Propylthiotetramethylcyclopentadienyl complexes of iron, titanium and zirconium. Structural characterization of [η⁵-C₅Me₄SCH₂CH₂CH₃]₂TiCl₂

$$[\eta^5\text{-}C_5Me_4SCH_2CH_2CH_3]_2TiCl_2$$

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Abstract

The use of the propylthio substituted tetramethylcyclopentadienylsodium salt leads to octamethyl-1,1′-di(propylthio)ferrocene and dichlorodi(propylthiotetramethylcyclopentadienyl)zirconium or titanium(IV). The structure of $[\eta^5\text{-}C_5Me_4SCH_2CH_2CH_3]_2TiCl_2$ has been established by X-ray analysis (orthorhombic, *Pbca*, $a = 16.767(1)$, $b = 16.247(3)$, $c = 19.002(3)$ Å, $V = 5176.2(9)$ Å³, $Z = 8$, $R_F = 0.052$). The complexes have been characterized by ^1H and ^{13}C NMR and electrochemical studies.

Keywords: Cyclopentadienyl; Sulphur; Ferrocene; Zirconium; Titanium

1. Introduction

The association of early transition metals to electron-rich metals such as rhodium is of great interest because of the potential cooperative reactivity of two widely different metals.

Among the various bridging modes via a heteroatom such as P or S we have been interested in bimetallic compounds in which the metal atoms are maintained close to each other by a short bridge as for $[AsPh_4][(\eta^5\text{-}C_5Me_5)_2Zr(\mu\text{-}S)_2Rh(CO)_2]$ [1]. In the presence of triphenylphosphine, this complex initiates the carbonylation of ethene to give acrolein.

We have also been interested in the preparation of bimetallic compounds in which the metal atoms are linked via a substituted cyclopentadienyl ring bearing a pendant functional group such as a phosphido group in $Fe(\eta^5\text{-}C_5Me_4PPh_2)_2M(CO)_4$, M = Cr, Mo, W [2].

By analogy, a linkage between two metallic centres using a cyclopentadienyl with a thioether substituent may be considered. As far as we know, chemistry in this field has been performed in the ferrocene series [3],

but no reports concerning the bent metallocenes have as yet appeared in the literature.

The present work reports on the generation of thioether substituted cyclopentadienides and on the formation of the corresponding substituted metallocenes.

2. Results and discussion

Sulphur substituted cyclopentadienyl ligands are present in chelating substituted ferrocenes such as $Fe(\eta^5\text{-}C_5H_4SR)_2$, $Fe(\eta^5\text{-}C_5H_4SR)(\eta^5\text{-}C_5H_5)$ [3] and cyclopentadienyl tricarbonyl manganese and rhenium compounds such as $Mn(\eta^5\text{-}C_5H_4SR)(CO)_3$ [4]. The sulfido groups have been introduced by the standard method of lithiation of the organometallic precursor. This synthetic strategy is not applicable to the synthesis of substituted bent metallocenes $M(\eta^5\text{-}C_5H_4SR)_2Cl_2$ which incorporate a Group 4 transition metal, because of the inability to form substituted derivatives by ring-substitution routes. We have studied an alternative approach consisting in the initial preparation of sulphur substituted cyclopentadienes and their transformation into the corresponding cyclopentadienides. In a following step, the metallocene products are obtained by

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reaction of the salts with a convenient metal chloride. In order to prepare a new sulphur substituted cyclopentadienyl we turned our interest towards tetramethylcyclopentadienyl chemistry. Among the reasons of interest in such species, there are firstly the advantageous properties of this substituted ligand (solubility, crystallizability, stabilization of metallocene derivatives) and also the reason which arises from the observation that a preliminary tetramethyl substitution may prevent the undesirable by-products, mainly polyalkylthiocyclopentadienes, which are formed in the case of cyclopentadiene itself [5,6].

The preparation of the suitable cyclopentadienyl salt has been achieved by reaction of propylsulfenylchloride or dipropyldisulfide with tetramethylcyclopentadienylsodium or lithium salt followed by reaction with one equivalent of sodium hydride (Scheme 1).

Sodium hydride was found to react with a mixture of propylthiotetramethylcyclopentadiene isomers in refluxing tetrahydrofuran but not in diethylether. This was not surprising because the aromatisation of substituted tetramethylcyclopentadienes usually occurs at relatively high temperatures [7].

The sodium salt 1, $C_5Me_4S^nPrNa$, was produced with a reasonable yield (40%) as a white powder soluble in etheral solvents and insoluble in alkanes and aromatics.

When a THF suspension of Fe_2Cl_4, 3THF was treated with four equivalents of 1 solubilized in THF the compound $Fe(\eta^5-C_5Me_4S^nPr)_2$ 2 was isolated (Scheme 2).

