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Novel titana-2,4-cyclopentadienes by 1,1-alkylboration

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Abstract

Bis(trimethylsilyl)amino-(2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl)-titanium dichloride (**3**) and bis(2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl)-titanium dichloride (**4**) were prepared and converted into the di(1-alkynyl)titanium derivatives, $(Me_3Si)_2N[(CH_2Me_2Si)_2N]Ti(C{\equiv}C\text{–}R)_2$ (**5**) and $[(CH_2Me_2Si)_2N]_2Ti(C{\equiv}C\text{–}R)_2$ (**6**) [R = Me (**a**), Ph (**b**), $SiMe_3$ (**c**)]. The reaction of **5a** and **5b** with trialkylboranes such as Et_3B leads almost quantitatively to titana-2,4-cyclopentadienes **7a** and **7b**, in which a diethylboryl group functions as a substituent in 3-position. In the same manner, **6b** reacts with Et_3B or Pr_3B to titana-2,4-cyclopentadienes **8b** or **9b**, respectively. It is proposed that these reactions proceed by 1,1-alkylboration. Compound **5c** also reacts with Et_3B, however, a complex mixture was obtained. All products were characterised by ^1H-, ^{11}B-, ^{13}C-, ^{15}N- and ^{29}Si-NMR spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Alkynes; Amides; 1,1-Organoboration; Titanacyclopentadienes

1. Introduction

Bis(silylamino)titanium dichlorides can be considered as attractive starting materials for the synthesis of new organometallic titanium complexes. However, until recently such dichlorides were available only in low yield [1] or as mixtures with other compounds, e.g. aminotitanium trichlorides [2]. We have reported on the clean synthesis of silylaminotitanium trichlorides such as **1** by the reaction of bis(silylamino)plumbylenes with an excess of titanium tetrachloride, $TiCl_4$ [3]. The so far unknown 2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl)titanium trichloride (**2**) was also prepared by this method. Treatment of these trichlorides with lithium *N*-silylamides provides a convenient access, in many cases, to bis(silylamino)titanium dichlorides, in which the silylamino groups can be identical or different [4]. Here we report on the synthesis of bis(trimethylsilyl-amino)-(2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl)titanium dichloride (**3**) and bis(2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl)titanium dichloride (**4**), and on the successful conversion of **3** and **4** into the corresponding di(1-alkynyl) derivatives **5** and **6** (Scheme 1). These complexes are rare examples [5], in which the titanium bears both 1-alkynyl and amino groups. First attempts to make use of the alkynyl functions were made in 1,1-alkylboration reactions which are known to work well for numerous 1-alkynylmetal compounds of main group metals [6], and for alkynylplatinum(II) derivatives [7,8]; however, compounds of type $Cp_2Ti(C{\equiv}C\text{–}R)_2$ have been found to react very sluggishly with trialkylboranes [9], accompanied by extensive decomposition.

2. Results and discussion

2.1. Synthesis of the starting materials **1–6**

The reaction of an excess of $TiCl_4$ with bis[-bis(trimethylsilyl)amino]plumbylene [10] affords bis(trimethylsilyl)aminotitanium trichloride (**1**) in high yield (Scheme 1a) as reported [3], and in an analogous way 2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl-titanium trichloride (**2**) is accessible (Scheme 1b). In contrast to $TiCl_4$ itself, these trichlorides react cleanly with various lithium silylamides to give bis(*N*-silylamino)titanium dichlorides [4]. We have now built on these results in order to prepare the new titanium dichlorides **3** and **4** (Scheme 1a and b) with the intention to synthesise di(1-alkynyl)titanium compounds **5**

