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1 Bis-Sulfoxide Ligands

Synthesis and Characterization of a Novel Bis-Sulfoxide and Its Evaluation as a Ligand in P-Block Chemistry

Noémi Deak,^[a,b] Olivier Thillaye du Boullay,^[a] Sonia Mallet-Ladeira,^[c] Ionuț-Tudor Moraru,^[b] David Madec,^{*,[a]} and Gabriela Nemes^{*,[b]}

Abstract: A new aryl bis-sulfoxide derivative was designed, synthesized and structurally characterized in solution and in solid state. The chemical behaviour of the newly obtained 1,3-(*para*-tolylsulfinyl)-5-*tert*-butyl-benzene **2** was evaluated to-

wards tin, silicon and phosphorus containing derivatives. In the case of Sn(II) derivative, the potential of bis-sulfoxide **2** as a pincer type ligand was suggested.

Introduction

The importance of compounds containing sulfinyl groups gained focus lately thanks to their proven role in organic synthesis, catalysis, pharmaceutical or material chemistry.^[1–5] These compounds are successfully used in catalytic reactions, or as reagents in asymmetric synthesis.^[3–8]

Derivatives containing two sulfinyl groups with different roles, in the chemical processes are also known. For example, the bis-sulfoxide derivatives are used as ligands in the stabilisation of transition metal or lanthanide complexes or as ligand in transition metal-catalyzed reactions or in various catalytic processes.^[5,7,9–18] In most of the cases the coordination to the metal center is realized through the sulfur atom of the sulfinyl group,^[5,11,14,15,18–23] however, coordination through the oxygen atom is also a possibility, some examples are presented in the literature.^[12,14,23–26]

The synthesis of the sulfoxides can be realized by different methods such as the arylation of sulfenate anions by a coupling reaction, a nucleophilic substitution or an electrophilic attack, with the formation of a C–SO bond,^[27–31] or by oxidation of a sulfide through a thioether as intermediary derivative.^[32–39]

The most common method of obtaining sulfoxides is by oxidation of thioethers^[5] using various oxidizing agents.^[3,4] It is challenging to obtain a selective oxidation, because there is the possibility of obtaining both the sulfoxide and the sulfone moieties. However, several methods were developed for selective oxidation, obtaining only a sulfoxide unit.^[3,4]

Following our scientific interest focused on the synthesis of new organic compounds that can function as O,C,O-chelating aryl-pincer-type ligands, containing either two sulfonyl groups in their structure (bis-sulfone),^[40,42] or one sulfonyl and one sulfinyl moiety (sulfone-sulfoxide),^[43] we have expanded our research on the bis-sulfoxides derivatives having in mind their ability to stabilize metallocenes. A significant feature of the sulfoxide groups connected to an aromatic ring, that is considered in this work, is their powerful directing effect in *ortho* position, as it is well known in the literature.^[2] We envisioned a derivative, where the synergistic effect of the *ortho*-directing sulfoxide group and the bulky *t*Bu group, connected in *para* position of the central aromatic ring (blocking the *meta* positions, that are also *ortho* position considering the sulfinyl groups), would lead to the selective deprotonation in the *ortho* position (C1) in the presence of deprotonating agents.^[40,41] This characteristic of the bis-sulfoxide derivative makes it ideal for the role of an O,C,O-chelating ligand. To the best of our knowledge, there are no examples of ligands containing sulfinyl moieties used for the stabilization of group 14 metallocenes beside the recently reported germylene-sulfoxide ligand used for obtaining transition metal complexes.^[44]

In this study we present the synthesis and the structural characterization of the new bis-sulfoxide derivative 1,3-(*para*-tolylsulfinyl)-5-*tert*-butyl-benzene **2** and its reactivity towards heavy elements of the *p* block, such as Si(IV), Sn(II) and P(III).

Results and Discussion

The new bis-sulfoxide compound, 1,3-(*para*-tolylsulfinyl)-5-*tert*-butyl-benzene **2** was obtained through an oxidation reaction of the newly obtained bis-thioether **1**. (Scheme 1).

[a] Dr. N. Deak, O. Thillaye du Boullay, Dr. D. Madec
Laboratoire Hétérochimie Fondamentale et Appliquée (UMR 5069), Université de Toulouse, CNRS,
118 Route de Narbonne, 31062 Toulouse, France
E-mail: madec@chimie.ups-tlse.fr
http://www.lhfa.cnrs.fr

[b] Dr. N. Deak, I.-T. Moraru, Prof. Dr. G. Nemes
Facultatea de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai,
str. Arany Janos, nr. 11, 400028, Cluj-Napoca, Romania
E-mail: gabriela.nemes@ubbcluj.ro
http://www.chem.ubbcluj.ro/pagini/anorganica/clcpe/

[c] S. Mallet-Ladeira
Institut de Chimie de Toulouse, FR2599, Université Paul Sabatier, UPS,
118 Route de Narbonne, 31062 Toulouse, France

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000728.

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Scheme 1. Synthesis of bis-thioether **1** and bis-sulfoxide **2**.

