## Structure Determination of a Lithiated Titanium-Sulfone

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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.<sup>1</sup> 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 phophorus, 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.<sup>2</sup> In contrast, it is, for example, wellknown 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.<sup>3</sup> The lacking structural information for the occurring intermediates stimulated us to shed some light on the structures of geminal lithium-titanium organodimetallics.<sup>4</sup> Herein we report the synthesis and first crystal structure of a complex derived from such a lithiated titaniumsulfone.



The reaction of (phenylsulfonyl)trimethylsilylmethane (1) with 2 equiv of *n*BuLi in diethyl ether and transmetalation with ClTi-(OiPr)<sub>3</sub> 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  $C_2$  symmetric cluster.<sup>5</sup> **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)<sub>2</sub> four-membered-ring motif, which shows a small

- (1) (a) Marek, I.; Normant, J.-F. Chem. Rev. 1996, 96, 3241-3267. (b) Thomson, C. M. Dianion Chemistry in Organic Synthesis; CRC Press: Boca (2) (a) Müller, J. F. K.; Neuburger, M.; Zehnder, M. Helv. Chim. Acta
- 1997, 80, 2182-2190. (b) Müller, J. F. K.; Batra, R. J. Organomet. Chem. 1999, 27-32.
- (3) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. Angew. Chem., Int. Ed. 1985, 24, 608-609
- (4) (a) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. Angew. Chem., Int. Ed. 1985, 24, 696-697. For NMR investigations on a lithium-titanium-sulfone see:
- (b) Vollhardt, J. Ph.D. Thesis, Darmstadt, 1990.

(5) X-ray data for 3: space group P1, a = 15.53(2) Å, b = 18.45(1) Å, c = 24.71(1) Å,  $\alpha = 107.73(4)^\circ$ ,  $\beta = 101.23(5)^\circ$ ,  $\gamma = 101.55(6)^\circ$ , V = 6352-(8) Å<sup>3</sup>, Z = 2, R = 0.1082,  $R_w = 0.1259$ , GOF = 1.0586.

deviation from planarity and serves presumably as a template for crystallization.<sup>6</sup> Each chlorine atom is coordinated with four lithium atoms in a distorted tetrahedral geometry. The two Li atoms in that (Li-Cl)<sub>2</sub> 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 16membered ring with the atomic sequence (O-S-O-Li)<sub>4</sub>. However, a Li–C( $\alpha$ ) bond has not been formed, but Ti–C( $\alpha$ ) bonds. Each titanium builds with the  $C(\alpha)$  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,  $O(22)-Ti(21)-O(24) = 169.5(5)^{\circ}$ ). Similar metalla-four-membered-ring chelates have been found before in a titanium-cyclopropyl sulfone,<sup>7</sup> a lithiated cyclopropyl sulfone,<sup>8</sup> several lithium sulfoximines,9 and a dilithiated sulfone.10 A second four-membered-ring Ti-O-Li-O is fused along the titaniumsulfonyl oxygen contact, inducing an overall six-membered-ring motif Ti-O-Li-O-S-C. The rather long Ti-O distances to the sulforyl 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 monotitanated sulfone and are responsible for the deviation from a tetrahedral to a trigonal bipyramidal coordination geometry around each Ti atom.<sup>7</sup> Each Ti atom satisfies its coordination sphere by three O-bound isopropylate molecules. The  $Ti-C(\alpha)$  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),<sup>7a</sup> but sligthly longer than in a Ti-bound bis-(phosphoranimine) (2.008(4) Å).<sup>7b</sup> Interestingly the S–C( $\alpha$ ) bonds show distances of 1.621(7) - 1.648(7) Å which are significantly shorter than the S-C( $\alpha$ ) bond of 1.725(4) Å in a titanium sulfone,<sup>7a</sup> but are closer to the S–C( $\alpha$ ) bond length of lithiated (trimethylsilylphenylsulfonyl)methane<sup>11</sup> (1.625 Å). This can be explained on one hand by the strong Coulombic attraction of the remaining negative charge at the  $C(\alpha)$  atom to the positively polarized S atom and on the other hand by an enhanced  $n_{\rm C} - \sigma *_{\rm S-Ph}$  interaction.<sup>12</sup> The Si-C( $\alpha$ ) distances in **3** are in general shorter compared to typical Si-C distances (1.802(6) - 1.794(7))Å vs 1.888(2) Å in Si(CH<sub>3</sub>)<sub>3</sub>),<sup>13</sup> suggesting that the Si-substituent plays also a role in charge stabilization.

