Controlled Hydrolysis of Tripodal Titanium Amido Halides: The Influence of the Ligand Periphery upon the Basicity of the Amido-N Functions☆

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Hydrolysis of the tripodal amidotitanium halides $H_3CC(CH_2NSiMe_3)_3TiX$ (X = Cl: **1a**; Br: **1b**) in the presence of Et_3N affords the linear μ-oxo-bridged complex $[H_3CC(CH_2NSiMe_3)_3Ti]_2$ (μ-O) (**3**) which was characterized by X-ray crystallography. Treatment of $H_3CC(CH_2N\textit{i}Pr)_3TiX$ (X = Cl: **2a**; Br: **2b**), obtained in low yields, under the same conditions only leads to decomplexation of the amido ligand. Under conditions of very slow exposure to H_2O the primary addition product of water across two Ti–N bonds in **2a** could be isolated and was characterized as $[H_3CC(CH_2\text{-}\overline{N\textit{i}Pr)_2CH_2NH\textit{i}Pr]}Ti(\mu\text{-}Cl)]_2(\mu\text{-}O)$ (**4**), the crystal structure analysis establishing a triply bridging central $Ti(\mu\text{-}O)(\mu\text{-}Cl)_2Ti$ unit. Deprotonation with two molar equivalents of *n*BuLi and subsequent LiCl elimination afforded the μ-oxo complex $[H_3CC(CH_2N\textit{i}Pr)_3Ti]_2(\mu\text{-}O)$ (**5**).

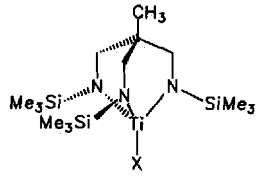
We have recently studied the coordinative capabilities of several types of novel tripodal amido ligands[1] which have found applications both in main group[2] and transition metal chemistry[3]. In particular, these have provided the key to the stabilization of unsupported early-late heterobimetallic complexes[4] and have generated unusual complex geometries of the heavier transition elements[5].

All the tripodal amido complexes studied so far have been *N*-alkyl/silyl or *N*-aryl/silyl substituted, a situation which enhanced their thermal and chemical stability. Particularly, the sensitivity towards hydrolysis of the M–N bonds upon *N*-silylation is markedly decreased, an observation which is consistent with earlier reports in this area[6]. Of the ligand systems studied those containing a neopentane framework were found to be ideally suited for coordination to first row transition elements, especially tetravalent titanium and vanadium.

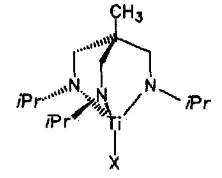
In this paper we demonstrate how the replacement of the peripheral trimethylsilyl groups in the neopentane-derived systems $H_3CC(CH_2NSiMe_3)_3TiX$ (X = Cl: **1a**; Br: **1b**) by sterically equivalent isopropyl groups affects the behaviour of the tripodal amides in controlled hydrolyses. In other words, it should be demonstrated how the change in basicity at the donor functions of the ligands influences the reaction pathways while leaving the steric situation essentially unchanged.

Results and Discussion

The isopropyl substituted analogues of **1a, b** were obtained by the same method as previously described. Reaction of the lithium amide $[H_3CC\{CH_2N(Li)\textit{i}Pr\}_3]_2$[1a] with $TiX_4(thf)_2$ (X = Cl, Br) led to product mixtures from which the target products **2a, b** could be isolated in low yield after work up by distillation. The low yields are in part due to the decreased thermal stability of alkyl substituted amides which is consistent with the detailed investigations into this matter reported by Bürger et al.[7]. As a consequence, the chloro complex **2a** was only obtained with small amounts of contaminations due to thermal degradation; the higher stability of the bromo derivatives was previously noted in the synthesis of **1a, b**.



