1,2-Bis(trimethylsilyl)hydrazido Titanium Complexes

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The silylhydrazido titanium complexes $[Cl_2Ti\{N_2H(SiMe_3)_2\}_2]$ (**1**), $[ClTi\{N_2H(SiMe_3)_2\}_3]$ (**2**), and $[(Cl_2Ti)_2\{N_2(SiMe_3)\}_2]$ (**3**) have been synthesized by reactions of the appropriate (trimethylsilyl)hydrazines with $TiCl_4$ in solution. The reactions are driven by the elimination of Me_3SiCl or LiCl after the dilithiation of bis(trimethylsilyl)hydrazine. According to NMR, mass spectrometry, and X-ray structure determination, products **1** and **2** are formed by the reaction of one equivalent of $TiCl_4$ with two or three equivalents of hydrazine, whereas compound **3** results from the reaction of two equivalents of $TiCl_4$ with two equivalents of hydrazine. According to the results of single-crystal X-ray diffraction investigations, complexes **1** and **3** feature an η^2-coordination of the hydrazido moiety to the titanium. In the crystals of **3**, both a chair and a twist form of the six-membered TiN_2TiN_2 rings are found, corresponding to different donor coordination modes of the hydrazido ligands to titanium. Temperature-dependent ^{29}Si NMR investigations indicate that both coordination modes co-exist in solution at low temperatures, but not at room temperature.

Introduction

In the context of the search for molecules with nitrido bridges between main group elements and transition metals, we have investigated the reactions of silazanes with various metal chlorides.[1−3] The obtained compounds have been studied with regard to their applicability as molecular precursors for the synthesis of solid-state materials of the M/Si/N system. A highly desirable property of these precursor compounds would be an ability to maintain either particular structural elements or a specific Si:M molar ratio during the transformation from the molecule to the solid-state compound. This approach has been elegantly applied for the synthesis of the nitride $SiPN_3$ starting from molecular $Cl_3SiNPCl_3$.[4]

Recently, we have extended our studies to titanium complexes of silylhydrazines. In this area, Leigh et al. have previously reported the crystal structures of the hydrazido titanium complexes $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NHNMe_2)TiCl_2]$ and $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NPhNH_2)TiCl_2]$ and have collected analytical data pertaining to some other titanium complexes with both cyclopentadienyl and hydrazido ligands.[5] Recently, Park et al. synthesized further cyclopentadienyl-substituted hydrazido titanium complexes with the aim of generating new Ziegler−Natta catalysts.[6]

A further class of titanium complexes has been described by Winter et al. and by Mösch-Zanetti et al. Their complexes bear η^2-pyrazolato ligands rather than hydrazido ligands and no cyclopentadienyl ligands are used to stabilize them.[7,8]

We report herein on the synthesis and characterization of novel bis(trimethylsilyl)hydrazido titanium complexes without cyclopentadienyl ligands. The silylhydrazido titanium complexes $[Cl_2Ti\{N_2H(SiMe_3)_2\}_2]$ (**1**), $[ClTi\{N_2H(SiMe_3)_2\}_3]$ (**2**), and $[(Cl_2Ti)_2\{N_2(SiMe_3)\}_2]$ (**3**) have been synthesized by reaction of the appropriate silylhydrazines with $TiCl_4$. The products show η^2-coordination of the hydrazido moiety to titanium in the solid state. For **3**, both chair and twist forms of the six-membered TiN_2TiN_2 ring have been found in the solid state, corresponding to different donor coordination modes of the hydrazido ligands to titanium.

