Titanium and Zirconium Complexes Containing a Novel Dianionic Trifunctional Amido Ligand

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The novel tridentate diamidoamine ligands $[RC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]^{2-}$ (R = H, CH_3) have been synthesized and coordinated to Ti^{IV} and Zr^{IV} giving the pentacoordinate complexes $[MX_2\{RC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ (M = Ti, Zr; X = Cl, Br). The crystal structure analysis of $[TiBr_2\{HC(2\text{-}C_5H_4N)(CH_2NSiMe_3)\}]$ (**10b**) confirmed the involvement of the pyridyl function in the coordination to the metal centre occupying an apical position in the trigonal bipyramidal ligand polyhedron. Alkylation of $[TiCl_2\{H_3CC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ (**12a**) with one or two molar equivalents of [RMgCl] (R = $PhCH_2$, Me_3SiCH_2, Me_3SiC_2) yielded the mono- and dialkyl complexes $[TiClR\{H_3CC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ and $[TiR_2\{H_3CC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ in good yields. Depending on the steric demand of the alkyl group coordination or decoordination of the pyridyl group leads to four- or five-coordinate species. A crystal structure analysis of the pentacoordinate complex $[TiCl(CH_2SiMe_3)\{H_3CC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ (**16**) was carried out.

The development of polydentate amido ligands during the past five years and their use in the synthesis of high-valent transition metal complexes has added new structural motifs and reactive patterns to the coordination and organometallic chemistry of the early transition metals. Among the triamido ligand systems, which adopt tripodal or related arrangements, the azatranes studied by the groups of Verkade, Schrock and others[1][2][3][4][5] as well as the amido tripods developed in this laboratory[6][7][8] have been studied in most detail. While they have enabled the stabilization of otherwise elusive molecular stuctures and offered the possiblity to investigate their reactivity, the scope of their use is limited. This warrants continuing efforts in the area of ligand design[9] and, given the results of the approach mentioned above, polyfunctional derivatives of amido systems are attractive candidates when early transition metals are involved.

Our research has focussed on the metals of the titanium triad and the trianionic tripodal amido ligands employed have generated *monofunctional* M^{IV} complexes, i.e. compounds in which one anionic ligand (such as a halide) may be substituted to yield derivatives. In order to study the chemistry of *difunctional* compounds of the tetravalent metals, in which two anionic ligands may be displaced in subsequent conversions, it was necessary to develop dianionic amido ligands (Figure 1). This may be achieved in a trivial way by formal removal of an anionic "ligand arm" from the tripodal "claw" generating a simple chelate ligand of the type studied previously by Bürger[10] and others.[11][12] If the tridentate nature of the ligand should, however, be retained, an anionic amido function may be formally replaced by a neutral tertiary amino group. This may be achieved most readily by incorporation of a pyridine ring into the ligand framework.

We previously reported preliminary results related to the coordination of the type-A ligand $[HC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2]^{2-}$ to titanium(IV),[13] however, the presence of the apical proton, which offers the possibilty of 1,2-eliminations in the ligand framework, renders the ligand precursors excedingly difficult to isolate and to handle. These difficulties were also encountered by Henrick and Tasker in their synthesis of late transition metal complexes containg the amine $HC(2\text{-}C_5H_4N)(CH_2NH_2)_2$.[14]

In this paper we report the synthesis of a closely related ligand in which the apical position is occupied by a methyl group. The degradation pathway mentioned above therefore is avoided. Of particular intest was the degree to which the pyridyl-function participates in the coordination of the metal centre in amido complexes obtained with the potentially tridentate ligand.

Results and Discussion

A) Syntheses of the Amine Precursors for the Amido Ligands

The precursor material of a type-B ligand is the known 2-(2-pyridyl)propane-1,3-diamine which may be easily converted to the desired secondary amine **1** by silylation. However, as already indicated, the synthesis of this compound is complicated by its tendency (as well as its precursors) to undergo elimination.

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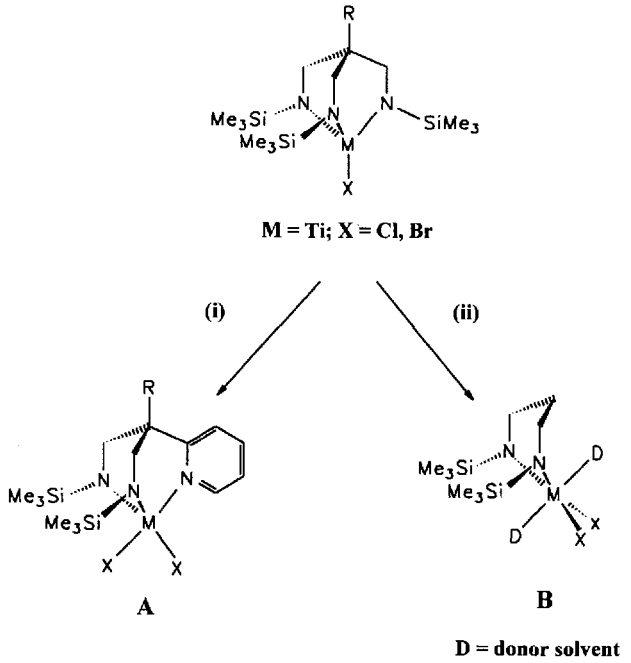
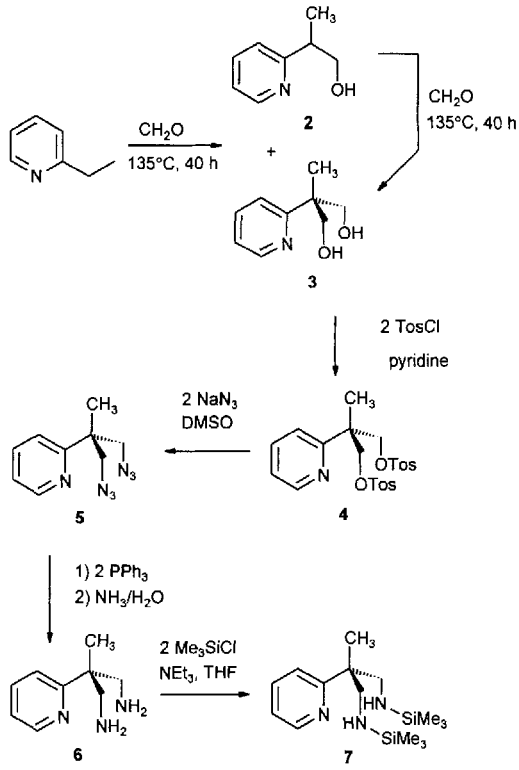
Figure 1. Amido complexes containing dianionic amido ligands which are formally derived from the tripodal amido complexes by (i) displacement of an anionic amido function by a neutral tetriary amino (pyridine) group or (ii) removal of an anionic amido "ligand arm"

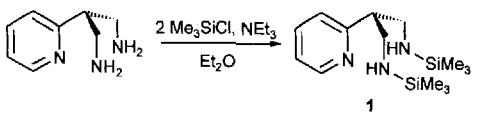


Scheme 1. Synthesis of the silylamine **6**



These difficulties made it desirable to block the apical C–H position by introducing a methyl group. Such a modified polyfunctional amido ligand precursor is prepared by means of the five-step synthetic route displayed in Scheme 1.

We note that a similar synthetic strategy recently was employed by Grohmann et al. in their synthesis of 2,6-bis[1,1'-bis(aminomethyl)ethyl]pyridine which they established as a pentacoordinate amine ligand in the coordination chemistry of the late transition metals.[15]

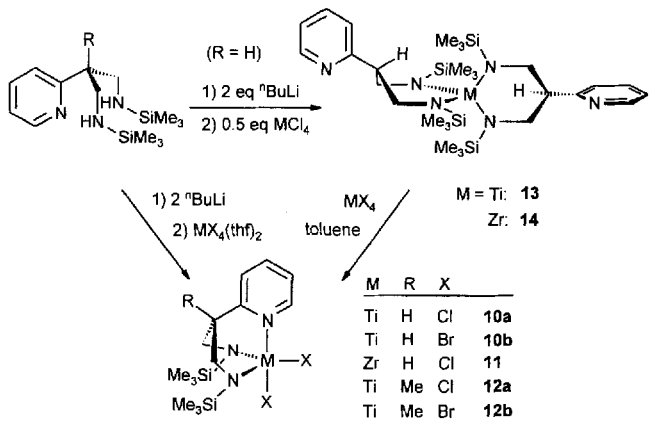


B) Synthesis and Structural Characterization of Pentacoordinate Ti and Zr Complexes

As in the synthesis of most other polydentate amido complexes the lithium amides derived from **1** and **7** by reaction with BuLi, **8** and **9**, are the amide transfer reagents of choice. Both of the lithium amides are dimeric species if generated in hydrocarbon solvents as was derived from NMR spectrocopy and cryoscopy in benzene. The crystal structures of $[Me_2Si\{N(Li)tBu\}_2]_2$ and $[Li[rac\text{-}N(tBuCH(Me)-CH(Me)NtBu\}Li]_2$ reported by, respectively, Bürger and Raston and their coworkers[16][17] give some indication as to the possible structures of **8** and **9** although this proposal will have to be substantiated in a future X-ray crystallographic study.