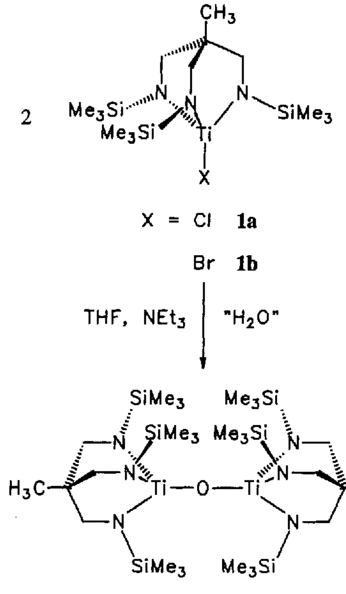
X = Cl **1a**
Br **1b**



X = Cl **2a**
Br **2b**

The introduction of a peripheral alkyl instead of a silyl group significantly changes the behaviour of the Ti complexes under conditions of controlled hydrolysis. Stirring of a solution of **1a, b** in thf (which was only dried over KOH and therefore still contained traces of moisture) and in the presence of triethylamine yielded a yellow, moderately air and moisture sensitive, crystalline compound which is only sparingly soluble in non-polar solvents. The product was identified as the Ti-oxo complex $[H_3CC(CH_2NSiMe_3)_3Ti]_2(\mu\text{-}O)$ (**3**) (eq. 1), the central Ti–O–Ti structure of which was established by X-ray crystallography (Figure 1).

The central oxygen atom is located on a crystallographic centre of symmetry, which relates the two halves of the molecule, and imposes linearity upon the Ti–O–Ti unit. The



(1)

3

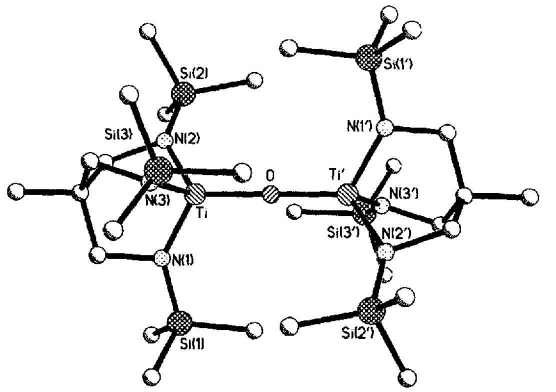


Figure 1. The structure of the centrosymmetric molecule of 3[a]

[a] Selected bond lengths [Å] and interbond angles [°]: Ti–O 1.810(1), Ti–N(1) 1.878(8), Ti–N(2) 1.896(7), Ti–N(3) 1.871(8), Si(1)–N 1.711(8), Si(2)–N 1.694(8), Si(3)–N 1.702(8); N(1)–Ti–O 117.5(3), N(2)–Ti–O 117.0(2), N(3)–Ti–O 116.7(2), N(1)–Ti–N(2) 101.6(4), N(1)–Ti–N(3) 100.5(4), N(2)–Ti–N(3) 100.5(3), Ti–O–Ti' 180.

Ti–O distance of 1.810(1) Å is somewhat shorter than those found in complexes of the general type $[Cp_2Ti(X)]_2O$ (X = ONO_2, Et, Cl, $OCOCF_3$) which have Ti–O bond lengths between 1.83 and 1.86 Å[8]. Linear Ti_2O units have also been found in $[(PhCH_2)_3Ti]_2O$ [*d*(Ti–O) = 1.798(0) Å] and $[(acen)(Cl)Ti]_2O$ [acen = *N,N'*-ethylenebis(acetylacetoneiminate)] [*d*(Ti–O) = 1.813(1) Å][9]. The Ti–N distances are between 1.871(8) and 1.896(7) Å and lie in the range previously established for complexes containing this type of tripodal amido ligands[3]. All nitrogen atoms possess a trigonal planar geometry which is characteristic of transition metal amido compounds[6].

In contrast to the reactivity of **1a**, **b**, treatment of **2a**, **b** with wet thf under identical conditions leads to the complete hydrolysis of the compounds generating the triamine $H_3CC(CH_2NH\textit{i}Pr)_3$. The Ti–N bond is thus the preferred point of attack instead of the Ti–halide bond as in **1a**, **b**. That the addition of H_2O indeed occurs at the Ti–N framework could was established by very slow hydrolysis of compound **2a**. Upon storage of a solution of **2a** (crude product) in pentane at room temperature, in a Schlenk tube which was only sealed with a rubber stopper, dark red crystals were (reproducibly!) formed over a period of 3–4 months. The complicated signal patterns in the NMR spectra of the product thus obtained indicated an oligomeric, probably dimeric, structure. The presence of a ν(N–H) band in the infrared spectrum was consistent with the partial protonation of the amido-*N* atoms. Single crystal X-ray structure analysis shows that compound **4** is indeed a product of the hydrolysis of **2a** and establishes a dinuclear structure in which the two Ti centres are triply linked by two chloro and an oxo ligand as shown in Figure 2.