Results and Discussion

The general synthetic approach for trimethylsilyl hydrazines is well established and some preparative methods for titanium complexes with alkyl-substituted hydrazido ligands have been described in the literature.[5,9] In order to avoid the formation of complexes with organic substituents at the metal center, we used $TiCl_4$ as the starting material. However, in several cases, we observed reduction of $TiCl_4$ by the trimethylsilylhydrazines as an unwanted side reaction. The undefined Ti^{III} species thus produced, which were deposited as green or brown precipitates, were not characterized further. Similar observations have been reported by Cotton et al., who recovered $[Ti_2Cl_9]^{3-}$ and $[Ti_3Cl_{12}]^{3-}$ from analogous precipitates.[10] In our investigations, the amorphous precipitates were carefully separated from the reaction mixtures in order to isolate the titanium hydrazido complexes without their decomposition.

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Scheme 1. Synthesis of **1**

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[+] Crystal structure analysis

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Reaction of $TiCl_4$ with two equivalents of 1,1,2-tris(trimethylsilyl)hydrazine, followed by elimination of two equivalents of Me_3SiCl, yielded the hydrazido titanium dichloride **1** (Scheme 1).

The elimination of Me_3SiCl could be qualitatively observed by ^{29}Si NMR spectroscopic monitoring of the reaction mixture. After the green Ti^{III} precipitate had been removed, **1** was isolated from the solution by crystallization at 0 °C. Once isolated, the crystals proved to be stable for several weeks, even at room temperature. It would seem that no intramolecular elimination of HCl or Me_3SiCl occurs, despite the fact that the relevant substituents are in close proximity in the molecule (Figure 1).

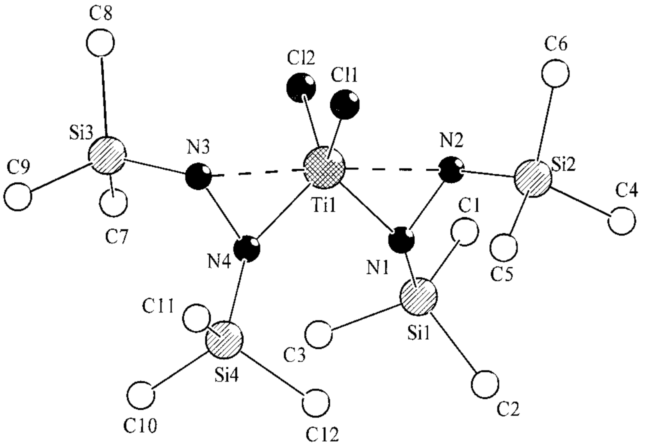


Figure 1. DIAMOND plot of the molecular structure of $Cl_2Ti[N_2H(SiMe_3)_2]_2$ (**1**)[11]

The X-ray crystal structure of **1** reveals the presence of two three-membered rings (Ti1−N1−N2 and Ti1−N4−N3) with N−N distances of 145 pm. In both cases, only one N atom (N1/N4) is actually bound to the titanium. Consequently, these N−Ti distances amount to just 189 pm, whereas the donor-coordinated N2/N3−Ti distances are about 215 pm. The corresponding bond angles are 60° at N2/N3 and 79° at N1/N4. The smallest angles are N1−Ti1−N2 and N3−Ti−N4, which measure 41° (Table 1).

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra confirm the molecular structure of **1**. The ^{29}Si NMR spectrum shows two characteristic signals at $\delta = 10.15$ and 23.03. The signal at $\delta = 10.15$ can be attributed to the Si attached to the covalently bound N atom, whereas that Si bound to the NH group gives rise to a ^{29}Si NMR signal further downfield at $\delta = 23.03$ (assigned by ^{1}H-coupled ^{29}Si NMR spectroscopy).

The mass spectrum clearly shows the molecular ion at $m/z = 468$. Mass spectrometry also revealed traces of a more volatile by-product, greater amounts of which could be generated from complex **1** and 1,1,2-tris(trimethylsilyl)hydrazine by Me_3SiCl elimination (Scheme 2). The reaction is very slow and its progress, including the elimination of Me_3SiCl, can be followed by NMR spectroscopy.

