, depending on the solvent used for crystallization (THF or toluene), two rotameric forms, *trans* or *cis*, were obtained (see the Supporting Information). DFT calculations, performed using the M06 level of theory, show that the energy barrier of the *cis*→*trans* rotation is low (1.6 kcal mol^{-1}) and that the *trans* rotamer is the most stable (−4.6 kcal mol^{-1}). Considering both repulsion energies and electronic energies, this stabilization is due to the steric effect (see the Supporting Information). However, owing to the low energy barrier and to the small energy gap between *cis* and *trans* rotamers, a free rotation process can occur in the reaction mixture.

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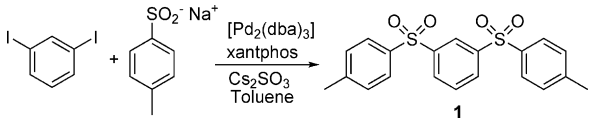
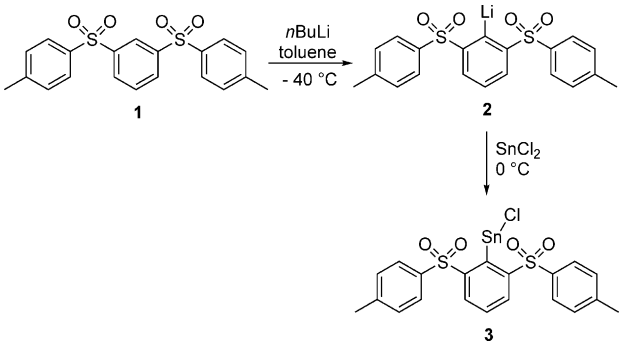
[**] We are grateful to the CNRS, UPS, and the ANR program (ANR-08-BLAN-0105-01) for financial support of this work.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406283.



Scheme 1. Synthesis of the bis-sulfone ligand **1**. Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

The lithiation of pincer systems with donor sites (such as N, P, O, and S atoms), facilitated by a so-called *ortho*-directed metalation group, is a useful method to obtain the corresponding lithiated derivatives in high yield.[11] Although a similar *ortho* directing effect has been well established for sulfonyl groups,[12] a noncoordinating solvent and a low reaction temperature were necessary to perform a regioselective lithiation. The reaction of ligand **1** with a slight excess of *n*BuLi (5%) in toluene at −40°C for 20 minutes resulted in the formation of **2** which was generally used for further reactions without purification (Scheme 2).



Scheme 2. Synthesis of the bis-sulfonyl aryl-based chlorostannylene **3**.

When quenching the reaction mixture with D_2O, the ^1H NMR spectrum of the mixture showed the formation of the corresponding deuterated compound in 90% yield (see the Supporting Information) with complete disappearance of the characteristic signal at $\delta = 8.47$ ppm which corresponds to the hydrogen atom on the *ipso* carbon of the central benzene cycle. Carbanion **2** could be isolated as extremely air-sensitive red-brown crystals from a mixture of toluene/THF. NMR spectroscopy investigations in the solution state were hampered by the fact that **2** was sparingly soluble in nonpolar solvents and by the presence of broad signals in the NMR spectrum. A single crystal X-ray diffraction study confirmed the structure of **2** (Figure 2).

Compound **2** crystallizes as a centrosymmetric dimer where the two organolithium fragments are connected by the sulfonyl groups forming a ten-membered ring of formula $Li_2S_2O_2C_4$. Interestingly, the aryl groups bridge the two lithium atoms through two-center two-electron (2c-2e) C_{ipso}–Li bonds whereas three-center two-electron (3c-2e) C_{ipso}–Li interactions are generally found in comparable Li-bound N,C,N aryl pincer systems.[13] This is probably as a result of the specific geometry and the steric hindrance of the sulfonyl moieties. In dimer **2**, each lithium center has a distorted tetrahedral geometry, where it is σ bonded to the *ipso* carbon of the central benzene cycle and coordinated to