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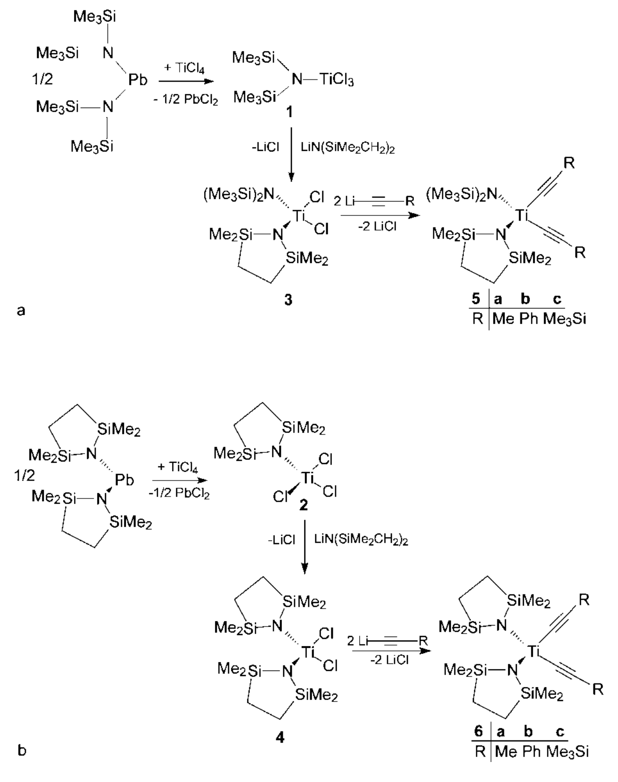
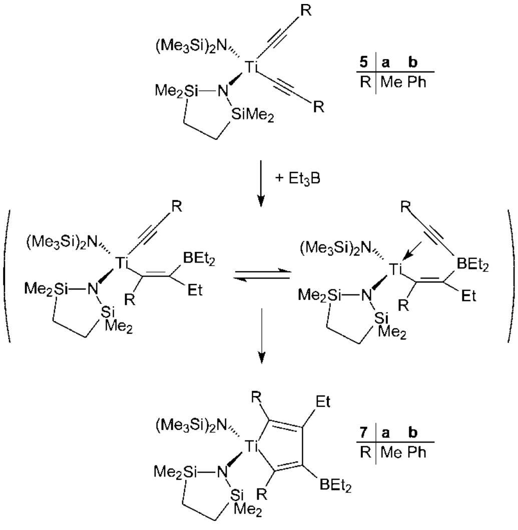
and **6** with amino groups at titanium. It turned out that the presence of two rather bulky amino groups is necessary for these compounds **5** and **6** to be formed, and to be sufficiently stable and reactive at the same time for use in further transformations. The combination of the different silylamino groups in **5** was particularly useful in this respect, as well as the use of two 2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl rings in **6**. Nevertheless, the complexes **5** and **6**, rearrange after some time into new compounds, possibly the result of titanium-induced C–C coupling of the alkyne units which can take place in various ways [11] and needs still to be clarified in the present cases.



Scheme 1.



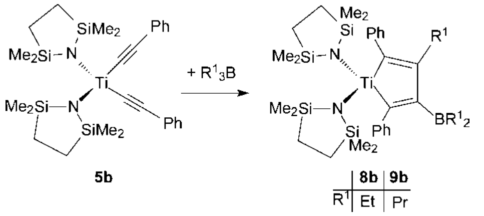
Scheme 2.

2.2. *1,1-Alkylboration of the di(1-alkynyl)titanium derivatives **5** and **6***

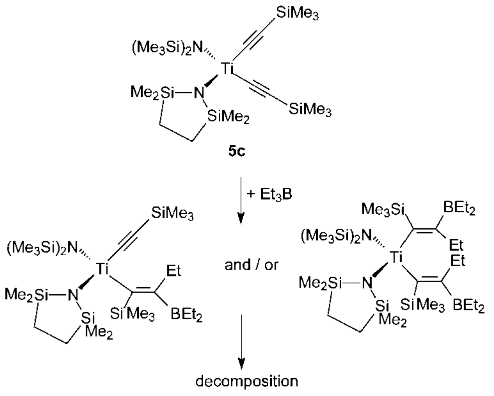
The reaction of the di(1-alkynyl)titanium derivatives **5a**, **b** with triethylborane and of **6a** with triethylborane or tripropylborane starts already <0 °C, and affords almost quantitatively the titana-2,4-cyclopentadienes **7**–**9** (Schemes 2 and 3). The metallacycles **7**–**9** could not be further purified, and attempts to isolate them free of solvent led to extensive decomposition. Decomposition into many unknown products became also evident for solutions of **7**–**9** in C_6D_6 or [D_8]toluene when the NMR spectra were measured at room temperature, and several hours of measurement time was required for certain experiments (e.g. ^{15}N-NMR spectra). However, the evidence from a consistent set of NMR data in solution is conclusive with respect to the proposed structures of **7**–**9** (vide infra). The substituent pattern at the five-membered ring is completely analogous to that of other metalla-2,4-cyclopentadienes obtained via 1,1-organoboration [6,8a,b]. Therefore, it is assumed that the mechanism (outlined in Scheme 2) which has been firmly established in other cases [6] will be the same here.