^{1}H, ^{13}C, and ^{29}Si NMR investigations unequivocally showed that **1** is completely transformed to **2** upon further reaction with the hydrazine. The ^{29}Si NMR spectrum of **2** features two signals at $\delta = 7.86$ and 13.78. The signal at $\delta = 7.86$ can be assigned to the silyl group attached to the covalently bound N atom by ^{1}H-coupled ^{29}Si NMR spectroscopy.

In the mass spectrum, the molecular ion of **2** ($m/z = 608$) could not be detected, but the fragmentation was nevertheless in accordance with the assumed composition. The calculated mass distributions of the ions at $m/z = 463$ and $m/z = 389$ correspond to the loss of two and three $SiMe_3$ groups, respectively. Unfortunately, **2** could not be obtained in crystalline form.

As known from the literature, the dilithiation of 1,1- and 1,2-substituted bis(trimethylsilyl)hydrazines invariably gives 1,2-substituted products.[12−14] Thus, after lithiation of a mixture of the bis(trimethylsilyl)hydrazines followed by treatment with $TiCl_4$, a titanium complex **3** with 1,2-substituted hydrazido ligands was obtained (Scheme 3).

In this reaction, a binuclear titanium complex is formed, in which the two N atoms of the hydrazido ligands are each bound to different Ti atoms. The X-ray crystal structure reveals that each covalently-bound N atom (e.g. N1) at one Ti atom (e.g. Ti2) is also involved in donor coordination to the other Ti atom (e.g. Ti1).

The X-ray crystal structure of **3** (Figure 2) also reveals that there are two different conformers **3a** and **3b** in the unit cell, which are present in a 1:2 molar ratio. Both of these are derived from the same six-membered ring system **3**, as shown in Scheme 3. The two conformers have the same composition and connectivity, but a different donor coordination of the N atoms to the Ti atoms (Scheme 4).

In the major conformer **3b**, both N atoms at Ti1 (N2 and N3) are involved in donor coordination to Ti2 on different sides of the ring, resulting in a twisted molecule with a twofold axis passing through Ti1 and Ti2. The second conformer **3a** has an inversion center and the N atoms coordinate on the same side of the six-membered ring with a parallel orientation of the hydrazido ligands, thereby leading to a chair conformation.

In both conformers, the Ti−Ti distances are very similar (271.7 and 271.8 pm). In both molecules, four TiN_2 three-membered rings with a covalent Ti−N bond measuring 194−198 pm and a weaker Ti−N donor bond measuring 214−228 pm are found.

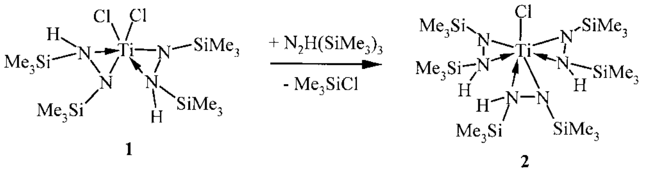
The N−N bond lengths are 136 pm in **3a** and 138 pm in **3b**. The corresponding bonding angles at titanium are about 38° in both conformers. The Ti−N−N bonding angles at the donor-coordinated N atom are about 58−63°, while the angles at the N atom closer to Ti are in the range 77−85°.

The two conformers have comparable angles and distances in their TiN_2 rings and can thus be expected to be very similar in energy. A comparison of the coordination modes of the silylhydrazines to the titanium atoms in **1**, **3a**, and **3b** likewise reveals no significant differences (Table 1).

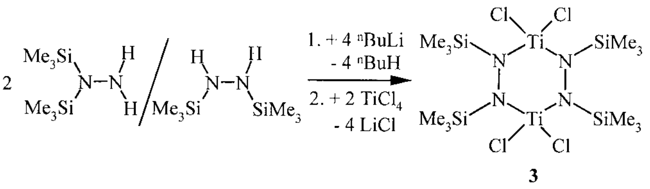
A comparison of the structural parameters of the Ti−N−N three-membered rings in complexes **1**, **3a**, and **3b** with those of similar structural units in hydrazido titanium complexes reported in the literature[5,6] again reveals that the bond lengths and angles are all very similar, making this a characteristic structural feature.