Similarly, treatment of $ZrCl_4$ or $TiCl_3$, 3THF with 1 and usual work-up led to the new bent dicyclopentadienyl metallocenes of titanium $Ti(\eta^5-C_5Me_4S^nPr)_2Cl_2$ 3 and zirconium $Zr(\eta^5-C_5Me_4S^nPr)_2Cl_2$ 4 (Scheme 2). $TiCl_4$ oxidizes partially the cyclopentadienide, and $HfCl_4$ did not yield any dicyclopentadienyl metallocene in the same conditions.

The dissymmetric arrangement $Zr(\eta^5-C_5Me_4S^nPr)(\eta^5-C_5H_5)Cl_2$ 5 was also readily formed by the reaction of 1 with a monocyclopentadienyl complex of zirconium, $Zr(\eta^5-C_5H_5)Cl_3$, DME.

Complexes 2 to 5 were characterized by elemental analyses, ^1H and ^{13}C NMR and mass spectrometry. The
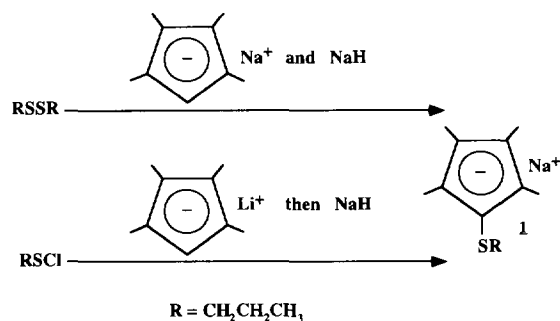
Scheme 2.

Scheme 1.
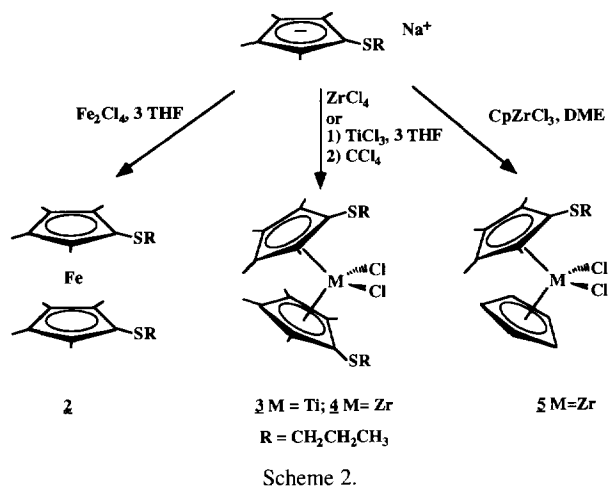
^1H NMR spectrum of the $C_5Me_4S^nPr$ part shows a typical triplet, sextuplet, triplet appearance for the protons of the propyl chain and two singlets for the methyl groups. The most shielded singlet is assigned to the methyl groups at the β position on the ring. This assignment is proposed by comparison with the spectrum observed for $Fe[\eta^5-C_5Me_3(S^nPr)_2]_2$ [8] but looks inverted with respect to that proposed for $Fe(\eta^5-C_5Me_4PPh_2)_2$ [2]. As expected, the ^{13}C NMR data (Table 1) show a deshielding of the ring carbon atoms in the $\eta^5-C_5Me_4S^nPr$ ligand with respect to the values observed for $\eta^5-C_5Me_4H$. This observation may be ascribed to the electron-withdrawing property of the propylthio group. Another characteristic is the reversed chemical shifts for the α and β ring carbons with respect to the ipso carbon when the $C_5Me_4S^nPr$ ligand is compared to the $C_5H_4S^nPr$ one [6].

The EI mass spectra of 2–5 exhibit the molecular ion (2, m/e 446 (M^+, 100%); 3, m/e 509 (M^+, 18%); 4, m/e 553 (M^+, 43%); 5, m/e 420 (M^+, 88%)) in the expected isotope pattern. The major fragments arise from the loss of cyclopentadienyl ligands from the molecular ion (see Section 4).

The electrochemical reduction of $M(\eta^5-C_5Me_4S^nPr)_2Cl_2$ (M = Ti 3 or Zr 4) in non-aqueous solution has been examined by linear potential sweep voltammetry. As expected, three for 3 and two for 4 monoelectronic stages were seen [9,10], but only the first one-electron reduction will be discussed (Table 1).

In the case of complex 3 (M = Ti), this first stage is dependent on the solvent, the supporting electrolyte and the sweep rate. The study of the influence of the two first factors (solvent, electrolyte) is in progress, and we report here the results of the voltammetry in tetrahydrofuran. We have observed a pseudo-reversible behaviour only in this solvent and at very slow sweep rates. When other solvents (dimethylformamide, dichloromethane) are used the system becomes irreversible.