Titana-2,4-cyclopentadienes have been obtained so far mainly as titanocene derivatives by various routes focusing on reduction of Cp_2TiCl_2 in the presence of alkynes [12] or starting from the Cp_2Ti generating complex $Cp_2Ti(\eta^2\text{-}Me_3Si\text{–}C{\equiv}C\text{–}SiMe_3)$ [13]. Ancillary 2,6-diaminopyridines with bulky aryl groups linked to the amino nitrogen atoms are required to stabilise 1,1-bis(amino)titana-2,4-cyclopentadienes [14]. Some titana-2,4-cyclopentadiene derivatives with bulky aryloxo ligands were obtained, by reduction of $(ArO)_2TiCl_2$ in the presence of alkynes [15a], and others were generated in situ by reduction of $(^iPrO)_2TiCl_2$ together with alkynes. All known titana-2,4-cyclopentdienes were found to be extremely reactive in further catalytic or stoichiometric reactions.

The fact that the reaction of both **5c** and **6c** with Et_3B does not lead to titana-2,4-cylopentadienes, at least not in significant amounts, indicates that some potential intermediates are unstable, and other reaction



Scheme 3.



Scheme 4.

Table 1
^{13}C-, ^{15}N-, ^{29}Si-NMR data [a] of the aminotitanium trichlorides **1** and **2**, aminotitanium dichlorides **3** and **4** and bis[bis(trimethylsilyl)amino]titanium dichloride

Compound	δ^{13}C(SiMe)	δ^{13}C(other)	δ^{15}N	δ^{29}Si
1	4.2 (56.0)	–	+26.3	11.8
2	1.0 (55.7)	8.5 (55.7)	+26 [b]	28.4
[(Me$_3$Si)$_2$N]$_2$ TiCl$_2$	5.1 (56.8)	–	−51.3	4.3
3	5.3 (56.7)	–	−48.8	4.3
	2.3 (55.1)	9.2 (55.1)	−64.0	20.3 (≡C–Si)
4	2.2 (55.2)	9.3 (55.2)	−58.4	20.2

[a] All measurements in C$_6$D$_6$ solutions at 25 ± 1 °C. All coupling constants to ^{29}Si (±0.1 Hz) are given in brackets.

[b] ^{14}N-NMR measurement.

pathways are preferred which may be only side reactions in the cases of **5a**, **b** and **6b**. In the cases of **5c** and **6c**, it can be assumed, in analogy to other trimethylsilylethynyl derivatives [6], that the first 1,1-alkylboration products, the alkenyltitanium derivatives, do not possess the desired configuration for further intramolecular reactions (Scheme 4). We have shown that the 1,1-alkylboration is reversible [6], and that finally the ring formation dominates. However, in the case of titanium compounds, it appears that decomposition routes are more competitive. Thus, one potential way of decomposition may involve Ti-alkynyl/B-ethyl exchange after which the ethyltitanium compounds decompose via β-hydrogen elimination.

2.3. NMR spectroscopic results

^{13}C-, ^{15}N-, and ^{29}Si-NMR data of **1**–**4** are given in Table 1 together with data of the bis(bis(trimethylsilylamino)titanium dichloride. Table 2 lists the ^{13}C-, ^{15}N-, and ^{29}Si-NMR data of the di(1-alkynyl)titanium derivatives **5** and **6**, and Table 3 contains the ^{13}C-, ^{11}B-, ^{15}N-, and ^{29}Si-NMR data of the metallacycles **7**–**9**.

The NMR data of **3** and **4** are similar to those of other bis(silylamino)titanium dichlorides. In solution, compounds **3** and **4** are monomers, indicated by the sharp ^{14}N-NMR signals, and even equilibria of weak association must be discarded because of the sharp ^{15}N- and ^{29}Si-NMR signals (Fig. 1).

There is also no indication of association of the 1-alkynyl derivatives **5** and **6** in solution, where sharp ^{13}C-NMR signals of the alkynyl carbon atoms are observed in addition to sharp ^{15}N- and ^{29}Si-NMR signals. The ^{13}C(alkynyl)-NMR signals of **5** and **6** appear at slightly higher frequency (Cα) and markedly lower frequency (Cβ) when compared with Cp$_2$Ti(C(α)≡C(β)–R)$_2$ [16]. The ^{15}N-NMR signals of **5** and **6** are shifted to lower frequency when compared with **3** and **4** which indicates that the titanium atom becomes less electron deficient than in **3** and **4**. There is also a slight shielding of the ^{29}Si nuclei in **5** and **6** with respect to **3** and **4**.