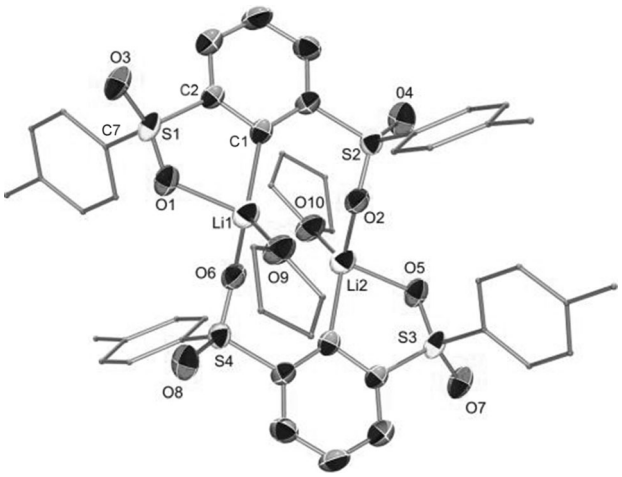


Figure 2. Molecular structures of compound **2** in the solid state (ball-and-stick model). Thermal ellipsoids are set at 50% probability. For clarity, hydrogen atoms and the co-crystallized solvent molecules are omitted and tolyl groups are simplified by representation as a stick model. Selected bond lengths [Å] and bond angles [°]: S1–O1 1.458(2), S1–O3 1.444(2), S2–O2 1.451(2), S2–O4 1.445(2), Li1–O1 2.068(6), Li1–O6 (or Li2–O2) 1.941(6), Li1–O9 1.923(10); O1-S1-O3 117.9(2), O2-S2-O4 117.6(2), O3-S1-C2 109.6(2), O1-S1-C2 107.2(2), O3-S1-C7 107.5(2), S1-O1-Li1 116.7(2), O1-Li1-C1 84.5(2), C1-C2-S1 115.7(2), C2-C1-Li1 112.8(3).

two oxygen atoms of two different sulfonyl groups and to an oxygen atom of a THF molecule. The largest deviation from the ideal tetrahedral angle is found for the C1-Li-O1 angle (84.5(2)°) which occurs because of the formation of a five-membered cycle by coordination of the lithium atom to the adjacent sulfonyl group. This heterocycle is nearly coplanar with the phenyl backbone with the sulfur atom lying 0.061 Å and the oxygen 0.351 Å out of the plane defined by the other atoms. No significant variations are detected between S→O dative bond (S1–O1, 1.458(2); S2–O2, 1.451(2) Å) and the S=O free bonds (S1–O3, 1.444(2); S2–O4, 1.445(2) Å). These values are marginally longer than those obtained in the starting bis-sulfonyl compound **1**. As a result of the different coordination modes of the sulfonyl groups to the lithium atoms (intra or inter), different values were detected for the Li–O bond lengths: 2.068(6) Å for Li1–O1 in the five-membered cycle and 1.941(6) Å for Li1–O6 within the bridge. This binding mode using bis-sulfonyl groups is unknown for main-group metal compounds and to our knowledge, there are very few examples with one sulfonyl group, for instance the monomeric 3-fluoro-2-lithio-1-phenyl-sulfonylbenzene which has a longer Li–O bond length (2.258(8) Å).[14] The Li–O (THF) bond lengths are in the range of the values obtained in organolithiated compounds.[15]

The reaction of the in situ generated lithiated compound **2** with $SnCl_2$ in toluene at 0°C (Scheme 2) afforded the chlorostannylene **3** which is obtained, after workup, as a white solid in a moderate yield of 54%. Compound **3** has been characterized by multinuclear magnetic resonance spectroscopy in solution. The solid-state structure was determined by single-crystal X-ray diffraction analysis of crystals obtained from a CH_2Cl_2 solution of **3** at low temperature (Figure 3).

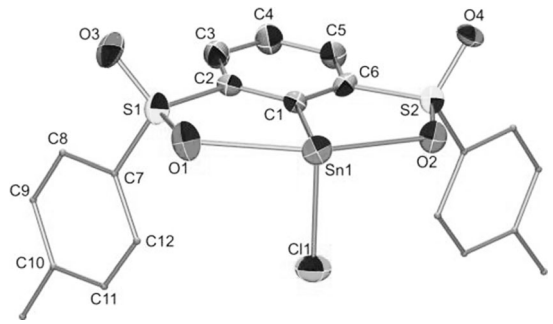


Figure 3. Molecular structure of compound **3**·CH_2Cl_2 in the solid state (ball-and-stick model). Thermal ellipsoids were set at 50% probability. For clarity, hydrogen atoms and the co-crystallized solvent molecules are omitted and tolyl groups are simplified by representation as a stick model. Selected bond distances [Å] and bond angles [°]: S1–O1 1.455(7), S1–O3 1.434(7), S2–O2 1.452(7), S2–O4 1.460(7), Sn1–O1 2.458(7), Sn1–O2 2.543(7), Sn1–Cl1 2.454(3); O1-S1-O3 118.7(4), O2-S2-O4 117.3(4), O1-S1-C2 105.1(4), C1-Sn1-Cl1 91.1(2), C1-Sn1-O1 73.2(3), O1-Sn1-O2 145.1(2).