Fig. 1 shows the cyclic voltammogram obtained with

Table 1
Electrochemical and ^{13}C NMR data

	$E_{1/2} = (E_{pc} + E_{pa})/2$ (V/ESC)	^{13}C NMR $\{^1H\}$ Cp ring
Fe(η^5-C$_5$Me$_4$H)$_2$	0.19	71.2 80.6 80.7 78.7 [b]
Fe(η^5-C$_5$Me$_4$S^{n}Pr)$_2$	0.35	77.8 82.1 84.8 82.3 [b]
Ti(η^5-C$_5$Me$_4$H)$_2$Cl$_2$	−1.04 [a]	113.1 125.1 135.8 127.0 [b]
Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$Cl$_2$	−0.88 [a]	119.8 134.2 134.4 131.4 [b]
Zr(η^5-C$_5$Me$_4$H)$_2$Cl$_2$	−1.88	110.0 120.9 129.7 122.2 [b]
Zr(η^5-C$_5$Me$_4$S^{n}Pr)$_2$Cl$_2$	−1.73	114.4 128.9 130.4 126.6 [b]
Zr(η^5-C$_5$Me$_4$S^{n}Pr)(η^5-C$_5$H$_5$)Cl$_2$	−1.74	

[a] $E_{1/2} = E_{1/2}$ apparent $= E_2° + (RT/F)\ln(1 + K_2)$.
[b] Mean value of δ^{13}C of five Cp carbon atoms.

a scan rate of 0.2 V s^{-1}. The reduction peak a is followed by two oxidation peaks b and c. The ratio I_{pa}/I_{pc} (peaks a and b) is 0.66. When the scan rate increases, the ratio I_{pa}/I_{pc} decreases and the relative height of peak c increases. The results suggest an electrochemical–chemical (EC) mecanism for the reduction process [11]. More precisely, the situation can be described by using a square scheme (Scheme 3). Such a cyclic scheme has been used for the qualitative interpretation of different types of voltammogram obtained for Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$ in various solvents [9]. We discuss below the determination of apparent $E_{1/2}$ for the reduction of 3 on the basis of the square scheme.

At slow sweep rates the recombination of Cl$^-$ takes place. The mechanism is restricted to the half of the square scheme (Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$Cl$_2$ ↔ Ti(η^5-C$_5$Me$_4$SPr)$_2$Cl$_2^-$ ↔ Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$ClL) and can
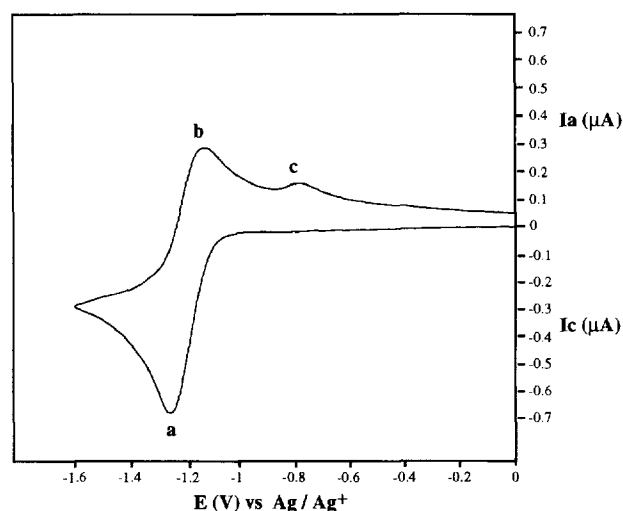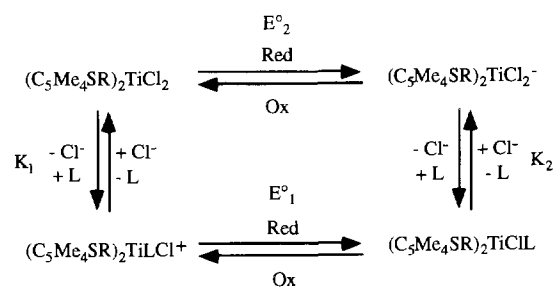

Fig. 1. Cyclic voltammogram of 3. Platinum electrode: diameter 2 mm; $v = 200$ mV s^{-1}. THF; Bu$_4$NPF$_6$: 0.5 M; 3: 10^{-3} M. $\Delta E_p = $ 80 mV; $I_{pa}/I_{pc} = 0.6$.

become equivalent to a reversible electrochemical reaction followed by a reversible chemical reaction (EC scheme). When $v = 0.2$ V s^{-1} (Fig. 1), where $I_{pa}/I_{pc} = $ 0.66, it can be deduced from the theory of Nicholson and Shain [13] that the reduction peak is shifted towards the negative potentials (the theoretical variation in peak potential is approximately equal in that case to 20 mV). The half sum of the oxidation and reduction peaks gives the apparent $E_{1/2}$ of the Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$Cl$_2$/Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$ClL couple defined in Table 1 with a shift equal to about 10 mV.

We have used thin-layer linear sweep voltammetry for determining unambiguously this apparent $E_{1/2}$ (Fig. 2).

At the slow sweep rates ($v = 5 \times 10^{-3}$ V s^{-1}) used in this technique, the ratio I_{pa}/I_{pc} of the system Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$Cl$_2$/Ti(η^5-C$_5$Me$_4$S^{n}Pr)$_2$ClL is equal to 1 and the difference between E_{pa} and E_{pc} comes from the ohmic drop. So here the apparent $E_{1/2}$ is equal to the half sum of the peak potentials E_{pa} and E_{pc}.