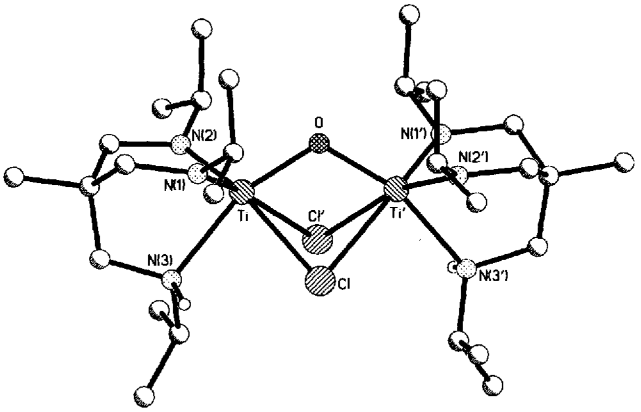
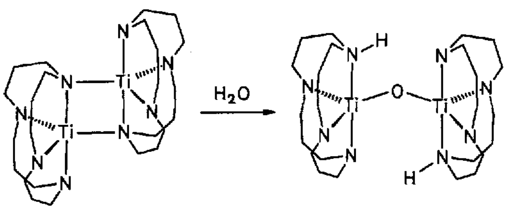


Figure 2. The structure of 4, showing the C_2 molecular symmetry[a]

[a] Selected bond lengths [Å] and interbond angles [°]: Ti–Cl 2.640(2), Ti–Cl' 2.778(2), Ti–O 1.841(4), Ti–N(1) 1.879(6), Ti–N(2) 1.916(6), Ti–N(3) 2.285(6); Cl–Ti–O 80.8(1), Cl–Ti–N(1) 93.5(2), Cl–Ti–N(2) 165.2(2), Cl–Ti–N(3) 81.2(2), O–Ti–N(1) 103.8(2), O–Ti–N(2) 108.1(2), O–Ti–N(3) 160.5(2), N(1)–Ti–N(2) 95.7(3), N(1)–Ti–N(3) 84.5(3), N(2)–Ti–N(3) 88.2(2), Ti–Cl–Ti' 70.0(1), Ti–O–Ti' 115.3(4).

The molecule has crystallographically imposed C_2 symmetry with the oxo-O atom lying on the twofold axis which relates the two halves of the molecule. The central $Ti(\mu\text{-}Cl)_2(\mu\text{-}O)Ti$ arrangement is unprecedented in transition metal chemistry[10]. One molecule of H_2O has formally added across two Ti–N bonds, protonating N3 and N3' and forming the Ti–O–Ti fragment. The titanium oxygen distance of 1.841(4) Å is significantly longer than that found in the linear unit of **3**, an observation which is consistent with previous reports on Ti–oxo complexes[8,9]. However, the Ti1–O1–Ti1' angle of 115.3(4)° is unusually small, marking a *structural extreme* in the chemistry of transition metal oxo-complexes[10], which is to be seen as a consequence of geometry imposed by the additional μ-Cl bridges. The Ti1–N3 distance of 2.285(6) Å is typical for Ti amine complexes[11] while the Ti–N(amido) bond lengths of *d*(Ti1–N1) = 1.879(6) and *d*(Ti1–N2) = 1.916(6) Å lie within the usual range found for titanium amido complexes[12–15]. As expected, the amine nitrogen atom N3 is not trigonally planar configurated but tetrahedrally distorted, the NH proton was located directly in the structure analysis.

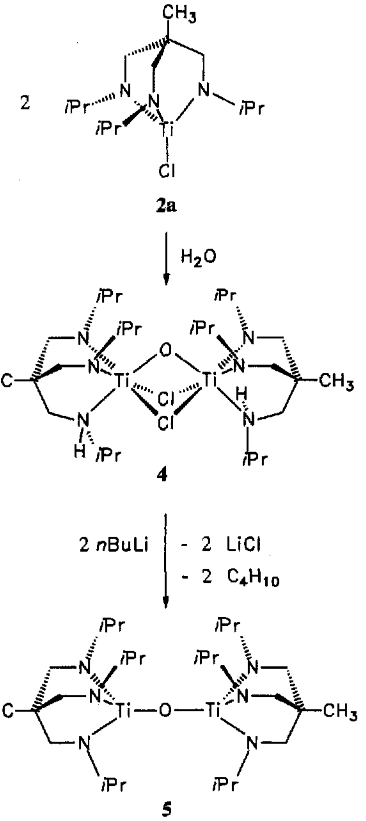
There is one previous example in the literature of the formal addition of H_2O across two Ti−N bonds. Power and coworkers reported the addition of water to the macrocyclic titanium tetramide $[(TiN_4C_{12}H_{24})_2]$ generating the μ-oxo-bridged species $[O(TiN_4C_{12}H_{25})_2]_2$ in which two amido-N atoms are also converted to amine functions (see eq. 2)[16].