In its turn, derivative **1** was obtained, by a cross-coupling
71 reaction of 1,3-dibromo-5-*tert*-butylbenzene and *para*-toluene
thiol, catalysed by a palladium-xantphos complex, using a mod-
ified method described in literature.^[29]

The bis-thioether **1**, used as starting product, was isolated as
a white powder and completely characterized by NMR spectro-
76 scopy and X-ray analysis. The ¹H NMR spectrum showed char-
acteristic signal for the H1, a triplet at $\delta = 6.82$ ($^4J_{HH} = 1.7$ Hz),
while in the ¹³C NMR the signal for the C1 atom is at 126.9 ppm.
Suitable crystals for X-ray diffraction were obtained in CH₂Cl₂.
The solid-state structure of **1** is shown in Figure 1, together
81 with the most significant geometrical parameters.

Figure 1. Solid state structure of 1,3-(*para*-tolyl sulfide)-5-*tert*-butylbenzene **1** (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and angles [deg]: C2–S1 1.771(2) S1–C7 1.777(2), C6–S2 1.773(2), S2–C7' 1.771(2), C2–S1–C7 103.76(10), C6–S2–C7' 103.01(10).

The bis-thioether **1** crystallizes in the orthorhombic space
group ($P2_12_12_1$), with three molecules in the unit cell. Since all
three molecules present similar geometric parameters data for
one molecule is presented. It is to note that the tolyl groups
86 are placed in an almost parallel position with the C–S–C bond
angle at 103°.

The bis-thioether **1** was oxidized to obtain a mixture of 1,3-
(*para*-tolylsulfinyl)-5-*tert*-butylbenzene **2** together with the
previously described bis-sulfone^[40] and sulfone-sulfoxide,^[43]
derivatives previously reported by our team. Though in the lit- 91
erature several studies are presented on the oxidation of sulf-
ides to sulfoxides or sulfones using different solvents, catalysts
and oxidants, on various substrates,^[3–5,14,32,35,36,45] none of
them mention the selective formation of a sole compound in
the case when two sulfide groups are present in the molecule. 96
In order to obtain bis-sulfoxide **2**, two oxidation methods were
tested, following procedures described in the literature^[38,46,47]
but adapted to the present case; one where the oxidation is
realized by adding hydrogen-peroxide to the bis-thioether **1** in
anhydrous acetic acid, and a second method, where *m*CPBA 101
was added to a solution of the new bis-thioether **1** in CH₂Cl₂.
The second method proved to be more efficient, affording not
only slightly higher yield, but considerably lower reaction time,
one hour compared to 24 hours. Bis-sulfoxide **2** was purified by
column chromatography using as eluent either a mixture of 106
cyclohexane and ethyl acetate (8:2) or toluene and ethyl acetate
(8:2). The new bis-sulfoxide **2** was separated as a mixture of 50–
50 % of the *meso* and *dl* diastereomers, according to the ¹H
NMR studies.

The *dl* diastereomer could be separated from the mixture in 111
a small quantity by fractional crystallization in acetone. It was
characterized by NMR spectroscopy and single-crystal X-ray dif-
fraction.

In the ¹H NMR spectra a downfield shift can be observed for
the H1 from 6.82 ppm in the bis-thioether **1** to 7.50 ppm (*dl* 116
isomer, *t*, $^4J_{HH} = 1.6$ Hz) and 7.58 ppm (*meso* isomer, *t*, $^4J_{HH} =$
1.6 Hz) in bis-sulfoxide **2**, which suggests the presence of the
sulfinyl groups. After the assignment of the signals in the ¹H
NMR of bis-sulfoxide **2-dl** with two dimensional NMR analysis,
the signals for the *meso* isomer could also be assigned. The 121
numbering scheme used in NMR analysis is presented in
Scheme 1.

The ratio of each diastereomer was determined from the ¹H
NMR, where the signals for the H3 and H5 appear as two dou-
blet signals at 7.71 and 7.74 ppm ($^4J_{HH} = 1.6$ and 1.6 Hz), which 126
can be distinguished very easily. In the case of the signals for
the other protons, these overlap in some part.

The signals for the *meso* and *dl* isomers of bis-sulfoxide **2** in
the ¹³C NMR spectra are very close of each other, with a differ-
ence of 0.02–0.1 ppm (0.77–10.41 Hz). 131

Crystals of the bis-sulfoxide **2-dl** suitable for X-ray analysis
were separated from acetone and the molecular solid-state
structure is presented in Figure 2.

Bis-sulfoxide **2** crystallizes in a monoclinic space group
($C 2/c$), (with a molecule of acetone in the crystal lattice) and 136
the structure shows that tolyl groups of the bis-sulfoxide are
situated on the same side of the central aromatic ring. The
S=O bond lengths of 1.499(1) Å and 1.493(1) Å are in the range
of S=O bonds found in sulfoxides presented in the literature
(1.478–1.515 Å).^[48–50] O...H interactions was observed between 141
the O atoms of the sulfoxide groups and the H atoms of the
aromatic ring (O2–H5 2.525 and O1–H1 2.603 Å) intramolecular

Figure 2. Molecular structure of compound **2-dl** in solid state (50 % probability level for the thermal ellipsoids). For clarity, the solvent and hydrogen atoms are omitted; tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and bond angles [deg]: S1–O1 1.493(1); S2–O2 1.499(1); O1–S1–C2 106.80(6); O2–S2–C6 106.42(6); C1–C6–S2 118.71(9).

short contacts similar to those found for sulfoxides **2.35–2.97 Å**.^[49]

The separation of the two diastereomers of bis-sulfoxide **2** was attempted through an HPLC experiment (see details in ESI, Figure S25) on a chiral column and it was shown that it is possible to separate the *dl* and the *meso* diastereomers, but also the *d*- and *l*-enantiomers. However, the experiment was performed on an analytical column, and so far, it could not be realized on 151 a bigger scale.