Table 1. Selected distances [pm] and angles [°] of **1**, **3a**, and **3b**; ESDs in parentheses

	1	**3a** (chair)	**3b** (twist form)
Ti−Ti	–	271.81(17), Ti3−Ti3A	271.72(11), Ti1−Ti2
N−N	146.1(5), N1−N2 145.7(6), N3−N4	136.3(5), N5−N6	138.2(5), N1−N2 137.7(5), N3−N4
N−Ti (covalent bond)	189.3(4), N1−Ti1 188.0(4), N4−Ti1	197.3(4), N5−Ti3 196.5(4), N6−Ti3A	193.6(4), N1−Ti2 194.8(4), N2−Ti1 197.9(4), N3−Ti1 198.2(4), N4−Ti2
N−Ti (donor bond)	214.0(4), N2−Ti1 215.9(5), N3−Ti1	222.0(4), N6−Ti3 219.4(5), N5−Ti3A	227.3(4), N1−Ti1 228.2(4), N2−Ti2 219.2(4), N3−Ti2 214.0(4), N4−Ti1
N−Ti−N	41.90(15), N1−Ti1−N2 41.26(16), N3−Ti1−N4	37.35(14), N5−Ti3−N6	37.25(13), N1−Ti1−N2 37.14(13), N1−Ti2−N2 38.81(13), N3−Ti1−N4 38.12(13), N3−Ti2−N4
Ti−N (covalent bond)−N	78.1, N2−N1−Ti1 79.8, N3−N4−Ti1	81.2(3), N6−N5−Ti3 80.3(3), N5−N6−Ti3A	85.1(2), N2−N1−Ti2 84.2(2), N1−N2−Ti1 76.9(2), N4−N3−Ti1 79.2(2), N3−N4−Ti2
Ti−N (donor bond)−N	60.0(2), N1−N2−Ti1 59.0(2), N4−N3−Ti1	62.0(2), N6−N5−Ti3A 61.4(2), N5−N6−Ti3	58.5(2), N2−N1−Ti1 57.7(2), N1−N2−Ti2 62.7(2), N4−N3−Ti2 64.3(2), N3−N4−Ti1



Scheme 2. Synthesis of **2**



Scheme 3. Synthesis of **3**

At room temperature, the ^{29}Si NMR spectrum of **3** features only one signal at $\delta = 24.87$. Low-temperature measurements in CD_2Cl_2 were then performed in order to ascertain whether the two conformations **3a** and **3b** co-exist in solution or only in the solid state (Figure 3).

The variable-temperature ^{29}Si NMR spectra confirm the existence of a six-membered ring without N donor coordination at room temperature. On lowering the temperature, increasing amounts of the two conformers **3a** and **3b** are formed in the solution. Two new signals appear in the spectra, downfield shifted by about 4 and 7 ppm. This downfield shift is due to the withdrawal of electron density from the N and Si atoms as a result of the donor coordination of the N atoms to the titanium. Spectral measurements in non-polar [D$_8$]toluene gave the same results, hence the formation of a donor complex with the solvent can be excluded. Low-temperature ^{1}H NMR spectra did not give useful results for further interpretation because the shift dif-