The synthesis of the amidotitanium- and -zirconium halide complexes is most conveniently achieved by reaction of the lithium amides **8** and **9** with $[TiX_4(thf)_2]$ or $[ZrCl_4(thf)_2]$ in a 1:1 molar ratio yielding the complexes $[MX_2\{RC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ (R = H, M = Ti, X = Cl, Br: **10a, b**; M = Zr, X = Cl: **11**; R = CH_3, M = Ti, X = Cl, Br: **12a, b**] (Scheme 2). An alternative synthetic route to **10** and **11** is via the spirocyclic compounds **13** and **14**, which may then be converted to the desired amido halide complexes by conproportionation with the metal tetrahalides or their THF-adducts (Scheme 2).

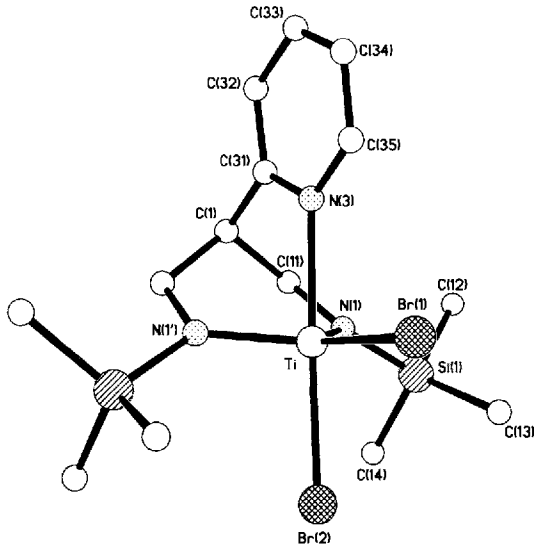
Scheme 2. Synthesis of the Ti and Zr complexes **10**–**14**



Both synthetic strategies were first reported by Bürger et al. in the 1970's for the synthesis of amido halide complexes containing bidentate amido ligands.[10] There is no indication of a participation of the pyridine functions in the

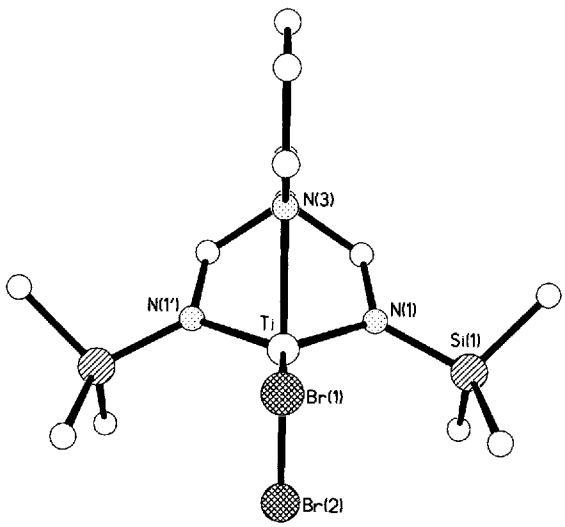
coordination at the metal centre. This is reflected in the diagnostic chemical shift of the *ortho*-protons at the pyridine rings (**13**: δ = 8.47; **14**: δ = 7.92) and we therefore formulate both complexes as tetra-coordinate species.

Figure 2a. The molecular structure of **10b**[a]



[a] Selected bond lengths [Å] and angles [°]: Ti–Br(1) 2.496(3), Ti–Br(2) 2.508(3), Ti–N(3) 2.263(12), Ti–N(1) 1.839(8), Si(1)–N(1) 1.750(9); Br(2)–Ti–Br(1) 90.2(1), N(3)–Ti–Br(1) 86.7(3), N(3)–Ti–Br(2) 176.9(3), N(1)–Ti–Br(1) 125.9(3), N(1)–Ti–Br(2) 96.5(3), N(1)–Ti–N(3) 85.4(3), N(1)–Ti–N(1') 106.5(5).

Figure 2b. A view parallel to the crystallograpic mirror plane of **10b**

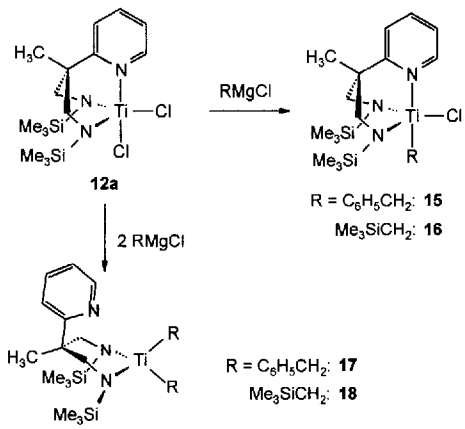


A single crystal X-ray structure analysis of compound **10b** established the penta-coordinate structure of this class of compounds (Figure 2a). The molecular structure of **10b** possesses exact C_s symmetry with the pyridine ring atoms, the apical C-atom, Br(1), Br(2), and Ti lying in the crystallographic mirror plane. The arrangement of the ligand donor atoms around the Ti^{IV} centre is slightly distorted trigonal bipyramidal. Both the amido-N atoms and Br(2)(lie in the equatorial plane of the idealized trigonal bipyramid while the axial positions are occupied by the pyridine-N atom and Br(1) [N(3)–Ti–Br(1) = 176.9(3)°]. As may be seen in the view of the molecule depicted in Figure 2a, the pyridine ring is slightly tilted with respect to the Ti–N1 vector. This is a consequence of the structural constraints imposed by the ligand framework and somewhat reminiscent of the coordination of oligopyridine ligands to transition metals.[18]

C) Synthesis and Structural Characterization of Organometallic Derivatives of $[TiX_2\{H_3CC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$

The coordination of the pyridyl-N atom to the Ti centre and thus the fivefold coordination of the complexes as a whole depends on the steric demand of the other ligands, particularly that of the third equatorial ligand. This is evident from the results of mono- and dialkylation of the dichlorotitanium complex **12a** (Scheme 3). Upon reaction of **12a** with one molar equivalent of the Grignard reagents RMgCl (R = $C_6H_5CH_2$, Me_3SiCH_2) the monoalkyl complexes **15** and **16** are obtained.

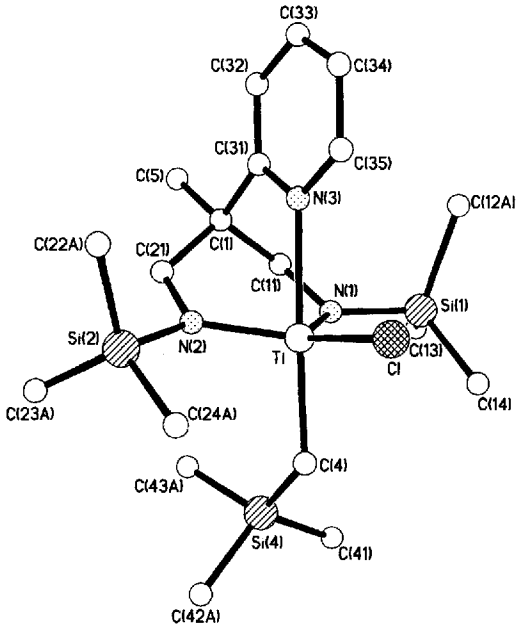
Scheme 3. Synthesis of the mono- and dialkyl Ti complexes **15**–**18**



The coordination of the pyridyl group is inferred from the low-field ^{1}H-NMR shift of H^6 in the pyridyl ring [**15**: δ = 9.03; **16**: δ = 9.31 in comparison to the respective chemical shifts of the same resonance in non-coordinated species which is observed at δ ≈ 8.5, or below]. The axial position of the alkyl ligand in both complexes was established by ^{1}H-NOESY experiments and confirmed for **16** by a single crystal X-ray structure analysis. Although disorder of the trimethylsilyl groups of the complex led to fairly high esd's on all parameters, the overall geometric features of the complex are well established and displayed in Figure 3a and 3b along with the principal bond parameters.