R = CH$_2$CH$_2$CH$_3$ R = solvant

K$_1$ = ([(C$_5$Me$_4$SR)$_2$TiLCl$^+$][Cl$^-$] /[((C$_5$Me$_4$SR)$_2$TiCl$_2$)]

K$_2$ = ([((C$_5$Me$_4$SR)$_2$TiClL][Cl$^-$]/ [((C$_5$Me$_4$SR)$_2$TiCl$_2^-$)])

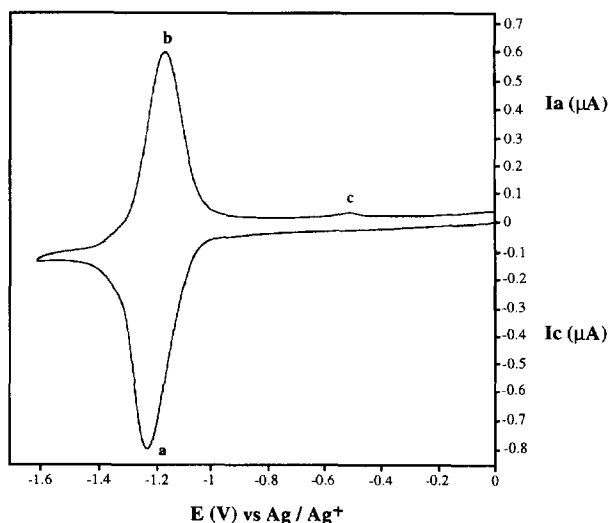Scheme 3. The square scheme for the complex 3; K_1, K_2, $E_1°$, $E_2°$ are defined in Refs. [9,10,12].

Fig. 2. Thin-layer cyclic voltammogram of 3. Platinum electrode: diameter 2 mm; $v = 5\,\mathrm{mVs^{-1}}$. THF; Bu_4NPF_6: 0.5 M; 3: 10^{-3} M. $I_{pa}/I_{pc} = 0.94$.

In the case of complex 4 (M = Zr), the system is reversible whatever the scan rate. By analogy with $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ [9,10], one may assume that there is no cleavage of the Zr–Cl bond. A one-electron reduction yields the corresponding anion $Zr(\eta^5\text{-}C_5Me_4SPr)_2Cl_2^-$ ($E_{1/2} = E_2^\circ$). A comparable result is obtained with the dissymmetric species $Zr(\eta^5\text{-}C_5Me_4S^nPr)(\eta^5\text{-}C_5H_5)Cl_2$ 5.

The electrochemical behaviour of the ferrocene derivative 2 has been examined in THF (Table 1). In the case of 2 the presence of one thiol substituent makes the one-electron oxidation more difficult by about 160 mV with respect to the corresponding octamethyl-ferrocene. On this basis the sulphur atom shows electron-withdrawing properties.

The introduction of the propylthio group in the bent metallocenes 3, 4 and 5 increases the redox potential by about 150 mV with respect to values found for the $M(\eta^5\text{-}C_5Me_4H)_2Cl_2$.

If it is assumed (in the case of Ti) that the SR substituent has no influence on the equilibrium constant (K_2, Scheme 3) of the chemical reaction in the EC mechanism, it is clear from the potential values given in Table 1 that the propylthio group behaves as a good electron-withdrawing substituent. Thus, whatever the nature of the metallocene (parallel, Fe; or bent, Ti or Zr), the electrochemical behaviour of substituted derivatives is similar. However, this is not the case for the corresponding complexes with $C_5H_4S^nPr$ ligand [6] where the propylthio group acts as slightly electron-withdrawing for $M(\eta^5\text{-}C_5H_4S^nPr)_2Cl_2$ (M = Ti, Zr, Hf) and as very slightly electron-donating for $Fe(\eta^5\text{-}C_5H_4S^nPr)_2$.

3. Description of the structure of $[\eta^5\text{-}C_5(CH_3)_4SCH_2CH_2CH_3]_2TiCl_2$ 3

The crystal structure of 3 is built of discrete organometallic molecules. They exibit (Fig. 3) a pseudo-tetrahedral geometry typical of bent $M(\eta^5\text{-}C_5H_5)_2X_2$ metallocenes. The Ti–Cp (geometrical centre of C_5 rings) distances of 2.14 Å correspond very well to those observed in the structures of $Ti(\eta^5\text{-}C_5Me_5)_2Cl_2$ (2.13 Å) [14] and of $[Ti(\eta^5\text{-}C_5Me_4PPh_2)_2Cl_2]Mo(CO)_4$ (2.14 Å) [15], but are longer than in the non-substituted $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ (2.06 Å) [16] and in some mono-substituted titanocene dichlorides [17]. The Cp–Ti–Cp angle of 137.0° in 3 is close to that of 137.4° found for permethylated complex, but much larger than the 131.0° observed for $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$. The corresponding value in Ti $\cdots$ Mo bimetallic is slightly higher (138.4°) due to the cis-complexation of $(C_5Me_4PPh_2)$ ligands on the $Mo(CO)_4$ unit. Thus, the C_5Me_5, $C_5Me_4PPh_2$ and $C_5Me_4S^nPr$ ligands exert a similar steric influence on the geometry of titanocenes.

