Reactions of ring-substituted titanocene dichlorides with thiocyanate ions: Synthesis of new S-bonded thiocyanato titanocene complexes, and crystal structure of (^{t}Bu–C$_5$H$_4$)$_2$Ti(NCS)$_2$

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Abstract

The asymmetrical titanocene dichloride (1,3-^{t}Bu$_2$-C$_5$H$_3$)(^{t}Bu$_2$-C$_5$H$_4$)TiCl$_2$ (I) has been prepared from (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ and (^{t}Bu–C$_5$H$_4$)Li. The reactions of I and of (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$TiCl$_2$ with an excess of ammonium thiocyanate afforded the S-bonded thiocyanato complexes (1,3-^{t}Bu$_2$-C$_5$H$_3$)(^{t}Bu–C$_5$H$_4$)Ti(SCN)$_2$ (IV) and (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$Ti(SCN)$_2$ (V) respectively. A similar reaction of (^{t}Bu–C$_5$H$_4$)$_2$TiCl$_2$ with excess ammonium thiocyanate produced the S-bonded thiocyanato complex (^{t}Bu–C$_5$H$_4$)$_2$Ti(SCN)$_2$ (II) as a minor product and the N-bonded thiocyanato complex (^{t}Bu–C$_5$H$_4$)$_2$Ti(NCS)$_2$ (III) as the major product. Similar reaction of (^{t}Bu–C$_5$H$_4$)$_2$TiCl$_2$ with ammonium thiocyanate in 1:1 molar ratios gave (^{t}Bu–C$_5$H$_4$)$_2$Ti(Cl)(NCS) (VI). Crystal structure of III was determined.

Key words: Titanium; Metallocene; Thiocyanate; Chloride; Crystal structure

1. Introduction

Ring-substituted derivatives of titanocene dichlorides continue to be of interest because of the significant changes in reactivity, stability, catalytic activity and other properties brought about by the substituents [1–9]. Several alkyl-substituted cyclopentadienyl titanium complexes have been prepared and studied, but little work has been reported on the tert-butyl-substituted analogues [10–13]. Because of the expected steric and electronic effects of tert-butyl substituted cyclopentadienyl ligands, we thought it of interest to examine their effects on the reactivity of the titanium centre.

Since ambidentate ligands and in particular the thiocyanate ion are sensitive to their chemical environment, their bonding modes give a clear picture of the relative softness or hardness of the metal centre in their complexes [14]. Thus reactions of the thiocyanate ion with (^{t}Bu–C$_5$H$_4$)$_2$TiCl$_2$, (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$TiCl$_2$ and the newly prepared compound (1,3-^{t}Bu$_2$-C$_5$H$_3$)-(^{t}Bu–C$_5$H$_4$)TiCl$_2$ have been examined and the results are reported below.

2. Experimental details

All reactions were conducted under dinitrogen by Schlenk techniques. tert-Butylcyclopentadiene and 1,3-di-tert-butylcyclopentadiene were prepared as previously described [15,16]. Dichlorobis-(η^5-tert-butylcyclopentadienyl titanium (IV) (^{t}Bu–C$_5$H$_4$)$_2$TiCl$_2$ was prepared by the method reported for (1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$TiCl$_2$ [13].

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Infrared spectra were recorded on a Pye–Unicam SP3-100 spectrophotometer and ^{1}H NMR spectra on a Bruker WP 80SY spectrometer with Me$_4$Si as internal standard. Mass spectra were recorded on a Finngan MAT 112 mass spectrometer. Elemental analyses were performed by M–H–W Laboratories, Phoenix, AZ, USA.

