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Synthesis and structure of sulfonamido cyclopentadiene titanium complexes: X-ray structure of $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)Cl_2$

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Abstract

The reaction of $Ti(NMe_2)_4$ with the bidentate ligand $C_5H_4CH_2CH_2NHSO_2C_6H_4CH_3$ yields the titanium sulfonamido cyclopentadiene complex $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)(NMe_2)_2$. This compound reacts with two equivalents Me_3SiCl to give the novel dichloride complex $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)Cl_2$ whose molecular structure was determined by single crystal X-ray crystallography. © 1998 Elsevier Science S.A.

Keywords: Titanium; Sulfonamido; Cyclopentadiene; Crystal structure

1. Introduction

The synthesis of metal complexes, in particular of Group 4 metals, with chelating cyclopentadiene ligands has received considerable attention. In particular Lewis base functionalized cyclopentadienes in which the cyclopentadiene is bonded via a bridge to a group containing an amine [1,2], ether [3], amide [4] or alkoxide [5] group.

Recently we described a facile synthesis of ethylsulfonamido substituted cyclopentadiene and indene ligands [6,7]. These compounds were obtained using a simple two step procedure starting from amino alcohols. Because of the ease of preparation of these compounds it is possible to synthesize a variety of these ligands and this was demonstrated by the synthesis of chiral, enantiomerically pure sulfonamide indene ligands.

It is our expectation that a bidentate sulfonamido cyclopentadiene ligand binds strongly with Group 4 metals and forms stable complexes. Given that the pK_a of sulfonamides are typically about 12–15, (in the same range as cyclopentadienes), and the pK_a of HNR_2 is typically around 40, it is anticipated that the metal sulfonamido bond will be less susceptible to aminolysis or alcoholysis then, for example, amine functionalized cyclopentadiene complexes.

The synthesis of cyclopentadiene complexes using the aminolysis reaction of tetradialkylamide metal precursors is now a well established route. It was first described for the synthesis of Group 4 metal complexes [8]. This route has also been used to prepare cyclopentadienyl-amide complexes of titanium, zirconium and hafnium with bidentate ligands [4,9]. It was further developed for the preparation of ansa-bisindenyl complexes of zirconium [10]. This study reports on the aminolysis reaction of the novel sulfonamido cyclopentadiene ligands $C_5H_4CH_2CH_2NHSO_2C_6H_4CH_3$ (**1**) and $C_9H_4CH_2CH_2NHSO_2C_6H_4CH_3$ (**2**) with $Ti(NR_2)_4$ (R = Me, Et).

2. Results and discussion

The reaction of ligand **1** with $Ti(NMe_2)_4$ in benzene or toluene proceeds fast at room temperature and is completed in only a few minutes to yield compound **3** which could be isolated in 85% yield. The reaction of the same ligand **1** with $Ti(NEt_2)_4$ in benzene on the