The Cl–Ti–Cl angle of 93.4° is intermediate between the values found for the substituted complexes (92.9° (C_5Me_5) and 91.7° ($C_5Me_4PPh_2$)) and for the non-substituted one (94.5°). This X–M–X angle in bent metallocenes correlates with the electronic structure of the metal centre (d^0, d^1, d^2) and corresponds to the formal occupation of the $1a_1$ frontier orbital in the Lauher–Hoffmann [18] model. In the case of titanocene (Ti(IV), d^0) this molecular orbital may be partially populated in the presence of donor substituents on the cyclopentadienyl rings. Thus, formally, one may expect that the C_5Me_4SR ligand behaves as a poorer donor than the C_5Me_5.

The conformation of cyclopentadienyl rings is intermediate between the staggered and eclipsed ones; the S1 Cp1 Cp2/S2 Cp2 Cp1 dihedral angle being equal to
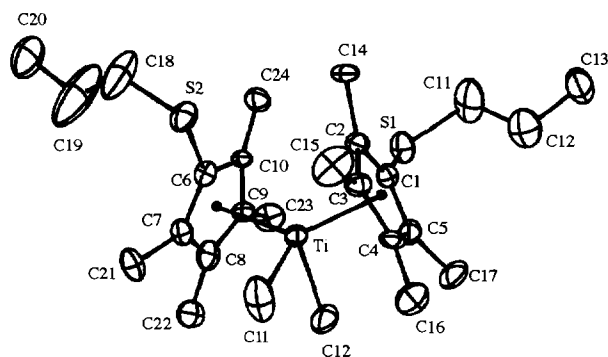

Fig. 3. ORTEP drawing of 3. Selected bond distances (Å) and angles (deg): Ti–Cp2, 2.136; Ti–Cl$_1$, 2.333(2); Ti–Cl$_2$, 2.333(2); Cp1–Ti–Cp2, 137.0; Cl$_1$–Ti–Cl$_2$, 93.36.

117°. All substituents are bent away from the best planes of C_5 rings. The largest deviations involve, as expected, the C14 and C24 atoms (approximately 0.4 Å). In fact, these atoms (methyl groups) are located in the far side from the chlorides, where the rings are close to one another. There is no particular feature concerning the C–C and S–C distances.

4. Experimental details

4.1. General considerations

Except when otherwise indicated, all manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried by distillation over appropriate drying agents. Propyl disulfide was obtained from Fluka Chemika, distilled under vacuum and stored under argon. Sodium hydride (50% oil dispersion, Aldrich Chemical Co.) was washed with hexane and stored under argon. Zirconium tetrachloride, from Merck, was sublimed before being stored under argon. $TiCl_3$, 3THF [19], $CpZrCl_3$, DME [20] were prepared according to published methods. For Fe_2Cl_4, 3THF a modification of the original synthesis [21] was used: 5 g of $FeCl_2$ was refluxed in 90 ml of THF for 45 min, the brown coloured solvent was then changed, and the procedure begun again until the solvent remained colourless. Finally, 5 g (30%) of a light brown solid, very sensitive to moisture, was obtained and stored under argon. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument in C_6D_6 (^1H) and $CDCl_3$ (^{13}C) at room temperature, if not stated otherwise, and were referenced internally using the residual solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). Mass spectra were obtained by a Kratos concept IS spectrometer operating at 70 eV. Melting points were determined with a Kofler apparatus. Elemental analyses were performed by the Service Central d'Analyses du CNRS, Vernaison.

4.2. $NaC_5Me_4SCH_2CH_2CH_3$ 1

(a) To a mixture of tetramethylcyclopentadienyl-sodium (1.95 g, 13.5 mmol) and NaH (0.43 g, 18 mmol) in 120 ml of THF were added dropwise 2.12 ml (13.5 mmol) of propyl disulfide. Quickly, a dense white suspension appeared and the resulting mixture was refluxed for 40 h. The white solid and excess of NaH were removed by filtration, washed by THF (2 × 10 ml) and the orange filtrate evaporated to dryness. The crude brown product was washed with pentane to give a white solid (1.33 g, 45%).

(b) To a solution of propyl disulfide (0.68 ml, 4.3 mmol) and three drops of triethylamine in 20 ml of dichloromethane, at −50°C, was slowly added (1 h

30 min) a solution of sulfuryl-chloride (0.35 ml, 4.3 mmol) in 20 ml of dichloromethane. After the end of the addition, the reaction mixture was slowly warmed to room temperature, affording a yellow solution. The solvent was then removed under reduced pressure. The yellow liquid residue was diluted with 20 ml of THF and slowly added to a suspension of tetramethylcyclopentadienyllithium (1.12 g, 8.74 mmol) in 30 ml of THF, at −50°C. Then the solution was left to warm. The solvent was removed under reduced pressure and the residue was extracted with ether (3 × 10 ml) to give a yellow solution. The solvent was again taken off and 20 ml of THF, followed by NaH (0.21 g, 8.7 mmol) was added. The mixture was refluxed for 12 h. The excess of NaH was removed by filtration, washed with THF (2 × 5 ml) to give a brown solution. The solvent was removed and the brown residue was washed with pentane, leading to a white solid (0.69 g, 36%).

