DALTON

Regioselective reactions of isothiocyanates with the titanocene vinylidene fragment [Ti(=C=CH$_2$)(η-C$_5$Me$_5$)$_2$]. Crystal and molecular structure of [Ti{SC(=NC$_6$H$_{11}$)C=CH$_2$}(η-C$_5$Me$_5$)$_2$]†

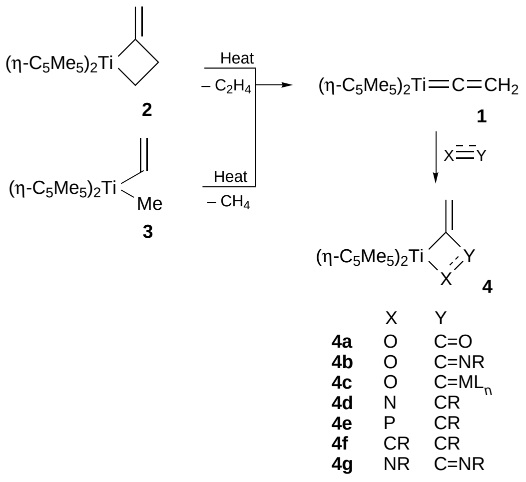
Rüdiger Beckhaus,*[a] Javier Sang,[a] Trixie Wagner[a] and Uwe Böhme[b]

[a] *Department of Inorganic Chemistry, Technical University Aachen, Professor-Pirlet-Strasse 1, D-52062 Aachen, Germany*
[b] *Department of Inorganic Chemistry, Leipziger Strasse, Technical University Bergakademie Freiberg, D-09596 Freiberg, Germany*

The titanocene vinylidene intermediate [Ti(=C=CH$_2$)(η-C$_5$Me$_5$)$_2$] **1** formed by ethane or methane elimination from [Ti(CH$_2$CH$_2$C=CH$_2$)(η-C$_5$Me$_5$)$_2$] **2** or [Ti(CH=CH$_2$)Me(η-C$_5$Me$_5$)$_2$] **3** respectively, reacted with isothiocyanates RNCS (R = C$_6$H$_{11}$ **a**, Ph **b** or Bu^t **c**) by a [2 + 2] cycloaddition, to give the titanathietane complexes [Ti{SC(=NR)C=CH$_2$}(η-C$_5$Me$_5$)$_2$]. The crystal structure of the R = C$_6$H$_{11}$ complex has been determined. In all cases the regioisomer in which the sulfur atom is bonded to titanium is observed as the primary product. Upon heating in the presence of pyridine a rearrangement to the regioisomeric titanacyclobutane derivative [Ti{C(=NR)SC=CH$_2$}(η-C$_5$Me$_5$)$_2$] was observed. The regioselectivity of the formation of the complexes **5** and **7** is discussed on the basis of *ab initio* calculations at the Hartree–Fock level of theory, with an effective core potential basis set.

Recent interest in ambidentate ligands, especially the thiocyanate ion which can co-ordinate *via* the sulfur or the nitrogen atoms or both, probably results from two principal considerations. The ambidentate nature of SCN$^-$ may be interpreted in terms of sulfur being a ‘soft’ and nitrogen a ‘hard’ base. When it is the only ligand present in a complex its mode of bonding generally follows the hard (M–NCS) or soft (M–SCN) pattern throughout the Periodic Table. However, the nature of other ligands in a complex may determine whether the metal functions as a hard ion and forms isothiocyanato complexes, or as a soft ion and forms thiocyanato complexes. Steric factors in bulky ligands also may alter the nature of thiocyanate co-ordination.[1] In the case of electron-poor transition metals the N-bonding mode of the thiocyanate ion is dominant,[2] but also examples of S-bonding modes are known.[2b] Additionally to the ambivalent character in different end-on co-ordination modes of the SCN$^-$ ion, side-on co-ordinations are known for isothiocyanates RSCN.[3] The ambivalent behaviour can also be observed in [2 + 2] cycloaddition reactions of isothiocyanates and metal–ligand double bonds. Thus C=N[4] and C=S addition products[4c,5a–c] are found.

The large variety of reactions involving the titanocene vinylidene intermediate [Ti(=C=CH$_2$)(η-C$_5$Me$_5$)$_2$] **1**[6] and carbon dioxide, ketenes, isocyanates,[7] transition-metal carbonyls,[8] nitriles and phosphaalkynes,[9] alkynes[10a,b] and carbodiimides[11] leads to four-membered titanacycles **4** of high thermal stability (Scheme 1). The regioselectivity can be explained in accordance with the polarities of the unsaturated compounds used in the cycloadditions towards the polarized titanium–carbon double bond (Ti$^{\delta+}$=C$^{\delta-}$) of **1**. Large differences in the partial charge of the unsaturated substrates (*e.g.* isocyanates, nitriles, alkynes) lead to stereochemically pure compounds, the more negative carbon being bonded to titanium.[7,9,10a,b] Regioisomers are obtained by using substrates with small differences in their partial charges. In a series of such studies we were interested in the behaviour of isothiocyanates RNCS towards the vinylidene intermediate **1**, in order to determine the accessibility of titanathietanes **5**. Owing to lower differences in the polarity of the NCS unit in isothiocyanates, compared to isocyanates, the formation of the regioisomers **6** and **7** should also be possible.