2.1. Preparation of η^5-1,3-di-tert-butylcyclopentadienyl-η^5-tert-butylcyclopentadienyl titanium(IV) dichloride $(1,3\text{-}^tBu_2\text{-}C_5H_3)(^tBu\text{-}C_5H_4)TiCl_2)(1)$

A 1.6 M hexane solution (6.5 ml) of n-butyllithium was added dropwise at 0°C to a hexane solution (75 ml) containing (1.2 g, 0.01 mol) of tert-butylcyclopentadiene. The mixture was allowed to warm with stirring to room temperature, and stirring was continued for a further 1 h. The mixture was then cooled to 0°C and a hexane solution (75 ml) of (3.3 g, 0.01 mol) of $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_3$ was added slowly. Stirring was continued for 2 h, the solvent then evaporated under vacuum at 20°C and the residue washed with cold hexane. The product was taken up in dichloromethane, and the solution filtered through Celite and then cooled to $-30°C$ to give red crystals of I (yield, 2.8 g (67%); melting point (m.p.), 192–195°C). Anal. Found: C, 63.04; H, 7.87; Cl, 17.00. $C_{22}H_{34}Cl_2Ti$ calc.: C, 63.31; H, 8.15; Cl, 17.03%. ^{1}H NMR (CDCl$_3$): 6.55–6.29 (m,7H); 1.33–1.22 (m,27H) ppm. Mass spectroscopy (MS): m/z 417.

2.2. Preparation of di-thiocyanato-S-bis(η^5-tert-butyl-cyclopentadienyl)titanium(IV) $(^tBu\text{-}C_5H_4)_2Ti(SCN)_2)$ (II) and di-thiocyanato-N-bis(η^5-tert-butylcyclopentadienyl)titanium(IV) $((^tBu\text{-}C_5H_4)_2Ti(NCS)_2)$ (III)

Hexane (150 ml) was added to a mixture of 2.0 g (5.6 mmol) of $(^tBu\text{-}C_5H_4)_2TiCl_2$, 1.27 g (16.7 mmol) of dried ammonium thiocyanate and 1.0 g of magnesium granules. The mixture was refluxed for 4 h, the red solution was cooled to room temperature and the solvent was evaporated under vacuum. The residue was washed three times with 25 ml portions of hexane. The washings were combined concentrated and kept at $-30°C$. Very fine golden-green needles of (II) were obtained (yield, 0.20 g (8.8%)); m.p., 170°C (decomposition), Anal. Found: C, 58.95; H, 6.46; N, 6.70. $C_{20}H_{26}N_2S_2Ti$ calc.: C, 59.11; H, 6.40; N, 6.90%, IR (KBr): 3000w, 2880m, 2044vs, 2008vs, 690s cm^{-1}. ^{1}H NMR (CDCl$_3$): 6.42 (s,8H); 1.30 (s,18H) ppm. Dichloromethane (75 ml) was added to the residue, and the solution obtained was filtered through Celite, concentrated, at $-30°C$ to give dark-red crystals of III (yield, 1.2 g (63%)). (m.p., 216–218°C). Anal. Found: C, 58.83; H, 6.66; N, 6.72. $C_{20}H_{26}N_2S_2Ti$ calc.: C, 59.11; H, 6.40; N, 6.90%. IR (KBr): 3000w, 2880m, 2048vs,

2010vs, 850s cm^{-1}. ^{1}H NMR (CDCl$_3$); 6.42 (s,8H); 1.30 (s,18H) ppm.

2.3. Preparation of di-thiocyanato-S-η^5-1,3-di-tert-butylcyclopentadienyl η^5-tert-butylcyclopentadienyl titanium(IV) $((1,3\text{-}^tBu_2\text{-}C_5H_3)(^tBu\text{-}C_5H_4)Ti(SCN)_2)$ (IV)

Hexane (150 ml) was added to a mixture of 2.0 g (4.8 mmol) of $(1,3\text{-}^tBu_2\text{-}C_5H_3)(^tBu\text{-}C_5H_4)TiCl_2$, 1.1 g (14.5 mmol) of dried ammonium thiocyanate and 1.0 g of magnesium granules. The mixture was refluxed for 4 h, and the yellowish-brown solution then filtered through Celite, concentrated and kept at $-30°C$ to give very fine golden-green needles of IV (yield, 0.80 g (36%)) (m.p., 235–237°C (decomposition)). Anal. Found: C, 62.16; H, 7.48; N, 6.17. $C_{24}H_{34}N_2S_2Ti$ calc.: C, 62.34; H, 7.36; N, 6.06%. IR (KBr): 3100w, 2895m, 2055vs, 2020vs, 710m cm^{-1}. ^{1}H NMR (CDCl$_3$): 6.11–6.68 (m,7H), 1.28 (s(br),27H) ppm.