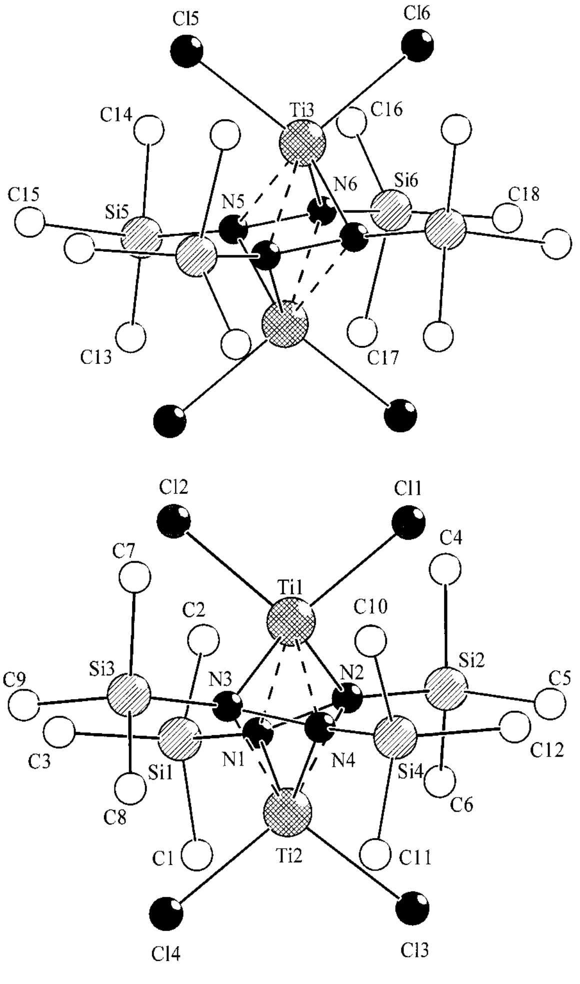
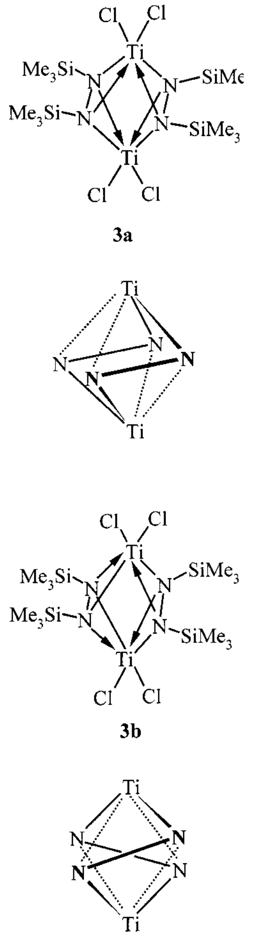


Figure 2. DIAMOND plot of the molecular structure of $(Cl_2Ti)_2[N_2(SiMe_3)]_2$ (**3a/3b**)[11]



3a

3b

Scheme 4. The two conformers **3a** and **3b** are found to be present in the solid

ferences of the trimethylsilyl protons in the spectra at different temperatures were too small.