Scheme 1

Results and Discussion

The vinylmethyl derivative **3** reacts with 1 equivalent of isothiocyanates RNCS (R = C$_6$H$_{11}$ **a**, Ph **b** or Bu^t **c**) at room temperature by liberation of methane to give the metallacyclobutanes **5a**–**5c** (Scheme 2) which can be isolated as brown crystals of high thermal stability [m.p. 110 (decomp.) **5a**, 139–140 (decomp.) **5b** and 129 °C (decomp.) **5c**]. The products **5a** and **5b** with the sulfur atom in the α position are formed exclusively. When using Bu^{t}NCS the reaction product contains **5c** and the regioisomer **7c** in a 10 : 1 ratio. Isomers of **5**, indicating [2 + 2] cycloadditions involving the C=N bond (forming **6**), are not found during the synthesis. The mass spectra of **5** exhibit the expected molecular peaks and the formation of a (η-C$_5$Me$_5$)$_2$-Ti=S fragment in a first step, similar to the fragmentation behaviour of the titanaoxetanes **4b**, where a (η-C$_5$Me$_5$)$_2$Ti=O fragment is also observed.

The ^{1}H and ^{13}C NMR data for the titanathietanes **5** are listed

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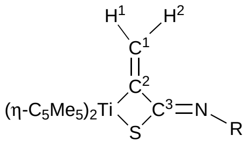
† *Non-SI unit employed*: $E_h \approx 4.36 \times 10^{-18}$ J.

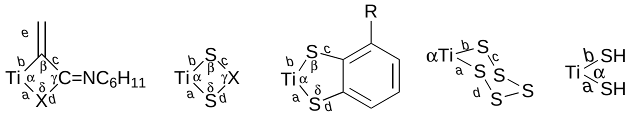
Table 1 NMR Data for the titanathietanes **5**[a]



		^1H (J_{HH}/Hz)				^{13}C			
	R	C_5Me_5	H^1 (*endo*)	H^2 (*exo*)	Δ^b	C_5Me_5	C^1	C^2	C^3
5a	C_6H_{11}	1.69	3.91 (d, 2.8)	6.92 (d, 2.8)	3.01	12.4 124.6	110.1	196.0	149.7
5b	Ph	1.64	4.06 (d, 2.4)	7.06 (d, 2.4)	3.00	12.4 125.0	112.2	195.9	153.4
5c	Bu^t	1.68	3.74 (d, 2.8)	6.97 (d, 2.8)	3.23	12.7 124.9	109.5	195.7	149.0

[a] Listed in ppm *vs.* $SiMe_4$; solvent was C_6D_6 and temperature = 25 °C. [b] $\Delta = |\delta(H^2) - \delta(H^1)|$.

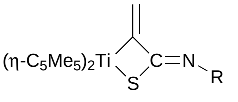
Table 2 Selected bond distances (Å) and angles (°) in complex **5a** compared to those of similar structure types



5a (X = S) **8** (X = S)
4b (X = O) **9** (X = SiMe2)
10
11
12

Complex	*a*	*b*	*c*	*d*	*e*	Ref.
5a	2.466(1)	2.156(3)	1.484(5)	1.795(3)	1.320(4)	This work
4b	1.983(2)	2.121(3)	1.477(4)	1.348(3)	1.325(4)	7(*a*)
8	2.413(4)	2.413(4)	2.041(5)	2.041(5)	—	13(*a*)
9	2.454(1)	2.454(1)	2.110(1)	2.110(1)	—	13(*b*)
10	2.418(3)	2.389(3)	1.76(1)	1.76(1)	—	13(*c*)
11	2.422(1)	2.448(1)	2.059(2)	2.058(1)	—	13(*d*)
12	2.409(2)	2.418(3)	—	—	—	14

	α	β	γ	δ	Ref.
5a	70.45(9)	99.5(2)	109.2(2)	80.9(1)	This work
4b	67.6(1)	87.2(2)	107.9(2)	96.7(2)	7(*a*)
8	84.44(9)	76.34	105.3(1)	76.34	13(*a*)
9	87.1	83.4	105.5	83.4	13(*b*)
10	81.4(1)	97.4(4)	—	95.9(4)	13(*c*)
11	94.6	—	—	—	13(*d*)
12	94.8(1)	—	—	—	14



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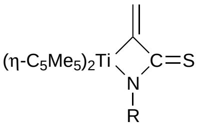

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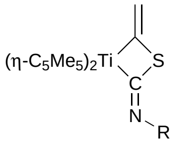

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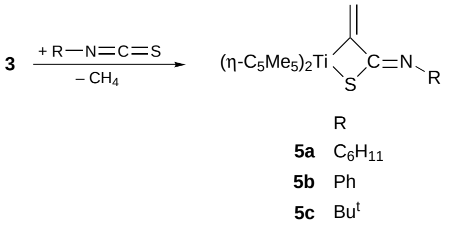


Scheme 2

in Table 1. Especially the value of the difference Δ of the chemical shifts of H^1 and H^2 in **5a**–**5c** appears to be a characteristic feature of the new complexes. The low-field signals in the ^{13}C NMR spectra are consistent with the metal-bonded C^2 atom (δ 195.7–196.0), whereas the chemical shifts of C^1 and C^3 are in the expected range.

