Journal of Organometallic Chemistry, *461* (1993) 75–80

JOM 23745

Synthesis and crystal structure of two titanasilazanes

Yu.E. Ovchinnikov [a], M.V. Ustinov [b], V.A. Igonin [a], Yu.T. Struchkov [a], I.D. Kalikhman [b] and M.G. Voronkov [b]

[a] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Acad. Sci., Vavilov St. 28, Moscow, 117813 (Russian Federation)*

[b] *Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Acad. Sci., Favorsky St. 1, Irkutsk, 664033 (Russian Federation)*

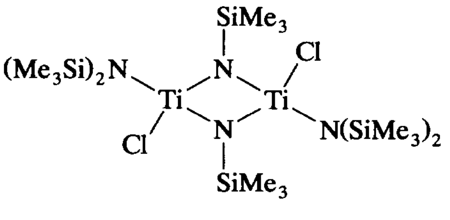
(Received February 28, 1993)

Abstract

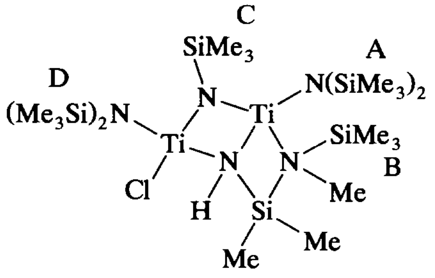
Interaction of $TiCl_4$ and $LiN(SiMe_3)_2$ produces two titanasilazanes, whose structure is established by an X-ray study. In both structures, Ti^{IV} atoms are tetra-coordinated. Geometrical parameters of the centrosymmetrical molecule of the first compound are unexceptional. In the bicyclic frame of the second complex, the bond lengths are: Ti–N 1.866–2.034(3), Si–N(sp^3) 1.890(4) Å.

1. Introduction

Investigations of various elements bis(silyl)amino derivatives has been a sufficiently actively developing area of organometallic chemistry for a long time [1]. Synthesis of silazanide titanium derivatives [2–7] is not on the last place in this field. Here we report the studies on the cyclic titanasilazanes **I** and **II**, that were prepared in the course of investigations on reactions resulting in compounds with Ti–Si bonds [8]. X-ray structural data show that the geometrical parameters of molecule **I** are close to those of titanasilazanes of similar structure. On the contrary, the bond lengths in molecule **II** bicyclic frame are rather unusual, though the structures of this type have not been known either for Ti, or its analogs, *viz*. Zr and Hf.



(I)



(II)

2. Experimental details

2.1. Preparation of I and II

All operations were carried out *in vacuo*. Solvents were dried over a sodium mirror and distilled directly before experiments. $LiN(SiMe_3)_2$ was prepared from ^nBuLi and $HN(SiMe_3)_2$ according to [2]. NMR spectra were measured with a Jeol FX 90Q spectrometer, mass spectra were registered with a Varian MAT 212 instrument. Assignment of NMR signals was performed according to ratios of integral intensity values and literature data [6,7].

The solution of 6.05 g (36.24 mM) of $LiN(SiMe_3)_2$ in 80 ml of THF was added on cooling and shaking to the solution of 1.97 g (10.35 mM) of $TiCl_4$ in 25 ml of hexane. The reaction mixture was kept for one day at room temperature, decanted from the LiCl precipitate and then the air moisture sensitive compounds **I** and **II**

Correspondence to: Dr. Yu.E. Ovchinnikov or Professor Yu.T. Struchkov.

Elsevier Sequoia S.A.

were isolated by recrystallization from hexane in the *ca.* 1 : 1 ratio (each in 17% of the total reaction mass).

I: ^{1}H NMR (C_6H_6, rel. TMS): δ 0.46 (s, $=NSiMe_3$); 0.54 (s, $-N(SiMe_3)_2$) ppm; integral intensities ratio 1 : 2. Mass spectrum (m/z, ion): 660 (4%) M^+, 645 (33%) $(M - Me)^+$, 499 (7%) $[M - HN(SiMe_3)_2]^+$, 145 (100% $[M - Ti_2Cl_2(NSiMe_3)N(SiMe_3)_2Me]^+$.