2.4. Preparation of di-thiocyanato-S-bis(η^5-1,3-di-tert-butylcyclopentadienyl-titanium(IV) $(1,3\text{-}^tBu_2\text{-}C_5H_3)_2Ti(SCN)_2)$ (V)

The proceeding described immediately above was repeated but starting from 2.0 g (4.2 mmol) of $(1,3\text{-}^tBu_2\text{-}C_5H_3)_3TiCl_2$, 1.0 g (13.2 mmol) of dried ammonium thiocyanate and 1.0 g of magnesium granules. Very fine golden-green needles of V were obtained (yield, 1.3 g (60%); m.p., 247–248°C (decomposition)). Anal. Found: C, 64.38; H, 8.24; N, 5.62. $C_{28}H_{42}N_2S_2Ti$ calc.: C, 64.86; H, 8.11; N, 5.41%. IR (KBr): 3100w, 2990m, 2052vs, 2020vs, 710m cm^{-1}. ^{1}H NMR (CDCl$_3$): 6.68 (t,2H), 6.14 (d,4H); 1.28 (s,36H) ppm. MS: m/e 518.

2.5. Preparation of chlorothiocyanato-N-bis(η^5-tert-butylcyclopentadienyl)titanium(IV) $(^tBu\text{-}C_5H_4)_2Ti(Cl)(NCS))$ (VI)

The procedure described above was repeated but starting from 2.0 g (5.6 mmol) of $(^tBu\text{-}C_5H_4)_2TiCl_2$, 0.43 g (5.6 mmol) of dried ammonium thiocyanate and 1.0 g of magnesium granules. Orange-red crystals of VI were obtained (yield, 1.4 g (65%); m.p. 138–140 (decomposition)). Anal. Found: C, 59.38; H, 6.84; N, 3.72. $C_{19}H_{26}ClNSTi$ calc.: C, 59.45; H, 6.77; N, 3.65%. IR (KBr): 3000w, 2890m, 2032vs, 830s cm^{-1}. ^{1}H NMR (CDCl$_3$): 6.46 (m,8H), 1.31 (s,18H) ppm.

2.6. Crystal structure analysis for $(^tBu\text{-}C_5H_4)_2Ti(NCS)_2$ (III)

Suitable crystals were obtained by recrystallization from dichloromethane.

Crystal data were as follows: $C_{20}H_{26}N_2S_2Ti$; molecular mass, 406; monoclinic; space group, $C2/c$ (No. 15) [17] with $a = 1907(1)$ pm, $b = 811.1(3)$ pm, $c = 1466.1(6)$

TABLE 1. Atomic coordinates for III, with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq} ($Å^2$)
Ti(1)	0.5000	0.6488(2)	0.7500	0.0166(5)
S(1)	0.4981(1)	0.1960(2)	0.9595(1)	0.0332(7)
N(1)	0.5003(2)	0.4764(6)	0.8499(3)	0.024(2)
C(1)	0.6241(3)	0.6852(7)	0.6092(4)	0.025(2)
C(2)	0.5885(3)	0.8368(7)	0.6410(4)	0.027(2)
C(3)	0.5828(3)	0.8681(8)	0.7382(5)	0.025(2)
C(4)	0.6141(3)	0.7329(7)	0.7657(5)	0.025(2)
C(5)	0.6420(3)	0.6163(7)	0.6858(4)	0.024(2)
C(6)	0.6913(3)	0.4663(8)	0.6773(5)	0.029(2)
C(7)	0.6609(4)	0.3112(7)	0.6476(5)	0.034(3)
C(8)	0.7728(3)	0.5034(9)	0.5927(5)	0.040(3)
C(9)	0.7003(4)	0.4349(9)	0.7746(5)	0.041(3)
C(10)	0.4987(3)	03587(7)	0.8983(4)	0.019(2)