The structure of compound **5a** was confirmed by X-ray analysis. The ORTEP[12] plot is shown in Fig. 1, relevant bond distances and angles, compared to those of similar structure types, in Table 2. The crystal chemistry of this and related titanacyclobutanes (**4b**,[7a] **4d**, **4e**[9]) will be the subject of a forthcoming paper.[7b] The geometry of **5a** shows a planar titanacycle. Thietanes are characterized by an angle of 154(4)° between the CCC and the CSC planes.[15] The solid-state structural data for **5a** are consistent with a metallacycle formalism. The Ti–C(2) bond is longer as in the titanacyclobutane **2** [2.068(6) Å][6c] and also longer than in titanacyclobutenes [**4f** (R = Me), 2.104(3) Å].[10a] More interesting is the slight elongation of the Ti–S bond compared to those of other sulfur-containing metallacycles **8**–**10**[13] and particularly to the non-cyclic titanocene sulfide $[Ti(SH)_2(\eta\text{-}C_5Me_5)_2]$ **12**.[14] Generally, the small ring size of

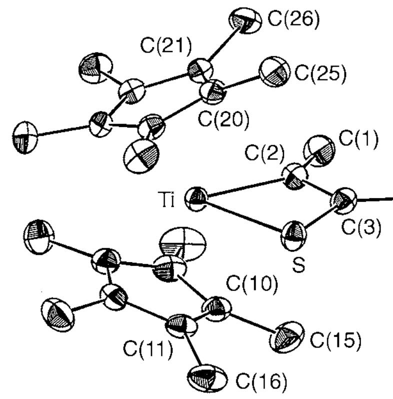
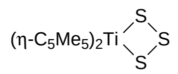


Fig. 1 An ORTEP drawing of [$\overline{\text{Ti}\{\text{SC}(=\text{NC}_6\text{H}_{11})\text{C}}=\text{CH}_2\}(\eta\text{-C}_5\text{Me}_5)_2$] **5a** (30% ellipsoids)



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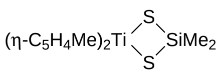

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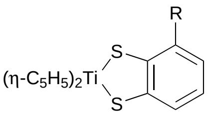

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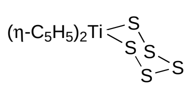
R = C(O)N(H)CH$_2$Ph



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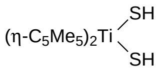

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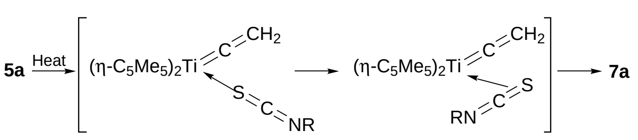
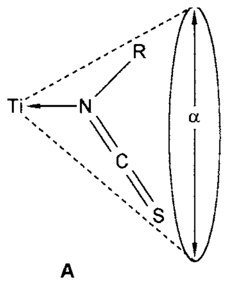
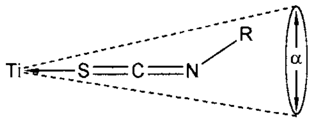


13 **14**

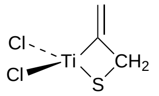
Scheme 3



A



B



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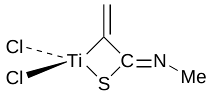

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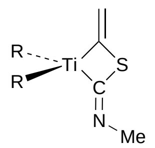
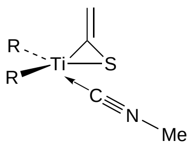




17a = Cl
17b = C$_5$H$_5$

18a = Cl
18b = C$_5$H$_5$

heterotitanacyclobutanes $\overline{\text{Ti–X–CC}}$ (X = O, N or S) leads to longer Ti–X distances as in larger rings or non-cyclic compounds, due to the lowering of X→Ti π-bonding interactions as a result of smaller Ti–X–C angles in four-membered rings. Thus the Ti–S bond distances increase from **12** [2.409(2)] to the five-membered rings **11** and **10** [2.422(1), 2.418(3)] and to the four-membered rings **8**, **9** and **5a** [2.413(4), 2.454(1) and 2.466(1)].

The exocyclic C=C double bond C(1)–C(2) [1.320(4) Å] is relatively short, compared to those in **4f** [1.377(4) Å, R = Me,[10a] 1.342(5) Å, R = CCSiMe$_3$ or SiMe$_3$[10b]], but similar to **4d** [1.337(3)], **4e** [1.326(8)][9] and **4f** [1.322(8), R = SiMe$_3$ or Ph].[10a] The value of the distance *e* is indicative of the reactivity of the methylenetitanacycles. A long distance characterizes stable complexes, a shorter distance points to a tendency to cycloreversion reactions (forming **1**), as found for **2** (*e* = 1.321 Å),[6c] **4e** and **4f**. Additionally the C(2)–C(3) bond in **5a** is longer than in **4b**. As a consequence of the larger sulfur atom in **5a** compared to the oxygen in the oxetanes **4b**, a longer distance Ti · · · C(3) of 2.881(3) in **5a** compared to 2.52 Å in **4b** is found. The value of the angle α in **5a** (Table 2) is in the expected range for four-membered titanacycles[6a] exhibiting a lower value compared to the more sulfur-rich compounds **8** and **9** and especially to larger rings or non-cyclic titanocene derivatives like **11** and **12**, as discussed before.

The orientation of the substituents in the cyclobutanes can be attributed to the polarity of the isothiocyanate molecule and the strongly nucleophilic α-C atom in the vinylidene **1** ($\text{Ti}^{\delta+}=\text{C}^{\delta-}=\text{CH}_2$). However, the nitrogen atom in RNCS exhibits the most negative partial charge (Pauling electronegativity values: S, 2.5; C, 2.5; N, 3.0) and a N-co-ordination mode **A** is expected. Calculated electron densities for the optimized structure of MeNCS (Mulliken values, basis set 6-31G*) confirmed that the most negative charge was on the nitrogen atom (S, −0.21; C, +0.31; N, −0.45). On the other hand, the primary co-ordination mode **A** exhibits a larger space requirement (α) compared to the S-co-ordination mode **B**. In particular, the rod-like shape of isothiocyanate molecule RNCS seems to be the reason for a preferred S-end-on co-ordination mode and formation of the CS-cycloaddition products **5** instead of a CN cycloaddition to the regioisomer **6**. Furthermore, isothiocyanates normally undergo nucleophilic attack at the carbon atom and not, like many other carbon–sulfur double bond-containing molecules, thiophilic attack.[16]