DFT calculations were performed on the diastereomers of bis-sulfoxide **2** in order to gain further insight on their stability, isomerization and racemization barriers. The optimized molecular structures of all possible isomers of derivative **2** are illustrated in Figure 3. Their computed relative energies are also depicted. However, energy gaps between isomers are very small, calculated differences among the investigated series being of at most 0.4 kcal mol^{−1} (see Figure 3). It is thus expected that all species would coexist in solution at room temperature. 161 In addition, *cis-trans* isomerization barriers were assessed by means of DFT investigations, for both *meso* and *dl* diastereomers (Figure S26 and S27). As expected, *cis-trans* transformations are barrier-less, with calculated rotation barriers of at most 2 kcal mol^{−1}. 166

Racemization barriers of the investigated enantiomers were also calculated by DFT means. To the best of our knowledge there is no previous theoretical study assessing racemization barriers on bis-sulfoxide species. However, racemization mecha-

Figure 3. DFT optimized molecular structures of all possible diastereomers of bis-sulfoxide **2**. Computed relative energies are also depicted (all displayed energies contain thermal enthalpy corrections).

171 nisms on sulfoxide molecules are well documented. The pio-
neering work of Mislow and co-workers revealed several possi-
ble racemization pathways of sulfoxide derivatives, involving ei-
ther pyramidal inversion or either homolytic C–S bond break-
ing.^[51–52] In addition, it has been shown than benzyl- and allyl-
176 sulfoxides undergo more complex rearrangement mecha-
nisms.^[53–54] Subsequent computational explorations performed
on sulfoxide molecules brought further clarification on the race-
mization mechanism of these species, highlighting an en-
hanced kinetic accessibility for the pyramidal inversion pathway
181 than for the C–S bond cleavage one.^[55] Concerning the racemi-
zation of the bis-sulfoxide enantiomers, we have considered in
the present DFT study both the pyramidal inversion and the
homolytic bond dissociation routes. However, calculations em-
phasize that the pyramidal inversion pathway requires a signifi-
186 cantly lower barrier than the homolytic bond cleavage route.
The energy gap between the computed barriers of the two
mechanisms is of ca. 18 kcal mol^{–1} (see Figure S28 for compar-
isons). Figure 4 illustrates the racemization route, occurring via
pyramidal inversion, for the *cis* enantiomers of the bis-sulfoxide
191 derivative. Inter-conversion of the two enantiomers involves the
meso trans derivative, as an intermediate, whereas the com-
puted transition states (TS) structures, corresponding to the py-
ramidal inversion of the sulfur atoms of each of the sulfoxide
groups, display the same energy. The TS structures display trig-
onal planar geometries at the sulfur atom. The computed race-
mization barrier for the *cis* bis-sulfoxide enantiomers is of
35.9 kcal mol^{–1}. Barrier heights of the same order of magnitude
were additionally calculated for the inter-conversion of the *trans*
enantiomers (36 kcal mol^{–1}, see Figure S29 for details). Notewor-
201 thy, the computed racemization barriers of these bis-sulfoxides
enantiomers are in line with previously reported values for the

pyramidal inversion of mono-sulfoxide species, for which barrier
heights of 38.7–47.1 kcal mol^{–1} were obtained.^[55]

In order to demonstrate the reactivity of bis-sulfoxide **2** de-
rivative, a deprotonation experiment was realized. The deproto-
206 nation reaction of the H1 occurs selectively in the presence of
LDA, due to the fact that the two sulfinyl groups have strong
ortho director effect, thus favouring lithiation in this position.
The carbanion of the bis-sulfoxide ligand was obtained by add-
ing LDA to a solution of bis-sulfoxide **2** (50 % *dl* and 50 % *meso* 211
mixture calculated from the ¹H NMR) in THF at low temperature.

To find the optimal conditions for the deprotonation, the
lithiated derivative **3** (Scheme 2) was quenched with D₂O. The
¹H NMR spectra of the deuterated compound **4** showed that
the deprotonation is complete and almost quantitative (< 5 % 216
starting material left). The efficiency of the deprotonation was
followed by the disappearance of the triplet signal at 7.58 ppm
for the H1 in the ¹H NMR of the *dl*-isomer of bis-sulfoxide **2**
(the signal for the H1 proton of the *meso* isomer at 7.50 ppm
is overlapping with other signals, it's disappearance cannot be 221
followed as clearly).

Considering that the stabilization of group 14 metallocenes
with different type of ligands is a continuing interest for our
group,^[51–59] we evaluated the O,C,O pincer-type ligand behav-
iour of bis-sulfoxide **2** towards Sn(II). In this respect, lithium 226
derivative **3** was treated with SnCl₂ at low temperature, and the
formation of the bis-sulfoxide stannylene [2,6-(*para*-tolyl-
sulfinyl)-4-*tert*-butyl-phenyl-chlorostannylene] **5** was confirmed
by ¹H NMR spectroscopy, where the disappearance of the triplet
signal at 7.58 ppm for the H1 proton of the *dl*-isomer bis-sulfox- 231
ide **2** is observed (the signal for the H1 proton of the *meso*
isomer at 7.50 ppm is overlapping with other signals, it's disap-

Figure 4. Racemization pathway suggested for the *cis* enantiomers of bis-sulfoxide **2**; the mechanism occurs via sulfur pyramidal inversion.