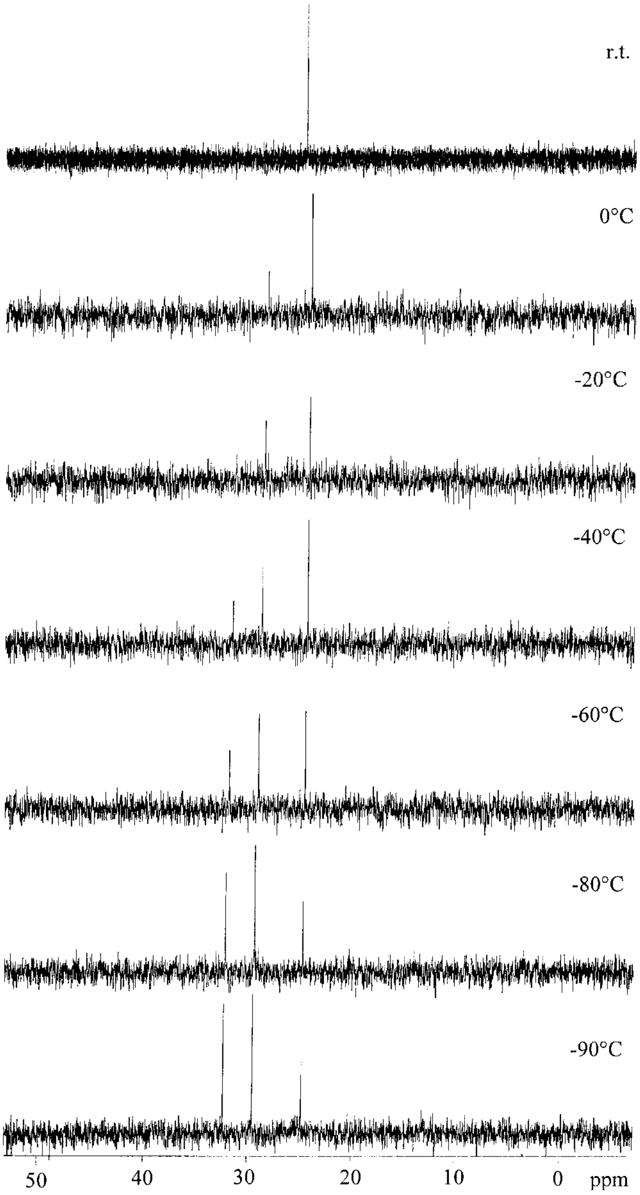


Figure 3. ^{29}Si NMR spectra of **3** at different temperatures

Conclusion

As a common structural feature, all 1,2-bis(trimethylsilyl)hydrazido titanium complexes described in this paper have a Ti−N−Si bridge with an η^2-coordinated N−N moiety at titanium. The X-ray crystal structure of **1** reveals N atoms that are either covalently bound to Ti or coordinated to Ti through a weaker donor bond. For the two conformers of **3**, N atoms with both a covalent and a donor bond to Ti are found in the solid state. These examples show that the synthesis of a variety of related transition metal hydrazides should be possible.

Experimental Section

General Remarks: All reactions were performed under an atmosphere of dry argon. The solvents were dried by standard methods. All glassware was heated to 100 °C, evacuated, and filled with dry argon several times prior to use. NMR spectra were recorded on Jeol GSX-270 and EX-400 spectrometers at 20 °C. Chemical shifts were determined by reference to the solvent resonances as internal standards. ^{29}Si NMR spectra were measured using the INEPT pulse sequence (TMS as external standard). Mass spectra (MS) were recorded on a Finnigan MAT spectrometer.

Elemental analysis was attempted, but due to the extreme sensitivity of the compounds the values obtained for **1** deviate from the expected composition. Likewise, it proved impossible to obtain reliable results for **2** and **3**.

Bis[*N*,*N'*-bis(trimethylsilyl)hydrazido]titanium Dichloride, $Cl_2Ti[N_2H(SiMe_3)_2]_2$ (1): 1,1,2-Tris(trimethylsilyl)hydrazine (0.70 g, 2.82 mmol) was dissolved in *n*-pentane (100 mL) at room temp. The resulting solution was cooled to −40 °C, whereupon $TiCl_4$ (0.84 mL, 0.77 mmol) was added dropwise. A green precipitate formed and the mixture was stirred at −10 °C for 2 h. The precipitate was then removed from the yellow solution by filtration and the filtrate was concentrated under reduced pressure at 0 °C. Yellowish crystals were obtained, which were recrystallized from *n*-pentane at 0 °C. The product proved to be stable under argon atmosphere at room temp. for several weeks. Yield: 0.32 g (89%). − ^{1}H NMR ($CDCl_3$): δ = 0.23 [s, 18 H, NSi(CH_3)$_3$], 0.42 [s, 18 H, NHSi($C\mathit{H}_3$)$_3$], 4.19 [s, 2 H, N*H*Si(CH_3)$_3$]. − ^{13}C NMR ($CDCl_3$): δ= −0.4 [NSi(CH_3)$_3$], 0.2 [NHSi(CH_3)$_3$]. − ^{29}Si NMR ($CDCl_3$): δ = 10.15 [NSi(CH_3)$_3$], 23.03 [NHSi(CH_3)$_3$] (assigned by ^{1}H-coupled ^{29}Si NMR spectroscopy). − MS (CI, *i*-butane): *m*/*z* (%) = 471 (9), 470 (23), 469 (12), 468 (27) [M$^+$], 455 (5), 453 (5) [M$^+$ − Me], 438 (3) [M$^+$ − 2 Me], 437 (8), 436 (17), 435 (47), 434 (48), 433 (91) [M$^+$ − Cl], 432 (32), 431 (9), 389 (6), 360 (3) [M$^+$ − Cl − SiMe$_3$], 228 (3), 227 (4), 192 (4), 178 (6), 177 (17), 176 (100) [HN$_2$(SiMe$_3$)$_2$ + 1], 175 (23) [HN$_2$(SiMe$_3$)$_2$], 174 (27) [N$_2$(SiMe$_3$)$_2$], 161 (5), 147 (10), 146 (60) [2SiMe$_3$], 132 (5), 130 (10). − $C_{12}H_{38}Cl_2N_4Si_4Ti$: calcd. C 30.69, H 8.16, N 11.93; found C 30.77, H 8.36, N 11.96.