(8) Hollstein, W.; Harms, K.; Marsch, M.; Boche, G. Angew. Chem., Int. *Ed.* **1988**, *27*, 846–847. (9) (a) Müller, J. F. K.; Neuburger, M.; Zehnder, M. *Acta Crystallogr.* **1997**,

(c) (a) Mullet, J. P. K., Neuburger, M., Zehnder, M. Acta Crystalog. 1997, (C3, 419–422. (b) Müller, J. F. K.; Batra, R.; Spingler, B.; Zehnder, M. *Helv. Chim. Acta* **1996**, 79, 820–826. (c) Gais, H.-J.; Lenz, D.; Raabe, G. *Tetrahedron Lett.* **1995**, 36, 7437–7441. (d) Gais, H.-J.; Dingerdissen, U.; Krüger, C.; Angermund, K. J. Am. Chem. Soc. **1987**, 109, 3775–3776. (e) Gais, H.-J.; Erdelmeier, I.; Lindner, H. J.; Vollhardt, J. Angew. Chem., Int. Ed. 1986, 25, 938-939

(10) (a) Müller, J. F. K.; Neuburger, M.; Spingler, B. *Angew. Chem., Int. Ed.* Submitted. (b) Gais, H.-J.; Vollhardt, J.; Günther, H.; Moskau, D.; Lindner, H. J.; Braun, S. J. Am. Chem. Soc. 1988, 110, 978-980.

(11) Boche, G. Angew. Chem., Int. Ed. 1989, 28, 277-297.

(12) (a) Salzner, U.; Schleyer, P. v. R. J. Am. Chem. Soc. 1993, 115, 10231–10236. (b) Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. J. Am. Chem. Soc. **1987**, 109, 4184–4188.

(13) Fjeldberg, T.; Seip, R.; Lappert, M. F.; Thorne, A. J. J. Mol. Struct. **1983**, *99*, 295–296.

<sup>(6) (</sup>a) Jokisch, A.; Schmidbaur, H. Inorg. Chem. **1999**, 38, 3014–3016. (b) Snaith, R.; Wright, D. S. In Lithium Chemistry: A Theoretical and Experimental Overview; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Intersience: New York, 1995; pp 227–295. (c) Barr, D.; Doyle, M. J.: Mulvey, P. R.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. J. Chem. Soc., Chem. Commun. **1989**, 318–319. (d) Barr, D; Clegg, W.; Mulvey, R. E.; Snaith, R. J. Chem. Soc., Chem. Commun. **1984**, 79–80. (7) (a) Gais, H.-J.; Vollhardt J.: Lindner H.J.: Paulus H. Angow. Chem.

<sup>(7) (</sup>a) Gais, H.-J.; Vollhardt, J.; Lindner, H. J.; Paulus, H. Angew. Chem., *Int. Ed.* **1988**, *27*, 1540–1542. (b) Cavell, R. G.; Kamalesh Babu, R. P.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805–5806.



Figure 1. Stereo plot of the molecular structure of 3. H atoms and the phenyl-, isopropyl-, and methyl-C atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.



Figure 2. Newman projections along the S(1)-C(10) (A) and S(21)-C(30) bonds (B) in 3.

## Scheme 1

$$\begin{array}{c} \bigoplus \\ Li \\ X \bigoplus \\ M \end{array} \begin{array}{c} R \\ M \end{array} \begin{array}{c} X = \text{Typical acceptor substituent:} \\ C(O)R, SO_2R, S(O)(NR)R, S(O)R, SR, CN... \\ M = \text{Ti, Zr, Zn, Cu...} \\ R = \text{SiR}_3, \text{Ph, SR, OR, NC, N(R)}_{2...} \end{array}$$

The Newman projections along the  $C(\alpha) - S$  bonds in A and **B** demonstrate that the lone pair at the  $C(\alpha)$  atom adopts a gauche conformation between the two sulfonyl oxygen atoms which allows a significant  $n_C - \sigma^*_{S-Ph}$  interaction for the stabilization of this geometry (see Figure 2). Obviously, the  $C(\alpha)$  atoms are fairly close to planarity as indicated by its sum of angles ( $\Sigma$  angles  $C(\alpha) = 359.40^{\circ}/358.76^{\circ}$ , the  $|\alpha + \beta|$  values (187.98°, 171.46°), and the distances of the C( $\alpha$ ) atoms to the Ti-S-Si plane (0.06 Å in A and 0.08 Å in B), suggesting a sp<sup>2</sup>-hybridized C atom.