The unstable titana-2,4-cyclopentadienes **7**–**9** had to be identified by multinuclear magnetic resonance spectroscopy. The relevant ^{1}H-NMR signals showed the presence of a chiral titanium centre in **7a**,**b** by splitting of the ^{1}H-NMR signals of the 4-CH$_2$ group as well as by the complex pattern of the ^{1}H(BCH$_2$) signals, and by doubling of the ^{1}H(SiMe$_2$) signals. The ^{11}B-NMR sig-

Table 2
^{13}C-, ^{15}N-, ^{29}Si-NMR data [a] of the di(1-alkynyl)-bis(silylamino)titanium compounds **5** and **6**

No.	δ^{13}C (α)	δ^{13}C (β)	δ^{13}C (SiMe$_3$)	δ^{13}C (SiMe$_2$)	δ^{13}C (SiCH$_2$)	δ^{13}C (R)	δ^{29}Si	δ^{15}N
5a	148.9	92.1	5.8 (56.2)	3.37 (54.9)	10.0 (54.9)	3.40	−0.5, 16.0	−72.8, −88.0
5b	157.6	95.2	5.7 (56.2)	3.4 (54.9)	9.9 (54.9)	122.1 [b]	0.1, 16.8	−62.5, −79.9
5c	175.8 (9.1)	100.3 (73.7)	5.7 (56.3)	3.3 (55.0)	9.8 (55.0)	−0.1 (55.7)	0.0, 16.7, −20.7 (≡C–Si)	−60.2, −78.1
6a	146.2	92.3	–	3.3 (54.9)	10.2 (54.9)	3.4	15.9	−80.4
6b	154.7	95.5	–	3.3 (54.9)	10.2 (54.9)	122.2 [c]	16.3	−70.3
6c	173.3 (9.1)	100.6 (73.7)	–	3.2 (55.0)	10.1 (55.0)	0.0 (55.9)	16.5, −20.9 (≡C–Si)	−68.4

[a] All measurements in C$_6$D$_6$ solutions at 25 ± 1 °C. All coupling constants to ^{29}Si (±0.1 Hz) are given in brackets.

[b] Other ^{13}C-NMR data: 132.7 (o), 128.57 (m), 128.63 (p).

[c] Other ^{13}C-NMR data: 132.7 (o), 128.57 (m), 128.62 (p).

Table 3
^{11}B-, ^{13}C-, ^{15}N-, ^{29}Si-NMR data [a] of the bis(silylamino)titana-2,4-cyclopentadienes **7**–**9**

No.	**7a**	**7b**	**8b**	**9b**
δ^{13}C (2)	218.1	222.4	218.5	218.5
δ^{13}C (3)	146.9 (br)	150.6 (br)	149.9 (br)	149.8 (br)
δ^{13}C (4)	132.9	135.7	135.5	134.4
δ^{13}C (5)	212.5	216.1	211.6	212.0
δ^{13}C (Me(2,5))	22.6/25.3	–	–	–
δ^{13}C (Ph-i)	–	146.8/148.0 [b]	146.7/147.5 [c]	146.7/147.6 [d]
δ^{13}C (R^1)	32.7/14.0	31.1/13.8	31.7/14.1	41.2/23.1/14.7
δ^{13}C (BR^1)$_2$	22.6 (br)/9.5	22.7 (br)/9.6	22.7 (br)/9.5	34.0 (br)/19.2/9.2
δ^{13}C (SiMe$_3$)	6.1 (55.4)	5.9 (55.6)	–	–
δ^{13}C (SiMe$_2$)	3.6/3.9 (54.1)	3.5/3.7 (53.7)	3.1/3.4 (54.1)	3.1/3.4 (54.2)
δ^{13}C (SiCH$_2$)	10.7	10.4	10.6	10.6
δ^{29}Si (SiMe$_3$)	−5.1	−3.6	–	–
δ^{29}Si (SiMe$_2$)	12.0	11.9	11.4	11.4
δ^{15}N(NSiMe$_3$)	−147.3 (2.2)	−126.6	–	–
δ^{15}N(NSiMe$_2$)	−152.7 (3.3)	−131.3	−129.8 (1.9)	−129.8
δ^{11}B	84 ± 3	84 ± 3	84 ± 3	84 ± 3

[a] All measurements in C$_6$D$_6$ solutions at 25 ± 1 °C, except **7a** (measured in [D$_8$]toluene). Coupling constants to ^{29}Si (±0.1 Hz) are given in brackets; (br) denotes a broad signal due to partially relaxed ^{13}C–^{11}B-coupling.