Heating compound **5a** in the presence of pyridine at 80 °C for 20 min results in isomerization to **7** (85%). The pyridine is not incorporated in the reaction product, but without it no isomerization takes place. As mentioned before, the reaction of **1** with Bu^{t}NCS leads to a small amount of **7c** (**5c**:**7c** = 10:1), which cannot be separated. Owing to the relatively long Ti–S and the C(2)–C(3) bond distances in **5a**, a reactive Ti–S bond is expected, indicating the possibility of a cycloreversion of **5**. Thus the formation of ring-opened intermediates **13** and **14** seems to be possible, which can rearrange to the second CS-cycloaddition product **7**. During the isomerization the colour changes from brown to light yellow. The NMR spectra clearly indicate the four-membered ring structure of **7**, which can be seen from the *exo*-CH$_2$ group at δ 4.19 and 7.91 for **7a**. In the ^{13}C NMR spectrum a second titanium-bonded carbon atom can be observed (δ 204.5, **7a**), instead of the signal δ 149.7 for the β-C=N carbon atom in **5a**.

To understand the reaction course **5** ⟶ **7**, the geometries of the titanium complexes **15**, **16** and **17**/**18** were investigated by *ab initio* calculations at the restricted Hartree–Fock (RHF) level of theory (see Experimental section). In our *ab initio* calculations the C$_5$Me$_5$ groups of the real molecules **5** and **7** were replaced by chloride ligands, which has been shown in other studies to provide a good theoretical substitute for the actual bent metallocene system.[17] The optimized geometries and the atomic charge distributions and bond-overlap populations of **15**, **16** and **18a** are shown in Figs. 2 and 3. The geometry of **16** is in good agreement with the structure found for **5a**. The total energies of the optimized structures **15**, **16** and **18a** are shown in Table 3. The calculation of single-point energies by second-order Møller–Plesset perturbation (MP2) results in a lowering of the total energy of these systems. This stabilization effect is similar for **16** and **18a**. The smaller molecule **15** shows a smaller effect, as expected.

Table 3 Total energies (E) and energy differences of complexes **15**, **16** and **18a** [E_h; kJ mol^{-1} (in parentheses)]

	15	**16**	**18a**	E(**16**) − E(**18a**)
E^{RHF}	−115.582 53	−131.259 45	−131.284 75	0.025 3 (66.4)
$E^{\mathrm{MP2/RHF}}$	−116.071 11	−131.921 67	−131.938 37	0.016 7 (43.8)
$E^{\mathrm{RHF}} - E^{\mathrm{MP2/RHF}}$	−0.488 58	−0.662 22	−0.653 62	

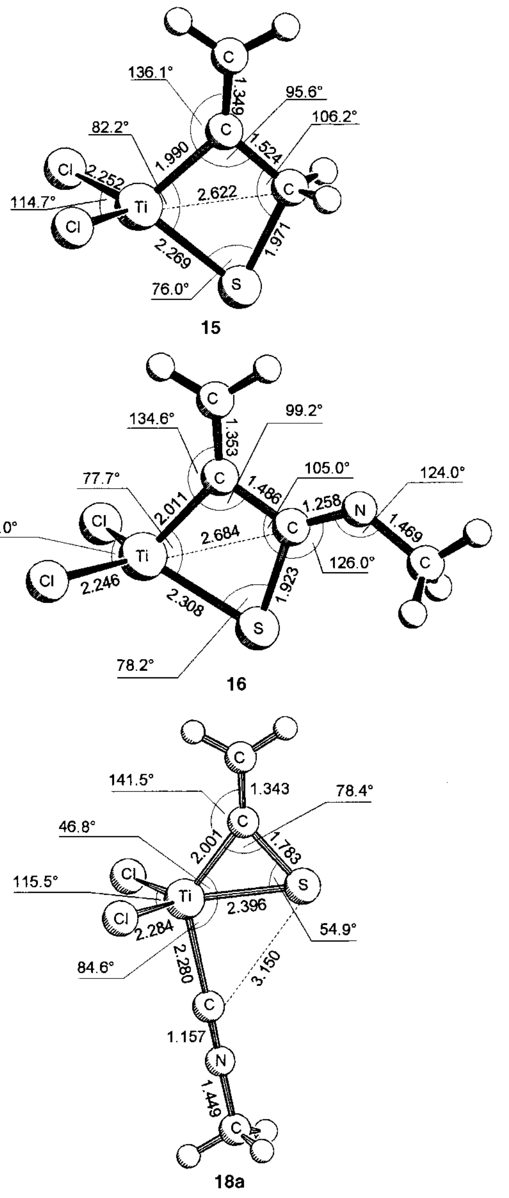


Fig. 2 Optimized geometries of complexes **15**, **16** and **18a** at the RHF level; distances in Å