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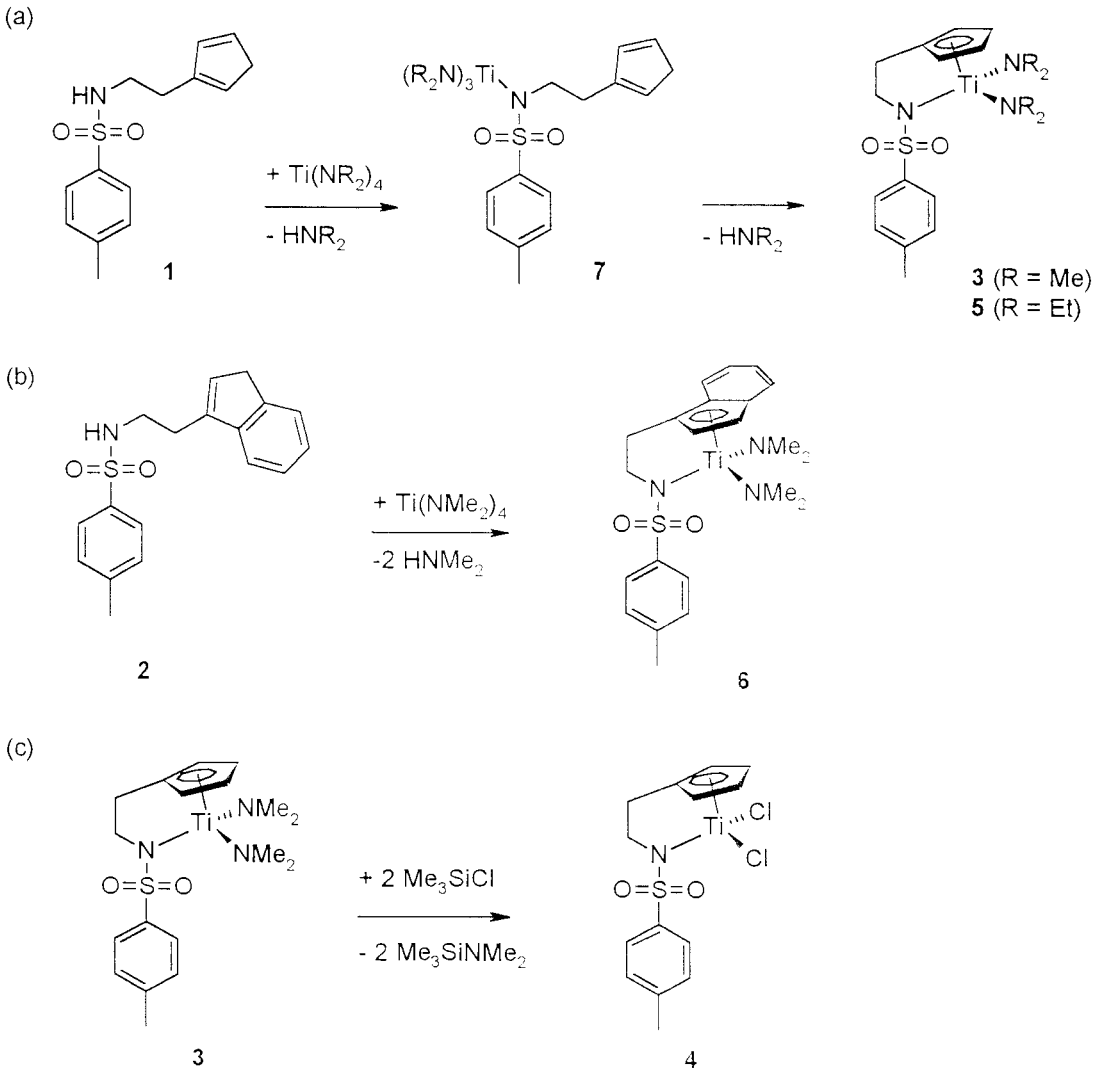
other hand proceeds in a step wise fashion. In the first and fast step the sulfonamido NH reacts with the metal precursor to eliminate one equivalent diethylamine to yield intermediate complex $Ti(C_5H_5CH_2CH_2NSO_2C_6H_4CH_3)(NMe_2)_3$ (**7**) in which the cyclopentadiene ring has not yet coordinated to the titanium center (Scheme 1a). The ^1H NMR spectrum of the reaction mixture, recorded immediately after mixing, clearly shows the disappearance of the NH signal and the appearance of signals which can be attributed to diethylamine. The signals for the cyclopentadiene protons remain unchanged. At this stage of the reaction there is no NMR evidence for the coordination of the cyclopentadiene ring to the metal center. Heating the reaction mixture to reflux (or better, in refluxing toluene) over a period of several days with a slow, continuous purge of nitrogen over the top of the reflux condenser in order to drive of the liberated amine, drives the reaction to completion with the formation of compound **5** which can be clearly identified in the ^1H and ^{13}C NMR spectra by the triplets for the coordinated cyclopentadiene protons at 5.53 and 5.48 ppm and the carbon signals at 113.3 and 110.8 ppm respectively.