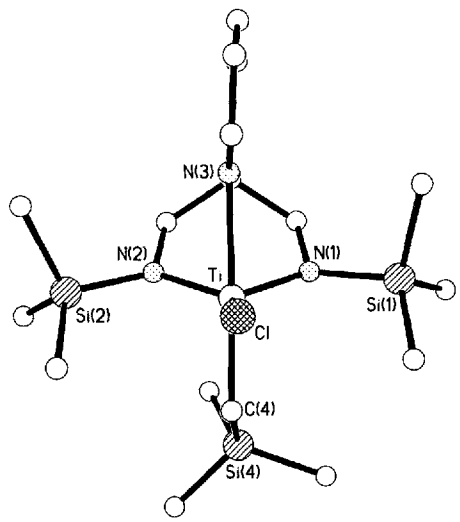
In the case of **16**, molecules in the crystal possess idealized C_s symmetry with the pyridine ring, C(1), C(4), Si(4), Ti, and Cl atoms lying close to the plane. Remarkably, the distortion of **16** with respect to an idealized trigonal bipyramidal coordination geometry is slightly more pronounced than in **10b**. [N(3)–Ti–C(4) = 174.9(4)°]. The pyridine-N–Ti distance [Ti–N(3) 2.376(8) Å] is significantly longer than the corresponding metal ligand distance in **10b**. Whether this is a consequence of the different trans-axial

Figure 3a. The molecular structure of **16** (one orientation of the disordered $SiMe_3$ groups is shown)[a]



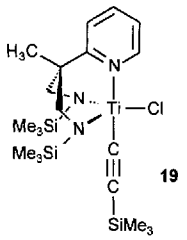
[a] Selected bond lengths (Å) and angles (°): Ti–Cl 2.344(3), Ti–N(1) 1.864(7), Ti–N(2) 1.873(7), Ti–N(3) 2.376(8), Ti–C(4) 2.144(9), Si(1)–N(1) 1.773(8), Si(2)–N(2) 1.746(7), Si(4)–C(4) 1.866(11); N(1)–Ti–N(2) 107.7(3), N(1)–Ti–C(4) 101.5(4), N(2)–Ti–C(4) 100.7(4), N(1)–Ti–Cl 121.6(3), N(2)–Ti–Cl 126.2(2), C(4)–Ti–Cl 90.0(3), N(1)–Ti–N(3) 82.4(3), N(2)–Ti–N(3) 81.1(3), C(4)–Ti–N(3) 174.9(4), Cl–Ti–N(3) 85.1(2).

Figure 3b. A view parallel to the virtual mirror plane of **16**



ligands or due to geometric contraints imposed by the ligand framework cannot be distinguished at this stage. All the other metric parameters are similar to those of **10b** as well as related titanium amidohalides and pyridine adducts and therefore do not require further discussion.[19]

In contrast to the monoalkylation products **15** and **16** the dialkyl complexes **17** and **18** adopt a tetrahedral configuration in solution, with the pyridyl group being a mere pendant ligand, as deduced from the ^{1}H-NMR spectroscopic data [H[6]: **17**: δ = 8.26; **18**: δ = 8.47]. An equilibrium between the proposed four- and a possible five-coordinate isomer in solution cannot be completely ruled out although low temperature NMR studies performed between 190 and 210 K give no indication of the presence a second isomer. Even if a trigonal bipyramidal isomer is present, this would only be so in very small quantities since the ^{1}H-NMR chemical discussed above are clearly indicative of a dominance of the open tetrahedral form.



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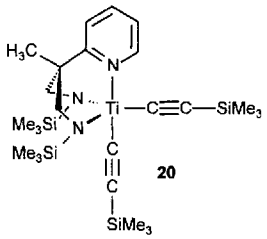

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The importance of the steric interaction between the ligands in **15**–**18** in the determination of the complex geometry gains additional support through the structures of the products of the reaction of **12a** with the lithium acetylide $Li[C_2SiMe_3]$. Both the product of mono substitution **19** as well as the diacetylide **20** adopt a trigonal bipyramidal coordination geometry with the pyridyl function acting as a ligand at the Ti centres [H[6]: **19**: δ = 9.31; **20**: δ = 9.99]. The low steric demand of the rod shaped alkynyl ligands favours the five coordinate structures established by NMR spectroscopy.

Conclusions

The introduction of a neutral donor function in a tridentate amido ligand enables a flexible adjustment of the coordination of the polyfunctional ligand to the steric requirements of the other ligand present in complexes of tetravalent titanium and, potentially, other early transition metals. In particular the "hemilabile" nature of the the pyridine coordination opens up the posibility of masking lower coordination numbers and thus free coordination sites at the metal centres. Preliminary further studies have indicated that the new {(ligand)Ti} fragment has considerable potential in the chemistry of mononuclear Ti imido complexes.[20] These and other aspects of the coordination chemistry of the diamido-amine ligands and the organometallic chemistry of its complexes is the focus of current and future work in our laboratory.

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Experimental Section

All manipulations were performed under dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures

and saturated with Ar. The deuterated solvents used for the NMR-spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4-Å molecular sieves. – The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded with a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, and 39.76 MHz, respectively) with tetramethylsilane as reference. – Infrared spectra were recorded with Perkin-Elmer 1420 and Bruker IRS 25-FT-spectrometers. – Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. – The compounds 2-(2-pyridyl)propane-1,3-diamine[14] and $[MX_4(thf)_2]$ (M = Ti, Zr; X = Cl, Br)[21] were prepared by literature methods. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of the Compounds

1) *Preparation of* $H_3CC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (**6**)

a) $H_3CCH(2\text{-}C_5H_4N)(CH_2OH)$ (**2**) *and* $H_3CC(2\text{-}C_5H_4N)(CH_2OH)_2$ (**3**): A mixture of 2-ethylpyridine (150 ml, 140.6 g, 1.31 mol) and an aqueous solution of formaldehyde (40%, 450 ml, 6.53 mol) was heated at 135°C for 40 h in a 1-l stirring autoclave. After cooling to room temperature, the solvent was removed in vacuo. Vacuum distillation yielded the product of monohydroxymethylation **2** (yield: 49%) as a pale yellow oil and **3** (yield: 16%) as an orange viscous oil. The yield of **3** could be increased to 48% by reaction of **2** with 4 equivalents of formaldehyde under the same conditions.

2: B. p. 115°C/0.2 Torr. – ^{1}H NMR ($CDCl_3$, 295 K), δ = 1.13 [d, ^3J(HH) = 7.0 Hz, CH_3], 2.90 [tq, ^3J(HH) = 6.0 Hz, C*H*CH_2OH], 3.66 (d, CHC*H*$_2$OH), 6.89–7.03 (m, H^3/H^5), 7.43 [dt, $^3J(H^3H^4) = {}^3J(H^5H^4)$ = 7.6, $^4J(H^4H^6)$ = 1.3 Hz, H^4], 8.26 [ddd, $^3J(H^5H^6)$ = 4.8, $^5J(H^3H^6)$ = 0.9 Hz, H^6]. – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K), δ = 16.6 (CH_3), 42.5 (*C*HCH$_2$OH), 66.5 (CH*C*H$_2$OH), 121.0, 121.9 (C^3/C^5), 136.3 (C^4), 148.2 (C^6) and 164.0 (C^2). – IR (neat): $\tilde{\nu}$ = 3330vs br. cm^{-1}, 3025s, 2980s, 2945s, 2890s, 1608vs, 1582s, 1488s, 1448s, 1390m, 1340m, 1310m, 1290w, 1250w, 1220w, 1165m, 1122m, 1090s, 1060vs, 1035vs, 1012s, 992m, 952vw, 912w, 900w, 800s, 765s. – $C_8H_{11}NO$ (137.18): calcd. C 70.07, H 8.08, N, 10.21; found C 69.79, H 7.89, N 10.14.

3: B. p. 143°C/0.2 Torr. – ^{1}H NMR ($CDCl_3$, 295 K) δ = 1.16 (s, CH_3), 3.74 [d, ^2J(HH) = 11.1, CH(C*H*HOH)$_2$], 3.94 [d, CH(CH*H*OH)$_2$], 7.14 [ddd, $^3J(H^5H^4)$ = 7.6 Hz, $^3J(H^5H^6)$ = 4.9 Hz, $^4J(H^5H^3)$ = 1.0 Hz, H^5], 7.31 [ddd, $^3J(H^3H^4)$ = 7.8 Hz, $^5J(H^3H^6)$ = 1.0 Hz, H^3], 7.66 [dt, $^4J(H^4H^6)$ = 1.8 Hz, H^4] and 8.43 (ddd, H^6). – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K) δ = 19.7 (CH_3), 45.7 [*C*(CH$_2$OH)$_2$], 69.3 [C(*C*H$_2$OH)$_2$], 121.5, 121.7 (C^3/C^5), 137.0 (C^4), 147.8 (C^6) and 165.1 (C^2). – IR (neat): $\tilde{\nu}$ = 3350 vs br. cm^{-1}, 2990 s, 2920 s, 2865 s, 1715 vw, 1688 s, 1563 m, 1469 s, 1428 s, 1285 w, 1245 w, 1205 w, 1192 m, 1101 m, 1085 m, 1045 vs, 998 m, 965 w, 895 vw, 843 vw, 785 s, 748 s. – $C_9H_{13}NO_2$ (167.21) calcd. C 64.65, H 7.84, N 8.38; found C 64.47, H 7.67, N, 8.29.