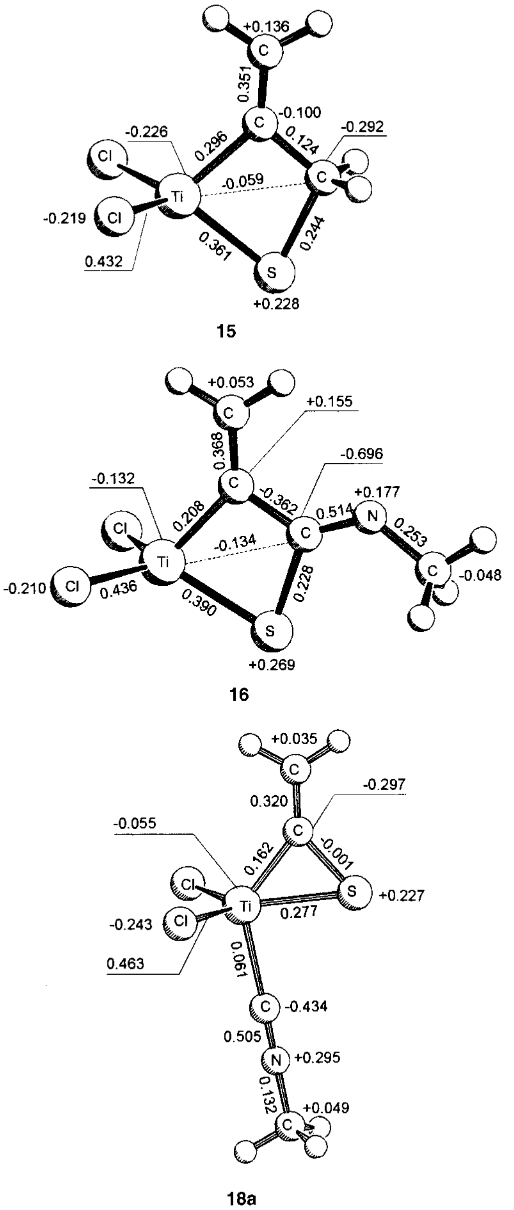
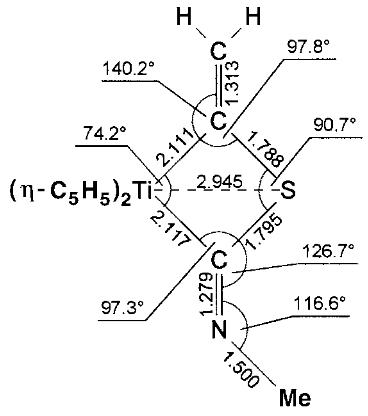


Fig. 3 Atomic charge distributions and bond-overlap populations of complexes **15**, **16** and **18a** obtained by Mulliken population analysis at the RHF level

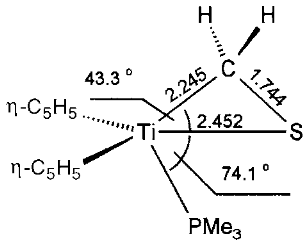
Whereas structure **16** converged well during optimization, the starting geometry **17a** led straightforwardly to the optimized structure **18a**. The fully optimized geometry of **18a** is more stable than **16** (66.4 kJ mol^{-1} at the restricted Hartree–Fock level, 43.8 kJ mol^{-1} at the MP2 level). The geometries of the four-membered titanacycles **15** and **16** are similar. Replacement of the CH_2 group in **15** by a C=NMe group in **16** leads to elongation of the Ti–C, Ti–S, Ti–C and C=C (*exo*-methylene group) bond lengths. The bond lengths S–C and C–C are shorter in **16** by 0.048 and 0.038 Å, respectively. This reflects the peculiar effect of the C=NMe group on the titanathietane ring in **16**: on one hand there are longer bonds between titanium and its ligands, on the other shorter bonds between the C=NMe group and its neighbours. The repulsive interaction (−0.362) between the α- and β-carbon in the four-membered ring is the most striking feature of the Mulliken-overlap population analysis of **16** (Fig. 3). Therefore it becomes probable that the kinetic product **16** undergoes a ring-opening reaction at the internal C–C bond with rearrangement to the thermodynamic stable product **18a**. It was found in our experiments that **5a** rearranges to **7** upon heating. The structure **18a** represents a titanium thioketene complex with co-ordinated methyl isocyanide.

Obviously the formation of complex **18a** reflects the degradation of isothiocyanates to isocyanides typical of late-transition-metal SCNR complexes,[3a,18a,b] but also in the case of



17b

Fig. 4 Optimized geometry of complex **17b** (RHF level, basis set STO-3G); distances in Å



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Lewis-acid metallocenes $Si(C_5Me_5)_2$.[5a] The existence of η^2-C,S bonded thioketene derivatives[19] as calculated in **18a** and comparable structures are also known in the case of titanium complexes.[20] However, in the case of the formation of **7** from **5** there are no hints regarding the presence of a co-ordinated isocyanide in the IR spectra [expected for ν(C=N) in Ti–CN–R complexes with RNC as σ donors (2200,[21] 2260–2310 cm^{-1}[22]) or as π-acceptor ligands (2038, 1937 cm^{-1}[23])]. Only the typical ν(CN) band of an iminoacyl structure[24] is observed in the case of **7a** (1541 cm^{-1}), which is only consistent with the model structure **17** and **7** in the real molecules. The mass spectra of **7a** shows the expected molecular peak.

Comparison of complex **18a** with the titanocene thioformaldehyde complex $[Ti(\eta^2\text{-}SCH_2)(\eta\text{-}C_5H_5)_2(PMe_3)]$ **19**, which was isolated and structurally characterized some years ago,[20a] shows that there are great similarities in the co-ordination geometry of the C–S fragment at titanium. The Ti–S and C–S bond lengths exhibit only small differences of 0.056 and 0.039 Å, respectively. The bond length Ti–C in the model complex **18a** is shorter than in **19** by 0.244 Å. The angles C–Ti–S are similar with 46.8° in **18a** and 43.3° in **19**. The differences between **18a** and **19** can be attributed to the different donor molecules CNMe and PMe_3 and to the substitution of the C_5H_5 ligand by Cl atoms.