(2)

It should be noted that a primary hydrolysis product similar to **4** could not be detected for the *N*-silylated species **1a**, **b**. If **4** is treated with two molar equivalents of *n*BuLi at −40°C in toluene the Ti_2O complex analogous to **3**, $[H_3CC(CH_2N\mathit{i}Pr)_3Ti]_2(\mu\text{-}O)$ (**5**), is generated in high yield (Scheme 1). Its formation from **4** is to be seen as a double dehydrochlorination resulting from initial deprotonation of the amine functions and subsequent elimination of LiCl.

Scheme 1. Reaction sequence leading to **4** and **5**



Conclusions

In this paper we have offered insight into the reaction pathways by which hydrolysis of transition metal amido complexes may occur. The isopropyl-substituted Ti amides **2a**, **b** are sufficiently basic at the N-donor functions to permit the isolation and structural characterization of the product of H_2O addition across two Ti−N bonds. That such intermediates are not observed in the hydrolysis the $SiMe_3$-functionalized complexes attests to the decreased basisity of the amido-donor functions. This along with the comparatively more vigorous reaction conditions in their hydrolysis confirms the notion of the increased chemical stability of the silyl-amido complexes.

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Experimental

All experiments were performed under dried Argon in standard (Schlenk) glassware which was flame-dried prior to use. Solvents were dried according to standard procedures and saturated with argon. The deuterated solvents used for the NMR-spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried with 4-Å-molecular sieves.

^{1}H, ^{13}C, ^{29}Si NMR: Bruker AC 200 spectrometer with a B-VT-2000 variable temperature unit (a 200.13, 50.32, and 39.76 MHz, respectively). – IR: Bruker IRS 25 FT. – Elemental analyses: Microanalytical laboratory of the Chemistry Department at Würzburg. – Melting points: Differential thermal analysis. – $H_3CC(CH_2NH\mathit{i}Pr)_3$[1a] and $H_3CC(CH_2NSiMe_3)_3TiX$ (X = Cl, Br)[3a] were prepared as reported previously by us. $TiX_4(THF)_2$ (X = Cl, Br) was prepared according to literature procedures[17]. All other chemicals used as starting materials were obtained commercially and used without further purification.

1) *Preparation of* $[H_3CC(CH_2N\mathit{i}Pr)_3TiX]$ (**2a**, **b**): To a stirred solution of 1.94 g (8.23 mmol) of $H_3CC(CH_2NH\mathit{i}Pr)_3$ in 80 ml of pentane, which was cooled to −40°C, was slowly added 24.75 mmol of *n*BuLi (9.9 ml of a 2.5 M solution in hexanes). The reaction mixture was warmed to room temp. and, after the butane evolution had subsided, heated under reflux for a short period of time. After the solution of the lithiated amine had been stirred at room temp. for another 30 min, it was cooled to −50°C, then 8.98 mmol of solid $TiX_4(THF)_2$ (X = Cl, Br) were added. The reaction mixture was warmed to room temp. over a period of 15 h, filtered through a G3 frit and the solvent of the filtrate removed in vacuo. Vacuum distillation of the residue yielded **2a** and **2b** as dark red oils [Yields: **2a** (crude product): 410 mg (15%), **2b**: 270 mg (9%)]. The ^{1}H-NMR spectrum indicated the presence of ca. 10% impurities in **2a**. A satisfactory elemental analysis of the chloro complex could thus not be obtained.

2a: B.p. 145°C/0.02 Torr. – ^{1}H NMR (C_6D_6, 295 K): δ = 1.14 (s, 3H, CH_3C), 1.24 [d, 18H, $CH(CH_3)_2$, $^{3}J_{HH}$ = 6.3 Hz], 3.06 [sept, 3H, $CH(CH_3)_2$], 3.41 (s, 6H, CH_2N). – $\{^{1}H\}^{13}C$ NMR (C_6D_6, 295 K): δ = 23.5 (CH_3C), 25.0 [$CH(CH_3)_2$], 42.2 (CH_3C), 57.6 [$CH(CH_3)_2$], 65.4 (CH_2N).