TABLE 2. Selected bond distances (Å) and bond angles (°) for III

Ti(1)-N(1)	2.026(5)	N(1)-Ti(1)-N(1a)	92.7(3)
Ti(1)-C(1)	2.402(5)	C(3)-Ti(1)-C(3a)	80.8(3)
Ti(1)-C(2)	2.328(6)	C(1)-C(5)-C(4)	105.0(5)
Ti(1)-C(3)	2.336(6)	C(5)-C(1)-C(2)	109.4(5)
Ti(1)-C(4)	2.383(7)	C(1)-C(2)-C(3)	108.4(6)
Ti(1)-C(5)	2.471(6)	C(2)-C(3)-C(4)	107.2(5)
C(1)-C(2)	1.385(8)	C(3)-C(4)-C(5)	110.0(6)
C(1)-C(5)	1.420(1)	C(5)-C(6)-C(7)	112.8(6)
C(2)-C(3)	1.41(1)	C(5)-C(6)-C(8)	106.6(5)
C(3)-C(4)	1.387(9)	C(5)-C(6)-C(9)	111.8(5)
C(4)-C(5)	1.420(8)	C(7)-C(6)-C(8)	107.8(5)
C(5)-C(6)	1.511(9)	C(7)-C(6)-C(9)	109.7(5)
C(6)-C(7)	1.521(1)	C(8)-C(6)-C(9)	107.8(6)
C(6)-C(8)	1.547(7)	Ti(1)-N(1)-C(10)	169.7(5)
C(6)-C(9)	1.53(1)	N(1)-C(10)-S(1)	177.7(5)
N(1)-C(10)	1.182(8)	C(1)-C(5)-C(6)	127.2(5)
C(10)-S(1)	1.594(6)	C(4)-C(5)-C(6)	127.2(6)

pm and $\beta = 64.66(4)°$; $V = 2049(1) \times 10^6$ pm^3; $d_{calc} = 1.317$ g cm^{-3}; $Z = 4$; $\mu = 0.63$ mm^{-1}; $F(000) = 912$.

The cell constants and reflections were measured at a temperature of 173 K on a Siemens (Nicolet Syntex) R3m/V diffractometer with a graphite monochromator, λ(Mo Kα) = 71.073 pm. An ω scan with a scan speed 1.9° min^{-1} $\leqslant \omega \leqslant$ 29.3° min^{-1}, $\Delta w = 0.75°$ and a scan range 2° $\leqslant 2\theta \leqslant 40°$. There were 1353 independent significant reflections (I $\geqslant 2\sigma$). The structure was solved by use of the programs SHELX 76 [18], SHELXTL PLUS [19] by direct methods. Hydrogen atoms were placed in the calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged at $R_1 = 0.0621$, $R_w = 0.0583$. Atomic coordinates are given in Table 1 and selected bond distances and bond angles in Table 2 [32*].

3. Discussion

The asymmetrical substituted titanocene dichloride complex (1,3-^{t}Bu$_2$-C$_5$H$_3$)(^{t}Bu-C$_5$H$_4$)TiCl$_2$ (I) was obtained with a fairly good yield by reaction of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ with (^{t}Bu-C$_5$H$_4$)Li. Compound I was characterized by elemental analysis and ^{1}H NMR and mass spectroscopy. It crystallizes as red needles and is stable in the solid state.

The reaction of (^{t}Bu-C$_5$H$_4$)$_2$TiCl$_2$ with a threefold excess of ammonium thiocyanate in the presence of magnesium † gave the red compound III as the major product and the golden-green compound II as the minor product. Elemental analysis reveals that the two compounds have the same molecular formula and con-

tain two thiocyanato groups that have replaced the two chloride ions originally present. The two compounds also gave exactly the same ^{1}H NMR spectra (see Fig. 2).