To gain a better insight into the influence of the spacer ligand chloride in comparison with any cyclopentadienyl system, we performed the optimization of the cyclopentadienyl-substituted model complexes **17b** and **18b** with basis set STO-3G.‡ We found that the structure **17b** is a minimum in this system for this primitive basis set (Fig. 4). Therefore we conclude that the chloride ligands with their higher electronegativity and different space filling than C_5H_5 are the reason for the unexpected minimum structure **18a** in our Cl_2Ti model system.

Conclusion

We have demonstrated that the reaction of the titanocene vinylidene intermediate $[Ti(=C=CH_2)(\eta\text{-}C_5Me_5)_2]$ **1** with isothiocyanates yields titanathietane complexes **5**. Only one regioisomer is formed, where the sulfur atom is in the α position of the metallacycle. The regioselectivity can be explained in terms of the shape of the isothiocyanate and the stereochemistry of **1**. On heating in the presence of pyridine, **5** can be isomerized to a second C=S cycloaddition product **7**. C=N-Cycloaddition products are not observed. The isomerization of **5** to **7** shows that the lower polarity of the C=S unit in the RNCS molecule allows the formation of a second isomer. In this context the behaviour of titanathietanes is quite different from that of titanaoxetanes, which react to give Ti=O (classical behaviour) or by cycloreversion to give Ti=C bonds (non-classical behaviour).[6a,b,8] A similar comparison of different reactivities between homologous compounds can be made between aza- and phospha-titanacyclobutenes. For the former only one regioisomer is observed; the latter exhibit also α,β regioisomers.[9] This behaviour can also be attributed to the lower polarity of the C=X bond used in cycloaddition reactions.

Experimental

General considerations

The preparation and handling of the described compounds were performed under rigorous exclusion of air and moisture under a nitrogen atmosphere, using standard vacuum-line and Schlenk techniques. All solvents were dried with appropriate drying agents and distilled under a nitrogen atmosphere. Deuteriated solvents were degassed by freeze–pump–thaw cycles and dried over molecular sieves (3, 4 Å) prior to use. Proton and ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuteriated solvents (C_6D_6, δ 7.15 for ^1H NMR, δ 126.96 for ^{13}C NMR). Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, infrared spectra as KBr pellets on a Perkin-Elmer 1720X FT-IR spectrometer. Elemental analyses were carried out at the Analytische Laboratorien in Lindlar, Germany. The titanocene complexes $[Ti(CH=CH_2)Me(\eta\text{-}C_5Me_5)_2]$[8,25] and $[\overline{Ti(CH_2CH_2C}=CH_2)(\eta\text{-}C_5Me_5)_2]$[26a,b] were prepared by literature procedures. The isothiocyanates were obtained from Aldrich.

Preparations

(4-Cyclohexylimino)(3-methylene)-2,2-bis(η^5-pentamethylcyclopentadienyl)-1-thia-2-titanacyclobutane 5a. To a solution of complex **3** (366.0 mg, 1.015 mmol) in hexane (40 cm^3) was added cyclohexyl isothiocyanate (150.6 mg, 1.066 mmol) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The hexane was partially removed under reduced pressure until crystallization took place (0 °C), yielding **5a** after decantation as brown, octahedral crystals (m.p. 110 °C), suitable for structure determination. Yield 0.265 g, 54% (Found: C, 72.25; H, 9.2; N, 2.75; S, 6.35. $C_{29}H_{43}NSTi$ requires C, 71.75; H, 8.95; N, 2.9; S, 6.6%). NMR (C_6D_6): ^1H (500 MHz), δ 1.28–1.37 (1 H, t/m, *J* 3.5), 1.51–1.58 (2 H, t/m, *J* 3.5), 1.58–1.65 (1 H, m), 1.80–1.85 (1 H, m), 1.85–1.92 (3 H, m), 2.17 (2 H, m) (all CH_2 ring), 1.69 [30 H, s, $C_5(CH_3)_5$], 3.91 [1 H, d, *J* 2.8, =C*H*H(*cis*)], 4.20 (1 H, t/t, *J* 9.9/4.0, NCH) and 6.92 [1 H, d, *J* 2.8 Hz, =CH*H*(*trans*)]; ^{13}C-{^1H} (125 MHz), δ 12.4 [$C_5(CH_3)_5$], 25.7, 26.8, 34.2 (all CH_2 ring), 60.2 (=NCH), 110.1 (=CH_2), 124.6 [$C_5(CH_3)_5$], 149.7 (C=N) and 196.0 (Ti–C=). Electron impact (EI) mass spectrum (111 °C): *m*/*z* 485 (*M*, 28), 460 (40), 350 [$(C_5Me_5)_2Ti=S$, 33], 318 [$(C_5Me_5)_2Ti$, 100], 279 (10), 271 (30), 256 (17), 215 [$(C_5Me_5)Ti=S$, 20], 181 (19), 159 (12), 136 (C_5Me_5H, 39), 119 (53), 105 (26), 91 (23), 83 (11), 77 (11) and 55 (18%); exact mass 485.2596 ($C_{29}H_{43}NSTi$), calculated 485.2596. IR (KBr): 3076w, 3022w, 2985w, 2956m, 2927vs, 2848s, 2722w, 1630w, 1539vs [ν(C=N)], 1491m, 1448m, 1379vs, 1343w, 1255w, 1180w, 1165w, 1120m, 1058w, 1019m, 1006m, 979m, 960m,

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‡ This basis set and cyclopentadienyl instead of pentamethylcyclopentadienyl ligands for the geometry optimization of **17b** and **18b** were chosen in order to obtain results in a reasonable time.

902m, 891w, 843w, 792w, 713m, 627w, 619w, 593w, 556m, 475w, 458w, 434w and 406m cm^{-1}.