2b: B.p. 151°C/0.02 Torr. – ^{1}H NMR (C_6D_6, 295 K): δ = 1.10 (s, 3H, CH_3C), 1.21 [d, 18H, $CH(CH_3)_2$, $^{3}J_{HH}$ = 6.4 Hz], 3.04 [sept, 3H, $CH(CH_3)_2$], 3.34 (s, 6H, CH_2N). – $\{^{1}H\}^{13}C$ NMR (C_6D_6, 295 K): δ = 23.5 (CH_3C), 25.0 [$CH(CH_3)_2$], 43.0 (CH_3C), 57.2 [$CH(CH_3)_2$], 65.2 (CH_2N). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1} w, 2924 vs, 2868 s, 2820 s, 1460 m, 1376 s, 1356 m, 1320 m, 1248 m, 1176 vs, 1144 s, 1124 s, 1068 w, 1044 w, 1008 w, 960 vs, 840 m, 784 m. – $C_{14}H_{30}BrN_3Ti$ (368.23): calcd. C 45.67, H 8.21, N 11.41; found C 46.56, H 8.42, N 10.94.

2) *Preparation of* $[H_3CC(CH_2NSiMe_3)_3Ti]_2(\mu\text{-}O)$ (**3**): To a stirred solution of 380 mg (0.83 mmol) of $H_3CC(CH_2NSiMe_3)_3TiX$

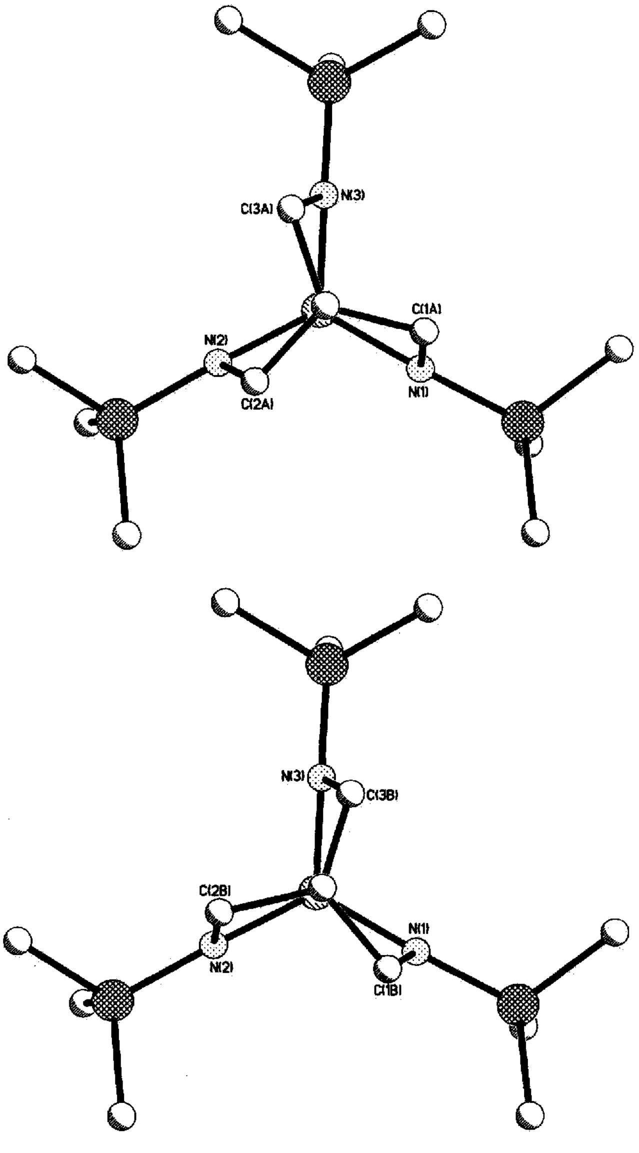
(**1a, b**) in 50 ml of THF (dried with KOH) 5 ml (36.0 mmol) of NEt_3 was added. The reaction mixture was stirred for 3 d and the solvent evaporated in vacuo. The residue was extracted with 20 ml of pentane, the extract filtered and the solvent removed in vacuo. The residue was dissolved in 5 ml of toluene and the solution stored at −30 °C. **4** was isolated as a highly crystalline yellow solid [Yield: 231 mg (72%)]. M.p. 104 °C (dec.). – ^1H NMR (C_6D_6, 295 K): δ = 0.33 [s, 27 H, $Si(CH_3)_3$], 1.02 (s, 3 H, CH_3C), 3.51 (s, 6 H, CH_2N). – $\{^1H\}^{13}C$ NMR (C_6D_6, 295 K): δ = 1.5 [$Si(CH_3)_3$], 26.3 (CH_3C), 49.6 (CH_3C), 61.9 (CH_2N). – $\{^1H\}^{29}Si$ NMR (C_6D_6, 295 K): δ = −1.2. – IR (hexanes): $\tilde{\nu}$ = 2964 cm^{-1} vs, 2932 vs, 2900 vs, 2868 vs, 1460 s, 1380 m, 1248 m, 1036 w, 988 vw, 924 w, 864 vs, 760 w. – $C_{28}H_{72}N_6OSi_6Ti_2$ (773.19): calcd. C 43.50, H 9.39, N 10.87; found C 43.60, H 9.88, N 10.93.