Similarly, the reaction of the indene ligand **2** with $Ti(NMe_2)_4$ in benzene also proceeds in a stepwise fashion (Scheme 1b). The first step is the rapid reaction of the sulfonamido group with the metal precursor with the liberation of an equivalent of dimethylamine. The ^1H NMR spectrum of the mixture immediately after mixing again clearly shows the disappearance of the sulfonamido NH, the appearance of dimethylamine and a small shift in the *p*-toluene proton signals. The indenyl signal at 5.84 ppm (CH) remains virtually unchanged. In order for this reaction to reach completion it is necessary to reflux the reaction mixture in toluene for several days. Compound **6** was formed exclusively and shows the characteristic ^1H and ^{13}C signals for a coordinated indene at 6.19 and 5.94 ppm (doublets) and



Scheme 1.

117.9 and 99.6 ppm respectively. The lower reactivity of ligand **2** towards $Ti(NMe_2)_4$ reflects the higher pK_a of indene when compared with cyclopentadiene and it is not uncommon that the amine elimination reactions with indenyl compounds require more forcing condition than cyclopentadiene.

The indene ligand **2** exhibits planar chirality and as a result complex **6** is chiral. This manifests itself in the ^1H and ^{13}C NMR spectra. For example, two signals are observe in the ^1H NMR spectrum for the two dimethylamide groups at 3.45 and 2.48 ppm and two signals at 51.8 and 46.9 ppm in the ^{13}C NMR. Also, the proton signals for the ethylene bridge show a ABCD pattern as expected.

The bis amide complexes **3**, **5**, and **6** were all obtained as extremely air sensitive dark orange powders. Purification of these compounds can be accomplished by careful washing with a minimum amount of pentane to yield analytically pure compounds. The compounds are extremely soluble in aromatic solvents but only sparingly soluble in pentane or hexane.

In a preliminary investigation in the chemical properties of the novel compounds **3** was reacted, in toluene, with two equivalents of Me_3SiCl (Scheme 1c). The compound $Ti(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)Cl_2$ (**4**) precipitated from the reaction mixture overnight as a yellow solid and was isolated in 50% yield. The same compound was also prepared in 87% in one pot synthesis.

Yellow crystals of **4** suitable for a X-ray crystallographic structure determination were obtained from $CDCl_3$. Fig. 1 shows the structure of compound **4** with selected bond lengths and angles.

Compound **4** is a monomeric complex. The geometry about the central titanium atom is a slightly deformed tetrahedron with equal angles Cg–Ti–Cl1 and Cg–Ti–Cl2 of 111.0° and 110.6° respectively and a smaller angle Cg–Ti–N of 101.0° (Cg is the center of gravity of the cyclopentadiene carbon atoms). The bond C9–C10 bends out of the plane of the cyclopentadiene ring, towards the titanium atom, by about 6.8°. The nitrogen atom has a trigonal planar geometry and although the angles are not equal, the sum of the angles is 358.5°. The atoms Ti, N, S, O2 and C10 are all within one plane with the largest deviation of the mean plane of 0.049 Å for S. This plane is oriented almost perpendicular to the plane of the cyclopentadiene ring at an angle of 85.7°.