(3-Methylene)-2,2-bis(η^5-pentamethylcyclopentadienyl)(4-phenylimino)-1-thia-2-titanacyclobutane 5b. A reaction of complex **3** (271.2 mg, 0.7525 mmol) in hexane (30 cm^3) with phenyl isothiocyanate (106.8 mg, 0.7901 mmol) was carried out using the same procedure as in the case of **5a**. Owing to the low solubility of **5b** in hexane the reaction mixture was filtered, yielding **5b** as brown microcrystals, m.p. 139–140 °C (decomp.). Yield 0.310 g, 86% (Found: C, 71.0; H, 8.1; N, 2.7. $C_{29}H_{37}NSTi$ requires C, 72.65; H, 7.8; N, 2.9%). NMR (C_6D_6): ^1H (500 MHz), δ 1.64 [30 H, s, $C_5(CH_3)_5$], 4.06 [1 H, d, *J* 2.4, =C*H*H-(*cis*)], 7.01 (1 H, t/m, *J* 7.2, *p*-H), 7.06 [1 H, d, *J* 2.4, =CH*H*(*trans*)], 7.37 (1 H, t/m, *J* 8.0, *m*-H) and 7.50 (2 H, d/m, *J* 8.5 Hz, *o*-H); $^{13}C-\{^1H\}$ (125 MHz), δ 12.4 [$C_5(CH_3)_5$], 112.2 (=CH_2), 122.7 (*m*-C), 125.0 [$C_5(CH_3)_5$], 128.3 (*p*-C), 129.8 (*o*-C), 153.4 (C=N), 156.8 (*ipso*-C) and 195.9 (Ti–C=). EI mass spectrum (151 °C): *m*/*z* 479 (*M*, 19), 445 (3), 389 (3), 380 (13), 353 (23), 350 [$(C_5Me_5)_2Ti{=}S$, 9], 345 (9), 318 (23), 317 (26), 297 (13), 279 (14), 265 (100), 250 (63), 235 (16), 218 (60), 194 (6), 167 (21), 162 (36), 147 (51), 134 (68), 130 (57), 121 (47), 119 (92), 105 (43), 93 (30), 91 (36), 77 (48) and 57 (35%); exact mass 479.2128 ($C_{29}H_{37}NSTi$), calculated 479.2126. IR (KBr): 3074w, 3060w, 3029w, 2959m, 2905s, 1819w, 1593s, 1530vs [ν(C=N)], 1485m, 1431m, 1378vs, 1262s, 1222s, 1165w, 1103m, 1069w, 1021m, 1002w, 991m, 908s, 846m, 803s, 765s, 695vs, 622w, 608m, 548m, 500w and 420m cm^{-1}.

(4-*tert*-Butylimino)(3-methylene)-2,2-bis(η^5-pentamethylcyclopentadienyl)-1-thia-2-titanacyclobutane 5c. A reaction of complex **3** (205.1 mg, 0.5691 mmol) in hexane (20 cm^3) with *tert*-butyl isothiocyanate (68.8 mg, 0.598 mmol) was carried out using the same procedure as in the case for **5a**. Similar work-up gave **5c** as yellow-brown needles, m.p. 129 °C (decomp.). Yield 0.191 g, 73% (Found: C, 69.6; H, 9.55; N, 2.85. $C_{27}H_{41}NSTi$ requires C, 70.55; H, 9.0; N, 3.05%). NMR (C_6D_6): ^1H (500 MHz), δ 1.68 [30 H, s, $C_5(CH_3)_5$], 1.82 [9 H, s, $NC(CH_3)_3$], 3.74 [1 H, d, *J* 2.8, =C*H*H(*cis*)] and 6.97 [1 H, d, *J* 2.8 Hz, =CH*H*(*trans*)]; $^{13}C-\{^1H\}$ (125 MHz), δ 12.7 [$C_5(CH_3)_5$], 29.8 [$C(CH_3)_3$], 54.8 [$C(CH_3)_3$], 109.5 (=CH_2), 124.9 [$C_5(CH_3)_5$], 149.0 (C=N) and 195.7 (Ti–C=). EI mass spectrum (91 °C): *m*/*z* 459 (*M*, 8), 402 (4), 356 (13), 350 [$(C_5Me_5)_2Ti{=}S$, 19], 337 (22), 318 (76), 317 (76), 279 (8), 277 (9), 268 (12), 221 (29), 202 (24), 149 (27), 143 (100), 135 (72), 121 (47), 119 (91), 105 (35), 91 (30), 88 (27), 87 (30), 71 (33) and 57 (47%); exact mass 459.2441 ($C_{27}H_{41}NSTi$), calculated 459.2439. IR (KBr): 3040w, 2962vs, 2901vs, 1808w, 1556vs [ν(C=N)], 1490m, 1475w, 1452m, 1432m, 1379vs, 1351s, 1262w, 1227s, 1209s, 1109s, 1065w, 1020s, 962s, 915w, 901s, 803m, 772w, 711w, 651w, 595w, 556m, 539m, 505w and 470w cm^{-1}.