II: ^{1}H NMR (C_6H_6, rel. TMS; for groups designation see the structural formula of **II**): δ 0.33(A), 0.36(B), 0.46(C), 0.55(D) ppm. Mass spectrum (m/z, ion): 697 (4%) M^+, 682 (2%) $(M - Me)^+$, 536 (2%) $[M - HN(SiMe_3)_2]^+$, 454 (15%) $[M - TiClN(SiMe_3)_2]^+$, 366 (4%) $[M - (NSiMe_3(SiMe_2)N(SiMe_3)_2Me]^+$, 145 (100%) $[HN(SiMe_3)_2MeH]^+$.

TABLE 1. Atomic coordinates ($\times 10^4$, $\times 10^3$ for H) and equivalent isotropic thermal parameters (Å$^2 \times 10^3$) in structure I

Atom	*x*	*y*	*z*	*U*
Ti(1)	310(1)	1170(1)	5966(1)	18(1)
Cl(1)	−1148(2)	2755(2)	5921(1)	30(1)
Si(1)	3778(2)	1532(2)	7505(1)	22(1)
Si(2)	1403(2)	2655(2)	8620(1)	26(1)
Si(3)	1931(2)	2588(2)	3892(1)	21(1)
N(1)	1864(5)	1726(5)	7369(3)	20(1)
N(2)	975(4)	988(4)	4528(3)	18(1)
C(1)	4231(7)	874(8)	6089(5)	34(2)
C(2)	5385(7)	3488(8)	8126(6)	37(2)
C(3)	3977(8)	83(8)	8405(6)	38(3)
C(4)	3555(7)	2220(7)	3197(5)	29(2)
C(5)	391(7)	2836(7)	2800(5)	31(2)
C(6)	2812(7)	4386(7)	5052(5)	30(2)
C(7)	2452(9)	2398(9)	10000(5)	40(3)
C(8)	1965(9)	4792(8)	8628(6)	40(3)
C(9)	−790(8)	1750(9)	8673(6)	40(3)
H(11)	524(8)	81(7)	626(5)	40(20)
H(12)	338(9)	−43(9)	561(7)	80(20)
H(13)	428(8)	137(8)	556(6)	40(20)
H(21)	638(8)	320(8)	818(6)	50(20)
H(22)	529(8)	386(8)	892(6)	50(20)
H(23)	521(9)	419(10)	769(7)	70(30)
H(31)	497(10)	2(9)	851(6)	60(20)
H(32)	323(9)	−99(9)	795(6)	50(20)
H(33)	382(13)	24(13)	915(10)	120(40)
H(41)	435(8)	202(8)	371(6)	40(20)
H(42)	390(8)	297(9)	270(6)	60(20)
H(43)	327(8)	135(9)	270(6)	50(20)
H(51)	−28(8)	303(7)	328(6)	40(20)
H(52)	93(8)	374(8)	250(5)	40(20)
H(53)	−13(8)	199(8)	216(6)	40(20)
H(61)	206(8)	465(7)	534(5)	40(20)
H(62)	344(7)	414(7)	557(5)	30(20)
H(63)	334(8)	523(8)	474(6)	50(20)
H(71)	208(7)	143(8)	1006(5)	30(20)
H(72)	371(11)	279(10)	1015(7)	80(30)
H(73)	234(9)	305(9)	1065(6)	60(20)
H(81)	175(9)	516(8)	926(6)	50(20)
H(82)	139(8)	501(8)	798(6)	50(20)
H(83)	293(11)	523(10)	863(8)	80(30)
H(91)	−106(10)	219(10)	939(8)	90(30)
H(92)	−163(9)	190(9)	803(7)	60(20)
H(93)	−88(10)	76(10)	881(7)	80(30)

2.2. *X-Ray structural study of I and II*

Crystals of **I** and **II**, suitable for X-ray diffraction experiments, were transferred under argon into pyrex capillaries, which were then sealed *in vacuo*.