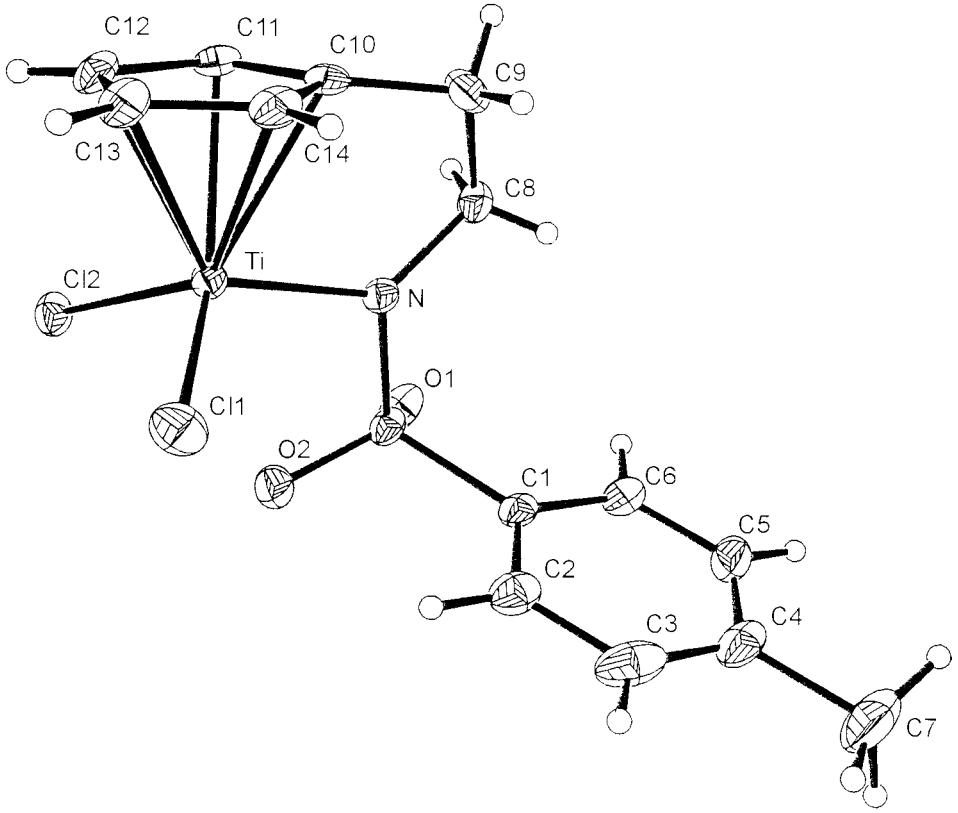


Fig. 1. View of the molecular structure of $Ti(\eta^5{:}\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)Cl_2$, **4**, with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to 30% probability [11]. Selected bond lengths (Å) and angles (°): Ti–N 1.963(2), Ti–Cl(1) 2.266(1), Ti–Cl(2) 2.289(1), Ti–Cg 2.024(3), Ti–O(2) 2.556(2), Ti–S 2.914(1), S–O(1) 1.432(2), S–O(2) 1.454(2), S–N 1.619(2), N–Ti–Cl(1) 112.35(7), N–Ti–Cl(2) 112.27(7), Cg–Ti–N 101.04, Cl(1)–Ti–Cl(2) 109.37(3), O(1)–S–O(2) 118.4(13), O(1)–S–N 111.63(13), O(2)–S–N 100.73(12), C(8)–N–S 118.65(18), C(8)–N–Ti 131.46(18), S–N–Ti 108.40(12).

The distance Cp–Ti of 2.024 Å is only slightly shorter than the distance found in e.g., $CpTi(N^iPr_2)_2Cl_2$ (2.035 Å) [12], $CpTiCl_3$ (2.04 Å) [13] and Cp_2TiCl_2 (2.059 Å) [14]. The Ti–N distance of 1.963 Å is approximately 0.1 Å longer than in e.g., $CpTi(N^iPr_2)_2Cl_2$ (1.865 Å) [12] or $C_5H_4CH_2CH_2N^iPrTiCl_2$ (1.864 Å). [1] This is a possible indication that a $N(p_\pi) \rightarrow M(d_\pi)$ bonding contribution is not as prominent as is the case for other titanium amide complexes. The close proximity of O2 to Ti, which could be interpreted as a bonding interaction of an oxygen lone pair towards Ti, may influence and diminish the $N(p_\pi) \rightarrow M(d_\pi)$ bonding interaction. The long Ti–N distance of 1.965 Å is more an indication of a Ti–N single bond which has been estimated to be 1.96–1.97 Å [15–17]. The two Ti–Cl bond distances differ by about 0.02(1) Å and are typical Ti–Cl distances for titanium amide complexes but are significantly shorter than in e.g., Cp_2TiCl_2 (2.36 Å) [14] and $(CH_2)_2(C_5H_4)_2TiCl_2$ (2.35 Å) [18]. The Ti–O2 distance of 2.556 Å is smaller than the sum of the van der Waals radii and this distance and the overall geometry of the complex suggests a bonding interaction between Ti and O2. The S–O1 distance is slightly smaller than the S–O2 distance by 0.02 Å. The molecular geometry of **4** in the solid state is chiral and this renders the two H atoms on C8 inequivalent as well as the two H atoms on C9. In solution, however, the ^{1}H NMR spectrum of **4** at room temperature shows a A_2X_2 pattern of two triplets for these protons indicating a dynamic system where O2 and O1 are exchanging coordination to the titanium.