Scheme 2. Reactivity study of bis-sulfoxide **2**.

pearance cannot be followed as clearly), as it can be seen on Figure S9 in ESI. The ^1H NMR spectrum for stannylene **5** shows a downfield shift of the signals for the aromatic protons in the 7.27–7.85 ppm region. In the ^{13}C NMR spectrum of the stannylene **5** the signals situated at 169.7 and 170.1 ppm (in CDCl_3) are characteristic for the *ipso* C1 atom of a group 14 metallylene.^[40,42,59]

The formation of product **5** was also confirmed by the ^{119}Sn NMR with the appearance of a sharp signal at 75 ppm and a broad one at 54 ppm. This is in agreement with the results previously observed in the case of the sulfone-sulfoxide stannylene,^[43] where signals were seen at 49.3 and 72.5 ppm. This observation also suggests that coordination of the oxygen atoms of the sulfinyl groups is likely in compound **5**, as it was proven for the sulfone-sulfoxide stannylene.^[43] The chemical shift for **5** observed at 75 and 50 ppm are downfield shifted compared to other O,C,O-chelating chlorostannylens (-99 ppm).^[60,61] Furthermore, in the mass spectrum peaks for $[\text{M} + \text{CH}_3\text{OH}]^+$ ($\text{C}_{24}\text{H}_{26}\text{O}_2\text{S}_2\text{SnCl} + \text{CH}_3\text{OH}$) at 597.0, $[\text{M} - \text{Cl}]$ ($\text{C}_{24}\text{H}_{25}\text{O}_2\text{S}_2\text{Sn}$) at 529.0 and a dimeric species $[\text{C}_{48}\text{H}_{50}\text{O}_4\text{S}_4\text{Sn}]^+$ at 939.2 can be observed (See S11 ESI), species that suggest the existence of the stannylene in the mixture. However, due to the sensitivity of the products, the mixture could not be separated and purified, thus further analysis was not realized.

For a better understanding of the chemical behaviour of bis-sulfoxide **2**, reaction with trimethylchlorosilane and chlorodiphenylphosphine, respectively was carried out. To the lithiated bis-sulfoxide **3**, obtained starting from a mixture of *dl* and *meso* isomers of the bis-sulfoxide **2**, a large excess of Me_3SiCl was added. According to the ^1H NMR analysis of the reaction mixture, the expected compound bis-sulfoxide trimethylsilane [2,6-(*para*-tolylsulfinyl)-4-*tert*-butyl-phenyl-trimethylsilane] **6** was obtained in a mixture that was purified by column chromatography, using as mobile phase a mixture of ethyl acetate and cyclohexane (1:9). One of the two diastereomers of compound **6** was separated from this mixture; the other one was recovered as a mixture of the two diastereomers.

Single crystals suitable for X-ray analysis were separated from a dichloromethane solution of the mixture of the two diastereomers of compound **6**. The solid-state structure is presented in Figure 5.

Figure 5. Molecular structure of compound **6** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, the solvent molecules and hydrogen atoms are omitted; tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and bond angles [deg]: S1–O1 1.500(2); S2–O2 1.501(2), C1–Si1 1.926(2); O1–S1–C2 106.79(9), O2–S2–C6 106.18(9), C1–C2–S1 121.25(14), C1–C6–S2 122.28(14), C6–C1–Si1 126.97(14), C2–C1–Si1 119.75(14).

Compound **6** crystallizes in a triclinic space group ($P\bar{1}$) with two molecules in the asymmetric unit. The solid state molecular structure shows the *meso* diastereomer of the compound, the *tolyl* groups are positioned on the same side of the central aromatic ring. The oxygen atoms are positioned in a way that doesn't make possible interactions with the silicon atom. This is in contrast with related Si(IV) derivatives, supported by {2,6-281 $[\text{P}(\text{O})(\text{OR})_2]_2$ -4-*t*Bu C_6H_2 } ligands,^[62] where weak O→Si coordinations were observed.

In a reaction of **2** with chlorodiphenylphosphine the formation of the new compound **7** (bis-sulfoxide diphenyl phosphine) was evidenced by multinuclear NMR spectroscopy. In the ^1H NMR spectra, the disappearance of the signals for H1 protons of the bis-sulfoxide **2** suggests the formation of compounds where the heteroatom is linked to the C1 carbon atom. In the ^{31}P NMR several signals can be observed in the -22 to -8.6 ppm region, an upfield shift compared to the starting ClPPh_2 from 81.8 ppm and characteristic for triaryl phosphines.^[63]