Yellow-green crystals of **I** are triclinic, at 150 K $a = 8.944(7)$, $b = 9.198(7)$, $c = 11.876(8)$ Å, $\alpha = 98.10(6)$, $\beta = 97.26(6)$, $\gamma = 109.09(6)°$, $V = 898(3)$ Å^3, $D_x = 1.224$ g cm^{-3}, $Z = 1$ ($C_{18}H_{54}N_4Si_6Ti_6Cl_2$), space group $P\bar{1}$, the molecule is in a special position (1). Unit cell parameters and intensities of 3706 reflections were measured with a Syntex $P2_1$ diffractometer (λ(Mo Kα), graphite monochromator, θ–2θ scan, $2\theta_{max} = 52°$). The structure was solved by direct methods and non-hydrogen atoms were refined by the full-matrix anisotropic least-squares technique. H atoms were localized in the difference Fourier map and refined isotropically. The final were calculated $R = 0.053$, $R_w = 0.062$ for 2765 reflections with $I > 3\sigma(I)$.

Red crystals of **II** are monoclinic, at 150 K $a = 11.579(3)$, $b = 32.764(7)$, $c = 11.596(3)$ Å, $\beta = 115.41(2)°$, $V = 3974(3)$ Å^3, $D_x = 1.168$ g cm^{-3}, $Z = 4$ ($C_{20}H_{61}N_5Si_7Ti_2Cl$), space group $P2_1/c$. Unit cell parameters and intensities of 3706 reflections were measured with a Syntex $P2_1$ diffractometer (λ(Mo Kα), graphite monochromator, θ–2θ scan, $2\theta_{max} = 52°$). The structure was solved by direct methods and refined by full-matrix least-squares anisotropically for non-hydrogen atoms and isotropically for all H atoms localized in the difference map. The final $R = 0.041$, $R_w = 0.041$ were calculated for 5382 reflections with $I > 3\sigma(I)$.

All calculations were carried out with an IBM PC/AT computer using the SHELXTL programs [9]. Atomic coordinates are given in Tables 1 and 2.

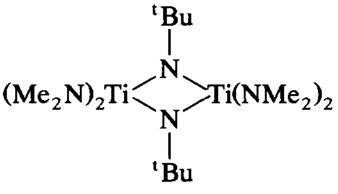
3. Discussion

The synthesis of **I** and **II** can be described by the scheme

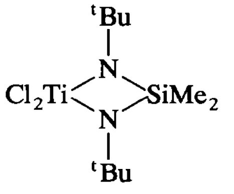
$$TiCl_4 + LiN(SiMe_3)_2 \xrightarrow[hexane]{THF} I + II + Me_3SiCl + LiCl \qquad (1)$$

Me_3SiCl interacts further with an excess of $LiN(SiMe_3)_2$ producing $(Me_3Si)_3N$. The above scheme is confirmed by [3–5], which show that on formation of 4-membered heteronuclear cycles similar to **I**, elimination of Me_3SiCl takes place, being faster in more polar media or in the presence of electron-donating molecules. Our results show that a comparatively low yield of $[(Me_3Si)_2N]_3TiCl$ (19%) in [2] is probably due to secondary (in the synthesis of this compound) cyclization processes, which in our case have led to the identification of compounds **I** and **II** in the present study.

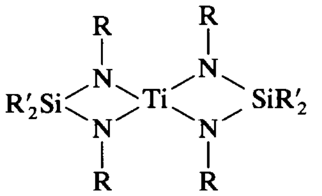
The general view of molecules **I** and **II** is presented in Figs. 1 and 2. Bond lengths and angles are listed in Tables 3 and 4. Structures of several tetra-coordinated Ti^{IV} complexes, structurally similar to **I** and **II**, are known. In comparing the geometrical parameters, $[(Me_3Si)_2N]_3TiCl$ (**III**) [5], the corresponding Me derivative $[(Me_3Si)_2N]_3TiMe$ (**IV**) [10] and complexes **V**–**VIII** [6,11–13] involving TiN_2Ti and TiN_2Si cycles represent the most interesting compounds.