3. Experimental

All manipulations were carried out under an inert atmosphere of nitrogen or argon or were carried out inside a glovebox (Innovative Technology). Solvents were dried using conventional methods. NMR spectra were recorded on a AC300 Bruker spectrometer. Elemental analysis were performed by Campbell Analytical Laboratory, University of Otago, Dunedin, New Zealand. $Ti(NMe_2)_4$ and $Ti(NEt_2)_4$ were prepared according to a literature method [19].

*3.1. Synthesis of $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)(NMe_2)_2$ (**3**)*

A solution of $C_5H_4CH_2CH_2N(H)SO_2C_6H_4CH_3$ (0.52 g, 2.0 mmol) dissolved in toluene (3 ml) was added dropwise to a solution of $Ti(NMe_2)_4$ (0.44 g, 2.0 mmol) in toluene (3 ml) at room temperature. The reaction mixture was stirred at room temperature for 2 h. The solvent was subsequently removed under reduced pressure. The crude product was washed once with pentane (5 ml) and dried in vacuo. An orange solid was isolated in a yield of 0.84 g, (1.68 mmol, 85%). Anal. Calc. for $C_{18}H_{27}N_3O_2STi$: C, 54.4; H, 6.8; N, 10.6. Found: C, 54.1; H, 6.8; N, 9.4. ^{1}H NMR (benzene-d_6) δ 7.73 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, C_6H_4), 6.67 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, C_6H_4), 5.53 (t, 2H, $^3J_{H-H}$ = 2.6 Hz, C_5H_4), 5.48 (t, 2H, $^3J_{H-H}$ = 2.6 Hz, C_5H_4), 3.45 (t, 2H, $^3J_{H-H}$ = 6.4 Hz, N–CH_2), 3.06 (s, 12H, NCH_3), 1.98 (t, 2H, $^3J_{H-H}$ = 6.4 Hz, CH_2–C–N), 1.85 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6) δ 141.9 (C_6H_4 para), 140.7 (C_6H_4 ipso), 136.9 (C_5H_4 ipso), 129.1 (CH of C_6H_4), 127.6 (CH of C_6H_4), 113.3 (CH of C_5H_4), 110.8 (CH of C_5H_4), 59.7 (NCH_2), 48.7 (NCH_3), 29.1 (CH_2–C–N), 21.1 (CH_3).

*3.2. Synthesis of $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)Cl_2$ (**4**)*