The signal for the major compound is found at -21.5 ppm (71 %) and in the ^1H NMR signals corresponding to the bis-sulfoxide-diphenyl phosphine could be identified. From the solution of this mixture in acetone, single crystals suitable for X-ray diffraction were separated. The multinuclear NMR analysis of the separated crystals showed the signals corresponding to the two compounds. In the ^{31}P NMR a signal can be seen at -21.5 ppm (major signal, 71 %) for the bis-sulfoxide diphenyl phosphine **7** and one at 31.8 ppm for the bis-sulfoxide diphenyl phosphine oxide **8**. In the ^1H NMR all the signals corresponding to these two compounds can be identified, signals characteristic to the H3 and H5 protons can be found at 8.20 ppm (d, 2H, $^3J_{\text{HH}} = 1.3$ Hz) for compound **7** and at 8.35 ppm (d, $^3J_{\text{HH}} = 2.6$ Hz) for compound **8**, with the ratio already seen in the ^{31}P NMR, both downfield shifted compared to the bis-sulfoxide **2** (from 7.71 and 7.74 ppm).

In the mixture both the $-\text{PPh}_2$ **7** and $-\text{P}(\text{O})\text{Ph}_2$ **8** derivatives are present, as a result of slow oxidation of the bis-sulfoxide diphenyl phosphine. The single-crystal X-ray analysis showed the *meso* diastereomer, with the tolyl groups positioned on the same side of the central aromatic ring (Figure 6). The P–C bond lengths [1.839(4) Å] are in agreement with values reported in literature.^[64]

Conclusion

In conclusion, the new 1,3-(*para*-tolylsulfinyl)-5-*tert*-butyl-benzene **2**, containing two sulfinyl groups in the *ortho* position of the central aromatic ring, was designed, synthesized and characterized. The synthesis of bis-sulfoxide **2** goes through the new bis-thioether **1** which was also structurally completely characterized. The new bis-sulfoxide **2** was obtained as a mixture of 50–50 % of the *meso* and *dl* diastereomers, but the qualitative separation of the two diastereomers was possible using chiral column. The HPLC experiment proves that it is possible to separate the *dl* and the *meso* diastereomers, but also the *d*- and *l*-enantiomers.

Reactions of lithiated 1,3-(*para*-tolylsulfinyl)-5-*tert*-butylbenzene **2** with trimethylchlorosilane and chlorodiphenylphosphine showed that deprotonation at the H1 of the bis-sulfoxide **2** and reactions with *p* block elements are possible. Furthermore, the bis-sulfoxide **2** was tested with the purpose to function as pincer ligand in the stabilization of divalent group 14 elements, thus a new stannylene was evidenced. However, due to the use of the bis-sulfoxide as a mixture of the two diastereomers *dl* and *meso* in the reactions, a mixture of isomers of the products was obtained as well.

The results presented here suggest that the newly obtained sulfinyl based compounds can be employed as ligands for the

Figure 6. Molecular structure of compounds **7** (a) and **8** (b) in the solid state (50 % probability level for the thermal ellipsoids). For clarity, the solvent molecules and hydrogen atoms are omitted; tolyl, *tert*-butyl and phenyl groups are simplified. Selected bond lengths [Å] and bond angles [deg]: S1–O1 1.490(3); S2–O2 1.485(4), C1–P1 1.839(4), P1–O3 (for **8**) 1.369(11); O1–S1–C2 105.95(18), O2–S2–C6 104.7(2), C1–C2–S1 120.6(3), C1–C6–S2 121.8(3), C6–C1–P1 117.0(3), C2–C1–P1 127.3(3).

stabilization of the organic compounds of the heavy *p* block elements.

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Experimental Section

Materials and Methods

All manipulations were performed in a dry, oxygen-free atmosphere of argon by using standard Schlenk-line and glove-box techniques.

346 The solvents were purified using MBRAUN SBS-800 purification system.

The NMR spectra were recorded with a Bruker Avance II 300 MHz apparatus, Bruker Avance 400 MHz apparatus and Bruker Avance 600 MHz apparatus using the following internal or external references: TMS for ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{29}Si NMR, SnMe₄ for ^{119}Sn , H_3PO_4 for ^{31}P NMR. Chemical shifts are expressed in parts per million (ppm). The NMR assignments were confirmed by COSY (^1H - ^1H), HSQC (^1H - ^{13}C), and HMBC (^1H - ^{13}C) experiments. Mass spectrometry (MS) spectra were measured with a Hewlett-Packard 5989A in the electron impact mode (70 eV). High-resolution mass spectrometry (HRMS) spectra were measured with a GCT Premier Waters in DCI mode (CH_4). Melting points were measured in a sealed capillary using the Stuart automatic melting point SMP40 apparatus.

The X-ray data were collected at 193(2) K on a Bruker - AXS APEX II Quazar diffractometer, equipped with a 30 W air-cooled microfocus source using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Phi- and omega-scans were used. The data were integrated with SAINT and an empirical absorption correction with SADABS was applied. The structures were solved by direct methods using SHELXS-97 and refined using a least-squares method on F^2 . All non-H atoms were refined with anisotropic displacement parameters.^[65–68] For **7** and **8**, tied-occupancy refinement confirmed that in the crystal two compounds crystallized together at a single site in the same unit cell, one containing the atom O3 with an occupancy of 0.27.