3) *Isolation of* $[\{H_3CC(CH_2NiPr)_2CH_2NHiPr\}Ti(\mu\text{-}Cl)]_2(\mu\text{-}O)$ (**4**): A solution of ca. 4.00 mmol of **2a** (crude product) in 20 ml of pentane was stored at room temp. After ca. 3 months precipitated dark red crystals of **4** [Yield: 285 mg (21%)]. – ^1H NMR ([D_8]toluene, 335 K): δ = 0.98 (s, 3 H, CH_3C), 1.01 [d, 6 H, $(CH_3)_2CHNH$, $^3J_{HH}$ = 6.7 Hz], 1.19 [d, 6 H, $(CH_3)_2CHN$, $^3J_{HH}$ = 6.7 Hz], 1.20 [d, 6 H, $(CH_3)_2CHN$, $^3J_{HH}$ = 6.7 Hz], 2.67 (d, 2 H, CH_2NHiPr, $^3J_{HH}$ = 8.6 Hz), 3.19 (d, 2 H, $CHHNiPr$, $^2J_{HH}$ = 12.7 Hz), 3.37 (d, 2 H, $CHHNiPr$), 3.90 [dsept, 1 H, $(CH_3)_2CHNH$, $^3J_{HH}$ = 2.0 Hz], 5.70 [sept, 2 H, $(CH_3)_2CHN$]. – $\{^1H\}^{13}C$ NMR ([D_8]toluene, 335 K): δ = 22.2 [$(CH_3)_2CHN$], 24.4 [$(CH_3)_2CHNH$], 26.5 (CH_3C), 42.7 (CH_3C), 49.5 [$(CH_3)_2CHNH$], 52.7 (CH_2NHiPr), 56.1 [$(CH_3)_2CHN$], 59.9 (CH_2NiPr). – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1} w, 3180 vw, 2930 vs, 2890 vs, 2840 s, 2810 s, 1622 vw, 1562 vw, 1445 vs, 1405 m, 1388 m, 1370 vs, 1355 s, 1340 s, 1318 s, 1302 m, 1250 w, 1225 w, 1155 vs, 1115 s, 1100 s, 1032 vs, 1012 m, 985 vs, 955 s, 910 s, 875 m, 820 s, 805 m, 790 m. – $C_{28}H_{62}Cl_2N_6OTi_2$ (665.51): calcd. C 50.53, H 9.39, N 12.63; found C 50.78, H 9.66, N 12.57.