To a solution of compound **3** (0.23 g, 0.58 mmol) in benzene (4 ml) was added a solution of Me_3SiCl (0.13 g, 1.20 mmol) in benzene (2 ml). The reaction mixture was stirred overnight at room temperature. The volume was reduced to 50% under reduced pressure. Pentane (10 ml) was added to the reaction mixture and a yellow solid was isolated via filtration. The crude product was washed with a small amount of pentane and dried under vacuo to yield 0.11 g (0.29 mmol, 50%) of compound **2** as a yellow solid. Anal. Calc. for $C_{14}H_{15}Cl_2NO_2STi$: C, 44.2; H, 4.0; N, 3.7. Found: C, 44.5; H, 4.3; N, 3.5. ^{1}H NMR ($CDCl_3$) δ 7.87 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, C_6H_4), 7.24 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, C_6H_4), 6.94 (t, 2H, $^3J_{H-H}$ = 2.6 Hz, C_5H_4), 6.39 (t, 2H, $^3J_{H-H}$ = 2.6 Hz, C_5H_4), 4.21 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, N–CH_2), 3.01 (t, 2H, $^3J_{H-H}$ = 7.0 CH_2–C–N), 2.36 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6) δ 148.7 (C_6H_4 *para*), 144.9 (C_6H_4 ipso), 134.4 (C_5H_4 ipso), 129.8 (CH of C_6H_4), 128.2 (CH of C_6H_4), 121.9 (CH of C_5H_4), 119.4 (CH of C_5H_4), 64.3 (NCH_2), 28.3 (CH_2–C–N), 21.6 (CH_3).

*3.3. One pot synthesis of $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)Cl_2$ (**4**)*

$Ti(NMe_2)_4$ (0.925 g, 4.1 mmol) was dissolved in toluene (5 ml). A solution of **1** (1.087 g, 4.1 mmol) in toluene (5 ml) was added and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo. The resulting dark orange oil was redissolved in toluene (5 ml). To this solution was added a solution of Me_3SiCl (0.897 g, 8.3 mmol) in toluene (5 ml). The reaction mixture was stirred overnight. The yellow precipitate was isolated via filtra-

[1] J.H. Teuben, P.-J. Sinnema, personal communication.

tion and dried in vacuo. Yield 1.365 g (3.6 mmol, 87%) of **4**.

3.4. Synthesis of $Ti(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2NSO_2C_6H_4CH_3)(NEt_2)_2$ (5)

To a solution of $Ti(NEt_2)_4$ (0.42 g, 1.25 mmol) in benzene (5 ml) was added **1** (0.32 g, 1.25 mmol). The mixture was heated to reflux for 3 days. The solvent was removed under reduced pressure to yield **5** as a dark orange oil. The ^1H and ^{13} NMR indicate a near quantitative conversion. ^1H NMR (benzene-d_6) δ 7.78 (d, 2H, $^3J_{H-H} = 8.1$ Hz, C_6H_4), 6.84 (d, 2H, $^3J_{H-H} = 7.9$ Hz, C_6H_4), 5.77 (t, 2H, $^3J_{H-H} = 2.6$ Hz, C_5H_4), 5.59 (t, 2H, $^3J_{H-H} = 2.6$ Hz, C_5H_4), 3.91 (m, 1H, N–CH_a), 3.40 (m, 1H N–CH_b), 3.33 (m, 1H, CH_a–C–N), 1.98 (m, 1H, CH_b–C–N), 2.38 (q, 4H, $^3J_{H-H} = 3.4$ Hz, N–CH_2(ethyl)), 2.36 (q, 4H, $^3J_{H-H} = 3.4$ Hz, N–CH_2(ethyl)), 0.95 (t, 6H, $^3J_{H-H} = 3.4$ Hz, N–C–CH_3(ethyl)), 0.94 (t, 6H, $^3J_{H-H} = 3.4$ Hz, N–C–CH_3(ethyl)), 1.95 (s, CH_3). ^{13}C NMR (benzene-d_6) δ 142.4, 140.6 (C_6H_4), 136.5 (C_5H_4 ipso), 129.1 (CH of C_6H_4), 127.7 (CH of C_6H_4), 113.1 (CH of C_5H_4), 109.5 (CH of C_5H_4), 59.4 (NCH_2), 47.6, 44.3 (NCH_2(ethyl)), 29.3 (CH_2–C–N), 21.2 (CH_3), 15.8, 15.2 (N–C–CH_3(ethyl)).