[b] Other ^{13}C-NMR data: 125.27/125.7 (o), 127.9/128.1 (m), 125.30/125.8 (p).

[c] Other ^{13}C-NMR data: 124.9/125.2 (o), 128.0/128.3 (m), 125.1/125.5 (p).

[d] Other ^{13}C-NMR data: 124.9/125.2 (o), 128.0/128.2 (m), 125.1/125.5 (p).

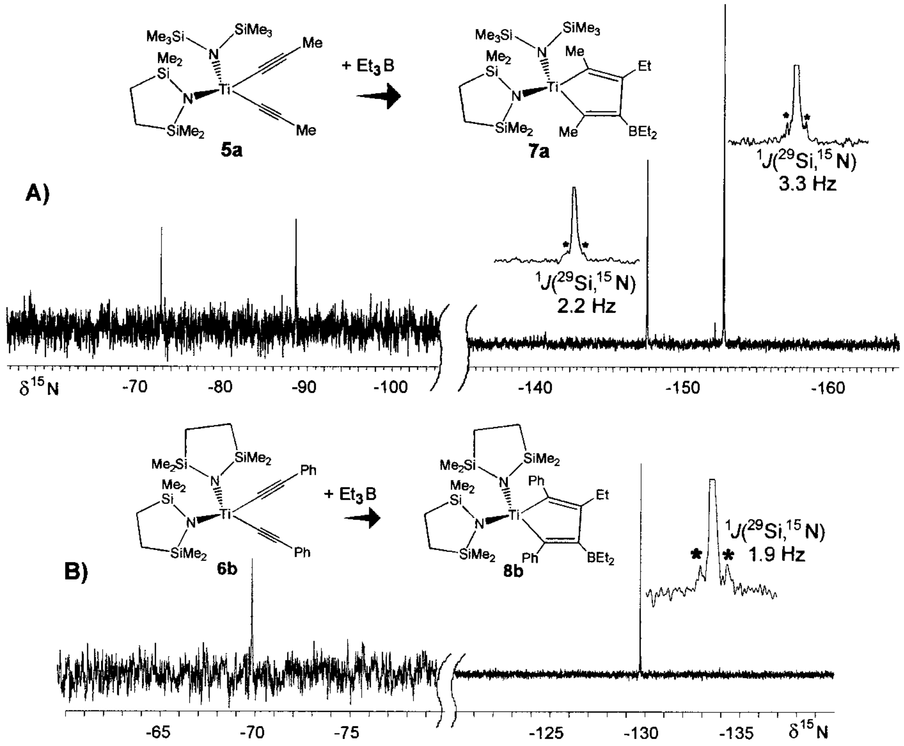


Fig. 1. ^{15}N-NMR spectroscopy was used for monitoring the formation of titana-2.4-cyclopentadienes. The simplicity of the spectra, and the large differences in the δ^{15}N values for starting materials and the products enables one to find the best conditions for the reactions. The ^{15}N-NMR signals are recorded by use of the INEPT pulse sequence (based on $^3J(^{15}N,^1H_{SiMe}) \approx 1.5$ Hz; refocused and ^{1}H decoupled). The ^{15}N resonances are visible after a short time (few minutes) as shown for the alkynes, and, after several hours, the ^{29}Si satellites according to $^1J(^{29}Si,^{15}N)$ (marked by asterisks) are also visible, as shown for the titana-2,4-cyclopentadienes.

nals are all very broad, difficult to detect in the presence of trialkylboranes which give intense ^{11}B-NMR signal in the same range, typical of triorganoboranes without significant CB(pp)π interactions [17]. Particularly helpful were consistent ^{15}N- (see Fig. 1), ^{29}Si- and ^{13}C-NMR data (Fig. 2). The ^{15}N nuclei become much