The ^{1}H NMR spectrum of **3** exhibits similar spectral features to those of the starting compound **1**. In the ^{13}C NMR spectrum, the signal attributable to the *ipso* carbon atom is shifted downfield ($\delta = 173.0$ ppm) in comparison to that of the bis-sulfone ($\delta = 126.5$ ppm), as detected in A[4b] and D[4c,d] analogues (Figure 1). The ^{119}Sn NMR signal for the Sn moiety in **3** appears at $\delta = -25.6$ ppm which is intermediate between the values measured in the related intramolecularly donor-stabilized chlorostannylenes [2,6-$(ROCH_2)_2$-C_6H_3]SnCl (R = Me, $\delta = 230$ ppm; R = *t*Bu, $\delta = 206$ ppm)[4f] and [2,6-{$P(O)(OR)_2$}$_2$-4-*t*Bu-C_6H_2]SnCl (R = Et, $\delta = -100$ ppm; R = *i*Pr, $\delta = -99$ ppm).[4c,d] This suggests that in **3** the S=O→Sn^{II} coordination is relatively strong and close to that the P=O→Sn^{II} coordination. The structure determination reveals a monomeric structure in the solid state (Figure 3). The most notable feature is the presence of the *cis* isomer with two oxygen atoms on the same side of the arene rings. The bis-sulfonyl ligand is bonded in a tridentate fashion to the tin center which exhibits a distorted trigonal bipyramidal geometry with the O atoms at the axial positions and the C1, Cl1, and the lone pair occupying the equatorial positions. The bond angle O1-Sn1-O2 (145.1(2)°) is smaller than that in the heteroleptic stannylene complex D (Figure 1, R = *i*Pr, R′ = *t*Bu) which has a O,C,O-coordinating pincer system (152.01(6)°).[4d] The two O→Sn donor bond lengths in **3** differ slightly (2.458(7) and 2.543(7) Å) but are close to those obtained in D (R = *i*Pr, R′ = *t*Bu; 2.430(2) and 2.427(2) Å).[4d] The Sn1–Cl1 distance (2.454(3) Å) is in the range of Sn–Cl distances in D (R = *i*Pr, R′ = *t*Bu; 2.4708(8) Å)[4d] and in A (2.488(3) Å).[4b] Interestingly, the intramolecular distances between the Cl atom and the H atoms of the tolyl groups (2.777 Å and 3.058 Å) suggest the presence of hydrogen bonds[16] if we consider the sum of the van der Waals radii for H and Cl atoms (2.95 Å,[17] 3.0 Å[18]). As in the lithiated compound **2**, no significant variation of the bond lengths or angles within the sulfonyl moieties could be identified, suggesting that the sulfonyl group constitutes a rigid system which is not influenced by the O→metal coordination. However, FTIR spectroscopy reveals a decrease of the ν(S=O) (1287 and 1146 cm^{-1}) when compared to those of **1** (1322 and 1158 cm^{-1}) that could indicate the formation of Sn–O contacts. Calculations were undertaken to gain further insight into some specific interactions and more precise information on the nature of the Sn–O interactions. Three isomers are found on the potential-energy surface (PES), two *cis* forms **3a** and **3b** and one *trans* form **3c** (see the Supporting Information). Low energetic variations were obtained. Nevertheless and in agreement with the experimentally determined X-ray structure, the **3a** isomer was calculated to be the most thermodynamically stable (−6.8 kcal mol^{-1}). In each of the isomers, natural bonding orbital (NBO) analysis reveals significant interactions between the oxygen lone-pair orbitals and the corresponding unoccupied p orbital of the tin atom ($\Sigma = 61.6$ kcal mol^{-1}). For the isolated compound **3a**, additional significant stabilization interactions were calculated. Interactions of this type can be detected between the lone pairs of electrons on the chlorine atom to the two σ^*_{CH} orbitals (around 12 kcal mol^{-1}; Figure 4).