371 Deposition Numbers 2019650, 2019651, 2019652, 2019653 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

376 Computational Details

Theoretical calculations were performed within the framework of the Density Functional Theory (DFT), using the *Gaussian 09* software.^[68] Molecular geometries were fully optimized without any symmetry constraints in THF using the SMD variation of the polarizable continuum solvation model^[69] (for TetraHydroFuran, $\epsilon = 7.4257$). The PBE0^[70] hybrid functional and the valence triple-zeta Def2-TZVP^[71] basis set were employed in all calculations. The optimization criteria were set to tight while the integration grid used within the calculations was of 99 radial shells and 950 angular points for each shell (99,950), known as the “ultrafine” grid in *Gaussian 09*. Calculations of the vibrational frequencies were performed in order to characterize the nature of the stationary points. Additionally, vibrational analyses were used to compute enthalpies within the framework of the harmonic approximation for vibrational contribution (further details on the thermodynamic equations are available in Ref.^[72]). Noteworthy, all reported energies throughout this study (relative energies between isomers, activation barriers, etc.) contain the thermal enthalpy corrections to the DFT energy.

Synthesis of Bis-thioether 1 [1,3-(para-Tolyl sulfide)-5-tert-butyl-benzene] (1): A mixture of Pd₂dba₃ (784 mg, 0.086 mmol, 5 mol-%) and Xantphos (991 mg, 1.71 mmol, 10 mol-%) in 5 mL of toluene was stirred for 5 minutes, then *p*-toluenethiol (6.380 g, 51.40 mmol, 3 equiv.), of 1,3-dibromo-5-tert-butylbenzene (5 g, 0.017 mmol, 1 equiv.), a KOH solution (50.9 mL, 50 % aqueous solution) and 80 mL of toluene were added. The biphasic system was heated to 90 °C for 48 h. After cooling to room temperature, 75 mL of CH_2Cl_2 was added and the layers separated. The aqueous phase was washed with 75 mL of CH_2Cl_2 , then all organic phases were washed with a saturated NaCl solution then dried on Na_2SO_4 . After evaporating all solvents, red oil remained. The obtained bis-thio-

ether was purified by column chromatography (cyclohexane) (6.18 g, yield = 95 %). ^1H NMR (CDCl_3) δ = 1.23 (s, 9H, tBu), 2.35 (s, 6H, Me), 6.82 (t, 1H, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, CH Ph), 7.10 (d, 4H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, *m*-CH Tol), 7.14 (d, 2H, $^4J_{\text{HH}} = 1.7 \text{ Hz}$, *m*-CH Ph), 7.24 (d, 4H, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, *o*-CH Tol). ^{13}C NMR (CDCl_3) δ = 21.3 (Me), 31.2 [$\text{C}(\text{CH}_3)_3$], 35.0 411 [$\text{C}(\text{CH}_3)_3$], 124.6, 126.9, 130.1, 130.7, 132.5, 137.8, 137.9, 152.8. M.p. 75–76 °C. MS (DCI NH_3) ($\text{C}_{24}\text{H}_{26}\text{S}_2$) [$\text{M} + 1$]⁺ 379.1. Elemental analysis calculated for $\text{C}_{24}\text{H}_{26}\text{S}_2$: C 76.14; H 6.92; found C 76.21; H 6.61.

Synthesis of Bis-sulfoxide 2 [1,3-(para-tolylsulfinyl)-5-tert-butyl-benzene] (2): Method I: To a solution of 5.4 g (0.014 mol) of bis-thioether **1** in 32 mL of glacial acetic acid, a solution of 2.6 mL of H_2O_2 (33wt.-%, 0.028 mmol, 2 equiv.) in 18 mL of glacial acetic acid was added dropwise. The mixture was stirred at room temperature for 48 hours, while a clear solution was obtained. A saturated solution of KOH was added to the reaction mixture until a neutral pH 421 was obtained. Then 25 mL of CH_2Cl_2 were added and the layers were separated. The aqueous layer was extracted six times with 25 mL of CH_2Cl_2 , the organic layers were united and washed twice with 50 mL of aqueous saturated NaCl solution then dried on Na_2SO_4 . After evaporating the solvent, a white sticky solid was obtained. The bis-sulfoxide **2** was separated from the mixture by column chromatography (cyclohexane/ethyl acetate, 8:2). It was obtained as a white powder a mixture of 50–50 % of the *meso* and *dl* diastereomers (3.4 g, 58 % yield). The *dl* isomer could be separated by fractional crystallization from acetone. Transparent crystals were 431 obtained of the *dl* diastereomer.