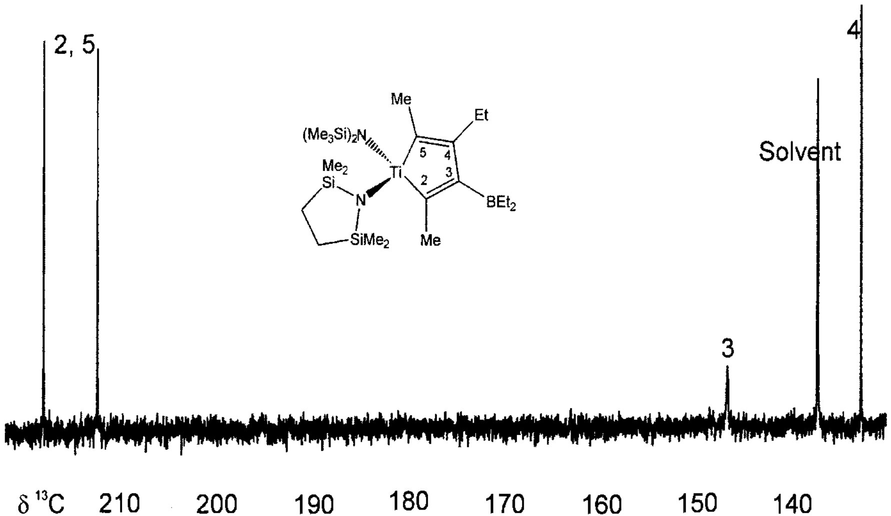


Fig. 2. 62.9 MHz ^{13}C{^{1}H}-NMR spectrum of the titana-2,4-cyclopentadiene **7a**, showing the range of the olefinic carbon atoms with the typical pattern of two sharp ^{13}C(2,5)-NMR signals at high frequencies, another one for ^{13}C(4) at lower frequency and a broad ^{13}C(C(3)–B)-NMR signal also at lower frequency.

more shielded in **7**–**9** than in the precursors **5** and **6** which can be interpreted, at least in part, by assuming (pd)π interactions between the butadiene system and titanium in the titana-2,4-cyclopentadienes [18]. Such interactions, or better the sum of π and σ interactions, are also indicated by the usual deshielding of ^{13}C(2,5) nuclei attached to titanium. The presence of the titana-2,4-cyclopentadiene ring with the boryl group in 3-position is confirmed by the observation of two signals for C(2,5) at high frequency, another sharp signal for C(4) at lower frequency, and a typically broad signal at moderately low frequency for C(3) linked to boron, all in the olefinic region (see Fig. 2). The broad signal is due to partially relaxed scalar ^{13}C–^{11}B coupling [19]. This characteristic pattern has been observed for all metalla-2,4-cyclopentadienes prepared by 1,1-organoboration [6,8a,b].

3. Experimental

Preparative work and handling of samples was carried out under an atmosphere of dry Ar, using oven-dried glassware and dry solvents. Starting materials were either commercial products (silylamines, BuLi (1.6 M in hexane), the alkynes, Et_3B, Pr_3B) or were prepared according to literature procedures (**1** [3]). NMR spectra were measured by using a Bruker ARX 250 spectrometer, equipped with a multinuclear unit. Chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ $(C_6D_5H) = 7.15$; $\delta^{13}C(C_6D_6) = 128.0$]; $\delta^{11}B$ $(Et_2O\text{–}BF_3) = 0$ for $\Xi(^{11}B) = 32.083971$ MHz, $\delta^{14}N$ (neat $MeNO_2$) $= 0$ for $\Xi(^{14}N) = 7.226455$ MHz, $\delta^{15}N$(neat $MeNO_2$) $= 0$ for $\Xi(^{15}N) = 10.676136$ MHz, and $\delta^{29}Si$ $(Me_4Si) = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz. ^{15}N-NMR spectra were measured by using the refocused INEPT pulse sequence with ^{1}H decoupling [20], and ^{1}H polarisation transfer was based on $^{3}J(^{15}N,^{1}H_{SiMe}) \approx 1.5$ Hz [21].

*3.1. Preparation of the bis(silylamino)titanium dichlorides **3** and **4***

One equivalent of the titanium trichloride **1** or **2** (ca. 50–100 mmol) was suspended in hexane (50 ml) at 0 °C, and one equivalent of 2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1-yl-lithium was added under vigorous stirring. The reaction mixture was allowed to warm up to room temperature (r.t.) and then stirred for 3 h. All insoluble material was filtered off, and the solvent was removed in vacuo to give the products as pure ($>95\%$ according to ^{1}H-NMR), yellow–orange or yellow oils.

3: yellow–orange oil; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^{1}H = 0.40$ (s, 18H, $SiMe_3$), 0.48 (s, 12H, $SiMe_2$), 0.53 (s, 4 H, $SiCH_2$). **4**: yellow oil; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^{1}H = 0.45$ (s, 24H, $SiMe_2$), 0.58 (s, 8 H, $SiCH_2$).

*3.2. Preparation of the di(1-alkynyl)bis(silylamino)titanium compounds **5** and **6***

Bis(silylamino)titanium dichloride **3** or **4** (1 mmol) in 0.5 ml C_6D_6 was added to a suspension of two equivalents of the respective lithiumalkynide Li–C≡CR in 0.5 ml C_6D_6 at 0 °C. The reaction mixture was allowed to warm up to r.t. After stirring the mixtures for 2–8 h (**4** reacts faster than **3**; Li–C≡CR with R = Me (**a**) reacts faster than R = Ph (**b**) and $SiMe_3$ (**c**)), the complete set of NMR data showed almost quantitative formation of the compounds **5** and **6**.