Tris[*N,N'*-tris(trimethylsilyl)hydrazido]titanium Chloride, ClTi-[N$_2$H(SiMe$_3$)$_2$]$_3$ (2): Compound **1** (0.69 g, 1.47 mmol) and 1,1,2-tris(trimethylsilyl)hydrazine (0.75 g, 3.01 mmol) were dissolved in $CHCl_3$ (100 mL) and the mixture was refluxed for at least 16 h. The solvent and the excess tris(trimethylsilyl)hydrazine were then removed under reduced pressure to leave a brown solid. Yield: 0.77 g (86%). − ^{1}H NMR ($CDCl_3$): δ = 0.05 [s, 27 H, NSi($C\mathit{H}_3$)$_3$], 0.11 [s, 27 H, NHSi($C\mathit{H}_3$)$_3$], 1.24 [s, 3 H, N*H*Si(CH_3)$_3$]. − ^{13}C NMR ($CDCl_3$): δ = 1.8 [NSi(CH_3)$_3$], 1.9 [NHSi(CH_3)$_3$]. − ^{29}Si NMR ($CDCl_3$): δ = 7.86 [NSi(CH_3)$_3$], 13.78 [NHSi(CH_3)$_3$] (assigned by ^{1}H-coupled ^{29}Si NMR spectroscopy). − MS (CI, *i*-butane): *m*/*z* (%) = 464 (4), 463 (8) [M$^+$ + 1 − 2Si(Me)$_3$], 392 (9), 391 (30), 390 (40), 389 (100) [M$^+$ − 3SiMe$_3$], 388 (14), 387 (12), 375 (10), 374 (15), 373 (31), 358 (13), 357 (29), 341 (8), 249 (11), 248 (32) [HN$_2$(SiMe$_3$)$_3$], 233 (11), 160 (5), 147 (26), 146 (17) [2 SiMe$_3$], 145 (13), 132 (17), 130 (12).