^1H NMR, δ (ppm), THF-d_8: 0.88 (t, CH_3, $J = 7.3$ Hz), 1.39 (sx, CH_2, $J = 7.3$ Hz), 1.97 (s, Me_β), 2.12 (s, Me_α), 2.16 (t, SCH_2, $J = 7.3$ Hz).

4.3. $Fe(\eta^5-C_5Me_4SCH_2CH_2CH_3)_2$ 2

To a suspension of Fe_2Cl_4, 3THF (0.32 g, 0.67 mmol) in 20 ml of THF, cooled at 0°C, was added a solution of propylthiotetramethylcyclopentadienylsodium (0.59 g, 2.7 mmol) in 15 ml of THF. The resulting suspension was stirred for 5 h to give a brown mixture. The solvent was removed under reduced pressure and replaced by diethyl ether (30 ml). The mixture was then treated with water and the organic layer collected. The water layer was extracted with diethyl ether and the combined organic extracts were washed with water before being dried over $MgSO_4$. After filtration, the solvent was removed and recrystallization from hexane gave a red powder (0.2 g, 33%), m.p. 101°C.

^1H NMR, δ (ppm): 0.78 (t, CH_3, $J = 7.3$ Hz), 1.39 (sx, CH_2, $J = 7.3$ Hz), 1.81 (s, Me_β), 2.03 (s, Me_α), 2.29 (t, SCH_2, $J = 7.3$ Hz). ^{13}C NMR: 10.4 (Me_α or Me_β), 10.7 (Me_α or Me_β), 14.2 (CH_3), 23.9 (CH_2), 38.5 (SCH_2), 77.8 (C_1), 82.1 ($C_{2,5}$), 84.8 ($C_{3,4}$).

MS, m/z (fragment, relative intensity): 446 (M^+, 100), 403 ($M^+ - C_3H_7$, 30), 372 ($M^+ - C_3H_6S$, 67), 329 ($Fe(C_5Me_4)C_5Me_4SH^+$, 23), 251 ($Fe(C_5Me_4SCH_2CH_2CH_3)^+$, 15), 119 ($C_5Me_4^+ - H$, 40).

Anal. Found: C, 64.83; H, 8.58; S, 14.15. $C_{24}H_{38}S_2Fe$ Calc.: C, 64.55; H, 8.57; S, 14.36%.

4.4. $Ti(\eta^5-C_5Me_4SCH_2CH_2CH_3)_2Cl_2$ 3

To a mixture of $TiCl_3$, 3THF (0.87 g, 2.3 mmol) in 20 ml of THF, at room temperature, was added a solution of 1.03 g (4.7 mmol) of propylthiotetramethylcyclopentadienylsodium in 20 ml of THF. The resultant

solution was stirred for 5 h to give a black mixture. Carbon tetrachloride (15 ml) was added to oxidise the Ti(III) species, the mixture becoming red brown. The solvents were removed under reduced pressure and recrystallization from hexane gave black crystals (0.42 g, 35%), m.p. 108 °C.

^{1}H NMR, δ (ppm): 0.75 (t, CH_3, $J = 7.0\,Hz$), 1.26 (sx, CH_2, $J = 7.0\,Hz$), 2.07 (s, Me_β), 2.18 (t, SCH_2, $J = 7.0\,Hz$), 2.36 (s, Me_α). ^{13}C NMR: 14.1, 14.5, 14.8 (CH_3, Me_α and Me_β), 23.7 (CH_2), 39.1 (SCH_2), 119.8 (C_1), 134.2 ($C_{2,5}$), 134.4 ($C_{3,4}$).

MS, m/z (fragment, relative intensity): 509 ($M^+ + H$, 18), 313 ($M^+ - C_5Me_4SCH_2CH_2CH_3$, 30), 235 ($TiC_5Me_4SCl^+$, 20), 195 ($C_5Me_4SCH_2CH_2CH_3^+$, 100), 153 ($C_5Me_4SH^+$, 14), 119 ($C_5Me_4^+ - H$, 17).

Anal. Found: C, 56.60; H, 7.44; S, 11.93. $C_{24}H_{38}Cl_2S_2Ti$ Calc.: C, 56.58; H, 7.52; S, 12.58%.

4.5. $Zr(\eta^5-C_5Me_4SCH_2CH_2CH_3)_2Cl_2$ 4

At $-40\,°C$, a solution of 0.82 g (3.7 mmol) of propylthiotetramethylcyclopentadienylsodium in 20 ml of THF was added to a mixture of $ZrCl_4$ (0.43 g, 1.85 mmol) in 30 ml of THF. When the addition was finished, the reaction mixture was left to warm at ambient conditions. The yellow solution was filtered and the white precipitate eliminated. The solvent was removed and the residue was recrystallized from hexane to give yellow crystals (0.56 g, 55%) of 4, m.p. 114 °C.