b) $H_3CC(2\text{-}C_5H_4N)(CH_2OTos)_2$ (**4**): To a solution of $H_3CC(2\text{-}C_5H_4N)(CH_2OH)_2$ (**3**) (50.0 g, 0.30 mol) in pyridine (400 ml), which was cooled to 0°C, toluenesulfonyl chloride (144 g, 0.75 mol) was added in small portions so as to keep the reaction temperature between 5 and 10°C. After stirring at ambient temperature for 16 h, the reaction mixture was poured into 1.5 l of ice/water The precipitate thus obtained was filtered off, washed with water (3 × 100 ml) and diethyl ether (2 × 100 ml) and dried in vacuo to yield **4** as a colourless solid (yield: 87%). M. p. 120°C. – ^{1}H NMR ($CDCl_3$, 295 K), δ = 1.30 (s, CH_3), 2.41 (s, Tos: CH_3), 4.23 (s, CH_2OTos), 7.04–7.15 (m, H^3/H^5), 7.27 [d, $^3J(H^2H^3)$ = 8.1 Hz, Tos: H^3], 7.55 [dt, $^3J(H^5H^4)$ = 7.7 Hz, $^4J(H^4H^6)$ = 1.9, H^4], 7.62 (d, Tos: H^2) and 8.28 [ddd, $^3J(H^5H^6)$ = 4.8 Hz, $^5J(H^3H^6)$ = 0.8 Hz, H^6]. – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K), δ = 19.3 (CH_3), 21.5 (Tos: CH_3), 44.7 [*C*(CH$_2$OTos)$_2$], 72.7 [C(*C*H$_2$OTos)$_2$], 120.7, 122.1 (C^3/C^5), 127.7 (Tos: C^3), 129.8 (Tos: C^2), 132.1 (Tos: C^4), 136.5 (C^4), 144.8 (Tos: C^1), 148.8 (C^6) and 159.0 (C^2). – IR (KBr): $\tilde{\nu}$ = 3032 m br. cm^{-1}, 2948 m, 2918 m, 2580 w, 2520 w, 1918 m, 1585 vs, 1568 s, 1472 s, 1455 s, 1435 s, 1398 s, 1355 vs, 1310 s, 1288 s, 1262 w, 1210 s, 1175 vs, 1130 s, 1095 vs, 1035 m, 1018 s, 978 vs, 945 vs, 893 m, 878 s, 845 vs, 812 vs, 783 vs, 752 s, 713 m. – $C_{23}H_{25}NO_6S_2$ (475.57): calcd. C 58.09, H 5.30, N 2.95, S 13.49; found C 57.84, H 4.95, N 2.65, S 13.86.

c) $H_3CC(2\text{-}C_5H_4N)(CH_2N_3)_2$ (**5**): A solution of $H_3CC(2\text{-}C_5H_4N)(CH_2OTos)_2$ (**4**) (146.6 g, 0.31 mol) and NaN_3 (60 g, 0.92 mol) in dmso (600 ml) was stirred at 70°C for 4 d. After cooling to room temperature, the reaction mixture was poured into water (600 ml) and the suspension extracted with diethyl ether (4 × 250 ml). The organic phase was dried with Na_2SO_4, filtered and the solvent evaporated in vacuo to yield crude **4** as an orange-brown oil which was used im the subsequent conversions (***CAUTION:*** *Alkyl azides are potentially hazardous chemicals!*). Yield of crude product: 83%. – ^{1}H NMR ($CDCl_3$, 295 K): δ = 1.35 (s, CH_3), 3.58 [d, ^2J(HH) = 12.0 Hz, C*H*HN$_3$], 3.70 (d, CH*H*N$_3$), 7.09 [ddd, $^3J(H^5H^4)$ = 7.4 Hz, $^3J(H^5H^6)$ = 4.8 Hz, $^4J(H^5H^3)$ = 1.0 Hz, H^5], 7.23 [ddd, $^3J(H^3H^4)$ = 8.0 Hz, $^5J(H^3H^6)$ = 0.8 Hz, H^3], 7.60 [dt, $^4J(H^4H^6)$ = 1.9 Hz, H^4] and 8.51 (ddd, H^6). – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K), δ = 20.7 (CH_3), 46.1 [*C*(CH$_2$N$_3$)$_2$], 57.8 [C(*C*H$_2$N$_3$)$_2$], 120.7, 121.9 (C^3/C^5), 136.4 (C^4), 148.8 (C^6) and 161.3 (C^2). – IR (neat): $\tilde{\nu}$ = 3090 vw cm^{-1}, 3050 vw, 2970 w, 2930 w, 2870 w, 2103 vs, 1588 m, 1570 w, 1468 m, 1435 m, 1380 w, 1290 s br., 1192 vw, 1180 vw, 1156 vw, 1118 vw, 1100 vw, 1050 vw, 995 vw, 942 vw, 790w, 750 m.

d) $H_3CC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (**6**): To a solution of $H_3CC(2\text{-}C_5H_4N)(CH_2N_3)_2$ (**5**) (55.0 g, 0.25 mol) in pyridine (60 ml) was added dropwise a solution of triphenylphosphane (160 g, 0.61 mol) in pyridine (220 ml) at 0°C. The reaction mixture was warmed to room temperature and stirred for 16 h. After warming to 60°C, the solvent was removed in vacuo, the warm viscous residue poured into an aqueous ammonia solution (10%, 600 ml) and virgously stirred for 16 h. After filtration, the precipitate was extracted with water (2 × 250 ml), the solvent of the filtrate removed in vacuo and the residue distilled to yield **6** as a pale yellow oil. Yield: 69%. B. p. 114°C/0.1 Torr. – ^{1}H NMR ($CDCl_3$, 295 K): δ = 1.05 (s, CH_3), 2.57 [d, ^2J(HH) = 12.8 Hz, C*H*HNH$_2$], 2.83 (d, CH*H*NH$_2$), 6.82 [ddd, $^3J(H^5H^4)$ = 7.8 Hz, $^3J(H^5H^6)$ = 4.8 Hz, $^4J(H^5H^3)$ = 1.1 Hz, H^5], 7.02 [ddd, $^3J(H^3H^4)$ = 8.0 Hz, $^5J(H^3H^6)$ = 1.0 Hz, H^3], 7.35 [dt, $^4J(H^4H^6)$ = 2.0 Hz, H^4] and 8.29 (ddd, H^6). – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K) δ = 20.2 (CH_3), 46.8 [*C*(CH$_2$NH$_2$)$_2$], 49.8 [C(*C*H$_2$NH$_2$)$_2$], 120.4, 121.0 (C^3/C^5), 135.6 (C^4), 148.3 (C^6) and 164.2 (C^2). – IR (neat): $\tilde{\nu}$ = 3370 s br. cm^{-1}, 3290 s br., 3080 w, 3050 w, 2960 s, 2920 s, 2860 s, 1583 vs, 1562 s, 1468 s, 1430 s, 1380 w, 1365 w, 1295 vw, 1165 w, 1090 w, 1043 m, 990 w, 845 s br., 785 s. – $C_9H_{15}N_3$ (165.24): calcd. C 65.42, H 9.15, N 25.43; found C 65.18, H 9.47, N 25.05.

2) *Preparation of the Silyl Amines* $RC(2\text{-}C_5H_4N)(CH_2NHSiMe_3)_2$ (R = H: **1**; CH_3: **7**): $RC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (R = H: **5**; CH_3: **6**) (17.0 mmol) and triethylamine (6.92 g, 68.4 mmol) were dissolved in thf (100 ml) and cooled to 0°C. The solution of $SiMe_3Cl$ (3.75 g, 34.5 mmol) in thf (20 ml) was added dropwise and the reaction mixture stirred for 3 h at room temperature. After filtration, the solvent was removed in vacuo and the residue distilled to yield **1** and **7** as colourless liquids.

1: Yield: 43%, b. p. 98°C/0.1 Torr. – ^{1}HNMR ($CDCl_3$, 295 K): δ = −0.15 [s, $Si(CH_3)_3$], 2.60 [quint, ^3J(HH) = 6.7 Hz, C*H*($CH_2NHSiMe_3)_2$], 2.94 [d, CH(C*H*$_2$NHSiMe$_3)_2$], 6.98 (m, H^3/H^5), 7.46 [dt, $^3J(H^3H^4) = {}^3J(H^5H^4)$ = 7.5 Hz, $^4J(H^4H^6)$ = 1.7 Hz, H^4] and 8.45 [ddd, $^3J(H^5H^6)$ = 4.8 Hz, $^5J(H^3H^6)$ = 1.0 Hz, H^6]. – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = −0.2 [$Si(CH_3)_3$], 44.4 [CH(*C*H$_2$NHSiMe$_3)_2$], 55.9 [*C*H(CH$_2$NHSiMe$_3)_2$], 121.1, 123.9 (C^3/C^5), 135.6 (C^4), 149.2 (C^6) and 162.7 (C^2). – ^{29}Si{^{1}H} NMR ($CDCl_3$, 295 K: δ = 3.5. – IR (neat): $\tilde{\nu}$ = 3395 m br. cm^{-1}, 3055 m br., 2995 m, 2940 vs, 2885 s, 2850 s, 1660 w br., 1585 vs, 1565 s, 1465 s, 1430 s, 1393 s, 1290 m, 1240 vs, 1180 m, 1100 vs, 867 vs, 833 vs, 742 vs. – $C_{14}H_{29}N_3Si_2$ (295.58): calcd. C 56.89, H 9.89, N 14.22; found C 56.96, H 10.01, N 15.09.

