

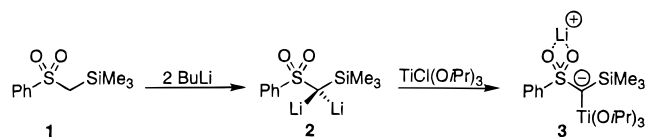
Structure Determination of a Lithiated Titanium–Sulfone

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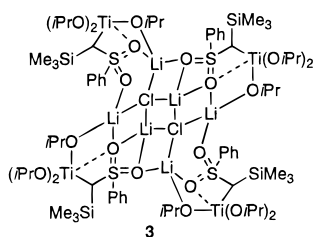
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Geminal dimetalated organometallics have captured a meaningful position as reagents in organic synthesis, due to the fact that the combination of multiple reactions in a single pot is highly efficient.¹ If there are two different metals bound to the same carbon atom of a compound, which is stabilized by an element of the third period, such as sulfur or phosphorus, a new stereocenter might be induced. This principle can be used for the asymmetric transformation of chiral information, but has rarely been applied in stereoselective reactions.² In contrast, it is, for example, well-known that in an achiral environment, that is in the absence of a chiral auxiliary, the addition of an aldehyde to a titanated dilithiosulfone proceeds in a highly diastereoselective fashion forming predominantly the *E*-alkenes.³ The lacking structural information for the occurring intermediates stimulated us to shed some light on the structures of geminal lithium–titanium organometallics.⁴ Herein we report the synthesis and first crystal structure of a complex derived from such a lithiated titanium–sulfone.



The reaction of (phenylsulfonyl)trimethylsilylmethane (**1**) with 2 equiv of *n*BuLi in diethyl ether and transmetalation with ClTi(O*i*Pr)₃ in hexane leads, after filtration of LiCl, smoothly to the lithium–titanium–sulfone **3** as yellow air-, temperature-, and moisture-sensitive crystals. Figure 1 shows an ORTEP plot of the tetrameric, approximate C₂ symmetric cluster.⁵ **3** consists of



four monolithiated titanium–sulfone units together with two molecules of LiCl. The center of the aggregate is characterized by a (Li–Cl)₂ four-membered-ring motif, which shows a small

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(5) X-ray data for **3**: space group P1, *a* = 15.53(2) Å, *b* = 18.45(1) Å, *c* = 24.71(1) Å, α = 107.73(4)°, β = 101.23(5)°, γ = 101.55(6)°, *V* = 6352(8) Å³, *Z* = 2, *R* = 0.1082, *R_w* = 0.1259, GOF = 1.0586.

deviation from planarity and serves presumably as a template for crystallization.⁶ Each chlorine atom is coordinated with four lithium atoms in a distorted tetrahedral geometry. The two Li atoms in that (Li–Cl)₂ ring are connected to a sulfonyl-oxygen and an oxygen atom of an isopropylate residue. Following the direction of the sulfonyl oxygen a six-membered ring is formed with the atomic sequence Li(1)–O(24)–S(21)–O(25)–Li(20)–Cl(1). In addition, two four-membered rings Li(1)–Cl(2)–Li(40)–O(24) are fused to the central (Li–Cl)₂ core. The 4 sulfonyl units form together with 4 external lithium atoms a 16-membered ring with the atomic sequence (O–S–O–Li)₄. However, a Li–C(α) bond has not been formed, but Ti–C(α) bonds. Each titanium builds with the C(α) atom and a sulfonyl-oxygen a (Ti–C–S–O) four-membered-ring chelate leading finally to a distorted trigonal bipyramidal coordination geometry on Ti. This view is supported by the angle deformation around the Ti atom (see, for example, O(22)–Ti(21)–O(24) = 169.5(5)°). Similar metalla-four-membered-ring chelates have been found before in a titanium–cyclopropyl sulfone,⁷ a lithiated cyclopropyl sulfone,⁸ several lithium sulfoximines,⁹ and a dilithiated sulfone.¹⁰ A second four-membered-ring Ti–O–Li–O is fused along the titanium–sulfonyl oxygen contact, inducing an overall six-membered-ring motif Ti–O–Li–O–S–C. The rather long Ti–O distances to the sulfonyl oxygen (range 2.258(9)–2.334(9) Å) are in line with the Ti–O bond length of 2.29(5) Å of a monolithated sulfone and are responsible for the deviation from a tetrahedral to a trigonal bipyramidal coordination geometry around each Ti atom.⁷ Each Ti atom satisfies its coordination sphere by three O-bound isopropylate molecules. The Ti–C(α) bond lengths in **3** are in the range of 2.036(7)–2.048(7) Å and shorter than in a titanated sulfone (2.174(4) Å),^{7a} but slightly longer than in a Ti-bound bis-(phosphoranimine) (2.008(4) Å).^{7b} Interestingly the S–C(α) bonds show distances of 1.621(7)–1.648(7) Å which are significantly shorter than the S–C(α) bond of 1.725(4) Å in a titanium sulfone,^{7a} but are closer to the S–C(α) bond length of lithiated (trimethylsilylphenylsulfonyl)methane¹¹ (1.625 Å). This can be explained on one hand by the strong Coulombic attraction of the remaining negative charge at the C(α) atom to the positively polarized S atom and on the other hand by an enhanced n_C–σ*_{S–Ph} interaction.¹² The Si–C(α) distances (1.802(6)–1.794(7) Å vs 1.888(2) Å in Si(CH₃)₃),¹³ suggesting that the Si-substituent plays also a role in charge stabilization.

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