^{1}H NMR, δ (ppm): 0.75 (t, CH_3, $J = 7.2\,Hz$), 1.27 (sx, CH_2, $J = 7.2\,Hz$), 2.02 (s, Me_β), 2.2 (t, SCH_2, $J = 7.2\,Hz$), 2.35 (s, Me_α). ^{13}C NMR: 13.4, 13.8 (Me_α and Me_β), 14.1 (CH_3), 23.7 (CH_2), 39.1 (SCH_2), 114.4 (C_1), 128.9 ($C_{2,5}$), 130.4 ($C_{3,4}$).

MS, m/z (fragment, relative intensity): 553 ($M^+ + H$, 43), 357 ($M^+ - C_5Me_4SCH_2CH_2CH_3$, 100), 313 ($ZrC_5Me_4SHCl_2^+$, 13), 277 ($ZrC_5Me_4SCl^+$, 48), 195 ($C_5Me_4SCH_2CH_2CH_3^+$, 12), 119 ($C_5Me_4^+ - H$, 20), 43 ($CH_2CH_2CH_3^+$, 38).

Anal. Found: C, 52.24; H, 7.06; S, 10.14. $C_{24}H_{38}Cl_2S_2Zr$ Calc.: C, 52.14; H, 6.93; S, 11.60%.

4.6. $Zr(\eta^5-C_5H_5)(\eta^5-C_5Me_4SCH_2CH_2CH_3)Cl_2$ 5

A solution of propylthiotetramethylcyclopentadienylsodium (0.23 g, 1.05 mmol) in 10 ml of THF, at room temperature, was added to a solution of $CpZrCl_3$, DME (0.38 g, 1.05 mmol) in 10 ml of THF. The yellow mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure, the product extracted with toluene and then recrystallized in heptane to give 5 as a yellow powder, m.p. 76 °C (0.26 g, 58%).

^{1}H NMR, δ (ppm): 0.73 (t, CH_3, $J = 7.3\,Hz$), 1.29 (sx, CH_2, $J = 7.3\,Hz$), 1.94 (s, Me_β), 2.0 (s, Me_α), 2.14 (t, SCH_2, $J = 7.3\,Hz$), 6.16 (s, C_5H_5). ^{13}C NMR: 13.4,

14.0 (Me_α and Me_β), 14.1 (CH_3), 23.7 (CH_2), 39.4 (SCH_2), 114.2 (C_1), 117.5 (C_5H_5), 129.5 ($C_{2,5}$), 130.1 ($C_{3,4}$).

MS, m/z (fragment, relative intensity): 420 (M^+, 43), 355 ($M^+ - C_5H_5$, 100), 277 ($ZrC_5Me_4SCl^+$, 46), 195 ($C_5Me_4SCH_2CH_2CH_3^+$, 18), 119 ($C_5Me_4^+ - H$, 55).

Anal. Found: C, 47.88; H, 5.76; S, 6.73. $C_{17}H_{24}Cl_2SZr$ Calc.: C, 48.32; H, 5.72; S, 7.59%.

4.7. Electrochemistry

Tetrabutylammoniumhexafluorophosphate, for electrochemical studies, obtained from Fluka Chemika, was recrystallized twice from absolute alcohol, then vacuum dried at 100 °C, before being stored under argon. The cyclic voltammetry data were carried out using a Tacussel UAP4 unit, and recorded with a Nicolet 3091 Digital Oscillograph (Madison, WI), and subsequently reproduced on an XY recorder (Sefram TGM.164). The electrochemical experiments were carried out at room temperature, under argon atmosphere on a vacuum line, in THF, with 0.5 M tetrabutylammoniumhexafluo-

Table 2
Crystallographic data for $[\eta^5-C_5(CH_3)_4(S^nPr)]_2TiCl_2$

molecular formula	$TiS_2Cl_2C_{24}H_{38}$
formula weight (g)	509.50
colour, dimension (mm^3)	red, $0.55 \times 0.35 \times 0.20$
crystal system	orthorhombic
space group	$Pbca$ (No. 61)
cell dimensions:	
a (Å)	16.767(1)
b (Å)	16.247(3)
c (Å)	19.002(3)
V (Å^3)	5176.2(9)
Z	8
ρ_{calc} (g cm^{-3})	1.308
$F(000)$	2160
radiation (Å)	λ(Mo Kα) 0.71073
scan type	$\omega - 2\theta$
scan speed (deg min^{-1})	0.75–4.00
scan width (deg)	$\Delta\omega = 0.7 + 0.347\tan\theta$
reflections measured	h 0–15
	k −23–23
	l 0–26
θ range (deg)	2–25
linear abs. μ (cm^{-1})	6.993
no. of reflections measured	10859
temperature (K)	296(1)
decay (%)	~5.8, corrected
cut off for observed data	$I \geq 3\sigma(I)$
no. of unique observed data (NO)	2691
no. of variables (NV)	371
$R(F)$	0.052
$Rw(F)$	0.049
weighting,	0.04
$w^{-1} = [\sigma^2(I) + (pF_0^2)^2]^{1/2}$, p	
GOF	1.093
ρ_{max} / ρ_{min} (DF)	0.597/ −0.128