7: Yield: 94%, b. p. 102°C/0.2 Torr. – ^{1}H NMR ($CDCl_3$, 295 K): δ = −0.10 [s, $Si(CH_3)_3$], 1.25 (s, CH_3), 2.79 [dd, ^2J(HH) = 12.8 Hz, ^3J(HH) = 9.0 Hz, C*H*HNHSiMe$_3$], 3.08 [dd, ^3J(HH) = 7.8 Hz, CH*H*NHSiMe$_3$], 7.04 [ddd, $^3J(H^5H^4)$ = 7.5 Hz, $^3J(H^5H^6)$ = 4.8 Hz, $^4J(H^5H^3)$ = 1.1 Hz, H^5], 7.23 [ddd, $^3J(H^3H^4)$ = 8.0 Hz, $^5J(H^3H^6)$ = 1.0 Hz, H^3], 7.56 [dt, $^4J(H^4H^6)$ = 1.9 Hz, H^4] and 8.55 (ddd, H^6). – ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 0.0 [$Si(CH_3)_3$], 20.6 (CH_3), 47.9 [*C*(CH$_2$NHSiMe$_3)_2$], 50.2 [C(*C*H$_2$NHSiMe$_3)_2$], 120.6, 122.0 (C^3/C^5), 135.7 (C^4), 148.7 (C^6) and 165.8 (C^2). – ^{29}Si{^{1}H} NMR ($CDCl_3$, 295 K): δ = 3.3. – IR (neat): $\tilde{\nu}$ = 3380 w cm^{-1}, 3080 vw, 3045 vw, 2940 s, 2890 m, 2850 m, 1583 m, 1562 w, 1465 m, 1428 m, 1396 m, 1245 vs, 1105 m, 1065 m, 1045 m, 870 s, 835 vs, 780 m, 743 s. – $C_{15}H_{31}N_3Si_2$ (309.60): calcd. C 58.19, H 10.09, N 13.57. found C 57.96, H 10.26, N 13.82.

3) *Preparation of the Lithium Amides [RC(2-C$_5$H$_4$N){CH$_2$N(Li)SiMe$_3$}$_2$]$_2$* (R = H: **8**; Me: **9**): To a solution of RC(2-C_5H_4N)($CH_2NHSiMe_3)_2$ (R = H: **1**; CH_3: **7**) (0.74 mmol) in toluene (5 ml) was added *n*-butyllithium (0.60 ml of a 2.5 M solution in hexanes, 1.50 mmol) at −30°C. The mixture was warmed to room temperature and then briefly heated. The volume of the solution was reduced to ca. 2 ml and stored at −35°C. Compounds **8** and **9** were obtained as colourless crystalline solids (yields 82% and 84%, respectively) which were filtered off and dried in vacuo.

8: ^{1}H NMR (C_6D_6, 295 K): δ = 0.21, 0.43 [s, $Si(CH_3)_3$], 2.91 [m, C*H*($CH_2NSiMe_3)_2$], 3.30 [m, CH(C*HH*NSiMe$_3)_2$], 3.62 [m, CH(CH*H*NSiMe$_3)_2$], 3.92 [m, CH(C*H*HNSiMe$_3)_2$], 6.42 [ddd, $^3J(H^5H^4)$ = 7.5 Hz, $^3J(H^5H^6)$ = 5.1 Hz, $^4J(H^5H^3)$ = 1.1 Hz, H^5], 6.65 [ddd, $^3J(H^3H^4)$ = 7.8 Hz, $^5J(H^3H^6)$ = 1.0 Hz, H^3], 6.91 [dt, $^4J(H^4H^6)$ = 1.8 Hz, H^4] and 8.13 (ddd, H^6). – ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ = 0.1, 3.4 [$Si(CH_3)_3$], 46.7, 52.4 [CH(*C*H$_2$NSiMe$_3)_2$], 55.8 [*C*H(CH$_2$NSiMe$_3)_2$], 121.1, 124.6 (C^3/C^5), 137.7 (C^4), 147.6 (C^6) and 166.8 (C^2). – ^{7}Li{^{1}H} NMR (C_6D_6, 295 K): δ = 0.26 and 0.78. – ^{29}Si{^{1}H} NMR (C_6D_6, 295 K): δ = −5.8 and −3.9. – $C_{28}H_{54}Li_4N_6Si_4$ (614.88): calcd. C 54.70, H 8.85, N 13.67; found C 54.22, H 9.27, N 13.33.

9: ^{1}H NMR (C_6D_6, 295 K): δ = 0.24, 0.46 [s, $Si(CH_3)_3$], 1.40 (s, CH_3), 3.10, 3.17 [d, ^2J(HH) = 13.8 Hz, C*H*HNSiMe$_3$], 3.48, 3.72 (d, CH*H*NSiMe$_3$), 6.47 [ddd, $^3J(H^5H^4)$ = 6.9 Hz, $^3J(H^5H^6)$ = 5.1 Hz, $^4J(H^5H^3)$ = 1.7 Hz, H^5], 6.95–7.11 (m, H^3/H^4) and 8.34 [ddd, $^4J(H^4H^6)$ = 1.8 Hz, $^5J(H^3H^6)$ = 1.1 Hz, H^6]. – ^{13}C{^{1}H}NMR (C_6D_6, 295 K): δ = 0.2, 4.4 [$Si(CH_3)_3$], 24.4 (CH_3), 50.7 [*C*(CH$_2$NSiMe$_3)_2$], 55.4, 58.6 [C(*C*H$_2$NSiMe$_3)_2$], 120.9, 121.7 (C^3/C^5), 137.7 (C^4), 147.3 (C^6) and 169.6 (C^2). – ^{7}Li{^{1}H} NMR (C_6D_6, 295 K): δ 0.16 and 0.88. – ^{29}Si{^{1}H} NMR (C_6D_6, 295 K): δ −7.6 and −4.4. – $C_{30}H_{58}Li_4N_6Si_4$ (642.94): calcd. C 56.04, H 9.09, N 13.07; found C 55.69, H 9.38, N 12.82.

4) *Synthesis of the Amido Halide Complexes [MX$_2${RC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}]* (**10**–**12**): To a solution of RC(2-C_5H_4N)($CH_2NHSiMe_3)_2$ (3.72 mmol) in 25 ml of pentane and 10 ml of diethyl ether, which was cooled at −40°C, was added 3.00 ml of a 2.5 M solution of *n*-butyllithium in hexanes (7.50 mmol). The reaction mixture was warmed to room temperature, then briefly refluxed and subsequently re-cooled to −60°C. Solid $TiX_4(thf)_2$ (X = Cl or Br) was added, the reaction mixture warmed to ambient temperature over a period of 16 h, the solvent removed in vacuo and the residue extracted with 4 × 30 ml of toluene. The combined extracts were concentrated to ca. 15 ml and stored at −35°C. Compounds [$TiCl_2${HC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**10a**), [$TiBr_2${RC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**10b**), [$TiCl_2${H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**12a**), and [$TiBr_2${H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**12b**) precipitated as yellow-orange microcrystalline solids and were isolated in yields of 48, 52, 61, 55%, respectively. The complex [$ZrCl_2${HC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**11**), was prepared in a similar way, using a mixture of 10 ml of pentane and 25 ml of diethyl ether as reaction medium and solid $ZrCl_4$ as starting material. The compound was obtained in only 21% yield employing this method and is therefore preferably synthesized by the aternative route described below.

10a: ^{1}H NMR (C_6D_6, 295 K): δ = 0.24 [s, $Si(CH_3)_3$], 3.07 [m, C*H*($CH_2NSiMe_3)_2$], 3.23 [dd, ^2J(HH) = 13.0 Hz, ^3J(HH) = 3.4 Hz, CH(CH*H*NSiMe$_3)_2$], 4.18 [dd, ^3J(HH) = 2.1 Hz, CH(C*H*HNSiMe$_3)_2$], 6.38 [ddd, $^3J(H^5H^4)$ = 7.5 Hz, $^3J(H^5H^6)$ = 5.5 Hz, $^4J(H^5H^3)$ = 1.4 Hz, H^5], 6.56 [ddd, $^3J(H^3H^4)$ = 7.5 Hz, $^5J(H^3H^6)$ = 0.9 Hz, H^3], 6.87 [dt, $^4J(H^4H^6)$ = 1.7 Hz, H^4] and 9.45 (ddd, H^6). – ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ = −0.2 [$Si(CH_3)_3$], 52.3 [*C*H(CH$_2$NSiMe$_3)_2$], 58.6 [CH(*C*H$_2$NSiMe$_3)_2$], 122.2, 122.3 (C^3/C^5), 138.7 (C^4/C^6), C^2 was not observed. – $C_{14}H_{27}Cl_2N_3Si_2Ti$ (412.35): calcd. C 40.78, H 6.60, N 10.19; found C 40.75, H 6.65, N 9.85.

10b: ^{1}H NMR (C_6D_6, 295 K): δ = 0.28 [s, $Si(CH_3)_3$], 3.06 [m, C*H*($CH_2NSiMe_3)_2$], 3.19 [dd, ^2J(HH) = 13.1 Hz, ^3J(HH) = 3.4 Hz, CH(CH*H*NSiMe$_3)_2$], 4.16 [dd, ^3J(HH) = 2.0 Hz, CH(C*H*HNSiMe$_3)_2$], 6.41 [ddd, $^3J(H^5H^4)$ = 7.6 Hz, $^3J(H^5H^6)$ = 5.6 Hz, $^4J(H^5H^3)$ = 1.4 Hz, H^5], 6.53 [ddd, $^3J(H^3H^4)$ = 7.6 Hz, $^5J(H^3H^6)$ = 0.9 Hz, H^3], 6.89 [dt, $^4J(H^4H^6)$ = 1.7 Hz, H^4] and 9.60 (ddd, H^6). – ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ = −0.2 [$Si(CH_3)_3$], 52.3 [*C*H(CH$_2$NSiMe$_3)_2$], 58.7 [CH(*C*H$_2$NSiMe$_3)_2$], 122.2, 122.4 (C^3/C^5), 138.7 (C^4/C^6), C^2 was not observed. – $C_{14}H_{27}Br_2N_3Si_2Ti$ (501.27): calcd. C 33.55, H 5.43, N 8.38; found C 33.50, H 5.50, N 8.10.