(V)



(VI)

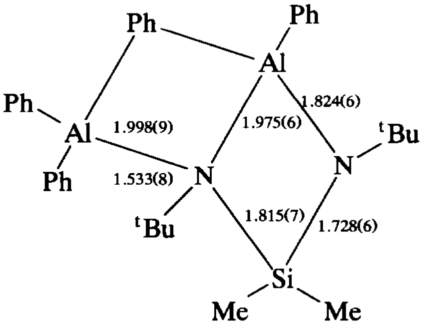


VII: $R = SiMe_3$, $R' = Ph$
VIII: $R = {}^tBu$, $R' = Me$

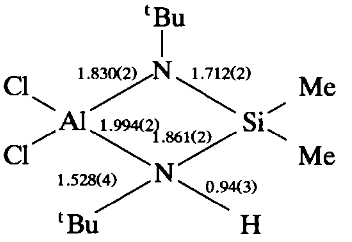
In all the structures considered, these cycles are planar or almost planar (within *ca.* ±0.05 Å) with close to square form (deviations of the endocyclic angles from 90° are within ±6°). The heterocycles of molecules **I** and **II** have the same form; moreover in **I** the central cycle is ideally planar (centrosymmetrical), but in **II** a slight non-planarity (±0.01 Å) of the Ti(2)N(4)Si(1)N(1) cycle and more pronounced non-planarity (±0.06 Å) of the Ti(1)N(1)Ti(2)N(2) cycle are observed. The Ti–N(sp^2) bond lengths in the structures considered are, as a rule, in the range 1.88–1.92 Å. The considerably shorter bond length of 1.829(5) Å in **VI** is evidently due to the influence of two electronegative Cl substituents at the Ti atom. The corresponding bond lengths in **III** (1.94(1) Å) and **IV** (1.935(7) Å) are only slightly out of the range mentioned, if rather significant standard deviations are taken into account (some influence in this respect can be also attributed to the non-cyclic character of the structures). The lengths of exo- and endo-cyclic Ti–N(sp^2) bonds are very similar, which testifies to a relatively low strain of the cycles. The Si–N(sp^2) bonds are in the range of approximately the same width of 1.74–1.78 Å, characteristic for this type of bond [14].

The geometric parameters of molecule **I** fully correspond with those indicated above. The observed deviations of the bond lengths in the bicyclic frame of complex **II** from "standard" values are evidently caused by the presence of a tetra-coordinated bridging nitrogen atom N(1). The N(1)–Ti(1) (2.034(3) Å) and N(1)–Ti(2) (2.018(4) Å) bond distances in **II**, which are close to the sum of the Ti and N covalent radii of 2.0 Å [15], prove these bonds to be ordinary, contrary to the usually increased bond orders of the Ti^{IV}–N(sp^2) [16], *e.g.* observed in **I**. However, even for the N(sp^2) atom, the N(1)–Si(1) bond (1.890(4) Å) is remarkably long.

As mentioned above, complexes of Ti and its analogs (related to **II**) have not been known previously, but for other metals, similar structures are described (*cf. e.g.* [17] and other publications by the same authors). It is interesting to compare bond lengths in the bicycle **II** and two alumasilazanes **IX** and **X** [18]. The first compound has a bicyclic structure quite similar to **II** and the second involves the bridging tetra-coordinated N atom with an H "substituent".



(IX)



(X)

In molecule **IX**, the Si–N(sp^3) and Si–N(sp^2) bond lengths are typical not only for similar aluminium compounds [19] but also for other organometallic compounds [17]. On the contrary, in molecule **X** the Si–N(sp^3) bond length is increased and approaches the analagous value in **II**, which is hardly accidental. Doubtless, in this case, the presence of an H substituent is essential, as the N(sp^3)–C and N(sp^3)–Al distances in molecules **IX** and **X** are equal. It is probably the same reason that causes the enormous N(1)–Si(1) bond elongation in **II**.

TABLE 2. Atomic coordinates ($\times 10^4$ for C, N; $\times 10^5$ for Ti, Cl, Si; $\times 10^3$ for H) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) in structure **II**