To obtain some insight into the solution structure of 3, <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in [D<sub>8</sub>]-THF at low temperatures.<sup>4b</sup> Whereas the <sup>1</sup>H NMR data showed only small changes, the examination by <sup>13</sup>C NMR spectroscopy revealed significant changes in chemical shifts on metalation. The most dramatic effect was observed for the C( $\alpha$ ) atom, which shifted  $\Delta \delta = 89$  ppm to a resonance at  $\delta = 138$  ppm downfield. Smaller changes were seen for the aromatic carbon atoms, the isopropyl C atoms, and the methyl groups on silicon. For comparison the chemical shift of the C( $\alpha$ ) carbon of a monotitanated sulfone<sup>3</sup> was observed at

 $\delta = 52.4$  ppm, whereas for a 2-fold titanated sulfone a  $\delta = 173$ ppm was found.<sup>7</sup> Therefore we conclude that in solution a Ti- $C(\alpha)$  double bond has not been formed; however, a carbenoid character cannot be completely excluded.14 The sp2 character of the C( $\alpha$ ) atom of **3** may explain the tremendous downfield shift.<sup>15</sup> However, the remaining negative charge at this carbon atom prevents an even stronger downfield shift as previously reported for a doubly titanated sulfone.<sup>7</sup> The aggregation state in solution is still not clear, but it is reasonable to assume that during the transmetalation step the in situ formed LiCl also acts in solution as a template for aggregation. A possible salt effect on the reactivity of such doubly metalated intermediates toward the reaction with electrophiles should not be neglected and is demonstrated by the powerful influence of lithium salt additives to a variety of chemical reactions.<sup>16</sup> The good solubility of **3** in ethereal and hydrocarbon solvents seems contradictory, but is attributed to the nonpolar isopropyl, trimethylsilyl and phenyl residues on the surface of the globular structure of 3. As a consequence of our investigations, the lithium-titanium sulfone **3** might be regarded as a transition metal substituted monolithio anion rather than a geminal dianionic organo(di)metallic. Remarkably, the chiral conformation along the  $C(\alpha)-S$  bonds in 3 suggests that these compounds might be useful synthetic intermediates in asymmetric reactions, especially in the presence of a chiral auxiliary as for instance a sulfoxide or sulfoximine group. The proper choice of the transition metal might lead to an enhanced configurational stability<sup>17</sup> of the anionic  $C(\alpha)$  atom and promises to direct the reactivity by its steric and electronic impact. Our further studies will focus on this novel concept for the creation of chiral configurationally stable carb(di)anions.

Supporting Information Available: Synthetic procedures and <sup>1</sup>H and <sup>13</sup>C NMR data (PDF). X-ray crystallographic file (CIF). This material is available free of charge on the Internet at http://pubs.acs.org.

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(14) (a) Seebach, D.; Hässig, R.; Gabriel, J. Helv. Chim. Acta 1983, 66, 308-337. (b) Mareda, J.; Rondan, N. G.; Houk, K. N.; Clark, T.; Schleyer, P. v. R. J. Am. Chem. Soc. **1983**, 105, 6997-6999. (c) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. Helv. Chim. Acta 1980, 63, 2046-2053. (d) Seebach, D.; Siegel, H.; Müllen, K.; Hiltbrunner, K. Angew. Chem., Int. Ed. 1979, 18, 784–785. (e) Seebach, D.; Hiltbrunner, K.; Siegel, H. Angew. Chem., Int. Ed. 1979, 18, 785-786.

(15) Kalinowski, H.-O.; Berger, S.; Braun, S. <sup>13</sup>C NMR Spektroskopie; G.

Thieme Verlag: Stuttgart, New York, 1984. (16) (a) Seebach, D.; Beck, K.; Studer, A. In *Modern Synthetic Methods*; Ernst, B., Leumann, C., Eds.; VCHA and VCH: Basel and Weinheim, 1995; Vol. 7, pp 3-178. (b) Loupy, E. A.; Tchoubar, B. Salt Effects in Organic and Organometallic Chemistry; VCH: Weinheim, 1992. (c) Reichardt, H.; Solvents and Solvent Effects in Organic Chemistry, 2nd ed.; VCH: Weinheim, 1988. (d) Seebach, D. Angew. Chem., Int. Ed. 1988, 27, 1624-1654

(17) (a) Reggelin, M.; Weinberger, H. Angew. Chem., Int. Ed. **1994**, 33, 489-491. (b) Kerrick, T.; Beak, P. J. Am. Chem. Soc. **1991**, 113, 9708-9710. (c) Hoppe, D.; Hintze, F.; Tebben, P. Angew. Chem., Int. Ed. **1990**, 29, 1422–1424. (d) Gais, H.-J.; Hellmann, G.; Günther, H.; Lopez, F.; Lindner, H. J.; Braun, S. Angew. Chem., Int. Ed. **1989**, 28, 1025–1027. (e) Still, W. C.; Mitra, A. J. Am. Chem. Soc. **1978**, 100, 1927–1928.