Compound II is highly soluble in hexane and its IR spectrum shows two very strong bands at 2044 and 2008 cm^{-1}, characteristic of ν(CN), and a medium band at 690 cm^{-1}, characteristic of ν(CS) [20–22].

Compound III is insoluble in hexane and its IR spectrum shows two very strong bands, at 2048 and 2010 cm^{-1}, characteristic of ν(CN), and a strong band at 850 cm^{-1}.

The first conclusion drawn from the above data is that II and III are isomers differing in the mode of attachment of the thiocyanato groups. An indication of the mode of coordination of the thiocyanato group can be obtained from vibrational spectroscopy, in particular the ν(CS) stretching frequency. It has been shown that ν(CS) appears in the range 780–860 cm^{-1} for the M–NCS isomer and 690–720 cm^{-1} for the M–SCN isomer [23]. The IR spectrum of II, which shows a band at 690 cm^{-1}, indicates that it is probably the S-bonded isomer, where that of III, which shows a strong band at 850 cm^{-1} and no band in 800–650 cm^{-1} region, indicates that it is the N-bonded isomer. This assignment is supported by the solubility behaviour in that II, judged to be the S-bonded isomer, is soluble in hexane as expected since it contains the less polar Ti–S bonds, where III, judged to be the N-bonded isomer, is insoluble because of its more polar Ti–N bonds. These conclusions were confirmed by determination of the crystal structure of III. Unfortunately, attempts to obtain crystals suitable for an X-ray study of II in various

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* Reference number with asterisk indicates a note in the list of references.

† The precise function of the Mg in the reaction is under inverstigation.

solvents were unsuccessful, very fine needles always being obtained.

We note that III was previously described [10] as a red–violet solid and its formula was assigned on the basis of elemental analysis and ^{1}H NMR spectra. No further details concerning its IR spectrum, its structure or the formation of other side products were given.

Reactions of $(1,3\text{-}^tBu_2\text{-}C_5H_3)(^tBu\text{-}C_5H_4)TiCl_2$ and $(1,3\text{-}^tBu_2\text{-}C_5H_3)_2TiCl_2$ with an excess of ammonium thiocyanate in the presence of magnesium gave the golden green complexes $(1,3\text{-}^tBu_2\text{-}C_5H_3)(^tBu\text{-}C_5H_4)$-Ti(SCN)$_2$ (IV), (yield, 36%) and $(1,3\text{-}^tBu_2\text{-}C_5H_3)_2$-Ti(SCN)$_2$ (V) (yield, 60%). The identities of IV and V were determined by mass and ^{1}H NMR spectroscopy and elemental analysis. Compounds IV and V are stable as solids in the air and are highly soluble in hexane and other organic solvents. Recrystallization of both compounds produced very fine needles unsuitable for X-ray structural study.

The IR (KBr) spectra of IV and V show two very strong bands at 2055 and 2020 cm^{-1} and 2052 and 2020 cm^{-1} respectively, characteristic of ν(CN) in addition to a medium band at 710 cm^{-1}, characteristic of ν(CS).

Since IV and V have characteristics (IR, solubility, colour and crystal type) very similar to those of II, they are probably the S-bonded thiocyanate isomers. A survey of the literature reveals that all titanocene complexes containing one or two Ti–NCS groups are red [24–28], whereas those containing two Ti–S bonds, e.g. $(C_5H_5)_2Ti(S_2C_2H_2)$ [29], $(C_5H_5)_2Ti(S_2C_2(CN)_2)$ [30] and $(C_5H_5)_2Ti(S_2C_6H_4)$ [31], are green, supporting the S-coordination mode of the thiocyanato groups in the green complexes IV and V.