Atom	*x*	*y*	*z*	*U*
Ti(1)	1206(5)	38332(2)	32300(5)	21(1)
Ti(2)	27964(5)	38873(2)	49020(5)	19(1)
Cl(1)	−15318(9)	41646(3)	33683(10)	39(1)
Si(1)	18254(9)	37502(3)	65432(9)	25(1)
Si(2)	12665(10)	46921(4)	28996(10)	30(1)
Si(3)	42089(10)	43006(4)	79455(9)	33(1)
Si(4)	−14920(10)	30787(4)	18881(9)	31(1)
Si(5)	1302(10)	34352(4)	6498(10)	36(1)
Si(6)	43909(10)	30420(3)	49295(10)	29(1)
Si(7)	51814(9)	38821(4)	44536(9)	29(1)
N(1)	1324(3)	3550(1)	4867(3)	36(1)
N(2)	1467(3)	4181(1)	3424(3)	23(1)
N(3)	−395(3)	3447(1)	1861(3)	25(1)
N(4)	3102(3)	4053(1)	6602(3)	26(1)
N(5)	4093(3)	3563(1)	4697(3)	23(1)
C(1)	587(5)	4057(2)	6772(5)	47(2)
C(2)	2311(6)	3309(2)	7656(5)	43(2)
C(3)	−413(5)	4818(2)	1742(6)	56(2)
C(4)	2310(6)	4822(2)	2089(6)	51(2)
C(6)	3879(9)	4205(3)	9362(5)	73(3)
C(7)	5847(5)	4102(2)	8353(5)	53(2)
C(8)	4195(6)	4859(2)	7693(5)	48(2)
C(9)	−3146(5)	3202(2)	707(6)	60(3)
C(10)	−1050(8)	2555(2)	1618(7)	60(3)
C(11)	−1546(5)	3058(2)	3477(5)	45(2)
C(12)	−1119(7)	3244(2)	−888(5)	69(3)
C(13)	634(14)	3925(4)	325(9)	126(6)
C(14)	1543(12)	3092(7)	1148(9)	193(9)
C(15)	2956(6)	2725(2)	4648(7)	50(3)
C(16)	5062(6)	2837(2)	3833(5)	47(2)
C(17)	5552(5)	2943(2)	6617(5)	42(2)
C(18)	4905(4)	4410(2)	4891(5)	38(2)
C(19)	4930(6)	3884(2)	2754(5)	52(2)
C(20)	6889(4)	3764(2)	5511(5)	41(2)
H(1)	126(4)	318(2)	482(4)	40(10)
H(11)	34(5)	427(2)	612(5)	70(20)
H(12)	98(5)	414(2)	756(5)	60(20)
H(13)	−4(6)	388(2)	661(6)	80(20)
H(21)	167(5)	312(2)	748(5)	50(20)
H(22)	265(5)	338(2)	855(6)	70(20)
H(23)	287(5)	318(2)	762(5)	50(20)
H(31)	−100(6)	488(2)	207(6)	90(20)
H(32)	−71(6)	459(2)	112(6)	70(20)
H(33)	−41(5)	509(2)	137(6)	70(20)
H(41)	211(7)	506(3)	188(8)	120(30)
H(42)	323(7)	482(2)	264(6)	100(20)
H(43)	224(6)	466(2)	156(6)	90(30)
H(51)	164(5)	527(2)	412(5)	60(20)
H(52)	122(5)	499(2)	464(5)	50(20)
H(53)	257(6)	498(2)	499(6)	70(20)
H(61)	450(5)	435(2)	1003(5)	60(20)
H(62)	320(5)	434(2)	925(5)	60(20)
H(63)	392(7)	390(3)	949(7)	110(30)
H(71)	646(6)	421(2)	914(6)	80(20)
H(72)	585(6)	380(3)	835(7)	110(30)
H(73)	614(7)	420(2)	783(7)	110(30)
H(81)	477(5)	497(2)	842(6)	70(20)
H(82)	337(5)	498(2)	748(5)	60(10)
H(83)	441(5)	493(2)	704(6)	80(20)
H(91)	−370(5)	300(2)	84(5)	70(20)
H(92)	−325(6)	320(2)	−15(6)	80(20)
H(93)	−342(6)	349(2)	85(6)	100(20)
H(101)	−165(6)	235(2)	160(6)	90(20)
H(102)	−29(6)	249(2)	225(6)	70(20)
H(103)	−90(7)	252(2)	93(7)	120(30)
H(111)	−174(4)	333(2)	373(4)	40(10)
H(112)	−76(5)	296(2)	413(5)	60(20)
H(113)	−217(5)	285(2)	349(4)	50(10)
H(121)	−133(6)	295(2)	−83(6)	80(20)
H(122)	−69(7)	321(3)	−138(8)	120(30)
H(123)	−201(11)	343(4)	−78(10)	240(50)
H(131)	−21(6)	406(2)	7(7)	230(20)
H(132)	158(10)	403(4)	125(11)	310(50)
H(133)	27(11)	402(4)	−65(12)	300(50)
H(141)	129(8)	294(2)	91(8)	290(30)
H(142)	215(8)	318(3)	196(9)	130(30)
H(143)	202(12)	324(4)	69(13)	200(60)
H(151)	269(5)	277(2)	532(5)	70(20)
H(152)	237(5)	280(2)	385(5)	50(20)
H(153)	312(6)	251(2)	455(6)	70(20)
H(161)	519(4)	255(2)	401(4)	50(10)
H(162)	580(6)	299(2)	402(5)	60(20)
H(163)	446(5)	290(2)	291(6)	70(20)
H(171)	565(5)	264(2)	679(5)	80(20)
H(172)	532(4)	304(1)	726(5)	60(10)
H(173)	642(6)	310(2)	687(5)	90(20)
H(181)	533(5)	465(2)	466(5)	70(20)
H(182)	527(5)	445(2)	577(5)	50(10)
H(183)	407(6)	452(2)	458(6)	80(20)
H(191)	553(5)	408(2)	263(5)	60(10)
H(192)	511(6)	363(2)	262(6)	80(20)
H(193)	410(7)	397(2)	225(7)	110(20)
H(201)	709(4)	380(1)	651(4)	30(10)
H(202)	743(5)	397(2)	524(5)	60(20)
H(203)	708(4)	353(2)	534(4)	40(10)