(2-Cyclohexylimino)(4-methylene)-3,3-bis(η^5-pentamethylcyclopentadienyl)-1-thia-3-titanacyclobutane 7a. Complex **5a** (140 mg, 0.288 mmol) was dissolved in pyridine (30 cm^3) (dried over KOH and distilled before use) and heated to 80 °C for 15 min. During that time the mixture changed from brown-red to vivid yellow. The pyridine was partially removed under reduced pressure until crystallization took place, yielding **7a** as a yellow powder. Yield 85% according to NMR spectroscopy. NMR (C_6D_6): ^1H (500 MHz), δ 1.01–1.11 (1 H, m), 1.13–1.22 (1 H, m), 1.25–1.35 (1 H, m), 1.45–1.51 (3 H, m), 2.24 (4 H, m) (all CH_2 ring), 1.67 [30 H, s, $C_5(CH_3)_5$], 4.19 [1 H, d, *J* 3.0, =C*H*H(*cis*)], 4.86 (1 H, t/t, *J* 7.5/4.0, NCH) and 7.91 [1 H, d, *J* 30 Hz, =CH*H*(*trans*)]; $^{13}C-\{^1H\}$ (125 MHz), δ 12.2 [$C_5(CH_3)_5$], 25.4, 26.1, 32.4 (all CH_2 ring), 54.3 (=NCH), 121.1 (=CH_2), 122.6 [$C_5(CH_3)_5$], 198.5 (Ti–C=) and 204.5 (C=N). EI mass spectrum (111 °C): *m*/*z* 486 (*M* + H, 2), 414 (5), 351 (5), 317 [$(C_5Me_5)_2$-Ti–H, 11], 305 (10), 272 (21), 170 (24), 136 (C_5Me_5H, 100), 121 (64), 119 (31), 105 (27), 98 (17), 93 (11), 91 (15), 88 (14), 71 (13) and 55 (11%); exact mass 485.2596 ($C_{29}H_{43}NSTi$), calculated 485.2596. IR (KBr): 3640s, 2978w, 2925vs, 2847s, 1541s [ν(C=N)], 1494m, 1449s, 1381vs, 1344m, 1261w, 1247w, 1192w, 1166m, 1132w, 1099w, 1065w, 1020w, 1002vs, 971m, 929m, 891m, 799s, 717s, 697s, 626w, 597w, 557s, 478m and 428m cm^{-1}.

Table 4 Crystal data and parameters of structure refinement for complex **5a**

Formula	$C_{29}H_{43}NSTi$
M	485.64
Space group (no.)	$P2_1/n$ (14)
Crystal symmetry	Monoclinic
a/Å	10.559(1)
b/Å	13.252(1)
c/Å	18.903(3)
γ/°	90.60(1)
U/Å^3	2644.9(9)
Z	4
D_c/g cm^{-3}	1.219
μ/cm^{-1}	35.78
T/°C	20
Radiation (λ/Å)	Cu-Kα (1.5418)
Crystal dimensions/mm	0.7 × 0.5 × 0.4
Measured reflections	4931
Scan range/°	$5 \leqslant \theta \leqslant 65$
Unique observed reflections [$I > 1.0\sigma(I)$]	3247
Parameters refined	289
R	0.054
R′ *	0.064
Goodness of fit	1.500

* Weighting scheme $w^{-1} = \sigma^2(F_o)$.

Ab initio and modelling calculations

The geometry of MeNCS was fully optimized at the restricted Hartree–Fock level of theory with the 6-31G* standard basis set,[28a,b] those of complexes **17b** and **18b** with basis set STO-3G[28] and titanium complexes **15**, **16** and **18a** with an effective core potential (ECP) basis set.[29a,b] The ECP replaces the innermost core orbitals for titanium and all core orbitals for the main-group elements (C, N, S, Cl). For titanium, orbitals 3s, 3p, 3d, 4s and 4p were treated explicitly by a double-ζ quality sp and a quadruple-ζ quality d basis set. For the main-group elements, ns and np were treated explicitly by a double-ζ basis set. It has been shown that this ECP basis set is suitable for transition-metal compounds of various kinds.[30a–c]

Although geometries are predicted accurately at the RHF level, energetics are expected to be poor if correlation energy is ignored. The correlation contribution was taken into consideration with single-point energy calculations (at the geometries obtained at the RHF level) according to Møller–Plesset second-order perturbation theory (MP2/RHF).[31] The atomic charges have been calculated from the fully optimized structures by Mulliken population analysis. The calculations have been carried out using the program packages SPARTAN 3.1[32] on an IBM RS6000-355 and GAMESS[33] on a CONVEX-C3420 computer.

Crystallography

Geometry and intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. A summary of crystallographic data, data collection and refinement parameters is given in Table 4. The monoclinic setting with a unique *c* axis was chosen for easier comparison between the structure of complex **5a** and the related but not isotypic structure of **4b** (R = C_6H_{11})[7a] which has similar unit-cell dimensions [$a = 9.904(3)$, $b = 13.780(3)$, $c = 19.342(4)$ Å, $\beta = 95.07(2)°$, $U = 2629(2)$ Å^3]. In both structures pairs of molecules are arranged in layers; they differ, however, with respect to the stacking of these layers along the *c* direction. A detailed comparison of these structures on the molecular and packing level will be published in a forthcoming paper.[7b] Although the crystal was sealed in a glass capillary, the intensities of three regularly measured check reflections indicated considerable anisotropic crystal decay (*ca.* 50%) which was taken into account by scaling the intensity data to the closest standard. Owing to this crystal instability the empirical absorption correction had to be performed by the DIFABS program[34] (minimum correction 0.822, maximum 1.165) after completion of the isotropic structure model. The structure was solved by direct methods[35] and refined on structure factors with the local version of the SDP program suite.[36] In the full-matrix least-squares refinement (based on F), all non-hydrogen atoms were assigned anisotropic displacement factors and hydrogen atoms were included riding on the corresponding carbon atoms [C−H 0.98 Å, $U_{iso}(H) = 1.3U_{eq}(C)$]. The highest fluctuations in a final Fourier-difference map amounted to 0.25 e $Å^{-3}$.

Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/527.

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