11: ^{1}H NMR (C_6D_6, 295 K): δ = 0.21 [s, 18 H, $Si(CH_3)_3$], 3.05 [m, 1 H, C*H*($CH_2NSiMe_3)_2$], 3.19 [dd, 2 H, CH(C*H*HNSiMe$_3)_2$, ^2J(HH) = 12.5 Hz, ^3J(HH) = 3.8 Hz], 3.90 [dd, 2 H, CH(CH*H*NSiMe$_3)_2$], 6.47 [ddd, 1 H, H^5, $^3J(H^5H^4)$ = 7.7 Hz, $^3J(H^5H^6)$ = 5.2 Hz, $^4J(H^5H^3)$ = 1.3 Hz], 6.57 [ddd, 1 H, H^3, $^3J(H^3H^4)$ = 7.7 Hz, $^5J(H^3H^6)$ = 0.9 Hz], 6.96 [dt, 1 H, H^4, $^4J(H^4H^6)$ = 1.7 Hz], 9.23 (ddd, 1 H, H^6). – {^{1}H}^{13}C NMR (C_6D_6, 295 K): δ = −0.3 [$Si(CH_3)_3$], 51.4 [*C*H(CH$_2$NSiMe$_3)_2$], 54.3 [CH(*C*H$_2$NSiMe$_3)_2$], 122.4, 123.4 (C^3/C^5), 139.7 (C^4), 148.4 (C^6), 158.2 (C^2). – {^{1}H}^{29}Si NMR (C_6D_6, 295 K): δ = 2.3. – $C_{14}H_{27}Cl_2N_3Si_2Zr$ (455.69): calcd. C 36.90, H 5.97,N 9.22; found C 36.81, H 6.08, N 9.07.

12a: ^{1}H NMR (C_6D_6, 295 K): δ = 0.25 [s, $Si(CH_3)_3$], 1.12 (s, CH_3), 3.18 [d, ^2J(HH) = 12.8 Hz, C*H*HNSiMe$_3$], 4.16 (d, CH*H*NSiMe$_3$), 6.53 [ddd, $^3J(H^5H^4)$ = 7.2 Hz, $^3J(H^5H^6)$ = 5.7 Hz, $^4J(H^5H^3)$ = 1.4 Hz, H^5], 6.90 [ddd, $^3J(H^3H^4)$ = 7.9 Hz, $^5J(H^3H^6)$ = 0.6 Hz, H^3], 7.12 [dt, $^4J(H^4H^6)$ = 1.8 Hz, H^4] and 9.59 (ddd, H^6). – ^{13}C{^{1}H} NMR (C_6D_6, 295 K): δ = −0.2 [$Si(CH_3)_3$], 22.4 (CH_3), 50.8 [*C*(CH$_2$NSiMe$_3)_2$], 65.8 [C(*C*H$_2$NSiMe$_3)_2$], 119.8, 122.4 (C^3/C^5), 139.1 (C^4), 148.4 (C^6) and 159.4 (C^2). – ^{29}Si{^{1}H} NMR

(C_6D_6, 295 K): δ = 6.5. – $C_{15}H_{29}Cl_2N_3Si_2Ti$ (426.37): calcd. C 42.26, H 6.86, N 9.86; found C 42.39, H 6.99, N 9.63.

12b: ^1H NMR (C_6D_6, 295 K): δ = 0.28 [s, $Si(CH_3)_3$], 1.13 (s, CH_3), 3.15 [d, ^2J(HH) = 13.4 Hz, C*H*HNSiMe$_3$], 4.15 (d, CH*H*NSiMe$_3$), 6.53 [ddd, $^3J(H^5H^4)$ = 7.3 Hz, $^3J(H^5H^6)$ = 5.8 Hz, $^4J(H^5H^3)$ = 1.3 Hz, H^5], 6.92 [ddd, $^3J(H^3H^4)$ = 7.8 Hz, $^5J(H^3H^6)$ = 0.5 Hz, H^3], 7.13 [dt, $^4J(H^4H^6)$ = 1.7 Hz, H^4] and 9.75 (ddd, H^6). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.1 [$Si(CH_3)_3$], 22.7 (CH_3), 50.9 [*C*($CH_2NSiMe_3)_2$], 66.0 [C(*C*$H_2NSiMe_3)_2$], 120.1, 122.4 (C^3/C^5), 139.3 (C^4), 149.1 (C^6) and 159.1 (C^2). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = 6.8. – $C_{15}H_{29}Br_2N_3Si_2Ti$ (515.27): calcd. C 34.96, H 5.67, N 8.15; found C 35.06, H 5.71, N 8.12.

5) *Synthesis of the Spirocyclic Amido Complexes [M{HC(2-C_5H_4N)($CH_2NSiMe_3)_2$}$_2$] (**13** and **14**) and Their Conversion to **10** and **11***: To a stirred solution of HC(2-C_5H_4N)($CH_2NHSiMe_3)_2$ (13.40 mmol) in 30 ml of pentane and 10 ml diethyl ether for M = Ti and toluene (50 ml) for M = Zr was added *n*-butyllithium (10.80 ml of a 2.5 M solution in hexanes, 27.00 mmol) at −40°C. The reaction mixture was warmed to room temperature, heated briefly under reflux and stirred at room temperature for 2 h. Solid [$TiCL_4(thf)_2$] or [$ZrCl_4(thf)_2$] (6.82 mmol) was added at −50°C. The reaction mixture was warmed to room temperature over a period of 15 h, filtered, the filtrate evaporated. The residue was extracted with 150 ml of pentane and the extract filtered and concentrated. The yellow (Ti) or colourless (Zr) powder was washed with 10 ml of cold pentane and then dried in vacuo.

[Ti{CH(2-C_5H_4N)($CH_2NSiMe_3)_2$}$_2$] (**13**): Yield: 69%. – ^1H NMR (C_6D_6, 295 K): δ = 0.30, 0.37 [s, $Si(CH_3)_3$], 3.71 (m), 4.48 (m), 6.59 [ddd, $^3J(H^5H^4)$ = 7.4 Hz, $^3J(H^5H^6)$ = 4.8 Hz, $^4J(H^5H^3)$ = 1.4 Hz, H^5], 6.92 [ddd, $^3J(H^3H^4)$ = 7.7 Hz, $^5J(H^3H^6)$ = 0.9 Hz, H^3], 7.04 [dt, $^4J(H^4H^6)$ = 1.9 Hz, H^4] and 8.47 (ddd, H^6). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.8, 1.4 [$Si(CH_3)_3$], 58.5, 58.8 [$CH(CH_2NSiMe_3)_2$], 60.0 [*C*$H(CH_2NSiMe_3)_2$], 121.6, 122.3 (C^3/C^5), 136.1 (C^4), 149.8 (C^6) and 162.6 (C^2). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.6 and 3.0. – $C_{28}H_{54}N_6Si_4Ti$ (635.00): calcd. C 52.96, H 8.57, N 13.23; found C 53.20, H 9.10, N 13.15.

[Zr{CH(2-C_5H_4N)($CH_2NSiMe_3)_2$}$_2$] (**14**): Yield: 76%. – ^1H-NMR (C_6D_6, 300 K): δ = −0.09, 0.55 [s, 18 H, $Si(CH_3)_3$], 3.20 [m, 2 H, H^c, C*H*($CH_2NSiMe_3)_2$], 3.48 [dd, 2 H, H^a, CH(C*H*HNSiMe$_3)_2$, $^2J(H^aH^b)$ = 11.6 Hz, $^3J(H^aH^c)$ = 4.7 Hz], 3.54 [dd, 2 H, $H^{a'}$, CH(CH*H*NSiMe$_3)_2$, $^2J(H^{a'}H^{b'})$ = 11.9 Hz, $^3J(H^{a'}H^c)$ = 1.4 Hz], 3.81 [dd, 2 H, $H^{b'}$, CH(CH*H*NSiMe$_3)_2$, $^3J(H^{b'}H^c)$ = 3.7 Hz], 3.91 [dd, 2 H, H^b, CH(C*H*HNSiMe$_3)_2$, $^3J(H^bH^c)$ = 1.6 Hz], 6.40 [ddd, 2 H, H^5, $^3J(H^5H^4)$ = 7.6 Hz, $^3J(H^5H^6)$ = 4.1 Hz, $^4J(H^5H^3)$ = 1.2 Hz], 6.68 [ddd, 2 H, H^3, $^3J(H^3H^4)$ = 7.6 Hz, $^5J(H^3H^6)$ = 0.9 Hz], 6.98 [dt, 2 H, H^4, $^4J(H^4H^6)$ = 1.8 Hz], 7.92 (ddd, 2 H, H^6). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 2.1 [$Si(CH_3)_3$], 53.3 [*C*$H(CH_2NSiMe_3)_2$], 54.1 [CH(*C*$H_2NSiMe_3)_2$], 120.2 (C^5), 123.8 (C^3), 138.6 (C^4), 149.3 (C^6), 163.0 (C^2). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = −3.0, −1.5. – $C_{28}H_{54}N_6Si_4Zr$ (678.34): calcd. C 49.58, H 8.02, N 12.39; found C 49.30, H 8.26, N 12.23.