To the best of our knowledge all the di-thiocyanato titanocene complexes previously reported involve the N-coordination mode [24–28], and so II, IV and V appear to be the first examples of S-bonded thiocyanato titanocene complexes. The formation of the S-coordination mode in our complexes could be attributed to the effect of *tert*-butyl substituents on the cyclopentadienyl rings; this might increase the electron density on the titanium centre, making it softer, which increases the opportunity for the soft sulphur atom to coordinate. This suggestion is consistent with the fact that, the greater the degree of substitution, the greater is the ease of the S-coordination mode, as indicated by the percentage yields of the complexes, namely (^tBu-$C_5H_4)_2Ti(SCN)_2$ (8.8%), $(1,3\text{-}^tBu_2\text{-}C_5H_3)(^tBu\text{-}C_5$-$H_4)Ti(SCN)_2$ (36%) and $(1,3\text{-}^tBu_2\text{-}C_5H_3)_2Ti(SCN)_2$ (60%).

It is note worthy that replacement of only one chloride ion of the titanocene dichloride by a thiocyanate ion is possible if 1 : 1 molar ratios are used.

Thus the reaction of (^tBu-$C_5H_4)_2TiCl_2$ with ammonium thiocyanate in 1 : 1 molar ratio in the presence of magnesium afforded (^tBu-$C_5H_4)_2Ti(NCS)Cl$ (VI), which was characterized by elemental analysis and ^{1}H NMR and IR spectroscopy. The IR (KBr) spectrum of VI shows a very strong band at 2035 cm^{-1}, characteristic of ν(CN) and a strong band at 830 cm^{-1}.

Finally, we note that the structural and electronic environment at titanium is affected not only by the substituents on the cyclopentadienyl ring but also by the other ligands. It is the effects of these ligands that are responsible for the significant difference between the molecular structures of (^tBu-$C_5H_4)_2TiCl_2$ and (^tBu-$C_5H_4)_2Ti(NCS)_2$, which have the tert-butyl groups in different positions, and also for the difference between the splitting patterns of the Cp-ring protons in the ^{1}H NMR spectra of II–VI and (^tBu-$C_5H_4)_2TiCl_2$ (Fig. 1). As shown in Fig. 1, the Cp-ring protons of (^tBu-$C_5H_4)_2TiCl_2$ give a symmetrical multiplet centred at 6.48 ppm, those of (^tBu-$C_5H_4)_2$-Ti(NCS)$_2$ (III) and (^tBu-$C_5H_4)_2Ti(SCN)_2$ (II) give a
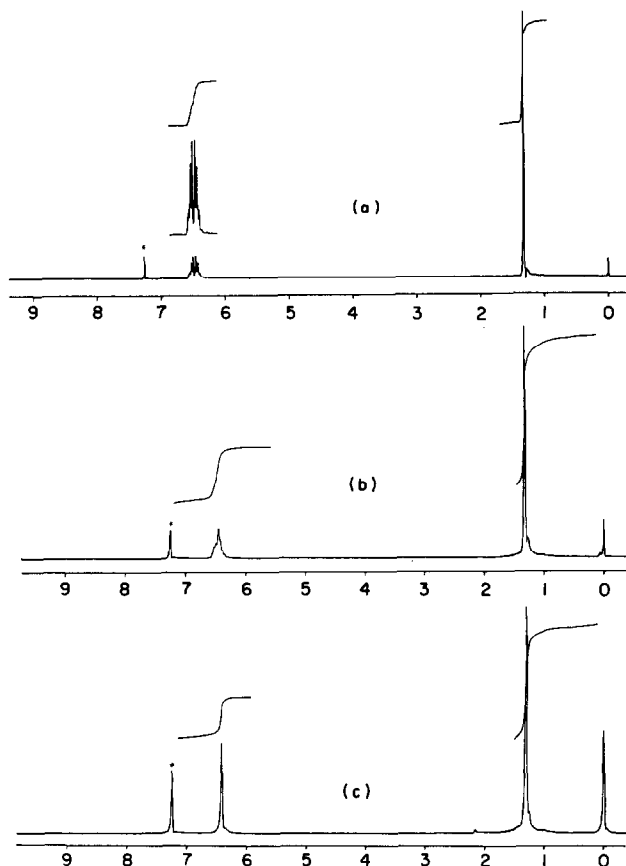
Fig. 1. ^{1}H NMR spectra of (a) (^tBu-$C_5H_4)_2TiCl_2$, (b) (^tBu-$C_5H_4)_2$ Ti(Cl)(NCS) and (c) (^tBu-$C_5H_4)_2Ti(SCN)_2$ ≡ (^tBu-$C_5H_4)_2Ti$ (NCS)$_2$. * = CDCl$_3$ peak.
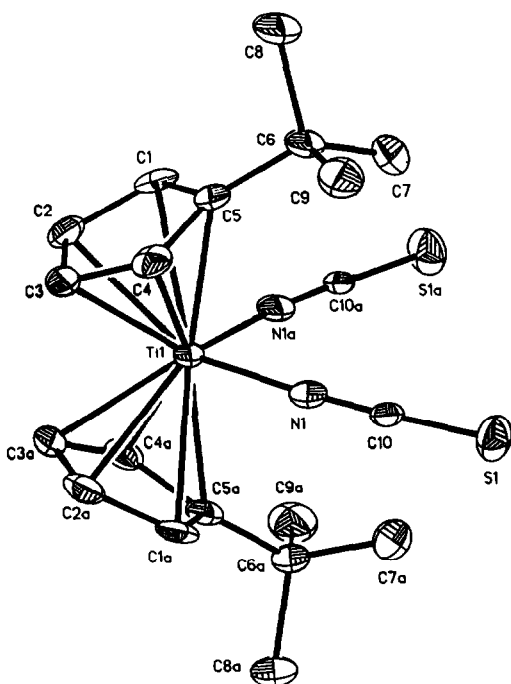
Fig. 2. Molecular structure of ('Bu-C$_5$H$_4$)$_2$Ti(NCS)$_2$ (III).