5a: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H = 0.52$ (s, 18H, $SiMe_3$), 0.60 (s, 12H, $SiMe_2$), 0.70 (s, 4H, $SiCH_2$), 1.44 (s, 6H, Me). **5b**: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H =$ 0.59 (s, 18H, $SiMe_3$), 0.70 (s, 12H, $SiMe_2$), 0.72 (s, 4H, $SiCH_2$), 6.91 (m, 6H, Ph), 7.43 (m, 4H, Ph). **5c**: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H = 0.09$ (s, 18H, $CSiMe_3$), 0.50 (s, 18H, $NSiMe_3$), 0.60 (s, 12H, $SiMe_2$), 0.63 (s, 4H, $SiCH_2$). **6a**: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H =$ 0.61 (s, 24H, $SiMe_2$), 0.72 (s, 8H, $SiCH_2$),1.43 (s, 6 H, Me). **6b**: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H = 0.69$ (s, 24H, $SiMe_2$), 0.73 (s, 8 H, $SiCH_2$), 6.92 (m, 6H, Ph), 7.46 (m, 4H, Ph). **6c**: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H = 0.11$ (s, 18H, $SiMe_3$), 0.63 (s, 24H, $SiMe_2$), 0.69 (s, 8 H, $SiCH_2$).

*3.3. 1,1-Alkylboration of the 1-alkynyltitanium compounds **5** and **6***

In an NMR tube, of the respective di(1-alkynyl)bis(silylamino)titanium compound (0.5 mmol) was dissolved in 0.5 ml of C_6D_6 (**5b** and **6b**) or in 0.5 ml of [D_8]toluene (**5a**, **c** and **6c**) and cooled to 0 or −20 °C, respectively. Then, trialkylborane (Et_3B **5b**, **c** and **6a**–**c** or Pr_3B **6b**; slight excess) was added and the solution was allowed to warm up to r.t. The reactions with alkynyl substituents R = Me (**a**), (**b**) led to the titana-2,4-cyclopenta-2,4-dienes **7a**, **7b**, **8b** and **9b** in essentially quantitative yield (NMR). The treatment of **5c** with Et_3B yielded a complex mixture of products which so far could not be analysed, whereas in the case of **6c** mainly decomposition products could be detected (Scheme 4).

7a: ^{1}H-NMR ([D_8]toluene, 250 MHz): $\delta^1H = 0.33$ (s, 18H, $SiMe_3$), 0.34 (s, 6H, $SiMe_2$), 0.35 (s, 6H,$SiMe_2$), 0.69 (s, 4H, $SiCH_2$), 0.98 (t, 3H, CCH_2CH_3), 1.05 (t, 6H, BCH_2CH_3), 1.40 (m, 4H, BCH_2), 1.91 (m, 2H, CCH_2), 2.13 (s, 3H, CMe), 2.28 (s, 3H,CMe). **7b**: ^{1}H-NMR (C_6D_6, 250 MHz), relevant signals: $\delta^1H =$ 0.28 (s, 18H, $SiMe_3$), 0.41 (s, 6H, $SiMe_2$), 0.43 (s, 6H, $SiMe_2$), 0.84 (s, 4H, $SiCH_2$), 0.92 (t, 6H, BCH_2CH_3), 1.25 (m, 4H, BCH_2), 1.70/2.30 (m, 2H, CCH_2), 6.90–7.30 (m, 10H, Ph). **8b**: ^{1}H-NMR (C_6D_6, 250 MHz): $\delta^1H = 0.36$ (s, 12H, $SiMe_2$), 0.40 (s, 12H, $SiMe_2$), 0.78 (s, 8H, $SiCH_2$), 6.), 0.89 (t, 3H, CCH_2CH_3), 0.95 (t, 6H, BCH_2CH_3), 1.28 (m, 4H, BCH_2), 2.06 (m, 2H, CCH_2), 6.85–7.30 (m, 10H, Ph). **9b**: ^{1}H-NMR (C_6D_6, 250 MHz), relevant signals: $\delta^1H = 0.30$ (s, 12H, $SiMe_2$), 0.35 (s, 12H, $SiMe_2$), 0.73 (s, 8H, $SiCH_2$), (m, 10H, Ph).