Bis[*N,N'*-bis(trimethylsilyl)hydrazido]-*N,N'*-bis(titanium dichloride) (Cl$_2$Ti)$_2$[N$_2$(SiMe$_3$)]$_2$ (3): A mixture of 1,1-bis(trimethylsilyl)hydrazine and 1,2-bis(trimethylsilyl)hydrazine (1.39 g, 7.89 mmol) was dissolved in *n*-pentane (80 mL) at room temp. and *n*-butyllithium (9.86 mL, 15.78 mmol, 1.7 M in *n*-pentane) was added dropwise. The colorless solution rapidly became yellow and a white precipitate was deposited. After stirring for 1 h, a solution of $TiCl_4$ (0.87 mL, 7.89 mmol) in *n*-pentane (60 mL) was added dropwise at −40 °C. A green precipitate formed and the mixture was stirred at −20 °C for 2 h. The green solid was then removed from the red solution by filtration and the filtrate was concentrated under reduced pressure. Red crystals were obtained, which proved to be stable under argon atmosphere for several weeks at −20 °C. Yield: 1.64 g (71%). − ^{1}H NMR ($CDCl_3$): δ = 0.50. − ^{13}C NMR ($CDCl_3$): δ = 2.3. − ^{29}Si NMR ($CDCl_3$): δ = 24.87. − MS (CI, *i*-butane): *m*/*z* (%) = 588 (4), 586 (6) [M$^+$], 584 (5), 573 (3), 571 (5) [M$^+$ − Me], 569 (4), 551 (19) [M$^+$ − Cl], 549 (15), 478 (14) [M$^+$ − Cl − SiMe$_3$], 476 (14), 397 (13), 395 (10), 362 (13), 360 (12), 342 (76) [M$^+$ − 2Cl − N$_2$(SiMe$_3$)$_2$], 340 (100) [M$^+$ − 2 − 2Cl − N$_2$(SiMe$_3$)$_2$], 326 (14), 324 (16), 310 (9), 308 (11), 193 (5), 190 (7), 146 (16) [2 SiMe$_3$].

X-ray Crystallographic Study: All crystals had to be handled with due care under argon in a Schlenk system. The selected crystals

Table 2. Crystallographic data of **1** and **3**

Compound	**1**	**3**
Chem. formula	$C_{12}H_{38}Cl_2N_4Si_4Ti$	$C_{12}H_{36}Cl_4N_4Si_4Ti_2$
Formula weight	469.62	586.41
Cryst. size [mm^3]	0.6 × 0.15 × 0.1	0.20 × 0.20 × 0.10
Cryst. system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [pm]	1186.04(4)	954.48(10)
b [pm]	1756.28(9)	4620.0(5)
c [pm]	1313.31(11)	988.20(11)
α [°]	90	90
β [°]	95.940(3)	94.194(2)
γ [°]	90	90
V [10^6 pm^3]	2721.2(3)	4346.0(8)
Z	4	6
d (calcd.) [Mg/m^3]	1.146	1.344
Radiation	Mo-K_α (graphite-monochromated)	Mo-K_α (graphite-monochromated)
	λ = 71.073 pm	λ = 71.073 pm
μ [mm^{-1}]	0.690	1.092
F (000)	1000	1824
Index range	$-10 \leq h \leq 9$	$-12 \leq h \leq 12$
	$-21 \leq k \leq 21$	$-51 \leq k \leq 49$
	$-16 \leq l \leq 16$	$-12 \leq l \leq 12$
2θ [°]	3.88−55.40	3.52−55.84
T [K]	183	193
Structure solution program	SHELXL-97	SHELXL-97
No. refl. collected	13769	24498
No. refl. unique	4136	8362
No. refl. observed (4σ)	2154	4425
R (int.)	0.1018	0.0779
No. variables	213	391
Weighting scheme	$w^{-1} = \sigma^2 F_0^2 + (0.0476P)^2$	$w^{-1} = \sigma^2 F_0^2 + (0.0491P)^2$
	$P = (F_0^2 + 2F_c^2)/3$	$P = (F_0^2 + 2F_c^2)/3$
GoF	0.776	0.963
Final *R* (4σ)	0.0510	0.0560
Final *wR*2	0.1146	0.1016
Larg. res. peak/hole [eÅ^{-3}]	0.380/−0.273	0.528/−0.659
Absorption correction	SADABS	SADABS
Max./min. transmission	1.000/0.8803	0.8986/0.8112

were covered with oxygen-free perfluoroether oil, mounted on a glass fiber, and transferred to the goniometer head of a Siemens SMART area detector. They were analyzed using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The structures were solved by direct methods (SHELXL-97[15]; see Table 2).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140716 (**1**) and -140715 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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