To a solution of [M{HC(2-C_5H_4N)($CH_2NSiMe_3)_2$}$_2$] (**13** or **14**) (5.40 mmol) in toluene (150 ml) was added [$MX_4(thf)_2$] (M = Ti, X = Cl, Br or M = Zr, X = Cl, respectively) (5.4 mmol) and the reaction mixture stirred at ambient temperatures for 72 h. After removal of the solvent in vacuo, the residue was washed with pentane (4 × 20 ml) and dried in vacuo. The remaining solid was recrystallised from thf (20 ml for M = Ti) or toluene (50 ml, M = Zr) to yield **10a** (78%), **10b** (82%), and **11** (72%). This is clearly the method of choice for the preparation of **11**.

6) *[TiCl($CH_2C_6H_5$){H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}]* (**15**): To a stirred solution of [$TiCl_2${H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**12a**) (1.32 g, 3.08 mmol) in diethyl ether (30 ml) was added dropwise $ClMgCH_2C_6H_5$ (2.48 ml of a 1.23 M solution in diethyl ether, 3.05 mmol) at −30°C. The mixture was warmed to room temperature over a period of 12 h, the solvents were removed in vacuo and the residue was extracted with pentane (40 ml). After filtration, the volume of the solution was reduced to ca. 10 ml and stored at −35°C. **15** precipitated as microcrystalline red solid. Yield: (0.73 g) 57%. – ^1H NMR (C_6D_6, 295 K): δ = 0.07 [s, $Si(CH_3)_3$], 0.90 (s, CH_3), 2.95 [d, ^3J(HH) = 12.8 Hz, C*H*HNSiMe$_3$], 3.51 (s, $CH_2C_6H_5$), 4.07 (d, CH*H*NSiMe$_3$), 6.48–7.34 [m, C_5H_4N, C_6H_5], and 9.03 [dd, $^3J(H^5H^6)$ = 5.4 Hz, $^4J(H^4H^6)$ = 1.2 Hz, H^6]. – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = −0.1 [$Si(CH_3)_3$], 22.5 (CH_3), 50.4 [*C*($CH_2NSiMe_3)_2$], 65.3 [CH(*C*$H_2NSiMe_3)_2$], 76.5 (*C*$H_2C_6H_5$), 120.1 (C^4 of C_6H_5), 120.2, 122.0 (C^3/C^5), 127.8, 127.9 (C^2, C^3 of C_6H_5), 138.2 (C^4), 146.0 (C^6), 153.7 (C^1 of C_6H_5) and 159.5 (C^2). – $C_{22}H_{36}ClN_3Si_2Ti$ (482.05): calcd. C 54.82, H 7.53, N 8.72; found C 54.68, H 7.39, N 8.63.

[TiCl(CH_2SiMe_3){H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**16**): To a stirred solution of [$TiCl_2${H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**12a**) (312 mg, 0.73 mmol) in diethyl ether (20 ml) was added dropwise $ClMgCH_2SiMe_3$ (0.31 ml of a 2.36 mM solution in diethyl ether, 0.73 mmol) at −30°C. The reaction mixture was warmed to room temperature over a period of 12 h, the solvents removed in vacuo and the residue extracted with pentane (30 ml). After filtration the volume of the solution was reduced to ca. 5 ml and stored at −35°C. **16** precipitated as crystalline yellow solid. Yield: 74%, m. p. 40°C (dec.). – ^1H NMR (C_6D_6, 295 K): δ = 0.11 [s, $Si(CH_3)_3$], 0.20 [s, $CH_2Si(CH_3)_3$], 0.96 (s, CH_3C), 2.20 (s, $TiCH_2$), 3.03 [d, ^2J(HH) = 13.1 Hz, C*H*HNSiMe$_3$], 4.32 (d, CH*H*NSiMe$_3$), 6.51 [ddd, $^3J(H^5H^4)$ = 7.3 Hz, $^4J(H^5H^3)$ = 1.5 Hz, H^5], 6.73 [dd, $^3J(H^3H^4)$ = 8.0 Hz, $^5J(H^3H^6)$ = 1.1 Hz, H^3], 6.98 [dt, $^4J(H^4H^6)$ = 2.0 Hz, H^4] and 9.31 (ddd, H^6). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.2 [$Si(CH_3)_3$], 3.4 [$CH_2Si(CH_3)_3$], 22.6 (CH_3), 50.6 [*C*($CH_2NSiMe_3)_2$], 65.8 [C(*C*$H_2NSiMe_3)_2$], 70.2 ($TiCH_2$), 119.9 (C^3), 121.9 (C^5), 138.1 (C^4), 146.4 (C^6) and 159.8 (C^2). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = −0.2 (CH_2SiMe_3) and 3.3 ($SiMe_3$). – IR (C_6H_6): $\tilde{\nu}$ = 2940 m cm^{-1}, 2860 w, 2800 w, 1580 s, 1560 w, 1240 s, 1160 w, 860 s, 830 s, 730 s. – $C_{19}H_{40}ClN_3Si_3Ti$ (478.14): calcd. C 47.73, H 8.43, N 8.79; found C 47.29, H 8.33, N 8.53.

7) *[Ti($CH_2C_6H_5$)$_2${H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}]* (**17**): To a stirred solution of [$TiCl_2${H_3CC(2-C_5H_4N)($CH_2NSiMe_3)_2$}] (**12a**) (610 mg, 1.43 mmol) in diethyl ether (20 ml) was added dropwise $ClMgCH_2C_6H_5$ (2.34 ml of a 1.23 M solution in diethyl ether, 2.88 mmol) at −30°C. The reaction mixture was warmed to room temperature over a period of 12 h, the solvents were removed in vacuo and the residue was extracted with pentane (30 ml). After filtration, the volume of of the solution was reduced to ca. 10 ml and stored at −35°C. **17** precipitated as microcrystalline red solid. Yield: 68%. – ^1H NMR (C_6D_6, 295 K): δ = 0.08 [s, $Si(CH_3)_3$], 0.79 (s, CH_3), 2.81, 3.13 (s, $CH_2C_6H_5$), 2.96 [d, ^2J(HH) = 13.1 Hz, C*H*HNSiMe$_3$], 3.69 (d, CH*H*NSiMe$_3$), 6.49 [ddd, $^3J(H^5H^4)$ = 8.0 Hz, $^4J(H^5H^3)$ = 1.1 Hz, H^5], 6.70 [dd, $^3J(H^3H^4)$ = 8.0 Hz, H^3], 6.99 [dt, $^4J(H^4H^6)$ = 1.1 Hz, H^4], 6.68–7.38 (m, C_6H_5) and 8.26 (dd, $^3J(H^5H^6)$ = 5.4 Hz, $^4J(H^4H^6)$ = 1.2 Hz, H^6). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.1 [$Si(CH_3)_3$], 23.4 (CH_3), 48.9 [*C*($CH_2NSiMe_3)_2$], 64.5 [CH(*C*$H_2NSiMe_3)_2$], 80.6, 81.9 (*C*$H_2C_6H_5$), 119.7 (C^3), 120.7, 121.9 (C^4 of C_6H_5), 121.8 (C^5), 126.3, 127.8 (C^2 of C_6H_5), 127.9, 129.3 (C^3 of C_6H_5), 137.7 (C^4), 144.7 (C^6), 150.9, 152.4 (C^1 of C_6H_5) and 161.1 (C^2). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = 0.2. – IR (C_6H_6): $\tilde{\nu}$ = 2980 m cm^{-1}, 2920 w, 2800 w, 1610 w, 1470 w, 1260 m, 850 s,

830 s, 760 m. – $C_{29}H_{43}N_3Si_2Ti$ (537.73): calcd. C 64.78, H 8.06, N 7.81; found C 64.64, H 7.91, N 8.07.