The principal distinction between complex **II** and alumasilazanes **IX** and **X** consists of the presence of an unpaired electron in molecule **II** due to a tetra-coordination of the N(1) atom. In favour of the assumption that molecule **II** is a stable radical is the intense red colour of its crystals, however ESR and NMR data do

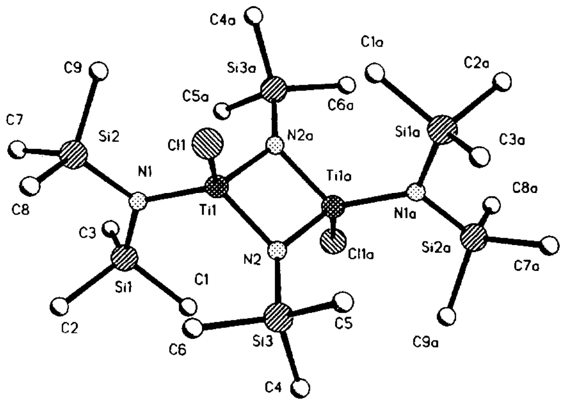


Fig. 1. General view of molecule I. H atoms are not shown.

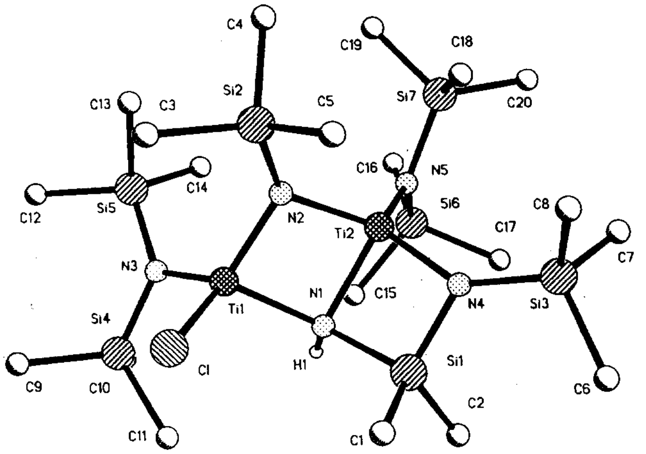


Fig. 2. General view of molecule II. H atoms are not shown (except H(1)).