singlet at 6.42 ppm and those of ('Bu-C$_5$H$_4$)$_2$-Ti(NCS)Cl (VI) give an asymmetrical multiplet centred at 6.46 ppm, showing clearly that the presence of chlorine atoms in the titanocene complex is responsible for the splitting of the ring protons.

3.1. Molecular structure of ('Bu-C$_5$H$_4$)$_2$Ti(NCS)$_2$ (III)

The molecular structure of III is illustrated in Fig. 2 and the bond lengths and angles are listed in Table 2 [32*]. The molecule has a C_{2v} symmetry, with the titanium atom lying on a twofold axis. The geometry around titanium is pseudotetrahedral with N(1)–T–N(1A) = 92.7°. The tert-butyl groups are located on the same side of the molecule above and below the plane of thiocyanato groups. The structure in this respect contrasts with that of ('Bu-C$_5$H$_4$)$_2$TiCl$_2$, in which the tert-butyl groups are situated on opposite sides of the molecule and directed away from each other and from the chlorine atom [11]. The average C–C distance (1.40 Å) around the cyclopentadienyl ring is in agreement with that reported for the dichloride analogue.

The Ti–C (ring) bond distances fall in the range 2.328 — 2.471 Å. The largest Ti–C distance involves the carbon atom bearing the tert-butyl group. A similar feature was observed for the dichloride analogue.

The bond distances Ti–N (2.026 Å) and the bond angles Ti–N–C (169.7°) and N–C–S (177.7°) show

clearly that both thiocyanato groups are coordinated through nitrogen as reported for related systems [14,33,34].