8) *[Ti(CH$_2$SiMe$_3$)$_2${H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}]* (**18**): To a stirred solution of [TiCl$_2${H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}] (**12a**) (370 mg, 0.87 mmol) in diethyl ether (20 ml) was added dropwise ClMgCH$_2$SiMe$_3$ (0.71 ml of a 2.46 M solution in diethyl ether, 1.74 mmol) at −30°C. The reaction mixture was warmed to room temperature over a period of 12 h, the solvents were removed in vacuo and the residue was extracted with pentane (30 ml). After filtration, the volume of the solution was reduced to ca. 10 ml and stored at −35°C. **18** precipitated as crystalline yellow solid. Yield: 71%. – ^{1}H NMR (C$_6$D$_6$, 295 K): δ = 0.21, 0.27 [s, CH$_2$Si(CH$_3$)$_3$], 0.34 [s, Si(CH$_3$)$_3$], 1.15, 1.44 (s, TiCH$_2$), 1.24 (s, CH$_3$), 3.77 [d, ^2J(HH) = 13.1 Hz, CHHNSiMe$_3$], 4.09 (d, CHHNSiMe$_3$), 6.56 (ddd, H^5), 7.03–7.08 (m, H^3,H^4) and 8.47 (ddd, H^6). – ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ = 1.1 [Si(CH$_3$)$_3$], 3.3, 3.4 [CH$_2$Si(CH$_3$)$_3$], 23.3 (CH$_3$), 53.1 [C(CH$_2$NSiMe$_3$)$_2$], 65.9 (TiCH$_2$), 67.7, 67.8 [C(CH$_2$NSiMe$_3$)$_2$], 120.7 (C^3), 121.4 (C^5), 136.4 (C^4), 148.0 (C^6) and 163.7 (C^2). – ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 295 K): δ = 1.5 (CH$_2$SiMe$_3$) and 1.7 (SiMe$_3$). – IR (C$_6$H$_6$): $\tilde{\nu}$ = 2960 m cm^{-1}, 2900 w, 1590 w,1580 w, 1440 w, 1240 s, 1090 w, 1020 m, 910 m, 850 s, 753 m. – $C_{23}H_{51}N_3Si_4Ti$ (529.90): calcd. C 52.13, H 9.70, N 7.93; found C 51.66, H 9.71, N 8.12.

9) *[TiCl(C≡CSiMe$_3$){H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}]* (**19**): To a stirred solution of [TiCl$_2${H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}] (**12a**) (210 mg, 0.49 mmol) in toluene (20 ml) was added Li[C≡CSiMe$_3$] (50 mg, 0.48 mmol) at −30°C. The reaction mixture was warmed to room temperature over a period of 12 h, the solvents were removed in vacuo and the residue was extracted with pentane (30 ml). After filtration, the volume of the solution was reduced to ca. 5 ml and stored at −35°C. **19** precipitated as crystalline yellow solid. Yield: 71%. – ^{1}H NMR (C$_6$D$_6$, 295 K): δ = 0.31 [s, C≡CSi(CH$_3$)$_3$], 0.33 [s, Si(CH$_3$)$_3$], 1.16 (s, CH$_3$), 3.19 [d, ^2J(HH) = 13.2 Hz, CHHNSiMe$_3$], 4.17 (d, CHHNSiMe$_3$), 6.59 [ddd, ^3J(H^{5}H^4) = 7.2 Hz, ^3J(H^{5}H^6) = 5.6 Hz, ^4J(H^{5}H^3) = 1.1 Hz, H^5], 6.96 [d, ^3J(H^{3}H^4) = 8.0 Hz, H^3], 7.22 [dt, ^4J(H^{4}H^6) = 1.8 Hz, H^4] and 9.31 (ddd, H^6). – ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ = 0.1 [NSi(CH$_3$)$_3$], 1.0 (C≡CSi(CH$_3$)$_3$), 22.8 (CH$_3$), 50.9 [C(CH$_2$NSiMe$_3$)$_2$], 65.0 [C(CH$_2$NSiMe$_3$)$_2$], 104.8 (C≡CSiMe$_3$), 119.9, 122.5 (C^3/C^5), 139.2 (C^4), 147.1 (C^6), 159.8 (C^2) and 171.8 (C≡CSiMe$_3$). – ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 295 K): δ = 3.2 (C≡CSiMe$_3$) and 4.5 (SiMe$_3$). – $C_{20}H_{38}ClN_3Si_3Ti$ (488.13): calcd. C 49.21, H 7.85, N 8.61; found C 48.95, H 7.90, N 8.41.

10) *[Ti(C≡CSiMe$_3$)$_2${H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}]* (**20**): To a stirred solution of [TiCl$_2${H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NSiMe$_3$)$_2$}] (**12a**) (402 mg, 0.94 mmol) in thf (20 ml) was added Li[C≡CSiMe$_3$] (198 mg, 1.90 mmol) at −30°C. The reaction mixture was warmed to room temperature over a period of 12 h, the solvents were removed in vacuo and the residue was extracted with pentane (30 ml). After filtration, the volume of the solution was reduced to ca. 10 ml and stored at −35°C. **20** precipitated as crystalline yellow solid. Yield: 64%. – ^{1}H NMR (C$_6$D$_6$, 295 K): δ = 0.34, 0.36 [s, C≡CSi(CH$_3$)$_3$], 0.37 [s, Si(CH$_3$)$_3$], 1.01 (s, CH$_3$), 3.11 [d, ^2J(HH) = 12.8 Hz, CHHNSiMe$_3$], 4.10 (d, CHHNSiMe$_3$), 6.58 (ddd, H^5), 6.78 [d, ^3J(H^{3}H^4) = 8.0 Hz, H^3], 6.99 [dt, ^4J(H^{4}H^6) = 1.8 Hz, H^4] and 9.99 (ddd, H^6). – ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K): δ = 0.3 [NSi(CH$_3$)$_3$], 0.8, 0.9 (C≡CSi(CH$_3$)$_3$), 22.9 (CH$_3$), 50.3 [C(CH$_2$NSiMe$_3$)$_2$], 64.5 [C(CH$_2$NSiMe$_3$)$_2$], 104.9, 108.7 (C≡CSi(CH$_3$)$_3$), 109.5, 121.9 (C^3/C^5), 138.7 (C^4), 148.9 (C^6), 159.6 (C^2) and 173.9, 174.1 (C≡CSiMe$_3$). – ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 295 K): δ = 3.3 (C≡CSiMe$_3$) and 3.3 (SiMe$_3$). – $C_{25}H_{47}N_3Si_4Ti$ (549.89): calcd. C 54.61, H 8.62, N 7.64; found C 54.89, H 8.90, N 7.48.

X-ray Crystallographic Study of **10b** *and* **16**

Crystal Data for **10b**: $C_{14}H_{27}Br_2N_3Si_2Ti$, M = 501.27, orthorhombic, *Pnma*, a = 13.900(3), b = 14.649(3), c = 10.523(2) Å, V = 2142.70 Å^3, Z = 4, $D_{calcd.}$ = 1.55 gcm^{-3}, μ(Mo-K_α) = 41.9 cm^{-1}, F(000) = 1008. An orange crystal of dimensions 0.30 × 0.35 × 0.45 mm was used in the data collection. Data were collected on a Philips PW1100 four-circle diffractometer using Mo-K_α radiation from a graphite monochromator by the method described previously.[22] Equivalent reflections were merged to give 749 unique reflections with $I/\sigma(I) > 3$. An absorption correction was applied to the data after initial refinement with isotropic thermal parameters for all atoms.[23] The positions of the titanium and two bromine atoms were deduced from a Patterson synthesis assuming the centrosymmetric space group *Pnma*.[24] The remaining non-hydrogen atoms to which they were bonded were located in subsequent difference Fourier syntheses. The thermal parameters of the H atoms were tied to two "free variables" which refined to final U values of 0.11 (aliphatic) and 0.12 (aromatic) Å^2. Anisotropic parameters were assigned to the titanium, bromine, silicon, nitrogen, and methyl carbon atoms in the final cycles of the full-matrix least-squares refinement which converged at R = 0.0479 and R_w = 0.0454 with weights of $1/\sigma^2(F)$ assigned to individual reflections.

Crystal Data for **16**: $C_{19}H_{40}ClN_3Si_3Ti$, M = 478.16, monoclinic, $P2_1/n$, a = 12.054(3), b = 16.833(3), c = 13.832(2) Å, β = 96.737(11)°, V = 2787.2(9) Å^3, Z = 4, $D_{calcd.}$ = 1.140 g cm^{-3}, μ(Mo-K_α) = 5.41 cm^{-1}, F(000) = 1024. All crystals inspected diffracted relatively weakly. An orange crystal of dimensions 0.44 × 0.36 × 0.24 mm was mounted under oil and data were collected at 173 K using a Siemens P4 diffractometer fitted with a Siemens LT2 low-temperature unit and graphite-monochromated Mo-K_α radiation. Of 8137 reflections measured, 3881 were unique in the θ range 1.91–23.00° (R_{int} = 0.226). No absorption correction was applied. The structure was solved by direct methods in space group $P2_1/n$. Extended areas of electron density were observed around the central Si of each SiMe$_3$ group in the molecule and six of the nine methyl carbon atoms were disordered over two sites of equal occupancy. All Si–CH$_3$ bonds were restrained to be equal. All hydrogen atoms were included in idealised positions with U_{iso}(H) = 1.2U_{eq}(C) for methylene and pyridine hydrogens and U_{iso}(H) = 1.5U_{eq}(C) for methyl hydrogen atoms. With the exception of methyl carbon atoms of SiMe$_3$ groups, all non-hydrogen atoms in the molecule were assigned anisotropic displacement parameters in the final cycles of full-matrix refinement on F^2. Refinement converged at R_1 = 0.0900, $wR2$ = 0.1496 [for data with $I > 2\sigma(I)$] and $wR2$ = 0.2440 (all data) for 220 parameters and 105 restraints. A weighting scheme $w^{-1} = \sigma^2F_o^2 + 0.0566[(F_o^2 + 2F_c^2)/3]$ was applied.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-100596 for **10b** and **16**, the names of the authors, and the journal citation.

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