not confirm such a proposal. Possibly, the efficiency of these spectral methods is influenced in this case by strong spin delocalization. Similar complexes are in general characterized by a complex stereoelectronic structure, *e.g.* in molecule **IX**, the fifth electron of the N(sp^3) atom is delocalized at least over two virtually identical N–Al bonds. A partial electron delocalization causes a strong influence of intramolecular interactions on the electron density distribution in metal–N(sp^2)–metal bridges [11]. Therefore, a sharp alternation of the Ti(1)–N(2) (1.866(3) Å) and N(2)–Ti(2) (1.993(3) Å) bond lengths observed in the bicycle **II** is not surprising as the Ti atoms have a different valent environment. Apparently, the non-equivalence of N(2)–Ti bonds results in a significant pyramidality of the N(2) atom coordination (its displacement out of the plane of bonded atoms reaches 0.25 Å). It is not excluded that the main reason for symmetry distortion of the Ti(1)N(2)Ti(2) bridge is the Cl substituent at the Ti(1) atom. Indeed, all Ti(2)–N(sp^2) bond lengths exceed the corresponding values for Ti(1), which can be caused by a smaller positive charge of Ti(2). However, some contribution to the elongation of the Ti(2) bonds can be provided by a significant deformation of its tetrahedral coordination towards a trigonal pyramid: the Ti(2) displacement out of the N(2)N(4)N(5) plane is only 0.18 Å (in the ideal tetrahedron 0.65 Å). This deformation is compulsory and is determined by the dihedral angle (121°) between the planes of the cycles, which is typical for similar bicyclic systems. The inherent molecular steric hindrances in **II** are not great because of the absence of short non-bonded contacts between atoms surrounding the bicyclic system, which is also emphasized by intense thermal vibrations of Me substituents at the Si(5) atom (Table 2).

TABLE 3. Relevant bond lengths (Å) in structures I and II

Structure I			
Ti(1)–Cl(1)	2.254(2)	Ti(1)–N(2a)	1.901(4)
Ti(1)–N(1)	1.918(4)	Si(1)–N(1)	1.768(5)
Ti(1)–N(2)	1.882(4)	Si(2)–N(1)	1.770(4)
		Si(3)–N(2)	1.767(4)
Structure II			
Ti(1)–Cl(1)	2.265(1)	Si(1)–N(1)	1.890(4)
Ti(1)–N(1)	2.034(3)	Si(1)–N(4)	1.756(4)
Ti(1)–N(2)	1.866(3)	Si(2)–N(2)	1.761(3)
Ti(1)–N(3)	1.914(3)	Si(3)–N(4)	1.737(3)
Ti(2)–N(1)	2.018(4)	Si(4)–N(3)	1.762(4)
Ti(2)–N(2)	1.993(3)	Si(5)–N(3)	1.754(4)
Ti(2)–N(4)	1.925(3)	Si(6)–N(5)	1.739(3)
Ti(2)–N(5)	1.936(3)	Si(7)–N(5)	1.751(4)

TABLE 4. Relevant bond angles (°) in structures I and II

Structure I			
Cl(1)Ti(1)N(1)	112.5(1)	Ti(1)N(1)Si(1)	126.0(2)
Cl(1)Ti(1)N(2)	106.6(2)	Ti(1)N(1)Si(2)	116.9(3)
Cl(1)Ti(1)N(2a)	112.8(1)	Si(1)N(1)Si(2)	116.9(2)
N(1)Ti(1)N(2)	119.8(2)	Ti(1)N(2)Si(3)	124.6(2)
N(1)Ti(1)N(2a)	116.8(2)	Ti(1)N(2)Ti(1a)	94.5(2)
N(2)Ti(1)N(2a)	85.5(2)	Si(3)N(2)Ti(1a)	137.8(2)
Structure II			
Cl(1)Ti(1)N(1)	114.4(1)	C(1)Si(1)C(2)	110.2(3)
Cl(1)Ti(1)N(2)	112.7(1)	Ti(1)N(1)Ti(2)	90.2(2)
Cl(1)Ti(1)N(3)	113.8(1)	Ti(1)N(1)Si(1)	125.9(2)
N(1)Ti(1)N(2)	87.9(1)	Ti(2)N(1)Si(1)	84.6(1)
N(1)Ti(1)N(3)	108.5(1)	Ti(1)N(2)Ti(2)	96.0(1)
N(2)Ti(1)N(3)	116.8(2)	Ti(1)N(2)Si(2)	124.0(2)
N(1)Ti(2)N(2)	85.0(1)	Ti(2)N(2)Si(2)	134.0(1)
N(1)Ti(2)N(4)	87.5(1)	Ti(1)N(3)Si(4)	114.1(2)
N(1)Ti(2)N(5)	113.0(1)	Ti(1)N(3)Si(5)	125.9(2)
N(2)Ti(2)N(4)	118.7(1)	Si(4)N(3)Si(5)	120.0(2)
N(2)Ti(2)N(5)	120.9(1)	Ti(2)N(4)Si(1)	91.2(1)
N(4)Ti(2)N(5)	117.9(1)	Ti(2)N(4)Si(3)	142.3(2)
N(1)Si(1)N(4)	96.8(2)	Si(1)N(4)Si(3)	125.7(2)
N(1)Si(1)C(1)	114.7(2)	Ti(2)N(5)Si(6)	129.2(2)
N(1)Si(1)C(2)	108.2(2)	Ti(2)N(5)Si(7)	110.0(2)
N(4)Si(1)C(1)	112.1(2)	Si(6)N(5)Si(7)	120.2(2)
N(4)Si(1)C(2)	114.4(2)		