rophosphate as supporting electrolyte. A standard three electrode configuration was used, with a platinum disc working electrode (diameter 0.8 or 2 mm), a platinum wire counter-electrode, and an $Ag/AgNO_3$ ($AgNO_3$: 0.01 M and Bu_4NPF_6: 0.2 M in CH_3CN) reference electrode. Before each experiment, the reference electrode was checked with an aqueous saturated calomel electrode.

4.8. X-ray analysis of $Ti(\eta^5\text{-}C_5Me_4SCH_2CH_2CH_3)_2Cl_2$ 3

A brown crystal of **5** grown from a solution in hexane was used for unit cell determination and data collection, carried out at 296(1) K on an Enraf–Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The pertinent crystallographic data are given in Table 2. All calculations were carried out by use of the Molen [22] package with neutral-atom scattering

Table 3
Positional parameters of all non-hydrogen atoms for [η^5-$C_5(CH_3)_4(S^nPr)]_2TiCl_2$

Atom	x	y	z	B (Å^2)
Ti	0.09170(5)	0.24073(8)	0.16416(4)	2.89(3)
Cp1	0.1863	0.3084	0.1149	—
Cp2	−0.0160	0.2683	0.2193	—
Cl1	0.1568(1)	0.1429(2)	0.2333(1)	8.25(6)
Cl2	0.0519(1)	0.1440(2)	0.08047(9)	7.00(6)
S1	0.07441(8)	0.4015(1)	0.02503(7)	4.65(5)
S2	0.07608(8)	0.3583(1)	0.32780(7)	4.28(5)
C1	0.1375(3)	0.3446(4)	0.0806(2)	3.0(2)
C2	0.1678(3)	0.3702(4)	0.1476(3)	3.0(2)
C3	0.2214(3)	0.3077(4)	0.1697(3)	3.3(2)
C4	0.2279(3)	0.2485(5)	0.1160(3)	3.1(2)
C5	0.1773(3)	0.2712(4)	0.0610(2)	3.4(2)
C6	0.0237(3)	0.3029(4)	0.2616(2)	3.2(2)
C7	0.0005(3)	0.2205(4)	0.2664(2)	3.3(2)
C8	−0.0429(3)	0.2025(5)	0.2051(3)	4.1(2)
C9	−0.0499(3)	0.2747(4)	0.1642(2)	2.8(2)
C10	−0.0116(3)	0.3411(4)	0.1992(2)	2.4(1)
C11	0.1454(5)	0.4752(6)	−0.0140(4)	8.4(3)
C12	0.1956(4)	0.4497(6)	−0.0677(4)	7.7(3)
C13	0.2507(4)	0.5137(5)	−0.0977(4)	6.5(2)
C14	0.1639(3)	0.4534(4)	0.1785(3)	3.9(2)
C15	0.2707(3)	0.3129(5)	0.2357(3)	6.4(2)
C16	0.2849(3)	0.1740(5)	0.1135(4)	5.7(2)
C17	0.1751(4)	0.2301(5)	−0.0131(3)	5.5(2)
C18	−0.0015(4)	0.4020(6)	0.3805(4)	9.6(3)
C19	−0.0645(5)	0.3728(8)	0.4010(5)	16.0(4)
C20	−0.1255(4)	0.4154(6)	0.4459(4)	8.4(3)
C21	0.0140(3)	0.1624(5)	0.3273(3)	4.7(2)
C22	−0.0869(3)	0.1202(5)	0.1909(3)	4.9(1) *
C23	−0.0996(3)	0.2827(5)	0.0992(3)	5.0(2)
C24	−0.0244(3)	0.4287(4)	0.1864(3)	3.1(2)

Starred atom, refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(4/3)^*[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos\gamma)^*B(1,2) + ac(\cos\beta)^*B(1,3) + bc(\cos\alpha)^*B(2,3)]$.

factors taken from the usual sources [23]. Intensities were corrected for Lorentz and polarization effects. Because of the low value of the linear absorption coefficient, no absorption correction was made. All non-hydrogen atoms could be located from three-dimensional Patterson and subsequent difference Fourier maps. These atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions (HYDRO) and included in the structure in a riding model with B_{iso} fixed at $1.3 B_{eq}$ for the carbon atoms bearing them. Good residuals, estimated standard deviations of bond distances and angles as well as the final peaks on the difference Fourier map confirm the correct quality of the structure of **5**. Positional parameters of non-hydrogen atoms are given in Table 3.

5. Supplementary material available

Anisotropic parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, full lists of bond distances and angles and least-squares planes.

Acknowledgements

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