Method II: To a solution of bis-thioether **1** (3 g, 7.9 mmol) in 50 mL of CH_2Cl_2 a solution of *m*CPBA (4.5 g, 26.2 mmol, 3 equiv.) in 50 mL of CH_2Cl_2 was added dropwise at 0 °C. The mixture was stirred at 0 °C for one hour and at room temperature for 20 minutes then 436 washed three times with 75 mL of an aqueous saturated solution of NaHCO_3 and all solvents evaporated. The bis-sulfoxide **2** was separated by column chromatography (cyclohexane/ethyl acetate, 8:2) as the mixture of the *meso* and *dl* diastereomers (0.8 g, 25 % yield). ^1H NMR (CDCl_3) *dl* isomer: δ = 1.29 (s, 9H, tBu), 2.36 (s, 6H, 441 Me), 7.23 (d, 4H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, *m*-CH Tol), 7.45 (d, 4H, $^3J_{\text{HH}} = 8.2 \text{ Hz}$, *o*-CH Tol), 7.50 (t, 1H, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, H1 Ph), 7.74 (d, 2H, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, *m*-CH Ph). *meso* isomer: δ = 1.28 (s, 9H, tBu), 2.37 (s, 6H, Me), 7.25 (d, 4H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, *m*-CH Tol), 7.48 (d, 4H, $^3J_{\text{HH}} = 8.2 \text{ Hz}$, *o*-CH Tol), 7.58 (t, 1H, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, H1 Ph), 7.71 (d, 2H, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, *m*-CH 446 Ph). ^{13}C NMR (CDCl_3) *meso* isomer δ = 21.6 (Me), 31.2 (tBu), 35.8 (C tBu), 118.3 (C1), 123.8 (C3, C5), 125.1 (C8, C12), 130.3 (C9, C11), 142.0 and 142.2 (C7, C10), 147.3 (C2, C6), 154.5 (C4). *dl* isomer δ = 21.6 (Me), 31.2 (tBu), 35.7 (C tBu), 118.4 (C1), 123.7 (C3, C5), 125.2 (C8, C12), 130.3 (C9, C11), 142.0 and 142.1 (C7, C10), 147.3 (C2, C6), 451 154.6 (C4). MS (DCI CH_4) ($\text{C}_{24}\text{H}_{26}\text{O}_2\text{S}_2$) [$\text{M} + 1$]⁺ 411.1439.

The separation of the two diastereomers of bis-sulfoxide **2** was shown by an HPLC experiment with an Agilent HPLC 1200 instrument on a chiral column [(*R,R*)-Whelk-O 1 Pirkle-type Chiral Column] at 30 °C using as mobile phase a mixture of hexane/2-propanol – 456 dichloromethane in the ratio 85:14:1.

Synthesis of Compounds 3 and 4: Method I: To a solution of 300 mg of bis-sulfoxide **2** (0.73 mmol) in 12 mL of THF cooled to –80 °C, a freshly prepared LDA solution in THF (0.80 mmol, 10 % excess) was added. The dark orange solution was stirred at this 461 temperature for 30 minutes then warmed up to –40 °C and stirred for another 30 minutes.

Method II: To a solution of 100 mg of bis-sulfoxide **2** (0.73 mmol) in 12 mL of THF (or toluene) cooled to –80 °C, a solution of LDA (prepared previously and kept as solid in the glovebox) in THF (or 466 toluene) (0.80 mmol, 10 % excess) was added. The dark orange solu-

tion was stirred at this temperature for 30 minutes then warmed up to -40°C and stirred for another 30 minutes.

To the solution of the lithiated compound **3** D_2O (1 mL) was added then stirred for 5 minutes at room temperature to obtain a light yellow solution. Solvents were evaporated and compound **4** was obtained as a white solid.

Synthesis of Bis-sulfoxide Stannylene [2,6-(para-tolylsulfanyl)-4-tert-butyl-phenyl-chlorostannylene] (5): The freshly prepared solution of the lithiated bis-sulfoxide **3** [prepared from 100 mg of bis-sulfoxide **2** (0.73 mmol)] was added to a solution of SnCl_2 (138.6 mg, 0.73 mmol, 1 equiv.) in 2 mL of THF (or toluene) at -40°C . The yellow mixture was stirred in the cooling bath for one hour then at room temperature for another hour. Solvents were evaporated; the solid was extracted with CH_2Cl_2 . A white solid was obtained as a mixture of compounds. ^1H NMR (CDCl_3) δ = 1.13–1.16 (tBu), 2.35–2.37 (Me), 7.27–7.30 (CH Tol), 7.34 (CH Tol/Ph), 7.69 (d, $^3J_{\text{HH}}$ = 8.1 Hz, CH Tol/Ph), 7.83 (d, $^3J_{\text{HH}}$ = 8.1 Hz, *m*-CH Tol). ^{13}C NMR (CDCl_3) δ = 21.6, 21.7 (Me), 31.1 (tBu), 35.3 (C tBu), 118.3–153.9 many signals, 169.7 and 170.1 (C1). ^{119}Sn (CDCl_3) δ = 75.1 (sharp); 54 (broad). MS (MS ESI+) ($\text{C}_{24}\text{H}_{25}\text{ClSnO}_2\text{S}_2$): $[\text{M} + \text{CH}_3\text{OH}]^+$ ($\text{C}_{24}\text{H}_{26}\text{O}_4\text{S}_2\text{SnCl} + \text{CH}_3\text{OH}$) at 597.0, $[\text{M} - \text{Cl}]$ ($\text{C}_{24}\text{H}_{25}\text{O}_2\text{S}_2\text{Sn}$) at 529.0, $[\text{C}_{48}\text{H}_{50}\text{O}_4\text{S}_4\text{Sn}]^+$ at 939.2.