Acknowledgment

References and notes

1 E. Samuel, *J. Organomet. Chem.*, *19* (1969) 87.
2 H.H. Printzinger and L.S. Bartlet, *J. Am. Chem. Soc.*, *92* (1970) 1105.
3 J.E. Bercaw, *J. Am. Chem. Soc.*, *96* (1974) 5087.
4 D. Feitler and G.M. Whitesides, *Inorg. Chem.*, *15* (1976) 466.
5 R. Jungst, D. Sekutowski, J. Davis, M. Luly and G. Stucky, *Inorg. Chem.*, *16* (1977) 1645.
6 F. Wochner, L. Zsolnai, G. Huttner and H.H. Brintzinger, *J. Organomet. Chem.*, *288* (1985) 69.
7 P. Jutzi and R. Dickbreder, *Chem. Ber.*, *119* (1986) 1750.
8 D.M. Bensley, Jr., and E.A. Mintz, *J. Organomet. Chem.*, *353* (1988) 93.
9 D.T. Mallin, M.D. Rausch, E.A. Mintz and A.L. Rheingold, *J. Organomet. Chem.*, *381* (1990) 35.
10 H. Koepf and N. Klouras, *Chem. Ser.*, *19* (1982) 122.
11 R.A. Howie, G.P. McQuillan and D.W. Thompson, *J. Organomet. Chem.*, *268* (1984) 149.
12 I.F. Urazowski, V.I. Ponomaryov, O.G. Ellert, I.E. Nifantev and D.A. Lemenovski, *J. Organomet. Chem.*, *356* (1988) 181.
13 I. Jibril, S. Abu Orabi, S.A. Klaib, W. Imhof and G. Huttner, *J. Organomet. Chem.*, *433* (1992) 253.
14 J.L. Burmeister, *Coord. Chem. Rev.*, *105* (1990) 77.
15 R. Reimschneider and R. Nehrig, *Z. Naturforsch*, *18b* (1963) 643.
16 L. Knothe, H. Prinzbach and E. Hadicke, *Chem. Ber.*, *114* (1981) 1656.
17 *International Tables for X-ray Crystallography*, Kynoch, Birmingham, 1974.
18 G.M. Sheldrick, SHELX76, *Program for Crystal Structure Determination*, University of Cambridge, 1976.
19 G.M. Sheldrick, SHELXTL PLUS, *Program for Crystal Structure Determination*, Universität Göttingen, 1988.
20 S.W. Lin and A.F. Schreiner, *Inorg. Chim. Acta.*, *5* (1971) 290.
21 M.F. Farona and A. Mojcici, *Inorg. Chem.*, *4* (1965) 857.
22 J. Besancon, D. Camboli and J. Tirouflet, *J. Organomet. Chem.*, *186* (1980) C15.
23 R.A. Baily, S.L. Kosak, T.W. Michelsen and W. Mills, *Coord. Chem. Rev.*, *6* (1971) 407.
24 A.M. Cardoso, R.J.H. Clark and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, (1980) 1156.
25 J. Besancon, D. Camboli, B. Trimaille, M. Collette and J. Tirouflet, *C.R. Acad. Sci. Paris*, *Ser. C, 287* (1978) 573.
26 V.K. Jain, N.K. Bhatia, K.C. Sharma and B.S. Garg, *J. Indian Chem. Soc.*, *57* (1980) 6.
27 J.L. Burmeister, E.A. Deardorff and C.E. Van Dyke, *Inorg. Chem.*, *8* (1969) 170.
28 R.K. Tuli, K. Chandra, R.K. Sharma, N. Kumar and B.S. Grag, *Trans. Met. Chem.*, *5* (1980) 49.
29 R.B. King and C.A. Eggeres, *Inorg. Chem.*, *7* (1968) 340.

30 M.A. Chaudhari and F.G.A. Stone, *J. Chem. Soc. A*, (1966) 838.

31 H. Koepf and M. Schmidt, *Angew. Chem. Int. Edn. Engl., 4* (1965) 953.

32 Further details for the X-ray structure are available from Fach informations zentrum Karlsruhe, Gesellschaft fur wissenschaft-lich-technische Information mbG, D-76344 Eggenstein-Leopolds-hafen, Germany, upon citation of the depository No. CSD-57150, the authors and references to this paper.

33 A.C. Villa, A.G. Manfredotti and C. Guastini, *Acta Crystallogr., Sect. B, 32* (1976) 909.

34 F.A. Cotton and M. Matusz, *Inorg. Chem., 26* (1988) 2127.