Certainly, a discussion of the structure of molecule **II**, based mainly on geometrical features cannot be considered conclusive and the relevant quantum chemical calculations are necessary to clear up all fine structural features.

References

1 U. Wannagat, *Pure Appl. Chem., 19* (1969) 329.
2 H. Burger and U. Wannagat, *Monatsh. Chem., 94* (1963) 761.
3 S.K. Vasisht, R. Sharma and V. Goyal, *Ind. J. Chem., A, 24* (1985) 37.
4 N.W. Alcock, M. Pierce-Butler and G.R. Willey, *J. Chem. Soc., Dalton Trans.*, (1976) 707.
5 C. Airoldi, D.C. Bradley, H. Chudzynska, M.B. Hursthouse,

K.M.A. Malik and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1980) 2010.

6 W.D. Beiersdorf, D.J. Brauer and H. Burger, *Z. Anorg. Allg. Chem., 475* (1981) 56.

7 H. Burger and W.D. Beiersdorf, *Z. Anorg. Allg. Chem., 459* (1979) 111.

8 M.V. Ustinov, D.A. Bravo-Zhivotovskii, I.D. Kalkhman, V.Yu. Vitkovskii, N.S. Vyazankin and M.G. Voronkov, *Metalloorg. Khim. (Russian J. Organomet. Chem.), 2* (1989) 343.

9 W. Robinson and G.M. Sheldrick, SHELX, in *Crystallographic Computing-Techniques and New Technologies*, Oxford University Press, Oxford, 1988, 366 pp.

10 D.C. Bradley, H. Chudzynska, J.D.J. Backer-Dirks, M.B. Hursthouse, A.A. Ibrahim, M. Motevalli and A.C. Sullivan, *Polyhedron, 9* (1990) 1423.

11 D.L. Thorn, W.A. Nugent and R.L. Harlow, *J. Am. Chem. Soc., 103* (1981) 357.

12 R.A. Jones, M.H. Seeberger, J.L. Atwood and W.E. Hunter, *J. Organomet. Chem., 247* (1983) 1.

13 D.J. Brauer, H. Burger, E. Essig and W. Geschwandtner, *J. Organomet. Chem., 190* (1980) 343.

14 E.Ya. Lukevits, O.A. Pudova and R.Ya. Sturkovich, *Molekulyarnaya struktura kremniiorganicheskikh soyedinenii*, Zinatne, Riga, 1988.

15 S.S. Batsanov, *Eksperimentalnye osnovy strukturnoi khimii*, Standarty, Moscow, 1986.

16 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc., 105* (1983) 7295.

17 M. Veith, W. Frank, F. Tollner and H. Lange, *J. Organomet. Chem., 326* (1987) 315.

18 M. Veith, H. Lange, O. Recktenwald and W. Frank, *J. Organomet. Chem., 294* (1985) 273.

19 T. Blumental, U. Wannagat, D.J. Brauer and H. Burger, *Monatsh. Chem., 114* (1983) 1271.