Synthesis of Bis-sulfoxide Trimethylsilane [2,6-(para-Tolylsulfanyl)-4-tert-butyl-phenyl-trimethylsilane] (6): To a solution of 100 mg of bis-sulfoxide **2** (0.24 mmol) in 4 mL of THF cooled to -80°C a freshly prepared LDA solution in THF (0.27 mmol, 10 % excess) was added dropwise. The orange solution was stirred at this temperature for 30 minutes, then a large excess of trimethylchlorosilane (0.5 mL) was added. After stirring at room temperature overnight, volatiles were evaporated and the product was purified by column chromatography (ethyl acetate:cyclohexane 2:8) (76 mg, 64 % yield). Transparent crystals of **6** were obtained in CH_2Cl_2 . *meso* diastereomer ^1H NMR (CDCl_3) δ = 0.54 (s, 9H, Me_3Si), 1.21 (s, 9H, tBu), 2.38 (s, 6H, Me), 7.19 (s, 8H, $J_{\text{Si-H}}$ = 9.0 Hz, *o*- and *m*-CH Tol), 8.05 (s, 2H, *m*-CH Ph). ^{13}C NMR (CDCl_3) δ = 4.8 (SiMe_3), 21.5 (Me), 30.8 (tBu), 35.7 (C tBu), 125.5 (C8, C12), 125.8 (C3, C5), 130.0 (C9, C11), 135.7 (C1), 141.2 (C10), 143.2 (C7), 153.5 (C2, C6), 155.6 (C4). ^{29}Si NMR (CDCl_3) δ = -2.18 . *dl* diastereomer ^1H NMR (CDCl_3) δ = 0.59 (s, 9H, Me_3Si), 1.11 (s, 9H, tBu), 2.36 (s, 6H, Me), 7.25 (d, 4H, $^3J_{\text{HH}}$ = 8.1 Hz, *m*-CH Tol), 7.31 (d, 4H, $^3J_{\text{HH}}$ = 8.4 Hz, *o*-CH Tol), 7.90 (s, 2H, *m*-CH Ph). ^{29}Si NMR (CDCl_3) δ = -1.85 . MS (MS ESI+) ($\text{C}_{27}\text{H}_{34}\text{O}_2\text{S}_2\text{Si}$) $[\text{M} + 1]^+$ 483.1858 (calculated for $\text{C}_{27}\text{H}_{35}\text{O}_2\text{S}_2\text{Si}$ 483.1848).

Synthesis of Bis-sulfoxide-diphenylphosphine 7 [2,6-(para-Tolylsulfanyl)-4-tert-butyl-phenyl-diphenylphosphine]: To a solution of 200 mg of bis-sulfoxide **2** (0.49 mmol) in 6 mL of THF cooled to -80°C , a solution of 103.4 mg of LDA (0.54 mmol, 1.1 equiv.) in 2 mL of THF was added at -80°C . After stirring the mixture for 30 minutes at this temperature, 0.12 mL of chlorodiphenylphosphine (0.66 mmol, 1.35 equiv.) was added. The mixture was stirred at room temperature overnight and volatiles were evaporated to obtain a yellow solid as a mixture of two diastereomers. Transparent crystals were separated in acetone.

Compound 7: ^1H NMR (CDCl_3) δ = 1.35 (s, 9H, tBu), 2.31 (s, 6H, Me), 7.06 (s, 8H, *o*- and *m*-CH Tol), 7.04–7.24 and 7.36–7.57 (m, PPh_2), 8.20 (d, 2H, H3 and H5, $^3J_{\text{HH}}$ = 1.3 Hz). ^{13}C NMR (CDCl_3) δ = 21.5 (Me), 31.0 (tBu), 36.2 (C tBu), 125.9 (CH PPh_2), 126.6 (d, $^3J_{\text{PH}}$ = 2.3 Hz, C3, C5), 128.8 (m, CH PPh_2), 129.8 (CH Tol), 132.3 (d, J_{PH} = 17.9 Hz, CH Tol), 132.8 (d, J_{PH} = 2.8 Hz, CH PPh_2), 133.8 (d, J_{PH} = 11.0 Hz) 141.0, 141.3, 142.2, 143.0, 152.7 and 154.1 (d, J_{PH} = 14.6 Hz) for C1, C2, C6, C7, C10 and PPh_2 , *ipso* 157.8 (C4). ^{31}P NMR (CDCl_3) δ = -21.5 .

MS (MS ESI+) ($\text{C}_{36}\text{H}_{35}\text{O}_2\text{PS}_2$) $[\text{M} + 1]^+$ 595.1907 (calculated for $\text{C}_{36}\text{H}_{36}\text{O}_2\text{PS}_2$ 595.1895).

Compound 8 (Bis-sulfoxide-diphenylphosphine oxide): ^1H NMR 531 (CDCl_3) δ = 1.32 (s, tBu), 2.33 (s, Me), 7.06 (s, 8H), 7.04–7.24 and 7.36–7.57 (m, *o*- and *m*-CH Tol, PPh_2), 8.35 (d, H3 and H5, $^3J_{\text{HH}}$ = 2.6). ^{13}C NMR (CDCl_3) δ = 30.8 (tBu), 125.5 (C8, C12), 126.7 (C3, C5), 129.1 (d, J_{PH} = 12.6 Hz, CH PPh_2), 129.7 (CH Tol), 132.4 (d, J_{PH} = 10.6 Hz, CH Tol), 159.0 (C4). ^{31}P NMR (CDCl_3) δ = 31.8. MS (MS ESI+) 536 ($\text{C}_{36}\text{H}_{35}\text{O}_3\text{PS}_2$) $[\text{M} + 1]^+$ 611.1857.

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