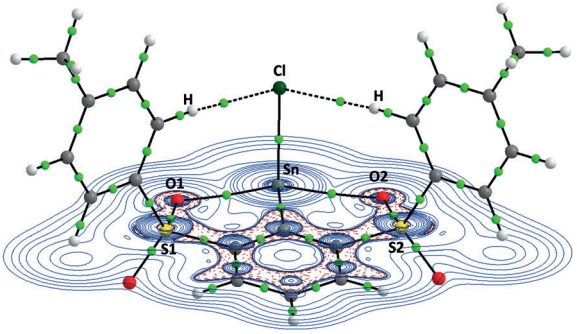


Figure 4. Theoretical isocontours of $\rho(\mathbf{r}_b)$ in compound **3** including BCPs (green dots). Positive contours are shown as solid blue lines and negative contours as broken red lines.

Focusing on the nature of the Sn–O interactions, topological analyses, specifically atoms in molecules (AIM) calculations, indicate bond critical points (BCP) between the Sn and O atoms. The electron density $\rho(r)$ at these BCP are found to be very low (0.037 e/a.u^3) and the Laplacian of the density at the BCP is found to be positive. Also, this interaction can be described as hydrogen-bond-like in nature. Importantly, AIM confirms the NBO results concerning the Cl···H bond. In fact, the electron density at the BCP of the Cl···H bond is found at 0.0131 a.u. with a Laplacian of the density at 0.039 a.u. (Figure 4).

In summary, we have shown the efficiency of a novel O,C,O pincer system for the stabilization of a low-valent tin species. The main advantages of this type of ligand are the straightforward synthesis of the bis-sulfone ligand and the regioselective preparation of the corresponding lithiated derivative. Additionally, an original chlorostannylene complex was preferentially obtained in the *cis* form with the two nonbonded oxygen atoms of the sulfonyl groups located on the same side. DFT calculations are in agreement with this result. The stabilization of this form can be explained not only by a significant Sn–O interaction but also by the presence of hydrogen bonds with the chloride atom. Ongoing studies aim

to modulate the ligand backbone and stabilize other Group 14 low-valent compounds. The reactivity of the so-obtained chlorostannylene complex is still under investigation in our group.

Experimental Section

All manipulations with air-sensitive materials were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk line and glovebox techniques. NMR spectra were recorded with a Bruker Avance II 500: ^{1}H (500 MHz), ^{13}C (125 MHz), ^{119}Sn (112 MHz) at 298 K.

3: A solution of *n*BuLi (0.5 mL of a 1.6 M solution in hexanes, 0.81 mmol) was added dropwise to a solution of **1** (0.30 g, 0.78 mmol) in toluene (12 mL) at −40 °C. The solution was stirred for 20 min and was then added to a suspension of $SnCl_2$ (0.15 g, 0.78 mmol) in toluene (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2 (2 × 10 mL). After removal of insoluble components by filtration, the filtrate was evaporated and the residue was triturated with diethyl ether (20 mL) and allowed to stand overnight at −20 °C. A white solid was obtained after supernatant removal at this temperature to give **3** (0.23 g, 54 %). Crystallization from CH_2Cl_2 at −24 °C gave yellow crystals suitable for a single-crystal X-ray diffraction study. M.p. 128–130 °C; ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 2.41$ (s, 6H, CH_3), 7.35 (d, $^{3}J_{HH} = 8.0$ Hz, 4H, C9-H), 7.50 (t, $^{3}J_{HH} = 7.7$ Hz, 1H, C4-H), 7.80 (d, $^{3}J_{HH} = 7.7$ Hz, 2H, C3-H), 8.07 ppm (d, $^{3}J_{HH} = 8.3$ Hz,4H, C8-H); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 21.9$ (CH_3), 128.8 (C8), 130.6 (C9), 130.8 (C4), 132.5 (C3), 135.5 (C7), 146.0 (C10), 146.3 (C2), 173.0 ppm (C1); ^{119}Sn NMR ($CDCl_3$): $\delta = -25.6$ ppm; HRMS (CI-CH_4) *m/z*: calcd for $C_{22}H_{22}ClO_4S_2Sn$: 568.9670 $[M+C_2H_5]$; found: 568.9656.

CCDC-1007686 (**1**-*trans*), 1007685 (**1**-*cis*), 1007687 (**2**), and 1007688 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting information (experimental procedures, physicochemical and structural data, and DFT calculations for **1**, **2**, and **3**) are available on the WWW under http://www.angewandte.org.

Received: June 16, 2014
Revised: November 7, 2014
Published online: November 27, 2014

Keywords: carbene homologues · density functional calculations · NMR spectroscopy · pincer ligands · tin

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