3.5. Synthesis of $Ti(\eta^5:\sigma\text{-}C_9H_6CH_2CH_2NSO_2C_6H_4CH_3)(NMe_2)_2$ (6)

To a solution of $Ti(NMe_2)_4$ (0.68 g, 3.0 mmol) in benzene (5 ml) was added $C_9H_7CH_2CH_2N(H)SO_2C_6H_4CH_3$ (0.94 g, 3.0 mmol) as a solid in small portions over a period of 30 min. The reaction mixture was refluxed for two days with a slow stream of argon blowing over the top of the reflux condenser to remove liberated dimethylamine. The solvent was removed under reduced pressure. The crude product was subsequently washed with a small amount of pentane to yield compound **3** (1.13 g, 2.52 mmol, 84%) as a dark orange solid. An analytically pure sample could be obtained by precipitation of a toluene solution with pentane. Anal. Calc. for $C_{22}H_{29}N_3O_2STi$: C, 59.1; H, 6.5; N, 9.4. Found: C, 59.2; H, 6.7; N, 9.0. ^1H NMR (benzene-d_6) δ 7.85 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4), 7.27 (d, 1H, $^3J_{H-H} = 7.3$ Hz), 7.20 (d, 1H, $^3J_{H-H} = 7$ Hz), 6.93 (d, 2H, $^3J_{H-H} = 8.0$ Hz, C_6H_4), 6.81 (m, 2H), 6.19 (d, 1H, $^3J_{H-H} = 3.1$ Hz, indenyl-C_5), 5.94 (d, 2H, $^3J_{H-H} = 3.1$ Hz, indenyl-C_5), 4.37 (m, 1H, NCH), 3.90 (m, 1H, NCH), 3.45 (s, 6H, NCH_3), 2.71 (m, 1H, CH–C–N), 2.48 (s, 6H, NCH_3), 2.33 (m, 1H, CH–C–N), 2.02 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6) not all aromatic signals observed, δ 129.1, 125.2, 124.8, 124.7, 122.1, 117.9 (indenyl-C_5 CH), 99.6 (indenyl-C_5 CH), 60.9 (N–CH_2), 51.8 (NCH_3), 46.9 (NCH_3), 27.6 (CH_2–C–N), 22.2 (CH_3).

4. X-ray structure determination of 4

Suitable crystals of compound **4** were obtained by crystallization form $CDCl_3$. A yellow crystal ($0.35 \times 0.30 \times 0.20$ mm^3) was selected. Data were collected at room temperature. The unit cell dimensions and intensity data were obtained using a Siemens CCD detector mounted on a P4 diffractometer and controlled by SMART software. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of two sets of exposures. In the first, each exposure covered 0.3° for a total of 52° in omega. The second run covered 360 degrees in phi (the mounting axis) also using 0.3° increments between frames. The crystal to detector distance was 4.0 cm. All frames were processed using program SAINT to give raw data sets which were corrected empirically for absorption using SADABS [cf. Blessing, Acta Cryst., A51, 1995, 33]. Graphite monochromator, λ(MoKα) = 0.71073 Å. Triclinic system, space group *P*-1, $a = 7.434(1)$ Å, $b = 7.476(1)$ Å, $c = 15.174$ (1) Å, $\alpha = 100.25$ (1)°, $\beta = 99.12$ (1)°, $\gamma = 103.72$ (1)°. $V = 788.15$ (11) Å^3, $\delta_{calc} = 1.602$ Mg m^{-3}, $Z = 2$, absorption coefficient = 1.016 mm^{-1}, F(000) = 388. Of the 2942 reflections collected 2105 were unique ($R_{int} = 0.0160$). The structure was solved by direct methods using SHELXS-96 (Sheldrick, 1990). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from difference Fourier maps and included in the final refinement with fixed isotropic thermal paramenters related to their parent atoms U(H) = 1.2 U_{eq}(C) and U(H) = 1.5 U_{eq}(C–Me) for H7*abc*. Final refinement was done by full-matrix least-squares refinement using SHELXL-96 (Sheldrick, 1996). Final *R* indices [$I > 2\sigma(I)$] $R_1 = 0.0329$, $wR_2 = 0.0895$. *R* indices (all data) $R_1 = 0.0367$, $wR_2 = 0.0920$. Tables of atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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