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References

[1] F. Jäger, H.W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, Chem. Ber. 130 (1997) 399.

[2] U. Wannagat, H. Bürger, Monatsh. Chem. 94 (1963) 761.

[3] B. Wrackmeyer, J. Weidinger, W. Milius, Z. Anorg. Allg. Chem. 624 (1998) 98.

[4] B. Wrackmeyer, J. Weidinger, Z. Naturforsch. Teil B 54 (1999) 1391.

[5] (a) P. Boe, J. Organomet. Chem. 107 (1976) 139;
(b) R.H. Cragg, M.F. Lappert, B.P. Tilley, J. Chem. Soc. A (1967) 947.

[6] B. Wrackmeyer, Coord. Chem. Rev. 145 (1995) 125.

[7] A. Sebald, B. Wrackmeyer, J. Chem. Soc. Chem. Commun. (1983) 309.

[8] (a) A. Sebald, B. Wrackmeyer, J. Chem. Soc. Chem. Commun. (1983) 1293;
(b) A. Sebald, B. Wrackmeyer, J. Organomet. Chem. 304 (1986) 271;
(c) B. Wrackmeyer, A. Sebald, J. Organomet. Chem. 544 (1997) 105.

[9] B. Wrackmeyer, unpublished results.

[10] M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, R. Riviere, M. Riviere-Baudet, J. Chem. Soc. Dalton Trans. (1977) 2004.

[11] U. Rosenthal, P.M. Pellny, F.G. Kirchbauer, V.V. Burlakov, Acc. Chem. Res. 33 (2000) 119.

[12] (a) V.B. Shur, E.G. Berkovich, M.E. Vol'pin, B. Lorenz, M. Wahren, J. Organomet. Chem. 228 (1982) C36;
(b) A. Famili, M.F. Farona, S. Thanedar, J. Chem. Soc. Chem. Commun. (1983) 435;
(c) M.B. Sabade, M.F. Farona, J. Organomet. Chem. 310 (1986) 311;
(d) S.M. Yousaf, M.F. Farona, Main Group Met. Chem. 15 (1992) 269.

[13] (a) U. Rosenthal, C. Lefeber, P. Arndt, A. Tillack, W. Baumann, R. Kempe, V.V. Burlakov, J. Organomet. Chem. 503 (1995) 221;
(b) V.V. Burlakov, A. Ohff, C. Lefeber, A. Tillack, W. Baumann, R. Kempe, U. Rosenthal, Chem. Ber. 128 (1995) 967;
(c) N. Peulecke, W. Baumann, R. Kempe, V.V. Burlakov, U. Rosenthal, Eur. J. Inorg. Chem. (1998) 419.

[14] F. Guerin, D.H. McConville, J.J. Vittal, Organometallics 16 (1997) 1491.

[15] (a) J.E. Hill, G. Balaich, P.E. Fanwick, I.P. Rothwell, Organometallics 12 (1993) 2911;
(b) H. Urabe, F. Sato, J. Am. Chem. Soc. 121 (1999) 1245;
(c) S. Yamaguchi, R.-Z. Jin, K. Tamao, F. Sato, J. Org. Chem. 63 (1998) 10060.

[16] (a) A. Sebald, P. Fritz, B. Wrackmeyer, Spectrochim. Acta 41A (1985) 1405 (some of the NMR data reported had been assigned to the wrong structure; see Ref. [16b] for the correct assignment);
(b) G.L. Wood, C.B Knobler, M.F. Hawthorne, Inorg. Chem. 28 (1989) 382.

[17] (a) H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR—Basic Principles and Progress, vol. 14, Springer, Berlin, 1978;
(b) B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 20 (1988) 61.

[18] E.T. Knight, L.K. Myers, M.E. Thompson, Organometallics 11 (1992) 3691.

[19] B. Wrackmeyer, Prog. NMR Spectrosc. 12 (1979) 227.
[20] (a) G.A. Morris, R. Freeman, J. Am. Chem. Soc. 101 (1979) 760;
(b) G.A. Morris, J. Am. Chem. Soc. 102 (1980) 428;
(c) D.P. Burum, R.R. Ernst, J. Magn. Reson. 39 (1980) 163.
[21] B. Wrackmeyer, E. Kupce, ^{15}N NMR of Silicon, Germanium, Tin and Lead-Nitrogen Compounds, in: M. Gielen (Ed.), Topics of Physical Organometallic Chemistry, vol. 4, Freund Publishing House, Tel Aviv, S, 1992, pp. 289–352.