4) *Preparation of* $[H_3CC(CH_2NiPr)_3Ti]_2(\mu\text{-}O)$ (**5**): To a stirred solution of 101 mg (0.15 mmol) of **4** in 5 ml of toluene, which was cooled to −40 °C, was slowly added 0.30 mmol of *n*BuLi (0.12 ml of a 2.5 M solution in hexanes). The reaction mixture was warmed to room temp., stirred for 20 min. and the solvent evaporated in vacuo. The residue was extracted with 20 ml of pentane, the extract filtered, and the volume of the solution reduced to ca. 2 ml. Storage at −78 °C yielded **3** as a red crystalline solid [Yield: 67 mg (75%)]. – ^1H NMR (C_6D_6, 295 K): δ = 1.12 (s, 6 H, CH_3C), 1.33 [d, 36 H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.5 Hz], 3.37 (s, 12 H, CH_2N), 3.46 [sept, 6 H, $CH(CH_3)_2$]. – $\{^1H\}^{13}C$ NMR (C_6D_6, 295 K): δ = 24.6 [$CH(CH_3)_2$], 27.5 (CH_3C), 43.5 (CH_3C), 56.8 [$CH(CH_3)_2$], 63.9 (CH_2N). – IR (hexanes): $\tilde{\nu}$ = 2810 s cm^{-1}, 2780 m, 1357 m, 1318 w, 1262 w, 1170 vs, 1120 w, 1070 w, 1020 w, 970 m, 840 vs, 808 vs, 728 s, 696 m. – $C_{28}H_{60}N_6OTi_2$ (592.58): calcd. C 56.75, H 10.21, N 14.18; found C 56.56, H 10.32, N 14.24.

4) *X-ray Crystallographic Study of* **3** *and* **4**: A clear, yellow crystal of **3** and a deep red crystal of **4**, both of prismatic habit, were mounted under argon in Lindemann capillary tubes. Using a Philips PW1100 diffractometer, with graphite-monochromated Mo-K_α radiation, unit cell parameters were determined by least-squares analysis of the setting angles of 25 reflections in the range $9 < \Theta < 12°$. Data for **3** and **4** were collected at 295 K in the Θ-range 3–25° with respective scan widths of 0.08 and 0.09° using the technique described previously[18]. For both crystals three standard reflections measured at intervals of 5 h showed no significant change in intensity. The data were corrected for Lorentz and polarisation effects and equivalent reflections merged to give 1917 (**3**) and 1708 (**4**) data with $I/\sigma(I) \geq 3.0$. Structure solution and refinement were carried out with the programs of the SHELX 86 and SHELX 76 software packages. The coordinates of the metal atom in **3** were deduced from Patterson syntheses, and for **4** the titanium atom and co-ordination sphere were located by direct methods. The remaining non-hydrogen atoms were located in subsequent difference-Fourier maps. For **3**, two sets of maxima were observed for the three methylene carbon atoms and were assigned half occupancy as atoms C(1a), C(2a), C(3a) and C(1b), C(2b), C(3b), corresponding to a 50:50 disorder of molecules with opposite twists of the tripod ligand as illustrated in Figure 3.

Figure 3. The two components of the disorder of the tripod ligand in the crystal structure of **3**



The position of the hydrogen atom on the amine nitrogen atom N(3) in **4** was located in a difference-Fourier map calculated using data with $\sin \Theta < 0.35$ and was included in structure factor calculation but its parameters were not refined. The remaining hydrogen atoms in **3** and **4** were included in idealised positions (C–H 1.08 Å) and all H-atoms were assigned fixed isotropic thermal parameters of 0.08 $Å^2$. Empirical absorption corrections were applied to both data sets using the program DIFABS[19]. Anistropic thermal parameters were assigned to the N, O, Si, and Ti atoms of **3** and all non-hydrogen atoms of **4** in the final cycles of full matrix least squares refinement; convergence occured at $R = 0.0737$ and $R_w = 0.0696$ for **3** and $R = 0.0519$ and $R_w = 0.0507$ for **4**, with weights of $1/\sigma^2 (F)$ assigned to individual reflections.

Table 1. Crystal data for **3** and **4**

	3	**4**
Empirical formula	$C_{28}H_{72}N_6OSi_6Ti_2$	$C_{28}H_{62}Cl_2N_6OTi_2$
Molecular mass	773.19	665.54
Crystal system	monoclinic	tetragonal
a [Å]	15.600(3)	12.447(3)
b [Å]	13.074(3)	-
c [Å]	11.398(3)	24.204(5)
β [°]	90.957(2)	-
V [Å^3]	2324.35	3749.87
Z	2	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.105	1.179
Space group	$P2_1/n$	$P4_12_12_1$
F000	836	1432
μ(Mo-K_α) [cm^{-1}][a]	5.1	5.8
no. of observed refl.	1917	1708
no. of refined params.	150	177
R/R_w	0.0737/0.0696	0.0519/0.0507

☆ Dedicated to Professor Dr. *Markus Wieber* on the occasion of his 60th birthday.

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